A Pseudostate Method for Computing Photon-Atom Scattering Cross-sections

Swaantje-Johanna Grunefeld
BAppSc (Hons)
Abstract

A computational method is developed for photon-atom scattering cross-sections given by the \( \mathbf{p} \cdot \mathbf{A} \) interaction, which dominates scattering at low frequencies. Our method is simple and intuitive, and has the advantage of being extremely adaptable - it can be extended to higher-order scattering processes and applied to any atom. The scattering cross-sections calculated in this thesis provide a more complete picture of the photon-atom interaction than is currently available, which is useful for high-precision atomic, molecular and optical (AMO) experiments and has applications in astrophysics and spectroscopy.

Our method utilises the atomic structure data produced by the non-relativistic code \texttt{patom}, developed by M. W. J. Bromley. This code models the atom to be in a box, which effectively discretises the continuum. The set of positive energy states that describe the continuum are referred to as pseudostates. The single-photon scattering cross-section calculations in this thesis are based on the computation of transition polarisabilities, which are also known as the Kramers-Heisenberg matrix elements. These describe the process where an atom initially in state \([i]\) transitions to state \([j]\) through the absorption and emission of one photon. We develop a method that uses the pseudostate information to compute the complex transition polarisabilities at frequencies both below and above ionisation energy.

Our pseudostate method is first applied to atomic hydrogen, and compared with the results of our semi-analytical calculations and literature values. These transition polarisabilities are then used to compute the various single photon scattering cross-sections off atomic hydrogen - Rayleigh and Raman scattering, as well as the photoionisation cross-section. Rayleigh scattering describes the elastic process where a photon of equal energy is absorbed and emitted. We show that the Rayleigh scattering cross-sections given by our pseudostate method are completely converged even for frequencies far above threshold. On the other hand, the Raman scattering cross-section is the inelastic process where an atom initially in state \([i]\) transitions to a bound state \([j]\) through the absorption and emission of photons of different energies. Though Raman scattering is often used in spectroscopy, there is only very little data for the cross-sections of Raman scattering off atomic hydrogen. Here we show that our method is able to calculate the various Raman scattering cross-sections. We also investigate the calculation of Compton scattering cross-sections with detailed convergence studies. We demonstrate that our total and differential Compton scattering cross-sections exhibit unresolved convergence issues related to box size and the use of free-to-free transition matrix elements.

Our pseudostate method is extended to higher-order processes as well, such as the calculation of two-photon ionisation cross-section and complex hyperpolarisability. Though the same free-to-free transition matrix elements are used in the hyperpolarisability calculation as in our calculation of Compton scattering cross-sections, we find that our hyperpolarisability results are converged and in agreement with literature. Our method is extremely adaptable, as it can not only be extended to multi-photon scattering calculations, but also easily be applied to atoms other than hydrogen. We present calculations of one valence electron systems - hydrogen isotopes, positronium, metastable helium, lithium and sodium. Finally, we show that our pseudostate method is limited to frequencies below the second ionisation threshold in the case of multi-photon processes. Further limitations and possible extensions to our method to more than one
active electron are discussed.
**Declaration by author**

This thesis is composed of my original work, and contains no material previously published or written by another person except where due reference has been made in the text. I have clearly stated the contribution by others to jointly-authored works that I have included in my thesis.

I have clearly stated the contribution of others to my thesis as a whole, including statistical assistance, survey design, data analysis, significant technical procedures, professional editorial advice, and any other original research work used or reported in my thesis. The content of my thesis is the result of work I have carried out since the commencement of my research higher degree candidature and does not include a substantial part of work that has been submitted to qualify for the award of any other degree or diploma in any university or other tertiary institution. I have clearly stated which parts of my thesis, if any, have been submitted to qualify for another award.

I acknowledge that an electronic copy of my thesis must be lodged with the University Library and, subject to the policy and procedures of The University of Queensland, the thesis be made available for research and study in accordance with the Copyright Act 1968 unless a period of embargo has been approved by the Dean of the Graduate School.

I acknowledge that copyright of all material contained in my thesis resides with the copyright holder(s) of that material. Where appropriate I have obtained copyright permission from the copyright holder to reproduce material in this thesis.
Publications during candidature

Conference abstracts:


Publications included in this thesis

No publications.
Contribution by others to the thesis

I acknowledge the contributions from Dr. Michael W. J. Bromley as my principal PhD supervisor and Dr. Yongjun Cheng for his help on deriving the complex polarisability formulas.

Statement of parts of the thesis submitted to qualify for the award of another degree

None.
Acknowledgements

This thesis has been a long and interesting journey, and there are many who have traveled with me.

I would like to thank my supervisor Michael Bromley, who has taught me the importance of thorough and careful research. Thank you for your guidance over these past few years, and for always taking the time to discuss when I had questions!

I would like to thank Yongjun Cheng for his help on puzzling out the complex polarisabilities, and Sergey Novikov for looking into our questions on hydrogen analytics. Thank you also to Li-Yan Tang for her hyperpolarisability data and Ivan Mikhaylov for sending us Compton scattering data.

I would also like to acknowledge the funding I received through the APA scholarship.

Thank you to Shu and Itia, for sharing the highs and lows of a PhD with me. You made this journey fun!

Most of all I’d like to thank my family, who have been with me every step of the way. Your encouragement has meant everything to me. Thank you to Theda and Wilko for always keeping my life bright with laughter and kindness. A thousand thank yous to my mum and dad, who have always supported me in everything that I have done. Thank you for your invaluable advice and endless patience.

A special thank you to my mum, who was the first to teach me about atoms and chemistry, and ignited the interest that has led me here.
Keywords

complex polarisability, complex hyperpolarisability, photon-atom scattering, Rayleigh, Raman, Compton, photoionisation, multi-photon ionisation, pseudostates

Australian and New Zealand Standard Research Classifications (ANZSRC)

ANZSRC code: 020201, Atomic and Molecular Physics, 80%
ANZSRC code: 020503, Nonlinear Optics and Spectroscopy, 20%

Fields of Research (FoR) Classification

FoR code: 0202, Atomic, Molecular, Nuclear, Particle and Plasma Physics, 80%
FoR code: 0205 Optical Physics, 20%
Contents

Abstract ................................................................. II
List of Figures .......................................................... XIII
List of Tables ........................................................... XVIII
List of Abbreviations .................................................. XXI

1 Introduction ......................................................... 1
   1.1 Scattering Cross-sections ......................................... 1
   1.2 Atomic Structure Code ............................................. 4
       1.2.1 Configuration Interaction ..................................... 5
   1.3 Method for Computing Cross-sections ............................ 10
   1.4 Stark Shift .......................................................... 11
       1.4.1 Polarisability .................................................. 12
       1.4.2 Hyperpolarisability .......................................... 13
   1.5 Above Threshold .................................................. 14
   1.6 A Brief History of Atomic Hydrogen ............................. 16
   1.7 Natural Units ....................................................... 18
       1.7.1 Units of Polarisability and Hyperpolarisability ............ 19
       1.7.2 Units of Cross-section ....................................... 19
   1.8 Thesis Outline ..................................................... 20

2 Complex Polarisability through Semi-analytics .................. 21
   2.1 Photon Interaction with an Atom ................................. 22
       2.1.1 Analytical Transition Matrix Elements ...................... 24
   2.2 Kramers-Heisenberg Matrix Elements ............................ 25
   2.3 Previous Methods for Calculating Polarisabilities .......... 27
   2.4 Complex Polarisability ........................................... 29
       2.4.1 Im₀[αᵢᵢ(ω)], Below Threshold ............................ 29
       2.4.2 Im₁[αᵢᵢ(ω)], Above Threshold .............................. 30
   2.5 Semi-Analytical Method .......................................... 33
       2.5.1 Below Ionisation Threshold (ω < 0.5 a.u.) ................. 34
## Contents

2.5.2 Above Ionisation Threshold ($\omega > 0.5$ a.u.) ... 37

3 Complex Polarisability through $p_{\text{atom}}$ 41

3.1 Atomic Structure ........................................... 41
3.1.1 Oscillator Strength ..................................... 42
3.2 Our Pseudostate Method .................................. 44
3.2.1 Below the Ionisation Threshold ($\omega < 0.5$ a.u.) ... 46
3.2.2 Above the Ionisation Threshold ($\omega > 0.5$ a.u.) ... 50
3.2.3 Initial $2s$ and $3s$ states ................................. 52
3.3 Langhoff et al. Pseudostate Method ......................... 53
3.4 Comparison of Pseudostate-based Polarisability Calculations 55
3.5 Alternative use of the Cauchy Principal Value Theorem ... 58
3.6 Pseudostate Packing ........................................... 60
3.7 Summary ....................................................... 60

4 Single Photon Scattering off Atomic Hydrogen 61

4.1 Previous Calculations ........................................ 61
4.1.1 Notes on $p \cdot A$ vs. $A^2$ ................................. 64
4.1.2 Previous $p \cdot A$ Calculations ......................... 65
4.2 Photoionisation ............................................... 66
4.3 Rayleigh Scattering ........................................... 67
4.3.1 Rayleigh Scattering $H(1s)$ ............................... 69
4.3.2 Rayleigh Scattering $H(2s)$ ............................... 70
4.3.3 Rayleigh Scattering $H(3s)$ ............................... 71
4.4 Raman Scattering .............................................. 72
4.4.1 Previous Calculations .................................... 72
4.4.2 Individual Transitions .................................... 73
4.4.3 Raman $1s$-$2s$ Transition ................................. 73
4.4.4 Raman $3s$-$3d$ Transition ................................. 74
4.4.5 Total Raman Scattering Cross-section .................... 76
4.4.6 Choosing the Ionisation Energy ......................... 78
4.5 Another Note on Convergence .................................. 83
4.6 Compton Scattering ............................................ 84
4.6.1 Semi-analytical Calculation .............................. 85
4.6.2 Pseudostate Calculation of Compton .................... 90
4.6.2.1 Differential Scattering Cross-section ................. 94
4.6.2.2 Total Compton Scattering Cross-section ............. 100
4.6.2.3 Lack of Convergence of Compton ................. 106
4.6.2.4 For Future Compton Studies ............................................. 108

5 Multi-photon Scattering ........................................................... 111

5.1 Two-Photon Ionisation ............................................................ 111

5.1.1 Below the Second Ionisation Threshold .................................... 113

5.2 Hyperpolarisability ............................................................... 115

5.2.1 Static (ω = 0) Hyperpolarisability ......................................... 118

5.2.1.1 Components of static hyperpolarisability ................................. 119

5.2.1.2 Attempt at Semi-analytic Calculation of γ_{BFF} ......................... 123

5.2.2 Complex (Dynamic) Hyperpolarisability .................................... 125

5.3 Relation of Two-Photon Ionisation to Imaginary Hyperpolarisability .......... 131

6 The Scattering Cross-sections of other Atoms .................................. 136

6.1 Isotopes of hydrogen .............................................................. 136

6.2 Positronium ................................................................. 138

6.3 Metastable Helium .............................................................. 141

6.4 Lithium ........................................................................ 146

6.4.1 Core Electrons .......................................................... 146

6.4.2 Dipole Polarisability .................................................... 147

6.4.3 Scattering Cross-sections ................................................ 149

6.4.4 Hyperpolarisability ..................................................... 151

6.4.4.1 Static Hyperpolarisability ........................................ 151

6.4.4.2 Dynamic Hyperpolarisability ....................................... 156

6.4.4.3 Improving Accuracy by using Experimental Energies ............... 158

6.5 Sodium ................................................................. 160

6.6 Summary ............................................................... 161

7 Above Threshold Ionisation ....................................................... 163

7.1 Two-Photon Ionisation Above Threshold .................................... 163

7.2 Future - Hyperpolarisability Above Threshold .................................. 167

8 Conclusion ....................................................................... 173

8.1 Alternative Methods .......................................................... 175

8.2 Outlook ................................................................. 178

Bibliography ................................................................. 180

A Derivation of Cross-section Formulae ............................................. 195

A.1 Time-Dependent Perturbation Theory ....................................... 195

A.2 Transitions involving a single Photon ..................................... 197
List of Figures

1.1 Rayleigh, Raman and Compton scattering diagrams ........................................ 2
1.2 Diagram of processes described by the interaction Hamiltonian. ........................ 3
1.3 Diagram showing continuum in analytic calculations vs. pseudostates in a finite-basis set calculation. ................................................................. 6
1.4 Plot of the energies (in atomic units) of atomic hydrogen for ($\varepsilon < 0$) bound states (left) and ($\varepsilon > 0$) pseudostates (right) for basis set size $N_\ell = 10, 11$ and 12. ............... 7
1.5 Plot of $r \psi_n$ for the first few $\ell = 0$ states of hydrogen. ................................ 8
1.6 Plot of $r \psi_n$ for the first few continuum states of hydrogen. ......................... 8
1.7 Diagram of the two-photon ionisation process. I.P. refers to the ionisation potential. 11
2.1 Absorption cross-section of atomic hydrogen with and without including decay. ...... 31
2.2 Diagram of Rayleigh scattering ................................................................. 33
3.1 Oscillator strengths of atomic hydrogen for transitions from 1s state to p states. .... 44
3.2 Normalised pseudostate oscillator strengths of atomic hydrogen for transitions from 1s state to p states. ................................................................. 45
3.3 Comparison of Im$_0[\alpha_{1s,1s}(\omega)]$ calculated for $\Gamma(\omega)$ with different frequency dependence. ................................................................. 48
3.4 Re$[\alpha_{1s,1s}(\omega)]$ calculated by our pseudostate method and compared with Gavrila’s calculation [1]. ................................................................. 50
3.5 Comparison of Im$_1[\alpha_{1s,1s}(\omega)]$ given by our pseudostate method with our semi-analytical calculation and data given by Gravrila [1]. ......................... 52
3.6 Re$[\alpha_{2s,2s}(\omega)]$ and Re$[\alpha_{3s,3s}(\omega)]$ of atomic hydrogen given by our pseudostate and semi-analytical method. ................................................................. 53
3.7 Comparison of the real 1s-1s polarisability at frequencies above threshold given by our pseudostate method and the Langhoff method. ......................... 56
3.8 Plots giving approximate values of Re$[\alpha_{1s,1s}]$ and Im$_1[\alpha_{1s,1s}]$ at $\omega = 0.6$ a.u. and $\omega = 1.0$ a.u. ................................................................. 59
4.1 Total cross-section given by the Klein-Nishina formula. .................................... 64
4.2 Photoionisation cross-section of the ground state of atomic hydrogen over the $1 - 100$ a.u. frequency range using our pseudostate calculation, the analytical formula and the FFAST [2] and XCOM [3] databases. ........................................................................................................... 67
4.3 Rayleigh scattering cross-section of the ground state of atomic hydrogen given by our pseudostate calculation, as well as the data given by Bergstrom et al. [4], Safari et al. [5] and the XCOM [3] database. .................................................................................................................. 70
4.4 Rayleigh scattering cross-section of H(2s) given by our pseudostate calculation, as well as data given by Gavrila et al. [6]. ................................................................................................................................. 71
4.5 Rayleigh scattering cross-section of H(3s) given by our pseudostate calculation, as well as data given by Florescu et al. [7]. ............................................................................................................................. 72
4.6 Raman 1s-2s scattering cross-section given by our pseudostate and semi-analytical calculation as well as the data given by Sadeghpour et al. [8]. .................................................................................. 74
4.7 Raman 3s-3d scattering cross-section given by our pseudostate and semi-analytical calculation as well as the data given by Florescu et al. [7]. .................................................................................. 75
4.8 Total Raman scattering cross-section of H(1s) given by our pseudostate method. ........................................................................................................................................................................................................ 77
4.10 $\ell = 0$ and $\ell = 2$ contribution to the total Raman scattering cross-section at $\omega = 1$ a.u., with respect to the number of bound states included in our semi-analytic calculation. .................................................................................. 78
4.9 Total Raman scattering cross-section of H(1s) for different basis set sizes and our semi-analytical calculation. ........................................................................................................................................ 78
4.11 $\ell = 0$ and $\ell = 2$ contribution to the total Raman scattering cross-section at $\omega = 2$ a.u., with respect to the number of bound states included in our semi-analytic calculation. .................................................................................. 79
4.12 Magnitude of the Raman scattering cross-sections $\sigma_{1s,ns}(\omega = 2)$ from initial 1s state to a state with $\ell = 0$ and energy $\varepsilon$ for various basis set sizes at frequency $\omega = 2$ a.u. .................................................................................. 80
4.13 Magnitude of the Raman transition from initial 1s state to a state with $\ell = 2$ and energy $\varepsilon$ for various basis set sizes at frequency $\omega = 2$ a.u. .................................................................................. 81
4.14 Oscillator strengths of atomic hydrogen from initial 1s state to states with angular momentum $\ell = 1$. .................................................................................................................................................................................................. 81
4.15 Plot of the total Raman scattering cross-section using new ionisation energy for different basis set sizes. .................................................................................................................................................................................................. 82
4.16 Total Raman scattering cross-section for atomic hydrogen given by our pseudostate and semi-analytical calculation. ........................................................................................................................................ 83
4.17 Diagram of Compton scattering. .................................................................................................................................................................................................. 84
4.18 Plot of the analytical free-to-free transition matrix elements from a state of energy $\varepsilon_1$ to a state of energy $\varepsilon_2 = 0.25$ a.u. as a function of energy $\varepsilon_1$. ........................................................................................................................................ 87
4.19 Number of loops needed for calculation of hypergeometric function (in Eqn. 4.17) to reach convergence to $10^{-10}$ plotted as a function of final state energy $\varepsilon_2$. .................................................................................. 89
4.20 Plot of the analytical transition matrix elements in velocity form for the transition between states with $\ell = 1$ and $\ell = 0$ in the continuum. ........................................................................................................................................ 90
4.21 Diagram showing the scattering processes (Raman, Compton, two-photon ionisation) described by transition polarisabilities. .......................................................... 92
4.22 Plot of the transition polarisability Re[α_{ε_f}(ω)] (in atomic units) of H(1s) given by our pseudostate method (N_ℓ = 120, 100 and 80 basis) for ℓ = 0 (a) and ℓ = 2 (b) final states with energy ε_f. .......................................................... 93
4.23 Differential Compton scattering cross-section for atomic hydrogen at incident photon frequency near ω = 5 a.u. .......................................................... 96
4.24 Differential Compton scattering cross-section for atomic hydrogen at incident photon frequency near ω = 2 a.u. .......................................................... 97
4.25 Differential Compton scattering cross-section for atomic hydrogen at incident photon frequency near ω = 1 a.u. .......................................................... 98
4.26 Differential Compton scattering cross-section at ω = 0.998, 1.93 and 4.94 a.u. for varying λ_0 and λ_2, and keeping λ_1 constant. .......................................................... 99
4.27 Our ℓ = 0 and ℓ = 2 contribution to the total Compton scattering cross-section for atomic hydrogen, in comparison with data given by Bergstrom et al. [4] and Drukarev et. al [9]. 101
4.28 Rayleigh, Compton, and Rayleigh + Raman + Compton scattering cross-section given by our pseudostate method, in comparison with cross-sections given by the FFAST database. 102
4.29 Comparison of differential Compton scattering cross-section given by our pseudostate calculation for only ℓ = 0 final states with the differential cross-section given by Drukarev et al. [9] .......................................................... 102
4.30 Comparison of Compton scattering cross-section given by our pseudostate calculation for only ℓ = 0 final states with the cross-section given by Drukarev et al. [9] .......................................................... 102
4.31 Plot of the total and individual contributions to the Compton scattering cross-section given by our pseudostate calculation and compared with Drukarev et al. and Bergstrom et al. .......................................................... 103
4.32 Plot of the total Compton scattering cross-section (in units of σ_T) for λ_ℓ between 0.40 and 1.00, and N_ℓ = 120, 100 and 80. .......................................................... 104
4.33 Plot of ℓ = 2 differential Compton scattering cross-section at ω = 5 a.u. for λ_ℓ between 0.40 and 0.50. .......................................................... 106
4.34 Plot of the ℓ = 0 (left) and ℓ = 2 (right) contribution to the total Compton scattering cross-section (in units of σ_T) for varying λ_ℓ and N_ℓ. .......................................................... 107
4.35 ℓ = 0 differential Compton scattering cross-section for varying λ_ℓ and varying basis set size N_ℓ. .......................................................... 107
4.36 Free-to-free transition matrix elements from an initial ℓ_i = 1 state to a final state of ℓ_f = 0 or ℓ_f = 2 .......................................................... 108
4.37 Normalisation of free-to-free transition matrix elements from an initial ℓ_i = 1 state to a final state of ℓ_f = 0 or ℓ_f = 2 .......................................................... 109
5.1 Diagram of two-photon ionisation process for frequency $\omega > \varepsilon_{IP}$. ........................................ 112
5.2 Matrix elements of the two-photon ionisation process in atomic hydrogen given by our pseudostate calculation, and data given by Chan et al. [10] and Veniard et al. [11]. .......... 114
5.3 Two-photon ionisation cross-sections given by our pseudostate calculation and compared with Chan et al. [10]. ................................................................. 115
5.4 Diagram of hyperpolarisability from an initial state with $\ell = 0$ ................................................................. 116
5.5 $\gamma_{BBB}, \gamma_{BFF} + \gamma_{FBB} + \gamma_{FBB}$ and $\gamma_{BBF}$ with respect to the number of bound states included in the calculation ................................................................. 120
5.6 $\gamma_{BFF}$ as a function of the cut-off used in the integration. ................................................................. 124
5.7 Plot of (a) $\text{Re}[\gamma(\omega)]$ and (b) $\text{Im} \gamma(\omega)$ of H(1s) (in atomic units) given by our pseudostate calculation ($N_\ell = 120$ basis) for frequencies $\omega < E_{IP}/2$. ........................................... 127
5.8 $\gamma_{0101}$ and $\gamma_{0121}$ for frequencies above $E_{IP}/2$ given by our pseudostate calculation. .................. 128
5.9 Plot of $\text{Re}[\gamma(\omega)]$ of H(1s) given by our pseudostate calculation ($N_\ell = 120$ basis), Pan et al. [12] and Manakov et al. [13] for frequencies $\omega > E_{IP}/2$. Note that the calculation by Manakov et al. [13] uses a different definition for the hyperpolarisability. ........................................... 129
5.10 $\text{Im} \gamma_{0101}$ and $\text{Im} \gamma_{0121}$ from pseudostate calculation for frequencies above $E_{IP}/2$. ........ 130
5.11 $\text{Im} \gamma(\omega)$ at $\omega > E_{IP}/2$ from our pseudostate calculation, as well as Manakov et al. [13] and Pan et al. [12]. ......................................................... 130
5.12 $\text{Re} \gamma(\omega)$ and $\text{Im} \gamma(\omega)$ at $\omega = 0.3$ a.u. found by adding a small imaginary term $i\Delta$ to the energies in the hyperpolarisability and extrapolating to $\Delta = 0$. ........................................... 132
5.13 Plot comparing $\text{Im} \gamma(\omega)$ given by our pseudostate calculation with data from Pan et al. [12] and Chan et al. [10] for frequencies below the second ionisation threshold. .... 134
5.14 Plot of all scattering cross-sections of atomic hydrogen calculated with our pseudostate method. ......................................................... 135

6.1 Single-photon scattering cross-sections of ground state hydrogen isotopes ($^3$H, H, D and T). ......................................................... 138
6.2 Scattering cross-sections of positronium given by our pseudostate method. ......................................................... 140
6.3 Comparison of differential Compton scattering cross-sections in positronium from our pseudostate calculation and data given by Kaliman et al. [14]. ......................................................... 141
6.4 Our differential Compton scattering cross-sections for positronium for varying $N_\ell$ and $\lambda_\ell$, compared with differential cross-section data given by Kaliman et al. [14]. ......................................................... 142
6.5 The scattering cross-sections of metastable helium given by our pseudostate calculation up to photon frequency of 100 a.u. ......................................................... 143
6.6 Rayleigh and photoionisation cross-section found by applying our pseudostate method to a one-electron and two-electron code respectively. ......................................................... 144
6.7 Raman scattering cross-section of metastable helium found by applying our pseudostate method to one-electron and two-electron atomic structure code. ......................................................... 144
6.8 $\text{Re}[\gamma(\omega)]$ of metastable helium given by our pseudostate calculation. .......................... 145
6.9 $\text{Re}[\alpha(\omega)]$ of lithium given by our pseudostate method at frequencies below and above threshold. ................................................................. 148
6.10 The various single photon scattering cross-sections of atomic lithium, using our pseudostate calculation. ................................................................. 150
6.11 Compton scattering cross-section of atomic lithium for varying basis set size $N_e$. .............. 151
6.12 Compton scattering cross-section of atomic lithium for varying $\lambda_e$. ................................. 152
6.13 $\text{Re}[\gamma(\omega)]$ and $\text{Im}[\gamma(\omega)]$ of lithium given by our pseudostate calculation. ................. 157
6.14 Two-photon ionisation cross-section of Li($2s$) given by our pseudostate method and compared with data given by Mizuno [15]. ................................. 158
6.15 Rayleigh and photoionisation cross-sections of atomic sodium. ............................................. 160

7.1 Diagram showing two photon ionisation at frequency $\omega > \varepsilon_{IP}$ ............................................. 164
7.2 Diagram showing second possible approximation to the two-photon ionisation process at frequencies above ionisation energy $\varepsilon_{IP}$. ............................................. 165
7.3 $\sigma_{010}^{(2)}$ and $\sigma_{012}^{(2)}$ contribution to the two-photon ionisation cross-section for frequencies above threshold, using an approximation. ......................... 166
7.4 Diagram showing our approximation to the two-photon ionisation process at frequencies above ionisation energy $\varepsilon_{IP}$. ............................................. 166
7.5 $\sigma_{010}^{(2)}$ and $\sigma_{012}^{(2)}$ contribution to the two-photon ionisation cross-section for frequencies above threshold, using a second approach to the approximation. .......... 167
7.6 Hyperpolarisability of atomic hydrogen at frequencies above threshold without removing unphysical poles due to the pseudostates. ................................. 169

8.1 Scattering cross-sections of helium given by applying our pseudostate method to a two-electron atomic structure code and compared with previous calculations. ................. 176
8.2 Compton scattering cross-sections of helium given by applying our pseudostate method to a two-electron atomic structure code. ............................................. 177

A.1 Diagram showing relation between $\mathbf{r}$, $\mathbf{k}$ and $\mathbf{e}^{(\alpha)}$ vectors. ................................. 205

C.1 Plot of the normalised oscillator strengths for initial $1s$ state with new states added between the existing pseudostates using linear interpolation. ......................... 214
C.2 Plot comparing the unnormalised oscillator strengths from the old set and new set of states, where two new states are added in between each existing pseudostate. ................................. 214
C.3 Plot of the energy density of the original set of pseudostates and the new set of pseudostates given by pseudostate packing. ................................. 215
C.4 Plot of $\text{Re}[\alpha_{1s,1s}(\omega)]$ at frequencies below and above threshold, with and without pseudostate packing. ................................. 215
List of Tables

2.1 Extrapolation of the bound state sum $\alpha_{1s,1s}^B(0)$ to an infinite number of bound states in semi-analytical calculation of atomic hydrogen .................................. 36
2.2 Convergence of $\alpha_{1s,1s}^C(0)$ in semi-analytical calculation of atomic hydrogen w.r.t. the number of panels used in integration. ......................................................... 36
2.3 Extrapolation of the bound state sum $\alpha_{1s,1s}^B(\omega)$ to an infinite number of bound states at frequencies below threshold in our semi-analytical calculation of atomic hydrogen. .... 36
2.4 Convergence of $\alpha_{1s,1s}^C(\omega)$ with respect to the number of panels used in the integration at frequencies below threshold in our semi-analytical calculation of atomic hydrogen. .... 37
2.5 Extrapolation of $\alpha_{1s,1s}^B(\omega)$ in our semi-analytical calculation of atomic hydrogen at frequencies above ionisation energy. ......................................................... 38
2.6 Convergence of $\alpha_{1s,1s}^C(\omega)$ with respect to the number of panels used in the integration for frequencies above threshold in our semi-analytical calculation of atomic hydrogen. .... 39
2.7 Comparison of $\Re[\alpha_{1s,1s}(\omega)]$ (in atomic units) given by our semi-analytical calculation with the data given by Gavrila [16]. The contribution of the bound states to the total polarisability, $\alpha^B/(\alpha^B + \alpha^C)$ is also presented as a percentage. ............... 39
3.1 Convergence $\Re[\alpha_{1s,1s}(\omega)]$ and $\Im[\alpha_{1s,1s}(\omega)]$ at frequencies above threshold w.r.t. basis set size in our pseudostate calculation. ......................................................... 51
3.2 Comparison of $\alpha_{1s,1s}(\omega)$ given by our pseudostate method with the Langhoff method, our semi-analytical calculation and data given by Gavrila [1] at frequencies below threshold. 57
3.3 Comparison of $\alpha_{1s,1s}(\omega)$ given by our pseudostate calculation, the Langhoff method and our semi-analytical calculation at frequencies just above threshold. ............................. 57
3.4 Comparison of $\alpha_{1s,1s}(\omega)$ given by our pseudostate calculation and the Langhoff method at frequencies above threshold. ......................................................... 58
4.1 Comparison of the photoionisation cross-section of ground state atomic hydrogen given by our pseudostate calculation and the analytic expression. ............................. 68
4.2 Comparison of the photoionisation cross-section of ground state atomic hydrogen given by the FFAST database and the analytic expression. ............................. 68
4.3 Comparison of the transition matrix elements $T_{ij}$ given by the analytic expressions [17] and the normalised transition matrix elements $T^P_{ij}$ given by patom for transitions from state $i$ with $\ell = 1$ to state $j$ with $\ell = 2$. .................................................. 75

4.4 Convergence of free-to-free transition matrix element $T^V_{\ell_1 \ell_2}$ with respect to changing $N_{\max}$. .......................................................... 88

4.5 Compton scattering cross-section of atomic hydrogen and the contribution from $\ell = 0$ and $\ell = 2$ final states for various $N_\ell$ and $\lambda_\ell$. .................................................. 105

5.1 Hyperpolarisability components with respect to the maximum principal quantum number $n$ in the sum given by the pseudostate calculation using $N_\ell = 120$ basis set. .................................................. 121

5.2 Hyperpolarisability components with respect to the maximum principal quantum number $n$ in the sum given by the pseudostate calculation using $N_\ell = 100$ basis set. .................................................. 122

5.3 Hyperpolarisability components with respect to the maximum principal quantum number $n$ in the sum given by the pseudostate calculation using $N_\ell = 80$ basis set. .................................................. 123

5.4 $\text{Re}[\gamma(\omega)]$ and $\text{Im}_0[\gamma(\omega)]$ below the first ionisation threshold from pseudostate calculation with comparison to Shelton [18]. .................................................. 126

5.5 Convergence of $\text{Re}[\gamma(\omega)]$, $\text{Im}_0[\gamma(\omega)]$ and $\text{Im}_1[\gamma(\omega)]$ at above threshold frequency ($\omega = 0.3$ a.u.) for pseudostate calculations with increasing basis set size $N_\ell$. .................................................. 131

6.1 Energies, in atomic units, of the lowest states ($1s, 2s, 2p, 3s, 3d$) in the hydrogen isotopes $\infty\text{H}, \text{H}, \text{D}$ and T. .................................................. 137

6.2 Comparison of the $\text{Re}[\alpha(\omega)]$ of isotopes of hydrogen at several frequencies below threshold. .................................................. 137

6.3 Comparison of the Rayleigh and Raman scattering cross-sections of isotopes of hydrogen at several frequencies below threshold. .................................................. 139

6.4 $\gamma_{0101}(\omega)$, $\gamma_{0121}(\omega)$ and the total hyperpolarisability $\gamma(\omega) = \gamma_{0101}(\omega) + \gamma_{0121}(\omega)$ for metastable helium at frequencies above threshold given by our pseudostate calculation. .................................................. 146

6.5 Existing theoretical and experimental values of lithium polarisability of the ground state. .................................................. 148

6.6 Comparison of $\text{Re}[\alpha(\omega)]$ of lithium given by Manakov et al. and our pseudostate method at frequencies above threshold .................................................. 149

6.7 List of some of the calculations of static hyperpolarisability of lithium, in atomic units. .................................................. 152

6.8 Contributions to static hyperpolarisability of lithium involving excitation of one core and one valence electrons. .................................................. 156

6.9 Comparison of the energies (in atomic units) given by patom ($N_\ell = 120$ basis) with the experimental energies given by NIST [19]. .................................................. 159

6.10 Comparison of the oscillator strengths given by patom ($N_\ell = 120$ basis) with those given by Tang et al. [20] .................................................. 159

6.11 Hyperpolarisability calculated by replacing the first few energies and oscillator strengths with more accurate data. .................................................. 159
B.1 Table of energies (in atomic units) and oscillator strengths for a $N_\ell = 10$ and $\lambda_\ell = 0.5$ Laguerre basis set, as well as the sum of the oscillator strengths for initial states 1s, 2s, 3s and 3d. The numbers in brackets (x) denote ($\times 10^x$).

D.1 Static $\alpha$ and $\gamma$ of atomic hydrogen for various basis set sizes.

D.2 Re[$\alpha(\omega)$] of atomic hydrogen at frequencies below threshold for different basis set sizes.

D.3 Im$_0[\alpha_{1s,1s}(\omega)]$ of atomic hydrogen at frequencies below threshold for different basis set sizes.

D.4 Re[$\gamma(\omega)$] of atomic hydrogen at frequencies below threshold for different basis set sizes.

D.5 Im$_0[\gamma(0.2)]$ of atomic hydrogen for various basis set sizes.

D.6 Raman 1s-2s scattering cross-section of atomic hydrogen for different basis set sizes at frequencies below and above ionisation threshold.

D.7 3s-3d cross-section of atomic hydrogen for different basis set sizes at frequencies below and above ionisation threshold.

D.8 Total Raman scattering cross-section of atomic hydrogen with respect to basis set sizes at frequencies below and above ionisation threshold.

D.9 Rayleigh, Raman and photoionisation cross-sections of atomic hydrogen at frequencies above threshold for various $N_\ell$ and $\lambda_\ell$. 

XX
**List of Abbreviations**

**AMO**  Atomic, Molecular and Optical

**ATI**  Above Threshold Ionisation

**DFWM**  Degenerate Four Wave Mixing

**LTO**  Laguerre Type Orbital

**STO**  Slater Type Orbital
This page intentionally left blank.
Chapter 1

Introduction

How does a photon scatter off an atom? This is a very simple question, but one that surprisingly has not been entirely answered. Most atomic physics textbooks will teach about scattering processes such as Rayleigh, Raman, and Compton scattering, but do not present a plot of these processes. The scattering cross-sections for high-frequency photons are well-known, but there have been far fewer calculations of the photon-atom scattering cross-sections for low-frequency photons. In this thesis I develop a simple and intuitive method for computing the photon-atom scattering cross-sections for low photon frequencies. Our method relies on the computation of the complex polarisability and was first tested extensively on atomic hydrogen.

1.1 Scattering Cross-sections

The single-photon scattering processes considered in this thesis are Rayleigh, Raman, and Compton scattering, as depicted in Fig. 1.1. Rayleigh scattering is an elastic process where the incident photon $\omega$ and outgoing photon frequency $\omega'$ have equal energy, so $\omega = \omega'$. On the other hand, the Raman and Compton scattering processes are inelastic, where $\omega \neq \omega'$. After Raman scattering occurs, the electron is still bound to the atom, but after Compton scattering occurs, the atom is ionised. Since the photon must have enough energy to ionise the atom, Compton scattering can only occur at photon energies greater than ionisation energy.

The most common example of Rayleigh scattering is the scattering of sunlight by molecules (and atoms) in the atmosphere, resulting in our blue sky. As Rayleigh scattering has a $\omega^4$ dependence in the regime of visible light, the higher frequency is scattered more and we see a blue sky. Rayleigh scattering of low-frequency photons is also relevant in astrophysics, as it is used in modeling the atmosphere of exo-planets [21, 22] and hot stars [23].

Rayleigh scattering has been considered as a non-invasive diagnostic tool [24] in biological and medical applications for photon energies of 1-150 keV [25]. Usually in medical applications, such as when destroying malignant diseases, the aim is to reduce the amount of photon scattering [26] as scattered pho-
1.1. Scattering Cross-sections

Figure 1.1: Diagrams of the single-photon scattering processes with schematic atomic levels of hydrogen shown for reference. I.P. is the ionisation potential, with bound states below I.P. and continuum above. (a) shows Rayleigh scattering, where the incident and outgoing photon are equal in frequency. After Rayleigh scattering occurs, the atom is in its initial state. (b) shows Raman scattering, where the atom ends in a different bound state from its initial state. In this case the incident and outgoing photons have different frequencies. (c) shows Compton scattering which results in ionisation. This process can occur only if the incident photon has sufficient energy to excite the electron into the continuum.

Compton scattering refers to the inelastic scattering process where a photon is emitted with different energy than the incident photon. The shift in wavelength between the incident and scattered light is referred to as the Compton effect. Classically the scattering of a photon off a free electron is described by the Thomson cross-section, which is independent of the photon frequency. This is true for low frequencies, but at higher frequencies the cross-sections are dependent on photon frequency and scattering angle. The relativistic Klein-Nishina formula, developed in 1928 using quantum electrodynamics, successfully
describes the photon scattering off a free electron at both low and high photon frequencies below vacuum-pair production at \( \sim 1 \) GeV. Since the Klein-Nishina formula describes the scattering off a free electron, it needs to be modified to describe the scattering off an electron bound to an atom. Compton scattering off an atom is often approximated by multiplying the Klein-Nishina formula by an ‘incoherent scattering factor’ which takes into account the difference between scattering off a bound and a free electron [4].

Compton scattering is usually considered, both experimentally and theoretically, at high incident photon frequencies (x-ray to \( \gamma \)-ray regime) [30]. Experimental measurements of Compton scattering are usually done with synchrotron radiation, which has the benefit of higher photon flux in comparison to conventional radioactive x-ray sources [31]. Compton scattering of x-ray photons is used as a diagnosis tool in the medical field [32] as well as non-destructive testing and 3D imaging [32].

The total and differential scattering cross-sections play an important role in the modeling of radiation transport in materials. As the radiation passes through a material, a range of photon-matter interactions can occur - the photons can be absorbed or scattered, and can ionise the material. Ionizing radiation is used in radiation therapy to kill cancer cells. The photon transport is modeled using methods such as the Monte Carlo technique [33] which are used to determine how the material is ionised and where the energy is deposited. This modeling is also important for medical imaging applications. As an example, GEANT4 [34] is a software toolkit which is often used for radiation transport calculations. However, in order to accurately model this behaviour, the cross-sections of the various photon-atom processes are needed as input.

The photon-atom interaction can be written in terms of a non-relativistic Hamiltonian derived from the Lorentz force law [35], given by

\[
H_{\text{int}} \equiv -\frac{e}{2m_e c} \mathbf{p} \cdot \mathbf{A} - \frac{e}{2m_e c} \mathbf{A} \cdot \mathbf{p} + \frac{e^2}{2m_e c^2} \mathbf{A}^2 \equiv -\frac{e}{m_e c} \mathbf{p} \cdot \mathbf{A} + \frac{e^2}{2m_e c^2} \mathbf{A}^2 ,
\]

where \( \mathbf{p} \) is the momentum of the electron, \( \mathbf{A} \) is the vector potential, \( m_e \) refers to the electron mass, \( e \) is the charge and \( c \) refers to the speed of light. The first term describes the photon-atom interaction depicted in Figs. 1.2 (a) and (b), and the second term describes the interaction given by 1.2 (c).

Figure 1.2: Feynman diagrams of the photon-atom interaction involving the absorption and emission of one photon. (a) and (b) describe the \( \mathbf{p} \cdot \mathbf{A} \) and \( \mathbf{A} \cdot \mathbf{p} \) interactions, where a photon is first absorbed and then emitted, and vice-versa. (c) describes the \( \mathbf{A}^2 \) interaction where the photon is simultaneously absorbed and emitted.
There are various ways for the photon-atom interaction in single-photon scattering processes to occur, as depicted in Fig 1.2. At low frequencies the scattering process is more likely to occur via the process described in Fig 1.2 (a) and (b), where first one photon is absorbed and some time later a photon is emitted (or vice-versa). On the other hand, the interaction given in Fig 1.2 (c), where a photon is simultaneously absorbed and emitted, dominates at high incident photon frequencies [36].

Since the $A^2$ term dominates at high energies, the $p \cdot A$ term is usually neglected in calculations of scattering at high photon frequencies. Historically, the scattering cross-sections given by the $p \cdot A$ term was quite difficult to calculate, as the formula given by perturbation theory involves an infinite summation and integration. In contrast, many different methods were developed to compute the scattering cross-sections given by the $A^2$ interaction term [2–4, 37]. The various methods used to compute the scattering cross-sections given by the $A^2$ and $p \cdot A$ interaction terms will be discussed in Chapter 4.

Currently the scattering cross-sections used as input for modeling are usually taken from cross-section databases [33] such as the NIST-based XCOM [3], FFAST [2] and XXAMDI [38] databases. NIST refers to the National Institute of Standards and Technology. For example, the XCOM database [3] presents theoretical cross-sections for x-ray photon scattering off neutral atoms. These cross-sections are calculated by neglecting the $p \cdot A$ interaction, which is a valid approximation for high-frequency incident photons. On the other hand, in this thesis I have developed a method for computing the various scattering cross-sections governed by the $p \cdot A$ interaction using bound and pseudostate information. Pseudostates will be defined in the next section. These scattering cross-sections will give a more complete scattering picture than currently available through the existing databases, as the $p \cdot A$ interaction is the dominant process at low frequencies. The atomic structure code that produces the pseudostate information used in our method is introduced in the next section.

### 1.2 Atomic Structure Code

The new computational method developed in this thesis to compute the polarisabilities and scattering cross-sections is referred to as the ‘pseudostate method’, since a defining feature of the method is the presence of pseudostates in our calculation. Our method utilises the atomic structure data produced by the non-relativistic, single-electron code patom, developed by M. W. J. Bromley [39]. This code uses a finite basis set of Laguerre functions, which effectively models the atom to be in a box.

The properties of an atom, such as the energies and oscillator strengths of atomic states, can be found by solving either the non-relativistic Schrödinger equation or the relativistic Dirac equation. patom solves the non-relativistic Schrödinger equation using a basis set of Laguerre functions and applying the configuration interaction method. For completeness I will briefly introduce these methods here. For more details, please see references [39–44].
1.2.1 Configuration Interaction

How are the wavefunctions built? In the (variational) configuration interaction method, the trial wavefunctions are built as a sum of configurations,

$$\psi = \sum_{i=1}^{N_s} c_i \Phi_i ,$$  \hspace{1cm} (1.2)

where $\Phi_i$ corresponds to the different configurations. In a one-electron atom, the configurations are the set of single-particle orbitals given by

$$\Phi_i = \frac{P_{i\ell_i}(r)}{r} Y_{\ell_i m_i}(r) ,$$  \hspace{1cm} (1.3)

where $P_{i\ell_i}(r)$ is the radial function and $Y_{\ell_i m_i}$ a spherical harmonic.

The radial function $P_{i\ell_i}(r)$ is given by the set of basis functions $\chi_{\alpha,\ell_i}$,

$$P_{i\ell_i}(r) = \sum_{\alpha} d_{\alpha i} r \chi_{\ell_i m_i}(\hat{r}) ,$$  \hspace{1cm} (1.4)

where $d_{\alpha i}$ is the expansion coefficient. There are several different types of basis functions, such as Slater-type orbitals (STO) or Laguerre-type orbitals (LTO). patom uses Laguerre-type orbitals, which will be discussed in more detail in 3.1.

From Schrödinger’s equation we then have an eigenvalue problem:

$$\sum_{i=1}^{N_s} \left( \langle \Phi_j | H | \Phi_j \rangle - \epsilon \langle \Phi_i | \Phi_j \rangle \right) c_i = 0 ,$$  \hspace{1cm} (1.5)

where $j = 1, \ldots, N_s$. This eigenvalue problem gives a set of eigenvalues $\epsilon$, which have corresponding eigenvectors $\{c_i\}$ and give the wavefunction $\psi$.

The variational method can be used to optimise the parameters in the trial wavefunction. The energy of a trial wavefunction $\Psi_t$ must be greater than the ground state energy $\epsilon_0$:

$$\epsilon_0 \leq \epsilon_t = \frac{\langle \psi_t | H | \psi_t \rangle}{\psi_t \psi_t} .$$  \hspace{1cm} (1.6)

The optimised parameters are found by searching for the values where the variation in energy is minimised,

$$\delta \epsilon = \delta \langle \psi_t | H | \psi_t \rangle = 0 .$$  \hspace{1cm} (1.7)

The eigenvalues given by the eigenproblem in Eqn. 1.5 can be negative or positive in energy. The eigenstates with negative energies correspond to bound states, whilst eigenstates with positive energies correspond to pseudostates. Both the bound states and pseudostates are stationary states, since they are eigenstates of the Hamiltonian for one particular basis set. Though the energy of the pseudostates change
for a different basis set, these are also stationary states.

Fig. 1.3 compares the structure of atomic hydrogen in an analytic calculation versus a calculation using a finite-basis set. The states with positive energy correspond to electrons that are not bound to the atom. In theory, an electron that is not bound to the nucleus should be able to have any positive energy. However, due to the fact that the basis sets are finite, only a finite number of positive energy states can be described in the calculation. These are an approximation to the continuum, and are not physical (unlike the bound states). For this reason the discrete positive energy states are referred to as pseudostates.

Figure 1.3: Comparison of the atomic structure of hydrogen in an analytic calculation with a calculation using a finite-basis set. A finite-basis set effectively models the atom to be in a box and discretises the continuum. Rather than a continuous function describing the continuum (as in the analytic calculation), the finite-basis set produces a set of unphysical ‘pseudostates’ approximating the continuum. The energies of these pseudostates are dependent on the basis set.

In order to show the behaviour of bound and pseudostates with respect to basis set, I have plotted the energies of $\ell = 0$ states in Fig. 1.4 for calculations with $N_\ell = 10, 11$ and 12 basis functions. In Fig. 1.4 (left) we can see the appearance of an extra bound state as $N_\ell = 10 \rightarrow 11$, as well as the lowering of eigenstate energy as per the Hylleraas-Undheim Theorem [45] for $N_\ell = 11 \rightarrow 12$. This plot shows that the lowest-lying bound states are accurately calculated and do not change for $N_\ell = 10, 11$ and 12, and the energy of the higher excited bound states become more accurate as we increase basis set size. On the other hand, the plot of pseudostates (positive energies) in Fig. 1.4 (right) clearly shows that the pseudostates vary as the basis set is changed. This demonstrates that the pseudostates are not physical states.

Though the basis sets are finite, they are able to build accurate representations of low-lying bound states. This is because the wavefunctions for bound states are localised near the nucleus and have only a few oscillations. The more functions are included in the basis set, the better the description of the bound states, particularly for bound states with higher energy (which have more oscillations in the wavefunction).

Throughout this thesis I usually use a large basis of $N_\ell = 120$ for $\ell = 0, ..., 5$. This was found to be an adequate representation of the continuum by studying convergence with respect to basis set size. $N_\ell = 120$ was as large as possible with numerical integration (quad-precision) and gives a finer discretisation of the
Figure 1.4: Plot of the energies (in atomic units) of atomic hydrogen for ($\varepsilon < 0$) bound states (left) and ($\varepsilon > 0$) pseudostates (right) for basis set size $N_{\ell} = 10, 11$ and 12. Only energies of $\ell = 0$ states are included. Note (left) the appearance of an extra bound state as $N_{\ell} = 10 \rightarrow 11$, whilst $N_{\ell} = 11 \rightarrow 12$ only results in (variational) lowering of eigenstate energies as per the Hylleraas-Undheim theorem [45]. (Right) Arrows indicate how pseudostate energies change as basis set size is increased. Though it cannot be clearly seen on this plot, note that the lowest lying $N_{\ell} = 10$ pseudostate changed in $N_{\ell} = 11$ to a bound state.
continuum. \( N_\ell = 50 \) is used in past work with patom. Here we wanted as many pseudostates as possible to test our method.

Fig. 1.5 plots \( r \psi_n \), where \( \psi_n \) is the wavefunction of the first few states of angular momentum \( L = 0 \) given by patom, whilst Fig. 1.6 plots \( r \psi_n \) for three states with energy closest to \( \varepsilon = 2 \) a.u. The continuum states should be plane waves that extend to \( r \to \infty \), but instead of oscillating to infinity, the wavefunctions go to zero at some distance away from the nucleus. Effectively this models a soft-walled box which is dependent on the basis set size.

Later in this thesis I will refer to the number of bound states as \( N_B \) and the number of pseudostates \( N_P \). As this is a numerical variational method that approximates the bound states, there is no definition that allows us to calculate the number of bound states given by a certain basis set without solving the eigenvalue problem. However, it is known that the larger the basis set, the greater the number of bound states \( N_B \). Similarly, there is no definition relating \( N_B \) and \( N_P \), except that as we increase the basis set, both the number of bound and pseudostates tend to increase.

The analytic expressions for wavefunctions of atomic hydrogen are well-known, so why use a numerical approach? The analytic expressions describe the complete set of atomic eigenstates, whereas my numerical approach only has a finite set of eigenstates. The reason I use this numerical approach is because the final aim is to calculate scattering cross-sections for any atom. Hydrogen is the only atom for which exact expressions are known. Even helium (with only two electrons) must be solved numerically. In this thesis I develop a numerical method for calculating scattering cross-sections that is based on pseudostates - my ‘pseudostate method’. My method is tested on atomic hydrogen, which has the advantage that I can also compare with semi-analytical results (calculated in Chapter 2). Since my method is numerical and uses only a finite number of eigenstates, it can be applied to atoms other than hydrogen, as shown in Chapter 6.

In Chapter 6 I have calculated polarisabilities and scattering cross-sections for positronium, metastable
1.2. Atomic Structure Code

helium, lithium and sodium. `patom` builds the wavefunctions for positronium in exactly the same way as for hydrogen, but a reduced mass of $M = 1/2$ is used instead. Like hydrogen, a basis set of Laguerre-type orbitals are used to build the wavefunctions for metastable helium, lithium and sodium. Though lithium and sodium have a single valence electron like hydrogen, they also have core electrons.

The core-direct and core-exchange potentials $V_{dir}$ and $V_{exc}$ are calculated exactly using a Hartree-Fock calculation and Slater-type orbitals. A core-polarisation potential is tuned to improve the accuracy of the frozen core calculation. The wavefunctions of the valence electrons are orthogonal to the core, to prevent them from collapsing into the core electron wavefunctions. Detailed information on the core electron calculation in `patom` is given in reference [39]. Though metastable helium has two electrons, the wavefunctions can be built by `patom` (which is a single-electron code) by considering the $2^3S_1$ state to be the ground state and considering the other electron as the core electron.

A large amount of atomic data produced by this code has already been published to investigate positron-atom scattering, where polarisability is important to describe the distortion of the electron by a positive charge ($e^+$) [39–41]. It has also been used to compute various atomic properties such as Van der Waal’s coefficients for positronium-atom interactions [42], atomic hydrogen [43], as well as alkali-metal and alkaline-earth-metals [44]. `patom` produces a list of energies for all states in the calculation, as well as the transition matrix elements between each of these states. More detail can be found in reference [39]. I have used this data to develop a computational method for producing photon-atom scattering cross-sections.

Various basis functions can be used in finite-basis set calculations, such as B-splines, Gaussian functions, Hylleraas functions or Laguerre functions. The Laguerre functions used in `patom` have the advantage of being orthogonal and produce a set of pseudostates that give a good description of the continuum. The finite basis set method has been previously used to compute Rayleigh and photoionisation cross-sections [5, 46]. However, our method utilises pseudostates to compute the complete set of Rayleigh, Raman, Compton, and photoionisation cross-sections as well as two-photon ionisation and higher-order scattering processes.

The LTOs in our pseudostate method have been previously used to accurately compute the higher-order Van der Waals coefficients up to $C_{16}$ [43] and even coefficients up to $C_{30}$ [47]. As these calculations use the same LTOs and transition matrix elements as in our method, we had good reason to believe that our pseudostate method would be able to accurately compute the various scattering cross-sections. Though we have been able to compute the Rayleigh, Raman and photoionisation cross-sections with our pseudostate method, it turns out that it does not give converged Compton scattering cross-sections as we vary the box size. These results are presented and discussed in Chapter 4.
1.3 Method for Computing Cross-sections

Our calculation of the cross-sections relies on the computation of the atomic polarisability. For example, the Rayleigh scattering cross-section is related to the polarisability $\alpha_{ii}(\omega)$ by [8, 46, 48]

$$\sigma_i = \sigma_T \omega^4 |\alpha_{ii}(\omega)|^2,$$

(1.8)

where $\omega$ is the incident photon frequency and $\sigma_T$ is the Thomson cross-section which describes the scatter off a free electron (discussed further shortly). An expression for the polarisability can be derived from the $\mathbf{p} \cdot \mathbf{A}$ Hamiltonian and second-order perturbation theory. Qualitatively the polarisability describes the deformation of the electron charge cloud when an electric field is applied, inducing a dipole moment. The polarisability describes the process where an atom initially in state $|i\rangle$ absorbs and emits a photon of frequency $\omega$ to end in the same state $|i\rangle$.

The polarisability can also be generalised to describe the process where an atom initially in state $|i\rangle$ absorbs a photon of frequency $\omega$ and emits a photon of frequency $\omega'$, resulting in a transition to the final state $|j\rangle$. We refer to this as the transition polarisability, which is given by the Kramers-Heisenberg matrix element [48] (ignoring fine-structure) to be

$$\alpha_{ij} = \sum_t C_{i,t,j} \left[ \frac{\langle j|z|t\rangle \langle t|z|i\rangle}{\epsilon_{ti} - \omega} + \frac{\langle j|z|t\rangle \langle t|z|i\rangle}{\epsilon_{ti} + \omega} \right],$$

(1.9)

where $C_{i,t,j}$ is a coefficient dependent on the angular momentum of the initial, intermediate and final states. The derivation of this expression is briefly presented in Chapter 2 and presented in more detail in Appendix A. The transition polarisability involves a sum over the (intermediate) bound states and an integral over the (intermediate) continuum. In our pseudostate method we compute this by performing a sum over all intermediate states in our system.

Like the Rayleigh scattering cross-section, the Raman scattering cross-section is also related to the transition polarisability. Only very few calculations of the Raman scattering cross-section have been done by considering the $\mathbf{p} \cdot \mathbf{A}$ interaction term [7, 8]. In comparison, the method developed in this thesis allows us to compute the Raman scattering cross-section for any initial and final bound state. We have also attempted to apply our pseudostate method to the calculation of the Compton scattering cross-sections. However this calculation gives interesting lack of convergence issues which are considered in detail in Chapter 4.

In our pseudostate method we also use the transition polarisability to compute the two-photon ionisation cross-section. This cross-section describes the process where two photons are absorbed, exciting the electron to the continuum and ionising the atom. This process is illustrated in Fig. 1.7 and shows that the atom is ionised for photon energy greater than half the ionisation energy. This is referred to as the first (or two-photon) ionisation threshold. The ionisation energy is then referred to as the second (or single-photon) ionisation threshold.
The two-photon ionisation cross-section is related to the imaginary hyperpolarisability, which is another atomic property which we have been able to compute with our pseudostate method. The expression for hyperpolarisability is derived from fourth-order perturbation theory and describes scattering processes involving four photons, such as degenerate four wave mixing (DFWM), the DC Kerr effect and third-harmonic generation. Our pseudostate method is able to compute the complex hyperpolarisability at frequencies both below and above the first ionisation threshold.

The polarisability and hyperpolarisability computed by our method are useful not only for calculating the single- and multi-photon scattering processes but also for computing the Stark shift.

## 1.4 Stark Shift

The Stark shift refers to the shift in energy of an atomic state when perturbed by an electric field. The second and fourth order corrections to the energy of state $n$ are given by the polarisability and hyperpolarisability respectively. The energy of state $n$ when perturbed by an electric field $E$ with frequency $\omega$ is

$$
\varepsilon_n(\omega) = \varepsilon_n^{(0)} + \Delta \varepsilon_n = \varepsilon_n^{(0)} + \varepsilon_n^{(2)}(\omega) + \varepsilon_n^{(4)}(\omega) + \ldots ,
$$

where $\varepsilon_n^{(0)}$ is the energy of the $n$th unperturbed state and $\Delta \varepsilon_n$ is the Stark shift of the state. The second-order energy correction is given by

$$
\varepsilon_n^{(2)}(\omega) = -\frac{1}{2} \alpha_{nn}(\omega) E^2 ,
$$

where $\alpha_{nn}(\omega)$ is the frequency-dependent polarisability and $E$ is the magnitude of the electric field. The polarisability has both a scalar and tensor component [49], given by

$$
\alpha_{nn}(\omega) = \alpha_{nn}^{(0)} + \alpha_{nn}^{(2)} g_2(\ell, m) ,
$$

where $\alpha_{nn}^{(0)}$ is the scalar component and $\alpha_{nn}^{(2)}$ the tensor component. $g_2(\ell, m)$ is a coefficient that is dependent on the angular moment $\ell$ of state $n$, and the magnetic quantum number $m$ (see reference [20] for definition of $\alpha_{nn}^{(2)}$ and $g_2(\ell, m)$). The tensor component is non-zero only for $\ell > 0$, as $g_2(\ell, m) = 0$ for $\ell = 0$. Throughout this thesis I have considered only $s$-state atoms, for which the polarisability contains only a scalar component. The reason for this is that the primary goal was to develop and test our
1.4 Stark Shift

Once this has been done, it is simply a matter of applying our pseudostate method to calculate the tensor polarisability.

The fourth-order contribution to the Stark shift is given by

\[ \varepsilon_n^{(4)}(\omega) = -\frac{1}{4!} \gamma_n(\omega) E^4, \]  

(1.13)

where \( \gamma_n \) is the second hyperpolarisability. The “first” hyperpolarisability is the third-order term, which is zero due to atomic symmetry, but is seen in crystals and molecules [50]. The second hyperpolarisability will be referred to simply as hyperpolarisability throughout this thesis. The hyperpolarisability has scalar and tensor terms [20],

\[ \gamma_n = \gamma_n^{(0)}(\omega) + \gamma_n^{(2)}(\omega) g_2(\ell, m) + \gamma_n^{(4)}(\omega) g_4(\ell, m), \]  

(1.14)

where \( \gamma_n^{(0)} \) is the scalar hyperpolarisability, and \( \gamma_n^{(2)} \) and \( \gamma_n^{(4)} \) are the tensor terms. The definitions for \( \gamma_n^{(2)}, g_2(\ell, m), \gamma_n^{(4)} \) and \( g_4(\ell, m) \) can be found in reference [20]. However, these will not be stated here as I consider only s-state atoms in this thesis, where the hyperpolarisability has only the scalar component \( \gamma_n^{(0)} \). The coefficients \( g_2(\ell, m) \) and \( g_4(\ell, m) \) are non-zero only for states with \( \ell > 0 \). Our pseudostate method will be extended to the calculation of the hyperpolarisability in Chapter 5, and the definition and calculation of \( \gamma_n^{(0)} \) will be presented there.

Note that the polarisability and hyperpolarisability are dependent on the polarisation of light, i.e. whether linear, circular or even elliptical polarisation is considered. Though in this thesis all calculations are done with linear polarisation, it is also possible to apply our method to calculation of polarisabilities and hyperpolarisabilities with varying polarisation. The overall definition of hyperpolarisability can be written as a function of the linear and circular polarisation [13], such that

\[ \gamma_{jklm} = (\gamma_n - \gamma_c) \delta_{jk} \delta_{lm} + \frac{1}{2} \gamma_c (\delta_{jl} \delta_{km} + \delta_{jm} \delta_{kl}) \]

where \( j, k, l, m = x, y, z \), the linear polarisation is given by \( \gamma = \gamma_{zzzz} \) and the circular polarisation \( \gamma_c = 2\gamma_{zzxz} \). However, in this thesis only the linear polarisation is considered, and \( \gamma = \gamma_{zzzz} \) is meant when referring to the hyperpolarisability symbol, \( \gamma \), throughout this thesis. See references [13] and [51] for more discussion on the calculation of polarisability or hyperpolarisability with linear and circular polarisation. The expression for calculating the frequency-dependent hyperpolarisability (for linear polarisation) is presented in Chapter 5.

### 1.4.1 Polarisability

The static polarisability \( \alpha_{nm}(\omega) \) is known for very many atoms [52], but the frequency-dependent polarisability is less well-known. The polarisabilities have applications in atomic clock and AMO experiments which rely on measuring the frequency of a specific transition to very high precision. Since the lasers in the experiment influence the energy of the atomic states, the frequency of the transition is dependent on
the wavelength of these lasers. To avoid this, the laser wavelength is chosen to be where both states in the transition shift in energy by the same amount. This is referred to as the magic wavelength and is found by determining where the polarisability of the states are equal.

As a consequence of this, there have been very many calculations of the atomic polarisability $\alpha_{nn}(\omega)$ for many atoms. However, far fewer papers have been published that consider the polarisability as a complex term. In fact, the polarisability has two imaginary terms, related to the finite linewidth due to non-zero decay rate of the atomic states and the possibility of ionisation respectively. Though there have been many calculations of the real part of the polarisability, most calculations consider only incident photon energies less than the ionisation energy. Gavrila [1, 16] derived analytic expressions for the polarisability of atomic hydrogen at frequencies above threshold as early as 1967, but these apply only to hydrogenic atoms. In this thesis I present a method for computing the complex polarisability at frequencies both below and above threshold in a unified calculation. The advantage of the computational method introduced in this thesis is that it can be applied to any atom and any initial state.

The polarisability of atomic hydrogen will be considered using semi-analytic methods in Chapter 2. Chapter 3 will present our computational method for computing the polarisability using the energies and transition matrix elements provided by $\text{patom}$. These complex polarisabilities will be used in Chapter 4 to compute the various scattering cross-sections involving the absorption of one photon.

### 1.4.2 Hyperpolarisability

The hyperpolarisability, with minor modifications, describes four-photon processes such as degenerate four wave mixing (DFWM) [18] where two-photons are absorbed, and two emitted, i.e. elastic scattering of two-photons. Our computational method of the complex polarisibility is extended to the complex hyperpolarisability at frequencies both below and above the first ionisation threshold. In comparison to the polarisability, there have been far fewer calculations of the hyperpolarisability as the contribution to the Stark shift is usually considered negligible. See Thakkar et al. for a good introduction to hyperpolarisabilities [52].

Most calculations consider only the static hyperpolarisability, where $\omega = 0$ a.u, and far fewer consider the dynamic hyperpolarisability particularly, at frequencies above the ionisation threshold. A previous calculation of the hyperpolarisability at frequencies above threshold was done by Manakov et al. in 1986 [13] and 2004 [53] for atomic hydrogen, using Green’s functions. Pan et al. [12] have also computed the hyperpolarisability of atomic hydrogen above threshold in 1991 using a complex rotation method. Takamoto et al. [54] have also presented a plot of the real and imaginary component of the hyperpolarisability for strontium, though the method of calculation of the imaginary hyperpolarisability was not discussed.

Originally the rapidly increasing accuracy of atomic clocks was the motivation of this thesis for considering theoretically the frequency dependent hyperpolarisability and scattering cross-sections. Over recent years atomic clocks have reached extraordinary levels of accuracy and stability. Single-ion clocks
have reached systematic uncertainties of \(3 \times 10^{-18}\) \[55\] and optical lattice clocks are currently the most accurate and stable, with systematic uncertainties down to \(2.1 \times 10^{-18}\) \[56\].

As mentioned previously, the magic wavelength refers to the wavelength of light at which the polarisability of both clock states are equal. Though the hyperpolarisability also influences the shift in energy of the atomic states, it is usually neglected in calculations of the magic wavelength. The relative energy shift of the transition from the hyperpolarisability term has been considered theoretically for the Sr optical lattice clock in 2003 \[57\] to be as small as \(5 \times 10^{-18}\) at the 800nm wavelength. Though the higher order contribution is extremely small and difficult to measure, atomic clocks are pushing the systematic uncertainties down to the \(10^{-18}\) level and possibly even smaller in the future. The small effect of the hyperpolarisability will become significant as the clocks become more and more accurate. This was our original motivation for developing a pseudostate method that is able to compute the frequency dependent hyperpolarisability at frequencies both below and above threshold.

In this thesis I have extended the computational method for the complex polarisability to the complex hyperpolarisability for frequencies both below and above the first ionisation threshold. In Chapter 5 I show that the real hyperpolarisability calculated with our method is in agreement with the data presented by Pan et al. \[12\].

### 1.5 Above Threshold

In this thesis I apply our pseudostate method to the calculation of single and two-photon cross-sections as well as polarisability and hyperpolarisability. As I have mentioned previously, the polarisability has been calculated many times at frequencies below threshold, but there are far fewer calculations of hyperpolarisability. Similarly there have been many calculations of the two-photon ionisation cross-section over the years, but only few calculations of the Raman and Compton scattering cross-section (due to the \(\mathbf{p} \cdot \mathbf{A}\) interaction).

Most papers have calculated only one or two of these various properties, instead of applying a single method and computing all cross-sections. Rather than presenting an overview for the literature each of the individual cross-section or polarisabilities here, I will discuss the literature in the relevant Chapters. However, there is one difficulty that is common to all calculations in this thesis, and that is calculation at frequencies above threshold.

Though there have been many calculations of polarisability below threshold, there have been relatively few at frequencies above threshold and far fewer calculations of the hyperpolarisability above threshold. These calculations are difficult at frequencies above threshold because they involve expressions with a denominator \(\varepsilon_t - \varepsilon_i - \hbar \omega\) (see for example Eqn. 1.9), where \(|t\rangle\) is the intermediate state energy, \(\varepsilon_i\) is the initial state energy and \(\omega\) is the frequency of the electric field. Since the polarisability involves an integral over the continuum energy \(\varepsilon_t\), this denominator results in an unphysical pole when \(\hbar \omega = \varepsilon_t - \varepsilon_i\).
Several different approaches have been used to calculate the polarisabilities or cross-sections at frequencies above threshold. The papers I will discuss below are not an exhaustive list but gives an overview of some of the methods present in literature:

- **Analytical Approach**: Gavrila [1, 16] derived analytic expressions for the Kramers-Heisenberg matrix elements of atomic hydrogen for initial $1s$ and $2s$ states for frequencies above ionisation threshold. In this approach the integral is evaluated analytically. This analytical approach was also used by Florescu et al. [7] to find the transition polarisabilities for the $3s-3s$ and $3s-3d$ transitions at frequencies above threshold.

- **Analytical Approach**: Gavrila [58, 59] also derived analytic expressions for the differential Compton scattering cross-section of atomic hydrogen. These expressions were later used by Drukarev et al. [9] and Bergstrom et al. [4] to compute the Compton scattering cross-section of atomic hydrogen. These are the only two calculations of Compton scattering cross-section of atomic hydrogen (for the $p \cdot A$ interaction). The disadvantage of using an analytical approach to calculate the cross-sections at frequencies above threshold is that this is only valid for atomic hydrogen or hydrogenic atoms. On the other hand, methods based on a finite-basis set atomic structure calculation should be applicable to many atoms.

- **Sturmian expansion of Green’s functions**: Manakov et al. have computed both the hyperpolarisability [13, 53] and polarisability [60] at frequencies above threshold. This method computes the polarisabilities and hyperpolarisabilities by writing these in terms of the Coulomb Green’s functions and using the properties of Sturmian functions to find converging values at frequencies above threshold. This method should be handled with care, as the imaginary polarisability of lithium given by Manakov et al. [60] is in disagreement with our calculation and other literature values.

- **Complex Rotation Method**: This method was originally used to find resonances energies and resonance widths and later for the calculation of ionisation cross-sections [61]. The complex rotation method involves rotating the radial coordinates into the complex plane, such that the (above threshold) energies have both a real and imaginary part [62, 63]. Pan et al. [12] have combined this method with Dalgarno-Lewis to compute the complex second and fourth order energy correction (related to the complex polarisability and hyperpolarisability respectively). Since the energies are complex in this method, they no longer have to deal with the pole due to the energy difference in the denominator, and are able to compute at frequencies above threshold. Since the imaginary hyperpolarisability is also related to the two-photon ionisation process, they are able to calculate this cross-section as well. However, they have presented only calculations of the polarisability where initial and final state are equal, and no calculations of single-photon scattering cross-sections.

- **Principal Value Approach**: Cormier et al. [64] have calculated the above threshold ionisation (ATI) cross-section by adding a small imaginary term $i\Delta$ into the denominator and tuning this to zero. In
this way they can extrapolate $\Delta$ to 0 and determine the ATI cross-section. I call this the principal value approach as it is effectively removing the effect of the pole by integrating around it in the integral plane (i.e. principal value integration).

- Pseudostate Approach: ATI refers to the process where more than one photon is absorbed and the atom is ionised. In this process more photons are absorbed than needed to ionise the atom. Bachau et al. [65,66] have also calculated the ATI cross-section with a method similar to the one I will apply in this thesis. In their method they have removed the effect of the unphysical pole by removing the state causing this divergence from the calculation. They use a set of Slater type orbitals (STOs) which are dependent on the parameter $\eta$ and the relation of this parameter to the atomic energies is known. Thus they can vary this parameter to give a state with energy that corresponds to the incident photon frequency, and remove this state from the calculation. In this way they can remove the effect of the unphysical pole. Though they have shown that they are able to compute the above threshold ionisation cross-section in this way, they do not seem to have extended this method to the calculation of other scattering cross-sections.

- Time-Dependent Schrödinger Equation: In later papers Bachau and co-workers [67–69] have computed the stimulated Raman and Compton scattering cross-sections, but these do not use the approach they have applied in their ATI cross-section calculations. Instead these scattering cross-sections are calculated using either the analytic expressions derived by Gavrila et al. or by solving the time-dependent Schrödinger equation.

In Chapters 2 and 3 I will show how we remove the effect of the unphysical pole at frequencies above threshold, in the semi-analytical and pseudostate calculation respectively. In the next section I will present the first calculations of the polarisabilities, hyperpolarisability and scattering cross-sections in atomic hydrogen.

1.6 A Brief History of Atomic Hydrogen

Atomic hydrogen is a suitable test atom as it has only one valence electron, and no core electrons. It is also the only atom which can be exactly described by analytical functions. For this reason I have first tested our pseudostate method with atomic hydrogen in Chapters 2 to 5 before applying our pseudostate method to other atoms in Chapter 6. An overview of the first calculations for atomic hydrogen for polarisabilities, hyperpolarisability and scattering cross-sections are given in the following timeline:

1925: Kramers and Heisenberg [70] derive the Kramers-Heisenberg expression.

1926: First calculations of static polarisability of atomic hydrogen independently by Epstein, Waller and Wentzel [71–73].
1929: Gordon [17] derives general analytic expressions (containing hypergeometric functions) for the transition matrix elements of atomic hydrogen. In Chapter 2 these analytic expressions will be used in a semi-analytical calculation of the hydrogen polarisability.

1931: Two-photon absorption predicted by Goeppert-Mayer [74].

1949: First analytic calculation of static hyperpolarisability of atomic hydrogen by Sewell [75].

1964: First calculation of two-photon ionisation cross-section by Zernik et al. [76,77]. This was followed by calculation by Gontier et al. in 1968 [78] and Chan et al. in 1969 [10]. In Chapter 5 our method for the complex polarisabilities will be extended to the calculation of the two-photon ionisation cross-sections as well.

1967: Gavrila [1, 16] derives analytic expressions for elastic scattering of atomic hydrogen. The polarisability of the ground state hydrogen presented in these papers was used to validate both the semi-analytical calculation in Chapter 2 and pseudostate calculation in Chapter 3.

1969: Gavrila [79] derives analytic expressions for the Compton scattering of the ground state of atomic hydrogen and demonstrated the presence of the infra-red divergence in the differential Compton scattering. Gavrila further investigated the Compton scattering of atomic hydrogen in 1972 [58,59].

1979: In 1979 Gavrila [6] also derived the expressions for elastic scattering of the \( n = 2 \) states of atomic hydrogen.

1985: Florescu et al. [7] use a similar method to Gavrila to derive the analytic expression for Rayleigh scattering of the \( n = 3 \) states of atomic hydrogen and the “Raman” 3s-3d scattering cross-sections.

1986: Manakov et al. [13] compute the complex hyperpolarisability of the ground and excited states of atomic hydrogen. They have stated that this is the ‘first correct calculation’ of the hyperpolarisability at above threshold frequencies. In 2004 Manakov et al. [53] also presented the complex hyperpolarisability of excited states of atomic hydrogen.

1987: Shelton [18] computes the frequency dependent hyperpolarisability of atomic hydrogen at frequencies below threshold for various four photon scattering processes (e.g. DFWM, DC Kerr). The hyperpolarisability given by Shelton is used in Chapter 5 to validate my hyperpolarisability calculation of atomic hydrogen below threshold.

1991: S-matrix method is used to consider the Compton scattering cross-section (\( \mathbf{A}^2 \) and \( \mathbf{p} \cdot \mathbf{A} \) contribution) by Suric et al. [80], including relativistic corrections.

1992: Sadeghpour et al. [8] computes the Raman 1s-2s scattering cross-section of atomic hydrogen at frequencies below threshold. This is the only Raman scattering cross-section data for the ground state of atomic hydrogen. In Chapter 4 I show that our method agrees with the calculation by
Sadeghpour \textit{et al.} and compute the Raman scattering cross-sections at above threshold frequencies as well. Thus, I present the first calculation of the \textit{total} Raman scattering cross-section, which is a sum over all the possible Raman scattering transitions.

\textbf{1993:} In their extensive discussion of Compton scattering from bound electrons in 1993, Bergstrom \textit{et al.} \cite{4} present the $p \cdot A$ contribution to Compton scattering of atomic hydrogen calculated from Gavrila’s expressions (derived in 1969). In Chapter 4 I will show that our calculation gives Compton scattering cross-sections that are up to three orders of magnitude larger than those presented by Bergstrom \textit{et al.}.

\textbf{2010:} Drukarev \textit{et al.} \cite{9} present the total and differential Compton scattering cross-sections of atomic hydrogen, using the expressions derived by Gavrila in 1969. The differential Compton scattering cross-sections presented by Drukarev \textit{et al.} are compared against our differential Compton scattering cross-sections in Chapter 4.

\section{1.7 Natural Units}

The system of atomic units is often used in atomic physics in order to simplify formulae. The numerical factors in equations are reduced by effectively setting

\begin{equation}
    e = m_e = h = 4\pi\varepsilon_0 = 1,
\end{equation}

where $e$ is the electric charge, $m_e$ is the electron mass, $\varepsilon_0$ is the vacuum permittivity and $h = h/2\pi$ where $h$ is Planck’s constant. In atomic units the hydrogen energy levels are then given simply by

\begin{equation}
    E_n = -\frac{1}{2n^2}.
\end{equation}

Since $h = 1$, then energy and frequency are equivalent in atomic units ($E = \omega$). Though atomic units are convenient for theoretical work, others usually prefer units such as electronvolts (eV) or wavelength (nm). The fundamental constants used in the conversions are taken from NIST CODATA 2014 \cite{81}. The energy conversion from atomic units to eV and J is given by

\begin{equation}
    1 \text{ a.u.} = 1 E_h = 27.21138602 \text{ eV} = 4.359744650 \times 10^{-18} \text{ J},
\end{equation}

where $E_h$ refers to the Hartree energy. The atomic units of energy can be converted to frequency using

\begin{equation}
    1 \text{ a.u.} = 4.1341373 \times 10^{16} \text{ s}^{-1}.
\end{equation}
1.7. Natural Units

1.7.1 Units of Polarisability and Hyperpolarisability

Computation of the polarisability and hyperpolarisability forms a significant part of this thesis, so it is important to have a discussion of the units used in the calculation of these values. Throughout this thesis the polarisability and hyperpolarisability are purely written in atomic units. I will present here the conversion from atomic units to SI units for polarisability and hyperpolarisability, only for the sake of completeness. Other common unit conversions are given in Mitroy et al. [49].

From the Stark shift formula,
\[ \varepsilon_n(\omega) = \varepsilon_n^{(0)} - \frac{1}{2} \alpha_{nn}(\omega) E^2 - \frac{1}{24} \gamma_n(\omega) E^4 - \ldots \]  
(1.17)

we know the polarisability \( \alpha_{nn} \) must have units of energy divided by electric field squared. The units of energy and electric field strength can be rewritten such that

\[ \frac{\text{units of energy}}{(\text{units of electric field})^2} = \frac{E_h}{(E_h/ea_0)^2} = \frac{e^2 a_0^2}{\alpha^2 m_e c^2}. \]

From this we can find the conversion from 1 a.u. of polarisability to SI units to be [49]

\[ \frac{e^2 a_0^2}{E_h} \equiv 4\pi \varepsilon_0 a_0^3 = 1.64878 \times 10^{-41} \text{ C}^2 \text{s}^2 \text{kg}^{-1}, \]
(1.18)

where often \( 4\pi \varepsilon_0 \) is neglected since \( 4\pi \varepsilon_0 = 1 \) in atomic units. The units of hyperpolarisability can be found using the same method, giving [52]

\[ \frac{\text{units of energy}}{(\text{units of electric field})^4} = \frac{E_h}{(E_h/ea_0)^4} = \frac{(4\pi \varepsilon_0)^3 a_0^7}{e^2} = 6.23538 \times 10^{-65} \text{ C}^4 \text{m}^4 \text{J}^{-3}. \]

1.7.2 Units of Cross-section

Scattering cross-sections are given in units of area, and are related to the probability of scattering [35]. Classically, the cross-section is easy to envisage, such as for the case of a particle scattered off a ball. Here the cross-section corresponds to the physical cross-sectional area of the scattering target. At smaller scales, such as for the case of photon scattering off an atom, the amount of scattering is determined by photon-atom interactions. In this case the cross-section defines the ‘effective’ scattering area, rather than the actual area of the atom. Atomic scattering cross-sections are often written in terms of barn (b) which corresponds approximately to the cross-sectional area of a uranium nucleus, where 1b = 10^{-24} cm².

Instead, in this thesis, all cross-sections are normalised by the Thomson cross-section, \( \sigma_T \). The Thomson cross-section is the cross-section of light scattered by a free electron, and is given by [35]
\[ \sigma_T = \frac{8\pi}{3} r_e^2 \approx 6.6525 \times 10^{-29} \text{m}^2 = 0.66525 \times 10^{-24} \text{cm}^2 \equiv 0.66525 \text{b} \equiv 2.3756 \times 10^{-8} a_0^2, \tag{1.19} \]

where \( r_e \) refers to the classical electron radius and \( a_0 \) refers to the Bohr radius, i.e. the Thomson cross-section is very small in atomic units. The Thomson cross-section was named after J. J. Thomson, who first derived this cross-section classically [35].

It is convenient to normalise against the Thomson cross-section, as it allows for a more intuitive understanding of the cross-sections. At very large incident photon energies, we expect the cross-section of Rayleigh scattering for the hydrogen atom to go to \( 1\sigma_T \), as the system approaches the behaviour of scattering of light by a free electron. At incident photon energies much larger than the binding energy of the electrons, we can predict an asymptotic value of \( 2\sigma_T \) for atomic helium, as this system would have a cross-section similar to that of two independent free electrons.

1.8 Thesis Outline

The transition polarisabilities are introduced in Chapter 2 and computed at frequencies both below and above threshold for atomic hydrogen using a semi-analytical method. In Chapter 3 our pseudostate method is explained and used to compute the transition polarisabilities for atomic hydrogen. Our pseudostate method is extended to the calculation of Raman, Rayleigh, Compton and photoionisation cross-sections in Chapter 4. In this Chapter I also compute the Compton scattering cross-sections with our pseudostate method and show that our calculation does not converge with varying box size. The pseudostate method is extended to the case of two-photon ionisation and hyperpolarisability in Chapter 5. Finally, the various scattering cross-sections are computed for a range of atoms in Chapter 6. In Chapter 7 I will discuss the application of our pseudostate method to the calculation of two-photon ionisation cross-section at photon energies greater than ionisation energy.
Chapter 2

Complex Polarisability through Semi-analytics

The first atom we have considered in our calculation of the single photon scattering cross-sections is hydrogen, as it is the simplest atom with only one electron. As any undergraduate student learns, the hydrogen atom is also the only atom which can be solved analytically. In fact, analytic expressions have been derived for the transition matrix elements of any transition in atomic hydrogen [17], which allows us to calculate the polarisabilities of atomic hydrogen with a semi-analytical method. Semi-analytic means we use (known) analytic matrix elements but perform sums and integrals numerically. In this Chapter I present the semi-analytical calculation of the complex polarisabilities of atomic hydrogen, before introducing our more general numerical method in Chapter 3.

As has been discussed in the introduction, the polarisability is of particular interest in spectroscopy and atomic clock applications, which measure the energy levels of atoms to extreme precision. Our calculations of atomic hydrogen may also be relevant to recent benchmark experiments in antihydrogen [82]. This experiment observes the $1s$-$2s$ transition in antihydrogen with the aim of comparing with the same transition in atomic hydrogen. The standard model predicts that the spectra of antihydrogen should be the same as that of its matter counterpart [82]. As such, any polarisabilities or cross-sections we compute for atomic hydrogen should also be applicable to antihydrogen, and will give a better understanding of the photon-atom interactions that occur in their experiment.

At first glance it may seem as if the atomic polarisability has been completely understood, as it plays a vital role in atomic clocks and has been computed for many atoms [83]. The polarisability describes how easily an electron cloud can be distorted when an electric field is applied, and is often given by the formula [49]

$$\alpha_{ii}(\omega) = \sum_{t} \frac{f_{it}}{\omega_{ti}^{2} - \omega^{2}}, \quad (2.1)$$

where $f_{it}$ is the oscillator strength of the transition from state $i$ to intermediate state $t$ and $\omega_{ti}$ is the energy difference between states $t$ and $i$ ($\omega_{ti} = \omega_{t} - \omega_{i}$). This simple formula belies the true complexity of the atomic polarisability, as it does not show that the polarisability has imaginary components.

Though it has been known for many years that the refractive index has a real and imaginary component [84], it is less well-known that the polarisability is also a complex quantity. As shown in Section 2.4, the
polarisability has two imaginary terms and should in reality be written as
\[ \alpha_{ii}(\omega) = \text{Re}[\alpha_{ii}(\omega)] + i\text{Im}_0[\alpha_{ii}(\omega)] + i\text{Im}_1[\alpha_{ii}(\omega)] , \] (2.2)
where the two imaginary parts are related to the finite linewidth of an atomic state and the possibility of ionising the atom, respectively.

Eqn. 2.1 describes the polarisability of an atom initially in state \( i \) and ending in state \( i \), i.e. the process where a photon of energy \( \hbar \omega \) is absorbed and emitted and the atom ends back in the initial state \( i \). However, the polarisability can actually be written more generally to describe the transition from initial state \( i \) to state \( j \) through the absorption of a photon of energy \( \hbar \omega \) and emission of a photon of energy \( \hbar \omega' \). This transition is described by the Kramers-Heisenberg matrix element, which is also referred to as the ‘transition polarisability’ and denoted as \( \alpha_{ij}(\omega) \). We next look at the transition matrix elements, then in Section 2.2 I give a short derivation of the Kramers-Heisenberg matrix element formula and explain the origin of the two imaginary parts of the polarisability.

### 2.1 Photon Interaction with an Atom

If we consider an atom in state \( i \) under an applied electric field, there is a possibility that the atom will absorb or emit a photon and transition to state \( j \). The photon-atom interaction is given by
\[ H_{\text{int}} = -\frac{e}{mc} \mathbf{p} \cdot \mathbf{A} + \frac{e^2}{2mc^2} \mathbf{A}^2 , \] (2.3)
where \( \mathbf{A} \) is the quantised radiation field [35] given by
\[ \mathbf{A}(r,t) = cA_0 \sum_k \frac{1}{\sqrt{\omega}} \left[ \sum_{\alpha=1}^2 \left( a_{k,\alpha}(t)e^{i\alpha \mathbf{k} \cdot \mathbf{r}} + a_{k,\alpha}^\dagger(t)e^{i\alpha \mathbf{k} \cdot \mathbf{r}} \right) \right] , \] (2.4)
where \( A_0 = \sqrt{2\pi \hbar/4\pi \varepsilon_0 V} \), \( \mathbf{e}^{(\alpha)} \) is the polarisation vector and \( a_{k,\alpha} \) and \( a_{k,\alpha}^\dagger \) are the annihilation and creation operators respectively. \( \mathbf{A} \) is assumed to be in a cubic box with volume \( V \). The \( \mathbf{A}^2 \) term in the interaction Hamiltonian describes the process where the number of photons in the field are changed by 0 or \( \pm 2 \) photons, whereas the \( \mathbf{p} \cdot \mathbf{A} \) interaction term results in a change of \( \pm 1 \) photons in the field.

The transition involving the absorption of a photon can be written as (see appendix A.2 for derivation)
\[ \langle j M_j | H_{\text{int}} | i M_i \rangle = -ieA_0 \sqrt{\omega} \langle j M_j | (\mathbf{r} \cdot \mathbf{e}^{(\alpha)}) | i M_i \rangle e^{-i\omega t} , \] (2.5)
where \( \langle j M_j | (\mathbf{r} \cdot \mathbf{e}^{(\alpha)}) | i M_i \rangle \) is referred to as the dipole transition matrix element. Throughout this thesis we will consider only linear polarisation, where
\[ \mathbf{r} \cdot \mathbf{e}^{(\alpha)} = [x,y,z] \cdot [0,0,1] = z = r \cos \theta . \] (2.6)
The dipole transition matrix element is dependent on the initial and final magnetic quantum number \((m_i \text{ and } m_f)\). However, these can be factored out of the transition matrix element by the Wigner-Eckart theorem, given by [85]

\[
\langle j\ell jm_j | T_q^k | i\ell im_i \rangle = (-1)^{\ell_j - m_j} \sqrt{2\ell_j + 1} \begin{pmatrix} \ell_j & k & \ell_i \\ m_j & q & -m_i \end{pmatrix} \langle j\ell j || T_q^k || i\ell i \rangle ,
\]

(2.7)

where \(T_q^k\) is the tensor operator of rank \(k\) with components \(q = -k, -k+1, ..., k-1, k\).

\(\langle j\ell j || T_q^k || i\ell i \rangle\) is referred to as the reduced transition matrix element and is independent of the magnetic quantum numbers \(m\). \(\begin{pmatrix} \ell_j & k & \ell_i \\ m_j & q & -m_i \end{pmatrix}\) is a Wigner-3j symbol which is closely related to the Clebsch-Gordon coefficients and is non-zero only when the conditions \(m_j + q = m_i\) and \(|\ell_j - k| \leq \ell_i \leq \ell_j + k\) are satisfied.

The dipole moment operator \((r \cdot e^{(\alpha)})\) is a spherical tensor operator of rank \(k = 1\) [85], and is often written in terms of a modified spherical harmonic

\[
C_q^k(\theta, \phi) = \left( \frac{4\pi}{2k+1} \right)^{\frac{1}{2}} Y_{kq}(\theta, \phi) .
\]

(2.8)

In the case of a dipole moment operator, \(k = 1\), but in the case of a quadrupole moment transition \(k = 2\) and in the case of an octupole moment, \(k = 3\). The spherical harmonics for \(k = 1\) are given by [85]

\[
Y_{10}(\theta, \phi) = \sqrt{\frac{3}{4\pi}} z = \sqrt{\frac{3}{4\pi}} \cos \theta ,
\]

(2.9)

\[
Y_{1\pm1}(\theta, \phi) = \mp \sqrt{\frac{3}{8\pi}} \frac{(x \pm iy)}{r} = \mp \sqrt{3} \frac{\sin \theta e^{\pm i\phi}}{8\pi} .
\]

(2.10)

Given that the dipole operator has a rank of \(k = 1\), then the transition matrix element is given by

\[
\langle j\ell jm_j | rC_q^1 | i\ell im_i \rangle = (-1)^{\ell_j - m_j} \sqrt{2\ell_j + 1} \begin{pmatrix} \ell_j & 1 & \ell_i \\ m_j & q & -m_i \end{pmatrix} \langle j\ell j || rC_q^1 || i\ell i \rangle ,
\]

(2.11)

and must obey the dipole selection rule \(|\ell_j - 1| \leq \ell_i \leq \ell_j + 1\). If we assume that the incident light is linearly polarised in the z-direction, then the dipole transition matrix element is given by

\[
\langle j\ell jm_j | rC_0^1 | i\ell im_i \rangle = (-1)^{\ell_j - m_j} \sqrt{2\ell_j + 1} \begin{pmatrix} \ell_j & 1 & \ell_i \\ m_j & 0 & -m_i \end{pmatrix} \langle j\ell j || rC_0^1 || i\ell i \rangle .
\]

(2.12)

Finally, we can write the matrix element describing the absorption of a photon with frequency \(\omega\) as

\[
\langle j\ell jm_j | H_{\text{int}} | i\ell im_i \rangle = i \sqrt{\frac{1}{2V}} \sqrt{\alpha} (-1)^{\ell_j - m_j} \sqrt{2\ell_j + 1} \begin{pmatrix} \ell_j & 1 & \ell_i \\ m_j & 0 & -m_i \end{pmatrix} \langle j\ell j || rC_0^1 || i\ell i \rangle e^{-i\omega},
\]

(2.13)
2.1. Photon Interaction with an Atom

and the matrix element describing the emission of a photon with frequency $\omega'$ by

$$
\langle j\elljm|H_{int}|i\ell'mi\rangle = i\sqrt{\frac{1}{2V}}\sqrt{\omega'}(-1)^{\ell_j-m_j}\sqrt{2\ell_j+1}\left(\begin{array}{cc}
\ell_j & 1
m_j & -m_i
\end{array}\right)\langle j\ell_j|z|i\ell_i\rangle e^{i\omega't},
$$

(2.14)

where we assume linearly polarised light.

2.1.1 Analytical Transition Matrix Elements

Though atomic hydrogen is perhaps not the most relevant atom for most high precision AMO experiments, the simple structure of atomic hydrogen means it is uniquely suitable to be used as a test atom. Simple analytic expressions for the dipole transition matrix elements from ground state atomic hydrogen, H(1s), can be found in atomic physics monographs such as Bethe et al. [86] and Sobelman [87]. Bethe et al. [86] give the analytic formula for transition matrix elements from $1s$-np bound (bound-bound) states to be

$$
T_{1s, np} = \langle 1s||z||np \rangle = 2^4n^{7/2}(n-1)^{n-5/2}n^{n+5/2},
$$

(2.15)

and Sobelman [87] give the 1s-$\epsilon p$ continuum (bound-free) transition matrix elements to be

$$
T_{1s, \epsilon p} = \langle 1s||z||\epsilon p \rangle = 2^4\frac{1}{(2\epsilon + 1)^{5/2}}e^{-\frac{2}{\sqrt{2\epsilon}}\tan^{-1}(\sqrt{2\epsilon})}(1 - e^{-\frac{2}{\sqrt{2\epsilon}}})^{-1/2},
$$

(2.16)

These analytic expressions are summed and integrated to compute the polarisability and Rayleigh scattering cross-section of an atom initially in the ground state of hydrogen.

General expressions for the transition matrix elements were derived by Gordon in 1929 [17] for a bound-to-bound state transition, bound-to-free state transition and free-to-free state transition. The transition between a bound state $n$ with angular momentum $\ell$ to a bound state $n'$ with angular momentum $\ell - 1$ is given by [17]

$$
T_{ij} = \frac{(-1)^{n'-\ell}(4nn')^{\ell+1}}{4(2\ell - 1)!}\sqrt{(n+\ell)(n-\ell)}\left(\prod_{s=1}^{2\ell-1}\sqrt{(n+\ell-s)(n'+\ell-s)}\right)\left(\frac{n-n'}{n+n'}\right)^{n+n'-2\ell-2}
\times 2F_1\left(\ell+1-n,\ell-n',2\ell,\frac{-4nn'}{(n-n')^2}\right) - \left(\frac{n-n'}{n+n'}\right)^2 2F_1\left(\ell-1-n,\ell-n',2\ell,\frac{-4nn'}{(n-n')^2}\right),
$$

(2.17)

where $2F_1(a,b;c;z)$ is the hypergeometric function given by

$$
2F_1(a,b;c;z) = \sum_{n=0}^{\infty} \frac{(a)_n(b)_n}{(c)_nn!}z^n,
$$

(2.18)

where $z$ is a complex number.

The transition from a bound state $n$ with angular momentum $\ell - 1$ to a continuum state with energy $\epsilon$
and angular momentum $\ell$ is given by [17]

$$
T_{ne}^\ell = i(i\mu)^{3/2}(-1)^{n-\ell} \frac{\sqrt{(\mu^2 + \ell^2)}(4i\mu n)^{\ell+1}}{4(2\ell - 1)!\sqrt{1 - e^{-\pi \sqrt{2/\epsilon}}}} \left( \frac{(i\mu - n)^{i\mu+n-2\ell+2}}{(i\mu + n)^{i\mu+n}} \prod_{s=1}^{2\ell-1} \sqrt{(n + \ell - s)(i\mu + \ell - s)} \right)
$$

$$
\times \left[ F\left( \ell + 1 - i\mu, \ell - n, 2\ell, \frac{-4i\mu n}{(i\mu - n)^2} \right) - \left( \frac{(i\mu - n)}{(i\mu + n)} \right)^2 F\left( \ell - 1 - i\mu, \ell - n, 2\ell, \frac{-4i\mu n}{(i\mu - n)^2} \right) \right],
$$

(2.19)

where $\mu = 1/\sqrt{2\epsilon}$.

These formulae are introduced here as they play an important role in the semi-analytical calculation presented in Section 2.5. In Section 2.5 I will present a semi-analytical method for calculating the polarisability of atomic hydrogen using these analytic expressions for the transition matrix elements of atomic hydrogen. Only bound-to-bound or bound-to-free transition matrix elements are required for our semi-analytical calculation of the polarisability, so the analytic expression for the free-to-free transition matrix elements has not been introduced. The analytical free-to-free transition matrix elements will be introduced in Chapter 4 when we compute the Compton scattering cross-sections, which involves the transition between two states in the continuum.

Eqns. 2.17 and 2.19 will also be used for a semi-analytical calculation of the Raman scattering cross-sections in Chapter 4. I will show that the analytical transition matrix elements for transitions to a $\ell = 2$ state must be multiplied by a factor of $\sqrt{2}$ to give the correct cross-sections. The missing $\sqrt{2}$ is due to the reduced matrix element $\langle \ell' = 2|C_0||\ell = 1 \rangle = \sqrt{2}$ [87], which will be discussed in Section 4.4.4. For now this can be ignored, as I will calculate the polarisability of ground state hydrogen in this Chapter, which involves only $\ell = 0$ and $\ell = 1$ states. A brief overview of the derivation of the polarisability formula is given in the next section.

### 2.2 Kramers-Heisenberg Matrix Elements

Let us consider the process where an atom initially in state $i$ absorb then emits a photon (or vice-versa), to end in final state $j$. See Appendix A.5 for the derivation. Second-order time-dependent perturbation theory gives the transition amplitude of this process to be

$$
c_i^{(2)}(t) = \frac{1}{i\hbar} e^2 A_0^2 \sqrt{\omega\omega'} \sum_n \left[ \frac{\langle j|\ell,m_j|\mathbf{r}\cdot\mathbf{e}(\alpha')\rangle \langle n|\ell,m_n|\mathbf{r}\cdot\mathbf{e}(\alpha)\rangle}{(\epsilon_n - \epsilon_i - \hbar\omega)} \right] \left( \begin{array}{c} f \langle j|\ell,m_j|\mathbf{r}\cdot\mathbf{e}(\alpha')\rangle \langle n|\ell,m_n|\mathbf{r}\cdot\mathbf{e}(\alpha)\rangle i\ell, m_i \rangle \frac{1}{(\epsilon_n - \epsilon_i + \hbar\omega')} \int_0^t e^{i(\omega_j + \omega' - \omega)t'} dt' \end{array} \right), \quad (2.20)
$$

where $\mathbf{e}(\alpha)$ is the polarisation of the incident photon with frequency $\omega$ and $\mathbf{e}(\alpha')$ is the polarisation of the outgoing photon with frequency $\omega'$. Though there is also a first-order transition amplitude corresponding
to the $A^2$ term in the interaction Hamiltonian, the $A^2$ term is negligible at low frequencies. In this thesis only the $\mathbf{p} \cdot \mathbf{A}$ interaction term is considered. The differential scattering cross-section with respect to solid angle $\Omega$ is given by (see Appendix A for derivation)

$$
\frac{d\sigma_{ij}}{d\Omega} = \omega \omega^3 r_e^2 \sum_n \left[ \frac{\langle j \ell jm \mid (\mathbf{r} \cdot \mathbf{e}(\alpha)) \mid n \ell mn \rangle \langle n \ell mn \mid (\mathbf{r} \cdot \mathbf{e}(\alpha)) \mid i \ell mi \rangle}{\omega_{ni} - \omega} + \frac{\langle j \ell jm \mid (\mathbf{r} \cdot \mathbf{e}(\alpha)) \mid n \ell mn \rangle \langle n \ell mn \mid (\mathbf{r} \cdot \mathbf{e}(\alpha)) \mid i \ell mi \rangle}{\omega_{ni} + \omega'} \right] \frac{2}{\omega_{ni} + \omega'} \right]^2, \quad (2.21)
$$

where $r_e$ is the classical electron radius.

Delserieys et al. [48] derived expressions for the cross-section with and without fine structure. The cross-section expression given by Delserieys et al., with fine structure is

$$
\sigma_{ij} = \sigma_T \frac{32\omega^3}{(2J + 1)} \sum_{K=0}^{2K+1} |A_{j'ij}^{(K)}(\omega)|^2, \quad (2.22)
$$

where the initial state $|i\rangle$ has angular momentum $\ell_i$, spin $S$ and total angular momentum $J$. The final state $|j\rangle$ has angular momentum $\ell_j$ and total angular momentum $J'$, and the intermediate state $n$ has angular momentum $\ell_n$.

The cross-section is dependent on $A_{j'ij}^{(K)}(\omega)$ which is given by [48]

$$
A_{j'ij}^{(K)} = (-1)^{J+S-\ell} \sqrt{(2J'+1)(2J+1)} \left\{ \begin{array}{ccc}
S & \ell_j & J' \\
K & \ell_i & J \\
\end{array} \right\} \\
\times \sum_n \left\{ \begin{array}{ccc}
\ell_i & \ell_j & K \\
1 & 1 & \ell_n \\
\end{array} \right\} \left[ \frac{\langle j \ell_j \mid z \mid n \ell_n \rangle \langle n \ell_n \mid z \mid i \ell_i \rangle}{\epsilon_n - \epsilon_i - \omega} + (-1)^K \frac{\langle j \ell_j \mid z \mid n \ell_n \rangle \langle n \ell_n \mid z \mid i \ell_i \rangle}{\epsilon_n - \epsilon_i + \omega'} \right]. \quad (2.23)
$$

If the fine-structure is not resolved, then the cross-sections must be averaged such that

$$
\bar{\sigma}_{ij} = \frac{\sum_{J'J} (2J+1)\sigma_{ij}}{(2\ell_i + 1)(2S + 1)}. \quad (2.25)
$$

An atom initially in state $|i\rangle$ with angular momentum $\ell_i = 0$ can end in final state $|j\rangle$ with angular momentum $\ell_j = 0$ or $\ell_j = 2$. The cross-section for the transition from initial state $|i\rangle$ ($\ell_i = 0$) to final state $|j\rangle$ ($\ell_j = 0$) is given by

$$
\sigma_{i1/2j1/2} = \sigma_T \omega \omega^3 \frac{1}{9} \sum_n \left[ \frac{\langle j \ell_j \mid z \mid n \ell_n \rangle \langle n \ell_n \mid z \mid i \ell_i \rangle}{\epsilon_n - \epsilon_i - \omega} + \frac{\langle j \ell_j \mid z \mid n \ell_n \rangle \langle n \ell_n \mid z \mid i \ell_i \rangle}{\epsilon_n - \epsilon_i + \omega'} \right]^2, \quad (2.26)
$$

whilst the transition from initial state $|i\rangle$ ($\ell_i = 0$) to final state $|j\rangle$ ($\ell_j = 2$) is given by

$$
\sigma_{i1/2j3/2} = \sigma_T \omega \omega^3 \frac{2}{45} \sum_n \left[ \frac{\langle j \ell_j \mid z \mid n \ell_n \rangle \langle n \ell_n \mid z \mid i \ell_i \rangle}{\epsilon_n - \epsilon_i - \omega} + \frac{\langle j \ell_j \mid z \mid n \ell_n \rangle \langle n \ell_n \mid z \mid i \ell_i \rangle}{\epsilon_n - \epsilon_i + \omega'} \right]^2, \quad (2.27)
$$
and

\[ \sigma_{1/2j} = \sigma_T \omega \omega^3 \left| \frac{3}{4S} \sum_n \left[ \frac{\langle j|l_n|n\rangle \langle n|l_n|z|i\rangle}{\varepsilon_n - \varepsilon_i - \omega} + \frac{\langle j|l_n|n\rangle \langle n|l_n|z|i\rangle}{\varepsilon_n - \varepsilon_i + \omega'} \right] \right|^2. \quad (2.28) \]

Since we neglect the fine-structure in our calculation, we must average the cross-sections to give

\[ \bar{\sigma}_{ij} = \frac{\sum_{J,J'}(2J+1)\sigma_{ij}}{(2L+1)(2S+1)} = \frac{1}{2}(2\sigma_{1/2j} + 2\sigma_{1/2j}) \]
\[ = \sigma_T \omega \omega^3 \left| \frac{1}{3} \sum_n \left[ \frac{\langle j|l_n|n\rangle \langle n|l_n|z|i\rangle}{\varepsilon_n - \varepsilon_i - \omega} + \frac{\langle j|l_n|n\rangle \langle n|l_n|z|i\rangle}{\varepsilon_n - \varepsilon_i + \omega'} \right] \right|^2. \quad (2.29) \]

Then we can write the cross-section expression as

\[ \sigma_{ij} = \sigma_T \omega \omega^3 \left| \alpha_{ij}(\omega) \right|^2, \quad (2.30) \]

where the transition polarisability is given by

\[ \alpha_{ij}(\omega) = \sum_n C_{i,n,j} \left[ \frac{\langle j|l_n|n\rangle \langle n|l_n|z|i\rangle}{\varepsilon_n - \varepsilon_i - \omega} + \frac{\langle j|l_n|n\rangle \langle n|l_n|z|i\rangle}{\varepsilon_n - \varepsilon_i + \omega'} \right], \quad (2.31) \]

where \( C_{i,n,j} = 1/3 \) for \( \ell_i = 0, \ell_n = 1 \) and \( \ell_j = 0 \) or 2. In Appendix A.7 I present my attempt at deriving the cross-section expression without fine-structure using LS-coupling matrix elements. Throughout this thesis I will use the expressions presented by Delserieys et al. [48], in the form written above.

Though I have presented the general expression for the transition polarisability in Eqn. 2.32, in this Chapter I will consider only the polarisability of Rayleigh transitions (where \( i = j \)). The transition polarisabilities, where \( i \neq j \), are needed to compute the Raman scattering cross-sections and will be considered in Chapter 4.

### 2.3 Previous Methods for Calculating Polarisabilities

Polarisabilities have been calculated for H [1, 16], Li [88, 89], He [90] and a host of other atoms [52]. Even the polarisability for atoms with a large number of electrons, such as Rb [91], Yb [92] and Er [93] have been calculated. Historically one of the main difficulties of calculating the polarisability has been the sum over the intermediate bound states in the Kramers-Heisenberg matrix element. The main two methods that were developed to deal with this infinite sum was the Dalgarno-Lewis method and using Green’s functions.

In 1955, Dalgarno and Lewis presented a method for computing the infinite sum by transforming the sum into a differential equation [94]. In the Dalgarno-Lewis method, the Hamiltonian is given by \( H = H_0 + V \) where \( H_0 \) is the unperturbed Hamiltonian and \( V \) is the perturbation. From perturbation
theory the first order energy is given by \( E_n^{(1)} = \langle n|V|n \rangle \) and the second-order energy is given by the usual

\[
E_n^{(2)} = \sum_{m \neq n} \frac{\langle n|V|m \rangle \langle m|V|n \rangle}{E_n^{(0)} - E_m^{(0)}}. \tag{2.33}
\]

An operator \( F \) is chosen to satisfy \([F,H_0]|n\rangle = (V - E_n^{(1)})|n\rangle\), and can be used to remove the summation from Eqn. 2.33 since

\[
E_n^{(2)} = \sum_{m \neq n} \frac{\langle n|V|m \rangle \langle m|V|n \rangle}{E_n^{(0)} - E_m^{(0)}} = \langle n|VF|n \rangle - E_n^{(1)} \langle n|F|n \rangle. \tag{2.34}
\]

Now the function of \( F \) can be found by solving differential equations and the second-order Stark shift is calculated without calculating the sum. One of the first calculations relevant to this thesis, that used this Dalgarno-Lewis method, was the calculation of two-photon ionisation by Zernik [76, 77]. Another example of an application of Dalgarno-Lewis method is the calculation of multi-photon ionisation cross-sections by Radhakrishnan [95].

Of course, the Dalgarno-Lewis method has also been used in calculations of polarisability. As an example, Pan et al. have used the Dalgarno-Lewis method in their calculation of the polarisability and hyperpolarisability of atomic hydrogen [96]. They have combined the Dalgarno-Lewis method with the complex rotation method in order to compute the polarisability and hyperpolarisability at frequencies both below and above the ionisation threshold [12]. Their method, and other methods for computing the polarisability at frequencies above threshold, will be discussed in Section 2.4.2.

The other method often used in the calculation of the polarisability is the Coulomb Green’s function method. The Green’s function for an operator \( H \) is [97]

\[
G(E) = \frac{1}{E - H}, \tag{2.35}
\]

which, upon multiplication of the projection operator and applying the closure relation, gives

\[
G(E) = \sum_m \frac{|m\rangle \langle m|}{E - E_m}. \tag{2.36}
\]

From this, \( G(x,x') \) can be defined as [97]

\[
G(x,x';E) = \sum_m \frac{\langle x|m \rangle \langle m|x' \rangle}{E - E_m}, \tag{2.37}
\]

or alternatively as

\[
(E - H)G(x,x';E) = \delta(x - x'). \tag{2.38}
\]

There are many known properties and theorems for the Green’s function, such as the fact that the solution
2.4 Complex Polarisability

In Section 2.2 I have presented the transition polarisability and its relation to the scattering cross-sections. However, the polarisability expression given in Eqn. 2.32 is purely real. As introduced in Eqn. 2.2, the polarisability should be complex valued. The imaginary term \( \text{Im}_1 \left[ \alpha_{ii}(\omega) \right] \) is non-zero only at frequencies above threshold, and is related to the photoionisation process. A different imaginary term \( \text{Im}_0 \left[ \alpha_{ij}(\omega) \right] \) is related to the linewidth of the bound states, and is non-zero at frequencies both below and above ionisation threshold. These are now discussed.

2.4.1 \( \text{Im}_0 \left[ \alpha_{ii}(\omega) \right] \), Below Threshold

The \( \text{Im}_0 \left[ \alpha_{ii}(\omega) \right] \) is related to the linewidth of the transition between bound states. The decay rate of an atomic state is related to the linewidth of the state, and should be included in the polarisability by writing the energies as a complex term \([35, 98]\),

\[
\varepsilon_j \rightarrow \varepsilon_j - i \frac{\Gamma_j}{2},
\]

for \( \phi(x) \) in the equation

\[
\mathcal{L} \phi(x) = u(x), \tag{2.39}
\]

where \( \mathcal{L} \) refers to a linear operator, can be given in terms of the Green’s function

\[
\phi(x) = \int G(x,x')u(x')dx', \tag{2.40}
\]

since

\[
\mathcal{L} \phi(x) = \int \delta(x-x')u(x')dx' = \int \mathcal{L} G(x,x')u(x')dx' = \mathcal{L} \int G(x,x')u(x')dx'. \tag{2.41}
\]

The Green’s functions can be used to calculate the polarisability, such as the analytical derivation by Gavrila in 1967 [16] of elastic scattering in hydrogen or the numerical calculation by Manakov et al. in 2007 [60] of the polarisabilities of alkali-metal atoms.

In the following section I will introduce the imaginary component of the polarisabilities at frequencies below and above threshold. At frequencies below threshold, the polarisability calculation is simple. There have been many calculations of atomic polarisabilities (see Mitroy et al. [49] for an overview of polarisabilities below threshold), but only few calculations of the real polarisability at frequencies above threshold. At frequencies above the ionisation energy, divergences occur which prevent easy integration across the continuum energy. I will discuss some of the calculations (both numerical and analytical) that have computed the real polarisability at frequencies above threshold in Section 2.4.2.
2.4. Complex Polarisability

where \( \Gamma_i \) refers to the linewidth of state \( i \).

In our semi-analytical calculation presented in this Chapter, the decay terms will be neglected, so no \( \text{Im}_0[\alpha_{ii}(\omega)] \) is given. However, the \( \text{Im}_0[\alpha_{ii}(\omega)] \) is calculated in our pseudostate method and so will be discussed in detail in Chapter 3 with respect to the form and frequency dependence of the decay rate.

As shown in Eqn. 2.31, the polarisability is related to the single-photon scattering cross-section. If \( \Gamma \) is neglected in the polarisability calculation, the corresponding cross-section diverges to \( \infty \) on resonance. An example of this is also found in the absorption cross-section. The absorption cross-section describes the process where a single photon is absorbed, exciting the electron from its initial state \( |i\rangle \) to a final bound state \( |f\rangle \). The expression for the absorption cross-section can be derived from Fermi’s Golden rule to be

\[
\sigma_{\text{abs}} = \frac{3}{2} \pi c^3 \varepsilon_f \varepsilon_i \sigma_T \frac{|\langle i|z|f\rangle|^2 \delta(\varepsilon_f - \varepsilon_i - \varepsilon)}{2 \pi (\Delta \varepsilon)^2 + \Gamma_f^2 / 4},
\]

(2.42)

where the delta function ensures that energy is conserved. However, in this expression the linewidths have not been included. This results in an absorption cross-section that diverges on resonance with zero linewidth (see Fig. 2.1, dashed lines).

A more accurate calculation of the absorption cross-section is done by replacing the delta function with

\[
g(\varepsilon_f) = \frac{\Gamma_f}{2 \pi (\Delta \varepsilon)^2 + \Gamma_f^2 / 4},
\]

(2.43)

where \( \Delta \varepsilon = \varepsilon_f - \varepsilon_i - \varepsilon \). \( g(\varepsilon_f) \) is the ‘normalised spectral width’ [101] and is dependent on the line-width \( \Gamma_f \). The form of \( g(\varepsilon_f) \) gives a Lorentzian lineshape of the resonance. Fig. 2.1 plots the absorption cross-section using the delta function (as in Eqn. 2.42) or with \( g(\varepsilon) \) (see Eqn. 2.43). The cross-section was calculated using the analytic expression for the bound-bound transition matrix elements (Eqn. 2.15).

The absorption cross-section occurs at frequencies below threshold, as it describes the process where a photon is absorbed and an electron is excited to a bound state. Photoionisation is a very similar process that occurs at frequencies above threshold, where a photon is absorbed and the electron initially in state \( |i\rangle \) is excited into the continuum. The expression for the photoionisation cross-section (given in the next section) is also very similar to the absorption cross-section, and is related to the other imaginary polarisability, \( \text{Im}_1[\alpha_{ii}(\omega)] \).

2.4.2 \( \text{Im}_1[\alpha_{ii}(\omega)] \), Above Threshold

Resonances occur in the polarisability due to the \((\varepsilon_n - \varepsilon_i - \hbar \omega)^{-1}\) term (see Eqn. 2.32), when \( \hbar \omega = \varepsilon_n - \varepsilon_i \). These resonances at frequencies below threshold correspond to the energies of the bound states. As such, the resonances are physical and expected. However, this is no longer the case at frequencies above threshold. As atomic hydrogen has no discrete states above threshold, we expect no resonances to occur. Instead, the polarisability of atomic hydrogen should be a smooth function at frequencies above threshold.

In our semi-analytical calculation, the polarisability should be written as a sum over the bound states
2.4. Complex Polarisability

Figure 2.1: Plot of the absorption cross-section (in units of $\sigma_T$) calculated from Eqn. 2.42 with decay (using $g(\varepsilon)$ given in Eqn. 2.43) and without decay (using the delta function). The transition matrix elements were calculated using the analytic expression (Eqn. 2.15).

and an integral over the continuum, such that the continuum contribution to the polarisability is given by

$$\alpha_{ii}^c(\omega) = \sum_{\ell_n} C_{i,n,i} \int_0^\infty \frac{\langle i|l_i|\ell_i\rangle \langle \varepsilon_n\ell_n|r|\ell_i\ell_i\rangle}{\varepsilon_n - \varepsilon_i - \omega} + \frac{\langle i|l_i|\ell_i\rangle \langle \varepsilon_n\ell_n|r|\ell_i\ell_i\rangle}{\varepsilon_n - \varepsilon_i + \omega'} d\varepsilon_n. \quad (2.44)$$

However, a pole occurs at $\varepsilon_n = \omega + \varepsilon_i$ in the integral

$$I = \int_0^\infty \frac{\langle i|l_i|\ell_i\rangle \langle \varepsilon_n\ell_n|r|\ell_i\ell_i\rangle}{\varepsilon_n - \varepsilon_i - \omega} d\varepsilon_n. \quad (2.45)$$

To avoid the (unphysical) divergence, we apply Cauchy’s Principal Value Theorem,

$$\int_0^\infty \frac{f(x)}{x-a-i0} dx = \mathcal{P} \int_0^\infty \frac{f(x)}{x-a} dx + i\pi f(x)|_{x=a}, \quad (2.46)$$

which effectively integrates across a pole in the complex plane, resulting in a solution that has a real and imaginary part. $\mathcal{P}$ refers to the principal value integral. Applying this to our polarisability integral given in Eqn. 2.45 gives

$$I = \mathcal{P} \int_0^\infty \frac{\langle i|l_i|\ell_i\rangle \langle \varepsilon_n\ell_n|r|\ell_i\ell_i\rangle}{\varepsilon_n - \varepsilon_i - \omega} d\varepsilon_n + i\pi \langle i|l_i|\ell_i\rangle \langle \varepsilon_n\ell_n|r|\ell_i\ell_i\rangle |_{\varepsilon_n=\omega+\varepsilon_i}. \quad (2.47)$$

Therefore, the imaginary polarisability $\text{Im}[\alpha_{ii}(\omega)]$ is given by

$$\text{Im}[\alpha_{ii}(\omega)] = \sum_{\ell_n} \pi C_{i,n,i} \langle i|l_i|\ell_i\rangle \langle \varepsilon_n\ell_n|r|\ell_i\ell_i\rangle |_{\varepsilon_n=\omega+\varepsilon_i}. \quad (2.48)$$
which is related to the photoionisation cross-section by [102]

\[ \sigma_I(\omega) = \frac{3}{2} c^3 \omega \sigma_T \text{Im}[\alpha_{ii}(\omega)]. \]  

(2.49)

The well-known derivation of the photoionisation cross-section and its relation to the imaginary polarisability is given in Appendix A.4 and will be computed for atomic hydrogen in Chapter 4.

In Chapter 4 I will validate our semi-analytical and numerical calculation of \( \text{Im}[\alpha_{1s,1s}(\omega)] \) by converting to photoionisation cross-section and comparing with the known analytical function of photoionisation cross-section for hydrogen. The photoionisation cross-section of the ground state of a hydrogen-like atom is given by the analytic expression in atomic units [87]

\[ \sigma_I = \frac{2^6 \pi}{\alpha^3 Z^2} \left( \frac{\omega_\Gamma}{\omega} \right)^4 \frac{e^{-4\kappa \text{arccot}\kappa}}{1 - e^{-2\pi \kappa}} \sigma_T, \]  

(2.50)

where \( \omega_\Gamma = |\varepsilon_{1s}|/\hbar \) and \( \kappa^2 = \omega_\Gamma/(\omega - \omega_\Gamma) \). Here \( \alpha \) refers to the fine-structure constant and \( Z \) is the nuclear charge.

In Chapter 3 I will compare \( \text{Im}[\alpha_{1s,1s}(\omega)] \) given by our semi-analytical and pseudostate calculation against data presented for ground state atomic hydrogen by Gavrila. In 1967 Gavrila presented an analytical calculation of the Kramers-Heisenberg matrix element at frequencies both below and above threshold [1, 16] for the \( 1s-1s \) transition of atomic hydrogen using Coulomb Green’s functions. The data presented for the complex matrix elements show significant disagreement with our \( \text{Im}[\alpha_{1s,1s}(\omega)] \). This will be discussed in Section 3.2.2.

Whilst we consider semi-analytics in this Chapter, there have been a range of both analytic and numerical methods for computing the complex polarisabilities. A few years after his paper on elastic scattering from the \( 1s \) state of atomic hydrogen, Gavrila also derived analytic expressions for the \( 2s \) Rayleigh scattering process [6]. Similarly, Florescu et al. [7] utilised the same analytical procedure as Gavrila’s papers and presented Rayleigh and Raman scattering cross-section data for the \( 3s \) and \( 3d \) states of atomic hydrogen at frequencies both below and above threshold.

Manakov et al. [60] have computed the transition polarisability at frequencies below and above threshold for alkali-metal and noble gas atoms. The below threshold frequencies were calculated using the Fues potential model and the Sturmian expansion of the Green’s function, allowing the integrals to be done analytically. However, this method cannot be used for above threshold frequencies, and instead they use the properties of the Sturmian functions to transform the Green’s function to a form that gives convergence above ionisation energies as well. The Sturmian expansion of the Green’s function contains a free parameter that can be chosen such that the matrix elements converge [53]. In their method they state that the simple model potential gives good estimates of the polarisabilities at above threshold frequencies, which may be used for applications that do not need high-precision values. Manakov et al. have also used this method to compute the hyperpolarisability for atomic hydrogen at above threshold frequencies [53].

Pan et al. [12, 96] have also computed the complex polarisability of atomic hydrogen, by combining
the complex rotation method with the Dalgarno-Lewis method involving inhomogeneous differential
equations. This method allows them to compute the Re[$\alpha_{ii}(\omega)$] and Im[$\alpha_{ii}(\omega)$] at frequencies above
threshold. Interestingly, they have also applied their method to the calculation of the fourth-order AC
Stark shift, effectively calculating the hyperpolarisability. This will be considered when we extend our
calculation to the hyperpolarisability in Chapter 5. Though Pan et al. [12] have presented an effective
method for computing the complex polarisabilities of hydrogenic atoms, I would like to point out that the
numerical method I will develop in this thesis is simpler than the approach by Pan et al.

In the 1970s Langhoff et al. presented a pseudostate method for computing the complex polarisabilities [46, 90, 103] at frequencies below and above threshold. Langhoff et al. extract a set of ‘principal pseudostates’ from a pseudospectrum and apply the Stieltjes imaging technique. This method will be
discussed in detail in Section 3.3 as it has similarities to the numerical method for computing polarisabilities I will develop in the next Chapter. The results from our semi-analytical and numerical method will
be compared in Section 3.4 with the method by Langhoff et al.

In the next section I introduce our semi-analytical calculation of the polarisability of hydrogen, and
in Chapter 3 I will develop our numerical method. Our transition polarisabilities will be used to compute
the various single-photon scattering cross-sections in Chapter 4. In Chapter 5 I will extend our method to
the hyperpolarisability, and demonstrate that our calculation is in good agreement with data from Pan et
al. [12].

2.5 Semi-Analytical Method

The semi-analytical calculation for the Rayleigh transition polarisability of H(1s) is presented in this
section. We call our calculation using the analytical transition matrix elements a ‘semi-analytical’ calcu-
lation since all integrals are integrated numerically.

Figure 2.2: Diagram of a Rayleigh transition occurring from the ground state of hydrogen. A Rayleigh
transition is an elastic scattering process, where the absorption and emission of a photon of frequency $\omega$
(or vice-versa), causes the electron to transition to all intermediate states $t$ and back to the initial state $i$. 
As depicted in Fig. 2.2, the Rayleigh scattering describes the process where an atom absorbs and then emits (or vice-versa) a photon of frequency $\omega$. This process involves summing over all transitions from the initial state to the infinite number of intermediate states $t$, and from these intermediate states $t$ back to the initial state $i$. The static $1s-1s$ polarisability for the ground state of hydrogen is well-known [52], and is given by

$$\alpha_{1s,1s}(0) = 4.5 \text{ a.u.} \quad (2.51)$$

In this section the dynamic (frequency-dependent) $1s-1s$ polarisability is computed to test our semi-analytical method and ensure it can be used to reliably compute the transition polarisabilities for which there are no literature values, such as $\alpha_{1n,n}$ for $n \geq 3$. The formula for transition polarisability between states $|i\rangle$ and $|j\rangle$ is

$$\alpha_{ij}(\omega) = \sum_{t} C_{i,t,j} \left[ \frac{\langle j|z|t\rangle\langle t|z|i\rangle}{\epsilon_{ti} - \omega} + \frac{\langle j|z|t\rangle\langle t|z|i\rangle}{\epsilon_{ij} + \omega} \right]$$

$$+ \int_{0}^{\infty} C_{i,\epsilon,j} \left[ \frac{\langle j|z|\epsilon\rangle\langle \epsilon|z|i\rangle}{\epsilon - \epsilon_{i} - \omega} + \frac{\langle j|z|\epsilon\rangle\langle \epsilon|z|i\rangle}{\epsilon - \epsilon_{j} + \omega} \right] d\epsilon, \quad (2.52)$$

where $C_{i,t,j} = 1/3$ and $C_{i,\epsilon,j} = 1/3$ from Delserieys et al. [48] for initial $\ell_{i} = 0$. The sum will be referred to as the bound contribution $\alpha^{B}$ and the integral as the continuum contribution $\alpha^{C}$, such that $\alpha_{ij}(\omega) = \alpha_{ij}^{B}(\omega) + \alpha_{ij}^{C}(\omega)$. The linewidths could be trivially added to avoid divergences at bound states, but for now I have not included these, which allows us to neglect the imaginary term $\text{Im}_{0}[\alpha_{ij}(\omega)]$ in this semi-analytical calculation.

### 2.5.1 Below Ionisation Threshold ($\omega < 0.5 \text{ a.u.}$)

A straight-forward computation of the sum over bound states in Eqn. 2.52 has slow convergence with respect to the number of bound states in the calculation. Instead of explicitly computing the sum to a large number of bound states, I have extrapolated the bound sum using a power series extrapolation method as used by Bromley et al. [104] and Mitroy et al. [105]. In these papers they extrapolated the convergence of the ground state of He with respect to the number of Laguerre functions $N$ or maximum angular momenta $L$ using a power series.

Here the increment $\Delta \alpha_{N}^{B}$ refers to the difference in the bound sum $\alpha^{B}$ for a sum over $N$ and $N - 1$ bound states, so

$$\Delta \alpha_{N}^{B} = \sum_{t}^{N} C_{i,t,j} \left[ \frac{\langle j|z|t\rangle\langle t|z|i\rangle}{\epsilon_{ti} - \omega} + \frac{\langle j|z|t\rangle\langle t|z|i\rangle}{\epsilon_{ij} + \omega} \right] - \sum_{t}^{N-1} C_{i,t,j} \left[ \frac{\langle j|z|t\rangle\langle t|z|i\rangle}{\epsilon_{ti} - \omega} + \frac{\langle j|z|t\rangle\langle t|z|i\rangle}{\epsilon_{ij} + \omega} \right]$$

$$= C_{i,N,j} \left[ \frac{\langle j|z|N\rangle\langle N|z|i\rangle}{\epsilon_{ti} - \omega} + \frac{\langle j|z|N\rangle\langle N|z|i\rangle}{\epsilon_{ij} + \omega} \right], \quad (2.53)$$
If we assume that the increments have the form [105]

\[ \Delta \alpha_N^B \sim \frac{a}{N^p}, \quad (2.54) \]

then \( p \) can be found by the use of three points \( \alpha_N, \alpha_{N-1}, \text{ and } \alpha_{N-2} \), where

\[ p = \ln \left( \frac{\Delta \alpha_{N-1}^B}{\Delta \alpha_N^B} \right) / \ln \left( \frac{N}{N-1} \right). \quad (2.55) \]

Once the value of \( p \) is known, the series can be extrapolated to \( N \to \infty \). Using this method, the increment \( \Delta \alpha_N^B \) is fitted to the series

\[ \Delta \alpha_N^B = \frac{a}{N^p} + \frac{b}{N^{p+1}} + \frac{c}{N^{p+2}} + \ldots \quad (2.56) \]

However, in order to determine where we should truncate this series, I have considered extrapolations using different number of terms in Eqn. 2.56, i.e. I have calculated \( c_p = a/N^p, c_{p,p+1} = a/N^p + b/N^{p+1} \) and \( c_{p,p+1,p+2} = a/N^p + b/N^{p+1} + c/N^{p+2} \). These are discussed in references [104–106]. Note that I simply applied a spreadsheet provided by Bromley to obtain the extrapolation results (see Mitroy et al. [106] for details).

The static polarisability is known analytically to be exactly \( \alpha_{1s}(0) = 4.5 \text{ a.u.} \) [52]. When the bound contribution is extrapolated using \( N = 10, 11, 12, 13 \) (details given in Table 2.1), the static polarisability is \( \alpha_{1s}(0) = 4.49999856 \text{ a.u.} \), whilst including \( N = 700 \) bound states without extrapolating gives \( \alpha_{1s}(0) = 4.49999362 \text{ a.u.} \). In both calculations, the continuum contribution was calculated to be \( \alpha_c = 0.83674210 \text{ a.u.} \). Evidently the extrapolation is more accurate even when 700 bound states are included in the calculation. Table 2.1 demonstrates that our extrapolated value for the bound contribution is in agreement with the value given by Langhoff et al. [107].

The continuum integral is computed by first transforming to an integral from 0 to 1, splitting this integral into \( N_{\text{panels}} \) intervals or ‘panels’, and performing 16 point Gaussian integration on each. In this way we can check convergence of the integral against the number of panels \( N_{\text{panels}} \). Table 2.2 demonstrates that the continuum contribution to the static polarisability is converged to a large number of significant figures even at 10 panels.

I have shown that we are able to compute the bound and continuum contribution to the static polarisability for frequencies below threshold, as presented in Tables 2.3 and 2.4. As we can apply the extrapolation method detailed above, we have established the bound sum convergence obeys a power series with empirically determined \( p = 3 \) the likely answer. The bound contribution at frequencies above threshold can be computed using the same method, but the continuum integral at frequencies above threshold involves integration over a pole.
Table 2.1: Bound polarisability sum $\alpha^B_{1s,1s}(0)$ (in atomic units) computed using analytical transition matrix elements, for different number of bound states ($N$) in the calculation. The bound polarisability is extrapolated using a power series, where $p$ is the power. Rows $c_3,c_3,4,c_3,4,5$ and $c_3,4,5,6$ show the bound polarisability extrapolated to infinity when adding increasingly higher order terms in the extrapolation. $\alpha^B_{1s,1s}(0)$ calculated by Langhoff et al. [107] is also shown. The total $\alpha_{1s,1s}(0)$ was calculated using $\alpha^C_{1s,1s}(0) = 0.8367420956$.

<table>
<thead>
<tr>
<th>$N$</th>
<th>$\alpha^B_{1s,1s}(0)$</th>
<th>$\alpha_{1s,1s}(0)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>3.6343635555</td>
<td>4.4711056511</td>
</tr>
<tr>
<td>11</td>
<td>3.6392460075</td>
<td>4.475981031</td>
</tr>
<tr>
<td>12</td>
<td>3.6429834772</td>
<td>4.4797255728</td>
</tr>
<tr>
<td>13</td>
<td>3.6459089539</td>
<td>4.4826510495</td>
</tr>
<tr>
<td>$\infty$ ($c_3$)</td>
<td>3.6635179637</td>
<td>4.5002600593</td>
</tr>
<tr>
<td>$\infty$ ($c_3,4$)</td>
<td>3.6631512915</td>
<td>4.4998933871</td>
</tr>
<tr>
<td>$\infty$ ($c_3,4,5$)</td>
<td>3.6632627464</td>
<td>4.5000048420</td>
</tr>
<tr>
<td>$\infty$ ($c_3,4,5,6$)</td>
<td>3.6632564615</td>
<td>4.499985571</td>
</tr>
<tr>
<td>700 Bound States</td>
<td>4.49999362</td>
<td></td>
</tr>
<tr>
<td>Langhoff et al. [107]</td>
<td>3.66326</td>
<td></td>
</tr>
</tbody>
</table>

Table 2.2: Convergence of the (real) polarisability continuum integral $\alpha^C_{1s,1s}(0)$ (in atomic units) with respect to the number of panels used in the integration. Each panel is computed using 16 point Gaussian integration.

<table>
<thead>
<tr>
<th>$N_{panels}$</th>
<th>$\alpha^C_{1s,1s}(0)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>0.836742095067</td>
</tr>
<tr>
<td>20</td>
<td>0.836742095486</td>
</tr>
<tr>
<td>30</td>
<td>0.836742095564</td>
</tr>
<tr>
<td>40</td>
<td>0.836742095591</td>
</tr>
<tr>
<td>50</td>
<td>0.836742095604</td>
</tr>
<tr>
<td>60</td>
<td>0.836742095611</td>
</tr>
<tr>
<td>70</td>
<td>0.836742095615</td>
</tr>
<tr>
<td>80</td>
<td>0.836742095618</td>
</tr>
<tr>
<td>90</td>
<td>0.836742095620</td>
</tr>
<tr>
<td>100</td>
<td>0.836742095621</td>
</tr>
</tbody>
</table>

Table 2.3: Convergence of the bound (real) polarisability sum $\alpha^B_{1s,1s}(\omega)$ at frequencies below ionisation energy (in atomic units). The bound sum is extrapolated by a polynomial series extrapolation, where $p$ is the power. The extrapolated bound polarisability value is given for increasing orders included in the polynomial series extrapolation.

<table>
<thead>
<tr>
<th>$N$</th>
<th>$\omega$ (a.u.)</th>
<th>0.1</th>
<th>0.2</th>
<th>0.3</th>
<th>0.4</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>3.894882</td>
<td>4.971016</td>
<td>9.410633</td>
<td>-18.44362</td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>3.899981</td>
<td>4.976847</td>
<td>9.418335</td>
<td>-18.42964</td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>3.903877</td>
<td>4.981309</td>
<td>9.424221</td>
<td>-18.41899</td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>3.906926</td>
<td>4.984799</td>
<td>9.428823</td>
<td>-18.41069</td>
<td></td>
</tr>
<tr>
<td>$\infty$ ($c_3$)</td>
<td>3.925277</td>
<td>5.005810</td>
<td>9.456523</td>
<td>-18.36072</td>
<td></td>
</tr>
<tr>
<td>$\infty$ ($c_3,4$)</td>
<td>3.924888</td>
<td>5.005336</td>
<td>9.455804</td>
<td>-18.36258</td>
<td></td>
</tr>
<tr>
<td>$\infty$ ($c_3,4,5$)</td>
<td>3.925007</td>
<td>5.005481</td>
<td>9.456028</td>
<td>-18.36197</td>
<td></td>
</tr>
<tr>
<td>$\infty$ ($c_3,4,5,6$)</td>
<td>3.925000</td>
<td>5.005472</td>
<td>9.456011</td>
<td>-18.36204</td>
<td></td>
</tr>
</tbody>
</table>
Table 2.4: Convergence of the (real) polarisability continuum integral \( \alpha_{1s,1s}^C(\omega) \) (in atomic units) for various frequencies with respect to the number of panels used in the integration. Each panel is computed using 16 point Gaussian integration.

<table>
<thead>
<tr>
<th>( N_{\text{panels}} )</th>
<th>( \omega ) (a.u.)</th>
<th>( \text{Re} )</th>
<th>( \text{Im} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>0.1</td>
<td>0.859298781121</td>
<td>936200288481</td>
</tr>
<tr>
<td>20</td>
<td>0.2</td>
<td>0.859298781566</td>
<td>936200289028</td>
</tr>
<tr>
<td>30</td>
<td>0.3</td>
<td>0.859298781650</td>
<td>936200289130</td>
</tr>
<tr>
<td>50</td>
<td>0.4</td>
<td>0.859298781692</td>
<td>936200289183</td>
</tr>
<tr>
<td>90</td>
<td></td>
<td>0.859298781709</td>
<td>936200289203</td>
</tr>
<tr>
<td>100</td>
<td></td>
<td>0.859298781710</td>
<td>936200289205</td>
</tr>
</tbody>
</table>

2.5.2 Above Ionisation Threshold (\( \omega > 0.5 \text{ a.u.} \))

The main difficulty of computing above threshold polarisabilities is that a pole occurs in the integrand due to the denominator of the term \( (\varepsilon - \varepsilon_i - \hbar \omega)^{-1} \) in Eqn. 2.52 when \( \varepsilon - \varepsilon_i = \hbar \omega \). In order to integrate across this pole, we must apply the Cauchy principal value method, where

\[
\int_0^\infty \frac{f(x)}{x-a-i0} \, dx = \mathcal{P} \int_0^\infty \frac{f(x)}{x-a} \, dx + i\pi f(x)|_{x=a}, \tag{2.57}
\]

such that the continuum contribution is then given by the resonant (\( -\omega \)) and off resonant (\( +\omega \)) terms.

\[
\alpha_{ij}^C(\omega) = \int_0^\infty C_{i\varepsilon,j} \frac{\langle j|z||\varepsilon\rangle\langle \varepsilon||z|i \rangle}{\varepsilon - \varepsilon_j - \omega} \, d\varepsilon + \mathcal{P} \int_0^\infty C_{i\varepsilon,j} \frac{\langle j|z||\varepsilon\rangle\langle \varepsilon||z|i \rangle}{\varepsilon - \varepsilon_i - \omega} \, d\varepsilon + i\text{Im}_1[\alpha_{ij}(\omega)], \tag{2.58}
\]

where \( \text{Im}_1[\alpha_{ij}(\omega)] = \pi C_{i\varepsilon_i + \omega,j} \langle j|z||\varepsilon_i + \omega\rangle\langle \varepsilon_i + \omega||z||i \rangle \), noting that \( \varepsilon_i < 0 \) for initial bound states. The calculation of \( \text{Im}_1[\alpha_{ij}(\omega)] \) is trivial, as it is analytic. The results of the exact calculation of \( \text{Im}_1[\alpha_{ij}(\omega)] \) using the analytical transition matrix elements will be compared with our numerical calculation and literature values in Section 3.2.2.

The real polarisability \( \text{Re}[\alpha(\omega)] = \text{Re}[\alpha^B(\omega)] + \text{Re}[\alpha^C(\omega)] \) is more complicated to calculate than \( \text{Im}_1[\alpha(\omega)] \) at frequencies above threshold. The bound contribution \( \text{Re}[\alpha^B(\omega)] \) can be computed in the same way as previously, and details of the bound contribution at frequencies \( \omega = 0.6 \) and 1.0 a.u. are given in Table 2.5. Here the bound sum is again extrapolated in order to gain a good approximation to the bound contribution. The first term in the integral in Eqn. 2.58 can be computed in the same way as previously - splitting the integral into \( N \) panels and integrating each panel with 16 point Gaussian integration.

However, the integral containing the pole,

\[
\int_0^\infty C_{i\varepsilon,j} \frac{\langle j|z||\varepsilon\rangle\langle \varepsilon||z|i \rangle}{\varepsilon - \varepsilon_j - \omega} \, d\varepsilon, \tag{2.59}
\]

cannot be integrated in this way. Longman [108] presented a method for integrating a function \( h(x) \) from
2.5. Semi-Analytical Method

Table 2.5: Convergence of the bound (real) polarisability sum \( \text{Re}[\alpha^{B\text{re}}_{1s,1s}](\omega) \) (in atomic units) at frequencies above the ionisation energy. The bound sum is extrapolated by a polynomial series extrapolation, where \( p \) is the power. \((-1)\) denotes \( \times 10^{-1} \).

<table>
<thead>
<tr>
<th>( N_{\text{panels}} )</th>
<th>Photon Frequency (a.u.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>-2.8615051 -6.6394498(-1)</td>
</tr>
<tr>
<td>11</td>
<td>-2.8720254 -6.6553694(-1)</td>
</tr>
<tr>
<td>12</td>
<td>-2.8801466 -6.6675987(-1)</td>
</tr>
<tr>
<td>13</td>
<td>-2.8865454 -6.6771975(-1)</td>
</tr>
<tr>
<td>( p )</td>
<td>3</td>
</tr>
<tr>
<td>( \infty (c_3) )</td>
<td>-2.9250608 -6.7349744(-1)</td>
</tr>
<tr>
<td>( \infty (c_3,4) )</td>
<td>-2.9253513 -6.7344568(-1)</td>
</tr>
<tr>
<td>( \infty (c_3,4,5) )</td>
<td>-2.9252898 -6.7346101(-1)</td>
</tr>
<tr>
<td>( \infty (c_3,4,5,6) )</td>
<td>-2.9252766 -6.7346043(-1)</td>
</tr>
</tbody>
</table>

\( x = -a \) to \( x = a \) with a pole at \( x = 0 \). The integral can be rewritten as

\[
\int_{-a}^{a} h(x)dx = \int_{0}^{a} [h(x) + h(-x)]dx. \tag{2.60}
\]

Since the aim is to integrate

\[
f(\varepsilon) = \frac{(j||z||\varepsilon)||z||i)}{\varepsilon - \varepsilon_i - \omega}, \tag{2.61}
\]

from \( 0 \to \infty \) which has a pole at \( \varepsilon = \varepsilon_i + \omega \), we must first rewrite the integral to be the same form as Eqn. 2.60. This can be done by splitting the integral into two parts, e.g.

\[
\int_{0}^{\infty} f(\varepsilon)d\varepsilon_i = \int_{0}^{2(\varepsilon_i+\omega)} f(\varepsilon)d\varepsilon + \int_{2(\varepsilon_i+\omega)}^{\infty} f(\varepsilon)d\varepsilon. \tag{2.62}
\]

The first integral \( I_1 \) must be integrated symmetrically across the pole at \( \varepsilon_i + \omega \). Rearranging this to the same form of the integral in Eqn. 2.60, gives

\[
I_1 = \int_{0}^{2(\varepsilon_i+\omega)} f(\varepsilon)d\varepsilon = \int_{\varepsilon_i + \omega}^{\varepsilon_i + \omega} f(u - \varepsilon_i - \omega)du, \tag{2.63}
\]

and applying Longman’s method gives

\[
I_1 = 2\int_{0}^{\varepsilon_i + \omega} (f(u - \varepsilon_i - \omega) + f(-u + \varepsilon_i + \omega))du, \tag{2.64}
\]

which can be integrated numerically as usual. The second integral in Eqn. 2.62 does not have a pole, and so can also be integrated normally since Gaussian integration does not compute at boundaries. Each integral is computed by splitting into \( N_{\text{panels}} \) panels and applying 16 point Gaussian integration. The continuum contribution is given with respect to the number of panels \( N_{\text{panels}} \) in Table 2.6 and shows very
good convergence even at a small number of panels.

Table 2.6: Convergence of the real polarisability continuum integral $\text{Re}[\alpha_{1s1s}(\omega)]$ (in atomic units) at frequencies above threshold, with respect to the number of panels used in the integration. Each panel is computed using 16 point Gaussian integration. $(-1)$ denotes $\times 10^{-1}$.

<table>
<thead>
<tr>
<th>$N_{\text{panels}}$</th>
<th>$\omega$ (a.u.)</th>
<th>0.6</th>
<th>1.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>$-3.725066416112(-1)$</td>
<td>$-5.325192456317(-1)$</td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>$-3.725066423038(-1)$</td>
<td>$-5.325192456196(-1)$</td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>$-3.725066425120(-1)$</td>
<td>$-5.325192456182(-1)$</td>
<td></td>
</tr>
<tr>
<td>40</td>
<td>$-3.725066426108(-1)$</td>
<td>$-5.325192456180(-1)$</td>
<td></td>
</tr>
<tr>
<td>50</td>
<td>$-3.725066426686(-1)$</td>
<td>$-5.325192456180(-1)$</td>
<td></td>
</tr>
<tr>
<td>60</td>
<td>$-3.725066427067(-1)$</td>
<td>$-5.325192456181(-1)$</td>
<td></td>
</tr>
<tr>
<td>70</td>
<td>$-3.725066427337(-1)$</td>
<td>$-5.325192456182(-1)$</td>
<td></td>
</tr>
<tr>
<td>80</td>
<td>$-3.725066427538(-1)$</td>
<td>$-5.325192456183(-1)$</td>
<td></td>
</tr>
<tr>
<td>90</td>
<td>$-3.725066427695(-1)$</td>
<td>$-5.325192456184(-1)$</td>
<td></td>
</tr>
<tr>
<td>100</td>
<td>$-3.725066427819(-1)$</td>
<td>$-5.325192456185(-1)$</td>
<td></td>
</tr>
</tbody>
</table>

I have demonstrated that the $\text{Re}[\alpha_{1s1s}(\omega)]$ is converged for our semi-analytical method. Table 2.7 gives an overview of the polarisability computed by our semi-analytical method compared with the data presented by Gavrila [16]. This table also shows the contribution to the polarisability from the bound state sum. Evidently the bound states have a very large contribution to the polarisability which generally becomes greater as the frequency approaches threshold and then drops off above threshold. I have not given a percentage at $\omega = 0.4$ a.u., as the bound state contribution was $\alpha^B = -18.36204$ and the continuum contribution $\alpha^C = 1.539376$. We can apply this same semi-analytical method to compute the transition polarisabilities of Raman processes (where an atom initially in state $i$ absorbs a photon of frequency $\omega$, emits a photon of frequency $\omega'$ and ends in the final state $j$ where $i \neq j$). Raman scattering will be considered in detail in Chapter 4.

In this Chapter I have introduced the complex polarisability and presented a semi-analytical calculation of the polarisability of atomic hydrogen. This semi-analytical calculation has shown the contribution

Table 2.7: Comparison of $\text{Re}[\alpha_{1s1s}(\omega)]$ (in atomic units) given by our semi-analytical calculation with the data given by Gavrila [16]. The contribution of the bound states to the total polarisability, $\alpha^B / (\alpha^B + \alpha^C)$ is also presented as a percentage.

<table>
<thead>
<tr>
<th>$\omega$ (a.u.)</th>
<th>Polarisability</th>
<th>% Bound states</th>
<th>Gavrila</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>4.4999986</td>
<td>81.4</td>
<td>-</td>
</tr>
<tr>
<td>0.1</td>
<td>4.7842988</td>
<td>82.0</td>
<td>4.784300</td>
</tr>
<tr>
<td>0.2</td>
<td>5.9416723</td>
<td>84.2</td>
<td>5.941675</td>
</tr>
<tr>
<td>0.3</td>
<td>10.563885</td>
<td>89.5</td>
<td>10.56389</td>
</tr>
<tr>
<td>0.4</td>
<td>-16.822664</td>
<td>-</td>
<td>-16.822644</td>
</tr>
<tr>
<td>0.6</td>
<td>-3.2977832</td>
<td>88.7</td>
<td>-3.29786</td>
</tr>
<tr>
<td>1.0</td>
<td>-1.2059797</td>
<td>55.8</td>
<td>-1.205980</td>
</tr>
</tbody>
</table>
of the bound and free states to the polarisability and demonstrated that the convergence of the bound state sum obeys a power series. Though the semi-analytical method presented in this method has been able to compute the polarisability, I have shown that the convergence can be relatively slow with respect to the number of bound states in the calculation. Another disadvantage of this method is that it can only be used for atomic hydrogen or other one-electron models as it requires analytic expressions of the transition matrix elements. In Chapter 3 I will develop a simple computational method to compute the complex polarisability for any atom. This computational method uses pseudostates to compute the complex polarisability at frequencies below and above threshold, and is validated for atomic hydrogen against previous calculations as well as the results given in this Chapter. In the next Chapter I will demonstrate that our numerical calculation of \( \text{Im} \left[ \alpha_{ii} (\omega) \right] \) is in agreement with our exact calculation using the analytical transition matrix elements, but in disagreement with results from Gavrila [1].
Chapter 3

Complex Polarisability through \texttt{patom}

In the previous Chapter the complex polarisability of atomic hydrogen was calculated with a semi-analytical method. Our semi-analytical method used the analytic expressions for hydrogen transition matrix elements derived by Gordon [17] in 1929. In this Chapter a method is developed for computing the complex polarisability using the energies and transition matrix elements provided by \texttt{patom}. Before this project, the energies and transition matrix elements given by \texttt{patom} have only previously been used to compute dynamic (real) polarisability below threshold. The one exception to this was the calculation by Tang \textit{et al.} [89] of the 3s lithium polarisability at a frequency just above threshold (energy of 0.00045 a.u. above ionisation energy) using \texttt{patom}.

In the calculation by Tang \textit{et al.} [89] the same method was used for above threshold frequencies as for the below threshold calculation. This was only possible because the continuum contribution to this polarisability was much smaller than the bound contribution, and so the uncertainty in the continuum calculation was not as important. As I will discuss in this Chapter, a different approach is needed to compute the polarisability at frequencies above threshold than at frequencies below threshold, due to the presence of unphysical pseudostates. In this Chapter I develop a numerical method for computing the polarisability calculation at frequencies above threshold using the pseudostate information given by \texttt{patom}.

Throughout this thesis I will refer to this numerical method as our “pseudostate method”. Note that this refers to our method for calculating the polarisabilities and scattering cross-sections, and should not be confused with the calculation of pseudostate information (energies and oscillator strengths) performed by \texttt{patom}.

3.1 Atomic Structure

In our calculation, \texttt{patom} uses a basis set of Laguerre type orbitals (LTO), given by [39]

\[ \chi_{\alpha}(r) = N_{\alpha} r^{\ell+1} e^{-\lambda_{\ell} r} L_{n_{\alpha}-\ell-1}^{(2\ell+2)}(2\lambda_{\ell} r) , \] (3.1)
3.1. Atomic Structure

where

$$N_{\alpha} = \sqrt{\frac{(2\lambda_\ell)^{2\ell+3}(n_\alpha - \ell - 1)!}{(\ell + n_\alpha + 1)!}},$$

(3.2)

and \(L^{(2\ell+2)}_{n_\alpha - \ell - 1}(2\lambda_\ell r)\) is a Laguerre polynomial, given by [39]

$$L^{(2\ell+2)}_{n_\alpha - \ell - 1}(2\lambda_\ell r) = \frac{(n_\alpha + \ell + 1)!}{(n_\alpha - \ell - 1)!(2\ell + 2)!}M(-n_\alpha - \ell - 1, 2\ell + 3, 2\lambda_\ell r),$$

(3.3)

where \(M(-n_\alpha - \ell - 1, 2\ell + 3, 2\lambda_\ell r)\) refers to a confluent hypergeometric function [41]. \(n_\alpha\) is the index given by \(N_\ell \leq \ell + 1 \geq n_\alpha \geq \ell + 1\) where \(N_\ell\) refers to the number of Laguerre functions with \(\ell\) angular momentum. The advantage of these Laguerre basis functions is that they can be optimised by changing only one variable, \(\lambda_\ell\), and are orthogonal. Larger values of \(\lambda_\ell\) bring the wavefunction closer in to the nucleus \((r = 0)\).

Unless specifically stated, the number of orbitals \(N_\ell\) will be the same for each partial wave \(\ell\). A simple way to check convergence is to run the calculation for different values of \(N_\ell\) as increasing the basis set size should lead to a more accurate description of the atom and more closely packed pseudostates. We will also look at the calculation with varying \(\lambda_\ell\). The energy and transition matrix element data for a small basis set \((N_\ell = 10)\) is given in Table B.1 of Appendix B, which can be used for example calculations for cross-sections of several Rayleigh and Raman transitions.

In the previous Chapter, the reduced transition matrix elements were discussed, and the analytic expressions for atomic hydrogen were presented. The most important difference between the semi-analytical calculation in the previous Chapter and the method developed in this Chapter is that now we have a set of pseudostates approximating the continuum. These pseudostates are a result of the atom-in-a-box model used by patom which discretises the continuum. The number of pseudostates increases for larger basis set size, whilst the oscillator strengths decrease as the number of pseudostates increases. In the following section the oscillator strengths given by patom will be considered in detail.

### 3.1.1 Oscillator Strength

patom produces reduced transition matrix elements that are independent of magnetic quantum number. The dimensionless oscillator strengths are related to these reduced transition matrix elements by [49]

$$f_{ij} = \frac{2\epsilon_{ji}}{3(2\ell_i + 1)} \frac{|\langle i | rC^1(\vec{r}) | j \rangle|^2}{},$$

(3.4)

and in a perfect calculation must obey the Thomas-Reiche-Kuhn sum rule

$$\sum_j f_{ij} = 1.$$  

(3.5)
In terms of our pseudostate calculation, this can be written as

\[
\sum_j f_{ij}^P + \sum_j f_{ij}^P \approx 1 ,
\]

(3.6)

where the sum over all oscillator strengths should tend to 1 for large basis set sizes. \(f_{ij}^P\) refers to the oscillator strengths given by \texttt{patom}. The example data set in Table B.1 in Appendix B demonstrates that the Thomas-Reiche-Kuhn sum-rule is obeyed in our pseudostate calculation, as the oscillator strengths for initial \(1s\), \(2s\), \(3s\) and \(3d\) states add to 1 within at least four significant figures.

As we add more pseudostates to our calculation (by using a larger basis set), the oscillator strength of each pseudostate must be smaller in order to still satisfy the Thomas-Reiche-Kuhn sumrule. The oscillator strengths of atomic hydrogen in the ground state (1s) computed by \texttt{patom} has been plotted in Fig. 3.1 for three different basis set sizes (\(N_\ell = 80, 100,\) and 120). Ionisation threshold is at \(\varepsilon = 0\) a.u. Fig. 3.1 demonstrates that the oscillator strengths to bound states (\(\varepsilon < 0\)) are unchanged for different basis sets, except at energies near threshold, and that the oscillator strengths to pseudostates (\(\varepsilon > 0\)) become smaller as the basis set size is increased.

The inset of Figure 3.1 shows that continuum behaviour starts below \(\varepsilon = 0\) a.u. These high energy bound states near ionisation threshold are referred to as Rydberg states. Since these Rydberg states exhibit continuum behaviour, it invites the question whether the ionisation threshold should really be at \(\varepsilon = 0\) au., or at the energy where the oscillator strengths have pseudostate behaviour. Note that this threshold approaches \(\varepsilon = 0\) a.u. when more Laguerres are used. The choice of ionisation energy has significant implications to the scattering cross-sections, which will be examined in Section 4.4.6. I will show that the Rydberg states have a large contribution to the cross-section, and so we must consider carefully if the contribution from these states should be considered as ‘continuum’ or ‘bound’. This distinction is particularly important when computing the Raman and Compton scattering cross-sections.

The pseudostate oscillator strengths can be normalised such that they agree with the analytic expression for the oscillator strength of hydrogen. The normalisation was found by considering the Thomas-Reich-Kuhn sum-rule in the analytical description and approximating the integral as a sum over pseudostates, so

\[
\sum_j f_{ij}^P + \int_0^\infty f_{i,\varepsilon} \varepsilon d\varepsilon \approx \sum_j f_{ij} + \sum_j f_{ij} \rho(\varepsilon_j)^2 = \sum_j f_{ij}^P + \sum_j f_{ij}^P, \tag{3.7}
\]

where \(f_{ij}^P\) refers to the \texttt{patom} oscillator strengths and \(\rho(\varepsilon_j)\) to the energy density of pseudostate \(j\). From this we know that the pseudostate oscillator strengths must be equivalent to the analytical oscillator strength multiplied by the energy density \(\rho(\varepsilon_j)\), so

\[
f_{ij}^P = f_{i,\varepsilon_j} \rho(\varepsilon_j)^2, \tag{3.8}
\]
3.2. Our Pseudostate Method

Figure 3.1: Plot of the oscillator strengths $f_{ij}^P$ for transitions from initial $i = 1s$ state to state $j$ (with energy $\varepsilon_j$ and angular momentum $\ell_j = 1$). Three different basis sets are shown with $N_\ell = 120$, 100 and 80, where $N_\ell$ refers to the number of Laguerre-type orbitals for each $\ell$. The inset zooms in on the region near the ionisation energy, and shows that the oscillator strengths of Rydberg states exhibit continuum behaviour.

where the energy density $\rho(\varepsilon_j)$ is given by

$$\rho(\varepsilon_j) = \sqrt{\frac{\varepsilon_{j+1} - \varepsilon_{j-1}}{2}}. \quad (3.9)$$

Fig. 3.2 compares the oscillator strength given by the analytic expression with the pseudostate oscillator strengths normalised by the energy density, $f_{ji}^P/\rho(\varepsilon_j)^2$. The bound oscillator strengths are scaled by $n^3$ as is well known [99]. Fig. 3.2 shows that the normalised continuum oscillator strengths agree well with the analytical oscillator strengths. Since the Rydberg states show continuum behaviour, but only states with energy $\varepsilon_j > 0$ were normalised, the oscillator strengths of these Rydberg states do not agree with the analytical function.

3.2 Our Pseudostate Method

In the previous section I have introduced the concept of pseudostates that originate due to the presence of a “box” confining the atom in our system. These pseudostates are unphysical states that describe the continuum. Here I present our method for computing photon-atom scattering cross-sections using these pseudostates.

To distinguish between the normalised transition matrix elements given by the analytic expressions (Eqns. 2.15 and 2.16) and the unnormalised transition matrix elements produced by patom, let us write
3.2. Our Pseudostate Method

Figure 3.2: Plot of the analytic oscillator strengths $f_{ij}$ for transitions from initial $i = 1s$ state to state $j$ (with energy $\varepsilon_j$ and angular momentum $\ell_j = 1$). The bound state oscillator strengths are scaled by $n^3$ and the pseudostate oscillator strengths have been normalised by $1/\rho(\varepsilon_j)^2$. Three different basis sets are shown with $N_\ell = 120, 100$ and $80$, where $N_\ell$ refers to the number of Laguerre-type orbitals for each $\ell$. The analytic oscillator strengths were calculated using the analytic expressions given in Eqns. 2.15 and 2.16. The inset shows that the bound and normalised pseudostate oscillator strengths are in agreement with the analytic function, except for Rydberg states.

The analytic oscillator strengths were calculated using the analytic expressions given in Eqns. 2.15 and 2.16. The inset shows that the bound and normalised pseudostate oscillator strengths are in agreement with the analytic function, except for Rydberg states.

The normalised transition matrix element as

$$T_{\varepsilon i} = \langle \varepsilon | z | i \rangle,$$

and use the notation $T_{\varepsilon i}^P$ to refer to the unnormalised transition matrix element. The relation between the bound-to-free transition matrix elements is given by

$$T_{\varepsilon i} = \frac{T_{\varepsilon i}^P}{\rho(\varepsilon_i)} \quad (3.11)$$

where $\rho(\varepsilon_i) = \sqrt{(\varepsilon_{i+1} - \varepsilon_{i-1})/2}$ is the energy density. For the boundary case i.e., at the highest pseudostate energy, the energy density is given by $\rho(\varepsilon_i) = \sqrt{\varepsilon_i - \varepsilon_{i-1}}$.

In the previous Chapter I have considered the calculation of the polarisabilities using analytic expressions for the transition matrix elements. The transition polarisability is given as a sum over the bound states and integral over the continuum,

$$\alpha_{ij}(\omega) = \sum_i C_{i,t,j} \left[ \frac{T_{jt} T_{ti}}{\varepsilon_{ti} - \omega + \varepsilon_{tj} + \omega} \right] + \int_0^\infty C_{i,\varepsilon,j} \left[ \frac{T_{je} T_{\varepsilon i}}{\varepsilon - \varepsilon_i - \omega} + \frac{T_{je} T_{\varepsilon i}}{\varepsilon - \varepsilon_j + \omega} \right] d\varepsilon \quad (3.12)$$

where $C_{i,t,j} = 1/3$ and $C_{i,\varepsilon,j} = 1/3$ from Delserieys et al. [48] for initial $\ell_i = 0$. We must modify this expression for the pseudostate calculation such that the sum over the bound states is a sum over all bound
states $N_B$ and the continuum integral is approximated as a sum over all pseudostates $N_P$,

\[
\alpha_{ij}(\omega) = \sum_{t}^N C_{i,t,j} \left[ \frac{T_{ji}^P T_{ti}^P}{\epsilon_i - \omega} + \frac{T_{ji}^P T_{ti}^P}{\epsilon_j + \omega} \right] + \sum_{t}^N C_{i,t,j} \left[ \frac{T_{ji}^P T_{ti}^P}{\epsilon_t - \epsilon_i - \omega} + \frac{T_{ji}^P T_{ti}^P}{\epsilon_t - \epsilon_j + \omega} \right] (3.13)
\]

\[
= \sum_{i}^N C_{i,t,j} \left[ \frac{T_{ji} T_{ti}}{\epsilon_i - \omega} + \frac{T_{ji} T_{ti}}{\epsilon_j + \omega} \right] + \sum_{t}^N C_{i,t,j} \left[ \frac{T_{ji} T_{ti}}{\epsilon_t - \epsilon_i - \omega} + \frac{T_{ji} T_{ti}}{\epsilon_t - \epsilon_j + \omega} \right] \Delta \epsilon_t, \quad (3.14)
\]

where $\Delta \epsilon_t = (\epsilon_{t+1} - \epsilon_{t-1})/2$.

### 3.2.1 Below the Ionisation Threshold ($\omega < 0.5$ a.u.)

In Section 2.4 the two imaginary components of the polarisability had been introduced, and the complex polarisability (at frequencies below threshold) is given by

\[
\alpha_{ij}(\omega) = \text{Re}[\alpha_{ij}(\omega)] + i\text{Im}[\alpha_{ij}(\omega)], \quad \forall \omega < \epsilon_{IP}
\]

where the $\text{Im}[\alpha_{ij}(\omega)]$ is related to the decay rates of the atomic states. $\text{Im}[\alpha_{ij}(\omega)]$ was discussed only briefly, and was not calculated in our semi-analytical method. The origin of this term is the decay rate of an atomic state such that the energies can be written as a complex term [35, 98] given by,

\[
\epsilon_j \rightarrow \epsilon_j - \frac{i\Gamma_j}{2},
\]

where $\Gamma_j$ refers to the linewidth of state $i$. Unlike our semi-analytical method, the decay rates will be included in our pseudostate method.

The exact formula implemented by paxom to calculate the linewidth is [109]

\[
A_{ij}^{(k)} = A_0 \frac{A^{(k)} \epsilon_{ij}^{2k+1}}{(2\ell + 1)C^{2k+1}} |\langle \psi_i | r^k C^{(k)}(\hat{r}) | \psi_j \rangle|^2, \quad (3.15)
\]

where $A_0$ and $A^{(k)}$ are constants (see reference [109] for more details). The Einstein coefficient is related to the decay rate $\Gamma_i$ and lifetime $\tau_i$ by [109]

\[
\frac{1}{\tau_i} = \Gamma_i = \sum_{k=1}^2 \Gamma_i^{(k)} = \sum_{k=1}^2 \left( \sum_{j: \epsilon_j < \epsilon_i} A_{ij}^{(k)} \right), \quad (3.16)
\]

where the $k = 1$ dipole and $k = 2$ quadrupole contributions are included.

The literature is somewhat ambiguous about the exact implementation of this decay term. Some papers have added the decay term as a negative value $(-i\Gamma/2)$ [8, 110], while others have added a negative decay term $(-i\Gamma/2)$ in the absorption term and a positive decay term $(+i\Gamma/2)$ in the emission term [102, 111, 112]. Some groups have included the decay term only in the absorption term [8], whilst others
3.2. Our Pseudostate Method

have included the decay term in both absorption and emission terms [110, 111]. The decay term has been calculated as the decay rate of the intermediate state $t$ only [8], $\Gamma = \Gamma_t$, or as the sum of the initial $i$ and intermediate state $t$ [111] $\Gamma = \Gamma_i + \Gamma_t$. Bonin et al. [102] have used the decay term as an average

$$\Gamma_{lk} = \frac{\Gamma_k + \Gamma_l}{2} + \Gamma'_{lk},$$

(3.17)

where $\Gamma'_{lk}$ is a dephasing rate constant.

Finally, some papers have included the decay term as a constant, whilst others have used a frequency dependent term. The choice of frequency dependence of the decay term has been considered in detail by Wijers [110]. Wijers has considered several criteria, such as that there should be no singular behaviour and causality should not be violated. These criteria must be met when choosing the frequency dependence of the decay. Wijers has also shown that the frequency dependent decay must be zero at zero frequency $\Gamma(0) = 0$. The consequence of this is that the imaginary polarisability $\text{Im}_0[\alpha_{ij}(\omega)] = 0$ at $\omega = 0$. Since the polarisability has only a real part at $\omega = 0$, the complex polarisability must refer to the polarisability at a non-zero frequency, i.e. the dynamic polarisability. The frequency dependence given by Wijers

$$\Gamma_t(\omega) = (\Gamma_t)^2 \frac{2\omega_i^2\omega^2}{\omega_i^4 + \omega^4},$$

(3.18)

where $\omega_i = \omega_t - \omega_i$.

We know that the wavefunctions given by path-templates are stationary, since the wavefunctions (given by the finite-basis set) are eigenstates and thus do not change with time. However, if time-dependent decay is included, then the wavefunctions are quasistationary. A quasistationary wavefunction has the form [113]

$$\Psi(r, \theta, \phi, t) = \psi(r, \theta, \phi) e^{-i\tilde{\epsilon}/\hbar},$$

where $\tilde{\epsilon} = \epsilon - i\Gamma/2$, where $\Gamma > 0$ is purely real. A consequence of having a negative imaginary part to the energy, is that $\psi(r, \theta, \phi)$ grows exponentially for $r \to \infty$. See Baz et al. [113] for a nice discussion on quasistationary wavefunctions. As I mentioned previously, it is not uncommon for either $+i\Gamma$ or $-i\Gamma$ to be used in the Kramers-Heisenberg matrix elements in the literature. The initial reason that I chose to use $-i\Gamma$ in my calculations was because Sakurai [35] includes the decay using $\epsilon_j \to \epsilon_j - i\Gamma_j$ in his derivation of the Kramers-Heisenberg matrix element. $-i\Gamma$ was also used by Sadeghpour et al. [8] and Wijers [110]. The choice of $\pm i\Gamma$ affects the sign of $\text{Im}_0[\alpha(\omega)]$, which is related to the (complex) index of refraction. However, in this thesis $\text{Im}_0[\alpha(\omega)]$ is used only to calculate the Rayleigh and Raman scattering cross-sections. The cross-sections are related to $|\alpha(\omega)|^2$ (see Eqn. 2.31), which corresponds to $\text{Re}[\alpha(\omega)]^2 + \text{Im}_0[\alpha(\omega)]^2$. Mathematically, the sign of the decay term does not affect the shape of the Lorentzian in the resonant part of the cross-section.

In our pseudostate method the imaginary decay term has been included as per Wijers, such that the complex polarisability is given by
Figure 3.3: Plot of the \( \text{Im} \left[ \alpha_{1s,1s}(\omega) \right] \) term using the ‘new frequency dependence’ given in Eqn. 3.21, Wijers frequency dependence given in Eqn. 3.18, and a constant decay term for the 1s-1s transition. A basis set of \( N_\ell = 120 \) was used, where \( N_\ell \) refers to the number of Laguerre-type orbitals for each \( \ell \).

\[
\alpha_{ij}(\omega) = \sum_t C_{i,t,j} \left[ \frac{T_{ji}^P T_{ii}^P}{\epsilon_{ti} - \omega - i \frac{\Gamma_{ii}(\omega)}{2}} + \frac{T_{ji}^P T_{ij}^P}{\epsilon_{tj} + \omega - i \frac{\Gamma_{tj}(\omega)}{2}} \right],
\]

but our frequency-dependent decay term \( \Gamma_{ii}(\omega) \) is given by

\[
\Gamma_{ii}(\omega) = \Gamma_i(\omega) + \Gamma_t(\omega).
\]

These decay rates are closely related to the linewidth of each state. Since a linewidth of the continuum makes no physical sense, the decay rates of the pseudostates are set to zero, so

\[
\Gamma_t = 0 \quad \text{if } \epsilon_t > \epsilon_{IP}.
\]

In the frequency dependence given by Wijers, the decay term becomes small at very large frequencies, but does not go to zero. This means that even for extremely high-frequency photons, there will still be an imaginary term in the polarisability related to the decay of a bound state. This is demonstrated in Fig. 3.3, where I have plotted the imaginary polarisability related to decay, \( \text{Im} \left[ \alpha_{1s,1s}(\omega) \right] \), using different functions for the frequency dependence of the decay term. \( \text{Im} \left[ \alpha_{1s,1s}(\omega) \right] \) is non-zero for all frequencies \( \omega > 0 \) when the decay term given by Eqn. 3.18 is used [110].

I have also considered a different frequency dependence for the decay term, which is referred to as “New freq. dep.” in Fig. 3.3. For this frequency dependence I have assumed that the decay must be zero at frequencies above the ionisation energy. By setting the decay to zero above threshold, the \( \text{Im} \left[ \alpha_{ij}(\omega) \right] \) term is also zero above threshold. To ensure that the \( \Gamma_{ii}(\omega) \to 0 \) as \( \omega \to \epsilon_{IP} \) and is symmetric, I have
3.2. Our Pseudostate Method

used (in atomic units)

\[ \Gamma_{it}(\omega) = (\Gamma_i + \Gamma_t) \left( \frac{(\epsilon_{IP} - |\omega|)^2 (|\omega| - 2\epsilon_{ti} + \epsilon_{IP})^2}{(\epsilon_{IP} - \epsilon_{ti})^4} \right), \quad \omega < \epsilon_{IP}, \]

and \( \Gamma_{it}(\omega) = 0, \quad \omega > \epsilon_{IP}. \) The real and imaginary polarisabilities are calculated using the frequency dependence of the linewidth given in Eqn. 3.21 and are converged at frequencies below threshold (see Appendix D Tables D.2 and D.3).

Though I have shown that the frequency-dependence of Eqn. 3.21 gives converged values for \( \text{Im}_0[\alpha_{1s,1s}(\omega)] \), difficulties arise when we consider an initial state that is not the ground state. Let us consider, for example, \( \text{Re}[\alpha_{3s,3s}(\omega)] \) of atomic hydrogen. In this case resonances will occur at frequencies below ionisation energy, corresponding to the case where the intermediate bound state \( t \) has energy \( \epsilon_t - \epsilon_i = \omega. \) However, there is now an intermediate state lower in energy then the initial state - the 2p state - which will result in a resonance above the ionisation energy. The resonance above threshold can be seen in our calculation of the 3s-3s transition polarisability in upcoming Section 3.2.3. This resonance is real as it is due to the bound state, and so must have a non-zero linewidth and decay rate. However, the frequency-dependence given in Eqn. 3.21 sets the decay to zero at frequencies above ionisation energy. For this reason the decay rate cannot have the frequency-dependence given in Eqn. 3.21. For the remainder of this thesis the frequency-dependence given by Wijers (Eqn. 3.18) will be used for the decay rate.

The real polarisability of the 1s-1s transition in atomic hydrogen is presented in Fig. 3.4. Our pseudostate calculation is compared with both our semi-analytical calculation as well as the analytical calculation by Gavrila [1]. The real part of the matrix element \( M \) given by Gavrila’s data is related to the transition polarisabilities by \( \text{Re}[\alpha_{1s,1s}] = \text{Re}[M(\omega)]/\omega^2. \) This relation of the polarisability to Gavrila’s matrix elements was pointed out by Sadeghpour et al. [8].

The dashed line referred to as “\( \text{Re}[\alpha] \) with poles” corresponds to our calculation of Eqn. 3.19 at frequencies both below and above threshold. We find that this calculation agrees with both our semi-analytical calculation and Gavrila’s values at frequencies below ionisation threshold. On the other hand poles occur at frequencies above ionisation energy that are not physical. These poles occur due to the \( \epsilon_{ti} - \omega \) denominator in the polarisability and occur when the photon frequency is on resonance with a pseudostate, i.e. \( \omega = \epsilon_t - \epsilon_i \) where \( \epsilon_i \) is the energy of a pseudostate. The poles above threshold are simply an artifact of our pseudostate calculation, and must be removed to give the real polarisability above threshold. The real polarisability without the pseudostate poles is also plotted in Fig. 3.4. Our method for computing this is presented in the following section.
3.2. Our Pseudostate Method

Figure 3.4: Plot of \(\text{Re}[\alpha_{1s,1s}(\omega)]\) given by our pseudostate method \((N_\ell = 120\) basis, where \(N_\ell\) is the number of Laguerre-type orbitals for each \(\ell\)), the semi-analytical method and Gavrila’s analytical calculation [16]. Our semi-analytical calculation used \(N = 800\) bound states and calculated the continuum integral by using \(N_{\text{panel}} = 100\) panels and applying 16 point Gaussian integration. “\(\text{Re}[\alpha_{1s,1s}(\omega)]\) with poles” (dashed line) is calculated from Eqn. 3.19, whilst \(\text{Re}[\alpha_{1s,1s}(\omega)]\) is computed using Eqn. 3.23, discussed in next section.

3.2.2 Above the Ionisation Threshold \((\omega > 0.5\ \text{a.u.})\)

At frequencies above the ionisation threshold, the polarisability (see Eqn. 3.12) has a pole in the continuum integral at \(\epsilon = \epsilon_i + \omega\) when \(\omega > |\epsilon_i|\). In the previous Chapter, the Cauchy principal value integral was used to integrate around this pole, resulting in an imaginary term \(\text{Im}[\alpha(\omega)]\) related to the ionisation cross-section. In the pseudostate calculation a pole also occurs when \(\epsilon_t = \epsilon_i + \omega\) when \(\omega > |\epsilon_i|\). We can transform our expression (Eqn. 2.58) for the continuum contribution \(\alpha^c\) at frequencies above threshold such that it is written in terms of a pseudostate sum. This is given by

\[
\alpha^c(\omega) = \int_0^\infty C_{i,e,j} \frac{T_{je} T_{ei}}{\epsilon - \epsilon_j + \omega} d\epsilon + \mathcal{P} \int_0^\infty C_{i,e,j} \frac{T_{je} T_{ei}}{\epsilon - \epsilon_i - \omega} d\epsilon + i\pi C_{i,e,j} T_{je} T_{ei} \bigg|_{\epsilon = \epsilon_t + \omega},
\]

\[
= \sum_{j}^{N_p} C_{i,j} \frac{T_{je}^P T_{ei}^P}{\epsilon_t - \epsilon_j + \omega} + \sum_{j \neq \epsilon_i + \omega}^{N_p} C_{i,j} \frac{T_{je}^P T_{ei}^P}{\epsilon_t - \epsilon_i - \omega} + i\pi C_{i,j} T_{je}^P T_{ei}^P \bigg|_{\epsilon = \epsilon_t + \omega},
\]

where the imaginary part gives \(\text{Im}[\alpha_{ij}(\omega)]\). This method removes the pseudostate from the sum when \(\epsilon_t = \omega + \epsilon_i\), where \(\epsilon_t\) is the energy of the pseudostate. Therefore, we compute the polarisability above threshold at discrete frequencies that fulfill the condition \(\omega = \epsilon_t - \epsilon_i\) where the \(\epsilon_t\) are discretised pseudostate energies.

We are now able to compute the polarisability at frequencies both below and above ionisation energy. The real polarisability given by this method for the \(1s-1s\) transition is plotted in Fig. 3.4, and shows good
agreement with both our semi-analytical calculation and Gavrila’s data [1] above threshold. The convergence of $\text{Re}[\alpha_{1s,1s}(\omega)]$ and $\text{Im}_1[\alpha_{1s,1s}(\omega)]$ for this method is presented in Table 3.1 for frequencies above threshold. Though the convergence is relatively slow, our pseudostate method gives the real polarisability accurate to within 1% by $N_\ell = 20$ for $\omega = 0.6$ a.u. and $N_\ell = 40$ for $\omega = 1.0$ a.u. (as compared to Gavrila’s $\text{Re}[M]/\omega^2$ data [1]).

Table 3.1: Convergence of $\text{Re}[\alpha_{1s,1s}(\omega)]$ and $\text{Im}_1[\alpha_{1s,1s}(\omega)]$ polarisabilities (in atomic units) at frequencies above threshold with respect to the basis set size in the pseudostate calculation. $N_\ell$ refers to the number of Laguerre-type orbitals for each $\ell$ in the basis. At above threshold frequencies, the polarisability can only be computed on frequencies corresponding to pseudostate energies. Since these pseudostate energies change for different basis sets, each calculation has a different set of frequencies above threshold. The convergence was investigated at specific frequencies for all basis sets by interpolating between the closest two frequencies.

<table>
<thead>
<tr>
<th>$N$</th>
<th>$\omega = 0.6$ a.u. $\text{Re}[\alpha_{1s,1s}(\omega)]$</th>
<th>$\omega = 1.0$ a.u. $\text{Re}[\alpha_{1s,1s}(\omega)]$</th>
<th>$\omega = 0.6$ a.u. $\text{Im}<em>1[\alpha</em>{1s,1s}(\omega)]$</th>
<th>$\omega = 1.0$ a.u. $\text{Im}<em>1[\alpha</em>{1s,1s}(\omega)]$</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>-3.2625</td>
<td>-1.1576</td>
<td>2.4503</td>
<td>0.3431</td>
</tr>
<tr>
<td>30</td>
<td>-3.2780</td>
<td>-1.1809</td>
<td>2.4847</td>
<td>0.3598</td>
</tr>
<tr>
<td>40</td>
<td>-3.2846</td>
<td>-1.1892</td>
<td>2.4958</td>
<td>0.3642</td>
</tr>
<tr>
<td>50</td>
<td>-3.2879</td>
<td>-1.1923</td>
<td>2.4998</td>
<td>0.3646</td>
</tr>
<tr>
<td>60</td>
<td>-3.2898</td>
<td>-1.1940</td>
<td>2.5010</td>
<td>0.3642</td>
</tr>
<tr>
<td>80</td>
<td>-3.2921</td>
<td>-1.1959</td>
<td>2.5027</td>
<td>0.3632</td>
</tr>
<tr>
<td>100</td>
<td>-3.2934</td>
<td>-1.1970</td>
<td>2.5035</td>
<td>0.3625</td>
</tr>
<tr>
<td>120</td>
<td>-3.2943</td>
<td>-1.1980</td>
<td>2.5042</td>
<td>0.3621</td>
</tr>
</tbody>
</table>

Gavrila [1] -3.29779 -1.20598

The imaginary polarisability $\text{Im}_1[\alpha_{1s,1s}(\omega)]$ for hydrogen given by this method is presented in Fig. 3.5, which is in good agreement with the purely-analytical calculation given in the previous Chapter. I have also plotted the imaginary part of the matrix element $M$ given by Gavrila as $\text{Im}_1[M]/\omega^2$ and $\text{Im}_1[M]/\omega^4$ [1].

Gavrila’s matrix element $M$ is related to the Kramers-Heisenberg matrix element $\mathcal{M}$ (for elastic scattering) by

$$\mathcal{M} = (\mathbf{s} \cdot \mathbf{s'})M, \quad (3.24)$$

where $\mathbf{s}$ and $\mathbf{s'}$ are the initial and final polarisation of the elastically scattered photon. From Gavrila’s definition of the differential Rayleigh scattering cross-section,

$$d\sigma = r_e^2|\mathcal{M}|^2d\Omega, \quad (3.25)$$

we know that our polarisability $\alpha$ is related to $M$ by

$$M = \omega^2\alpha. \quad (3.26)$$
Though I have shown in Fig. 3.4 that our real polarisability is in good agreement with \( \text{Re}[M]/\omega^2 \), our imaginary polarisability values are in significant disagreement with \( \text{Im}_1[M]/\omega^2 \). We have better agreement with \( \text{Im}_1[M]/\omega^4 \), though we are still in disagreement at lower energies. Note that this disagreement is relatively large as Fig. 3.5 is plotted on a log scale. Though we are in disagreement with the imaginary values presented by Gavrila, I will show in Chapter 4 that our \( \text{Im}_1[\alpha_{ii}(\omega)] \) calculation is correct by validating against the photoionisation cross-sections.

Figure 3.5: Plot of imaginary \( \text{Im}_1[\alpha_{1s,1s}(\omega)] \) polarisability (in atomic units) given by our pseudostate method \((N_\ell = 120 \text{ basis, where } N_\ell \text{ is the number of Laguerre-type orbitals for each } \ell)\), the purely-analytical (exact) method given in the previous Chapter, and Gavrila’s analytical calculation [1] (with two different scalings).

### 3.2.3 Initial 2s and 3s states

Let us now consider Rayleigh transitions from excited states. The 2s-2s transition polarisability is given in Fig. 3.6 (a) and the 3s-3s transition polarisability is given in Fig. 3.6 (b). These figures show good agreement for our pseudostate and semi-analytical method at frequencies below and above threshold frequencies. The values given by Chandrasekharan et al. [114] at \( \omega = 0 \) also agree with our calculations.

The 3s-3s transition polarisability in Fig. 3.6 (b) exhibits a pole at \( \omega = 0.0694 \text{ a.u.} \) which corresponds to the energy difference between the 3s and 2p state. The 2p state of atomic hydrogen has a large linewidth, and the pole corresponding to this state should have a width related to the 2p linewidth. As I have previously stated, this indicates that the frequency-dependence I had constructed in Eqn. 3.21 cannot be used, as it would give \( \Gamma = 0 \). The Wijer’s frequency dependence given by Eqn. 3.18 is used instead.
3.3. Langhoff et al. Pseudostate Method

Langhoff et al. presented a pseudostate method for computing the polarisability, photoionisation and Rayleigh scattering cross-sections in several papers in the 1970s [46, 90, 103]. An explanation of this method is also given in reference [115]. The method by Langhoff et al. extracts a set of ‘principal pseudostates’ from a pseudospectrum and applies the Stieltjes imaging technique. These principal pseudostates are chosen such that their energy \( \tilde{\varepsilon}_j \) and oscillator strengths \( \tilde{f}_j \) reproduce the oscillator strength

Figure 3.6: Plot of (a) \( \text{Re}[\alpha_{2s,2s}(\omega)] \) and (b) \( \text{Re}[\alpha_{3s,3s}(\omega)] \) given by our pseudostate and semi-analytical calculation and compared with the analytic polarisability at \( \omega = 0 \) a.u. given by Chandrasekharan et al. [114]. Our pseudostate calculation used a basis of \( N_\ell = 120 \), where \( N_\ell \) is the number of Laguerre-type orbitals for each \( \ell \). Our semi-analytical calculation used \( N = 800 \) bound states and calculated the continuum integral by using \( N_{\text{panel}} = 100 \) panels and applying 16 point Gaussian integration.
3.3. Langhoff et al. Pseudostate Method

sum rules,

\[ S(k) = \sum_{j=1}^{n} \tilde{\epsilon}_j f_j \]  

(3.27)

Langhoff et al. consider this as a moment problem, and refers to the oscillator strength sum rules as spectral moments. The differential distribution of the oscillator strengths is then approximated as

\[ g(\tilde{\omega}_j) = \tilde{g}_j = \frac{\tilde{f}_j + \tilde{f}_{j+1}}{2(\tilde{\epsilon}_{j+1} - \tilde{\epsilon}_j)} , \]

(3.28)

where

\[ \tilde{\omega}_j = \frac{1}{2}(\tilde{\epsilon}_j + \tilde{\epsilon}_{j+1}) . \]

The \( g(\tilde{\omega}_j) \) used by Langhoff et al. is similar to our normalised oscillator strengths which are given by the (almost) centred-approximation \( f_{ij} = f_{ij}^B / (\epsilon_{j+1} - \epsilon_{j-1}) \). However, we compute at frequencies that correspond to pseudostate energies, whilst Langhoff et al. consider frequencies that correspond to the average of two of their ‘principal pseudostate’ energies.

When the frequency is below the ionisation threshold, the real polarisability is given by Langhoff et al. to be

\[ \text{Re}[\alpha(\omega)] = \sum_i \frac{\tilde{F}_i}{\epsilon_i^2 - \omega^2} + \sum_j \frac{\tilde{g}_j}{2\omega} \ln \left( \frac{(\tilde{\epsilon}_j + \omega)(\tilde{\epsilon}_{j+1} - \omega)}{(\tilde{\epsilon}_{j+1} + \omega)(\tilde{\epsilon}_j - \omega)} \right) . \]

(3.29)

In the notation used by Langhoff et al. the oscillator strengths of the bound states are denoted as \( \tilde{F}_j \).

Unlike our pseudostate method, the continuum contribution in the Langhoff method is transformed into a \( \ln \) function rather than the simpler summation given by our method. The reasoning for this is that Langhoff et al. rewrite the continuum integral as a sum over the pseudostate intervals, and integrate each interval,

\[ \alpha(\omega) = \sum_i \frac{\tilde{F}_i}{\epsilon_i^2 - \omega^2} + \int_0^{\infty} \frac{\tilde{g}(\epsilon)}{(\epsilon - \epsilon_n)^2 - \omega^2} d\epsilon \approx \sum_i \frac{\tilde{F}_i}{\epsilon_i^2 - \omega^2} + \sum_k \int_{\tilde{\epsilon}_k}^{\tilde{\epsilon}_{k+1}} \frac{\tilde{g}(\epsilon)}{(\epsilon - \tilde{\epsilon}_n)^2 - \omega^2} d\epsilon , \]

(3.30)

\[ = \sum_i \frac{\tilde{F}_i}{\epsilon_i^2 - \omega^2} + \sum_k \int_{\tilde{\epsilon}_k}^{\tilde{\epsilon}_{k+1}} \frac{\tilde{g}_k}{2\omega} \left( \frac{1}{\epsilon - \tilde{\epsilon}_n - \omega} - \frac{1}{\epsilon - \tilde{\epsilon}_n + \omega} \right) d\epsilon , \]

(3.31)

where \( \epsilon_n \) is the ground state energy and \( \tilde{g}_k \) is the continuum oscillator strength at energy halfway between \( \epsilon_k \) and \( \epsilon_{k+1} \). From this the polarisability (at below threshold frequencies) is then given to be

\[ \alpha(\omega) = \sum_i \frac{\tilde{F}_i}{\epsilon_i^2 - \omega^2} + \sum_k \int_{\tilde{\epsilon}_k}^{\tilde{\epsilon}_{k+1}} \frac{\tilde{g}_k}{2\omega} \left( \frac{1}{\epsilon - \tilde{\epsilon}_n - \omega} - \frac{1}{\epsilon - \tilde{\epsilon}_n + \omega} \right) d\epsilon \]

(3.32)

\[ \approx \sum_i \frac{\tilde{F}_i}{\epsilon_i^2 - \omega^2} + \sum_k \frac{\tilde{g}_k}{2\omega} \left[ \ln |\epsilon - \tilde{\epsilon}_n - \omega| - \ln |\epsilon - \tilde{\epsilon}_n + \omega| \right]_{\tilde{\epsilon}_k}^{\tilde{\epsilon}_{k+1}} . \]

(3.33)

\[ = \sum_i \frac{\tilde{F}_i}{\epsilon_i^2 - \omega^2} + \sum_k \frac{\tilde{g}_k}{2\omega} \left[ \ln \left( \frac{(\tilde{\epsilon}_{k+1} - \tilde{\epsilon}_n - \omega)(\tilde{\epsilon}_k - \tilde{\epsilon}_n + \omega)}{(\tilde{\epsilon}_{k+1} - \tilde{\epsilon}_n + \omega)(\tilde{\epsilon}_k - \tilde{\epsilon}_n - \omega)} \right) \right] . \]

(3.34)
Note that this derivation was initially pointed out to me by Dr. Cheng and Dr. Bromley, and provided the initial motivation for our simpler approach.

At above threshold frequencies, Langhoff et al. gives the real polarisability to be

\[
\text{Re}[\alpha(\tilde{\omega}_j)] = \sum_i \frac{\tilde{F}_i}{\varepsilon_i^2 - \tilde{\omega}_j^2} + \sum_{k \neq j} \int_{\tilde{\epsilon}_k}^{\tilde{\epsilon}_{k+1}} \frac{\tilde{g}_k}{2\tilde{\omega}_j} \left( \frac{1}{\varepsilon - \tilde{\epsilon}_n - \tilde{\omega}_j} - \frac{1}{\varepsilon - \tilde{\epsilon}_n + \tilde{\omega}_j} \right) d\varepsilon
\]

\[
+ \int_{\tilde{\epsilon}_j}^{\tilde{\epsilon}_{j+1}} \frac{\tilde{g}_j}{2\tilde{\omega}_j} \left( -\frac{1}{\varepsilon - \tilde{\epsilon}_n + \tilde{\omega}_j} \right) d\varepsilon,
\]

and the imaginary part is given by

\[
\text{Im}[\alpha(\tilde{\omega}_j)] = \pi \frac{\tilde{g}_j}{2\tilde{\omega}_j}.
\]

It is evident that our method given by Eqn. 3.23 is simpler than the method presented by Langhoff et al., but the true test of the methods occurs when we compare their convergence and accuracy. When comparing the two methods, we refer to the method presented by Langhoff et al. as the ‘Langhoff method’. The true Langhoff method would have constructed moments, for example, by compressing many pseudostates down to just a few.

### 3.4 Comparison of Pseudostate-based Polarisability Calculations

Let us now compare \(\text{Re}[\alpha_{1s,1s}(\omega)]\) for the various methods at frequencies both below and above ionisation threshold. Fig. 3.7 plots \(\text{Re}[\alpha_{1s,1s}(\omega)]\) given by our pseudostate method, the Langhoff method, our semi-analytical calculation as well as data from Gavrila [1]. The inset in Fig. 3.7 shows the behaviour of the various calculations near threshold. From this we can see that our pseudostate calculation tends to \(\text{Re}[\alpha_{1s,1s}(\omega)] \approx -4.4\) at the ionisation threshold, whilst the Langhoff method gives diverging values of the polarisability. Though our semi-analytical calculation is no longer equal to our pseudostate calculation at frequencies directly above threshold, it has much better agreement than with the Langhoff method.

Let us make a closer comparison of the different methods by considering the convergence of the polarisability below threshold in Table 3.2. The data shows that the polarisability calculated with our pseudostate method is converged to more than 10 significant figures. On the other hand, the Langhoff method is converged to only three significant figures. The polarisability computed with our pseudostate calculation is in agreement with Gavrila’s values, whilst our semi-analytical calculation is accurate to five significant figures (since we do not do the extrapolation of the bound states to \(N \to \infty\)).
3.4. Comparison of Pseudostate-based Polarisability Calculations

Figure 3.7: Plot of $\text{Re}[\alpha_{1s,1s}(\omega)]$ at frequencies above threshold given by our pseudostate method and the Langhoff method. This plot demonstrates good agreement between the two methods at higher frequencies, whereas there is significant discrepancy at frequencies close to threshold (shown in inset). At low frequencies the semi-analytical calculation is in better agreement with our pseudostate method than the Langhoff method. Our semi-analytical calculation used $N = 800$ bound states and calculated the continuum integral by using $N_{\text{panel}} = 100$ panels and applying 16 point Gaussian integration.

Our pseudostate and the Langhoff method compute the polarisability above threshold at different frequencies. In order to compare these methods at the same frequencies, I have linearly interpolated between the closest values. Table 3.3 presents the convergence at frequencies very close to threshold. The slight disagreements between the various methods (our pseudostate, semi-analytical and Langhoff method) indicate that it is very difficult to compute the polarisability near threshold.
3.4. Comparison of Pseudostate-based Polarisability Calculations

Table 3.2: Comparison of Re[α_{1s,1s}(\omega)] (in atomic units) given by our pseudostate method with the Langhoff method, our semi-analytical calculation and data given by Gavrila [1] at frequencies below threshold. Our pseudostate method and the Langhoff method were applied to the same basis set of \( N_\ell = 120, 100 \) and 80, where \( N_\ell \) is the number of Laguerre-type orbitals for each \( \ell \). Our semi-analytical calculation used \( N = 800 \) bound states and calculated the continuum integral by using \( N_{\text{panel}} = 100 \) panels and applying 16 point Gaussian integration.

<table>
<thead>
<tr>
<th>Frequency (a.u.)</th>
<th>0.1</th>
<th>0.2</th>
<th>0.3</th>
<th>0.4</th>
</tr>
</thead>
<tbody>
<tr>
<td>( N_\ell = 120 )</td>
<td>4.78430034299754</td>
<td>5.94167486099454</td>
<td>10.563888867155</td>
<td>-16.8226453544919</td>
</tr>
<tr>
<td>( N_\ell = 100 )</td>
<td>4.78430034299754</td>
<td>5.94167486099454</td>
<td>10.563888867155</td>
<td>-16.8226453544919</td>
</tr>
<tr>
<td>( N_\ell = 80 )</td>
<td>4.78430034296586</td>
<td>5.94167486094312</td>
<td>10.563888866971</td>
<td>-16.8226453556444</td>
</tr>
</tbody>
</table>

Table 3.3: Comparison of Re[α_{1s,1s}(\omega)] (in atomic units) given by our pseudostate calculation, the Langhoff method and our semi-analytical calculation at frequencies just above threshold. Our pseudostate method and the Langhoff method were applied to the same basis sets of \( N_\ell = 80, 100, 120 \), where \( N_\ell \) is the number of Laguerre-type orbitals for each \( \ell \). The values from our pseudostate method and Langhoff method were found at the frequencies given in this table by linear interpolation of the closest values. Our semi-analytical calculation used \( N = 800 \) bound states and calculated the continuum integral by using \( N_{\text{panel}} = 100 \) panels and applying 16 point Gaussian integration.

<table>
<thead>
<tr>
<th>Frequency (a.u.)</th>
<th>0.51</th>
<th>0.52</th>
<th>0.53</th>
<th>0.54</th>
</tr>
</thead>
<tbody>
<tr>
<td>Our Pseudostate Method</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( N_\ell = 120 )</td>
<td>-4.233</td>
<td>-4.119</td>
<td>-4.008</td>
<td>-3.900</td>
</tr>
<tr>
<td>( N_\ell = 100 )</td>
<td>-4.237</td>
<td>-4.121</td>
<td>-4.010</td>
<td>-3.901</td>
</tr>
<tr>
<td>( N_\ell = 80 )</td>
<td>-4.243</td>
<td>-4.125</td>
<td>-4.012</td>
<td>-3.902</td>
</tr>
<tr>
<td>Langhoff Method</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( N_\ell = 120 )</td>
<td>-4.150</td>
<td>-4.070</td>
<td>-3.972</td>
<td>-3.872</td>
</tr>
<tr>
<td>( N_\ell = 100 )</td>
<td>-4.136</td>
<td>-4.062</td>
<td>-3.966</td>
<td>-3.866</td>
</tr>
<tr>
<td>( N_\ell = 80 )</td>
<td>-4.087</td>
<td>-4.039</td>
<td>-3.951</td>
<td>-3.854</td>
</tr>
<tr>
<td>Semi-analytical</td>
<td>-4.207</td>
<td>-4.103</td>
<td>-3.999</td>
<td>-3.894</td>
</tr>
</tbody>
</table>

Table 3.4 gives the polarisability at \( \omega = 0.55, 0.6, 0.8 \) and 1.0 a.u. for the Langhoff method and our pseudostate method. Our semi-analytical calculation is in good agreement with Gavrila’s data, and we can also see that our pseudostate calculation is more accurate than the Langhoff method at the lower frequencies (\( \omega = 0.55, 0.6 \) a.u.).
3.5 Alternative use of the Cauchy Principal Value Theorem

The imaginary $\text{Im} \{ \alpha_{ii}(\omega) \}$ is related to the photoionisation cross-section through the optical theorem. In the semi-analytical and pseudostate method above the $\text{Im} \{ \alpha \}$ polarisability was found by applying the Cauchy Principal Value theorem. There is also an alternative method for applying the Cauchy Principal Value theorem, which for example was used by Cormier et al. [64] to compute the multi-photon ionisation cross-sections. Rather than applying the Cauchy principal value theorem directly, the pole in the integral is computationally avoided by adding a small imaginary term $i\Delta$, so

\[
\alpha_{ii}(\omega) = \sum_{t} C_{i,t,j} \left[ \frac{\langle i|z|t\rangle \langle t|z|i \rangle}{\epsilon_{ti} - \omega} + \frac{\langle i|z|t\rangle \langle t|z|i \rangle}{\epsilon_{tj} + \omega} \right] + \int_{0}^{\infty} C_{i,e,j} \left[ \frac{\langle i|\epsilon|e\rangle \langle e|z|i \rangle}{\epsilon - \epsilon_{i} - \omega - i\Delta} + \frac{\langle i|\epsilon|e\rangle \langle e|z|i \rangle}{\epsilon - \epsilon_{j} + \omega} \right] d\epsilon .
\]

Cormier et al. [64] computed multi-photon ionisation cross-sections by decreasing this imaginary term $i\Delta$ and extrapolating to zero. The polarisability tends to some real and imaginary value before
diverging as $\Delta$ becomes small. This divergence occurs when $\Delta$ becomes smaller than the energy spacing between the pseudostates, i.e. the integrand varies sharply when $\Delta \to 0$ and the energy spacing is too large to take this into account, resulting in a divergence [64]. I have applied this method, as shown in Fig. 3.8 to compute the polarisability at $\omega = 0.6$ and 1.0 a.u. The energy spacing to the two nearest pseudostate from below and above are indicated by the vertical dashed lines. For the case where $\omega = 1.0$ a.u., the energy spacing to the nearest pseudostate is very small and can be barely seen on the plots. From Fig. 3.8 we can see that the divergence occurs when $\Delta$ is greater than the energy difference to the nearest pseudostate.

Figure 3.8: Plot of $\Re[\alpha_{1s,1s}]$ (left) and $\Im[\alpha_{1s,1s}]$ (right) at frequency $\omega = 0.6$ a.u. (a),(b) and $\omega = 1.0$ a.u. (c),(d). The solid black line gives the polarisability computed with the small imaginary $\Delta$ term, and the grey dashed line gives the polynomial extrapolation. The pseudostate calculation uses a basis of $N_{\ell} = 120$, where $N_{\ell}$ is the number of Laguerre-type orbitals for each $\ell$. The polarisability given by our semi-analytical calculation is plotted at $\Delta = 0$. Our semi-analytical calculation used $N = 800$ bound states and calculated the continuum integral by using $N_{\text{panel}} = 100$ panels and applying 16 point Gaussian integration. The black vertical dashed lines indicate the energy spacing to the nearest pseudostates.

In Fig. 3.8 I have compared the polarisabilities given by this method with the result from our semi-analytical method. Though the two methods do seem to agree, it is evident that the method used by Cormier et al. has a very large uncertainty, as the extrapolated value is dependent on where and how the extrapolation is done. In Fig. 3.8 I have extrapolated the real and imaginary polarisabilities using
3.6 Pseudostate Packing

One drawback of our pseudostate method is that we can only compute at specific frequencies above threshold. Our method results in a set of values above threshold corresponding to frequencies on resonance with a pseudostate. We have developed a method we refer to as “pseudostate packing”, where our aim is to pack new pseudostates between existing pseudostates. This method would be particularly useful in computing the hyperpolarisability and two-photon ionisation cross-sections at frequencies above threshold (discussed in Chapters 5, 6 and 7). Our pseudostate method should be easily extended to these calculations above threshold if we were able to add new pseudostates that are half the energy of the existing pseudostates. The calculation of hyperpolarisability and two photon ionisation cross-sections above threshold using our pseudostate method is considered in Chapter 7.

Unfortunately I have been unable to develop a reliable pseudostate packing method to handle transitions involving two free states, which is needed for these higher order scattering calculations. As a result, our pseudostate packing method needs some more work before it can really be useful. For future work, details of our pseudostate packing method have been included in Appendix C and is not considered in any more detail here.

3.7 Summary

I have developed a simple method for computing the complex polarisability at frequencies both below and above threshold. This method has been validated for atomic hydrogen against previous calculations by Gavrila and our semi-analytical calculation presented in Chapter 2. The main advantage of the method presented in this Chapter is its adaptability - it can be applied to other atoms in different initial states and can also be extended to higher-order processes as well. The method presented in this Chapter will be used to compute the Rayleigh, Raman, and Compton scattering cross-sections in Chapter 4. In Chapter 5, 6, and 7 this method will be extended to multi-photon scattering processes as well.
Chapter 4

Single Photon Scattering off Atomic Hydrogen

In this Chapter our pseudostate method is applied to the computation of the single photon scattering cross-sections - Rayleigh, Raman, and Compton scattering. We focus on low frequencies (sub-keV energy) where the $\mathbf{p} \cdot \mathbf{A}$ interaction dominates (see Eqn. 1.1). The Rayleigh and Raman scattering cross-sections are validated against published data and our semi-analytical calculation. Our pseudostate method is also applied to the calculation of the Compton scattering cross-section, which appears to be up to three-orders of magnitude larger than previous calculations by Drukarev et al. [9] and Bergstrom et al. [4]. Our differential Compton scattering cross-sections are somewhat in agreement with the calculation by Drukarev et al. [9] if we neglect the contribution from $\ell = 2$. However, closer investigation of our Compton scattering cross-sections with respect to basis set size and box radius show that our Compton calculation exhibits convergence issues.

4.1 Previous Calculations

Two common methods for computing the Rayleigh scattering cross-section at high frequency are the form-factor method and the relativistic S-matrix approach [116]. The S-matrix method involves solving the second-order S-matrix amplitude [116], which is effectively the Kramers-Heisenberg matrix element. The states used in this calculation are solutions to the relativistic Dirac equation. Rather than computing the infinite sum over intermediate states, the S-matrix method usually applies the Dalgarno and Lewis method which transforms this sum into inhomogeneous differential equations to be solved [116]. This method uses the independent particle approximation (IPA) to reduce the problem from a many-particle problem to a single-particle problem. Unlike our calculation which uses the dipole approximation, the S-matrix method must include higher-order multipoles as well for the calculations to converge. For higher photon frequencies, the number of multipoles that must be included increases. Although the S-matrix calculation is more accurate than the form-factor approach, it is also more computationally expensive and so the form-factor approach is often used [117].

The S-matrix method was used by Suric et al. [80] to compute the differential scattering cross-sections
of atoms with many electrons, such as aluminium, lead, and holmium. Bergstrom et al. [4] also applied the S-matrix method to compute differential scattering cross-sections in a range of atoms such as hydrogen, carbon, copper and lead, whilst Kaliman et al. [118] computed the differential Compton scattering cross-section of metastable helium. The S-matrix calculation can be used for photon energies up to 1 MeV [119]. The disadvantage of this S-matrix method is that it is “computer-intensive” especially for atoms with many electrons [116]. Though the S-matrix method can compute the differential cross-sections at a range of frequencies, Bergstrom et al. consider the method “too time-consuming and unnecessary” [120] when computing cross-sections over scattering angle and photon frequency.

In the form-factor method the differential Rayleigh scattering cross-section is given (in atomic units) by [37]

\[
\frac{d\sigma}{d\Omega} = \frac{\alpha^2}{2}(1 + \cos^2 \theta)|f(q)|^2, \tag{4.1}
\]

where \( f(q) \) is the form-factor given by \( f(q) = \int \rho(r)e^{iq\cdot r}dr \), \( \rho(r) \) is the charge density and \( q \) is the momentum transfer. \( \alpha \) is the fine-structure constant. Note that \( \frac{d\sigma}{d\Omega}(\theta) = \frac{\alpha^2}{2}(1 + \cos^2 \theta) \) is the differential Thomson cross-section, which describes the scattering of a photon off a free electron. Effectively the form-factor modifies the differential Thomson cross-section to take into account scattering from a charge distribution [37]. Since the cross-section given by the form-factor approach is based on scattering off a free electron, the form-factor approach can only be used to describe scattering of high-energy photons (much larger than atomic binding energy).

NIST have published databases of theoretical scattering cross-sections that use this form-factor approach. An example of such a database is FFAST (Form-Factor, Attenuation, and Scattering Tables) [2]. As the name suggests, FFAST uses the form-factor method to determine the photon-atom scattering cross-section. As this method is intended for x-ray photon frequencies, the cross-sections have extremely large uncertainties in the low-energy regime we are interested in [2].

Another database I will compare against is the XCOM database [3], which presents scattering cross-sections for x-ray photons off neutral atoms. As our method is at low energies, it is only possible to compare against the lowest few data points of this database. XCOM provides the scattering cross-sections for ‘coherent’ and ‘incoherent’ scattering. The coherent scattering cross-section is determined from the differential Thomson formula and Hartree-Fock form-factor [3]. The incoherent scattering cross-sections were computed using the Klein-Nishina formula and Hartree-Fock incoherent scattering functions [3].

The incoherent scattering method is used to compute Raman and Compton scattering cross-sections [121]. This method very similar to the form-factor method of Rayleigh scattering. The incoherent scattering method considers how scattering off a bound electron differs from scattering described by the Klein-Nishina formula. This is quantified by the ‘incoherent scattering factor’ \( S(k) \) which gives the differential scattering cross-section

\[
\frac{d\sigma(\omega_1, \theta)}{d\Omega_2} = S(k) \left[ \frac{d\sigma}{d\Omega_2}\right]_{KN},
\]
when multiplied by the differential cross-section given by the Klein-Nishina formula [4]. The incoherent
cattering factor is given by [120]

\[ S(k) = \sum_f |\langle f|e^{ikr}|i \rangle|, \]

which involves a sum over the final states \( f \), where the final state is not equal to the initial state \( i \). It
is important to note that this approximate method gives the total inelastic scattering, so includes both
Raman and Compton scattering.

The (relativistic) Klein-Nishina formula is given (in atomic units) by [35]

\[ \left[ \frac{d\sigma}{d\Omega} \right]_{KN} = \frac{\alpha^2}{4} \left( \frac{\omega'}{\omega} \right)^2 \left[ \frac{\omega'}{\omega} + \frac{\omega}{\omega'} - 2 + 4 \cos^2 \theta \right], \]

where \( \alpha \) is the fine-structure constant. \( \omega \) and \( \omega' \) are the photon frequencies before and after scattering,
where \( \omega' \) is given by

\[ \omega' = \frac{\omega}{1 + \omega \alpha^2 (1 - \cos \theta)}, \]

in atomic units. This differential cross-section describes scattering of a photon off a free electron, taking
into account the change in outgoing frequency and dependence on scattering angle. At low frequencies,
when \( \omega \ll 1/\alpha^2 \) then \( \omega = \omega' \) and the differential cross-section given by the Klein-Nishina formula
becomes (in atomic units)

\[ \frac{d\sigma}{d\Omega} = \frac{\alpha^2}{2} (1 - \cos^2 \theta), \]

which corresponds to the differential Thomson cross-section.

The Klein-Nishina formula can be integrated over solid angle to give the total cross-section [122],

\[ \sigma = \frac{3}{4} \sigma_T \left[ \frac{1 + k}{k^2} \left( \frac{2(1 + k)}{1 + 2k} - \frac{1}{k} \ln(1 + 2k) \right) + \frac{1}{2k} \ln(1 + 2k) - \frac{1 + 3k}{(1 + 2k)^2} \right], \quad (4.2) \]

where \( k = \omega \alpha^2 \) is in atomic units. Fig. 4.1 plots the cross-section given by Eqn. 4.2 as a function of incident photon energy \( \epsilon \). This plot demonstrates that the relativistic effect only becomes important at very
high energies. Since our pseudostate method calculates at sub-keV energies, we expect the relativistic
effect to be negligible. A more important effect to consider in our calculation is the contribution of the
\( A^2 \) interaction term, which is discussed in the next section.
4.1. Previous Calculations

Figure 4.1: Plot of the total cross-section (in units of $\sigma_T$) given by the Klein-Nishina formula in Eqn. 4.2, as a function of incident photon energy (eV). For low energies (sub-keV) only small changes occur in the cross-section.

4.1.1 Notes on $p \cdot A$ vs. $A^2$

In Chapter 1 the photon-atom interaction Hamiltonian was introduced as

$$H_{int} = -\frac{e}{m_e c} p \cdot A + \frac{e^2}{2m_e c^2} A^2,$$

(4.3)

where $p$ is the momentum, $A$ is the vector potential, $m_e$ refers to the electron mass and $e$ to the charge.

All the methods for calculating the photon-atom scattering cross-sections introduced so far, except for the S-matrix method, have considered only the $A^2$ interaction and neglected the $p \cdot A$ interaction. The $A^2$ interaction dominates at higher photon frequencies, whilst the $p \cdot A$ term dominates at low frequencies [36]. In 1970, Eisenberger et al. [36] explored the contribution from the $p \cdot A$ and $A^2$ interactions (see their Appendix) and showed that the $A^2$ contribution to Compton scattering is greater when the incident photon energy is much greater than ionisation energy, $\hbar \omega \gg \epsilon_{IP}$. However, when $\omega, \omega' \sim \epsilon_{IP}$, as is the case in our pseudostate calculations, the $p \cdot A$ interaction dominates [36].

Varma et al. [123] and Florescu et al. [124] have considered the contribution of the $p \cdot A$ and $A^2$ terms in the interaction Hamiltonian to the above threshold ionisation (ATI) cross-sections of atomic hydrogen. Varma et al. found that ATI is dominated by the $A^2$ contribution at photon energies greater than 6.8 keV, whilst the interaction at low photon energies is completely described by the $p \cdot A$ contribution. Florescu et al. [124] computed the ATI of atomic hydrogen with fewer approximations. They also found that the $p \cdot A$ dominated the scattering at lower photon frequencies, and the $A^2$ contribution is small at energies below 50 keV. Both calculations agree that the $A^2$ term is negligible for small photon energies. In this thesis I consider the $p \cdot A$ contribution to the cross-sections for sub-keV energies.

In the Chapter 2 I have presented an expression for the scattering cross-section involving the absorp-
tion of a photon of frequency $\omega$ and emission of a photon of frequency $\omega'$ to be (Eqn. 2.31)

$$\sigma_{ij}(\omega) = \sigma_T \omega \omega' \left| \alpha_{ij}(\omega) \right|^2,$$

where $i$ refers to the initial state and $j$ to the final state of the atom. $\sigma_T$ refers to the Thomson cross-section and $\alpha_{ij}(\omega)$ refers to the complex transition polarisability (in atomic units). Since the transition polarisability describes only the $\mathbf{p} \cdot \mathbf{A}$ interaction and neglects the $\mathbf{A}^2$ interaction, the scattering cross-section calculated in this way is valid for low photon frequencies. There are far fewer calculations of the scattering cross-sections that consider the $\mathbf{p} \cdot \mathbf{A}$ interaction than the $\mathbf{A}^2$ interaction. In the next section I will give an overview of the Rayleigh, Raman and Compton scattering cross-section calculations that have considered the $\mathbf{p} \cdot \mathbf{A}$ interaction.

### 4.1.2 Previous $\mathbf{p} \cdot \mathbf{A}$ Calculations

There have been a series of papers by Gavrila [1,6,16] and Floresco et al. [7] that have analytically derived expressions for the Rayleigh scattering of the first few states of atomic hydrogen and published data for frequencies both below and above threshold. In 1967 Gavrila [16] used the Coulomb Green’s function to calculate the Kramers-Heisenberg matrix element of the hydrogen ground state $H(1s)$. Though he did not present the data in the form of cross-sections, the matrix elements can easily be converted using Eqn. 4.4. The same method was used by Gavrila in 1979 [6] to compute the Rayleigh scattering cross-sections of the $n = 2$ hydrogen states, and by Floresco et al. in 1985 [7] to compute the Rayleigh scattering cross-sections of the $n = 3$ states and the cross-section of the $3s-3d$ Rayleigh transition.

Safari et al. [5] have also computed the $\mathbf{p} \cdot \mathbf{A}$ contribution to the Rayleigh scattering cross-section for atomic hydrogen using a finite basis set consisting of B-splines and B-polynomials for the relativistic Dirac equation. Though they have presented Rayleigh scattering cross-section data computed with their finite-basis set method for frequencies between 0.5 keV and 10 keV, they have not explained how the calculations at frequencies above threshold were done. They compared the total Rayleigh scattering cross-section computed using the electric dipole approximation with the calculation including other multipoles and found that multipole contributions become significant at higher energies (above approximately 3 keV).

More data has been published for the Raman scattering cross-sections than for the corresponding transition polarisabilities, but even for these I have only been able to find data for the Raman $1s-2s$ [8,125] and $3s-3d$ [7] transitions. Saslow and Mills [125] investigated the cross-section of the $1s-2s$ Raman transition in atomic hydrogen in 1969 by numerical calculation. They used the analytic expressions for the atomic hydrogen matrix elements and truncated the sum over bound states to some large principal number $s$. Sadeghpour et al. [8] also investigated the Raman $1s-2s$ transition cross-section and computed the sum by applying the Dalgarno-Lewis method.

Following his analytical derivation of elastic scattering in 1967, Gavrila derived analytic expressions
describing inelastic (Compton) scattering of the ground state of hydrogen-like atoms in 1972 [58, 59]. These complicated analytic expressions were used by Bergstrom et al. in 1993 [4] and Drukarev et al. in 2010 [9] to compute the total Compton scattering cross-sections of atomic hydrogen. Bergstrom et al. computed the cross-section for frequencies approximately 100 eV - 1 keV whilst Drukarev et al. computed the cross-section for frequencies just above ionisation threshold to approximately 68 eV. Given that there are so few calculations of the Raman scattering cross-sections, it is perhaps not surprising that only two previous calculations have presented total Compton scattering cross-sections for atomic hydrogen (for the $p \cdot A$ interaction) [4, 9]. These calculations will be discussed in more detail in Section 4.6 when I present our computational method for the Compton scattering cross-section.

### 4.2 Photoionisation

Photoionisation refers to the process where a photon is absorbed and the atom is ionised, i.e. the photon must have energy greater than the ionisation energy ($\hbar \omega > \varepsilon_{IP}$). The cross-section formula of this process is derived in Appendix A.4 and is related to the imaginary polarisability $\text{Im}[\alpha_{ii}(\omega_j)]$ by [102]

$$\sigma_i(\omega_j) = \frac{4\pi}{c} \omega_j \text{Im}[\alpha_{ii}(\omega_j)]. \quad (4.5)$$

I have shown in the previous Chapter that our pseudostate method can compute $\text{Im}[\alpha_{ii}(\omega_j)]$, and so we are also be able to compute the photoionisation cross-section with our pseudostate method. Since our method computes $\text{Im}[\alpha_{ii}(\omega_j)]$ at specific frequencies corresponding to pseudostate energies $\varepsilon_j$ (where $\omega_j = \varepsilon_j - \varepsilon_i$), the photoionisation cross-section is also given at these points.

Previously our values for $\text{Im}[\alpha_{ii}(\omega)]$ of ground state atomic hydrogen was found to be in disagreement with the previous calculation by Gavrila [16] (see Fig. 3.5). Here we validate our method against the photoionisation cross-section, as an analytical expression is known for ground state hydrogen [87] (see Eqn. 2.50).

In Fig. 4.2 I plot the photoionisation cross-section given by our pseudostate calculation as well as the cross-section given by the analytic expression (Eqn. 2.50) over the frequency range of 1 – 100 a.u. (27.2 – 272 eV). We have found very good agreement with the analytic expression, validating our pseudostate calculation of the photoionisation cross-section. This can be more closely seen in Table 4.1. The photoionisation cross-section given by the FFAST [2] and XCOM [3] database is also given in Fig. 4.2. Only the lowest two data points from the XCOM database occurs in this frequency regime. On this logscale the FFAST and XCOM seem to be in good agreement with the analytical function at high frequencies. At these high frequencies our pseudostate calculation only has few datapoints, and our cross-section calculation drops in accuracy. However, it does show that pseudostates work up to high energies (see Table 4.1).

On the other hand, Fig 4.2 seems to show that the FFAST calculation is not in agreement with the analytical function at lower frequencies. This is shown more clearly in the inset of Fig. 4.2 which plots...
Figure 4.2: Plot of photoionisation cross-section (in units of $\sigma_T$) of H(1s) given by our pseudostate calculation ($N_{\ell} = 120$, where $N_{\ell}$ refers to the number of Laguerre-type orbitals for each $\ell$) and the analytical formula given in Eqn. 2.50 over the 1 – 100 a.u. frequency range. The photoionisation cross-section given by the FFAST [2] and XCOM [3] databases are also plotted, though there are only two datapoints given by the XCOM datapoints in this energy regime. The inset zooms in on the cross-section at frequencies near threshold.

the photoionisation cross-sections for near threshold frequencies. Fig. 4.2 shows that our pseudostate calculation is in good agreement with the analytical function, whereas the FFAST data drops in accuracy closer to threshold. Though it seems surprising that the FFAST database gives incorrect values for the photoionisation cross-section over this energy range, it does demonstrate that the data given by previous calculations must be handled with care. Evidently our calculation is more accurate close to threshold, and the FFAST database is more accurate at high frequencies. This is demonstrated in Tables 4.1 and 4.2, where the percentage difference between the analytical function and our pseudostate calculation as well as the FFAST database is given. The FFAST data and our pseudostate calculation are given in separate tables as our calculation gives datapoints at a different set of frequencies to those given by FFAST. Though we could interpolate our values, I have chosen to present the exact values here.

4.3 Rayleigh Scattering

The Rayleigh scattering cross-section is given by (see equation 2.31)

$$\sigma_{ii}(\omega) = \sigma_T \omega^4 \left| \alpha_{ii}(\omega) \right|^2.$$  

(4.6)

where $\alpha_{ii}(\omega)$ is the polarisability for which a computational method has been developed in the previous Chapter. The polarisability below threshold is simply
Table 4.1: Tabulated values of the photoionisation cross-section (in units of $\sigma_T$) of H(1$s$) at selected frequencies of some pseudostates given by our pseudostate calculation (using a $N_\ell = 120$ basis) and the analytic expression given in Eqn. 2.50. The percentage difference between these two calculations is also presented. The numbers in brackets (x) denote $10^x$.

<table>
<thead>
<tr>
<th>$\omega$ (a.u.)</th>
<th>Pseudostate Calculation</th>
<th>Analytical Formula</th>
<th>Percentage difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5003</td>
<td>9.467 (6)</td>
<td>9.464 (6)</td>
<td>0.0330</td>
</tr>
<tr>
<td>0.5099</td>
<td>8.991 (6)</td>
<td>8.993 (6)</td>
<td>0.0249</td>
</tr>
<tr>
<td>0.5207</td>
<td>8.499 (6)</td>
<td>8.502 (6)</td>
<td>0.0304</td>
</tr>
<tr>
<td>0.5502</td>
<td>7.331 (6)</td>
<td>7.334 (6)</td>
<td>0.0398</td>
</tr>
<tr>
<td>0.6022</td>
<td>5.742 (6)</td>
<td>5.745 (6)</td>
<td>0.0550</td>
</tr>
<tr>
<td>0.6998</td>
<td>3.804 (6)</td>
<td>3.807 (6)</td>
<td>0.0834</td>
</tr>
<tr>
<td>0.9996</td>
<td>1.399 (6)</td>
<td>1.402 (6)</td>
<td>0.170</td>
</tr>
<tr>
<td>2.082</td>
<td>1.632 (5)</td>
<td>1.640 (5)</td>
<td>0.481</td>
</tr>
<tr>
<td>2.998</td>
<td>5.399 (4)</td>
<td>5.439 (4)</td>
<td>0.742</td>
</tr>
<tr>
<td>4.938</td>
<td>1.145 (4)</td>
<td>1.160 (4)</td>
<td>1.29</td>
</tr>
<tr>
<td>10.28</td>
<td>1.098 (3)</td>
<td>1.129 (3)</td>
<td>2.80</td>
</tr>
<tr>
<td>60.27</td>
<td>2.722</td>
<td>3.264</td>
<td>16.6</td>
</tr>
<tr>
<td>120.3</td>
<td>2.105 (-1)</td>
<td>3.134 (-1)</td>
<td>32.8</td>
</tr>
</tbody>
</table>

Table 4.2: Comparison of the FFAST data [2] for the photoionisation cross-section (in units of $\sigma_T$) of H(1$s$) with the analytical expression given in Eqn. 2.50. The percentage difference between these is also presented. The numbers in brackets (x) denote $10^x$.

<table>
<thead>
<tr>
<th>$\omega$ (a.u.)</th>
<th>FFAST</th>
<th>Analytical Formula</th>
<th>Percentage difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5130</td>
<td>6.931 (6)</td>
<td>8.848 (6)</td>
<td>21.7</td>
</tr>
<tr>
<td>0.5484</td>
<td>5.840 (6)</td>
<td>7.398 (6)</td>
<td>21.1</td>
</tr>
<tr>
<td>0.7162</td>
<td>2.908 (6)</td>
<td>3.572 (6)</td>
<td>18.6</td>
</tr>
<tr>
<td>0.9998</td>
<td>1.185 (6)</td>
<td>1.401 (6)</td>
<td>15.4</td>
</tr>
<tr>
<td>2.083</td>
<td>1.495 (5)</td>
<td>1.638 (5)</td>
<td>8.69</td>
</tr>
<tr>
<td>3.108</td>
<td>4.598 (4)</td>
<td>4.869 (4)</td>
<td>5.56</td>
</tr>
<tr>
<td>4.959</td>
<td>1.116 (4)</td>
<td>1.145 (4)</td>
<td>2.56</td>
</tr>
<tr>
<td>10.33</td>
<td>1.116 (3)</td>
<td>1.110 (3)</td>
<td>0.530</td>
</tr>
<tr>
<td>62.59</td>
<td>2.890</td>
<td>2.872</td>
<td>0.600</td>
</tr>
</tbody>
</table>
where the $\text{Im}_0[\alpha_{ii}(\omega)]$ term originates from the non-zero linewidths of the atomic states. However, at frequencies above threshold, the complex polarisability has two imaginary terms, such that

$$
\alpha_{ii}(\omega) = \text{Re}[\alpha_{ii}(\omega)] + i\text{Im}_0[\alpha_{ii}(\omega)] + i\text{Im}_1[\alpha_{ii}(\omega)].
$$

This leads to the question of how the second imaginary term, $\text{Im}_1[\alpha_{ii}(\omega)]$, should be included in the Rayleigh scattering cross-section expression in Eqn. 4.6. From our calculation of the $1s-1s$ polarisability, we know that the $\text{Im}_1[\alpha_{ii}(\omega)]$ term is of the same magnitude as the $\text{Re}[\alpha_{ii}(\omega)]$ contribution at frequencies close to threshold (see Table 3.1), and so would be a large contribution to the Rayleigh scattering cross-section if it were included in Eqn. 4.6. Since I have shown in the previous section that the $\text{Im}_1[\alpha_{ii}(\omega)]$ term is related to the photoionisation cross-section, it will not be included in the Rayleigh scattering cross-section. In this section I will compute the Rayleigh scattering cross-section by including only the $\text{Re}[\alpha_{ii}(\omega)]$ and $\text{Im}_0[\alpha_{ii}(\omega)]$ terms and demonstrate good agreement with literature [6, 7, 16] for frequencies below and above threshold.

### 4.3.1 Rayleigh Scattering $\text{H}(1s)$

In Section 3.2 the $1s-1s$ (transition) polarisability was calculated using our pseudostate method and validated against the analytical calculation of Gavrila and our semi-analytical calculation. It was also shown that the $1s-1s$ polarisability converges at frequencies both below and above threshold. Since the $1s-1s$ polarisability has already been validated, our calculation of the Rayleigh scattering cross-section of the $1s$ state must also be correct. The Rayleigh scattering cross-section for the ground state of hydrogen is plotted at frequencies below and above threshold in Figs. 4.3(a) and 4.3(b). The Rayleigh scattering cross-section calculated with our pseudostate method tends to $1\sigma_T$ at high photon energies, as shown in Fig. 4.3. This is expected as at high-photon frequencies the hydrogen atom scatters like a free electron.

Bergstrom et al. have employed the S-matrix method to compute the photon-hydrogen scattering cross-sections. Fig. 29 in their 1993 paper [4] gives a plot of the various cross-sections for photon energies from $10^{-2}$ keV to $10^7$ keV. I have digitised values of their elastic scattering cross-section in Fig. 4.3 to demonstrate that their Rayleigh scattering does not show the correct behaviour below threshold. As mentioned above, we do not show the Gavrila results as they are indistinguishable from ours. XCOM [3] and Safari et al. [5] have presented values of the Rayleigh scattering cross-section at high frequencies, which is also plotted on Fig. 4.3. We show that the corrections included in their calculations become important for $\omega > 50$ ($\varepsilon > 1361$ eV).

Fig. 4.3 also plots the photoionisation cross-section of the hydrogen ground state. The photoionisation cross-section completely dominates the scattering process at frequencies just above threshold as it is more than six orders of magnitude larger than the Rayleigh scattering cross-section. As the photon frequency
becomes larger the probability of photoionisation cross-section drops off, until the photoionisation cross-section eventually has the same magnitude as the Rayleigh scattering cross-section at approximately \( \omega \approx 80 \text{ a.u.} \) (approximately 2177 eV).

Figure 4.3: Plot of Rayleigh and photoionisation cross-section (in units of \( \sigma_T \)) of \( \text{H}(1s) \) given by our pseudostate calculation (\( N_\ell = 120 \) basis set, where \( N_\ell \) refers to the number of Laguerre-type orbitals for each \( \ell \)), as well as the data given by Bergstrom et al. [4], Safari et al. [5] and the XCOM [3] database. Our \( 1s \) Rayleigh scattering cross-section is computed using the complex transition polarisability \( \alpha_{1s,1s}(\omega) = \text{Re}[\alpha_{1s,1s}(\omega)] + \text{Im}[\alpha_{1s,1s}(\omega)] \) where the frequency dependence of the damping \( \Gamma(\omega) \) is given by Eqn. 3.21. (a) shows lower energies (below and above threshold). (b) shows higher energies.

4.3.2 Rayleigh Scattering \( \text{H}(2s) \)

Previously I have shown that my semi-analytical calculation of the \( 2s-2s \) polarisability agrees very well with our pseudostate calculation, which indicates that our Rayleigh scattering cross-section of \( \text{H}(2s) \) must also be correct. There is cross-section data available for the \( \text{H}(2s) \) state calculated by Gavrila in 1979 [6] using similar analytical techniques to the calculation of the \( \text{H}(1s) \) Rayleigh scattering cross-section by Gavrila in 1967 [16]. Fig. 4.4 plots the photoionisation and Rayleigh scattering cross-section calculated using our pseudostate method and the data given by Gavrila [6]. Like the cross-sections presented for \( \text{H}(1s) \) in the previous section, the photoionisation cross-section for \( \text{H}(2s) \) also decreases rapidly, whilst the Rayleigh scattering cross-section again tends to \( 1\sigma_T \) at high photon frequencies. Note that there are kinks in the photoionisation cross-section at high frequencies (see Fig. 4.4 (b) ), since we only have few pseudostates at such high energies. In \( \text{H}(2s) \) the cross-over of Rayleigh and photoionisation cross-section occurs at \( \omega \approx 45 \text{ a.u.} \), which corresponds to approximately 1225 eV.
4.3. Rayleigh Scattering

Figure 4.4: Plot of Rayleigh and photoionisation cross-section (in units of $\sigma_T$) of H(2s) given by our pseudostate calculation ($N_\ell = 120$ basis set, where $N_\ell$ refers to the number of Laguerre-type orbitals for each $\ell$), as well as data given by Gavrila [6]. Our H(2s) Rayleigh scattering cross-section is computed using the frequency dependence of damping $\Gamma(\omega)$ given by Eqn. 3.18.

4.3.3 Rayleigh Scattering H(3s)

In 1985 Florescu et al. [7] have calculated the H(3s) Rayleigh scattering cross-section using the same analytical method as Gavrila [6]. This is compared with the Rayleigh scattering cross-section calculated with our pseudostate method in Fig. 4.5. The Rayleigh scattering cross-section has a pole above threshold due to the $(\omega_{nj} + \omega)^{-1}$ denominator in the polarisability (see equation 2.32) that corresponds to a photon frequency near resonance with the 3s-2p energy difference.

The $(\omega_{nj} + \omega)^{-1}$ term in the polarisability can be computed at all frequencies as it does not have any unphysical pseudostate poles. On the other hand, our pseudostate method must be applied to calculate the $(\omega_{ni} - \omega)^{-1}$ term in the polarisability at certain frequencies above threshold that correspond to pseudostate energies. These two terms are computed separately and then added ($(\omega_{ni} - \omega)^{-1}$ term is linearly interpolated) to give the total polarisability. The Rayleigh scattering cross-section calculated with this method is plotted in Fig. 4.5, as well as the photoionisation cross-section. We have included the damping in all bound states using the frequency dependence given in Eqn. 3.18, and set the damping of pseudostates to zero. Florescu et al. [7] have not included damping in their calculation. From Fig. 4.5 we can see that at this resonance frequency the Rayleigh scattering cross-section becomes greater than the photoionisation cross-section. The photoionisation cross-section drops off whilst the Rayleigh scattering cross-section in our calculation tends to $1 \sigma_T$, resulting in a cross-over at $\omega \approx 30$ a.u., which corresponds to approximately 816 eV.
Figure 4.5: Plot of Rayleigh and photoionisation cross-section (in units of $\sigma_T$) of H(3s) given by our pseudostate calculation ($N_{\ell} = 120$ basis set, where $N_{\ell}$ refers to the number of Laguerre-type orbitals for each $\ell$), as well as data given by Florescu et al. [7]. Our H(3s) Rayleigh scattering cross-section is computed using the frequency dependence of damping $\Gamma(\omega)$ given by Eqn. 3.18.

4.4 Raman Scattering

The Rayleigh scattering cross-section describes scattering that occurs where the incident and outgoing photons have the same energy. After Rayleigh scattering occurs, the atom is in the same state as before the scattering process. On the other hand, Raman scattering describes the scattering process where the photon emitted $\omega'$ has a different frequency to the photon absorbed $\omega$ and the atom ends in a final bound state $j$ that is not the initial state $i$ [126].

The Raman scattering cross-sections may be calculated in the same way as the Rayleigh scattering cross-sections, using the complex transition polarisabilities, where

$$\sigma_{ij}(\omega) = \sigma_T \omega^3 \left| \text{Re}\left[\alpha_{ij}(\omega)\right] + i\text{Im}\left[\alpha_{ij}(\omega)\right] \right|^2, \quad i \neq j.$$  \hspace{1cm} (4.9) 

4.4.1 Previous Calculations

Only very little data has been published on the transition polarisabilities of Raman transitions. Most of the calculations that have been mentioned above have only considered the Rayleigh transition. Chandrasekharan et al. [114] is one of the only papers to present data for Raman transition polarisabilities. They have have computed the static ($\omega = 0$) transition polarisability for various Raman transitions in the hydrogen atom for both ground and excited states. Lee et al. [127] has also presented a plot of the frequency-dependent transition polarisability of the 1s-2s Raman transition in atomic hydrogen.

There is more data published for the Raman transitions in terms of cross-sections, which is understandable as this has a more practical use than the Raman transition polarisabilities. Sadeghpour et al. [8]
have presented values for the $1s$-$2s$ Raman scattering cross-section in atomic hydrogen, as have Nussbaumer et al. [29]. Florescu et al. [7] have computed the cross-sections for both the Rayleigh transition from the $3s$ and $3d$ state as well as the Raman $3s$-$3d$ transition in atomic hydrogen.

Though it is clear now that there is little data of Raman transitions to validate our polarisability calculation against, the advantage of testing our computational method on atomic hydrogen is that we can compute the polarisabilities using a semi-analytical method as well. In the next section I present the transition polarisabilities of Raman transitions in atomic hydrogen, for our pseudostate method as well as our semi-analytical calculation.

### 4.4.2 Individual Transitions

In the previous Chapter a pseudostate method was developed for the complex transition polarisabilities and a semi-analytical calculation was also introduced. These methods have been used to compute the Rayleigh transition polarisabilities of the $1s$, $2s$ and $3s$ states of hydrogen. Since there is little literature data available for the complex transition polarisabilities of the Raman transitions in hydrogen, our calculation method must be validated against the available Raman scattering cross-section data. Here the methods developed in the previous Chapter will be used to compute the Raman $1s$-$2s$ and $3s$-$3d$ transition cross-sections and validated against data given by Sadeghpour et al. [8] and Florescu et al. [7] respectively.

### 4.4.3 Raman $1s$-$2s$ Transition

The Raman $1s$-$2s$ transition cross-section is plotted in Fig. 4.6 for our pseudostate method, semi-analytical calculation as well as the data given by Sadeghpour et al. [8]. Since Sadeghpour et al. have only presented data for below threshold frequencies, we must validate our method above threshold using the semi-analytical calculation. The Raman scattering cross-section is non-zero only at frequencies $\omega > 0.375$ a.u., as this corresponds to a photon having enough energy to excite the atom from the $1s$ state to the $2s$ state.

Fig. 4.6 shows that the semi-analytical calculation gives slightly larger cross-sections than the pseudostate method at frequencies above threshold. This seems to be due to convergence of the pseudostate method at frequencies above threshold. I have done some convergence studies (see Appendix D) and have shown that the $1s$-$2s$ cross-section is converged to nine significant figures below threshold and is converged to one significant figure above threshold. To the best of my knowledge this is the first calculation of the $1s$-$2s$ transition at frequencies above threshold. Convergence to more significant figures could be achieved by using larger basis sets. We find that $\sigma_{1s,2s}$ reaches a peak at approximately $\omega = 0.82$ a.u. = 22.3 eV above threshold and has a minimum just above threshold. The minimum is predicted at $\omega = 0.545$ a.u. = 14.83 eV and means that at this laser frequency it is very unlikely for the $1s$-$2s$ transition to occur.
\section*{4.4. Raman Scattering}

Figure 4.6: Plot of Raman 1s-2s scattering cross-section (in units of $\sigma_T$) given by our pseudostate ($N_\ell = 120$ basis set, where $N_\ell$ refers to the number of Laguerre-type orbitals for each $\ell$) and semi-analytical calculation as well as the data given by Sadeghpour et al. \cite{Sadeghpour1992}. Our semi-analytical calculation used $N = 800$ bound states and calculated the continuum integral by using $N_{\text{panel}} = 100$ panels and applying 16 point Gaussian integration.

4.4.4 Raman 3s-3d Transition

Before we consider our cross-sections for the 3s – 3d transition, let us take a closer look at the transition matrix elements involving a $\ell = 2$ state since this is our first calculation using $\ell = 2$ states. Upon comparison of the analytic expressions for the transition matrix elements given by Gordon \cite{Gordon1977} (Eqns. 2.17 and 2.19), we find that the $\text{patom}$ transition matrix elements to states with $\ell = 2$ is greater than the analytical result by a factor of $\sqrt{2}$. This is shown in Table 4.3 for both bound-to-bound and bound-to-free matrix elements. The $\text{patom}$ transition matrix elements are given for a basis set of $N_\ell = 120$ and $\lambda_\ell = 0.5$. The bound-to-free matrix elements are given for initial states 2p and 3p, and final pseudostates with energies nearest to $\varepsilon = 0.1, 0.2, 0.5$ and 1.0 a.u.. The analytical transition matrix elements (see Section 2.1.1) are not including the relation $\langle \ell | C_0^\dagger | \ell' \rangle = (-\ell)^{2\ell+\ell'+1} \sqrt{\ell_{\text{max}}}$ (where $C_0^\dagger$ is the modified spherical harmonic) \cite{87}, which would give the extra factor of $\sqrt{2}$ for the transition between $\ell' = 1$ and $\ell = 2$ or vice-versa. This is also seen by calculating the 3s-3d Raman scattering cross-section and comparing with the values given by Florescu et al. \cite{Florescu1985}. Note that the $\text{patom}$ transition matrix elements given in Table 4.3 differ in sign, which is due to the arbitrary choice of $e^{i\varphi}$ phase of wavefunction by $\text{patom}$.

The 3s-3d Raman transition was computed by Florescu et al. \cite{Florescu1985} in 1985 by a perturbative $\mathbf{p} \cdot \mathbf{A}$ calculation at frequencies above threshold. Fig. 4.7 plots the 3s-3d Raman scattering cross-section from our pseudostate calculation, our semi-analytical calculation and the values given by Florescu et al. \cite{Florescu1985}. Here the transition matrix elements to the 3d state have been multiplied by $\sqrt{2}$ in the semi-analytical calculation of the Raman 3s-3d scattering cross-section, resulting in good agreement with the literature values. Evidently we must ensure that the $\ell = 2$ transition matrix elements in our semi-analytical calculation are multiplied by $\sqrt{2}$ to give the correct results. From this point on, any transition matrix elements in our
Table 4.3: Comparison of the transition matrix elements $T_{ij}$ given by the analytic expressions [17] and the normalised transition matrix elements $T_{ij}^p$ given by pa\-tom for transitions from state $i$ with $\ell = 1$ to state $j$ with $\ell = 2$.

<table>
<thead>
<tr>
<th>initial state</th>
<th>final state</th>
<th>Analytical $T_{ij}$</th>
<th>Normalised $T_{ij}^p$</th>
<th>Pseudostate/Analytical</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bound-bound</td>
<td>2p</td>
<td>4.748</td>
<td>6.715</td>
<td>1.414</td>
</tr>
<tr>
<td></td>
<td>2p</td>
<td>1.710</td>
<td>2.418</td>
<td>1.414</td>
</tr>
<tr>
<td></td>
<td>3p</td>
<td>7.565</td>
<td>10.70</td>
<td>1.414</td>
</tr>
<tr>
<td></td>
<td>3p</td>
<td>2.968</td>
<td>4.198</td>
<td>1.414</td>
</tr>
<tr>
<td>Bound-free</td>
<td>2p</td>
<td>$\varepsilon = 0.10383$</td>
<td>2.159</td>
<td>3.053</td>
</tr>
<tr>
<td></td>
<td>2p</td>
<td>$\varepsilon = 0.20137$</td>
<td>0.998</td>
<td>1.411</td>
</tr>
<tr>
<td></td>
<td>2p</td>
<td>$\varepsilon = 0.49774$</td>
<td>0.233</td>
<td>-0.330</td>
</tr>
<tr>
<td></td>
<td>2p</td>
<td>$\varepsilon = 1.06184$</td>
<td>0.051</td>
<td>-0.073</td>
</tr>
<tr>
<td></td>
<td>3p</td>
<td>$\varepsilon = 0.10383$</td>
<td>2.258</td>
<td>3.193</td>
</tr>
<tr>
<td></td>
<td>3p</td>
<td>$\varepsilon = 0.20137$</td>
<td>0.864</td>
<td>1.221</td>
</tr>
<tr>
<td></td>
<td>3p</td>
<td>$\varepsilon = 0.49774$</td>
<td>0.167</td>
<td>-0.236</td>
</tr>
<tr>
<td></td>
<td>3p</td>
<td>$\varepsilon = 1.06184$</td>
<td>0.034</td>
<td>-0.047</td>
</tr>
</tbody>
</table>

semi-analytical calculation involving $\ell = 2$ states will be multiplied by $\sqrt{2}$. Fig. 4.7 has a pole above threshold which occurs due to the presence of the $2p$ state that is lower in energy than the final state.

Figure 4.7: Plot of Raman 3s-3d scattering cross-section (in units of $\sigma_T$) given by our pseudostate ($N_\ell = 120$ basis set, where $N_\ell$ refers to the number of Laguerre-type orbitals for each $\ell$) and semi-analytical calculation as well as the data given by Florescu et al. [7]. Our semi-analytical calculation used $N = 800$ bound states and calculated the continuum integral by using $N_{panel} = 100$ panels and applying 16 point Gaussian integration.

The Raman scattering cross-sections are completely converged (with respect to basis set size) at frequencies below threshold whilst the cross-sections above threshold have much slower convergence (see Table D.7 in Appendix D). However, our method has the advantage of being extremely simple and adaptable, and can easily be applied to the calculation of any transition in the atom. Improved
convergence could be achieved by simply increasing the basis set size.

4.4.5 Total Raman Scattering Cross-section

Our pseudostate method can easily calculate the transition polarisabilities and cross-sections for all other Raman transitions in the system, which enables us to compute the total Raman scattering cross-section. The total Raman scattering cross-section simply refers to the sum of the Raman transition cross-sections over all possible final states, such that

\[
\sigma_R(i) = \sum_{j : \epsilon_j < 0} \sigma_{ij}(\omega),
\]

where \(\sigma_{R,i}\) is the total Raman scattering cross-section for an atom initially in state \(i\). This total cross-section is useful as it describes the total possibility that an atom will absorb and emit a photon without being ionised or ending in the initial state (without further photon emission). To the best of my knowledge this is the first time that such a total Raman scattering cross-section has been computed for atomic hydrogen, indeed for any atom! For this reason we did not know what to expect for the behaviour of the total Raman scattering cross-section before performing the calculation.

Fig. 4.8 is a plot of the total Raman scattering cross-section given by our pseudostate calculation and semi-analytical calculation, as well as the cross-sections of the individual 1s-2s and 1s-3d transitions. As mentioned previously, the 1s-2s Raman scattering cross-section has a peak at approximately \(\omega = 0.82\) a.u. = 22.3 eV above threshold and has a minimum just above threshold at approximately \(\omega = 0.545\) a.u. = 14.83 eV. In fact we have found that all cross-sections from the initial 1s state to a final \(\ell = 0\) state have such a minimum at frequency above threshold. On the other hand, the cross-section from an initial 1s state to a final \(\ell = 2\) state do not exhibit a minimum.

Since there is no previous data to compare against for these cross-sections above threshold, we have compared the total Raman scattering cross-section from our pseudostate method with our semi-analytical calculation. Though it may seem as if our semi-analytical result agrees with our pseudostate calculation in Fig. 4.8, it is important to note that it is plotted on a log-scale spanning \(10^{-4}\) to \(10^{12}\). A clearer comparison is given in Fig. 4.8, which shows the cross-section given by our pseudostate method for changing basis set size \(N_\ell\) and our semi-analytical calculation.

Fig. 4.9 shows the total Raman scattering cross-section with respect to the number of Laguerre functions in the basis and compares against my semi-analytic calculation. From this we can see that the Raman scattering cross-section is converged at frequencies below threshold but does not seem to smoothly converge above threshold.

Additionally, we show that our pseudostate calculation is not in agreement with our semi-analytic calculation - the semi-analytic cross-sections drop off much faster than the pseudostate calculation. Since there are no previous calculations of the total Raman scattering cross-section it is difficult to determine which of the two, or if either of our calculations are correct. The convergence of the semi-analytic calculations
cross-section with respect to the number of final bound states in the calculation for $\omega = 1$ a.u. and 2 a.u. is shown in Figs. 4.10 and 4.11 respectively. Though our semi-analytic calculation is converged at $\omega = 1$ a.u., our semi-analytic calculation struggles to compute the cross-section accurately at higher frequencies (see convergence of $\ell = 2$ contribution at $\omega = 2$ a.u. in Fig. 4.11 (b)). The convergence of the total Raman scattering cross-section given by our pseudostate method will be investigated further in the next section.

Figure 4.8: Plot of the total Raman scattering cross-section (in units of $\sigma_T$) given by our pseudostate method and semi-analytic calculation, as well as the individual $1s-2s$ and $1s-3d$ Raman transition cross-sections. The $1s-2s$ cross-sections given by Sadeghpour et al. [8] is also shown. Our pseudostate calculation is done with a $N_\ell = 120$ basis set, where $N_\ell$ refers to then number of Laguerre-type orbitals for each $\ell$. 40 final bound states were included in our semi-analytic calculation, and $N = 800$ intermediate bound states. In the semi-analytic calculation, the continuum integral was calculated using $N_{\text{panel}} = 100$ panels and applying 16 point Gaussian integration.
4.4. Raman Scattering

Figure 4.10: Plot of the $\ell = 0$ contribution (a) and $\ell = 2$ contribution (b) to the total Raman scattering cross-section at $\omega = 1$ a.u. with respect to the number of bound states included in our semi-analytic calculation. Our semi-analytical calculation used $N = 800$ intermediate bound states and calculated the continuum integral by using $N_{\text{panel}} = 100$ panels and applying 16 point Gaussian integration.

![Graph](image1)

Figure 4.9: Plot of the total Raman scattering cross-section (in units of $\sigma_T$) for different basis set sizes (where $N_\ell$ refers to the number of Laguerre-type orbitals for each $\ell$) and our semi-analytic calculation. 40 final bound states were included in our semi-analytic calculation, and $N = 800$ intermediate bound states. In the semi-analytic calculation, the continuum integral was calculated using $N_{\text{panel}} = 100$ panels and applying 16 point Gaussian integration.

![Graph](image2)

4.4.6 Choosing the Ionisation Energy

As more functions are added to the basis set, more pseudostates are added to the system and the lowest-lying pseudostates become bound states. Therefore, as the basis set is increased, the number of bound states included in the total Raman scattering cross-section calculation increases. Fig. 4.9 shows that the total Raman scattering cross-section above threshold does not smoothly converge. Next, let us have a look at the contribution of each individual Raman transition to the total Raman scattering cross-section.
Figure 4.11: Plot of the $\ell = 0$ contribution (a) and $\ell = 2$ contribution (b) to the total Raman scattering cross-section at $\omega = 2$ a.u. with respect to the number of bound states included in our semi-analytic calculation. Our semi-analytical calculation used $N = 800$ intermediate bound states and calculated the continuum integral by using $N_{\text{panel}} = 100$ panels and applying 16 point Gaussian integration.

at $\omega = 2$ a.u., though note that our (linear) interpolation introduces some uncertainty. Figs. 4.12 and 4.13 plot the contribution from the individual Raman transitions for final states with $\ell = 0$ and $\ell = 2$ respectively for different basis sets, as well as our semi-analytic calculation. From these plots we can see that the contribution decreases with increasing final state energy but increases dramatically for final states near threshold. The large contribution from Rydberg states prevents the total Raman scattering cross-section from converging with respect to increasing basis set size.
4.4. Raman Scattering

Figure 4.12: Magnitude of the individual Raman scattering cross-sections $\sigma_{1s,ns}(\omega = 2)$ from the initial $1s$ state to a state with $\ell = 0$ and energy $\varepsilon$ for various basis set sizes at fixed frequency $\omega = 2$ a.u. above threshold. Our pseudostate calculation with different basis set size $N_\ell$ is compared against our semi-analytic calculation, which uses 800 intermediate bound states and 40 final bound states. The continuum integral was calculated using $N_{\text{panel}} = 100$ panels and applying 16 point Gaussian integration. (a) shows the contribution from all bound states (states with energy $\varepsilon < 0$). (b) zooms in on the final state energy $\varepsilon$ near threshold, and shows that our semi-analytic calculation differs from our $N_\ell = 120$ pseudostate calculation by approximately 17%.

Fig. 4.12 shows the semi-analytic calculation gives a slightly larger contribution for $\ell = 0$ states than the pseudostate calculation. This seems to be due to the slow convergence of the Raman scattering cross-sections in our pseudostate calculation above threshold. The slight discrepancy was also observed when comparing the $1s$-$2s$ Raman scattering cross-section for the two methods in Section 4.4.3. From Fig. 4.12 (b) we can see that the pseudostate method shows the same behaviour as the semi-analytic calculation (except for the Rydberg states) and is off by approximately 17%. The scattering cross-section contribution from the $\ell = 2$ final states is given in Fig. 4.13 for $\omega = 2$ a.u. and shows good agreement between our pseudostate and semi-analytic calculation. At lower frequencies the semi-analytic cross-section decreases as $\varepsilon \to 0$, but the semi-analytic calculation struggles to give convergence at frequencies $\omega \geq 2$ a.u. (see Fig. 4.10 and 4.11) and results in increasing $\sigma$ as $\varepsilon \to 0$ in Fig. 4.13. Evidently it is not straightforward to reach converged answers for both our pseudostate and semi-analytic calculations of the total Raman scattering cross-section.

In Chapter 3, the normalised oscillator strengths from $\text{patom}$ were introduced and plotted as a function of energy. It was shown that the oscillator strengths of the Rydberg states do not follow the same trend as the lower-lying bound states. The oscillator strengths of states just below and above the threshold for the $N_\ell = 120$ basis set calculation are also plotted in Fig. 4.14. Since these Rydberg states demonstrate continuum behaviour, a better choice of ionisation energy may be the energy where the continuum behaviour begins. This may also solve our convergence issues in the total Raman scattering cross-section calculation.
There are two possible ways of choosing the new ionisation energy. The ionisation can be chosen to be halfway between the state with the lowest oscillator strength and the previous one, as given by the dashed line labeled (a) in Fig. 4.14 or halfway between the state with the oscillator strength and the succeeding one as given by the dashed line labeled (b) in Fig. 4.14. The total Raman scattering cross-
section is now calculated with the new ionisation energy and plotted in Fig. 4.15. Fig. 4.15a shows the total Raman scattering cross-section using the new ionisation energy given by (a) in Fig. 4.14, whilst Fig. 4.15b shows the total Raman scattering cross-section using the new ionisation energy given by (b) in Fig. 4.14.

Figure 4.15: Plot of the total Raman scattering cross-section (in units of $\sigma_T$) using the original ionisation energy with a basis of $N_\ell = 120$ and the total Raman scattering cross-section using new ionisation energy for different basis set sizes of $N_\ell = 120, 100$ and 80. $N_\ell$ refers to the number of Laguerre-type orbitals for each $\ell$. (a) shows the cross-section when the ionisation energy is chosen to be halfway between the state with the lowest oscillator strength and the previous state. (b) shows the cross-section when the ionisation energy is chosen to be halfway between the state with the lowest oscillator strength and the following state.

Fig. 4.15 shows that by excluding these highest energy states, the total Raman scattering cross-section is diminished by at least an order of magnitude. Choosing the ionisation energy to be before or after the state with the lowest oscillator strength also changes the magnitude of the total Raman scattering cross-section, particularly at high photon frequencies. Though I have used the new ionisation energy, the total Raman scattering cross-section does not show convergence above threshold.

From here on the ionisation energy will be chosen to be the energy half-way between the state with lowest oscillator strength and the previous state (see (a) in Figs. 4.14 and 4.15). Now that we have changed the ionisation energy, let us compare again with our semi-analytic calculation. Fig. 4.16 shows the total Raman scattering cross-section given by our pseudostate calculation (for various basis sets $N_\ell$) and our semi-analytic calculation, as well as the $\ell = 0$ and $\ell = 2$ contribution in our semi-analytic calculation. We see that the semi-analytic calculation is in now in much better agreement with our pseudostate calculation given our new choice of ionisation energy. Some interesting behaviour is going on at frequencies just above threshold ($0.5 < \omega < 0.8$ a.u.). Our semi-analytic calculation has a peak in the total Raman scattering cross-section at approximately $\omega = 0.8$ a.u., whereas the cross-section increases as $\omega \rightarrow 0.5$ a.u. for our pseudostate calculation. The origin of this behaviour is not clear, nor do we know which of these calculations are correct, since these are the first calculations of total Raman scattering.
Figure 4.16: Plot of the total Raman scattering cross-section given by our pseudostate and semi-analytic calculation. The cross-section is given for a basis set of $N_\ell = 120$ and the original ionisation energy, as well as $N_\ell = 120, 100$ and 80 for the new ionisation energy. The semi-analytic calculation uses 800 intermediate bound states and 40 final bound states. The continuum integral in our semi-analytic calculation was calculated using $N_{panel} = 100$ panels and applying 16 point Gaussian integration.

4.5 Another Note on Convergence

The convergence of the Rayleigh, photoionisation, and total Raman scattering cross-sections are given in Table D.9 in Appendix D for ground state atomic hydrogen at several frequencies above threshold. These cross-sections are given for different basis set sizes and varying $\lambda_\ell$ (both of which changes the effective box radius), to demonstrate how changes in the basis set effects our results. We find that the Rayleigh scattering cross-sections are completely converged, even at frequencies as large as 100 a.u. (2721 eV).

In Section 4.2 I computed the photoionisation cross-section given by our pseudostate method and compared with the analytical results. I found that our photoionisation cross-section was in good agreement with the analytic expression at frequencies near threshold, but drift away from the analytical values at frequencies much larger than threshold. This is also reflected in our study of the photoionisation cross-section with respect to the basis set size and varying $\lambda_\ell$. In Table D.9 we find that the photoionisation is converged at low frequencies, but at high frequencies the photoionisation varies with $\lambda_\ell$ or $N_\ell$.

We do not expect very good convergence of the total Raman scattering cross-sections, since I have shown in Section 4.4.6 that these are very sensitive to the inclusion/exclusion of Rydberg states, i.e. the Raman scattering cross-section is polluted by the Compton scattering. We could consider the convergence of the sum of the Raman and Compton scattering cross-sections, but we find that the Raman scattering cross-section given in Table D.9 is much smaller than the Compton scattering cross-section shown in the
4.6 Compton Scattering

In the previous section I have presented the Rayleigh scattering cross-sections and cross-sections of Raman transitions. These cross-sections describe the probability of a transition occurring to a certain final state energy (or, equivalently, the probability of emitting a photon of certain frequency $\omega'$) given the absorption of an incident photon of frequency $\omega$. In this section I will present our calculation of the Compton scattering cross-section. After extensive convergence studies we have found that, unlike the Rayleigh or Raman scattering cross-sections, we find that our method does not give converged results for Compton scattering. Compton scattering refers to the process where a photon of frequency $\omega$ is absorbed, the atom is ionised and a photon of frequency $\omega'$ is emitted, as shown in Fig. 4.17. Unlike Rayleigh or individual Raman scattering cross-sections, the Compton scattering cross-section involves integration over all possible final state energies $\varepsilon$ (or, equivalently, over all outgoing photon frequencies $\omega'$). This is similar to the total Raman scattering cross-section which involves a sum over all possible final state energies.

Figure 4.17: Diagram of the Compton scattering process for incident photon frequency $\omega$ with schematic atomic levels of hydrogen shown for reference, where I.P. is the ionisation potential. The Compton scattering cross-section is found by summing over all intermediate states $t$ and integrating over all possible final states in the continuum with energy $\varepsilon$.

In Chapter 1 the photon-atom interaction was introduced as the sum of two terms - the $\mathbf{p} \cdot \mathbf{A}$ interaction and the $A^2$ interaction. There have been many calculations of the Compton cross-sections, but the overwhelming majority of these compute Compton scattering at high photon energies and neglect the $\mathbf{p} \cdot \mathbf{A}$ term. Methods such as the incoherent scattering method or impulse approximation consider only the $A^2$ contribution and so cannot be compared against our Compton calculation.

Gavrila published analytic expressions describing Compton scattering of hydrogen-like atoms in 1972 [58,59]. The analytic expression

$$d^3 \sigma = r_0^2 (\kappa_2 / \kappa_1) |\mathcal{M}|^2 d\kappa_2 d\Omega_2 d\Omega,$$

(4.11)
4.6. Compton Scattering

The differential Compton scattering cross-section, where $\kappa_1$ and $\kappa_2$ are the momenta of the initial and final photons, and $\Omega_2$ and $\Omega$ is the solid angles of the emitted photon and outgoing electron respectively. $\mathcal{M}$ is the matrix element of the Kramers-Heisenberg-Waller type. These analytic expressions were evaluated numerically to compute Compton scattering from the $p \cdot A$ interaction by Bergstrom et al. [4] and Drukarev et al. [9]. To the best of my knowledge this is the only data available for the $p \cdot A$ contribution to the Compton scattering cross-section.

Rather than applying these analytic expressions given for hydrogen-like atoms, we have considered an alternative approach. The total Compton scattering cross-section involves an integral over all possible final state energies,

$$\sigma_C = \int_{\epsilon_{\text{min}}}^{\epsilon_{\text{max}}} \frac{d\sigma_C}{d\epsilon'} d\epsilon' , \quad (4.12)$$

where $\epsilon_{\text{min}} = 0$ and $\epsilon_{\text{max}} = \omega - |\epsilon_i|$ since the largest possible energy that the electron can be excited to is $\omega - |\epsilon_i|$. Since in our calculation the atom is effectively confined in a box, the continuum is approximated by a set of pseudostates. As a result, the integral in Eqn. 4.12 will be approximated as a sum over pseudostates with energy below $\epsilon_{\text{max}} = \omega - |\epsilon_i|$. This has similarities with the total Raman scattering cross-section, which involves a sum over all possible final bound states,

$$\sigma_{\text{R,ij}}(\omega) = \sum_{j: \epsilon_j < 0} \sigma_{ij}(\omega) = \sum_{j: \epsilon_j < 0} \sigma_T \omega' |\alpha_{ij}(\omega)|^2 ,$$

where $\epsilon_j < \omega - |\epsilon_i|$ and $\omega' = \omega - |\epsilon_i| - \epsilon_j$.

Motivated by the Raman scattering cross-section, we have considered the intuitive ansatz

$$d\sigma_C = \sigma_T \omega' |\alpha_{ie'}(\omega)|^2 , \quad (4.13)$$

where the outgoing photon frequency

$$\omega' = \omega - |\epsilon_i| - \epsilon' , \quad (4.14)$$

and $\alpha_{ie'}(\omega)$ is the transition polarisability to a final pseudostate with energy $\epsilon$. Note that we are only considering linearly polarised light. In the following sections I will present the Compton scattering cross-sections given by our pseudostate method (by applying the ansatz in Eqn. 4.13) and comparing with the cross-sections calculated by Bergstrom et al. [4] and Drukarev et al. [9] using Gavrila’s analytic expressions.

4.6.1 Semi-analytical Calculation

The differential Compton scattering cross-section $\frac{d\sigma_C}{d\epsilon'}$ should be a continuous function with respect to the incident photon frequency. Since there are analytic expressions of the free-to-free transition matrix elements for atomic hydrogen [17], the differential Compton scattering cross-section can be described analytically. In the ansatz we are assuming (see Eqn. 4.13 in previous section), the differential Compton
scattering cross-section requires calculation of the complex polarisability, which is given by the same formula as previously,

\[
\alpha_{\varepsilon \varepsilon'}(\omega) = \sum_{i} C_{i, \varepsilon} \left[ \frac{\langle \varepsilon' | z | i \rangle \langle i | z | i \rangle}{\varepsilon_{i} - \varepsilon_{i} - \omega} + \frac{\langle \varepsilon' | z | i \rangle \langle i' | z | i \rangle}{\varepsilon_{i} - \varepsilon' + \omega} \right] + \int_{0}^{\infty} C_{i, \varepsilon} \left[ \frac{\langle \varepsilon' | z | \varepsilon' \rangle \langle \varepsilon' | z | i \rangle}{\varepsilon - \varepsilon_{i} - \omega} + \frac{\langle \varepsilon' | z | \varepsilon' \rangle \langle \varepsilon' | z | i \rangle}{\varepsilon - \varepsilon' + \omega} \right] d\varepsilon , \quad (4.15)
\]

but in this case the final state is a state of positive energy \( \varepsilon' \). This is the first calculation in this thesis that involves a free-to-free transition and requires a free-to-free transition matrix element (\( \langle \varepsilon' | z | \varepsilon' \rangle \)).

Gordon [17] derived an analytic expression for the free-to-free transition matrix element in 1929. The transition matrix element between a continuum state with energy \( \varepsilon_{1} \) and angular momentum \( L \) to a continuum state with energy \( \varepsilon_{2} \) and angular momentum \( L - 1 \), is

\[
T_{\varepsilon_{1} \varepsilon_{2}'} = \frac{i e^{\pi |\mu_{2} - \mu_{1}|/2}}{8(2L - 1)!(k_{1}k_{2})^{2}} \sqrt{\sinh(\pi \mu_{2})\sinh(\pi \mu_{1})} \sqrt{L^{2} + \mu_{2}^{2}} \left( \frac{4k_{1}k_{2}}{(k_{1} + k_{2})^{2}} \right)^{L+1} i(\mu_{1} - \mu_{2}) \ln \left| \frac{k_{1} + k_{2}}{k_{1} - k_{2}} \right| \quad (4.16)
\]

and \( k = \sqrt{2\varepsilon} \). We have used the formula as presented by Novikov et al. [128], which differs from Gordon’s formula by \( \frac{1}{k_{1}k_{2}} \). The hypergeometric function \( _{2}F_{1}(a, b, c; z) \) can be calculated using [129]

\[
_{2}F_{1}(a, b, c; z) = \sum_{n=0}^{N_{\max}} \frac{(a)_{n}(b)_{n}z^{n}}{(c)_{n}n!} , \quad (4.17)
\]

where \( z \) is a complex number.

The free-to-free transition matrix element can be written in different forms - length, velocity and acceleration. The form given in Eqn. 4.16 is in the length form, as notated by the superscript \( r \). The length form can be converted to the velocity form \( T_{\varepsilon_{1} \varepsilon_{2}}^{V} \) (Drukarev et al. [9] use velocity form and Green’s functions) or acceleration form \( T_{\varepsilon_{1} \varepsilon_{2}}^{V} \) using [128]

\[
(\varepsilon_{1} - \varepsilon_{2})^{2} T_{\varepsilon_{1} \varepsilon_{2}}^{r} = (\varepsilon_{1} - \varepsilon_{2}) T_{\varepsilon_{1} \varepsilon_{2}}^{V} = T_{\varepsilon_{1} \varepsilon_{2}}^{V} . \quad (4.18)
\]

The various forms of the free-to-free transition matrix element for the transition between state of energy \( \varepsilon_{2} = 0.25 \) a.u. and energy \( \varepsilon_{1} \) are plotted in Fig. 4.18. From 4.18 we can see that there is a pole in the transition matrix elements in the length and velocity forms, but the acceleration function does not
have a pole. The acceleration form is plotted in Fig. 4.18, zoomed in on the energy range where $\epsilon_1 \approx \epsilon_2$. Though the acceleration form does not have a pole, there is a dip in the transition matrix element when $\epsilon_1 \approx \epsilon_2$. Upon investigation of the origin of this dip, we have found that increasing the number of loops ($N_{\text{max}}$ in Eqn. 4.17) used in the calculation of the hypergeometric function narrows the dip. Therefore, it seems that this dip is not physical, but rather an artifact of our hypergeometric calculation.

Figure 4.18: Plot of the analytical free-to-free transition matrix elements from a state of energy $\epsilon_1$ to a state of energy $\epsilon_2 = 0.25$ a.u. as a function of energy $\epsilon_1$. (a) shows the length, velocity and acceleration form whilst (b) zooms in on the acceleration form of the transition matrix element near $\epsilon_1 = \epsilon_2$, and also shows the improved calculation of the transition matrix element (in acceleration form) once we apply a transformation (see Eqn. 4.19) to the hypergeometric function.

I have studied the dependence of the free-to-free transition matrix element on the number of loops used in the hypergeometric function in Table 4.4. Table 4.4 gives the transition matrix element between a state with energy $\epsilon_2 = 0.25$ a.u. and a state with energy $\epsilon_1$ for different number of loops $N_{\text{max}}$ in the hypergeometric function. The free-to-free transition matrix element involves the computation of two hypergeometric functions - here we use the same $N_{\text{max}}$ for both. Table 4.4 shows that the transition matrix element converges with respect to $N_{\text{max}}$ at energies away from $\epsilon_1 = \epsilon_2$, but at energies $\epsilon_1 \approx \epsilon_2$ the convergence of the transition matrix elements is extremely slow. The table has shown that close to the pole more than 10,000 loops are needed for convergence.
4.6. Compton Scattering

Table 4.4: Convergence of free-to-free transition matrix element $T_{\epsilon_1\epsilon_2}^{V}$ (in atomic units) with respect to changing $N_{\text{max}}$, where $N_{\text{max}}$ is the upper bound of the sum in the hypergeometric calculation (given in Eqn. 4.17). Here the initial state energy is $\epsilon_2 = 0.25 \text{ a.u.}$ and several final state energies, $\epsilon_1$, near $\epsilon_2$ are considered.

<table>
<thead>
<tr>
<th>$N_{\text{max}}$</th>
<th>0.20</th>
<th>0.22</th>
<th>0.24</th>
<th>0.26</th>
<th>0.28</th>
<th>0.3</th>
</tr>
</thead>
<tbody>
<tr>
<td>200</td>
<td>70.4996858</td>
<td>146.2</td>
<td>1019.8</td>
<td>896.7</td>
<td>112.0</td>
<td>47.733879</td>
</tr>
<tr>
<td>400</td>
<td>83.8640344</td>
<td>165.7</td>
<td>1045.9</td>
<td>921.3</td>
<td>126.0</td>
<td>55.880184</td>
</tr>
<tr>
<td>600</td>
<td>91.1410617</td>
<td>181.6</td>
<td>1067.3</td>
<td>940.8</td>
<td>137.1</td>
<td>60.761973</td>
</tr>
<tr>
<td>800</td>
<td>95.0727477</td>
<td>194.7</td>
<td>1087.4</td>
<td>958.7</td>
<td>146.2</td>
<td>63.783297</td>
</tr>
<tr>
<td>1000</td>
<td>97.1892976</td>
<td>205.5</td>
<td>1106.7</td>
<td>975.8</td>
<td>153.8</td>
<td>65.678941</td>
</tr>
<tr>
<td>2000</td>
<td>99.5342973</td>
<td>236.3</td>
<td>1196.4</td>
<td>1053.8</td>
<td>176.8</td>
<td>68.638853</td>
</tr>
<tr>
<td>3000</td>
<td>99.6382182</td>
<td>247.6</td>
<td>1277.3</td>
<td>1123.2</td>
<td>186.6</td>
<td>68.960779</td>
</tr>
<tr>
<td>4000</td>
<td>99.6428102</td>
<td>251.7</td>
<td>1350.5</td>
<td>1185.5</td>
<td>190.9</td>
<td>68.997146</td>
</tr>
<tr>
<td>5000</td>
<td>99.6430131</td>
<td>253.2</td>
<td>1416.7</td>
<td>1241.8</td>
<td>192.7</td>
<td>69.997146</td>
</tr>
<tr>
<td>6000</td>
<td>99.6430221</td>
<td>253.7</td>
<td>1476.6</td>
<td>1292.6</td>
<td>193.5</td>
<td>69.001819</td>
</tr>
<tr>
<td>7000</td>
<td>99.6430225</td>
<td>254.0</td>
<td>1530.6</td>
<td>1338.6</td>
<td>193.9</td>
<td>69.001876</td>
</tr>
<tr>
<td>8000</td>
<td>99.6430225</td>
<td>254.0</td>
<td>1579.4</td>
<td>1380.2</td>
<td>194.0</td>
<td>69.001883</td>
</tr>
<tr>
<td>9000</td>
<td>99.6430225</td>
<td>254.0</td>
<td>1623.5</td>
<td>1417.9</td>
<td>194.1</td>
<td>69.001884</td>
</tr>
<tr>
<td>10000</td>
<td>99.6430225</td>
<td>254.0</td>
<td>1663.3</td>
<td>1452.0</td>
<td>194.1</td>
<td>69.001884</td>
</tr>
</tbody>
</table>

We can ensure convergence in our calculations by truncating the sum when the difference between subsequent terms have reached a certain tolerance. Throughout this thesis I will be using a tolerance of $10^{-10}$. Of course, from Table 4.4 we can see that reaching the tolerance of $10^{-10}$ at energies $\epsilon_1 \approx \epsilon_2$ will require $N_{\text{max}}$ much larger than 10000. In order to be able to use these analytical transition matrix elements to compute scattering cross-sections, we need a more efficient method for computing $2F_1(a, b, c; z)$. For a more efficient method I have utilised the transformation for $2F_1(a, b, c; z)$ when $0.5 \leq z \leq 1$ [129, 130] to

\[
2F_1(a, b, c; z) = \frac{\Gamma(c)\Gamma(c-a-b)}{\Gamma(c-a)\Gamma(c-b)} 2F_1(a, b, a+b-c+1; w) + w^{c-a-b}\frac{\Gamma(c)\Gamma(a+b-c)}{\Gamma(a)\Gamma(b)} 2F_1(c-a, c-b, c-a-b+1; w) \tag{4.19}
\]

where $w = 1 - z$.

Fig. 4.19 compares the $N_{\text{max}}$ needed to achieve convergence to $10^{-10}$ in the transition matrix elements for the original and improved method. The two hypergeometric functions in Eqn. 4.16 require different number of loops to achieve the $10^{-10}$ convergence. In Fig. 4.19 $N_{\text{max}}$ refers to the maximum number of loops of the two functions. From this plot it is evident that applying the transformations of the hypergeometric functions [129], allows us to calculate the free-to-free transition matrix elements even at energies $\epsilon_1 \approx \epsilon_2$. The resulting free-to-free transition matrix element (see Fig. 4.18 (b)) still shows a kink at $\epsilon_1 \approx \epsilon_2$ but no longer has the large dip at $\epsilon_1 \approx \epsilon_2$ that our straight-forward calculation of hypergeometric function gave us.
Figure 4.19: Plot of the number of loops that are needed for the calculation of the hypergeometric function in the transition matrix element $T^{E_1 E_2}_{E_1 E_2}$ (given in Eqn. 4.17) to reach convergence to $10^{-10}$, where the initial state energy is $\varepsilon_1 = 1$ a.u. The number of loops needed is compared for a straight-forward computation of the hypergeometric function and for a calculation using transformations.

Having now resolved the origin of the dip in the acceleration form of the transition matrix elements, we can accurately compute the free-to-free transition matrix elements. Fig. 4.20 is a plot of the free-to-free transition matrix elements in the velocity form as a function of the initial and final state energy. The complex polarisabilities are calculated using the velocity form of the transition matrix elements, which means that the integrand of the continuum integral,

$$
\int_0^\infty C_{i,\varepsilon, j} \left[ \frac{\langle \varepsilon' || z || \varepsilon \rangle \langle \varepsilon || z || i \rangle}{\varepsilon - \varepsilon_i - \omega} + \frac{\langle \varepsilon' || z || \varepsilon \rangle \langle \varepsilon || z || i \rangle}{\varepsilon - \varepsilon' + \omega} \right] d\varepsilon ,
$$

now has two poles, at $\varepsilon = \varepsilon_i + \omega$ and $\varepsilon = \varepsilon'$. Although it is possible to compute such integrals involving the free-to-free transition matrix elements, as has been done for the case of two-photon ionisation by Veniard et al. [11], it is very complicated. In order to do this integration, we must split the integral into two - i.e. to integrate across each pole. We find that as we add more panels to the integral, the free-to-free transition matrix elements must be calculated for increasingly smaller energies. However we cannot calculate the analytical transition matrix elements $\langle \varepsilon' || z || \varepsilon \rangle$ in length form between states very close to threshold, as it involves cancellation of extremely large numbers. This difficulty also will be seen to occur in Section 5.2.1.1 in our calculation of the static hyperpolarisability of hydrogen using our semi-analytic calculation. Since the aim of this thesis is to develop a pseudostate method and not the semi-analytical calculation, I have chosen not to pursue this approach to the Compton scattering cross-section any further, but leave this section to document my calculations so far.
4.6. Compton Scattering

Figure 4.20: Plot of the analytical transition matrix elements in velocity form for the transition between states with $\ell = 1$ and $\ell = 0$ in the continuum.

4.6.2 Pseudostate Calculation of Compton

Let us consider the calculation of the Compton scattering cross-section using our pseudostate method instead. Previously I have shown that the pseudostate bound-to-free transition matrix elements are normalised by

$$T_{\varepsilon_t \varepsilon_i} = T_{\varepsilon_t \varepsilon_i}^P \rho(\varepsilon_t) \rho(\varepsilon_i) \left( \frac{2}{\varepsilon_{t+1} - \varepsilon_{t-1}} \right),$$

(4.21)

where $\rho(\varepsilon_t)$ is the energy density. The bound-to-free transition matrix element must be normalised in this way since our calculation uses a set of pseudostates to approximate the continuum. It follows that the free-to-free transition matrix element must be normalised in a similar way, but because both the initial state $\varepsilon_t$ and final state $\varepsilon_j$ in the transition are pseudostates, they must be normalised by

$$T_{\varepsilon_j \varepsilon_t} = \frac{T_{\varepsilon_j \varepsilon_t}^P}{\rho(\varepsilon_j) \rho(\varepsilon_t)}. \quad (4.22)$$

This normalisation must be taken into account when we transform our analytic expression for the complex transition polarisability to the pseudostate case. The complex transition polarisability is computed the
same as previously, but the final state is now a pseudostate with energy $\varepsilon_j$, such that

$$
\alpha_{\varepsilon j}(\omega) = \sum_l C_{i,l,j} \left[ \frac{\langle \varepsilon_j | z | l \rangle \langle l | z | i \rangle}{\varepsilon_i - \varepsilon_l - \omega} + \frac{\langle \varepsilon_j | z | l \rangle \langle l | z | i \rangle}{\varepsilon_i - \varepsilon_j + \omega} \right]
+ \int_0^\infty C_{i,\varepsilon,j} \left[ \frac{\langle \varepsilon_j | z | \varepsilon_j \rangle \langle \varepsilon_j | z | i \rangle}{\varepsilon - \varepsilon_i - \omega} + \frac{\langle \varepsilon_j | z | \varepsilon_j \rangle \langle \varepsilon_j | z | i \rangle}{\varepsilon - \varepsilon_j + \omega} \right] d\varepsilon
$$

$$
= \sum_l C_{i,l,j} \left[ \frac{T_{\varepsilon_j T_{ii}}}{\varepsilon_i - \varepsilon_l - \omega} + \frac{T_{\varepsilon_j T_{ii}}}{\varepsilon_i - \varepsilon_j + \omega} \right] + \int_0^\infty C_{i,\varepsilon,j} \left[ \frac{T_{\varepsilon_i T_{ii}}}{\varepsilon_i - \varepsilon_i - \omega} + \frac{T_{\varepsilon_i T_{ii}}}{\varepsilon_i - \varepsilon_j + \omega} \right] d\varepsilon
$$

$$
\approx \sum_l C_{i,l,j} \left[ \frac{T_{\varepsilon_j T_{ii}}^p}{\varepsilon_i - \varepsilon_l - \omega} + \frac{T_{\varepsilon_j T_{ii}}^p}{\varepsilon_i - \varepsilon_j + \omega} \right] + \frac{N_B}{N_P} \left[ \frac{T_{\varepsilon_i T_{ii}}^p}{\varepsilon_i - \varepsilon_i - \omega} + \frac{T_{\varepsilon_i T_{ii}}^p}{\varepsilon_i - \varepsilon_j + \omega} \right] \Delta \varepsilon_i,
$$

(4.23)

where $N_B$ is the number of bound states in the calculation, $N_P$ is the number of pseudostates and

$$
\Delta \varepsilon_i = \frac{\varepsilon_{i+1} - \varepsilon_i - 1}{2} = \rho(\varepsilon_i)^2,
$$

(4.24)

so the transition polarisability can be written as

$$
\alpha_{\varepsilon j}(\omega) = \sum_l \frac{N_B}{N_P} \sum_l \frac{C_{i,l,j}}{\rho(\varepsilon_j)} \left[ \frac{T_{\varepsilon_j T_{ii}}^p}{\varepsilon_i - \varepsilon_l - \omega} + \frac{T_{\varepsilon_j T_{ii}}^p}{\varepsilon_i - \varepsilon_j + \omega} \right] + \sum_l \frac{N_B}{N_P} \sum_l \frac{C_{i,l,j}}{\rho(\varepsilon_j)} \left[ \frac{T_{\varepsilon_i T_{ii}}^p}{\varepsilon_i - \varepsilon_i - \omega} + \frac{T_{\varepsilon_i T_{ii}}^p}{\varepsilon_i - \varepsilon_j + \omega} \right] \rho(\varepsilon_i)^2
$$

$$
+ \sum_l \frac{N_B}{N_P} \sum_l \frac{C_{i,l,j}}{\rho(\varepsilon_j)} \left[ \frac{T_{\varepsilon_j T_{ii}}^p}{\varepsilon_i - \varepsilon_i - \omega} + \frac{T_{\varepsilon_j T_{ii}}^p}{\varepsilon_i - \varepsilon_j + \omega} \right] \rho(\varepsilon_j)^2
$$

$$
= \sum_l \frac{N_B}{N_P} \sum_l \frac{C_{i,l,j}}{\rho(\varepsilon_j)} \left[ \frac{T_{\varepsilon_j T_{ii}}^p}{\varepsilon_i - \varepsilon_l - \omega} + \frac{T_{\varepsilon_j T_{ii}}^p}{\varepsilon_i - \varepsilon_j + \omega} \right] + \sum_l \frac{N_B}{N_P} \sum_l \frac{C_{i,l,j}}{\rho(\varepsilon_j)} \left[ \frac{T_{\varepsilon_i T_{ii}}^p}{\varepsilon_i - \varepsilon_i - \omega} + \frac{T_{\varepsilon_i T_{ii}}^p}{\varepsilon_i - \varepsilon_j + \omega} \right] \rho(\varepsilon_i)^2
$$

$$
+ \sum_l \frac{N_B}{N_P} \sum_l \frac{C_{i,l,j}}{\rho(\varepsilon_j)} \left[ \frac{T_{\varepsilon_i T_{ii}}^p}{\varepsilon_i - \varepsilon_i - \omega} + \frac{T_{\varepsilon_i T_{ii}}^p}{\varepsilon_i - \varepsilon_j + \omega} \right] \rho(\varepsilon_j)^2.
$$

(4.25)

Though this derivation is somewhat complicated, in the end we are effectively applying the same transition polarisability as for the Raman calculation. As shown in Fig. 4.21, the difference between the transition polarisabilities in our Raman and Compton calculations is that the transition polarisability in our Compton calculation has a final state in the continuum. In fact, as demonstrated in Fig. 4.21, our transition polarisability can also be applied to the calculation of the two-photon ionisation cross-section (see Chapter 7).

Our Compton scattering cross-section calculation involves the calculation of transition polarisabilities to all final pseudostates with energy $\varepsilon_f < \omega - |\varepsilon_i|$. As an example, the transition polarisability to a final pseudostate of approximately $\varepsilon_f \sim 4.5$ a.u. is plotted as a function of incident photon frequency $\omega$ for various basis set sizes $N_f$ in Fig. 4.22. Fig. 4.22 gives the final state energy $\varepsilon_f$ used for each calculation with basis $N_f = 120, 100$ and 80. In this plot, only the transition polarisabilities with outgoing photon frequency $\omega' > 0$ are relevant to our Compton calculation. Since $\omega' = \omega - (\varepsilon_f - \varepsilon_i)$, then the data relevant to our Compton calculation is at frequencies $\omega > \varepsilon_f - \varepsilon_i$. However, the transition polaris-
4.6. Compton Scattering

Figure 4.21: Diagram showing the scattering processes described by the transition polarisabilities from initial state \( i \) to final states \( f \). The transition polarisability to final bound state \( \varepsilon_f < 0 \) (Raman scattering), final pseudostate with energy \( \varepsilon_f - \varepsilon_i < \omega \) (Compton scattering) and final pseudostate with energy \( \varepsilon_f - \varepsilon_i = 2\omega \) are shown.

ability at frequency \( \omega = (\varepsilon_f - \varepsilon_i)/2 \) can be used to compute the two-photon ionisation cross-section (see Chapter 7). Difficulties emerge in our calculation of the two-photon ionisation cross-section as we do not necessarily have data points at exactly this frequency. This will be discussed in detail in Chapter 7.

The differential Compton scattering cross-section is thus given by

\[
\frac{d\sigma_C}{d\varepsilon_j} = \sigma_T \omega \varepsilon_j^3 |\alpha_{\varepsilon_j}(\omega)|^2
\]

\[
= \sigma_T \omega \varepsilon_j^3 \left| \sum_i N_i C_{i,t,j} \left[ \frac{T_{\varepsilon_j}^P T_{\varepsilon_i}^P}{\varepsilon_i - \varepsilon_j - \omega} + \frac{T_{\varepsilon_j}^P T_{\varepsilon_i}^P}{\varepsilon_i - \varepsilon_j + \omega} \right] + \sum_i N_i C_{i,t,j} \frac{T_{\varepsilon_j}^P T_{\varepsilon_i}^P}{\varepsilon_i - \varepsilon_j - \omega} + \frac{T_{\varepsilon_j}^P T_{\varepsilon_i}^P}{\varepsilon_i - \varepsilon_j + \omega} \right|^2
\]

\[
= \sigma_T \omega \varepsilon_j^3 \frac{1}{\rho(\varepsilon_j)^2} \left[ \sum_i N_i C_{i,t,j} \left[ \frac{T_{\varepsilon_j}^P T_{\varepsilon_i}^P}{\varepsilon_i - \varepsilon_j - \omega} + \frac{T_{\varepsilon_j}^P T_{\varepsilon_i}^P}{\varepsilon_i - \varepsilon_j + \omega} \right] \right]
\]

\[
+ \sum_i N_i C_{i,t,j} \left[ \frac{T_{\varepsilon_j}^P T_{\varepsilon_i}^P}{\varepsilon_i - \varepsilon_j - \omega} + \frac{T_{\varepsilon_j}^P T_{\varepsilon_i}^P}{\varepsilon_i - \varepsilon_j + \omega} \right]^2 \] (4.26)

Then the total Compton scattering cross-section is given by

\[
\sigma_C = \int_0^{\omega - |\varepsilon_i|} \frac{d\sigma_C}{d\varepsilon_j} d\varepsilon_j' \approx \sum_{j,\varepsilon_j < \omega - |\varepsilon_i|} \frac{d\sigma_C}{d\varepsilon_j} \Delta \varepsilon_j \approx \sum_{j,\varepsilon_j < \omega - |\varepsilon_i|} \frac{d\sigma_C}{d\varepsilon_j} \rho(\varepsilon_j)^2. \] (4.27)

The total Compton scattering cross-section can be written as

\[
\sigma_C(\omega) = \sum_{j,\varepsilon_j < \omega - |\varepsilon_i|} d\sigma_{\varepsilon_j}(\omega), \] (4.28)
4.6. Compton Scattering

Figure 4.22: Plot of the transition polarisability $\text{Re} [\alpha_{i\epsilon_f}(\omega)]$ (in atomic units) of H(1s) given by our pseudostate method ($N_\ell = 120, 100$ and $80$ basis) for $\ell = 0$ (a) and $\ell = 2$ (b) final states with energy $\epsilon_f$. 

![Graph showing transition polarisability](image)
and the differential Compton scattering cross-section as

$$\frac{d\sigma_C(\omega)}{d\epsilon_j} = \frac{d\sigma_{ie_j}(\omega)}{\Delta\epsilon_j},$$

where the $\rho(\epsilon_j)^2$ in Eqn. 4.27 cancels $1/\rho(\epsilon_j)^2$ in Eqn. 4.22 to give

$$d\sigma_{ie_j}(\omega) = \sigma_T \omega^3 \left| \sum_t C_{i,t,j} \left[ \frac{T_{\epsilon_j t}^P T_{t i}^P}{\epsilon_t - \epsilon_i - \omega} + \frac{T_{\epsilon_j t}^P T_{t i}^P}{\epsilon_t - \epsilon_i + \omega} \right] + \sum_t C_{i,t,j} \left[ \frac{T_{\epsilon_j t}^P T_{t i}^P}{\epsilon_t - \epsilon_i - \omega} + \frac{T_{\epsilon_j t}^P T_{t i}^P}{\epsilon_t - \epsilon_i + \omega} \right] \right|^2.$$  

This is the ansatz that we now test against previous calculations of Drukarev et al. \[9\] and Bergstrom et al. \[4\]. Though the derivation of 4.30 may seem complicated, we are effectively applying the total Raman scattering cross-section formula, but for final states in the continuum.

From this we can see that the total Compton scattering cross-section calculation requires only the un-normalised transition matrix elements given by $\rho(\epsilon)^2$. Since the complex transition polarisability above threshold can only be computed at certain frequencies $\omega$ that correspond to the difference between the initial and pseudostate energies, $\epsilon_t - \epsilon_i$, the Compton scattering cross-section can also only be computed at these frequencies as well.

### 4.6.2.1 Differential Scattering Cross-section

Before we calculate the total Compton scattering cross-section, let us examine the differential Compton scattering cross-section $d\sigma/d\omega'$. Often the differential cross-section refers to the differential with respect to solid angle, i.e. $d\sigma/d\Omega$, when dealing with (classical or quantum) particle scattering. In this section I will be considering the differential Compton scattering cross-section with respect to the outgoing photon frequency, i.e. $d\sigma/d\omega'$ where $\omega'$ is the outgoing photon frequency. The differential cross-section has previously been computed by Drukarev et al. \[9\] for atomic hydrogen in the ground state, and they kindly sent us their data for direct comparison.

Computing this differential cross-section allows us insight into the physics that occurs in the Compton scattering process, such as the infra-red divergence. The infra-red divergence refers to the divergence in the differential Compton scattering cross-section as the outgoing photon frequency $\omega'$ approaches zero, $\omega' \to 0$. This divergence is physical and occurs when a radiative process becomes indistinguishable from a radiationless process as the photon frequency becomes small \[4\]. In this case the corresponding radiationless process is the photoionisation process, where a photon is absorbed and an electron, but no photon, is emitted. This behaviour was shown to occur in the differential Compton scattering cross-section by Gavrila \[58, 79\] in his non-relativistic analytic calculation of Compton scattering of atomic hydrogen.

As the divergence in the radiative process corresponds to a radiationless process, a relation between these two processes can be found \[131\]. In the case of Compton scattering, the relation to the photoionisation process is given by Low’s theorem \[9\] at low outgoing photon frequencies ($\omega' \ll \omega, \epsilon_{IP}$) such
4.6. Compton Scattering

that

\[ \frac{d\sigma(\omega, \omega')}{d\omega'} = \sigma\ell(\omega)w(\omega, \omega'), \tag{4.31} \]

and

\[ w(\omega, \omega') = \frac{2}{3\pi} \frac{p^2}{m^2} \frac{1}{\omega'}, \tag{4.32} \]

where \( \sigma\ell \) is the photoionisation cross-section, \( p \) is the linear momentum of the electron given by \( p^2 = 2m(\omega - \epsilon_i \lambda) \) and \( m \) is the mass of the electron. Drukarev et al. [9] have computed both the differential cross-section using Gavrila’s analytic equations as well as using Low’s theorem, and have found that Low’s theorem gives a good approximation to the differential cross-section over a large range of the outgoing photon frequency \( \omega' \).

In our pseudostate calculation the differential Compton scattering cross-section is calculated using Eqns. 4.29 and 4.30. The differential Compton scattering cross-section cannot be accurately compared for different basis sets, since each calculation with a different basis set has a different set of incident photon frequencies. The differential cross-section can be investigated with respect to changing box radius by varying a different parameter, \( \lambda_\ell \). The Laguerre functions in our basis set were introduced in Chapter 3, and are given by Eqns. 3.1 and 3.2, where smaller \( \lambda_\ell \) gives a larger box and larger \( \lambda_\ell \) gives a smaller box. As a result, the pseudostate energies also change as we vary \( \lambda_\ell \).

Let us investigate the differential Compton scattering cross-sections given by our pseudostate method and compare with the differential cross-section data given by Drukarev et al. [9]. Drukarev et al. [9] have presented differential cross-sections for atomic hydrogen at \( \omega = 1, 2 \) and 5 a.u. We are not able to directly compare our differential cross-sections at exactly these frequencies, as our method can compute the Compton scattering cross-section only at certain frequencies corresponding to the energy difference between a pseudostate and the initial state. Our differential cross-sections can also only be computed at specific outgoing frequencies \( \omega' \) corresponding to \( \omega' = \omega - (\epsilon - \epsilon_i)/\hbar \) where \( \epsilon \) refers to a pseudostate energy and \( \epsilon_i \) to the initial state energy. However, if we run the calculation for various \( \lambda_\ell \), we have a different set of pseudostate energies for each calculation. We are then able to compute the Compton scattering cross-sections for a range of incident frequencies near \( \omega = 1, 2 \) and 5 a.u.

The differential Compton scattering cross-section given by Drukarev et al. [9] for incident frequency \( \omega = 5 \) a.u. and the differential Compton scattering cross-sections given by our pseudostate method for incident photon frequencies near \( \omega = 5 \) a.u. are plotted in Figs. 4.23 (a)-(d). Our pseudostate method is run for several calculations with \( \lambda_\ell \) varied for all \( \ell \) from \( \lambda_\ell = 0.49 \) to 0.51 in steps of 0.001. We have separated the differential Compton scattering cross-section given by our pseudostate method into the contribution from final \( \ell = 0 \) states (see Figs. 4.23 (a) and (b)) and final \( \ell = 2 \) states (see Figs. 4.23 (c) and (d)).

Fig. 4.23 (a) compares the differential Compton scattering cross-section given by our pseudostate method to final \( \ell = 0 \) states with the differential Compton scattering cross-section (to all final states) given by Drukarev et al. [9] at \( \omega = 5 \) a.u. The same features are present in our differential Compton scattering cross-section as in the differential cross-section presented by Drukarev et al., i.e. increasing \( d\sigma/d\omega' \) as
4.6. Compton Scattering

Figure 4.23: Plot of the differential Compton scattering cross-section \( d\sigma_C / d\omega' \), in units of \( \sigma_T \), for incident photon frequencies near \( \omega = 5 \) a.u. when varying \( \lambda_\ell \) from 0.49 to 0.51 in steps of 0.001 for all \( \ell \). The differential Compton scattering cross-section given by Drukarev et al. [9] at exactly \( \omega = 5 \) a.u. is plotted for comparison. (a) and (c) show the differential cross-section to final \( \ell = 0 \) and \( \ell = 2 \) states respectively, and exhibit bifurcation. (b) and (d) show the differential cross-section to final \( \ell = 0 \) and \( \ell = 2 \) states respectively, where the bifurcation has been removed by averaging.

\( \omega' \to 0 \) due to the infra-red divergence, and decreasing \( d\sigma / d\omega' \) as \( \omega' \) approaches the maximum outgoing frequency. However, the differential cross-sections given by our pseudostate method are bifurcated. Our calculation is alternatively over-estimating and under-estimating the differential cross-section, but the reason for this is not yet clear to us. In Fig. 4.23 (b) I have averaged out the bifurcation in our differential cross-section, and show that our differential Compton scattering cross-section to \( \ell = 0 \) final states is in good agreement with the differential Compton scattering cross-section (to all final states) given by Drukarev et al. at \( \omega = 5 \) a.u.

An important note to make here is that in a pseudostate calculation, the energy gap between successive pseudostates becomes larger and larger at higher energies (i.e. when \( \omega' \to 0 \)). This can also be seen on our plots of the differential cross-section, where there are fewer points at lower \( \omega' \) frequencies. This gives us a built-in cut-off when integrating the differential cross-section, which is dependent on the incident photon frequency. In comparison, Drukarev et al. have used a cut-off of 1 eV (\( \sim 0.03 \) a.u.) for all
4.6. Compton Scattering

Figure 4.24: Plot of the differential Compton scattering cross-section \( d\sigma_C/d\omega' \), in units of \( \sigma_T \), for incident photon frequencies near \( \omega = 2 \) a.u. when varying \( \lambda_\ell \) from 0.49 to 0.51 in steps of 0.001 for all \( \ell \). The differential Compton scattering cross-section given by Drukarev et al. [9] at exactly \( \omega = 2 \) a.u. is plotted for comparison. The bifurcation in the differential cross-sections are averaged out, and the differential cross-section to final \( \ell = 0 \) (left) and \( \ell = 2 \) (right) states are presented.

incident frequencies \( \omega \), which is much smaller than our built-in cut-off for \( \omega = 5 \) a.u. (see Fig. 4.23).

Fig. 4.23 (c) plots the differential Compton scattering cross-section to final \( \ell = 2 \) states from our pseudostate method, and the differential Compton scattering cross-section (to all final states) given by Drukarev et al. at \( \omega = 5 \) a.u. Again we can see that bifurcation occurs in our calculation of the differential Compton scattering cross-section in Fig. 4.23 (c). Fig. 4.23 (d) gives the differential Compton scattering cross-section to final \( \ell = 2 \) states by averaging out this bifurcation. We find that the differential Compton scattering cross-section to \( \ell = 2 \) states show very different behaviour than the differential Compton scattering cross-sections given by Drukarev et al. [9]. Our calculation of the differential cross-section in Figs. 4.23(c) and (d) do not show the infra-red divergence, but have a very large peak near the maximum outgoing photon frequency \( \omega' \). This behaviour was unexpected, as we have not seen this mentioned previously in the literature. Evidently our differential cross-section to final \( \ell = 0 \) states is in much better agreement with the differential cross-section given by Drukarev et al. This seems to indicate that Drukarev et al. have included only the \( \ell = 0 \) final states in their calculation.

The same behaviour is shown in Figs. 4.24 and 4.25 when comparing the differential cross-sections at incident frequencies \( \omega = 2 \) and 1 a.u. with the data given by Drukarev et al. In these plots the bifurcation in our differential cross-sections have been removed by averaging. \( \lambda_\ell \) is varied, for all \( \ell \), from 0.49 to 0.51 in steps of 0.001. The cut-off used by Drukarev et al. (1 eV) is also indicated in Fig. 4.25 to show that at \( \omega = 1 \) a.u. our calculation has a similar cut-off.

Our differential cross-sections to final \( \ell = 0 \) states show the same behaviour as the differential cross-sections given by Drukarev et al., though we seem to underestimate the differential cross-section at lower \( \omega' \) and overestimate at higher \( \omega' \). Our differential cross-sections to final \( \ell = 2 \) states show very different behaviour than the differential cross-sections given by Drukarev et al. as ours have a peak near the
4.6. Compton Scattering

Figure 4.25: Plot of the differential Compton scattering cross-section $d\sigma_C/d\omega'$, in units of $\sigma_T$, for incident photon frequencies near $\omega = 1$ a.u. when varying $\lambda_\ell$ from 0.49 to 0.51 in steps of 0.001 for all $\ell$. The differential Compton scattering cross-section given by Drukarev et al. [9] at exactly $\omega = 1$ a.u. is plotted for comparison. The bifurcation in the differential cross-sections are averaged out, and the differential cross-section to final $\ell = 0$ (left) and $\ell = 2$ (right) states are presented. The infra-red cut-off used in the calculation by Drukarev et al. is also indicated at 1 eV.

maximum outgoing frequency $\omega'$. This indicates that Drukarev et al. are including only the $\ell = 0$ final states in their calculation.

Though we are interested in investigating the effect of changing box size (by varying $\lambda_\ell$) on our differential cross-sections, so far we have not been able to do a direct comparison as we are unable to compute at the same incident frequency for different $\lambda_\ell$. The reason for this is that, as we change $\lambda_\ell$, all pseudostate energies are shifted and so we must compute at slightly different $\omega$ for each calculation. If instead we change only $\lambda_\ell$ for $\ell = 0$ and 2, and keep $\lambda_1$ constant at $\lambda_1 = 0.5$, then we are able to calculate the differential cross-section at the same $\omega$. We did this calculation in order to investigate the effect of changing box size on the differential cross-section.

Fig. 4.26 shows the differential Compton scattering cross-sections for incident photon frequencies $\omega$ = 0.998, 1.93 and 4.94 a.u., and to final $\ell = 0$ and $\ell = 2$ states. $\lambda_0$ and $\lambda_2$ are varied, whilst $\lambda_1$ is kept constant at $\lambda_1 = 0.5$. These differential cross-sections show some interesting oscillating behaviour, for which we have no physical explanation. It is possible that these oscillations are an artifact of changing $\lambda_\ell$ for only $\ell = 0$ and $\ell = 2$, which corresponds to $\ell = 0$ and $\ell = 2$ basis functions existing in a box of different size to the other $\ell$ functions. It is likely that these oscillations are an artefact of changing $\lambda_\ell$ differently for different $\ell$, as these oscillations do not occur if we change $\lambda_\ell$ equally across all $\ell$. For this reason we will always change all $\lambda_\ell$ equally for all $\ell$ when considering the effect of box size in the following sections.

In the next section we will compute the total Compton scattering cross-section and compare with the previous calculations by Drukarev et al. and Bergstrom et al. I will show that our Compton scattering cross-section to only $\ell = 0$ final states is in good agreement with the total Compton scattering cross-section given by Drukarev et al. and Bergstrom et al., but our Compton scattering cross-sections do not
Figure 4.26: Plot of the differential Compton scattering cross-section $d\sigma_C/d\omega'$, in units of $\sigma_T$. (a) and (b) give $d\sigma_C/(d\omega'\sigma_T)$ (for $\ell = 0$ and $\ell = 2$ final states respectively) at $\omega = 4.94$ a.u. for varying $\lambda_0$ and $\lambda_2$ from 0.5 to 0.53 in steps of 0.002. (c) and (d) give $d\sigma_C/(d\omega'\sigma_T)$ (for $\ell = 0$ and $\ell = 2$ final states respectively) at $\omega = 1.93$ a.u. for varying $\lambda_0$ and $\lambda_2$ from 0.5 to 0.524 in steps of 0.002. (e) and (f) give $d\sigma_C/(d\omega'\sigma_T)$ (for $\ell = 0$ and $\ell = 2$ final states respectively) at $\omega = 0.998$ a.u. when varying $\lambda_0$ and $\lambda_2$ from 0.49 to 0.51 in steps of 0.001. These calculations used a $N_{\ell} = 120$ basis set, with $\lambda_1$ is kept constant at $\lambda_1 = 0.5$. The differential Compton scattering cross-section given by Drukarev et al. [9] at exactly $\omega = 1, 2$ and 5 a.u. are also plotted.
converge with respect to $\lambda_\ell$.

### 4.6.2.2 Total Compton Scattering Cross-section

The total Compton scattering cross-section is computed by integrating the differential Compton scattering cross-section or summing as seen in Eqn. 4.28. As mentioned in the previous section, a cut-off must be used when integrating the differential Compton scattering cross-section to remove the infra-red divergence. In a pseudostate calculation the number of pseudostates become sparse at higher energies (i.e. when $\omega' \to 0$). This results in fewer points as $\omega' \to 0$, and gives us a built-in cut-off dependent on incident photon frequency $\omega$.

For frequency $\omega = 1$ a.u., the lowest $\omega'$ value (for which the differential cross-section is non-zero) is at approximately 1 eV (see Fig. 4.25). Drukarev et al. [9] have used a cut-off of 1 eV which is approximately equal to our built-in cut-off at $\omega = 1$ a.u.. In the next section I will show that the $\ell = 0$ contribution to the total Compton scattering cross-section given by our pseudostate calculation is in agreement with Drukarev et al. at $\omega = 1$ a.u., where we have the same cut-off. At higher frequencies our built-in cut-off in the differential cross-section becomes larger, whilst the cut-off used by Drukarev et al. is constant at 1 eV. Our $\ell = 0$ differential cross-section at $\omega = 5$ a.u. (see Fig. 4.23) is in good agreement with the previous calculation of differential cross-section by Drukarev et al. [9]. However, our built-in cut-off ($\sim 0.5$ a.u. $\equiv 13.6$ eV) is much larger than their cut-off at 1 eV, and so our $\ell = 0$ contribution to the total Compton scattering cross-section will be smaller than the cross-section given by Drukarev et al. as we are not including as much of the infra-red divergence.

In Fig. 4.27 our Compton scattering cross-section is plotted for $\ell = 0$ final states (a) and $\ell = 2$ final states (b), for various basis set sizes $N_\ell$. The Compton scattering cross-sections given by Drukarev et al. [9] and Bergstrom et al. [4] are also plotted. The data from Bergstrom et al. we present here was digitised from Fig. 29 in their paper [4] published in 1993.
4.6. Compton Scattering

Figure 4.27: Plot of the Compton scattering cross-section contribution, in units of $\sigma_T$, from $\ell = 0$ (left) and $\ell = 2$ (right) final states, computed with our pseudostate method (for basis set sizes $N_\ell = 80, 100$ and $120$, and $\lambda_\ell = 0.5$). The Compton scattering cross-sections given by Bergstrom et al. [4] and Drukarev et al. [9] are also plotted.

Our Compton scattering cross-section with $\ell = 0$ final states is in much better agreement with the previous data given by Drukarev et al. [9] and by Bergstrom et al. [4], than our total Compton scattering cross-section ($\ell = 0 + \ell = 2$ states). The differences between our $\ell = 0$ calculation and the previous data is likely due to the different cut-offs used in the calculation. On this log-scale our $\ell = 2$ Compton scattering cross-section seems to be converged with respect to basis set size $N_\ell$, but it is up to three orders larger in magnitude than the previous calculations by Bergstrom et al. and Drukarev et al. This discrepancy is extremely large, and seems to indicate that only the $\ell = 0$ states were included in the calculation by Bergstrom et al. and Drukarev et al. We will take a closer look at the convergence of our Compton scattering cross-section with respect to lambda at the end of this section.

We are also able to compare our calculation against scattering cross-sections given by the FFAST database, which were calculated using the form-factor method. Fig. 4.28 plots our Compton scattering cross-section, as well as our total (Rayleigh + Raman + Compton) scattering cross-section, and the scattering cross-section given by FFAST. The FFAST database gives the coherent + incoherent scattering cross-sections, which includes Rayleigh, Raman and Compton scatter. We find that, unlike the calculations by Drukarev et al. and Bergstrom et al., the FFAST cross-sections are in qualitative agreement with our calculation. Strangely, the FFAST cross-section seems to be in better agreement with our Compton scattering cross-section than our total cross-section, although the FFAST cross-section includes Rayleigh scattering as well.
4.6. Compton Scattering

Figure 4.28: Plot of our Rayleigh + Raman + Compton scattering cross-section, in units of $\sigma_T$, computed with our pseudostate method (basis set size $N_\ell = 120$), as well as our Rayleigh and Compton scattering cross-section. The coherent + incoherent scattering cross-sections presented by FFAST [2] are also plotted.

![Figure 4.28: Plot of our Rayleigh + Raman + Compton scattering cross-section, in units of $\sigma_T$, computed with our pseudostate method (basis set size $N_\ell = 120$), as well as our Rayleigh and Compton scattering cross-section. The coherent + incoherent scattering cross-sections presented by FFAST [2] are also plotted.](image)

Curiously, we have also found improved agreement between our $\ell = 0$ Compton scattering cross-section and the cross-sections given by Drukarev et al. divided by frequency, as shown in Fig. 4.30. However, closer investigation shows (Fig. 4.29) that in this case the differential cross-section is no longer in agreement with our calculation. The good agreement in Fig. 4.30 is possibly due to our built-in cut-off which changes as a function of frequency, thereby changing the total Compton scattering cross-section as a function of frequency.

Figure 4.29: Plot of the differential Compton scattering cross-section given by our pseudostate calculation (with $N_\ell = 120$ basis and varying $\lambda_\ell$) for only $\ell = 0$ final states, as well as the differential cross-section given by Drukarev et al. [9] and the data given by Drukarev divided by photon frequency $\omega$.

![Figure 4.29: Plot of the differential Compton scattering cross-section given by our pseudostate calculation (with $N_\ell = 120$, $\lambda_\ell = 0.5$ basis) for only $\ell = 0$ final states, as well as the differential cross-section given by Drukarev et al. [9] and the data given by Drukarev divided by photon frequency $\omega$.](image)

Figure 4.30: Plot of the Compton scattering cross-section given by our pseudostate calculation (with $N_\ell = 120$, $\lambda_\ell = 0.5$ basis) for only $\ell = 0$ final states, as well as the Compton scattering cross-section given by Drukarev et al. [9] and the data given by Drukarev divided by photon frequency $\omega$.

![Figure 4.30: Plot of the Compton scattering cross-section given by our pseudostate calculation (with $N_\ell = 120$, $\lambda_\ell = 0.5$ basis) for only $\ell = 0$ final states, as well as the Compton scattering cross-section given by Drukarev et al. [9] and the data given by Drukarev divided by photon frequency $\omega$.](image)
4.6. Compton Scattering

Fig. 4.31 shows the total cross-sections I have calculated from integrating the differential cross-section data given by Drukarev et al. with various cut-offs. Drukarev et al. gave the differential cross-section data at $\omega = 5 \text{ a.u.}$ which allows us to compare their calculation with the Bergstrom et al. calculation. Bergstrom et al. have, like Drukarev et al., based their calculation on the analytic expressions for the triple differential Compton scattering cross-section given by Gavrila [4]. Though the data presented by these two papers disagree, I have shown in Fig. 4.31 that the calculation by Drukarev et al. agrees with Bergstrom et al. once a larger cut-off is used, e.g. 20 eV seems to get agreement. Bergstrom et al. have used a cut-off of 10 eV, though they state that the cross-section is independent of cut-off [4]. In a later paper they state that the “cut-off is rarely low enough for the cut-off dependent infra-red divergence to be important for the integrated cross-section [120]. On the other hand, we have found that our truncation in the differential cross-sections given by Drukarev et al. show significant differences in the integrated Compton scattering cross-section.

So far I have computed the total Compton scattering cross-section for the ground state of atomic hydrogen using different basis set sizes, which disagrees with data given by Drukarev et al. [9] and Bergstrom et al. [4] by three orders of magnitude. Since our results are in good agreement with previous calculations if we do not include the $\ell = 2$ states, it seems to indicate that the two previous calculations have neglected this contribution.

Figure 4.31: Plot of the total Compton scattering cross-section, in units of $\sigma_T$, given by our pseudostate calculation (using $N_\ell = 120$, $\lambda_\ell = 0.5$ basis), as well as by Drukarev et al. [9] and Bergstrom et al. [4]. We show that the $\ell = 0$ final state contribution to the Compton scattering cross-section agrees well with both previous calculations, whilst the $\ell = 2$ final state contribution is several orders of magnitude larger. We also give the total Compton scattering cross-section at several frequencies ($\omega = 1, 2, 5 \text{ a.u.}$) calculated from the differential cross-section data given by Drukarev et al. using cut-offs of 1, 10 and 20 eV.

\[ \sigma_c/\sigma_T \]

Our convergence studies with respect to basis set size $N_\ell$ showed convergence in our Compton scattering cross-sections, which indicated that our calculation must be correct. However, it turns out that the
4.6. Compton Scattering

results we have shown so far are extremely misleading. We have found that the total Compton scattering cross-section varies significantly as $\lambda_\ell$ is changed (see Fig. 4.32). This is contrary to what we had expected (and assumed), as the outcome of calculations are usually expected to converge with respect to $N_\ell$. As an example, the Rayleigh scattering cross-section is converged with respect to $\lambda_\ell$ (see Table D.9). In most calculations $\lambda_\ell$ is chosen such that the results give fastest convergence.

Table 4.5 gives our total Compton scattering cross-section (and the $\ell = 0$ and $\ell = 2$ contribution) for changing basis set size $N_\ell$ and varying $\lambda_\ell$. We find that our total Compton scattering cross-section is converged at frequencies near threshold, but does not show convergence at frequencies far above threshold. Though our Compton scattering cross-section data in Table 4.5 is not necessarily converged, it still predicts the same order of magnitude. However, this is because I have presented data for only small $\lambda_\ell$ variation. For large variation in $\lambda_\ell$, as shown in Fig. 4.32, the total Compton scattering cross-section also varies in order of magnitude.

There are two factors that must be taken into account when investigating convergence with respect to $\lambda_\ell$. Firstly, in order to compare the Compton scattering cross-sections at the same frequencies for all calculations I had to interpolate between data points which adds some uncertainty to the cross-sections given at these frequencies. Secondly, and more importantly, a finite value for the Compton scattering cross-section can only be found by adding a cut-off to the infra-red divergence. In our pseudostate calculation this cut-off is naturally included, as the cut-off corresponds to the lowest energy pseudostate in our calculation. As a result, changing $N_\ell$ and $\lambda_\ell$ changes the energies of the pseudostates and so changes this cut-off. By having different cut-offs we are effectively including a different amount of the infra-red divergence in each calculation.

Figure 4.32: Plot of the total Compton scattering cross-section (in units of $\sigma_T$) for $\lambda_\ell$ between 0.40 and 1.00, and $N_\ell = 120, 100$ and 80.
4.6. Compton Scattering

Table 4.5: Total Compton scattering cross-section $\sigma_C(\omega)$, in units of $\sigma_T$, and the contribution from $\ell = 0$ and $\ell = 2$ final states in atomic hydrogen at several frequencies above threshold. This calculation was done with our pseudostate method and using basis set sizes $N_\ell = 80, 100$ and 120, and $\lambda_\ell = 0.49, 0.50$ and 0.51. The numbers in brackets (x) denote $10^x$.

<table>
<thead>
<tr>
<th>$\omega$ (a.u.)</th>
<th>$N_\ell$</th>
<th>$\lambda_\ell$</th>
<th>Compton</th>
<th>Compton (\ell = 0)</th>
<th>Compton (\ell = 2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.80</td>
<td>80</td>
<td>0.49</td>
<td>1.0942</td>
<td>2.1252 (-1)</td>
<td>8.8166 (-1)</td>
</tr>
<tr>
<td>0.80</td>
<td>80</td>
<td>0.50</td>
<td>1.0796</td>
<td>2.1262 (-1)</td>
<td>8.6698 (-1)</td>
</tr>
<tr>
<td>0.80</td>
<td>80</td>
<td>0.51</td>
<td>1.0659</td>
<td>2.1292 (-1)</td>
<td>8.5301 (-1)</td>
</tr>
<tr>
<td>0.80</td>
<td>100</td>
<td>0.49</td>
<td>1.1214</td>
<td>2.2165 (-1)</td>
<td>8.9976 (-1)</td>
</tr>
<tr>
<td>0.80</td>
<td>100</td>
<td>0.50</td>
<td>1.1075</td>
<td>2.2203 (-1)</td>
<td>8.8549 (-1)</td>
</tr>
<tr>
<td>0.80</td>
<td>100</td>
<td>0.51</td>
<td>1.0948</td>
<td>2.2230 (-1)</td>
<td>8.7252 (-1)</td>
</tr>
<tr>
<td>0.80</td>
<td>120</td>
<td>0.49</td>
<td>1.1452</td>
<td>2.2924 (-1)</td>
<td>9.1596 (-1)</td>
</tr>
<tr>
<td>0.80</td>
<td>120</td>
<td>0.50</td>
<td>1.1321</td>
<td>2.2986 (-1)</td>
<td>9.0222 (-1)</td>
</tr>
<tr>
<td>0.80</td>
<td>120</td>
<td>0.51</td>
<td>1.1198</td>
<td>2.3020 (-1)</td>
<td>8.8958 (-1)</td>
</tr>
<tr>
<td>4.00</td>
<td>80</td>
<td>0.49</td>
<td>4.2015</td>
<td>1.8181 (-2)</td>
<td>4.1833</td>
</tr>
<tr>
<td>4.00</td>
<td>80</td>
<td>0.50</td>
<td>3.9682</td>
<td>1.8148 (-2)</td>
<td>3.9500</td>
</tr>
<tr>
<td>4.00</td>
<td>80</td>
<td>0.51</td>
<td>3.7540</td>
<td>1.8039 (-2)</td>
<td>3.7360</td>
</tr>
<tr>
<td>4.00</td>
<td>100</td>
<td>0.49</td>
<td>4.1409</td>
<td>1.8038 (-2)</td>
<td>4.1229</td>
</tr>
<tr>
<td>4.00</td>
<td>100</td>
<td>0.50</td>
<td>3.9042</td>
<td>1.8365 (-2)</td>
<td>3.8859</td>
</tr>
<tr>
<td>4.00</td>
<td>100</td>
<td>0.51</td>
<td>3.6878</td>
<td>1.8692 (-2)</td>
<td>3.6692</td>
</tr>
<tr>
<td>4.00</td>
<td>120</td>
<td>0.49</td>
<td>4.0905</td>
<td>1.8484 (-2)</td>
<td>4.0720</td>
</tr>
<tr>
<td>4.00</td>
<td>120</td>
<td>0.50</td>
<td>3.8596</td>
<td>1.8748 (-2)</td>
<td>3.8408</td>
</tr>
<tr>
<td>4.00</td>
<td>120</td>
<td>0.51</td>
<td>3.6497</td>
<td>1.8853 (-2)</td>
<td>3.6308</td>
</tr>
<tr>
<td>20.0</td>
<td>80</td>
<td>0.49</td>
<td>2.2538</td>
<td>6.2742 (-4)</td>
<td>2.2532</td>
</tr>
<tr>
<td>20.0</td>
<td>80</td>
<td>0.50</td>
<td>2.1172</td>
<td>6.1528 (-4)</td>
<td>2.1166</td>
</tr>
<tr>
<td>20.0</td>
<td>80</td>
<td>0.51</td>
<td>1.9886</td>
<td>5.9930 (-4)</td>
<td>1.9880</td>
</tr>
<tr>
<td>20.0</td>
<td>100</td>
<td>0.49</td>
<td>2.1973</td>
<td>5.5326 (-4)</td>
<td>2.1968</td>
</tr>
<tr>
<td>20.0</td>
<td>100</td>
<td>0.50</td>
<td>2.0655</td>
<td>5.4693 (-4)</td>
<td>2.0649</td>
</tr>
<tr>
<td>20.0</td>
<td>100</td>
<td>0.51</td>
<td>1.9422</td>
<td>5.3625 (-4)</td>
<td>1.9417</td>
</tr>
<tr>
<td>20.0</td>
<td>120</td>
<td>0.49</td>
<td>2.1629</td>
<td>5.1492 (-4)</td>
<td>2.1623</td>
</tr>
<tr>
<td>20.0</td>
<td>120</td>
<td>0.50</td>
<td>2.0340</td>
<td>5.1173 (-4)</td>
<td>2.0335</td>
</tr>
<tr>
<td>20.0</td>
<td>120</td>
<td>0.51</td>
<td>1.9126</td>
<td>5.0393 (-4)</td>
<td>1.9121</td>
</tr>
<tr>
<td>100</td>
<td>80</td>
<td>0.49</td>
<td>7.7639 (-1)</td>
<td>3.8870 (-5)</td>
<td>7.7636 (-1)</td>
</tr>
<tr>
<td>100</td>
<td>80</td>
<td>0.50</td>
<td>7.3037 (-1)</td>
<td>3.7490 (-5)</td>
<td>7.3033 (-1)</td>
</tr>
<tr>
<td>100</td>
<td>80</td>
<td>0.51</td>
<td>6.8627 (-1)</td>
<td>3.5993 (-5)</td>
<td>6.8623 (-1)</td>
</tr>
<tr>
<td>100</td>
<td>100</td>
<td>0.49</td>
<td>6.9616 (-1)</td>
<td>2.0616 (-5)</td>
<td>6.9614 (-1)</td>
</tr>
<tr>
<td>100</td>
<td>100</td>
<td>0.50</td>
<td>6.4319 (-1)</td>
<td>1.9164 (-5)</td>
<td>6.4317 (-1)</td>
</tr>
<tr>
<td>100</td>
<td>100</td>
<td>0.51</td>
<td>5.9484 (-1)</td>
<td>1.7820 (-5)</td>
<td>5.9482 (-1)</td>
</tr>
<tr>
<td>100</td>
<td>120</td>
<td>0.49</td>
<td>6.6252 (-1)</td>
<td>1.8400 (-5)</td>
<td>6.6250 (-1)</td>
</tr>
<tr>
<td>100</td>
<td>120</td>
<td>0.50</td>
<td>6.2876 (-1)</td>
<td>1.8764 (-5)</td>
<td>6.2874 (-1)</td>
</tr>
<tr>
<td>100</td>
<td>120</td>
<td>0.51</td>
<td>5.9544 (-1)</td>
<td>1.8834 (-5)</td>
<td>5.9542 (-1)</td>
</tr>
</tbody>
</table>
4.6.2.3 Lack of Convergence of Compton

Since we are able to find the differential Compton scattering cross-section, we can check how much of the infra-red divergence is included in each calculation and observe the effect this has on the convergence. Since the $\ell = 2$ contribution is far larger than the $\ell = 0$ contribution, let us have a look at the $\ell = 2$ differential Compton scattering cross-section. Fig. 4.33 plots the $\ell = 2$ differential Compton scattering cross-section at $\omega = 5$ a.u. for $\lambda_\ell$ between 0.40 and 0.50. Each of these calculations have a different set of incident photon frequencies $\omega$, so the results were interpolated to do the comparison at $\omega = 5$ a.u.

Figure 4.33: Plot of $\ell = 2$ differential Compton scattering cross-section at $\omega = 5$ a.u. for $\lambda_\ell$ between 0.40 and 0.50, and $N_\ell = 120$. The inset zooms in on higher outgoing frequency $\omega'$, and shows that the peak varies significantly for changing $\lambda$.

The differential scattering cross-sections in Fig. 4.33 show that the peak near $\omega - |\epsilon|$ is the origin of most of the $\ell = 2$ scattering, as was also seen in the previous plots of differential cross-section. Since we only have very few points for low outgoing frequency, the contribution from the infra-red divergence is negligible. It is not clear to us why this peak near $\omega - |\epsilon|$ occurs in our $\ell = 2$ differential cross-section, and does not seem to be shown in any previous literature. Evidently the divergence in the total Compton scattering cross-section occurs because of the strong dependence of the differential cross-section on $\lambda_\ell$, rather than the contribution from the infra-red divergence.

Now let us have a look at the $\ell = 0$ and $\ell = 2$ contribution to the total Compton scattering cross-section for varying $\lambda_\ell$, as plotted in Fig. 4.34. Here we can see that the $\ell = 2$ contribution changes much more than $\ell = 0$ as we vary $\lambda_\ell$. Since the box radius increases as $\lambda_\ell$ is decreased, we had originally expected convergence as $\lambda_\ell$ becomes smaller. From these plots of the Compton scattering cross-section for varying $\lambda_\ell$ it is clear to see that this is not the case.
Figure 4.34: Plot of the $\ell = 0$ (left) and $\ell = 2$ (right) contribution to the total Compton scattering cross-section (in units of $\sigma_T$) for varying $\lambda_\ell$ and $N_\ell$.

We know that the large variation in the $\ell = 2$ Compton scattering cross-section is due to the change in peak magnitude of the $\ell = 2$ differential cross-section as $\lambda_\ell$ is changed. The $\ell = 0$ differential Compton scattering cross-section is plotted in Fig. 4.35 for a large range of $\lambda_\ell$ and different $N_\ell$. In the $\ell = 0$ differential cross-section the infra-red divergence is clearly seen. Here we can see that the infra-red cut-off, which changes as we vary $\lambda_\ell$ and $N_\ell$, will have a large impact on the $\ell = 0$ contribution to the Compton scattering cross-section. However, this change is negligible when considering the total Compton scattering cross-section as the $\ell = 2$ final states is orders of magnitude larger than the $\ell = 0$ contribution.

Figure 4.35: Plot of the $\ell = 0$ differential Compton scattering cross-section for varying $\lambda_\ell$ and varying basis set size $N_\ell$. The differential cross-section given by Drukarev et al. [9] is also plotted.
4.6.2.4 For Future Compton Studies

The Compton scattering cross-section is the first calculation I have presented in this thesis that uses free-to-free transition matrix elements. In principle we should be able to compute the Compton scattering cross-section correctly using our pseudostate method, since Bachau et al. [65, 66] have used a very similar method to calculate the above threshold ionisation cross-section which also involves free-to-free transitions. However, as discussed in the previous section, our Compton scattering cross-section calculation does not converge with respect to lambda.

In order to determine why this occurs, we have investigated the free-to-free transition matrix elements used in our pseudostate calculation. For future studies we present what the underlying matrix elements from our pseudostate calculations look like, and show that the analytic matrix elements from Eqn. 4.16 appear to be significantly different. Fig. 4.36 shows the free-to-free matrix elements given by \( \text{patom} \) for the transition from an initial \( \ell_i = 1 \) state with energy \( \varepsilon_i = 2 \) a.u. to \( \ell_f = 0 \) and \( \ell_f = 2 \) final states. The analytical transition matrix element given by Gordon [17] is also plotted. Evidently the transition matrix elements given by \( \text{patom} \) do not agree with the analytics and are not converged with respect to \( \lambda \). However, we do not expect the free-to-free \( \text{patom} \) transition matrix elements to be in agreement with the analytical function, as our free-to-free transition matrix elements should be normalised to remove any dependence on basis set.

Figure 4.36: Plot of the free-to-free transition matrix elements from an initial \( \ell_i = 1 \) state with energy \( \varepsilon_i = 2 \) a.u. to a final state of \( \ell_f = 0 \) (left) or \( \ell_f = 2 \) (right) given by \( \text{patom} \) and analytic expressions [17]. The transition matrix elements produced by \( \text{patom} \) are given for several calculations with \( \lambda = 0.4, 0.5 \) and 0.6.

Fig 4.37 plots the same \( \text{patom} \) transition matrix elements as in Fig. 4.36, but here we divide by the energy density of the initial state \( \rho(\varepsilon_i) \) and final state \( \rho(\varepsilon_f) \). In our differential Compton scattering cross-section calculation the normalisation \( T_{ij}/\rho(\varepsilon_i)\rho(\varepsilon_f) \) is used. However, from this plot we can see that our normalisation does not result in convergence across \( \lambda \), nor does it agree with the analytical function. The low energy limit in Fig. 4.37 suggests that the free-to-free transition matrix elements to \( \ell_f = 2 \) states are
Figure 4.37: Plot of the free-to-free transition matrix elements normalised by initial and final state energy density for transitions from an initial $\ell_i = 1$ state with energy $\varepsilon_i = 2$ a.u. to a final state of $\ell_f = 0$ (left) or $\ell_f = 2$ (right) given by patom and compared with analytic expressions [17]. The transition matrix elements produced by patom are given for several calculations with $\lambda = 0.4, 0.5$ and $0.6$.

four orders of magnitude larger than the analytic. As these transition matrix elements are included in the sum, this may explain why the $\ell = 2$ contribution to our Compton scattering cross-section is much larger than expected.

In our calculation of Compton scattering cross-section I have assumed that our free-to-free transition matrix elements are correct. This assumption seemed valid as I had previously calculated the static hyperpolarisability correctly using the same transition matrix elements as in our Compton calculation. My hyperpolarisability calculation will be discussed in detail in the next Chapter. Since the hyperpolarisability given by the free-to-free transition matrix elements was correct, there was no reason to believe it would not give the correct Compton scattering cross-sections. The only difference between the free–free transition matrix elements used in our hyperpolarisability calculation and in our differential cross-sections is that the hyperpolarisability calculation is independent of the normalisation since it sums over all states. On the other hand, our differential cross-sections are dependent on the normalisation of the free-to-free matrix elements.

It would be very useful to know whether the analytic transition matrix elements would give the same Compton scattering cross-sections as given by Drukarev et al. and Bergstrom et al. Unfortunately, there are various difficulties associated with this semi-analytical calculation (discussed in Section 4.6.1) which prevented us from calculating the Compton scattering cross-section using the analytic transition matrix elements. The Compton scattering cross-section calculation involves an integral over both the intermediate state energies but also the final state energies. In order to get convergence we need to use many panels in the integration, which requires calculation of the free-to-free analytic transition matrix elements between two very small energies.

The main difficulty in the semi-analytical calculation is that we are unable to compute the analytical transition matrix elements between two very small energies, as this involves the cancellation of two
extremely large numbers. For this reason I did not pursue the semi-analytic calculation of Compton scattering cross-section any further. These difficulties also occur in our semi-analytical calculation of hyperpolarisability, discussed in the next Chapter. However, it may be worth pursuing the semi-analytical calculation further in the future, in order to determine if this calculation agrees with the Compton calculations by Drukarev et al. and Bergstrom et al.

Another approach would be to rearrange the analytic expressions for differential Compton scattering cross-section by Drukarev et al. [9] such that it is written in terms of the Kramers-Heisenberg matrix element. This would allow us to compare the transition polarisabilities used in our Compton calculation with Drukarev et al. [9]. The difficulty here is that the analytic expressions given by Drukarev et al. are very complicated and attempts at rewriting the expressions in terms of transition polarisabilities have so far been unsuccessful.

In the next section I will show that our pseudostate method can be used to compute the two-photon ionisation cross-section at frequencies both below and above the first ionisation threshold. The free-to-free matrix elements discussed here will be used to compute the hyperpolarisability which are in good agreement with previous calculations. I will also discuss the relation of the two-photon ionisation cross-section to the hyperpolarisability.
Chapter 5

Multi-photon Scattering

In the previous Chapters our pseudostate method has been outlined and validated for the computation of transition polarisabilities and single photon scattering cross-sections (except Compton scattering). In this Chapter our pseudostate method is extended to the calculation of multi-photon processes: two-photon ionisation and the complex hyperpolarisability. I demonstrate that the two-photon ionisation cross-section and real hyperpolarisability calculated with our method are in agreement with previous values. Though our method can compute the two-photon ionisation cross-section and hyperpolarisability at frequencies above the first ionisation threshold, difficulties emerge when considering frequencies above the second ionisation threshold.

5.1 Two-Photon Ionisation

Two-photon ionisation refers to the process where two photons are absorbed and an electron is emitted, as depicted in Fig. 5.1. The lowest photon energy needed for two-photon ionisation to occur is at half the ionisation energy, $E_{IP}/2$. Two-photon ionisation was observed shortly after the invention of the laser [132, 133], and opened up the possibility of multi-photon ionisation with more than two photons and the study of above threshold ionisation (ATI) [134].

The first calculations of two-photon ionisation for atomic hydrogen were by Zernik et al. in 1964 [76, 77] who used the Dalgarno-Lewis technique. The two-photon ionisation cross-section was extended to more general multi-photon ionisation calculation by Bebb et al. [135] and up to twelve-photon ionisation rates of atomic hydrogen were presented. In the following years, many calculations of the multi-photon ionisation cross-section for atomic hydrogen [10, 11, 78, 95, 136–144] were done. The main difficulties of the two-photon ionisation calculations was the calculation of the second-order matrix element which contains, like the polarisability, an infinite sum and integral over the continuum. The same techniques I discussed in Chapter 2.3 - Dalgarno-Lewis method and Green’s functions - are used to find the two-photon ionisation cross-section.
5.1. Two-Photon Ionisation

The two-photon ionisation cross-section is given by Zernik et al. [77], “after some burdensome algebra”, to be

$$\sigma_i^{(2)} = \frac{2\pi^2\alpha}{15} \frac{I}{I_0} \omega a^2 \left[ \frac{2(\ell + 1)(\ell + 2)}{(2\ell + 3)(2\ell + 1)} |M_{\ell,\ell+1,\ell+2}|^2 + \frac{2\ell(\ell - 1)}{(2\ell - 1)(2\ell + 1)} |M_{\ell,\ell-1,\ell-2}|^2 \right. $$

$$\left. + \frac{(\ell + 1)(4\ell^2 + 8\ell + 5)}{(2\ell + 1)^2(2\ell + 3)} |M_{\ell,\ell+1,\ell+2}|^2 + \frac{\ell(4\ell^2 + 1)}{(2\ell + 1)^2(2\ell - 1)} |M_{\ell,\ell-1,\ell-2}|^2 \right]. \quad (5.1)$$

where \( a \) refers to the Bohr radius, \( I \) refers to the intensity and \( I_0 \) is the characteristic atomic field strength intensity [145]. To complicate matters, different values of \( I_0 \) are used across the literature. As an example, Zernik et al. [77] uses \( I_0 = 7.019 \times 10^{16} \text{W/cm}^2 \), whilst Gontier et al. [78] have used \( I_0 = 14.038 \times 10^{16} \text{W/cm}^2 \).

Eqn. 5.1 can be simplified for an atom initially in a state with \( \ell = 0 \) to be [10]

$$\sigma_i^{(2)} = 2\pi^2 \alpha I \frac{I}{I_0} \omega a^2 \left[ \frac{1}{9} M_{0,1,0}^2 + \frac{4}{45} M_{0,1,2}^2 \right]. \quad (5.2)$$

The cross-section in units of Thomson cross-section is given by

$$\sigma_i^{(2)} = \frac{3}{4} \frac{\pi \alpha I}{I_0} \omega \left[ \frac{1}{9} M_{0,1,0}^2 + \frac{4}{45} M_{0,1,2}^2 \right] \frac{a^2}{r_e^2} \sigma_T \quad (5.3)$$

$$= \frac{3\pi}{4\alpha^3} \frac{I}{I_0} \omega \left[ \frac{1}{9} M_{0,1,0}^2 + \frac{4}{45} M_{0,1,2}^2 \right] \sigma_T, \quad (5.4)$$

and the matrix elements \( M \) are given by

$$M_{\ell i,\ell_m,\ell_j} = \sum_m \frac{\langle e_j || z || m \rangle \langle m || z || i \rangle}{\epsilon_m - \omega} + \int_0^\infty \frac{\langle e_j || z || e \rangle \langle e || z || i \rangle}{\epsilon - \epsilon_i - \omega} d\epsilon. \quad (5.5)$$

where \( \ell_e = \ell_m \). The damping can be included, like in our polarisability calculation, by adding the decay rate of the bound states \(-i\Gamma_m(\omega)/2\) in the denominator. This would result in a matrix element \( M \) which has a real \( \text{Re}[M] \) part and two imaginary parts - \( \text{Im}_0[M] \) and \( \text{Im}_1[M] \). \( \text{Im}_0[M] \) is a result of the imaginary
damping term, and Im$_1 [M]$ is a result of removing the unphysical pole when $\omega = \varepsilon - \varepsilon_i$. In my calculations of two-photon ionisation presented here, I have not included the damping. In my calculation of two-photon ionisation cross-section in this section, only Re$[M]$ is used.

In the case of two-photon ionisation, the only possible final state for incident photons of frequency $\omega$ is $\varepsilon_f = 2\omega + \varepsilon_i$. The coefficients of the two-photon ionisation cross-sections are identical to the coefficients of the hyperpolarisability formula. This is expected, as essentially our expressions for $M_{0,1,0}^2$ and $M_{0,1,2}^2$ involve the same four transition matrix elements as in the calculation of the hyperpolarisability.

Several different expressions for two-photon ionisation have been presented in the literature. The expressions given by Refs [11, 146] have an extra factor of a wave-vector, whilst expressions given by Refs [126, 147] involve $\omega^2$. In our calculation I have used the expression given by Eqn. 5.4 and have chosen to set $I/I_0 = 1$ to obtain $\sigma^{(2)}_i$ in units of $\sigma_T$.

The calculation of two-photon ionisation can be separated into two frequency regimes - above the first ionisation threshold ($\varepsilon_{IP} > \omega > \varepsilon_{IP}/2$) and above the second ionisation threshold ($\omega > \varepsilon_{IP}$). Here I consider the two-photon ionisation that occurs when the incident photon frequency is below the second ionisation threshold ($\varepsilon_{IP} > \omega > \varepsilon_{IP}/2$).

5.1.1 Below the Second Ionisation Threshold

The two-photon ionisation cross-section describes the process where two photons of frequency $\omega$ are absorbed, exciting the electron to energy $2\omega - |\varepsilon_i|$. In our pseudostate calculation the excitation of an electron to the continuum is described by the transition to a pseudostate. As such the two-photon ionisation cross-section can only be computed at frequencies $\omega$ corresponding to half the energy of a pseudostate.

Presently we have chosen to increase the frequency grid of our calculation by computing the two-photon ionisation cross-sections for basis set sizes of various $\lambda_\ell$. The matrix elements for two-photon ionisation are presented in Fig. 5.2 and were computed for 21 basis sets with $\lambda_\ell$ between 0.49 and 0.51 for all $\ell$. A better description of the two-photon ionisation process can be given by simply increasing the basis set size. Fig. 5.2 plots the matrix element to a final state of $\ell = 0$ and to a final state of $\ell = 2$. We show good agreement with the matrix elements given by Chan et al. [10] if we divide our matrix elements to $\ell = 2$ final states by $\sqrt{2}$. This is not surprising as I have previously shown in section 4.4.1 that the transition matrix elements to $\ell = 2$ states in our pseudostate calculation differs from the analytic expressions by $\sqrt{2}$. Chan et al. [10] computed the matrix element of two-photon ionisation for atomic hydrogen by applying the Dalgarno and Lewis technique, where the integral over the continuum is found by solving inhomogeneous differential equations. Veniard et al. [11] have also presented the matrix elements to final states of $\ell = 2$ but these differ from both the results by Chan et al. and ours at low frequencies.

Veniard et al. have computed these matrix elements at frequencies both above the first and second ionisation threshold. Rather than applying the Dalgarno and Lewis method, or using the Coulomb Green’s
Figure 5.2: Plot of the matrix elements $M_{0,1,0}$ and $M_{0,1,2}$ of the two-photon ionisation process calculated using 21 basis sets with $\lambda$ between 0.49 and 0.51 and 120 Laguerre functions per partial wave. The matrix elements presented by Chan et al. [10] and Veniard et al. [11] are also plotted. Fig. (left) gives the $M_{0,1,0}$ matrix element as a function of incident photon frequency and Fig. (right) gives the $M_{0,1,2}$ matrix element.

functions, Veniard et al. have explicitly carried out the integral over the continuum using the analytic expressions for the free-to-free transition matrix elements derived by Gordon [17]. This calculation is very complicated, as it involves integration over the divergences in the free-to-free transition matrix elements and complicated hypergeometric functions.

The two-photon ionisation cross-sections computed from the matrix elements in Fig. 5.2 are given in Fig. 5.3. The total two-photon ionisation cross-sections is a sum of the cross-sections presented in these two figures. Here I have presented the two-photon ionisation cross-section to final states of $\ell = 0$ and $\ell = 2$ separately. Since our calculation chooses the frequency to be half the pseudostate energies, the cross-sections for $\ell = 0$ and $\ell = 2$ final states are computed at different frequencies. As a result, the two-photon ionisation cross-sections presented in Fig. 5.3 must be interpolated to the same set of frequencies before summing to find the total two-photon ionisation cross-section. The matrix elements given by Chan et al. [10] were used to compute the two-photon ionisation cross-sections for the individual $\ell = 0$ and $\ell = 2$ contributions.

We have successfully computed the two-photon ionisation cross-section above the first ionisation threshold with our pseudostate method and validated against the data given by Chan et al. [10]. The two-photon ionisation cross-section above the first ionisation threshold has poles, as these correspond to an incident photon having enough energy to excite the electron to a bound state. On the other hand, when the incident photon has energy greater than ionisation energy (above the second ionisation threshold), a single photon is sufficient to excite the electron to the continuum.

A disadvantage of our pseudostate method is that the pseudostate grid becomes sparse at higher energies, which means that there are only few frequencies at which the two-photon ionisation cross-section can be calculated near the second ionisation threshold. The pseudostate packing method introduced in Chapter 3.6 would be ideal to increase the number of pseudostates in the calculation. Unfortunately the
Figure 5.3: Plot of the two-photon ionisation cross-sections calculated using 21 basis sets with \( \lambda \) between 0.49 and 0.51 and 120 Laguerre functions per partial wave. The two-photon ionisation cross-sections calculated from the matrix elements by Chan et al. [10] are also plotted. The cross-sections are given for \( \ell = 0 \) (left) and \( \ell = 2 \) (right) final states. Note laser intensity is \( I = I_0 = 1 \) a.u.

Pseudostate packing method has not yet been successfully extended to calculations involving free-to-free transition matrix elements. The pseudostate packing method may be a suitable method to apply in the future when the behaviour of the free-to-free transition matrix elements in our pseudostate calculation are better understood.

Here I have shown how our pseudostate method can be easily applied to the calculation of the two-photon ionisation cross-section below the second ionisation threshold. However, this method cannot be easily applied to the calculation of the two-photon ionisation cross-section above the second ionisation threshold. Chapter 7 will discuss the challenges of calculating the two-photon ionisation cross-section, and introduce an approximate method.

### 5.2 Hyperpolarisability

Similar to the way that the single photon ionisation cross-section is related to the imaginary (dipole) polarisability, the two photon ionisation cross-section is related to the imaginary (second, dipole) hyperpolarisability. The hyperpolarisability was introduced at the very beginning of this thesis, in Section 1.4, where the fourth-order energy correction \( \varepsilon_n^{(4)}(\omega) \) is given by the hyperpolarisability \( \gamma_n(\omega) \), where

\[
\varepsilon_n^{(4)}(\omega) = -\frac{1}{4!}\gamma_n(\omega)E^4.
\]  

Note that in this thesis I consider only \( s \)-state atoms, so the hyperpolarisability has only a scalar component. However, our method can also be applied to the tensor hyperpolarisabilities for initial states with \( \ell \neq 0 \).
5.2. Hyperpolarisability

The hyperpolarisability gives the fourth-order energy correction to the Stark shift and describes processes involving four photons, such as degenerate four-wave mixing (DFWM). DFWM refers to the process where two photons of frequency $\omega$ are absorbed and two photons of frequency $\omega$ are emitted. The hyperpolarisability describes a process with four transitions, as depicted in Fig. 5.4. This is closely related to the two-photon absorption or ionisation cross-section as both involve the absorption of two photons of frequency $\omega$.

Figure 5.4: Diagram of hyperpolarisability from an initial state with $\ell = 0$. The two possible transition pathways for an electron initially in an $\ell = 0$ state are shown - (left) depicts one of the $\gamma_{0101}$ contributions and (right) depicts one of the $\gamma_{0121}$ contributions.

It is not surprising that there are far fewer calculations of the hyperpolarisability in comparison to the polarisability [52], as the expression for hyperpolarisability is derived from fourth-order time-dependent perturbation theory and involves four transition matrix elements and sums over three intermediate states [148]. In addition to this, the fourth-order energy correction given by the hyperpolarisability is usually much smaller than the polarisability and so is usually neglected in calculations of the Stark shift. As I have discussed in Chapter 1, in recent years atomic clocks have reached extremely high levels of precision and as such the hyperpolarisability contribution will become significant in the future. In this section I will extend our pseudostate method to the calculation of the atomic hyperpolarisability of the DFWM process, at frequencies above threshold.

The calculation of two-photon ionisation cross-section is split into two frequency regimes - above the first ionisation threshold and above the second ionisation threshold. Since the hyperpolarisability also involves the absorption of two photons, the hyperpolarisability calculation can be split into the same frequency regimes, i.e. below threshold, below second ionisation threshold and above second ionisation threshold. Like the atomic polarisability, the hyperpolarisability has two imaginary components - $\text{Im}_0[\gamma(\omega)]$ and $\text{Im}_1[\gamma(\omega)]$. $\text{Im}_0[\gamma(\omega)]$ is a result of including the linewidth of the states in the calculation, whilst $\text{Im}_1[\gamma(\omega)]$ is related to the possibility of ionisation. $\text{Im}_1[\gamma(\omega)]$ is related to the two-photon ionisation cross-section and is non-zero only at frequencies above threshold.

Most calculations of the hyperpolarisability have focused on the calculation of the static hyperpolarisability ($\omega = 0$) for various atoms using various computational approximations [52]. The hyperpolaris-
ability has been measured experimentally for only few atoms - mostly noble gas atoms [52, 149]. To the best of my knowledge, hyperpolarisability has not been measured for atomic hydrogen. However, recent advances in anti-hydrogen experiments [82] opens up the possibility of measuring the hyperpolarisability of anti-hydrogen. Though there is little experimental data available, the static hyperpolarisability of many atoms have been calculated [52]. On the other hand, hyperpolarisability data for non-zero frequencies is quite rare:

- In the case of atomic hydrogen, Shelton [18] calculated the dynamic hyperpolarisability using Sturmian Coulomb Green’s functions for a variety of four-photon processes, including the dc Kerr effect, electric-field-induced second harmonic generation (ESHG), third harmonic generation (THG) and degenerate four-wave mixing (DFWM). Though Shelton presented the frequency-dependent hyperpolarisability for the DFWM process in atomic hydrogen, only frequencies below threshold were considered.

- Manakov et al. [13, 53] have presented the complex hyperpolarisability of atomic hydrogen above ionisation threshold. They refer to their calculation as the ‘first correct calculation’ of the hyperpolarisability at above threshold frequencies. Manakov et al. [53] computed the complex hyperpolarisability at frequencies above threshold using the Sturmian expansion of the Green’s function. This method is similar to their calculation of the polarisability above threshold [60] which was discussed in Section 2.4.2.

- In 1988 Pan et al. [96] computed both the second- and fourth-order Stark shift for atomic hydrogen, using the Sturmian function expansion and the Coulomb Green’s function. Three years later they had extended this calculation to frequencies above threshold and computed the imaginary part of the energies by applying the complex rotation method [12]. We are able to convert these values for the real and imaginary part of the energies to Re[\( \gamma(\omega) \)] and Im[\( \gamma(\omega) \)].

- Takamoto et al. [54] have also presented a plot of the real and imaginary component of the hyperpolarisability for strontium, though the method of calculation of the imaginary hyperpolarisability was not discussed. This is important for atomic clocks, as the hyperpolarisability gives both the fourth-order Stark shift (from the real hyperpolarisability) and also describes the two-photon ionisation process (from the imaginary hyperpolarisability).

The static (\( \omega = 0 \)) hyperpolarisability is introduced in Section 5.2.1 and computed using our pseudostate method. I also demonstrate the difficulties of computing even the static hyperpolarisability using our semi-analytic methods. In Section 5.2.2 the complex (frequency-dependent) hyperpolarisability is computed with our pseudostate method.
5.2. Hyperpolarisability

5.2.1 Static ($\omega = 0$) Hyperpolarisability

The hyperpolarisability describes four photon processes and involves four transition matrix elements. The static ($\omega = 0$) hyperpolarisability is given by standard application of fourth-order perturbation theory [20]

$$\gamma(\omega = 0) = \frac{24}{\sqrt{\ell_i+1}} \sum_{\ell_j, \ell_m, \ell_t} G_{\ell_i, \ell_j, \ell_m, \ell_t} \left[ \sum_{jm} T_{ij} T_{jm} T_{mt} T_{ti} \delta(\ell_m, \ell_i) \delta(m, i) \sum_{jt} \frac{T_{ij} T_{ji} T_{jt} T_{ti}}{(\epsilon_j - \epsilon_i)(\epsilon_m - \epsilon_i)(\epsilon_t - \epsilon_i)^2} \right],$$

(5.7)

where $|i\rangle$ denotes the initial state and $|j\rangle, |m\rangle, |t\rangle$ denote the intermediate states. Note that Eqn. 5.7 gives the scalar hyperpolarisability. The hyperpolarisability involves a sum over all the bound states and an integral over the continuum states. The second term in Eqn. 5.7 describes the case where the electron returns to the initial state in the intermediate state. For the pseudostate calculation, the integral is simply approximated as a sum over the pseudostates, similar to the polarisability calculation.

The coefficient $G_{\ell_i, \ell_j, \ell_m, \ell_t}$ is given by Tang et al. [20] to be $G_{0,1,0,1} = \frac{1}{9}$ and $G_{0,1,2,1} = \frac{2}{45}$. On the other hand, Davydkin et al. [51] give the coefficients to be $G_{0,1,0,1} = \frac{1}{7}$ and $G_{0,1,2,1} = \frac{4}{45}$. This discrepancy in the hyperpolarisability formulae can be found throughout the literature. There is a discrepancy of $\sqrt{2}$ (originating from angular-momentum algebra) between the $\ell = 2$ transition matrix elements of the analytical and pseudostate calculation. See Section 4.4.4 for more details. Thus, applying the hyperpolarisability coefficient given by Davydkin et al. to the analytic transition matrix elements, and the coefficients from Tang et al. [20] to the pseudostate calculation, gives the correct hyperpolarisability for both cases.

Given that we are considering the ground state of atomic hydrogen, only the transitions

$$\ell_i = 0 \rightarrow \ell_j = 1 \rightarrow \ell_m = 0 \rightarrow \ell_t = 1 \rightarrow \ell_i = 0$$

and

$$\ell_i = 0 \rightarrow \ell_j = 1 \rightarrow \ell_m = 2 \rightarrow \ell_t = 1 \rightarrow \ell_i = 0$$

are possible due to the dipole selection rule. The contribution from the first transition pathway shown above will be referred to as $\gamma_{0101}$ and the second as $\gamma_{0121}$. The static hyperpolarisability $\gamma(\omega = 0)$ and the contributions from $\gamma_{0101}$ and $\gamma_{121}$ are shown to be converged to 11 significant figures in Appendix D Table D.1 for our pseudostate calculation using a basis set of $N_\ell = 20$, where $N_\ell$ refers to the number of Laguerre functions for each $\ell$. Our pseudostate calculation gives the static hyperpolarisability to be $\gamma(0) = 1333.125$ known to be exact [52] which also agrees with previous calculations by Shelton [18] and Tang et al. [20]. However, the static hyperpolarisability of hydrogen given by Manakov et al. [13] is approximately 125, digitised from their Fig. 2.

In the following section the contributions from the bound and free states to the static hyperpolarisability will be considered individually for both the pseudostate and semi-analytic calculation, and shown...
5.2. Hyperpolarisability

5.2.1.1 Components of static hyperpolarisability

There are two ways to split the hyperpolarisability - into the two transition pathways $\gamma_{0101}$ and $\gamma_{0121}$, or into the components involving bound and free states. The hyperpolarisability can be written as

$$\gamma = \gamma_{0101} + \gamma_{0121} = \gamma_{BBB} + \gamma_{FBB} + \gamma_{BBF} + \gamma_{FFB} + \gamma_{FBB} + \gamma_{BFF} + \gamma_{FFF},$$

where $B$ denotes a bound state ($\epsilon < \epsilon_{IP}$) and $F$ denotes a free state ($\epsilon > \epsilon_{IP}$). The sum over bound intermediate states $|j\rangle, |m\rangle$ and $|t\rangle$ is denoted as $\gamma_{BBB}$ and is given by

$$\gamma_{BBB} = \frac{24}{\sqrt{\ell_i + 1}} \sum_{\ell_j, \ell_m, \ell_t} G_{\ell_i, \ell_j, \ell_m, \ell_t}^\text{bound} \left[ \sum_{jmt} T_{ij} T_{jm} T_{mi} T_{ti} (\epsilon_j - \epsilon_i)(\epsilon_m - \epsilon_i)(\epsilon_t - \epsilon_i)^2 \delta(\ell_m, \ell_i) \delta(m, i) \right] .$$  (5.9)

The hyperpolarisability components involving two intermediate bound states and an intermediate free state are given by $\gamma_{BBF}$, $\gamma_{FBB}$ and $\gamma_{FFB}$, as shown in Eqns. 5.10 and 5.11.

$$\gamma_{BBF} = \frac{24}{\sqrt{\ell_i + 1}} \sum_{\ell_j, \ell_m, \ell_t} G_{\ell_i, \ell_j, \ell_m, \ell_t}^\text{bound} \left[ \sum_{jmt} T_{ij} T_{jm} T_{me} T_{ei} (\epsilon_j - \epsilon_i)(\epsilon_m - \epsilon_i)(\epsilon_t - \epsilon_i)^2 \delta(\ell_m, \ell_i) \delta(m, i) \right] .$$  (5.10)

$$\gamma_{FBB} = \frac{24}{\sqrt{\ell_i + 1}} \sum_{\ell_j, \ell_m, \ell_t} G_{\ell_i, \ell_j, \ell_m, \ell_t}^\text{bound} \left[ \sum_{jmt} T_{ij} T_{je} T_{me} T_{ei} (\epsilon_j - \epsilon_i)(\epsilon_m - \epsilon_i)(\epsilon_t - \epsilon_i)^2 \delta(\ell_m, \ell_i) \delta(m, i) \right] .$$  (5.11)

The hyperpolarisability component of transitions going from the initial state to a free-to-bound-to-free state is given by

$$\gamma_{FBB} = \frac{24}{\sqrt{\ell_i + 1}} \sum_{\ell_j, \ell_m, \ell_t} G_{\ell_i, \ell_j, \ell_m, \ell_t} \left[ \sum_{jm} \int_0^\infty \frac{T_{ij} T_{jm} T_{me} T_{ei}}{(\epsilon_j - \epsilon_i)(\epsilon_m - \epsilon_i)(\epsilon_t - \epsilon_i)^2} d\epsilon_i \delta(\ell_m, \ell_i) \delta(m, i) \right] .$$  (5.12)

$\gamma_{FBB}$ is a simpler calculation than $\gamma_{FBB}$ or $\gamma_{BFF}$ since it has only bound-to-free state transitions and no transitions between free states.

In the semi-analytic calculation the integration is done, as in the polarisability calculation, by splitting the integral into $N$ panels and computing each with 16 point Gaussian integration. The integral is computed in our pseudostate calculation by approximating the integral as a sum over pseudostates.
Figure 5.5: Plot of the hyperpolarisability components, $\gamma_{BBB}$, $\gamma_{BBF} + \gamma_{FBB}$, $\gamma_{FBB}$ and $\gamma_{BF}$. The sum is $\gamma_{BBB} + \gamma_{BBF} + \gamma_{FBB} + \gamma_{BF}$. $N = 120$ basis was used for the pseudostate calculation (denoted as points). The analytic values are the corresponding lines.

The various components of the hyperpolarisability ($\gamma_{BBB}$, $\gamma_{BBF} + \gamma_{FBB}$, $\gamma_{FBB}$ and $\gamma_{BF}$) are plotted in Fig. 5.5 with respect to the maximum principal quantum number, $n$, included in the calculation. I have shown that these components diverge with respect to the number of bound states in the sum, for both the semi-analytic and pseudostate calculation. This divergence can also be observed in our pseudostate calculation (see Tables 5.1, 5.2 and 5.3) for different basis set sizes (i.e. effectively changing the number of bound states in our calculation). Note that each calculation has a different number of states with $\varepsilon < 0$. Arnous et al. [145] have previously also shown that the $\gamma_{BBB}$ sum diverges with respect to the number of bound states in our calculation.

Fig. 5.5 demonstrates that both our semi-analytic and pseudostate calculation show the same divergence in the $\gamma_{BBB}$, $\gamma_{BBF}$, $\gamma_{FBB}$, $\gamma_{FBB}$ and $\gamma_{BF}$ components of the hyperpolarisability for principal quantum number $n < 15$. For $n \geq 15$ we see that our pseudostate calculation no longer agrees with our semi-analytic calculation. This is due to the Rydberg states in our pseudostate calculation, which exhibit continuum behaviour, i.e. a mixing of bound and pseudostates occurs for states near ionisation energy. We know that our pseudostate calculation gives the correct static hyperpolarisability when all components are added. This indicates that we cannot expect our semi-analytic calculation of the other components, $\gamma_{BBF} + \gamma_{FBB} + \gamma_{FF}$ to give the same values as in our pseudostate calculation. In the pseudostate calculation we find that $\gamma_{BBF} + \gamma_{FBB}$ diverges with respect to the number of bound states, and, of course, $\gamma_{FF}$ is not dependent on $n$ as it does not involve a sum over bound states.
Table 5.1: Hyperpolarisability components (in atomic units) with respect to the maximum principal quantum number \( n \) in the sum given by the pseudostate calculation using \( N_\ell = 120 \) basis set. The energy \( \varepsilon \) of each bound state given by \( \rho_{\text{atom}} \) is also presented. \( \{\text{BBF}\} \) refers to the hyperpolarisability component that involves all permutations of one intermediate free state and two intermediate bound states, i.e. \( \{\text{BBF}\} = \gamma_{\text{BBF}} + \gamma_{\text{BF B}} + \gamma_{\text{F BB}} \).

<table>
<thead>
<tr>
<th>( n )</th>
<th>( \varepsilon (\ell = 0) )</th>
<th>( \varepsilon (\ell = 1) )</th>
<th>( \varepsilon (\ell = 2) )</th>
<th>( \text{BBB} )</th>
<th>( {\text{BBF}} )</th>
<th>( \text{FBF} )</th>
<th>( \text{BFF+FFB} )</th>
<th>( \text{FFF} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>-0.1250000</td>
<td>-0.1250000</td>
<td></td>
<td>2132.839</td>
<td>-497.890</td>
<td>26.809</td>
<td>-675.193</td>
<td>4674.829</td>
</tr>
<tr>
<td>3</td>
<td>-0.0555556</td>
<td>-0.0555556</td>
<td>-0.0555556</td>
<td>2186.216</td>
<td>-591.423</td>
<td>68.987</td>
<td>-1133.261</td>
<td>4674.829</td>
</tr>
<tr>
<td>4</td>
<td>-0.0312500</td>
<td>-0.0312500</td>
<td>-0.0312500</td>
<td>2319.760</td>
<td>-655.136</td>
<td>117.391</td>
<td>-1522.156</td>
<td>4674.829</td>
</tr>
<tr>
<td>5</td>
<td>-0.0200000</td>
<td>-0.0200000</td>
<td>-0.0200000</td>
<td>2497.148</td>
<td>-719.971</td>
<td>169.782</td>
<td>-1870.649</td>
<td>4674.829</td>
</tr>
<tr>
<td>6</td>
<td>-0.0138889</td>
<td>-0.0138889</td>
<td>-0.0138889</td>
<td>2699.584</td>
<td>-790.807</td>
<td>224.675</td>
<td>-2189.822</td>
<td>4674.829</td>
</tr>
<tr>
<td>7</td>
<td>-0.0102041</td>
<td>-0.0102041</td>
<td>-0.0102041</td>
<td>2918.190</td>
<td>-867.855</td>
<td>281.113</td>
<td>-2485.670</td>
<td>4674.829</td>
</tr>
<tr>
<td>8</td>
<td>-0.0078125</td>
<td>-0.0078125</td>
<td>-0.0078125</td>
<td>3148.119</td>
<td>-950.322</td>
<td>338.481</td>
<td>-2762.085</td>
<td>4674.829</td>
</tr>
<tr>
<td>9</td>
<td>-0.0061728</td>
<td>-0.0061728</td>
<td>-0.0061728</td>
<td>3386.425</td>
<td>-1037.284</td>
<td>396.376</td>
<td>-3021.860</td>
<td>4674.829</td>
</tr>
<tr>
<td>10</td>
<td>-0.0050000</td>
<td>-0.0050000</td>
<td>-0.0050000</td>
<td>3631.172</td>
<td>-1127.907</td>
<td>454.531</td>
<td>-3267.117</td>
<td>4674.829</td>
</tr>
<tr>
<td>11</td>
<td>-0.0041322</td>
<td>-0.0041322</td>
<td>-0.0041322</td>
<td>3881.015</td>
<td>-1221.490</td>
<td>512.768</td>
<td>-3499.531</td>
<td>4674.829</td>
</tr>
<tr>
<td>12</td>
<td>-0.0034722</td>
<td>-0.0034722</td>
<td>-0.0034722</td>
<td>4134.985</td>
<td>-1317.468</td>
<td>570.970</td>
<td>-3720.413</td>
<td>4674.829</td>
</tr>
<tr>
<td>13</td>
<td>-0.0029586</td>
<td>-0.0029586</td>
<td>-0.0029586</td>
<td>4392.184</td>
<td>-1415.085</td>
<td>628.991</td>
<td>-3931.823</td>
<td>4674.829</td>
</tr>
<tr>
<td>14</td>
<td>-0.0025501</td>
<td>-0.0025501</td>
<td>-0.0025501</td>
<td>4641.061</td>
<td>-1514.842</td>
<td>687.996</td>
<td>-4126.677</td>
<td>4674.829</td>
</tr>
<tr>
<td>15</td>
<td>-0.0022022</td>
<td>-0.0022059</td>
<td>-0.0022095</td>
<td>4797.410</td>
<td>-1598.499</td>
<td>753.339</td>
<td>-4379.060</td>
<td>4674.829</td>
</tr>
<tr>
<td>16</td>
<td>-0.0018365</td>
<td>-0.0018501</td>
<td>-0.0018648</td>
<td>4843.872</td>
<td>-1700.262</td>
<td>859.045</td>
<td>-4609.792</td>
<td>4674.829</td>
</tr>
<tr>
<td>17</td>
<td>-0.0014009</td>
<td>-0.0014276</td>
<td>-0.0014574</td>
<td>4867.141</td>
<td>-1844.224</td>
<td>1033.580</td>
<td>-5262.705</td>
<td>4674.829</td>
</tr>
<tr>
<td>18</td>
<td>-0.0008922</td>
<td>-0.0009331</td>
<td>-0.0009793</td>
<td>4889.776</td>
<td>-2006.837</td>
<td>1419.199</td>
<td>-5868.359</td>
<td>4674.829</td>
</tr>
<tr>
<td>19</td>
<td>-0.0003155</td>
<td>-0.0003716</td>
<td>-0.0004353</td>
<td>4912.425</td>
<td>-2159.374</td>
<td>3430.259</td>
<td>-9525.013</td>
<td>4674.829</td>
</tr>
</tbody>
</table>
Table 5.2: Hyperpolarisability components (in atomic units) with respect to the maximum principal quantum number $n$ in the sum given by the pseudostate calculation using $N_\ell = 100$ basis set. The energy $\varepsilon$ of each bound state given by $\text{patom}$ is also presented. $\{\text{BBF}\}$ refers to the hyperpolarisability component that involves all permutations of one intermediate free state and two intermediate bound states, i.e. $\{\text{BBF}\} \equiv \gamma_{BBF} + \gamma_{BFB} + \gamma_{FBB}$.

<table>
<thead>
<tr>
<th>$n$</th>
<th>$\varepsilon (\ell = 0)$</th>
<th>$\varepsilon (\ell = 1)$</th>
<th>$\varepsilon (\ell = 2)$</th>
<th>BBB</th>
<th>[BBF]</th>
<th>FBF</th>
<th>BFF+FFB</th>
<th>FFF</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>-0.1250000</td>
<td>-0.1250000</td>
<td></td>
<td>2132.839</td>
<td>-501.424</td>
<td>27.011</td>
<td>-557.647</td>
<td>2930.868</td>
</tr>
<tr>
<td>3</td>
<td>-0.0555556</td>
<td>-0.0555556</td>
<td>-0.0555556</td>
<td>2186.216</td>
<td>-599.268</td>
<td>69.661</td>
<td>-934.962</td>
<td>2930.868</td>
</tr>
<tr>
<td>4</td>
<td>-0.0312500</td>
<td>-0.0312500</td>
<td>-0.0312500</td>
<td>2319.760</td>
<td>-668.808</td>
<td>118.882</td>
<td>-1251.697</td>
<td>2930.868</td>
</tr>
<tr>
<td>5</td>
<td>-0.0200000</td>
<td>-0.0200000</td>
<td>-0.0200000</td>
<td>2497.148</td>
<td>-741.304</td>
<td>172.526</td>
<td>-1531.462</td>
<td>2930.868</td>
</tr>
<tr>
<td>6</td>
<td>-0.0138889</td>
<td>-0.0138889</td>
<td>-0.0138889</td>
<td>2699.584</td>
<td>-821.903</td>
<td>229.198</td>
<td>-1783.731</td>
<td>2930.868</td>
</tr>
<tr>
<td>7</td>
<td>-0.0102041</td>
<td>-0.0102041</td>
<td></td>
<td>2918.190</td>
<td>-911.065</td>
<td>288.031</td>
<td>-2013.889</td>
<td>2930.868</td>
</tr>
<tr>
<td>8</td>
<td>-0.0078125</td>
<td>-0.0078125</td>
<td>-0.0078125</td>
<td>3148.119</td>
<td>-1008.243</td>
<td>348.499</td>
<td>-2225.589</td>
<td>2930.868</td>
</tr>
<tr>
<td>9</td>
<td>-0.0061728</td>
<td>-0.0061728</td>
<td>-0.0061728</td>
<td>3386.425</td>
<td>-1112.751</td>
<td>410.293</td>
<td>-2421.540</td>
<td>2930.868</td>
</tr>
<tr>
<td>10</td>
<td>-0.0050000</td>
<td>-0.0050000</td>
<td>-0.0050000</td>
<td>3631.172</td>
<td>-1223.992</td>
<td>473.242</td>
<td>-2603.850</td>
<td>2930.868</td>
</tr>
<tr>
<td>11</td>
<td>-0.0041322</td>
<td>-0.0041322</td>
<td>-0.0041322</td>
<td>3881.014</td>
<td>-1341.453</td>
<td>537.259</td>
<td>-2774.383</td>
<td>2930.868</td>
</tr>
<tr>
<td>12</td>
<td>-0.0034722</td>
<td>-0.0034722</td>
<td>-0.0034722</td>
<td>4134.378</td>
<td>-1465.772</td>
<td>602.524</td>
<td>-2931.033</td>
<td>2930.868</td>
</tr>
<tr>
<td>13</td>
<td>-0.0029548</td>
<td>-0.0029558</td>
<td>-0.0029567</td>
<td>4365.091</td>
<td>-1584.218</td>
<td>669.542</td>
<td>-3110.365</td>
<td>2930.868</td>
</tr>
<tr>
<td>14</td>
<td>-0.0024972</td>
<td>-0.0025067</td>
<td>-0.0025162</td>
<td>4473.534</td>
<td>-1733.719</td>
<td>762.177</td>
<td>-3200.845</td>
<td>2930.868</td>
</tr>
<tr>
<td>15</td>
<td>-0.0019812</td>
<td>-0.0020088</td>
<td>-0.0020387</td>
<td>4500.664</td>
<td>-1876.622</td>
<td>914.039</td>
<td>-3685.358</td>
<td>2930.868</td>
</tr>
<tr>
<td>16</td>
<td>-0.0013603</td>
<td>-0.0014093</td>
<td>-0.0014638</td>
<td>4516.517</td>
<td>-2272.639</td>
<td>1264.642</td>
<td>-3755.747</td>
<td>2930.868</td>
</tr>
<tr>
<td>17</td>
<td>-0.0006376</td>
<td>-0.0007100</td>
<td>-0.0007912</td>
<td>4531.004</td>
<td>-3262.578</td>
<td>3045.255</td>
<td>-5914.160</td>
<td>2930.868</td>
</tr>
<tr>
<td>18</td>
<td>-0.0000268</td>
<td></td>
<td></td>
<td>5961.289</td>
<td>-5998.048</td>
<td>4353.176</td>
<td>-5914.160</td>
<td>2930.868</td>
</tr>
</tbody>
</table>
5.2. Hyperpolarisability

Table 5.3: Hyperpolarisability components (in atomic units) with respect to the maximum principal quantum number \( n \) in the sum given by the pseudostate calculation using \( N_l = 80 \) basis set. The energy \( \varepsilon \) of each bound state given by \( p_{\text{atom}} \) is also presented. \( \{\text{BBF}\} \) refers to the hyperpolarisability component that involves all permutations of one intermediate free state and two intermediate bound states, i.e. \( \{\text{BBF}\} \equiv \gamma_{\text{BBF}} + \gamma_{\text{FBB}} + \gamma_{\text{FFB}} \).

<table>
<thead>
<tr>
<th>( n )</th>
<th>( \varepsilon (\ell = 0) )</th>
<th>( \varepsilon (\ell = 1) )</th>
<th>( \varepsilon (\ell = 2) )</th>
<th>BBB</th>
<th>[BBF]</th>
<th>FBF</th>
<th>FFF+FFB</th>
<th>FFF</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>-0.1250000</td>
<td>-0.1250000</td>
<td>2132.839</td>
<td>-494.331</td>
<td>26.317</td>
<td>-616.090</td>
<td>4852.645</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>-0.0555556</td>
<td>-0.0555556</td>
<td>2186.216</td>
<td>-586.671</td>
<td>67.348</td>
<td>-1020.791</td>
<td>4852.645</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>-0.0312500</td>
<td>-0.0312500</td>
<td>2319.760</td>
<td>-648.517</td>
<td>113.797</td>
<td>-1351.806</td>
<td>4852.645</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>-0.0200000</td>
<td>-0.0200000</td>
<td>2497.148</td>
<td>-710.034</td>
<td>163.234</td>
<td>-1636.157</td>
<td>4852.645</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>-0.0138889</td>
<td>-0.0138889</td>
<td>2699.584</td>
<td>-775.551</td>
<td>214.010</td>
<td>-1884.545</td>
<td>4852.645</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>-0.0102041</td>
<td>-0.0102041</td>
<td>2918.190</td>
<td>-844.810</td>
<td>265.031</td>
<td>-2103.002</td>
<td>4852.645</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>-0.0078125</td>
<td>-0.0078125</td>
<td>3148.119</td>
<td>-916.606</td>
<td>315.561</td>
<td>-2295.630</td>
<td>4852.645</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>-0.0050000</td>
<td>-0.0050000</td>
<td>3386.425</td>
<td>-989.645</td>
<td>365.102</td>
<td>-2465.508</td>
<td>4852.645</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>-0.0041317</td>
<td>-0.0041317</td>
<td>3631.155</td>
<td>-1062.717</td>
<td>413.283</td>
<td>-2615.890</td>
<td>4852.645</td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>-0.0034507</td>
<td>-0.0034562</td>
<td>3877.423</td>
<td>-1134.885</td>
<td>460.513</td>
<td>-2735.608</td>
<td>4852.645</td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>-0.0027809</td>
<td>-0.0028100</td>
<td>4059.223</td>
<td>-1195.930</td>
<td>508.112</td>
<td>-2931.586</td>
<td>4852.645</td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>-0.0020351</td>
<td>-0.0021049</td>
<td>4108.252</td>
<td>-1221.664</td>
<td>588.673</td>
<td>-2878.576</td>
<td>4852.645</td>
<td></td>
</tr>
<tr>
<td>14</td>
<td>-0.0019706</td>
<td>-0.0020351</td>
<td>4117.235</td>
<td>-1332.399</td>
<td>713.094</td>
<td>-3569.515</td>
<td>4852.645</td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>-0.0009975</td>
<td>-0.0011019</td>
<td>4120.554</td>
<td>-583.514</td>
<td>1045.569</td>
<td>-2577.461</td>
<td>4852.645</td>
<td></td>
</tr>
<tr>
<td>16</td>
<td>-0.0000183</td>
<td>-0.0001830</td>
<td>3009.057</td>
<td>1823.238</td>
<td>1579.495</td>
<td>-9931.310</td>
<td>4852.645</td>
<td></td>
</tr>
</tbody>
</table>

5.2.1.2 Attempt at Semi-analytic Calculation of \( \gamma_{\text{BBF}} \)

In this section I will detail my attempt at computing the \( \gamma_{\text{BBF}} \) and \( \gamma_{\text{FBB}} \) components using our semi-analytic calculation. Unlike the previous components computed with our semi-analytic calculation which involved only bound-to-bound or bound-to-free transitions, these components involve free-to-free transitions. \( \gamma_{\text{BBF}} \) is given by

\[
\gamma_{\text{BBF}} = \frac{24}{\sqrt{\ell_i + 1}} \sum_{\ell_j, \ell_m, \ell_t} G_{\ell_i, \ell_j, \ell_m, \ell_t} \sum_j \int_0^\infty \int_0^\infty T_{ij} T_{jm} T_{m\ell_i} \frac{T_{\ell_i\ell_j} T_{\ell_i\ell_t} T_{\ell_t\ell_i}}{(\varepsilon_j - \varepsilon_i)(\varepsilon_m - \varepsilon_i)(\varepsilon_t - \varepsilon_i)} d\varepsilon_i d\varepsilon_m, \quad (5.13)
\]

which involves integration over a pole in the free-to-free transition matrix element \( T_{\ell_m\ell_i} \) when \( \varepsilon_m = \varepsilon_i \). The pseudostate calculation is simple as the integral is approximated as a sum over the pseudostates. In the semi-analytic calculation the integration is done using the method by Longman [108] that I have previously used in the semi-analytic calculation of the above threshold polarisability. The integral over the free-to-free analytic transition matrix elements is known to be very difficult to evaluate [11].

The convergence of the semi-analytic calculation must be tested by changing the number of panels used in the integration. As more panels are added, the free-to-free transition matrix elements must be calculated for increasingly smaller energies. However we cannot calculate the analytic transition matrix elements between states very close to threshold, as it involves cancelling extremely large numbers. To avoid this I have added a cut-off \( \Delta \) into the integral over \( \varepsilon_m \). Fig. 5.6 shows the convergence of \( \gamma_{\text{BBF}} \) with...
5.2. Hyperpolarisability

respect to the energy cut-off $\Delta$ in the integral over $\epsilon_m$, for calculations using different maximum principal quantum number $n$ in the sum over bound states. $\gamma_{FFF}$ should give the same value, as the formulae are effectively identical.

Figure 5.6: Plot of the hyperpolarisability component $\gamma_{BFF}$ as a function of the cut-off used in the integration. Each line corresponds to a different maximum principal quantum number $n$ used in the calculation. The circles show the value of $\gamma_{BFF}$ when extrapolated to $\Delta \to 0$ for each $n$, by applying a polynomial fit as given by the gnumeric spreadsheet.

$\gamma_{BFF}$ in Fig. 5.6 seems to be converging with respect to the number of bound states, which is unexpected since all other components involving bound states diverge. Since the sum over all components in our semi-analytic calculation (excluding $\gamma_{BFF} + \gamma_{FFB} + \gamma_{FFF}$) diverge, the only way to get the correct hyperpolarisability value in our semi-analytic calculation is for $\gamma_{BFF} + \gamma_{FFB} + \gamma_{FFF}$ to diverge and cancel to give the finite value of hyperpolarisability. If $\gamma_{BFF} + \gamma_{FFB} + \gamma_{FFF}$ converges with respect to the number of bound states, then our total hyperpolarisability will diverge with respect to the number of bound states included in the calculation. Though it seems futile, I have extrapolated $\gamma_{BFF}$ with respect to the principal quantum number, and extrapolated the cut-off to $\Delta \to 0$, to give $\gamma_{BFF} \approx 34$.

The calculation of $\gamma_{FFF}$ would involve two free-to-free transition matrix elements, and three integrals over the continuum. One of the difficulties here is that, in order to accurately compute the integrals, we would need to compute the free-to-free transition matrix elements between very small energies. This is, as mentioned previously, not possible in our semi-analytic calculation as it involves the cancellation between extremely large numbers when we consider very small energies. Since we have shown that our pseudostate calculation does give the correct hyperpolarisability, even though most components diverge with respect to the number of bound states, I will go on to compute the frequency-dependent hyperpolarisability in the next section with our pseudostate calculation, rather than pursuing this semi-analytic calculation further.
5.2. Hyperpolarisability

5.2.2 Complex (Dynamic) Hyperpolarisability

The frequency dependence of the hyperpolarisability is directly related to the nonlinear process being considered [126]. Here I consider the degenerate four-wave mixing (DFWM) process which involves the absorption of two and emission of two photons of frequency $\omega$ [18], and is given by [98]

$$\gamma(-\omega; \omega_1, \omega_2, \omega_3) = \frac{24}{\sqrt{\ell_i + 1}} \sum_{\ell_j, \ell_m, \ell_t} G_{\ell_i, \ell_j, \ell_m, \ell_t} \left[ \sum_{jmt} f^a_{i,j,m,t}(-\omega; \omega_1, \omega_2, \omega_3) \right. \\
- \delta(\ell_m, \ell_i) \delta(m, i) \sum_{jt} f^b_{i,j,m,t}(-\omega; \omega_1, \omega_2, \omega_3) \right], \tag{5.14}$$

where the frequency dependence is given by

$$f^a_{i,j,m,t}(-\omega; \omega_1, \omega_2, \omega_3) = \frac{1}{6} \sum_P \left[ \frac{T_{ij} T_{jm} T_{mt} T_{ti}}{\left( \varepsilon_{ji} - \omega - i \frac{1}{2} \Gamma_{ij}(\omega) \right) \left( \varepsilon_{mi} + \omega_1 + \omega_2 - i \frac{1}{2} \Gamma_{im}(\omega_1 + \omega_2) \right) \left( \varepsilon_{ti} + \omega_1 - i \frac{1}{2} \Gamma_{it}(\omega_1) \right)} \right], \tag{5.15}$$

and

$$f^b_{i,j,m,t}(-\omega; \omega_1, \omega_2, \omega_3) = \frac{1}{6} \sum_P \left( \frac{T_{ij}^2 T_{ti}^2}{\left( \varepsilon_{ji} - \omega - i \frac{1}{2} \Gamma_{ij}(\omega) \right) \left( \varepsilon_{ti} - \omega_2 - i \frac{1}{2} \Gamma_{it}(\omega) \right)} \right), \tag{5.16}$$

where, in the case of DFWM, $\omega_{1,2} = \omega$, $\omega_3, \sigma = -\omega$. The sum over $P$ denotes a sum over all permutations of $\omega_1, \omega_2, \omega_3$ and $\omega_\sigma$, where the condition $-\omega_\sigma = \omega_1 + \omega_2 + \omega_3$ is satisfied.

The real $\text{Re}[\gamma(\omega)]$ component and imaginary $\text{Im}_0[\gamma(\omega)]$ component of the hyperpolarisability can be calculated using a similar method to the polarisability calculation, where $\text{Im}_0[\gamma(\omega)]$ stems from the decay rates of the bound states. The decay rate was included only for the bound states and $\Gamma(\omega) = 0$ for the continuum states. The real $\text{Re}[\gamma(\omega)]$ and imaginary $\text{Im}_0[\gamma(\omega)]$ part of the hyperpolarisability at frequencies $\omega < E_{IP}/2$ converge with respect to basis set size (see Appendix D, Tables D.5 and D.4).

A comparison of our pseudostate hyperpolarisability calculation with previous values of $\text{Re}[\gamma(\omega)]$ [18] is given in Table 5.4. Shelton [18] have computed the frequency dependent hyperpolarisability of atomic hydrogen for frequencies below half the ionisation energy, though they do not consider the imaginary hyperpolarisability. Although the pseudostate transition matrix elements between free states do not agree with the analytic transition matrix elements (in previous section), our pseudostate calculation
5.2. Hyperpolarisability

does agree with Shelton [18]. Re$[\gamma(\omega)]$ and Im$[\gamma(\omega)]$ are plotted in Figs. 5.7a and 5.7b for frequencies below $E_{IP}/2$. Our pseudostate calculation of $\gamma(\omega)$ was also validated (in a one-electron model) of lithium against unpublished calculations of hyperpolarisability by Tang.

Table 5.4: Real Re$[\gamma(\omega)]$ and imaginary Im$[\gamma(\omega)]$ (in atomic units) below the first ionisation threshold from pseudostate calculation with comparison to Shelton [18]. The numbers in brackets (x) denote $10^x$.

<table>
<thead>
<tr>
<th>$\omega$ (a.u.)</th>
<th>Ref [18]</th>
<th>Re$[\gamma(\omega)]$</th>
<th>Im$[\gamma(\omega)]$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1333.125</td>
<td>1333.125000</td>
<td>0.0000</td>
</tr>
<tr>
<td>0.01</td>
<td>1338.324538</td>
<td>1338.324538</td>
<td>0.0000</td>
</tr>
<tr>
<td>0.02</td>
<td>1354.104514</td>
<td>1354.104514</td>
<td>0.0000</td>
</tr>
<tr>
<td>0.03</td>
<td>1381.023883</td>
<td>1381.023883</td>
<td>0.0000</td>
</tr>
<tr>
<td>0.04</td>
<td>1420.066087</td>
<td>1420.066087</td>
<td>0.0000</td>
</tr>
<tr>
<td>0.05</td>
<td>1472.725496</td>
<td>1472.725496</td>
<td>0.0000</td>
</tr>
<tr>
<td>0.06</td>
<td>1541.148131</td>
<td>1541.148131</td>
<td>0.0000</td>
</tr>
<tr>
<td>0.07</td>
<td>1628.352964</td>
<td>1628.352964</td>
<td>0.0000</td>
</tr>
<tr>
<td>0.08</td>
<td>1738.580268</td>
<td>1738.580268</td>
<td>0.0000</td>
</tr>
<tr>
<td>0.09</td>
<td>1877.851100</td>
<td>1877.851100</td>
<td>0.0000</td>
</tr>
<tr>
<td>0.1</td>
<td>2054.896662</td>
<td>2054.896663</td>
<td>0.0000</td>
</tr>
<tr>
<td>0.11</td>
<td>2282.774667</td>
<td>2282.774666</td>
<td>0.0000</td>
</tr>
<tr>
<td>0.12</td>
<td>2581.853170</td>
<td>2581.853170</td>
<td>0.0000</td>
</tr>
<tr>
<td>0.13</td>
<td>2985.760254</td>
<td>2985.760254</td>
<td>0.0000</td>
</tr>
<tr>
<td>0.14</td>
<td>3554.518234</td>
<td>3554.518234</td>
<td>0.0000</td>
</tr>
<tr>
<td>0.15</td>
<td>4407.88456</td>
<td>4407.88456</td>
<td>0.0000</td>
</tr>
<tr>
<td>0.16</td>
<td>5829.175401</td>
<td>5829.175401</td>
<td>0.0000</td>
</tr>
<tr>
<td>0.17</td>
<td>8717.13094</td>
<td>8717.13094</td>
<td>0.0000</td>
</tr>
<tr>
<td>0.18</td>
<td>18606.29874</td>
<td>18606.29874</td>
<td>0.0000</td>
</tr>
<tr>
<td>0.19</td>
<td>-46389.0271</td>
<td>-5443.937450</td>
<td>5.0652 (-6)</td>
</tr>
<tr>
<td>0.2</td>
<td>-5443.937450</td>
<td>5.0652 (-6)</td>
<td></td>
</tr>
<tr>
<td>0.21</td>
<td>2523.436959</td>
<td>9.7807 (-5)</td>
<td></td>
</tr>
<tr>
<td>0.22</td>
<td>34619.06951</td>
<td>5.2818 (-3)</td>
<td></td>
</tr>
<tr>
<td>0.23</td>
<td>-3256.67269</td>
<td>6.3438 (-4)</td>
<td></td>
</tr>
<tr>
<td>0.24</td>
<td>-5513.67393</td>
<td>2.1307 (11)</td>
<td></td>
</tr>
</tbody>
</table>

At frequencies $\omega > E_{IP}/2$, spurious poles occur at $\epsilon_{mi} = 2\omega$. These spurious poles are caused by the presence of pseudostates in the continuum, and must be removed by using the same principal value method as used for the polarisability. Figs. 5.8a, 5.8b show the hyperpolarisability, $\gamma_{0101}(\omega)$ and $\gamma_{0121}(\omega)$, when the spurious poles are not removed ($N_{\ell} = 20$ calculation) and when the poles are removed for different basis set sizes ($N_{\ell} = 100, 110, 120$). The implementation of the principal value method in our pseudostate method removes the spurious poles, but keeps the physical resonances corresponding to bound states.

Im$[\gamma(\omega)]$ is the imaginary term originating from the principal value integration over the pole at $\epsilon_m = 2\omega + \epsilon_i$, which only appears in one of the terms (Eqn. 5.15) where two photons are absorbed and
5.2. Hyperpolarisability

Figure 5.7: Plot of (a) Re[\(\gamma(\omega)\)] and (b) Im[\(\gamma(\omega)\)] of H(1s) (in atomic units) given by our pseudostate calculation (\(N_\ell = 120\) basis) for frequencies \(\omega < E_{IP}/2\).

This gives us an imaginary term Im[\(\gamma(\omega)\)] related to the process of two photon absorption into the continuum [53], discussed further in the next section. However, in order to be able to remove the poles, the hyperpolarisability must be calculated at photon frequencies \(\omega = \epsilon_{mi}/2\).

We can compare our values for the real hyperpolarisability against the calculation given by Pan et al. [12] at frequencies above threshold. However, \(\gamma_{0101}\) and \(\gamma_{0121}\) in our pseudostate calculation are computed at a different set of frequencies so cannot be simply added to find the total. In order to find the total hyperpolarisability, \(\gamma = \gamma_{0101} + \gamma_{0121}\), we must first interpolate to a common set of frequencies. It is difficult to interpolate accurately above the second resonance, as there are only few data points. For this reason \(\gamma_{0101}\) and \(\gamma_{0121}\) at frequencies above the second resonance were simply added for nearest frequencies, rather than doing any interpolation. Therefore, the data presented in Figs 5.8a and 5.8b is more accurate than our total hyperpolarisability presented in Fig. 5.9.

We find that our real hyperpolarisability is in good agreement with the data given by Pan et al. [12] as shown in Fig. 5.9. On the other hand, the data I have digitised from the 1986 paper by Manakov et al. [13], is much smaller than both the data given by Pan et al. and our pseudostate calculation. My calculation of hyperpolarisability has a different frequency dependence to the hyperpolarisability data given by Manakov et al. [13]. Though the definition of hyperpolarisability was not explicitly given by
5.2. Hyperpolarisability

Figure 5.8: Plot of $\gamma_{0101}(\omega)$ and $\gamma_{0121}(\omega)$ of H(1s) given by our pseudostate calculation for frequencies $\omega > E_{IP}/2$. The $N_l = 20$ calculation shows the behaviour of the hyperpolarisability when the spurious poles originating from pseudostates are not removed, i.e. Eqn. 5.14, using the same code as Fig. 5.7a. The poles were removed in the calculation with $N_l = 100, 110$ and 120 basis.

Manakov et al. [13], two of the same authors published a paper in the same year [150]. In that paper, the definition of hyperpolarisability is indeed slightly different to the definition I have used in my thesis.

In their definition of hyperpolarisability, their equivalent to our term $f_{i,j,m,t}^{b}$ (Eqn. 5.16) has only four terms [150], unlike my definition which has six. The frequency-dependent hyperpolarisability formula given by Manakov et al. [150] agrees with the formalism by Davydkin et al. [51], but disagrees with the frequency-dependence used in my work (which agrees with Pan et al. [12]). My definition has two extra terms (in agreement with Pan et al. [12]):

$$
\frac{1}{6} \frac{T_{i}^{2}T_{i}^{2}}{(\epsilon_{ji} - \omega)(\epsilon_{ti} + \omega)(\epsilon_{ti} - \omega)} + \frac{1}{6} \frac{T_{i}^{2}T_{i}^{2}}{(\epsilon_{ji} + \omega)(\epsilon_{ti} + \omega)(\epsilon_{ti} - \omega)}.
$$

To check how these terms affect the calculation of hyperpolarisability, I have rerun my calculations without these two terms. This calculation should give the same frequency dependence as given by Manakov et al. [13]. However, I have found that this is not the case, and more work needs to be done in the future to resolve this difference before publication. As Manakov et al. [13] have used a different definition of hyperpolarisability, we cannot sensibly compare my calculations of real hyperpolarisability with the results provided by Manakov et al. [13].

The convergence of $\text{Re}[\gamma(\omega)]$, $\text{Im}_0[\gamma(\omega)]$ and $\text{Im}_1[\gamma(\omega)]$ is given for $\omega = 0.3$ a.u. in Table 5.5. Every basis set has a different set of frequencies, as shown in Figs. 5.8a, 5.8b, as the pseudostates have different energies for each basis set. The hyperpolarisability values at $\omega = 0.3$ a.u. were calculated by linearly extrapolating from the nearest frequencies. From Table 5.5 we can see that our $\text{Re}[\gamma(\omega)]$, $\text{Im}_0[\gamma(\omega)]$ and $\text{Im}_1[\gamma(\omega)]$ calculation converges with respect to basis set size.

Fig. 5.10 and 5.11 show the $\text{Im}_0[\gamma(\omega)]$ and $\text{Im}_1[\gamma(\omega)]$ given by our pseudostate calculation at frequen-
Figure 5.9: Plot of \( \text{Re}[\gamma'(\omega)] \) of H(1s) given by our pseudostate calculation \((N_{\ell} = 120 \text{ basis})\), Pan \textit{et al.} [12] and Manakov \textit{et al.} [13] for frequencies \( \omega > E_{IP}/2 \). Note that the calculation by Manakov \textit{et al.} [13] uses a different definition for the hyperpolarisability.

The imaginary hyperpolarisability \( \text{Im}_1[\gamma'\omega)] \) calculated by Manakov \textit{et al.} [13] is included for completeness in Fig. 5.11. However, their calculation likely uses a definition of hyperpolarisability that has a different frequency dependence from ours, and so cannot be used for validation of our method.

On the other hand, our imaginary hyperpolarisability \( \text{Im}_1[\gamma'\omega)] \) is in good agreement with the data given by Pan \textit{et al.} [12]. Pan \textit{et al.} [12, 96] have calculated the fourth-order contribution to the Stark shift rather than the hyperpolarisability. However, in their 1988 paper they had given the fourth-order energy in the static case to be \(-20.83008\) [96]. Since the static hyperpolarisability of atomic hydrogen is 1333.125, then

\[
\frac{\gamma(0)}{\epsilon^{(4)}(0)} = \frac{1333.125}{-20.83008} = -64 ,
\]

and so we determine the frequency-dependent hyperpolarisability from their consequent 1991 paper by multiplying their \( \epsilon^{(4)} \) data by -64. This is what is plotted in Fig. 5.11.

In order to further validate that the hyperpolarisability computed with our pseudostate method is correct, I have also used an alternative method to compute the \( \text{Re}[\gamma'\omega)] \) and \( \text{Im}_1[\gamma'\omega)] \). This method was first introduced in Section 3.5 as an alternative application of the Cauchy principal value method. In this method we avoid the pole by adding a small imaginary term \( i\Delta \) to the energies in the divergent hyperpolarisability equation and tune this to zero.

Fig. 5.12 shows the \( \text{Re}[\gamma'\omega)] \) and \( \text{Im}_1[\gamma'\omega)] \) given by this method when extrapolated to \( \Delta = 0 \). Like I have stated in the previous discussion of this method (Section 3.5), this method has a very large uncertainty since the final value is dependent on the extrapolation. The extrapolation for \( \text{Re}[\gamma'\omega)] \) and \( \text{Im}_1[\gamma'\omega)] \) was done by simply applying a linear (for \( \text{Re}[\gamma'\omega)] \)) and polynomial fit (\( \text{Im}_1[\gamma'\omega)] \)) as given
5.2. Hyperpolarisability

Figure 5.10: Plot of $\text{Im}_0[\gamma_{0101}]$ and $\text{Im}_0[\gamma_{0121}]$ of H(1s) given by our pseudostate calculation for frequencies $\omega > E_{IP}/2$. A $N_\ell = 20$ basis was used to show $\text{Im}_0[\gamma_{0101}]$ and $\text{Im}_0[\gamma_{0121}]$ without removing the spurious poles, whilst a large $N_\ell = 120$ basis was used for the calculation of the actual $\text{Im}_0[\gamma_{0101}]$ and $\text{Im}_0[\gamma_{0121}]$ values where the spurious poles were removed.

Figure 5.11: Plot of $\text{Im}_1[\gamma(\omega)]$ given by our pseudostate calculation ($N_\ell = 120$ basis), Manakov et al. [13] and Pan et al. [12] for frequencies $\omega > E_{IP}/2$. Note that Manakov et al. have used a different definition for hyperpolarisability.
Table 5.5: Convergence of $\text{Re}[\gamma(\omega)]$, $\text{Im}_0[\gamma(\omega)]$ and $\text{Im}_1[\gamma(\omega)]$ (in atomic units) at above threshold frequency ($\omega = 0.3$ a.u.) for pseudostate calculations with increasing basis set size $N_{\ell}$. The numbers in brackets (x) denote $10^x$.

<table>
<thead>
<tr>
<th>$N$</th>
<th>$\text{Re}$</th>
<th>$\text{Im}_0$</th>
<th>$\text{Im}_1$</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>-108939</td>
<td>-154.2 (-3)</td>
<td>6055.9</td>
</tr>
<tr>
<td>20</td>
<td>-19209</td>
<td>-2.223 (-3)</td>
<td>6114.6</td>
</tr>
<tr>
<td>30</td>
<td>-18876</td>
<td>-1.966 (-3)</td>
<td>6155.0</td>
</tr>
<tr>
<td>40</td>
<td>-18801</td>
<td>-1.886 (-3)</td>
<td>6166.9</td>
</tr>
<tr>
<td>50</td>
<td>-18822</td>
<td>-1.865 (-3)</td>
<td>6170.2</td>
</tr>
<tr>
<td>60</td>
<td>-18859</td>
<td>-1.862 (-3)</td>
<td>6171.0</td>
</tr>
<tr>
<td>70</td>
<td>-18893</td>
<td>-1.867 (-3)</td>
<td>6177.3</td>
</tr>
<tr>
<td>80</td>
<td>-18897</td>
<td>-1.861 (-3)</td>
<td>6179.3</td>
</tr>
<tr>
<td>90</td>
<td>-18903</td>
<td>-1.856 (-3)</td>
<td>6179.2</td>
</tr>
<tr>
<td>100</td>
<td>-18920</td>
<td>-1.857 (-3)</td>
<td>6179.4</td>
</tr>
<tr>
<td>110</td>
<td>-18931</td>
<td>-1.858 (-3)</td>
<td>6181.1</td>
</tr>
<tr>
<td>120</td>
<td>-18929</td>
<td>-1.854 (-3)</td>
<td>6181.3</td>
</tr>
</tbody>
</table>

by the gnumeric spreadsheet. Fig. 5.12 shows that the extrapolation gives approximate values for $\text{Re}[\gamma(0.3)]$ and $\text{Im}_1[\gamma(0.3)]$ that agree in magnitude with the values given by our pseudostate calculation. This, as well as the agreement with the scaled data from Pan et al. [12], gives us confidence that our pseudostate calculation is correct.

Like the two-photon ionisation cross-section, the calculation of hyperpolarisability cannot easily be extended to frequencies above the second ionisation threshold. The calculation at frequencies above the second ionisation threshold would require pseudostates with energies $\varepsilon_j$ and $\varepsilon_m$ that fulfill the condition

$$\varepsilon_j - \varepsilon_i = 2(\varepsilon_m - \varepsilon_i).$$

(5.19)

In Chapter 7 I will consider possible ways of extending our pseudostate method to compute the hyperpolarisability at frequencies above the second ionisation threshold.

### 5.3 Relation of Two-Photon Ionisation to Imaginary Hyperpolarisability

The imaginary hyperpolarisability ($\text{Im}_1[\gamma]$) is related to the possibility of two-photon ionisation. It turns out the relation of hyperpolarisability to two-photon absorption has been studied in more detail for molecules than atoms. The (second) hyperpolarisability of molecules is known to be related to the two-photon absorption cross-section by [151]

$$\sigma(\omega) = \frac{8\pi^2\hbar^2\omega^4}{n^2c^2L^4}\text{Im}_1[\gamma(\omega)],$$

(5.20)
5.3. Relation of Two-Photon Ionisation to Imaginary Hyperpolarisability

Figure 5.12: Plot of $\text{Re}[\gamma(\omega)]$ (left) and $\text{Im}_1[\gamma(\omega)]$ (right) at $\omega = 0.3$ a.u. found by adding a small imaginary term $i\Delta$ to the energies in the hyperpolarisability and extrapolating to $\Delta = 0$. The value given by our pseudostate calculation is also depicted at $\Delta = 0$ and shows good agreement with the extrapolation for both $\text{Re}[\gamma(\omega)]$ and $\text{Im}_1[\gamma(\omega)]$.

where the hyperpolarisability describes the DFWM process, $L$ is the “local field” factor (=1 for vacuum) and $n$ is the refractive index. In fact, several experiments have been done using degenerate four-wave mixing to measure the real and imaginary hyperpolarisabilities of various molecules [152, 153].

In terms of atoms, Manakov et al. [53] have related the imaginary hyperpolarisability $\text{Im}_1[\gamma]$ to the two-photon ionisation probability $W^{(2)}$ by

$$W^{(2)} = -2\text{Im}[E^{(4)}] = \frac{1}{4}\text{Im}_1[\gamma]I^2,$$  \hspace{1cm} (5.21)

where $I$ is the intensity of the field, whilst Takamoto et al. [54] have related the two-photon ionisation rate to the hyperpolarisability by

$$P_{2\omega} = 4\pi\text{Im}_1[\gamma]I^2,$$  \hspace{1cm} (5.22)

The difference in Eqns. 5.21 and 5.22 are due to the difference in the units used for hyperpolarisability in the two papers. Evidently we must choose the formula that uses atomic units. Though Eqn. 5.21 is in atomic units, we must also take care that the definition of $\gamma$ is the same as that which I have applied. Since our definition of hyperpolarisability differs from that used by Manakov et al. [13] (see discussion related to Fig. 5.9), I will not use Eqn. 5.21. Instead, let us consider the definition for two-photon ionisation cross-section provided by Arnous et al. [145].

Arnous et al. [145] have related the fourth-order matrix element, $\tau_i^{(4)}$, to the two-photon ionisation cross-section by

$$a_i^2\text{Im}_1[\tau_i^{(4)}] = -\frac{1}{4\pi} \frac{\sigma_i^{(2)}I_0}{\alpha\omega I},$$  \hspace{1cm} (5.23)
5.3. Relation of Two-Photon Ionisation to Imaginary Hyperpolarisability

where $\alpha$ is the fine-structure constant. This can be converted to units of Thomson cross-section such that

$$\frac{\sigma_i^{(2)}}{\sigma_T} = -\omega c^3 \frac{I}{I_0} \frac{3}{2} \text{Im}[\tau_i^{(4)}], \quad (5.24)$$

or

$$\text{Im}[\tau_i^{(4)}] = -\frac{\sigma_i^{(2)} I_0}{\sigma_T} \frac{2}{I} \frac{1}{3} \omega c^3. \quad (5.25)$$

where $c = 1/\alpha = 137.036$ in atomic units.

In our calculation we consider the Stark shift to be given by

$$\varepsilon_i(\omega) = \varepsilon_i^{(0)} - \frac{1}{2} \alpha_i(\omega) E^2 - \frac{1}{24} \gamma_i(\omega) E^4 - ... \quad (5.26)$$

which is the form given by Tang et al. [20] and Davydkin et al. [51]. On the other hand, Arnous et al. [145] have given the fourth-order energy correction to be

$$\varepsilon^{(4)} = \frac{1}{6} \frac{E^4}{E_0^4} \tau_i^{(4)}(\omega). \quad (5.27)$$

Note that, since $\text{Im}[\tau_i^{(4)}]$ calculated by Arnous et al. [145] is negative, their fourth-order matrix element must be equivalent to

$$\tau_i^{(4)}(\omega) = -\frac{1}{4} \gamma_i(\omega), \quad (5.28)$$

which allows us to rewrite Eqn. 5.24 as

$$\frac{\sigma_i^{(2)}}{\sigma_T} = \omega c^3 \frac{I}{I_0} \frac{3}{2} \text{Im}[\gamma_i]. \quad (5.29)$$

Let us compare this with the one-photon ionisation cross-section,

$$\frac{\sigma_i}{\sigma_T} = \frac{3}{2} c^3 \omega \text{Im}[\alpha] \quad (5.30)$$

which has the same factor of $\omega c^3 (3/2)$ but is not dependent on intensity.

There is an additional complication when doing this conversion, as various papers have used different values of $I_0$. For example, Arnous et al. have used $I_0 = 7.016 \times 10^{16} \text{Wcm}^{-2}$, whereas Gontier et al. [78] have used $I_0 = 14.038 \times 10^{16} \text{Wcm}^{-2}$. We can test the conversion given in Eqn. 5.29 by converting the two-photon ionisation cross-section given by Chan et al. [10] to imaginary hyperpolarisability. In this calculation we set $I/I_0 = 1$. However, since Chan et al. use $I_0 = 14.038 \times 10^{16} \text{Wcm}^{-2}$ instead of $I_0 = 7.016 \times 10^{16} \text{Wcm}^{-2}$ used by Arnous et al., we must use the equation

$$\frac{\sigma_i^{(2)}}{\sigma_T} = \omega c^3 \left( \frac{I}{2I_0} \right) \frac{3}{2} \frac{\text{Im}[\gamma_i^{(4)}]}{4}. \quad (5.31)$$
Figure 5.13: Plot comparing $\text{Im} \left[ \gamma(\omega) \right]$ given by our pseudostate calculation with data from Pan et al. [12] and Chan et al. [10] for frequencies below the second ionisation threshold.

Note that the factor of eight difference between Eqns. 5.31 and 5.24 was suggested by M. Bromley.

Fig. 5.13 plots $\text{Im} \left[ \gamma(\omega) \right]$ given by the two-photon ionisation cross-section data from Chan et al. [10] as well as the data from Pan et al. [12] and our pseudostate calculation. The conversion from the data given by Chan et al. [10] was done using Eqn. 5.31. We find that there is very good agreement between our imaginary hyperpolarisability. This indicates that we are now able to successfully compute the two-photon ionisation cross-section from the imaginary hyperpolarisability as well (at energies below the second ionisation threshold).

Let us now briefly compare the various scattering cross-sections we have computed for atomic hydrogen. In Fig. 5.14 I have presented all the scattering cross-sections of atomic hydrogen I have computed with our pseudostate method - the Rayleigh, Raman, Compton, photoionisation and two-photon ionisation cross-sections. Here we can see that, as expected, the two-photon ionisation cross-section has resonances that occur at the same frequencies as the Rayleigh and Raman scattering cross-section. At frequencies off-resonance, the two-photon ionisation cross-section is many orders of magnitude larger than the Rayleigh and Raman scattering cross-section. Note, however, that the two-photon ionisation cross-section is dependent on intensity, which will change the magnitude of the cross-section. Here I have set $I/I_0 = 1$. The two-photon ionisation cross-section is presented only for frequencies below the single-photon ionisation threshold. An extension of our pseudostate method for calculating the two-photon ionisation cross-section above the single-photon ionisation threshold is discussed in Chapter 7.
5.3. Relation of Two-Photon Ionisation to Imaginary Hyperpolarisability

Figure 5.14: Plot of the scattering cross-sections, in units of $\sigma_T$, of atomic hydrogen calculated with our pseudostate method (using basis $N_\ell = 120$, $\lambda_\ell = 0.5$). The Rayleigh, Raman and two-photon ionisation cross-sections are presented for frequencies below ionisation threshold (left). The Rayleigh, Raman, Compton, photoionisation and two-photon ionisation cross-sections are also presented for a frequency range of $0.1 - 100$ a.u. (right). In our two-photon ionisation cross-section calculation, we set $I/I_0 = 1$.

In this Chapter I have extended our pseudostate method to the calculation of the two-photon ionisation cross-sections and complex hyperpolarisability at frequencies up to the single-photon ionisation threshold. I have demonstrated that my calculation of complex $\gamma$ agrees with previous calculations and shown that we can convert our $\text{Im}[\gamma]$ to $\sigma_\ell^{(2)}$ and vice-versa. The hyperpolarisability is directly related to the fourth-order Stark shift, and so will be useful for determining the expected energy shift to higher accuracies for high-precision atomic experiments. Since our method is very simple, it can easily be used to compute the hyperpolarisability at frequencies below the second ionisation threshold for excited states, and for other atoms as well. This is particularly interesting for atoms such as lithium, for which there have been no previous calculations of the hyperpolarisability at frequencies above threshold.
Chapter 6

The Scattering Cross-sections of other Atoms

Whilst there is some uncertainty in Raman, and outstanding questions in Compton, we nonetheless, have developed a method that uses the properties of pseudostates to compute the single photon scattering and ionisation cross-sections in a unified calculation. All calculations so far have been done for atomic hydrogen, which is the simplest atom to study as there are no core electrons and can be described analytically. One of the advantages of our pseudostate-based methods are that they can be applied to other atoms as well. In this Chapter I will use our pseudostate method to compute the scattering cross-sections of various isotopes of hydrogen, as well as the scattering cross-sections for positronium, lithium, sodium and metastable helium. I will describe how the core electrons are included in our calculations for multi-electron atoms.

The results presented in this Chapter demonstrate the potential of our pseudostate method, as it allows us to compute the scattering cross-sections of many different atoms quite easily. Though photoionisation cross-sections have been calculated for many atoms, the Rayleigh and Raman scattering cross-sections are not as well-known. To the best of my knowledge, I present the first theoretical data for the Rayleigh and Raman scattering cross-sections of positronium. I also present preliminary results for the Rayleigh and Raman scattering cross-sections, and hyperpolarisability of metastable helium, as well as ground-state lithium and sodium. Though more convergence studies should be done for these atoms, I will show that we are able to apply our pseudostate method to calculate elastic and inelastic scattering cross-sections for various atoms.

6.1 Isotopes of hydrogen

If we have a set of bound and pseudostate energies, and the corresponding transition matrix elements for an atom, we are able to apply our pseudostate method to compute the various photon-atom scattering cross-sections. As a simple example, let us look at isotopes of hydrogen with one neutron (deuterium) and two neutrons (tritium). The change in mass of the nucleus results in a small shift in the energies of the atom and results in surprisingly large different scattering properties.
In the previous Chapters on photon-hydrogen scattering, the atom was considered to have an infinitely heavy nucleus. The finite mass of the nucleus can be included in our calculation by using the reduced mass
\[ M = \frac{m_1 m_2}{m_1 + m_2}. \] (6.1)

The atomic structure of protonium (hydrogen without a neutron, \( M = 0.9994557 \)), deuterium \((M = 0.9997278)\) and tritium \((M = 0.9998185)\) are given by altering the reduced mass. The energies of the first few states of the hydrogen isotopes are presented in Table 6.1, which shows that there is a difference of 0.0544\% in the energies for reduced mass \(M = 1\) (\( ^\infty H \)) and for the reduced mass \( M = 0.9994557 \) (H). In this section I compute the polarisability and scattering cross-sections of these isotopes. The polarisability for the hydrogen isotopes is presented for several frequencies in Table 6.2.

Table 6.1: Energies, in atomic units, of the lowest states \((1s, 2s, 2p, 3s, 3d)\) in the hydrogen isotopes - \( ^\infty H \), H, D and T.

<table>
<thead>
<tr>
<th>Energies (a.u.)</th>
<th>(^\infty H)</th>
<th>H</th>
<th>D</th>
<th>T</th>
</tr>
</thead>
<tbody>
<tr>
<td>1s</td>
<td>-0.50000000</td>
<td>-0.49972784</td>
<td>-0.49986388</td>
<td>-0.49990925</td>
</tr>
<tr>
<td>2p</td>
<td>-0.12500000</td>
<td>-0.12493196</td>
<td>-0.12496597</td>
<td>-0.12497731</td>
</tr>
<tr>
<td>2s</td>
<td>-0.12500000</td>
<td>-0.12493196</td>
<td>-0.12496597</td>
<td>-0.12497731</td>
</tr>
<tr>
<td>3d</td>
<td>-0.05555556</td>
<td>-0.05552532</td>
<td>-0.05554043</td>
<td>-0.05554547</td>
</tr>
<tr>
<td>3p</td>
<td>-0.05555556</td>
<td>-0.05552532</td>
<td>-0.05554043</td>
<td>-0.05554547</td>
</tr>
</tbody>
</table>

Table 6.2: Comparison of the real polarisability (in atomic units) of isotopes of hydrogen at several frequencies below threshold, calculated with a \( N_\ell = 120 \) basis set. The percentage difference between H and \( ^\infty H \) is also shown.

<table>
<thead>
<tr>
<th>( \omega ) a.u.</th>
<th>(^\infty H)</th>
<th>H</th>
<th>D</th>
<th>T</th>
<th>H/(^\infty H) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>4.500000</td>
<td>4.507363</td>
<td>4.503677</td>
<td>4.502451</td>
<td>0.163622</td>
</tr>
<tr>
<td>0.1</td>
<td>4.784300</td>
<td>4.792453</td>
<td>4.788376</td>
<td>4.787017</td>
<td>0.170412</td>
</tr>
<tr>
<td>0.2</td>
<td>5.941675</td>
<td>5.953530</td>
<td>5.947600</td>
<td>5.945624</td>
<td>0.199523</td>
</tr>
<tr>
<td>0.3</td>
<td>10.56389</td>
<td>10.59858</td>
<td>10.58121</td>
<td>10.57543</td>
<td>0.328383</td>
</tr>
<tr>
<td>0.4</td>
<td>-16.82265</td>
<td>-16.64420</td>
<td>-16.73310</td>
<td>-16.76288</td>
<td>1.06077</td>
</tr>
<tr>
<td>0.45</td>
<td>-17.64694</td>
<td>-16.93947</td>
<td>-17.28626</td>
<td>-17.40490</td>
<td>4.00902</td>
</tr>
</tbody>
</table>

The various single photon scattering cross-sections of \( ^\infty H \), H, D and T are plotted in Fig. 6.1. The difference in the cross-sections may not be obvious from these plots, so I have also presented a comparison of the cross-sections in Table 6.3 at several frequencies.

The cross-sections increase or decrease monotonically with increasing mass, as expected. We find that there is a surprisingly large difference in the polarisability as well as the Rayleigh and Raman scattering cross-sections between the hydrogen atom with a nucleus of infinite mass (\(^\infty H\)) and protonium.
6.2 Positronium

Positronium was first produced in 1951 [154] and refers to an atom consisting of an electron and its anti-particle, a positron. Since the positron and electron can annihilate, the atom is unstable and exists only for a short period of time. Ground state Ps have a mean lifetime of 142ns [155]. Much longer lifetimes can be achieved by exciting the Ps into high Rydberg states [156, 157]. Positronium are produced in vacuum when a positron beam is incident on material such as Au, Ti, Cu [158] or silica film [157]. Positronium formation is monitored by detecting the γ-rays that are emitted upon positron-electron annihilation. Positronium is used to study QED [159] and has applications in gravity measurements [160]. It is also

(H). The percentage difference between $^\infty$H and H for the Rayleigh and Raman scattering cross-sections are 8% and 13%, respectively, at $\omega = 0.45$. Evidently the difference in reduced mass results in a significant difference in the cross-sections, particularly at frequencies near threshold. On the other hand, the photoionisation cross-section changes only slightly for the different isotopes.

Figure 6.1: Plot of the single photon scattering cross-sections of ground state hydrogen isotopes - (a) $^\infty$H, (b) H, (c) D and (d) T given by our pseudostate method using a basis set with $N_\ell = 120$. 
Table 6.3: Comparison of the Rayleigh, Raman and photoionisation cross-sections (in units of $\sigma_T$) of isotopes of hydrogen at several frequencies calculated with a $N_\ell = 120$ basis set. The percentage difference between $^\infty$H and H is also shown.

<table>
<thead>
<tr>
<th>$\omega$ a.u.</th>
<th>$^\infty$H</th>
<th>H</th>
<th>D</th>
<th>T</th>
<th>H/$^\infty$H (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>0.00228895</td>
<td>0.00229676</td>
<td>0.00229285</td>
<td>0.00229155</td>
<td>0.341204</td>
</tr>
<tr>
<td>0.2</td>
<td>0.0564856</td>
<td>0.0567112</td>
<td>0.0565983</td>
<td>0.0565607</td>
<td>0.399394</td>
</tr>
<tr>
<td>0.3</td>
<td>0.903926</td>
<td>0.909871</td>
<td>0.906893</td>
<td>0.905903</td>
<td>0.657687</td>
</tr>
<tr>
<td>0.4</td>
<td>7.24484</td>
<td>7.09195</td>
<td>7.16791</td>
<td>7.19345</td>
<td>2.11033</td>
</tr>
<tr>
<td>0.45</td>
<td>12.7699</td>
<td>11.7666</td>
<td>12.2533</td>
<td>12.4220</td>
<td>7.85676</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>$\omega$ a.u.</th>
<th>$^\infty$H</th>
<th>H</th>
<th>D</th>
<th>T</th>
<th>H/$^\infty$H (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>0.00000</td>
<td>0.00000</td>
<td>0.00000</td>
<td>0.00000</td>
<td>-</td>
</tr>
<tr>
<td>0.2</td>
<td>0.00000</td>
<td>0.00000</td>
<td>0.00000</td>
<td>0.00000</td>
<td>-</td>
</tr>
<tr>
<td>0.3</td>
<td>0.00000</td>
<td>0.00000</td>
<td>0.00000</td>
<td>0.00000</td>
<td>-</td>
</tr>
<tr>
<td>0.4</td>
<td>0.0677208</td>
<td>0.0686900</td>
<td>0.0682041</td>
<td>0.0680427</td>
<td>1.43117</td>
</tr>
<tr>
<td>0.45</td>
<td>0.565780</td>
<td>0.493719</td>
<td>0.528346</td>
<td>0.540499</td>
<td>12.7366</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>$\omega$ a.u.</th>
<th>$^\infty$H</th>
<th>H</th>
<th>D</th>
<th>T</th>
<th>H/$^\infty$H (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.55</td>
<td>7.33801 x 10^6</td>
<td>7.33420 x 10^6</td>
<td>7.33659 x 10^6</td>
<td>7.33706 x 10^6</td>
<td>0.051921</td>
</tr>
<tr>
<td>0.6</td>
<td>5.79927 x 10^6</td>
<td>5.79699 x 10^6</td>
<td>5.79813 x 10^6</td>
<td>5.79851 x 10^6</td>
<td>0.039315</td>
</tr>
<tr>
<td>1.0</td>
<td>1.39778 x 10^6</td>
<td>1.39713 x 10^6</td>
<td>1.39746 x 10^6</td>
<td>1.39757 x 10^6</td>
<td>0.011208</td>
</tr>
<tr>
<td>2.0</td>
<td>1.85639 x 10^5</td>
<td>1.85538 x 10^5</td>
<td>1.85589 x 10^5</td>
<td>1.85606 x 10^5</td>
<td>0.017416</td>
</tr>
<tr>
<td>5.0</td>
<td>1.11214 x 10^4</td>
<td>1.11108 x 10^4</td>
<td>1.11161 x 10^4</td>
<td>1.11179 x 10^4</td>
<td>0.018278</td>
</tr>
</tbody>
</table>

used in anti-hydrogen experiments [161, 162].

Our atomic structure code calculates the atomic structure of positronium in the same way as for atomic hydrogen, but uses a reduced mass of $M = 1/2$, since positronium has a positron and electron, whereas the atom has a proton and an electron. The result of using a reduced mass that is half that of hydrogen are energy levels that are half that of atomic hydrogen. The transition matrix elements and energies produced by patom for positronium have been previously used to compute the $C_6$ dispersion coefficient of Ps-atom interactions for rare gases and alkali-metal atoms [163].

There are only very few calculations of the photon-positronium scattering cross-sections. One of the few calculations of scattering cross-sections were done by Kaliman et al. [14] in 2013. Kaliman et al. computed the photoionisation cross-section of positronium and used expressions derived by Gavrila [58, 59] for atomic hydrogen to compute the differential Compton scattering cross-section of positronium. Kaliman et al. investigated the contribution of $A^2$ and $p \cdot A$ contribution to the cross-section and found that the differential cross-section was dominated by the $p \cdot A$ contribution at low energies and $A^2$ at high energies. Kaliman et al. determined that the $A^2$ contribution can be neglected at incident photon frequencies lower than 0.3 keV [14].
I have applied our pseudostate method to compute the Rayleigh, Raman, Compton and photoionisation cross-sections of Ps, as presented in Fig. 6.2a. The photoionisation cross-section given by our pseudostate method is in good agreement with the values given by Kaliman et al. [14]. The Rayleigh scattering cross-section of positronium tends to $4\sigma_T$, in comparison to $1\sigma_T$ in atomic hydrogen. Fig 6.2b shows the Compton scattering cross-section of positronium, and the $\ell = 0$ and $\ell = 2$ contribution. Since positronium is a hydrogen-like atom, we expect to see similar behaviour to scattering in atomic hydrogen. We expect that this Compton scattering cross-section also diverges with respect to box radius, as was the case for our atomic hydrogen Compton calculation.

Figure 6.2: Plot of the scattering cross-sections of positronium given by our pseudostate method (using a $N_\ell = 120$ basis set). Fig. (a) gives the various single photon scattering cross-sections over a frequency range of 0.1-100 a.u. and demonstrates agreement between our photoionisation cross-section and data given by Kaliman et al. [14]. Fig. (b) shows the total Compton scattering cross-section and the contribution from the $\ell = 2$ and $\ell = 0$ final states. The same behaviour is shown as in atomic hydrogen, where the $\ell = 2$ contribution is several orders of magnitude larger than the $\ell = 0$ contribution.

I have found no previous calculations of the Compton scattering cross-sections to compare against, but Kaliman et al. [14] have presented differential Compton scattering cross-sections at relatively high incident photon frequencies in units of $r_0^2/m$ where $m$ is the electron rest mass. Fig. 6.3 compares our differential cross-section with the differential cross-section from Kaliman et al. [14] at incident photon frequency of approximately 11 a.u.. From this plot we can see that our differential Compton scattering cross-sections are very different to the data given by Kaliman et al. [14]. Here we see, like in our calculation of atomic hydrogen, that a bifurcation occurs in our differential cross-section calculation. This is particularly evident in Fig. 6.3 in the $\ell = 0$ differential cross-section, where one part of bifurcation becomes very small at approximately $\omega' = 9.5$ a.u..

Though we have shown in our hydrogen calculation that our Compton scattering cross-sections did not converge as we vary $\lambda_\ell$, we did find good agreement between our $\ell = 0$ differential cross-section and the differential cross-section given by Drukarev et al. [9]. On the other hand, we find that our $\ell = 0$
differential cross-section for positronium is at least four orders of magnitude smaller than the differential cross-section given by Kaliman et al. [14].

Figure 6.3: Plot of the differential Compton scattering cross-sections for outgoing photon frequency $\omega'$, as given by Kaliman et al. [14] for incident photon frequency $\omega = 11.02$ a.u. and our calculation (using $N_\ell = 120$ basis) at incident photon frequency $\omega = 11.14$ a.u.. The differential cross-section given by Kaliman et al. includes both the $A^2$ and $p \cdot A$ contribution, where the $A^2$ contribution results in the upturn at high outgoing photon frequency $\omega'$. The differential cross-section given by our pseudostate method is plotted as the $\ell = 0$ and $\ell = 2$ contribution and is smaller than the differential cross-section given by Kaliman et al. at low frequency $\omega'$ by several orders of magnitude.

I have investigated the convergence of the differential Compton scattering cross-section in positronium by varying $N_\ell$ and $\lambda_\ell$, as shown in Fig. 6.4. We find that, like our differential Compton cross-sections for atomic hydrogen, the differential cross-section to $\ell = 2$ final states in positronium have a peak near the maximum outgoing frequency. Of course, since we have pseudostates that shift in energy as we vary $N_\ell$ and $\lambda_\ell$, we are not able to directly compare our calculations for the same incident frequency $\omega$. However, we can see in Fig. 6.4 that our differential cross-sections seem to be converged with respect to $N_\ell$, but varying $\lambda_\ell$ changes the height of the peak in the $\ell = 2$ differential cross-section. This is the same behaviour as previously seen in our hydrogen calculation, and indicates that the Compton scattering cross-section is likely not converging with respect to $\lambda_\ell$.

### 6.3 Metastable Helium

The next interesting atom to consider is metastable helium, which refers to the helium atom in the first excited (spin-triplet) state, $2^3S_1$. This is referred to as the metastable state, as it has an extremely long lifetime at 7870 seconds [164]. An interesting experiment was done by Henson et al. in 2015 [165] on metastable helium, where they measured the tune-out wavelength to high-precision in order to test the QED prediction. The tune-out wavelength refers to the laser wavelength at which the Stark shift
Figure 6.4: Plot of the differential Compton scattering cross-sections for positronium with respect to the outgoing frequency $\omega'$, as given by Kaliman et al. [14] for incident photon frequency $\omega = 11.02$ a.u. and our calculation for varying basis set size $N_\ell$ (left) and varying $\lambda_\ell$ (right). Our differential Compton scattering cross-sections for $\ell = 0$ and $\ell = 2$ final states are given for $N_\ell = 100, 110, 120$ and $\lambda_\ell = 0.5$ (left), and for $N_\ell = 120$ and $\lambda_\ell = 0.42, 0.46, 0.50$ (right).

for a certain state is zero. The tune-out wavelength predicted by Mitroy and Tang [166] was found by calculating the polarisability, i.e. the second-order energy correction. We are interested in determining whether the fourth-order energy correction, given by the hyperpolarisability, would have an appreciable contribution to the energy shift and whether it can be neglected.

We are able to use the pseudostate method developed in the previous Chapters to compute the various single photon scattering cross-sections, as well as the hyperpolarisability of metastable helium. Though patom is a single-electron code, and helium is a two-electron atom, patom can be used to compute metastable helium as the $2^3S_1$ state can effectively be considered to be the ground state of the atom. The results presented here should be considered as preliminary results as no systematic convergence studies have been done so far.

Fig. 6.5 plots the various scattering cross-sections of metastable helium up to photon frequencies of 100 a.u.. We find that the scattering cross-sections have the expected behaviour, i.e. the photoionisation cross-section is very large at frequencies just above threshold and is comparable in magnitude to the Rayleigh scattering cross-section at very high ($\sim 100$ a.u.) frequencies. The Rayleigh scattering cross-section approaches $1\sigma_T$ at high frequencies, and the Raman scattering cross-section is very small above threshold. I have also plotted the Compton scattering cross-section here, to demonstrate that our Compton calculation consistently show the same behaviour across different atoms (i.e. that the Compton scattering cross-section is similar in magnitude to the Rayleigh scattering cross-section). Further investigations must be done into the convergence of the Compton scattering cross-sections of metastable helium and to determine the origin of the oscillations in the Compton scattering cross-section. The most likely explanation is due to the physical structure of the core-electron in the model, i.e. orthogonality of pseudostates and core electron. Note that the one-electron model is only applicable below 2.21 a.u. [167], as
the $2s2p$ resonance should be seen in the cross-section at that frequency.

Figure 6.5: Plot of the scattering cross-sections (Rayleigh, Raman, Compton and photoionisation) of metastable helium (in units of $\sigma_T$) given by our pseudostate calculation (using a basis set size of $N_{\ell=0} = 60, N_{\ell=1,2} = 55$) up to photon frequency of 100 a.u.. Note the vertical line indicates the core excitation energy to $2s2p$, above which our one-electron model is no longer applicable.

Preliminary results have been found by E. Kahl for the scattering cross-sections of metastable helium by applying our pseudostate method to a two-electron (non-relativistic) atomic structure code. The preliminary results for Rayleigh and photoionisation cross-sections are compared with my one-electron calculation in Fig. 6.6 and for the Raman scattering cross-section in Fig. 6.7. The cross-sections are in good agreement at frequencies below threshold. The Rayleigh scattering cross-section given by our one-electron calculation starts to drift off from the two-electron calculation at higher frequencies. Slight differences are expected since, in our calculation, we are approximating metastable helium as an atom with a single valence electron. Overall, it seems as if this gives a good approximation of the scattering cross-sections at low frequencies.

There is good agreement between the one- and two-electron calculation at frequencies below and just above threshold (to approximately $\omega \approx 0.2$ a.u.). However, the Raman scattering cross-sections are very different at frequencies $\omega > 0.2$ for the one- and two-electron calculation. This difference is likely due to the pollution of the Raman scattering cross-section by Compton scattering. In both the one- and two-electron code the new ionisation energy was used, such that fewer Rydberg states that exhibit continuum behaviour are included in the calculation. However, even the inclusion of a single extra Rydberg state would result in a very different total Raman scattering cross-section at frequencies above threshold.

The real hyperpolarisability of metastable helium is presented in Fig. 6.8 for frequencies both below and above the first ionisation threshold. In metastable helium the first ionisation threshold occurs at $-0.1752$ a.u. Below threshold the total ($\ell = 0$ and $\ell = 2$ contribution) is given by the solid line, whilst above threshold the $\ell = 0$ and $\ell = 2$ contribution are plotted separately.

The tune-out wavelength in the experiment by Henson et al. [165] is at $\lambda = 413.0938$ nm which
Figure 6.6: Plot of the Rayleigh and photoionisation cross-section found by applying our pseudostate method to a one-electron and two-electron code respectively.

Figure 6.7: Plot of the Raman scattering cross-sections at frequencies below (left) and above (right) threshold found by applying our pseudostate method to a one-electron and two-electron atomic structure code.
6.3. Metastable Helium

Figure 6.8: Plot of $\text{Re}[\gamma(\omega)]$ of metastable helium given by our pseudostate calculation (basis set $N_{\ell=0} = 60, N_{\ell=1, 2} = 55$). The solid lines give the real hyperpolarisability below threshold, whereas the points correspond to the $\ell = 0$ and $\ell = 2$ contribution to the hyperpolarisability.

The laser frequency corresponds to $\omega = 0.1103$ a.u. This laser frequency is above the ionisation threshold, and is depicted by a solid line in Fig. 6.8. We find that the $\ell = 0$ and $\ell = 2$ contribution to the hyperpolarisability have opposite signs, resulting in cancellations in the total hyperpolarisability.

We can find an approximate value of the real hyperpolarisability at the laser frequency by interpolating the two closest data points to the laser frequency and summing. Unfortunately, the interpolation of $\gamma_{0101}$ is quite difficult for $\omega = 0.1103$ a.u., as it lies very close to a pole in $\ell = 0$ and we have only few data points. A new calculation should be run for a different basis set to get a varying set of frequencies to do this interpolation. For now we can approximate the total hyperpolarisability at the laser frequency by simply summing the closest value, to give $\gamma = \gamma_0 + \gamma_2 = -2.0 \times 10^6$. This may be able to be measured in future experiments with more intense laser beam at $\lambda = 413.098$ nm.

$\gamma_{0101}$ and $\gamma_{0121}$ are positive and negative respectively at frequencies just above threshold. From Fig. 6.8 we see that these contributions seem to be nearly equal in magnitude, and seems to indicate that there may be a broad tune-out in the hyperpolarisability near $\omega = 0.1$ a.u.. This is further investigated in Table. 6.4, where I have calculated the total hyperpolarisability at frequencies just above threshold by interpolating $\gamma_{0121}$ and adding to $\gamma_{0101}$. From this we can expect the tune-out in the hyperpolarisability to occur at approximately $\omega \approx 0.0958$. 
Table 6.4: $\gamma_{0101}(\omega)$, $\gamma_{0121}(\omega)$ and the total hyperpolarisability $\gamma(\omega) = \gamma_{0101}(\omega) + \gamma_{0121}(\omega)$ for metastable helium (in atomic units) at frequencies above threshold given by our pseudostate calculation (basis set $N_{\ell=0} = 60, N_{\ell=1,2} = 55$). Our pseudostate calculation gives $\gamma_{0121}(\omega)$ at a different set of frequencies than $\gamma_{0101}(\omega)$. $\gamma_{0121}(\omega)$ is presented here for the same frequencies as $\gamma_{0101}(\omega)$ by linearly interpolating from the nearest values, which also allows us to calculate the total hyperpolarisability $\gamma(\omega)$.

<table>
<thead>
<tr>
<th>$\omega$ (a.u.)</th>
<th>$\gamma_{0101}(\omega)$</th>
<th>$\gamma_{0121}(\omega)$</th>
<th>$\gamma(\omega)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0880</td>
<td>875780.71</td>
<td>-528997.77</td>
<td>346782.93</td>
</tr>
<tr>
<td>0.0921</td>
<td>693980.54</td>
<td>-528102.57</td>
<td>165877.97</td>
</tr>
<tr>
<td>0.0969</td>
<td>560487.94</td>
<td>-613046.53</td>
<td>-52558.593</td>
</tr>
<tr>
<td>0.1025</td>
<td>491134.01</td>
<td>-900641.51</td>
<td>-409507.50</td>
</tr>
<tr>
<td>0.1089</td>
<td>473102.54</td>
<td>-2296303.7</td>
<td>-1823201.2</td>
</tr>
</tbody>
</table>

6.4 Lithium

Though I have used atomic hydrogen as a test atom through this thesis, I had initially studied atomic lithium at the very beginning of this work. The reason I had initially studied atomic lithium was that we were interested in the effect of the hyperpolarisability on atoms such as Sr that are used in atomic clock experiments. These atoms have many core electrons, so we first considered atomic lithium which has only two core electrons. However, the (static) hyperpolarisability of lithium is unusual in that the calculation involves very large cancellations which lead to relatively large uncertainties [52, 168]. In light of this we chose to use atomic hydrogen to test our calculations of complex polarisabilities and scattering cross-sections. In this section I will return to the calculation of atomic lithium and demonstrate how the core electrons are included in our method.

6.4.1 Core Electrons

Lithium has two core electrons that must be included in our calculation of the scattering cross-sections. As the core electrons are much more tightly bound than the valence electrons, the core electron contribution should be much smaller than the valence contribution and is often approximated rather than explicitly included in the wave-functions. The core electron can be excited to any of the $\ell = 1$ bound states, or even into the continuum. Though it is, in principle, possible to explicitly include the core electrons into the calculation for atomic lithium, this is not feasible for larger atoms with many core electrons. We choose to approximate the core behaviour through a single transition of the core electrons, which is referred to as the Mitroy method.

The Mitroy method was introduced in the computation of the polarisabilities and Van der Waals coefficients of positronium and the alkali and alkali-metal atoms [163, 169]. In this method the core behaviour is approximated by a single transition to a state of energy $\Delta$, which is varied to reproduce the known polarisability of the ionic core. The (exact) Thomas-Reiche-Kuhn sum-rule gives the sum over
the oscillator strengths to be

\[ N_j = \sum_i f_{ij}, \]  

(6.2)

where \( N_j \) is the number of electrons in a closed subshell \( j \). The ground state energy of the core electrons \( \varepsilon_i \) is given by the Koopman energy, which refers to the single-particle energy from a Hartree-Fock calculation [163]. The energy \( \Delta \) can be tuned by approximating the core polarisability as [163]

\[ \alpha_{\text{core}} = \sum_j \frac{N_j}{\varepsilon_j^2} \approx \sum_j N_j \frac{\Delta - \varepsilon_j}{(\Delta - \varepsilon_j)^2}, \]

where the core polarisability is known from experiment. Mitroy \textit{et al.} [169] have provided a list of \( \Delta \) energies for several alkali and alkali-metal atoms. In the case of atomic lithium \( \Delta \) is determined to be \( \Delta = 0.745 \) a.u. and is determined from the value of the ionic core calculated by Drachman \textit{et al.} [170] to be \( \alpha_{\text{core}} = 0.1925 \) a.u..

### 6.4.2 Dipole Polarisability

The polarisability of atomic lithium has been calculated through various methods over the years, such as with a coupled cluster method [171] or with a Hylleraas basis [20, 88]. Calculations with the Hylleraas basis [20, 88, 172, 173] that use three-electron wavefunctions are the most accurate, as they do not approximate the core electron interaction. Puchalski \textit{et al.} [172, 173] utilised a Hylleraas basis to investigate the relativistic and QED effect on lithium polarisability (both of which are small and will be ignored here). Other calculations of the lithium polarisability include the calculation by Hollauer \textit{et al.} [174] with an \( L^2 \) basis, Safronova \textit{et al.} [175] with a coupled-cluster (all-order) method and Li \textit{et al.} [176] with a model potential technique.

Table 6.5 gives the static polarisability given by (several) previous calculations and experiments for atomic lithium. The values given by our pseudostate method are also included, with and without the core electron contribution. Since our core electron approximation relies on the static polarisability of the core, our core contribution at \( \omega = 0 \) is exactly the core polarisability, but at non-zero frequencies the core polarisability is no longer exact. Curiously, the previous calculations give slightly different polarisabilities - Li \textit{et al.} and Merawa \textit{et al.} agree to four significant figures that the static polarisability of lithium is \( \alpha = 163.6 \) a.u., whereas the calculations by Pipin \textit{et al.} [177], Tang \textit{et al.} [88], Puchalski \textit{et al.} [172, 173] and Safronova \textit{et al.} [175] agree to four significant figures that the polarisability is \( \alpha = 164.1 \) a.u..

The most accurate experimental measurement of the lithium polarisability was done by Miffre \textit{et al.} [179] in 2006. Their experiment used an atom interferometer where the atoms in one arm passed through an electric field. Upon perturbation from the electric field, the ground state energy of the lithium atoms decrease and the kinetic energy of the atoms increase. This results in a phase shift that is measured in the interferometer and can be used to deduce the polarisability of lithium. The polarisability measured
Table 6.5: Some existing theoretical and experimental values of lithium static polarisability of the ground state in atomic units. Values given in brackets are uncertainties.

<table>
<thead>
<tr>
<th>Reference</th>
<th>(\alpha(\omega = 0)) (a.u.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pipin et al., 1992 [177]</td>
<td>164.1</td>
</tr>
<tr>
<td>Merawa et al., 1998 [178]</td>
<td>163.6</td>
</tr>
<tr>
<td>Mitroy et al., 2003 [169]</td>
<td>164.2</td>
</tr>
<tr>
<td>Tang et al., 2010 [88]</td>
<td>164.112(1)</td>
</tr>
<tr>
<td>Puchalski et al., 2011/2012 [172, 173]</td>
<td>164.1125(5)</td>
</tr>
<tr>
<td>Safronova et al., 2012 [175]</td>
<td>164.16(5)</td>
</tr>
<tr>
<td>Li et al., 2013 [176]</td>
<td>163.62</td>
</tr>
<tr>
<td>Miffre et al., 2006 [Experimental] [179]</td>
<td>164.2(1.1)</td>
</tr>
<tr>
<td>Present, without core</td>
<td>164.02</td>
</tr>
<tr>
<td>Present, with core</td>
<td>164.22</td>
</tr>
</tbody>
</table>

by the experiment has a much larger estimated uncertainty than the theoretical calculations by Tang et al. [88], Puchalski et al. [172, 173] and Safronova et al. [175], although it agrees remarkably well.

The calculation of atomic lithium static polarisability by Mitroy et al. in 2003 [169] also used the atomic structure information produced by the atomic structure code \texttt{patom} and used the core electron approximation we refer to as the Mitroy method. Table 6.5 demonstrates that our calculation is validated against the value given by Mitroy et al. [169]. Fig. 6.9 plots the real polarisability of atomic lithium at frequencies both below and above threshold, which is in good agreement with the data given by Tang et al. [88] at frequencies below threshold. In 2007 Manakov et al. [60] used a Sturmian expansion of the Green’s function to compute the real and imaginary polarisability at frequencies above threshold for atomic lithium, sodium, potassium, rubidium and cesium. Their data for \(\text{Re}[\alpha(\omega)]\) of atomic lithium is also presented in Fig. 6.9.

Figure 6.9: Plot of \(\text{Re}[\alpha(\omega)]\) of lithium calculated with our pseudostate method using a \(N_e = 120\) basis set at frequencies both below and above threshold. Our polarisability agrees extremely well with the data given by Tang et al. [88] at frequencies below threshold and Manakov et al. [60] above threshold.
6.4. Lithium

Though the real polarisability given by Manakov et al. [60] seems to be in good agreement with our calculation in Fig. 6.9, closer investigation (Table 6.6) shows that there are slight differences between our results. This difference is unlikely to be because we have included the core electron approximation in our calculation, since neglecting the core contribution gives a larger percentage difference. In the next section I will also demonstrate that the imaginary polarisability \( \text{Im}[\alpha(\omega)] \) given by Manakov et al. [60] produces photoionisation cross-sections that disagree with both the theoretical calculation by Hollauer et al. [174] and our pseudostate calculation.

Table 6.6: Comparison of the real polarisability (in atomic units) given by Manakov et al. [60] at frequencies above threshold with the values given by our pseudostate method \((N_\ell = 120 \text{ basis})\) when including core. The values from our pseudostate method were determined at these frequencies by linear interpolating the polarisability from the nearest frequencies.

<table>
<thead>
<tr>
<th>( \omega ) (a.u.)</th>
<th>Manakov et al. [60]</th>
<th>Pseudostate method</th>
<th>Percentage Difference (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2</td>
<td>-16.8</td>
<td>-19.4</td>
<td>15.7</td>
</tr>
<tr>
<td>0.25</td>
<td>-10.3</td>
<td>-12.4</td>
<td>20.3</td>
</tr>
<tr>
<td>0.3</td>
<td>-7.05</td>
<td>-8.78</td>
<td>24.5</td>
</tr>
<tr>
<td>0.4</td>
<td>-3.95</td>
<td>-5.15</td>
<td>30.3</td>
</tr>
<tr>
<td>0.6</td>
<td>-1.77</td>
<td>-2.36</td>
<td>33.2</td>
</tr>
<tr>
<td>0.8</td>
<td>-1.00</td>
<td>-1.29</td>
<td>28.9</td>
</tr>
<tr>
<td>1.0</td>
<td>-0.64</td>
<td>-0.76</td>
<td>19.4</td>
</tr>
</tbody>
</table>

6.4.3 Scattering Cross-sections

In general, the experimental measurements of scattering cross-sections are quite rare and often have some discrepancies with theoretical results, due to the difficulties in measuring cross-sections. An example of this discrepancy is found in the experimental measurement of the lithium photoionisation cross-section. The lithium photoionisation cross-sections were measured by Tunstead in 1953 [180], Marr in 1963 [181] as well as Hudson and Carter in 1965 [182] and 1967 [183]. The experimental results measured a larger value for the maximum photoionisation cross-section, as well as a smaller fall-off than theoretical prediction. Hollauer et al. [174] investigated the discrepancy between the theoretical and experimental results and found that it is not possible for lithium atoms to produce the maximum photoionisation cross-sections as measured in the experiment by Hudson and Carter [183]. They suggested that this is due to the photoionisation of lithium dimers, which had also been suggested by Hudson and Carter [183] themselves. Though experimental cross-sections are scarce, the agreement between several high-precision theoretical calculations utilising different methods allows for confidence in the theoretical photoionisation cross-sections. Evidently high-precision theoretical calculations are a valuable source of scattering cross-sections, due to the experimental difficulties of measuring the scattering cross-sections accurately.

I have plotted the Rayleigh, Raman, Compton, and photoionisation cross-section given by our pseudostate method for atomic lithium in Fig. 6.10. Our photoionisation cross-section is in agreement with
the theoretical calculation of photoionisation given by Hollauer et al. [174] but disagrees with the photoionisation calculated from the imaginary polarisability by Manakov et al. [60]. As in the case of atomic hydrogen, the Rayleigh scattering cross-section of atomic lithium tends to $1\sigma_T$ at large incident photon frequencies. However, the Compton scattering cross-section given by our pseudostate method is no longer smooth and exhibits oscillations (similar to He($^3S_e$)).

It is important to keep in mind that lithium has two core electrons which can also undergo excitation. Excitation to $1s2s^2$ occurs at 2.07 a.u. [184]. Since we are not including these core excitations in our scattering cross-sections, we can only trust the cross-sections below this energy. The total Compton scattering cross-section of atomic lithium is plotted in Fig. 6.11 for changing basis set size. In our hydrogen calculation we found that the Compton scattering cross-sections do not vary significantly with respect to $N_\ell$. In our lithium calculation we find that there are oscillations present in the Compton scattering cross-sections. We find that the oscillations at lower frequencies seems to be shift with changing basis set, though the oscillations at higher frequencies are very similar across all basis set sizes. The origin of these oscillations is not immediately clear.

Figure 6.10: Plot of the various single photon scattering cross-sections, in units of $\sigma_T$, off atomic lithium, using a basis of $N_\ell = 120$. Our photoionisation cross-section is in good agreement with the theoretical calculation by Hollauer et al. (data digitised from Fig. 3 in reference [174]), but disagrees with the photoionisation cross-sections calculated from the imaginary polarisability given by Manakov et al. [60]. The dashed vertical line shows the frequency at which excitation to $1s2s^2$ can occur, and so our calculation is only valid below this frequency.
6.4. Lithium

Figure 6.11: Plot of the Compton scattering cross-section, in units of $\sigma_T$, of atomic lithium for varying basis set size $N_\ell = 80, 100, 120$. The dashed vertical line shows the frequency at which excitation to $1s2s^2$ can occur, and so our calculation is only valid below this frequency.

We investigate the convergence of these Compton scattering cross-sections with respect to small changes in $\lambda_\ell$ in Fig. 6.12. Again, there are oscillations present in each calculation, though they seem to be shifted left with respect to increasing $\lambda_\ell$. These oscillations may be due to pseudostates in our calculation being orthogonal to the core electrons. The convergence at low energies with respect to $\lambda_\ell$ is not clear, but at high-energy the convergence seems to be showing the same behaviour as in our hydrogen calculation. A convergence study over a wider range of $\lambda_\ell$ should be done to give a better understanding of the convergence behaviour. It would also be interesting to look at the $\ell = 0$ and $\ell = 2$ contribution to the total and differential Compton scattering cross-section in the future, to see if this has the same behaviour as the hydrogen calculation.

6.4.4 Hyperpolarisability

6.4.4.1 Static Hyperpolarisability

As has been mentioned in the introduction to this section on atomic lithium, there have been extreme difficulties in calculating the static hyperpolarisability of lithium. This is best illustrated by quoting a paper by Maroulis et al. in 1989 [168], in which they stated, “basis set and correlation effects for $\gamma$ are so large that we cannot even be certain of its sign although we suggest its magnitude is less than $1.5 \times 10^4 e^A a_0^4 E_h^{-3}$.” There have been several calculations of lithium hyperpolarisability since this paper, which are listed in Table 6.7. We know now that the hyperpolarisability is approximately 5 times smaller than the value suggested by Maroulis et al. [168]. Table 6.7 demonstrates that although the calculations now agree on sign and approximate magnitude of the hyperpolarisability, only few significant figures are known. Pipin et al. [177] and Tang et al. [20] have used the Hylleraas basis in their calculation, whilst Kassimi et al. [185] and Jaszunski et al. [186] used the finite-field method. Cohen et al. [187] used atomic
6.4. Lithium

Figure 6.12: Plot of the Compton scattering cross-section, in units of $\sigma_T$, of lithium (using a $N_\ell = 120$ basis set) and varying $\lambda_{\ell=0}$ between 0.81-0.85, $\lambda_{\ell=1}$ between 0.51-0.55 and $\lambda_{\ell=2}$ 0.41-0.45 in steps of 0.01. These $\lambda_{\ell}$ were chosen since in the previous calculations $\lambda_{\ell=0} = 0.8, \lambda_{\ell=1} = 0.5$ and $\lambda_{\ell=2} = 0.4$ were used.

Table 6.7: List of some of the calculations of static hyperpolarisability of lithium, in atomic units.

<table>
<thead>
<tr>
<th>Reference</th>
<th>$\gamma(\omega = 0)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Maroulis et al., 1989 [168]</td>
<td>$4.3 \times 10^4$</td>
</tr>
<tr>
<td>Pipin et al., 1992 [177]</td>
<td>$3 \times 10^3$</td>
</tr>
<tr>
<td>Kassimi et al., 1994 [185]</td>
<td>$2900 \pm 300$</td>
</tr>
<tr>
<td>Jaszunski et al., 1996 [186]</td>
<td>3450</td>
</tr>
<tr>
<td>Cohen et al., 2005 [187]</td>
<td>3390</td>
</tr>
<tr>
<td>Tang et al., 2009 [20]</td>
<td>$3060 \pm 40$</td>
</tr>
<tr>
<td>Present, without core</td>
<td>1449</td>
</tr>
<tr>
<td>Present, with core</td>
<td>1406</td>
</tr>
</tbody>
</table>

model potentials to simulate the ionic core of lithium.

Let us consider the contribution of the core electrons to the hyperpolarisability. Like in the polarisability calculation, we apply the Mitroy method to approximate the core electron behaviour with a single transition. We find that including the core electrons in our calculation results in a very different value for the static hyperpolarisability (see Table 6.7).

The hyperpolarisability describes a process involving four transitions, where the final state is the same as the initial state. In the case of an atom with core electrons, it is possible for both a core electron and a valence electron to be excited in this process. As a result, the core and valence contribution cannot be cleanly separated in this calculation. All possible transitions must be taken into account when calculating the hyperpolarisability and all permutations must be considered. For example, if we consider the case where only core electrons undergo transitions, the possibilities are:
1. core electron excited, core electron de-excited, core electron excited, core electron de-excited
2. first core electron excited, second core electron excited, core electron de-excited, core electron de-excited.

Atomic lithium has two core electrons which is already taken into account since the core electron oscillator strength is 2. Later I will calculate the contribution to the hyperpolarisability from only core excitations, and will denote this as \( \Delta \gamma_c \). In the case where a core and a valence electron undergo transition, the various possible permutations are (in order of strength)

1. core excited, core de-excited, valence excited, valence de-excited
2. valence excited, core excited, core de-excited, valence de-excited
3. valence excited, valence de-excited, core excited, core de-excited
4. core excited, valence excited, core de-excited, valence de-excited
5. valence excited, core excited, valence de-excited, core de-excited
6. core excited, valence excited, valence de-excited, core de-excited

I will denote these contributions to the hyperpolarisability as \( \Delta \gamma_1 \), \( \Delta \gamma_2 \), \( \Delta \gamma_3 \), \( \Delta \gamma_4 \), \( \Delta \gamma_5 \) and \( \Delta \gamma_6 \) respectively. My calculated values for these contributions will be presented in Table 6.8, after I discuss the formulae needed to compute the transition matrix elements where two or three electrons are coupled.

The state of the atom can be written as a product of the core electron state \( |\ell_1 m_1\rangle \) and the valence electron state \( |\ell_2 m_2\rangle \) to be [188]

\[
\psi = |\ell_1 m_1\rangle |\ell_2 m_2\rangle ,
\]

which is the uncoupled representation. In the coupled representation, the state is given by [188, 189]

\[
\psi_j = \sum_{LM} |\ell_1 \ell_2 LM\rangle \langle \ell_1 \ell_2 LM|\ell_1 \ell_2 m_1 m_2\rangle ,
\]

where \( \langle \ell_1 \ell_2 LM|\ell_1 \ell_2 m_1 m_2\rangle \) is the Clebsch-Gordon given by

\[
\langle \ell_1 \ell_2 LM|\ell_1 \ell_2 m_1 m_2\rangle = (-1)^{-M+m_2-m_1} \binom{\ell_1 \ell_2 L}{m_1 m_2 -M} \sqrt{2L+1} .
\]

\( L \) is the total angular momentum which obeys the triangular condition [189]

\[
\ell_1 + \ell_2 \geq L \geq |\ell_1 - \ell_2|
\]

In the case of lithium the atomic state can be written in the uncoupled representation as

\[
|\ell_1 m_1, \ell_2 m_2, \ell_3 m_3\rangle = |\ell_1 m_1\rangle |\ell_2 m_2\rangle |\ell_3 m_3\rangle ,
\]

where the angular momentum vectors couple to a resultant \( L \) and \( M \) [189]. The coupled representation is
given by
\[ |\ell_1, (\ell_2 \ell_3) L_{23}; LM \rangle = \sum_{m_1, M_{23}} |\ell_1 m_1 \rangle |\ell_2 \ell_3 L_{23} M_{23} \rangle \langle \ell_1 L_{23} m_1 M_{23} |LM \rangle , \] (6.8)
where \( |\ell_2 \ell_3 L_{23} M_{23} \rangle \) is given by
\[ |\ell_2 \ell_3 L_{23} M_{23} \rangle = \sum_{m_2, m_3} |\ell_2 m_2 \rangle |\ell_3 m_3 \rangle \langle \ell_2 \ell_3 m_2 m_3 |L_{23} M_{23} \rangle . \] (6.9)

In the case of coupling between two electrons, the matrix element can be written as [190]
\[ \langle \ell_1 \ell_2 L || T^k (1) || \ell'_1 \ell'_2 L' \rangle = \delta_{\ell_2 \ell'_2} (-1)^{\ell_1 + \ell_2 + L' + k} \sqrt{(2L' + 1)(2\ell_1 + 1)} \left\{ \frac{\ell_1 \ell'_1 k}{L' L \ell_2} \right\} \langle \ell_1 || T^k (1) || \ell'_1 \rangle , \] (6.10)
where the operator \( T^k (1) \) acts on space 1. If the operator acts on space 2, then
\[ \langle \ell_1 \ell_2 L || T^k (2) || \ell'_1 \ell'_2 L' \rangle = \delta_{\ell_1 \ell'_1} (-1)^{\ell_1 + \ell_2 + L' + k} \sqrt{(2L' + 1)(2\ell_2 + 1)} \left\{ \frac{\ell_2 \ell'_2 k}{L' L \ell_1} \right\} \langle \ell_2 || T^k (2) || \ell'_2 \rangle . \] (6.11)

In the case where three electrons are coupled, the matrix element for an operator acting on the first electron is given by
\[ \langle \ell_1 \ell_2 L_{23}; L || T^k (1) || \ell'_1 \ell'_2 L'_{23} \rangle = \delta_{\ell_2 \ell'_2} (-1)^{\ell_1 + \ell_2 + L' + k} \sqrt{(2L' + 1)(2\ell_1 + 1)} \left\{ \frac{\ell_1 \ell'_1 k}{L' L \ell_2} \right\} \langle \ell_1 || T^k (1) || \ell'_1 \rangle , \] (6.12)
where \( \ell_2 + \ell_3 \geq \ell_{23} \geq |\ell_2 - \ell_3| \) and \( \ell_1 + \ell_{23} \geq L \geq |\ell_1 - \ell_{23}| \).

The angular momentum coupling of transition 3. in the list above (where first a core then a valence electron is excited, and then a core and then a valence electron is de-excited) is given by
\[
\begin{align*}
\langle \ell_c = 0, \ell_v = 0, L = 0 || r \cos \theta || \ell'_c = 1, \ell'_v = 0, L' = 1 \rangle &= \langle \ell_c = 1, \ell_v = 0, L = 1 || r \cos \theta || \ell'_c = 1, \ell'_v = 1, L' = 0 \rangle \\
\langle \ell_c = 1, \ell_v = 1, L = 0 || r \cos \theta || \ell'_c = 0, \ell'_v = 1, L' = 1 \rangle &= \langle \ell_c = 0, \ell_v = 1, L = 1 || r \cos \theta || \ell'_c = 0, \ell'_v = 0, L' = 0 \rangle \\
&= \sqrt{3} \begin{pmatrix} 0 & 1 & 1 \\ 1 & 0 & 0 \end{pmatrix} \langle \ell_c = 0 || r \cos \theta || \ell'_c = 1 \rangle \sqrt{3} \begin{pmatrix} 0 & 1 & 1 \\ 0 & 1 & 1 \end{pmatrix} \langle \ell_v = 0 || r \cos \theta || \ell'_v = 1 \rangle \\
&\times \sqrt{3} \begin{pmatrix} 1 & 0 & 1 \\ 1 & 0 & 1 \end{pmatrix} \langle \ell_c = 1 || r \cos \theta || \ell'_c = 0 \rangle \sqrt{3} \begin{pmatrix} 1 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix} \langle \ell_v = 1 || r \cos \theta || \ell'_v = 0 \rangle \\
&= \frac{1}{3} \langle \ell_c = 0 || r \cos \theta || \ell'_c = 1 \rangle \langle \ell_v = 0 || r \cos \theta || \ell'_v = 1 \rangle \langle \ell_c = 1 || r \cos \theta || \ell'_c = 0 \rangle \langle \ell_v = 1 || r \cos \theta || \ell'_v = 0 \rangle
\end{align*}
\]
or

\[
\langle \ell_c = 0, \ell_v = 0, L = 0 | r \cos \theta | \ell'_c = 1, \ell'_v = 0, L' = 1 \rangle \langle \ell_c = 1, \ell_v = 0, L = 1 | r \cos \theta | \ell'_c = 1, \ell'_v = 1, L' = 2 \rangle \\
\langle \ell_c = 1, \ell_v = 1, L = 2 | r \cos \theta | \ell'_c = 0, \ell'_v = 1, L' = 1 \rangle \\
\langle \ell_c = 0, \ell_v = 1, L = 1 | r \cos \theta | \ell'_c = 0, \ell'_v = 0, L' = 0 \rangle
\]

\[
= \sqrt{3} \begin{pmatrix}
0 & 1 & 1 \\
1 & 0 & 0
\end{pmatrix}
\langle \ell_c = 0 | r \cos \theta | \ell'_c = 1 \rangle \sqrt{5} \begin{pmatrix}
0 & 1 & 1 \\
2 & 1 & 1
\end{pmatrix}
\langle \ell_v = 0 | r \cos \theta | \ell'_v = 1 \rangle
\times \sqrt{9} \begin{pmatrix}
1 & 0 & 1 \\
1 & 2 & 1
\end{pmatrix}
\langle \ell_c = 1 | r \cos \theta | \ell'_c = 0 \rangle \sqrt{3} \begin{pmatrix}
1 & 0 & 1 \\
0 & 1 & 0
\end{pmatrix}
\langle \ell_v = 1 | r \cos \theta | \ell'_v = 0 \rangle
\]

\[
= \frac{\sqrt{5}}{3} \langle \ell_c = 0 | r \cos \theta | \ell'_c = 1 \rangle \langle \ell_v = 0 | r \cos \theta | \ell'_v = 1 \rangle \langle \ell_c = 1 | r \cos \theta | \ell'_c = 0 \rangle \langle \ell_v = 1 | r \cos \theta | \ell'_v = 0 \rangle
\]

Applying the formulae above and the Mitroy method allows us to calculate the static hyperpolarisability with core contributions. \( \gamma_{0101} \) and \( \gamma_{0121} \) refer to the hyperpolarisability, neglecting the core electrons, for the \( \ell_i = 0 \rightarrow \ell_j = 1 \rightarrow \ell_m = 0 \rightarrow \ell_i = 0 \) and \( \ell_i = 0 \rightarrow \ell_j = 1 \rightarrow \ell_m = 2 \rightarrow \ell_i = 1 \rightarrow \ell_i = 0 \) transition pathways respectively. We find \( \gamma_{0101} = 1459691 \) a.u. and \( \gamma_{0121} = 1461140 \) a.u., which are nearly equal in magnitude, but opposite in size. This results in a very large cancellation, and the total hyperpolarisability (neglecting the core contribution) is given by \( \gamma_{0101} + \gamma_{0121} = 1449 \) a.u.. Given that the hyperpolarisability of atomic lithium was calculated by Tang et al. [20], using a three-electron Hylleraas calculation, to be \( \gamma = 3060 \pm 40 \) a.u., our calculation is not very accurate.

Let us now consider the contribution from the core electrons to the static hyperpolarisability. As was listed above, \( \Delta \gamma_1, \Delta \gamma_2, \Delta \gamma_3, \Delta \gamma_4, \Delta \gamma_5 \) and \( \Delta \gamma_6 \) (given in Table 6.8) are the various contributions to the hyperpolarisability where both a core and a valence electron are excited, listed in order of strength. The total contribution from exciting a core and valence electron is \( \Delta \gamma_v = \Delta \gamma_1 + \Delta \gamma_2 + \Delta \gamma_3 + \Delta \gamma_4 + \Delta \gamma_5 + \Delta \gamma_6 = -43.3904 \) a.u.. Finally, the contribution to the hyperpolarisability from only core electron excitations is given by \( \Delta \gamma_c = -0.02385503 \) a.u.. Overall, the correction to the hyperpolarisability by including core electrons in the calculation, is given by \( \Delta \gamma_{core} = \Delta \gamma_c + \Delta \gamma_v = -43.4143 \) a.u.. Evidently the core contribution to the hyperpolarisability is very small with respect to the magnitude of \( \gamma_{0101} \) and \( \gamma_{0121} \), but due to the cancellations has a significant impact on the total hyperpolarisability. The static hyperpolarisability given by our calculation when including the core electrons is \( \gamma = 1406 \) a.u., in comparison to \( \gamma = 3060 \pm 40 \) a.u. given by Tang et al. [20]. However, in a later section I will show how our calculation of the static hyperpolarisability can be improved by replacing energies in our calculation with experimentally known values and replacing the oscillator strengths with more accurate values from the calculation by Tang et al. For now let us consider the frequency-dependent hyperpolarisability.
Table 6.8: All the different contributions to the hyperpolarisability (in atomic units) involving the excitation of one core electron and one valence electron. The transition pathways given by $\Delta \gamma_1$, $\Delta \gamma_2$, $\Delta \gamma_3$, $\Delta \gamma_4$, $\Delta \gamma_5$ and $\Delta \gamma_6$ were listed at the beginning of this section, and are sorted in order of strength. $\gamma_{cv}$ is the sum of all contributions involving the excitation of one core and one valence electron.

<table>
<thead>
<tr>
<th>$\Delta \gamma$</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta \gamma_1$</td>
<td>-115.2921</td>
</tr>
<tr>
<td>$\Delta \gamma_2$</td>
<td>71.29069</td>
</tr>
<tr>
<td>$\Delta \gamma_3$</td>
<td>-2.448946</td>
</tr>
<tr>
<td>$\Delta \gamma_4$</td>
<td>1.513456</td>
</tr>
<tr>
<td>$\Delta \gamma_5$</td>
<td>1.513456</td>
</tr>
<tr>
<td>$\Delta \gamma_6$</td>
<td>0.03299370</td>
</tr>
<tr>
<td>$\Delta \gamma_{cv}$</td>
<td>-43.3904</td>
</tr>
</tbody>
</table>

### 6.4.4.2 Dynamic Hyperpolarisability

Perhaps due to the difficulty of computing even the static hyperpolarisability, data for dynamic hyperpolarisability is scarce. Jaszunski et al. [186] give the first calculation of the frequency-dependent hyperpolarisability for the DC Kerr process. They also consider a power series expansion of the hyperpolarisability to give an approximate function of the hyperpolarisability at low frequencies, which would be useful to find the hyperpolarisability at a specific frequency for experiments without having to conduct the full calculation. Here we use the same formulae as presented in Chapter 5 for the frequency-dependent hyperpolarisability for the DFWM process, given by

$$\gamma(-\omega_{\sigma}; \omega_1, \omega_2, \omega_3) = \sum_{\ell_i, \ell_m, \ell_t} G_{\ell_i, \ell_j, \ell_m, \ell_t} \left[ \sum_{jmt} f_{i,j,m,t}^a(-\omega_{\sigma}; \omega_1, \omega_2, \omega_3) \right. \left. - \delta(\ell_m, \ell_i) \delta(m, i) \sum_{jtt} f_{i,j,m,t}^b(-\omega_{\sigma}; \omega_1, \omega_2, \omega_3) \right],$$

where the frequency dependence is given by

$$f_{i,j,m,t}^a(-\omega_{\sigma}; \omega_1, \omega_2, \omega_3) = \frac{1}{6} \sum_{p} \left[ \frac{T_{i,j}T_{j,m}T_{m,t}T_{t,i}}{(e_{ji} - \omega_{\sigma} - i\frac{1}{2} \Gamma_{ij}(\omega))(e_{mi} + \omega_1 + \omega_2 - i\frac{1}{2} \Gamma_{im}(\omega_1 + \omega_2))(e_{ti} + \omega_1 - i\frac{1}{2} \Gamma_{it}(\omega))} \right].$$

(6.13)
and

\[
\begin{align*}
 f_{ij,m,l}^b(-\omega; \omega_1, \omega_2, \omega_3) &= \frac{1}{6} \sum_{P} \left( T_{ij}^2 T_{ii}^2 \right) \left( \varepsilon_{ji} - \omega - i\frac{1}{2}\Gamma_{ij}(\omega) \right) \left( \varepsilon_{i\!i} + \omega_1 - i\frac{1}{2}\Gamma_{ii}(\omega_1) \right) \left( \varepsilon_{i\!i} - \omega_2 - i\frac{1}{2}\Gamma_{ii}(\omega) \right),
\end{align*}
\]

(6.15)

where, in the case of DFWM, \( \omega_{1,2} = \omega, \omega_3 = -\omega \). The sum over \( P \) denotes a sum over all permutations of \( \omega_1, \omega_2, \omega_3 \) and \( \omega_\sigma \), where the condition \( -\omega_\sigma = \omega_1 + \omega_2 + \omega_3 \) is satisfied. The coefficient \( G_{\ell_i,\ell_j,\ell_m,\ell_r} \) is given by Tang et al. [20] to be \( G_{0,1,0,1} = \frac{1}{9} \) and \( G_{0,1,2,1} = \frac{2}{45} \).

Tang et al. had presented a calculation of the static polarisability and hyperpolarisability of atomic lithium in 2009 [20] and extended this to the dynamic polarisability, but not the hyperpolarisability, in a subsequent paper [88]. Upon our request Li-Yan Tang calculated the frequency-dependent hyperpolarisability with her three-electron Hylleraas method and kindly sent us her data. We demonstrate agreement for the hyperpolarisability at frequencies below threshold in Fig. 6.13. The hyperpolarisability given by the Hylleraas calculation above the first ionisation threshold exhibits resonances due to pseudostates, as our pseudostate method was not applied. Our method also shows resonances, such as at approximately 0.14 a.u., which corresponds to resonance with a physical state.

Figure 6.13: Plot of frequency dependent \( \gamma(\omega) \) of atomic lithium (neglecting the core electron contribution) calculated using a \( N_f = 120 \) basis. \( \text{Re}[\gamma(\omega)] \) is presented (left) and compared with the values given by the Hylleraas calculation by Dr. Li-Yan Tang. \( \text{Im}[\gamma(\omega)] \) is presented (right), where \( \text{Im}[\gamma(\omega)] = \text{Im}[\gamma_{0101}(\omega)] + \text{Im}[\gamma_{0121}(\omega)] \)

\[
\begin{align*}
\text{Re}[\gamma(\omega)] \text{[a.u.]} \quad \text{Im}[\gamma(\omega)] \text{[a.u.]} \\
0 &\quad 0.05 &\quad 0.1 &\quad 0.15 &\quad 0.2 \\
0 &\quad 0.0 &\quad 0.1 &\quad 0.2 &\quad 0.3 \\
-1.5 \times 10^7 &\quad -1.0 \times 10^7 &\quad -0.5 \times 10^7 &\quad 0 &\quad 0.5 \times 10^7 \\
-1.5 \times 10^7 &\quad -1.0 \times 10^7 &\quad -0.5 \times 10^7 &\quad 0 &\quad 0.5 \times 10^7 \\
\end{align*}
\]

Since we apply the principal value method at frequencies above \( \omega > \varepsilon_{IP}/2 \), the hyperpolarisability is complex. In Fig. 6.13 I have presented both \( \text{Re}[\gamma(\omega)] \) and \( \text{Im}[\gamma(\omega)] \) of atomic lithium calculated using our pseudostate method. Since \( \text{Im}[\gamma_{0101}(\omega)] \) and \( \text{Im}[\gamma_{0121}(\omega)] \) are computed at a different set of frequencies, the total \( \text{Im}[\gamma(\omega)] \) was found by interpolating \( \text{Im}[\gamma_{0101}(\omega)] \) and adding to \( \text{Im}[\gamma_{0121}(\omega)] \). However, at higher frequencies there are not enough pseudostates to describe the resonances that should occur. At frequencies greater than 0.17 a.u., I have simply added the values of \( \text{Im}[\gamma_{0101}(\omega)] \) and
Figure 6.14: Plot of the two-photon ionisation cross-section (in units of $\sigma_T$) of Li$(2s)$ given by our pseudostate calculation (with a basis of $N_\ell = 120$). The two-photon ionisation cross-sections converted from the two-photon ionisation probabilities given by Mizuno [15] are also plotted. In my conversion I have assumed that Mizuno has used the unit flux corresponding to $F = I_0/h\omega$, where $I_0 = 14.038 \times 10^{16}$.

$\text{Im}[\gamma_{0121}(\omega)]$ for the nearest frequencies, instead of interpolating. I have previously shown in Section 5.3 that $\text{Im}[\gamma(\omega)]$ can be converted to the two-photon ionisation cross-section. For this reason we are now able to compute the two-photon ionisation cross-section for atomic lithium from the imaginary hyperpolarisability, as presented in Fig. 6.14. Though I have found no data to compare against for $\text{Im}[\gamma(\omega)]$ of lithium, the two-photon ionisation probabilities has been calculated by Mizuno [15]. Upon conversion, I have found good agreement between our calculations (see Fig. 6.14), which indicates that my calculation of $\text{Im}[\gamma(\omega)]$ of ground state atomic lithium must be correct.

### 6.4.4.3 Improving Accuracy by using Experimental Energies

Several theoretical calculations have improved the accuracy of their results by replacing the theoretical energies with experimentally measured energies. We have used the same approach to compute more accurate values of the hyperpolarisability.

The energies of states $n \leq 4$ (where $n$ is the principal quantum number) were replaced by the experimental energies given by NIST [19]. The oscillator strengths of the $2s-2p$, $2p-3d$ and $3d-4f$ transitions were replaced with the oscillator strengths given by Tang et al. [20], as the three-electron Hylleraas calculation has a more accurate description of the atom than our one-electron calculation. Of course, the hyperpolarisability of ground state lithium does not involve the $3d-4f$ transition. However, using the $2s-2p$ and $2p-3d$ oscillator strengths given by Tang et al. does result in a different value for the hyperpolarisability. The old and new values for oscillator strength and energies are presented in Tables 6.9 and 6.10.
### Table 6.9: Comparison of the energies (in atomic units) given by patom \((N_\ell = 120 \text{ basis})\) with the experimental energies given by NIST [19].

<table>
<thead>
<tr>
<th>(\ell)</th>
<th>patom</th>
<th>NIST</th>
</tr>
</thead>
<tbody>
<tr>
<td>2s</td>
<td>-0.1981406</td>
<td>-0.1981420</td>
</tr>
<tr>
<td>2p</td>
<td>-0.1302386</td>
<td>-0.1302349</td>
</tr>
<tr>
<td>3s</td>
<td>-0.0741685</td>
<td>-0.0741818</td>
</tr>
<tr>
<td>3p</td>
<td>-0.0572283</td>
<td>-0.0572356</td>
</tr>
<tr>
<td>3d</td>
<td>-0.0556113</td>
<td>-0.0556057</td>
</tr>
<tr>
<td>4s</td>
<td>-0.0386096</td>
<td>-0.0386154</td>
</tr>
<tr>
<td>4p</td>
<td>-0.0319702</td>
<td>-0.0319745</td>
</tr>
<tr>
<td>4d</td>
<td>-0.0312768</td>
<td>-0.0312736</td>
</tr>
</tbody>
</table>

### Table 6.10: Comparison of the oscillator strengths given by patom \((N_\ell = 120 \text{ basis})\) with those given by Tang et al. [20].

<table>
<thead>
<tr>
<th>(\ell)</th>
<th>patom</th>
<th>Tang et al</th>
</tr>
</thead>
<tbody>
<tr>
<td>2s-2p</td>
<td>0.7474820</td>
<td>0.7469563</td>
</tr>
<tr>
<td>2p-3d</td>
<td>0.6388382</td>
<td>0.6385685</td>
</tr>
<tr>
<td>3d-4f</td>
<td>1.0153298</td>
<td>1.0153771</td>
</tr>
</tbody>
</table>

Though it may seem that there are only slight differences between the original and new energies and oscillator strengths, these make a (relatively) huge difference to the calculation of the hyperpolarisability. The total hyperpolarisability is small relative to the magnitude of \(\gamma_{0101}\) and \(\gamma_{0121}\), i.e. \(\gamma/(|\gamma_{0101}| + |\gamma_{0121}|) = 0.000496\) and so small changes to the oscillator strengths and energies have a significant effect. Since \(\gamma_{0101}\) and \(\gamma_{0121}\) must be computed to very high accuracy in order to determine the total hyperpolarisability \(\gamma\) with relatively low uncertainty, it follows that the accuracy of the initial inputs (energies and oscillator strengths) have a large effect on the hyperpolarisability value. Our new values for the hyperpolarisability (with and without core contribution) are presented in Table 6.11.

### Table 6.11: The total static hyperpolarisability \(\gamma\), as well as \(\gamma_{0101}\) and \(\gamma_{0121}\) (in atomic units) are given, where we have replaced energy of the 2s state and first three \(\ell = 1\) states \((2p, 3p, 4p)\) with experimental values and replaced the oscillator strength of the 2s-2p transition with the oscillator strength given by Tang et al. [20]. Our calculation is presented with and without the core contribution, and is compared with the hyperpolarisability data given by Tang et al. [20].

<table>
<thead>
<tr>
<th>Core contribution?</th>
<th>(\gamma_{0101})</th>
<th>(\gamma_{0121})</th>
<th>(\gamma)</th>
</tr>
</thead>
<tbody>
<tr>
<td>neglected</td>
<td>-1456207</td>
<td>1459302</td>
<td>3095</td>
</tr>
<tr>
<td>included</td>
<td>-1456285</td>
<td>1459337</td>
<td>3052</td>
</tr>
<tr>
<td>Tang et al.</td>
<td>-1458643</td>
<td>1461682</td>
<td>3060±40</td>
</tr>
</tbody>
</table>

Tang et al. did some convergence studies of the static hyperpolarisability of lithium by computing the \(\gamma_{0101}\) and \(\gamma_{0121}\) for several basis set sizes, and extrapolating the convergence to give the total hyperpolarisability. Since the extrapolated value for \(\gamma_{0101}\) and \(\gamma_{0121}\) was not presented by Tang et al., we compare our values with \(\gamma_{0101}\) and \(\gamma_{0121}\) given by their largest basis set. We find that our values of \(\gamma_{0101}\) and \(\gamma_{0121}\) (including core contribution, and replacing the first energies and oscillator strengths as shown in Tables 6.9 and 6.10) are accurate to 99.8383\% and 99.8395\% respectively. Initially our calculation (with only valence electrons) of the lithium hyperpolarisability gave \(\gamma = 1449\) a.u., whilst replacing energies and oscillator strengths with more accurate values gives a hyperpolarisability of \(\gamma = 3095\) a.u. (by
neglecting core contribution) and \( \gamma = 3052 \text{ a.u.} \) (by neglecting core contribution). Simply by replacing a few of the energies and oscillator strengths with more accurate values, we are able to give a much more accurate value of the hyperpolarisability which is in agreement with the value given by Tang et al. [20] (\( \gamma = 3060 \pm 40 \text{ a.u.} \)). Note that our core treatment gives a small contribution that is on the same order as the \( \pm40 \) error in the results given by Tang et al.

6.5 Sodium

The next atom I will consider here is sodium. Like lithium, this atom has only one valence electron, though it has ten core electrons. These core electrons can be included in the Rayleigh scattering cross-section calculation through the use of the Mitroy method I introduced in my calculation of atomic lithium in Section 6.4. However, we expect the most interesting physics to occur due to the valence electron as it is less tightly bound than the core electrons and thus more likely to be excited. Fig. 6.15 plots the Rayleigh and photoionisation cross-section of sodium by considering only the valence electron. Note that at 1.13 a.u. the core electrons become important as this is the first excitation energy (to \( 2p^53s^2 \)) [191]. We can only consider energies below this as we do not include the core electrons exactly.

Figure 6.15: Rayleigh and photoionisation cross-section of atomic sodium given by our pseudostate calculation (using basis set of \( N_{\ell=0} = 43, N_{\ell=1} = 40 \) and \( N_{\ell=2} = 35 \)). The ionisation energy of sodium is at 0.189 a.u.

We are particularly interested in the photoionisation cross-section of atomic sodium, as this is expected to exhibit a dip which is known as the Cooper minimum. This Cooper minimum occurs when the matrix element passes through zero, which means that the cross-section approaches zero and then increases again. This was first found to occur in the photoionisation cross-sections of sodium and helium by Cooper in 1962 [192].

The photoionisation cross-section given by our pseudostate calculation for atomic sodium is shown
in Fig. 6.15, where we can see a dip occur at approximately $\omega = 0.25$ a.u. Cooper [192] gave a plot of the photoionisation cross-section of sodium for both experimental and theoretical results, and show a minimum at a wavelength of approximately 1900 Å, which corresponds to 0.24 a.u. This indicates that our pseudostate calculation gives the correct behaviour of the sodium photoionisation cross-section. As we have only few pseudostates in the frequency range of the Cooper minimum, we could only see a slight dip. In the future we could use more pseudostates to better map out the dip that occurs in our calculation. In future work we could also apply the core method to $\gamma(\omega)$ for sodium, as the cancellation is not as severe.

6.6 Summary

We have now applied our pseudostate method for the single and two-photon cross-sections to a range of atoms. The calculations in this Chapter show that our method can be used for atoms other than atomic hydrogen. As is expected, the various isotopes of hydrogen, as well as positronium, exhibit very similar cross-section behaviour to the hydrogen atom. I have also presented a relatively small calculation of the scattering cross-sections and hyperpolarisability of metastable helium, which demonstrates that we can use our pseudostate method for this atom as well. In the future we can use a larger basis set to compute the properties of metastable helium. These results, particularly the hyperpolarisability, may be useful in experiments such as the high-precision measurement of tune-out wavelength by Henson et al. [165] in metastable helium.

Though we have shown that our calculation of static hyperpolarisability of atomic lithium is not as accurate as the three-electron Hylleraas calculation, we have demonstrated that our method allows us to compute hyperpolarisabilities above threshold by removing the unphysical poles occurring due to the $(\varepsilon_{ii} - 2\omega)$ term in the denominator. Our core treatment is useful, as it shows that the core electrons have a small contribution to the hyperpolarisability. I have also shown that the photoionisation cross-section given by our pseudostate method for lithium is in agreement with Hollauer et al. [174] but disagrees with the data given by Manakov et al. [60]. I have also applied our pseudostate method to the Compton scattering cross-section, which exhibits oscillations. Further convergence studies need to be done to determine if our lithium Compton calculation diverges like our hydrogen Compton calculation.

Finally, I have also presented a calculation of the sodium atom for a small basis set. Even this small calculation shows the presence of the Cooper minimum, which verifies that our pseudostate calculation gives the correct behaviour of the cross-section. A calculation using a larger basis set for atomic sodium should be able to give a better description of the Cooper minimum. The calculations presented in this Chapter are the first step to applying our pseudostate method to larger atoms that are of interest in high-precision AMO experiments.

Now that I have demonstrated that our pseudostate method can be applied to different atoms, I will consider how our pseudostate method can be extended in future work. Chapter 7 will focus on the
possibility of extending our pseudostate calculation to two-photon ionisation and hyperpolarisability at frequencies above the second ionisation threshold. Chapter 8 will consider other applications/extensions of our pseudostate method.
Chapter 7

Above Threshold Ionisation

In this thesis I have developed our pseudostate method for computing the various single and multi-photon scattering cross-sections, and in the previous Chapter I have applied our method to various atoms. In this Chapter I will discuss the possibility of extending our pseudostate-based method to the calculation of multi-photon scattering cross-sections at frequencies above ionisation threshold.

Our pseudostate method was used in Chapter 5 to compute the two-photon ionisation cross-section at frequencies above the first ionisation threshold. The natural extension to this is to consider how our method can be extended to frequencies above the second ionisation threshold. This calculation is complicated by the fact that both the intermediate and the final states are now in the continuum. In this Chapter I will detail the first attempt at using our pseudostate method to compute the two photon ionisation cross-section at frequencies above the second ionisation threshold. I will also discuss the related calculation of the complex hyperpolarisability above the second ionisation energy and the difficulties associated with this.

The ‘first’ ionisation threshold refers to the lowest energy that the photons can have to ionise the atom through two-photon ionisation. This is also referred to as the two-photon ionisation threshold and occurs at $\varepsilon = 0.25$ a.u. in atomic hydrogen. The ‘second’ ionisation threshold refers to the energy a single photon must have to ionise the atom. This may also be referred to as the single photon ionisation threshold. This is shown in Fig. 7.1.

7.1 Two-Photon Ionisation Above Threshold

For photon energies greater than the second ionisation threshold, the absorption of a single photon is sufficient to excite the atom into the continuum. As a result, the calculation of the two-photon ionisation cross-section using our pseudostate method at frequencies above the second ionisation threshold involves both an intermediate and final state in the continuum, i.e. we want to describe this using pseudostates.
The two-photon ionisation cross-section starting in an $\ell_i = 0$ state is given by (see Section 5.1)

$$
\sigma_{i}^{(2)}(\omega_n) = \frac{3\pi I}{4\alpha^3 l_0} \omega \left[ \frac{1}{9} M_{010}^2 + \frac{4}{45} M_{012}^2 \right] \sigma_T
$$

(7.1)

where

$$
M_{\ell_i \ell_m \ell_j}(\omega) = \sum_{m \neq n} \frac{\langle \epsilon_j | z | \epsilon_m \rangle \langle \epsilon_m | z | i \rangle}{\epsilon_{mi} - \omega}
$$

(7.2)

where $\omega = \epsilon_n - \epsilon_i$ and $2\omega = \epsilon_j - \epsilon_i$. The pole at frequency $\omega = \epsilon_{mi}$ in the matrix element $M_{\ell_i \ell_m \ell_j}$ is avoided by removing the pseudostate with energy $\epsilon_n$ from the sum. As a consequence of this, the final state pseudostate energy $\epsilon_j$ must fulfill the condition

$$
\epsilon_j - \epsilon_i = 2(\epsilon_n - \epsilon_i)
$$

(7.3)

where $\epsilon_n$ is the energy of a pseudostate and $\epsilon_i$ is the energy of the initial state. This two-photon ionisation process is depicted in Fig. 7.1. If our pseudostates satisfied this condition, we would be able to easily compute the two-photon ionisation cross-section. Unfortunately, the energy of the pseudostates in our calculation do not satisfy Eqn. 7.3 and so I will consider here the possibility of computing the two-photon ionisation cross-section above the second ionisation threshold through approximate methods.

As our pseudostates are not able to fulfill the condition in Eqn. 7.3 exactly, I have instead chosen the nearest states which fulfill

$$
\epsilon_j - \epsilon_i \approx 2(\epsilon_n - \epsilon_i)
$$

(7.4)

This approximation essentially means that we are no longer computing the ionisation process involving the absorption of two identical photons, but rather the absorption of two photons of frequency $\omega'$ and $\omega''$. As a result the two photon ionisation cross-section should be written as

$$
\sigma^{(2)}(\omega) \rightarrow \sigma^{(2)}(\omega', \omega'')
$$

(7.5)
since the cross-section is dependent on both $\omega'$ and $\omega''$.

Let us rewrite this in terms of our pseudostate calculation. In our approximation, I choose the final state energy $\varepsilon_j$ first and then find the two nearest values to $\omega_{ni} \approx (\varepsilon_j - \varepsilon_i)/2$. This approximation is depicted in Fig. 7.2. This then gives us two values of the cross-section for given a final state $j$, where

$$
\sigma_{\ell_i, \ell_m, \ell_j}^{(2)}(\omega_{ni}, \omega_{jn}) = \frac{3\pi I}{4\alpha^3 I_0} \omega_{ni} \left[ G_{\ell_i, \ell_m, \ell_j} \sum_{m \neq n} \frac{\langle \varepsilon_j | z | \varepsilon_m \rangle \langle \varepsilon_m | z | \varepsilon_i \rangle}{\varepsilon_{mi} - \omega_{ni}} \right]^2 \sigma_T
$$

(7.6)

and

$$
\sigma_{\ell_i, \ell_m, \ell_j}^{(2)}(\omega_{n+1,i}, \omega_{j,n+1}) = \frac{3\pi I}{4\alpha^3 I_0} \omega_{n+1,i} \left[ G_{\ell_i, \ell_m, \ell_j} \sum_{m \neq n+1} \frac{\langle \varepsilon_j | z | \varepsilon_m \rangle \langle \varepsilon_m | z | \varepsilon_i \rangle}{\varepsilon_{mi} - \omega_{n+1,i}} \right]^2 \sigma_T
$$

(7.7)

Figure 7.2: Diagram showing our approximation to the two-photon ionisation process at frequencies above ionisation energy $\varepsilon_{IP}$. By choosing the nearest intermediate state to $\varepsilon = \varepsilon_{ji}/2$ from below (left) or from above (right), we now describe the process involving the absorption of photons of frequencies $\omega' = \omega_{n,i}$ and $\omega'' = \omega_{j,n}$ (left) or frequencies $\omega' = \omega_{n+1,i}$ and $\omega'' = \omega_{j,n+1}$ (right).

We can then average the two cross-sections ($\sigma_{\ell_i, \ell_m, \ell_j}^{(2)}(\omega_{ni}, \omega_{jn})$ and $\sigma_{\ell_i, \ell_m, \ell_j}^{(2)}(\omega_{n+1,i}, \omega_{j,n+1})$) to give an approximation to the two-photon ionisation cross-section that is plotted in Fig. 7.3. In Fig. 7.3 our two-photon ionisation cross-section is plotted on a log-scale, and compared with previous calculations by Karule [143] and Jayadevan et al. [146]. From this plot we can see that our approximation, whilst in qualitative agreement with literature, is not in quantitative agreement.

Next we use a different approach in our approximation, in an attempt to get better agreement with literature. A second approach to the approximation is to first choose the frequency $\omega' = \omega_{ni}$, and then find the second frequency $\omega''$ for the two closest pseudostate energies $\omega'' = \omega_{jn}$ and $\omega'' = \omega_{j+1,n}$. This process is depicted in Fig. 7.4.
7.1. Two-Photon Ionisation Above Threshold

Figure 7.3: Plot of the $\sigma_{010}^{(2)}$ and $\sigma_{012}^{(2)}$ contribution (in units of $\sigma_T$) to the two-photon ionisation cross-section calculated using the approximation discussed above (basis set $N_\ell = 120$) for frequencies up to $\omega = 30$ a.u. (left) and zoomed in to frequencies near threshold (right). The intensity was chosen to be $I = I_0$, as per Section 5.1. The two-photon ionisation cross-sections given by Karule [143] and Jayadevan et al. [146] are also plotted.

Figure 7.4: Diagram showing our approximation to the two-photon ionisation process at frequencies above ionisation energy $\varepsilon_{IP}$. By choosing the nearest final state to $\varepsilon = 2\omega - \varepsilon_i$ from below (left) or from above (right), we now describe the process involving the absorption of two photons of frequency $\omega'$ and $\omega''$, rather than the absorption of two photons of frequency $\omega$.

We average $\sigma_{i_1,\ell_1,m_1,j_1}^{(2)}(\omega_{i_1}, \omega_{j_1})$ and $\sigma_{i_2,\ell_2,m_2,j_2}^{(2)}(\omega_{i_2}, \omega_{j+1,n})$ to give our approximation to the two-photon ionisation, as shown in Fig. 7.5. We find that our approximation gives slightly different values for the two-photon ionisation cross-section depending on whether we chose the intermediate energy and chose the nearest possible final states or vice-versa. The first approximation we applied (presented in Fig. 7.3) gives a better estimate of the two-photon ionisation cross-section than the cross-sections presented in Fig. 7.5. Although our two-photon ionisation cross-section is in qualitative agreement, our approximation gives cross-sections that are larger than the values given by Karule [143] and Jayadevan et al. [146].

There have been several calculations of the two-photon ionisation cross-section for atomic hydrogen.
7.2 Future - Hyperpolarisability Above Threshold

Figure 7.5: Plot of the $\sigma_{010}^{(2)}$ and $\sigma_{012}^{(2)}$ contribution (in units of $\sigma_T$) to the two-photon ionisation cross-section calculated using the approximation discussed above (basis set $N_\ell = 120$) for frequencies up to $\omega = 30$ a.u. (left) and zoomed in to frequencies near threshold (right). The intensity was chosen to be $I = I_0$, as per Section 5.1. The two-photon ionisation cross-sections given by Karule [143] and Jayadevan et al. [146] are also plotted.

at frequencies above the second ionisation threshold. I have chosen to plot the data given by both Karule and Jayadevan et al. for the two-photon ionisation cross-section in the plots above, in order to show the good agreement between previous calculations. In fact, the two-photon ionisation cross-section above the second ionisation threshold for atomic hydrogen was calculated as early as 1965 by Zernik et al. [193] and 1970 by Klarsfeld [141]. Several different methods were used in these previous calculations of the two-photon ionisation cross-section. For example, Klarsfeld [141] and Karule [143] used analytical expressions for atomic hydrogen to calculate the two-photon ionisation cross-section, and found converged values by applying transformations to the hypergeometric functions. Jayadevan et al. [146] applied a variation of the Dalgarno and Lewis method, and solving the differential equation numerically.

Our method, as it is at the moment, cannot compete with the accuracy of these calculations for the two-photon ionisation cross-section. However, we should be able to increase the accuracy of our calculation for frequencies above threshold if we could apply the pseudostate packing method discussed in Section 3.6 and Appendix C. The pseudostate packing method would allow us to add pseudostates to the calculation that have the energies needed to compute the two-photon ionisation without approximation.

7.2 Future - Hyperpolarisability Above Threshold

In the previous section I have discussed our approximation of the two-photon ionisation cross-section at frequencies above the single photon ionisation threshold. In order to calculate this more accurately, we should develop the pseudostate packing method in the future. In principal we should then also be able to calculate the hyperpolarisability above threshold. In this section I will not compute the hyperpolarisabil-
ity, but I will discuss some interesting aspects of the imaginary hyperpolarisability at frequencies above ionisation threshold that should be considered in future work.

Our pseudostate method for computing the complex hyperpolarisability was introduced in Chapter 5 and computed at frequencies below and above the first ionisation threshold. The hyperpolarisability is given by

\[ \gamma(-\omega_\sigma; \omega_1, \omega_2, \omega_3) = \sum_{\ell_m,\ell_i,\ell_n} G_{i,m,l,n} \left[ \sum_{mn} f_{i,m,l,n}^a(-\omega_\sigma; \omega_1, \omega_2, \omega_3) \right. \]
\[ \left. - \delta(\ell_t, \ell_i) \delta(t,i) \sum_{mn} f_{i,m,l,n}^b(-\omega_\sigma; \omega_1, \omega_2, \omega_3) \right] \] (7.8)

where the frequency dependence is given by

\[ f_{i,m,l,n}^a(-\omega_\sigma; \omega_1, \omega_2, \omega_3) = \frac{1}{6} \sum_P \left[ \frac{\langle i|r|m\rangle \langle m|r|i\rangle \langle t|r|n\rangle \langle n|r|i \rangle}{(\epsilon_{mi} - \omega_\sigma - i\frac{1}{2} \Gamma_{im}(\omega_\sigma)) (\epsilon_{ti} + \omega_1 + \omega_2 - i\frac{1}{2} \Gamma_{it}(\omega_1 + \omega_2)) (\epsilon_{ni} + \omega_1 - i\frac{1}{2} \Gamma_{in}(\omega_1))} \right] \] (7.9)

and

\[ f_{i,m,l,n}^b(-\omega_\sigma; \omega_1, \omega_2, \omega_3) = \frac{1}{6} \sum_P \left[ \frac{\langle i|r|m\rangle \langle m|r|i\rangle \langle t|r|n\rangle \langle n|r|i \rangle}{(\epsilon_{mi} - \omega_\sigma - i\frac{1}{2} \Gamma_{im}(\omega_\sigma)) (\epsilon_{mi} + \omega_1 - i\frac{1}{2} \Gamma_{in}(\omega_1)) (\epsilon_{ni} - \omega_2 - i\frac{1}{2} \Gamma_{in}(\omega_2))} \right] \] (7.10)

where, in the case of DFWM, \( \omega_{1,2} = \omega, \omega_{3,\sigma} = -\omega \). The sum over P denotes a sum over all permutations of \( \omega_1, \omega_2, \omega_3 \) and \( \omega_\sigma \), where the condition \( -\omega_\sigma = \omega_1 + \omega_2 + \omega_3 \) is satisfied. This gives various sets of denominators (neglecting the decay term to simplify the expressions):

1. \((\epsilon_{mi} - \omega)(\epsilon_{ti} - 2\omega)(\epsilon_{ni} - \omega)\) describing absorption, absorption, emission, emission
2. \((\epsilon_{mi} + \omega)(\epsilon_{ti} + 2\omega)(\epsilon_{ni} + \omega)\) describing emission, emission, absorption, absorption
3. \((\epsilon_{mi} - \omega)(\epsilon_{ti})(\epsilon_{ni} - \omega)\) describing absorption, emission, emission, absorption
4. \((\epsilon_{mi} - \omega)(\epsilon_{ti})(\epsilon_{ni} + \omega)\) describing absorption, emission, absorption, emission
5. \((\epsilon_{mi} + \omega)(\epsilon_{ti})(\epsilon_{ni} - \omega)\) describing emission, absorption, emission, absorption
6. \((\epsilon_{mi} + \omega)(\epsilon_{ti})(\epsilon_{ni} + \omega)\) describing emission, absorption, absorption, emission

In Chapter 5 I computed the hyperpolarisability of hydrogen at frequencies below the second ionisation threshold \( \omega < \varepsilon_{IP} \). I showed that at \( \varepsilon_{IP}/2 < \omega < \varepsilon_{IP} \), an unphysical pole occurs (due to \( \epsilon_{ti} - 2\omega \) in the denominator) and can be removed by applying the Principal Value theorem. This results in an imaginary term that is related to the two-photon ionisation cross-section. See Section 5.3 for details.

Let us now discuss the (multiple) pole structures for frequencies above the second ionisation threshold
(\(\omega > \epsilon_{IP}\)). In this frequency regime a single photon has sufficient energy to ionise the atom. Poles will occur at \(\epsilon_{mi} = \omega\), \(\epsilon_{ti} = 2\omega\) and \(\epsilon_{ni} = \omega\) due to the terms \((\epsilon_{mi} - \omega)\), \((\epsilon_{ti} - 2\omega)\) and \((\epsilon_{ni} - \omega)\) in the denominator of the hyperpolarisability. These poles occur at \(\omega > \epsilon_{IP}\), but for \(H(1s)\) there are no bound states above ionisation energy, and so these poles must be unphysical. A straightforward calculation of the hyperpolarisability without removing the unphysical poles is shown in Fig. 7.6, where the poles due to \((\epsilon_{mi} - \omega)\) and \((\epsilon_{ni} - \omega)\) are indicated by crosses and the poles due to \((\epsilon_{ti} - 2\omega)\) are indicated by circles. The frequency range \(1 - 2\) a.u. was plotted as there are fewer pseudostates than just above threshold, and so it is easier to see each pole. In order to give the correct hyperpolarisability at frequencies above the ionisation threshold, we must remove the effect of these unphysical poles.

Figure 7.6: Plot of the hyperpolarisability of atomic hydrogen at frequencies above threshold without removing unphysical poles due to the pseudostates. The poles due to \((\epsilon_{mi} - \omega)\) and \((\epsilon_{ni} - \omega)\) in the denominator of the hyperpolarisability are indicated by crosses and the poles due to \((\epsilon_{ti} - 2\omega)\) are indicated by circles.

Let us first consider one of the simpler terms in the hyperpolarisability (item 4. in the list above), which has only one pole. We can remove this unphysical pole using the Principal Value theorem, to give

\[
\sum_{m,n,t} \frac{\langle i | r | m \rangle \langle m | r | t \rangle \langle t | r | n \rangle \langle n | r | i \rangle}{(\epsilon_{mi} - \omega)\epsilon_{ti}(\epsilon_{ni} + \omega)} = \sum_{m\neq j,n,t} \frac{\langle i | r | m \rangle \langle m | r | t \rangle \langle t | r | n \rangle \langle n | r | i \rangle}{(\epsilon_{mi} - \omega_{j})\epsilon_{ti}(\epsilon_{ni} + \omega_{j})} + i\pi \sum_{n,t} \frac{\langle i | r | j \rangle \langle j | r | t \rangle \langle t | r | n \rangle \langle n | r | i \rangle}{\epsilon_{ti}(\epsilon_{ni} + \omega_{j})} \tag{7.11}
\]

We can also apply the Principal Value theorem to the hyperpolarisability term which has both \((\epsilon_{mi} - \omega)\) and \((\epsilon_{ni} - \omega)\) in the denominator.
\[\sum_{m,n,t} |i| r |m\rangle \langle m | r |t\rangle \langle t | r | n\rangle \langle n | r | i\rangle \] 

\[
\frac{(\epsilon_{mi} - \omega)\epsilon_{ti}(\epsilon_{ni} - \omega)}{\epsilon_{mi} - \omega)\epsilon_{ti}(\epsilon_{ni} - \omega)} = \sum_{m\neq j,n\neq j,t} \frac{|i| r |m\rangle \langle m | r |t\rangle | t | r | n\rangle \langle n | r | i\rangle}{(\epsilon_{mi} - \omega)\epsilon_{ti}(\epsilon_{ni} - \omega)} \] 

\[+ i\pi \sum_{n,t} \frac{|i| r |j\rangle \langle j | r |t\rangle \langle t | r | n\rangle \langle n | r | i\rangle}{\epsilon_{ti}(\epsilon_{ni} - \omega)} \] 

\[= \sum_{m\neq j,n\neq j,t} \frac{|i| r |m\rangle \langle m | r |t\rangle | t | r | j\rangle \langle j | r | i\rangle}{(\epsilon_{mi} - \omega)\epsilon_{ti}} \] 

\[+ i\pi \sum_{n\neq j,t} \frac{|i| r |j\rangle \langle j | r |t\rangle \langle t | r | n\rangle \langle n | r | i\rangle}{\epsilon_{ti}^2} \] 

This gives us the expression

\[
\sum_{m,n,t} \frac{|i| r |m\rangle \langle m | r |t\rangle \langle t | r | n\rangle \langle n | r | i\rangle}{(\epsilon_{mi} - \omega)\epsilon_{ti}(\epsilon_{ni} - \omega)} = \sum_{m\neq j,n\neq j,t} \frac{|i| r |m\rangle \langle m | r |t\rangle | t | r | n\rangle \langle n | r | i\rangle}{(\epsilon_{mi} - \omega)\epsilon_{ti}(\epsilon_{ni} - \omega)} \] 

\[+ i\pi \sum_{n\neq j,t} \frac{|i| r |j\rangle \langle j | r |t\rangle \langle t | r | n\rangle \langle n | r | i\rangle}{\epsilon_{ti}^2} \] 

\[+ i\pi \sum_{m\neq j,t} \frac{|i| r |m\rangle \langle m | r |j\rangle \langle j | r | i\rangle}{(\epsilon_{mi} - \omega)\epsilon_{ti}} \] 

\[+ i\pi \sum_{m\neq j,t} \frac{|i| r |j\rangle \langle j | r |i\rangle \langle i | r | j\rangle \langle j | r | i\rangle}{\epsilon_{ti}} \] 

(7.13)

Let us now consider the term in the hyperpolarisability that has \((\epsilon_{mi} - \omega)(\epsilon_{ti} - 2\omega)(\epsilon_{ni} - \omega)\) in the
denominator. Applying the Principal Value theorem gives us

\[
\sum_{m,n,i} \frac{\langle i || r | m \rangle \langle m || r | t \rangle \langle t || r | n \rangle \langle n || r | i \rangle}{(\epsilon_{mi} - \omega)(\epsilon_{ti} - 2\omega)(\epsilon_{ni} - \omega)} = \sum_{m\neq j, n\neq j, t \neq j} \frac{\langle i || r | m \rangle \langle m || r | t \rangle \langle t || r | n \rangle \langle n || r | i \rangle}{(\epsilon_{mi} - \omega_j)(\epsilon_{ti} - 2\omega_j)(\epsilon_{ni} - \omega_j)}
\]

\[+ i\pi \sum_{n \neq t \neq j} \frac{\langle i || r | j \rangle \langle j || r | t \rangle \langle t || r | n \rangle \langle n || r | i \rangle}{(\epsilon_{mi} - \omega_j)(\epsilon_{ni} - \omega_j)}
\]

\[+ i\pi \sum_{m \neq j, n \neq j} \frac{\langle i || r | m \rangle \langle m || r | t \rangle \langle t || r | j \rangle \langle j || r | i \rangle}{(\epsilon_{mi} - \omega_j)(\epsilon_{ni} - 2\omega_j)}
\]

\[- \pi^2 \sum_{t \neq j} \frac{\langle i || r | j \rangle \langle j || r | n \rangle \langle n || r | i \rangle}{(\epsilon_{ti} - 2\omega_j)}
\]

\[+ i\pi \sum_{m \neq j, n \neq j} \frac{\langle i || r | m \rangle \langle m || r | j \rangle \langle j || r | n \rangle \langle n || r | i \rangle}{(\epsilon_{mi} - \omega_j)(\epsilon_{ni} - \omega_j)}
\]

\[- \pi^2 \sum_{n \neq j} \frac{\langle i || r | j \rangle \langle j || r | n \rangle \langle n || r | i \rangle}{(\epsilon_{mi} - \omega_j)}
\]

\[- \pi^2 \sum_{m \neq j} \frac{\langle i || r | m \rangle \langle m || r | j \rangle \langle j || r | n \rangle \langle n || r | i \rangle}{(\epsilon_{mi} - \omega_j)}
\]

\[- i\pi^3 \langle i || r | j \rangle \langle j || r | n \rangle \langle n || r | i \rangle \langle 2\omega + \epsilon_i \rangle \langle 2\omega + \epsilon_i || r | j \rangle \langle j || r | i \rangle.
\]

\[(7.15)\]

Previously I have shown that the imaginary polarisability above the ionisation threshold is related to the single photon ionisation cross-section and imaginary hyperpolarisability above the first ionisation threshold is related to the two-photon ionisation cross-section. It stands to reason that the imaginary hyperpolarisability terms at frequencies above the second ionisation threshold must also be related to some ionisation cross-section.

The imaginary hyperpolarisability above the first ionisation threshold had a simple relation to the two-photon ionisation cross-section (see Section 5.3). However, the hyperpolarisability above the second ionisation threshold is evidently not as simple, as it has imaginary terms that correspond to single and two photon absorption. These additional terms are related to corrections to the single photon ionisation cross-section [53]. Manakov et al. have computed the complex hyperpolarisability of hydrogen at frequencies both below and above the ionisation energy in 2004 [53] using the Sturmian expansion of the Coulomb Green’s function. In this paper they also discussed the meaning of the imaginary hyperpolarisability terms at frequencies above the second ionisation threshold. They have stated that the additional terms in the matrix elements, originating from the poles at \( \epsilon_{mi} - \omega, \epsilon_{ti} - 2\omega \) and \( \epsilon_{ni} - \omega \), give the correction term \( W^{(1-3)} \) to the single photon ionisation probability \( W_i \) such that [53]

\[ W_i = W^{(1)} + W^{(1-3)} \]

(7.16)

where \( W^{(1)} \) is the ionisation probability given by the imaginary polarisability.

The correction \( W^{(1-3)} \) can be negative, and so can diminish the total ionisation probability. This can
lead to an effect referred to as ‘stabilisation’, which describes a decrease in the rate of ionisation for increasing intensity, or a decrease in the total ionisation probability. Evidently there has been much interest in this stabilisation effect as several reviews have been written on this topic [194, 195]. In the future it may be worthwhile to extend our pseudostate method to the calculation of the imaginary hyperpolarisability above the second threshold, in order to consider the stabilisation effect in more detail. In the next, and last, Chapter I will briefly discuss other possible extensions to the method developed in this thesis, and summarise some the important aspects of the work presented in this thesis.
Chapter 8

Conclusion

In this thesis I have developed a pseudostate method for computing the various photon-atom scattering cross-sections. Our method involves calculation of the complex transition polarisabilities (Chapter 3) for frequencies both below and above ionisation threshold. I have presented a unified treatment of \( \text{Re} \{ \alpha_{ij}(\omega) \} \), \( \text{Im}_0 \{ \alpha_{ij}(\omega) \} \) and \( \text{Im}_1 \{ \alpha_{ij}(\omega) \} \), which allows us to compute the various single-photon scattering cross-sections (Chapter 4). I have extended our method to the calculation of complex hyperpolarisabilities which is used to compute the two-photon scattering cross-sections (Chapter 5). I have validated our method against previous calculations where possible and performed convergence studies. The method was first tested on atomic hydrogen, as this allowed us to do semi-analytical calculations for comparison as well (Chapter 2).

The advantage of our method is that it is very simple and intuitive and involves simply a sum over all states in our calculation. This means that our method can easily be extended to calculation of higher-order scattering processes (Chapter 5) and to other atoms (Chapter 6) as well. However, several important limitations of our method were found.

Previously we had shown that our Rayleigh scattering cross-section was completely converged and in good agreement with previous calculations for frequencies below threshold. I was also able to validate our Raman scattering cross-section for the 3s-3d transition in atomic hydrogen at frequencies above threshold. In Chapter 4 I present the 1s-2s Raman scattering cross-section in atomic hydrogen at frequencies above threshold calculated with both our semi-analytical and pseudostate method. To the best of my knowledge, this is the first calculation of the 1s-2s Raman scattering cross-section in atomic hydrogen above threshold. However, we find that there is a small residual error between our pseudostate and semi-analytical calculation for this cross-section, which I have not yet been able to resolve.

A significant limitation is the convergence (or lack there-of) in our Compton scattering cross-section calculation. At first I had studied the convergence of the single photon scattering cross-sections with respect to the number of basis functions \( N_\ell \) in our calculation, and showed that the Compton scattering cross-section appeared to be consistent for different \( N_\ell \). Though our Compton scattering cross-sections were much larger than the previous calculations, I was able to show that our Compton scattering cross-
sections and differential cross-sections are in good agreement with literature if the $\ell = 2$ states were neglected. This seemed to indicate that previous calculations have neglected the very large contribution from the $\ell = 2$ states.

The main difference between our Compton calculation and the other single-photon scattering cross-sections was the inclusion of free-to-free transition matrix elements. Our hyperpolarisability calculations also used these free-to-free transition matrix elements and was shown to be completely converged and in agreement with literature. This, as well as the convergence of the Compton scattering cross-section with respect to $N$, gave us confidence that our Compton scattering cross-sections must also be correct. Unfortunately, there is more to this story.

We have found that our Compton scattering cross-sections do not converge with respect to increasing box size. The radius of the box is governed by $\lambda_\ell$, where smaller $\lambda_\ell$ gives a bigger radius. The value of $\lambda_\ell$ is usually not expected to influence the outcome of the calculations, except for rate of convergence. As expected, varying $\lambda_\ell$ does not affect the Rayleigh and Raman scattering cross-sections or the hyperpolarisability. On the other hand, the total and differential Compton scattering cross-sections were shown to vary significantly as we changed $\lambda_\ell$. As yet I have been unable to determine the reason of this. Upon inspecting the differential Compton scattering cross-sections, I have found that the large $\ell = 2$ contribution to the Compton scattering cross-section was due to an anomalously high $\ell = 2$ contribution for outgoing photon frequencies approaching $\omega - \hbar \epsilon_{IP}$.

Perhaps the most important question to ask is whether it is even possible to compute the differential Compton scattering cross-section with our pseudostate method. We compute the differential cross-sections by finding the transition polarisability (for final state in the continuum with energy $\epsilon_j$) and using the relation (inspired from Raman),

$$d\sigma_C = \sigma_T \omega \omega' |\alpha_{ji}(\omega)|^2.$$  \hfill (8.1)

There are two main reasons we believe that our method should be able to compute $\alpha_{ji}(\omega)$ correctly, where $j$ is a pseudostate:

Firstly, Bachau et al. [65] used a very similar approach in 1990 to calculate the above threshold ionisation cross-section in hydrogen. This calculation also used a discrete basis and removed the intermediate state corresponding to an unphysical pole. This above threshold ionisation cross-section calculation essentially has the same properties as the transition polarisabilities needed in our Compton scattering cross-section calculation. As such, it indicates that our pseudostate calculation should, in principle, be able to compute these transition polarisabilities accurately.

Secondly, I have been able to compute the hyperpolarisability and show convergence with respect to both $N_\ell$ and $\lambda_\ell$. The same free-to-free transition matrix elements are used in this calculation as in our differential Compton calculation. As such, we would normally expect the transition polarisabilities to final states in the continuum to be converged.

Though we know that the same transition matrix elements are used in the hyperpolarisability and
Compton calculation, there is one major difference between the two. The hyperpolarisability calculation involves summing over all pseudostates, whereas the differential Compton scattering cross-section describes the transition to one specific pseudostate with an intermediate sum over pseudostates. As a consequence, the differential Compton scattering cross-section is dependent on the normalisation of the free-to-free transition matrix elements, whereas the hyperpolarisability is not. Upon closer investigation, I have found (see Fig. 4.37) that the free-to-free matrix elements are still dependent on $\lambda_\ell$ after I have applied the normalisation (dividing by energy density). This may be one of the reasons why our differential Compton scattering cross-sections are not converged with respect to $\lambda_\ell$.

I had originally attempted to verify our Compton scattering cross-sections by doing a quick semi-analytical calculation for hydrogen. However, this attempt was not successful as the integration involving free-to-free states was much more difficult than expected. This difficulty is also reflected in the literature, where only very few such semi-analytical calculations have been done. Verniard et al. [11] have been able to use this semi-analytical approach to compute the above threshold ionisation cross-section. Their semi-analytical method may also be a useful approach to consider in the future to check our Compton scattering cross-section calculations.

Another limitation of our method occurs in the calculation of hyperpolarisability and two-photon ionisation cross-section. In Chapter 7 I attempted to approximate the two-photon ionisation cross-section, but found that our results were in qualitative but not quantitative agreement with literature. In the future it would be useful to develop the pseudostate packing method, which would allow us to add extra pseudostates where necessary. Successful application of the pseudostate packing method would enable us to calculate the two-photon ionisation cross-section and imaginary hyperpolarisability at frequencies above the second ionisation threshold. As discussed in Chapter 7, this could give insight to some interesting physics, as the imaginary hyperpolarisability above the second threshold is related to both the single-photon ionisation cross-section and correction, as well as the two-photon ionisation cross-section.

8.1 Alternative Methods

The advantage of using pseudostates is that our method can be applied to any atom. As an example, the pseudostate method developed in this thesis was applied to metastable helium by Emily Kahl using a two-electron atomic structure code. Her data is in good agreement with the cross-sections given by my one-electron calculation, at least for lower frequencies (see Figs. 6.6 and 6.7).

The scattering cross-sections of ground state atomic helium is another interesting case to study, as like hydrogen, there have been only few calculations of these scattering cross-sections. One of the only cross-section calculations for helium was done by Grosges et al. [196], who have given the Compton scattering cross-section to be on the order of $1000\sigma_T$. This does not appear to be physical. Additionally, the calculations by Grosges et al. have large oscillations in the cross-sections above threshold, which are unexplained. Cross-sections have also been given by the FFAST database [2], but are not in agreement
with the data given by Grosges et al. [196]. This indicates that as yet the scattering cross-sections for helium are not known.

Since the cross-sections for He are not known, an ab-initio method for computing these photon-atom scattering cross-sections will be very useful. Two honours students have made independent attempts to apply my pseudostate method to atomic helium, using the two-electron finite-basis atomic structure code. Preliminary results of the first calculation of the helium scattering cross-sections (by E. Kahl) are presented in Fig. 8.1 and are compared with the previous calculation by Grosges et al. [196] and the scattering cross-section given by the FFAST database [2]. Though I have found good qualitative agreement between my calculation and FFAST data for atomic hydrogen, the cross-sections provided by E. Kahl for helium are not in agreement with the FFAST database. We need a better understanding of the calculations done in the FFAST database to determine why this disagreement occurs. Additionally, the Compton scattering cross-section presented by E. Kahl disagrees with the calculation by Grosges et al. [196] by several orders of magnitude. Though the preliminary data presented here seem to be consistent with the behaviour we have seen in hydrogen, the helium results should be handled with care, as several bugs have previously been found in this code.

Figure 8.1: Plot of the single photon scattering cross-sections (in units of $\sigma_T$) of ground state helium computed using our pseudostate method and a two-electron non-relativistic atomic structure code, computed by E. Kahl. The Rayleigh, Raman and Compton scattering cross-sections calculated by Grosges et al. [196] and the cross-sections for coherent and incoherent scattering given by the FFAST database [2] are also plotted. This plot was provided by E. Kahl.
Figure 8.2: Plot of the Compton scattering cross-section (in units of $\sigma_T$) of ground state helium computed using our pseudostate method and a two-electron non-relativistic atomic structure code, computed by G. Ruzzi Villacres. The Compton scattering cross-section is calculated with a basis set of $N_\ell = 50$ and $\lambda_\ell = 0.6, 0.7, 0.8, 0.9$ and 1.0. The Compton scattering cross-section calculated by Grosges et al. [196] is plotted.

G. Ruzzi Villacres has also (independently to E. Kahl) applied my pseudostate method to the calculation of helium, using the same energies and transition matrix elements as used by E. Kahl. However, his Compton scattering cross-section calculation gives a very different result (see Fig. 8.2), where the cross-section is of the same magnitude as those presented by Grosges et al. [196]. Like Grosges et al. [196], his Compton scattering cross-sections exhibit oscillations which vary significantly as we vary lambda. This indicates, that like hydrogen, the Compton scattering cross-sections calculated with our pseudostate method for helium are not physical. Since his code has been able to successfully reproduce my cross-sections for atomic hydrogen, we expect that the oscillations in helium are not due to a bug in the code. In order to gain a better understanding of the origin of these oscillations and the magnitude of the Compton scattering cross-section in helium, the differential Compton scattering cross-sections of helium will be investigated in the future.

The preliminary results given in Fig. 8.2 show very similar oscillatory behaviour to the data presented by Grosges et al. [196]. The oscillations in the Compton scattering cross-section are likely spurious, as these change significantly as lambda is varied. Due to the similarities between the calculation of G. Ruzzi Villacres and Grosges et al. [196], I would hypothesize that Grosges et al. [196] have also included a spurious contribution in their calculation. Evidently there have been only few calculations of the helium cross-sections, but even these should be investigated further.

My calculations as well as this calculation of ground state atomic helium is based on a non-relativistic atomic structure code, which means that the fine structure is not included in our cross-sections. Work
is also being done by E. Kahl on applying our pseudostate method to the relativistic multi-electron code known as AMBIT. Details of this atomic structure code is given in reference [197,198]. This should allow us to calculate more accurate scattering cross-sections that include relativistic effects and core electron physics.

The advantage of using pseudostates in our method is that we are able to apply our method to any atom. A potential alternative method we could use for frequencies above threshold, that also has the advantage of using pseudostates, is the complex rotation method. This method may be a useful alternative to the method I have developed in this thesis, as it should allow us to compute the complex polarisabilities at any frequency above threshold. Currently my method is limited to calculating the complex polarisability above threshold only at certain frequencies corresponding to pseudostate energies.

By rotating the coordinates into the complex plane, both our energies and transition matrix elements would be complex. This method was previously used by Pan et al. [12] to compute the complex second and fourth order energies in hydrogen at frequencies above threshold. In their calculation they avoided the sum-over-states by applying the Dalgarno-Lewis method. Once we have applied the complex rotation method, we can compute the the polarisabilities and hyperpolarisabilities the same way we do at frequencies below threshold, instead of applying the Dalgarno-Lewis method. Rescigno et al. [199] have also applied complex rotation method to find the complex polarisability. The advantage of applying the complex rotation method is that this removes the unphysical pole corresponding to a pseudostate, since the energy difference in the denominator is now complex. This method should allow us to compute both the hyperpolarisability and above-threshold ionisation cross-section at frequencies above the second ionisation threshold, and may be easier to implement than it would be to develop the pseudostate packing method. It may also be possible to extend this method to calculate the Raman and Compton scattering cross-sections.

8.2 Outlook

It is important to note that in all calculations in this thesis I have computed only one term in the interaction Hamiltonian, the \( p \cdot A \) interaction. It is known that the contribution from the \( A^2 \) interaction term is negligible at lower frequencies, so our assumption is valid near threshold. However, to describe the scattering accurately the \( A^2 \) term should also be included, particularly at high frequencies. In principle it should be possible to use the transition matrix elements and energies produced by \( p\cdot A \) to perform the \( A^2 \) scattering calculation. This may be an interesting direction to take in the future as it would allow us to directly compare the contribution of each interaction to the total scattering.

The pseudostate method developed in this thesis has a lot of potential, as it can be adapted and extended to calculations of other atomic properties and other atoms. Throughout this thesis I have considered only the scalar term of the polarisability and hyperpolarisability, as only \( s \)-state atoms were considered. However, it is also possible to compute the tensor terms with our method for linear, as well as
circular polarisation. Once fully implemented, the method developed in this thesis should be valid for any
atom. This method does require a set of pseudostates that give a good description of the continuum, in
order to calculate at frequencies above threshold. Of course, there are still problems that must be consid-
ered in multi-electron atoms, such as how to deal with autoionising states. Work is already in progress in
applying our pseudostate method to other atomic structure calculations and multi-electron atoms. Since
our method is quite simple and easily adaptable, it is suitable for easily running the cross-section calcu-
lations across many different atoms. A useful application of our method will be to build a cross-section
database to supplement the existing databases (e.g. XCOM, FFAST) of the $A^2$ scattering cross-sections.
Bibliography


[122] O Klein and Y Nishina. *On the Scattering of Radiation by free Electrons according to Dirac’s new relativistic Quantum Dynamics*, page 253. Translated by Dr Lars Bergström.


Appendix A

Derivation of Cross-section Formulae

In this Chapter I will present the derivation of the photoionisation and single-photon scattering cross-sections, as well as the polarisability using spherical tensor operators. I will draw on the textbooks by Friedrich [99, 200], Sakurai [35] and Band [201] in my derivation of the scattering cross-sections, and the angular momentum textbook by Zare [85] for the polarisability derivation. For completeness I have shown my derivation of the single-photon scattering cross-section expression in terms of transition polarisability in Section A.6 and derivation of the transition polarisability coefficients in Section A.7. As I will discuss in Section A.7, the expressions I have derived using LS-coupling matrix elements are not in agreement with expressions that I used in this thesis by Delserieys et al. [48], who have included fine-structure in their derivation.

In order to derive expressions for the single-photon scattering cross-sections, we require second-order time-dependent perturbation theory. I will introduce this briefly in the next section. Note that the derivations in Appendix A are done in SI units, as this allowed me to easily apply dimensional analysis. I have chosen to use SI units as this makes the derivation easier to follow than in atomic units, since factors like the electron charge $e$ are included in SI units but would be equal to 1 in atomic units. Therefore, factors such as electron charge would be hidden from the reader if the derivation were in atomic units. The formulae are converted to atomic units at the end of each derivation to be consistent with the system of units used in the main part of the thesis.

A.1 Time-Dependent Perturbation Theory

This follows the method as seen in Sakurai [35]. The atomic wavefunction is written as

$$|\psi\rangle = \sum_k c_k(t) |k\rangle e^{-iE_k t/\hbar},$$

(A.1)
where $|k\rangle$ is the eigenfunction and $E_k$ the energy of the unperturbed atom,

$$H |k\rangle = E_k |k\rangle . \tag{A.2}$$

Since we are considering a time-dependent hamiltonian, the time-dependent Schrödinger equation applies,

$$(H + H_{int}) |\psi\rangle = i \hbar \frac{\partial |\psi\rangle}{\partial t} , \tag{A.3}$$

and substituting Eqn. A.1 into the time-dependent Schrödinger equation gives

$$(H + H_{int}) \sum_k c_k |k\rangle e^{-iE_k t/\hbar} = i \hbar \sum_l \left( \dot{c}_l |l\rangle e^{-iE_l t/\hbar} - i \frac{E_l}{\hbar} c_l |l\rangle e^{-iE_l t/\hbar} \right) . \tag{A.4}$$

Expanding this gives simply

$$\sum_k H_{int} c_k |k\rangle e^{-iE_k t/\hbar} = i \hbar \sum_l \dot{c}_l |l\rangle e^{-iE_l t/\hbar} , \tag{A.5}$$

and multiplying by $\langle m|$ gives

$$\sum_k c_k \langle m| H_{int} |k\rangle e^{-iE_k t/\hbar} = i \hbar \dot{c}_m e^{-iE_m t/\hbar} , \tag{A.6}$$

so

$$\dot{c}_m = \frac{1}{i \hbar} \sum_k c_k \langle m| H_{int} |k\rangle e^{i(E_m - E_k) t/\hbar} = \frac{1}{i \hbar} \sum_k c_k \langle m| H_{int} |k\rangle e^{i\omega_{mk} t} . \tag{A.7}$$

Next we assume that at $t = 0$, the entire population is in a state $l$ ($c_l = 1$ and $c_m = 0$ where $m \neq l$). For first-order perturbation theory we assume that for a short time after the perturbation is turned on, $c_l \approx 1$, and $c_m$ is very small (where $m \neq l$). This approximation changes Eqn. A.7 to

$$\dot{c}_m = \frac{1}{i \hbar} \langle m| H_{int} |l\rangle e^{i\omega_{ml} t} . \tag{A.8}$$

The first-order approximation for $c_m(t)$ is then given by

$$c_m^{(1)}(t) = \frac{1}{i \hbar} \int_0^t \langle m| H_{int} |l\rangle e^{i\omega_{ml} t'} dt' . \tag{A.9}$$

We can now substitute the first-order approximation to $c_k$ back into Eqn. A.7, which gives

$$\dot{c}_m = \frac{1}{i \hbar} \langle m| H_{int} |l\rangle e^{i\omega_{ml} t} + \frac{1}{i \hbar} \sum_k c_k^{(1)} \langle m| H_{int} |k\rangle e^{i\omega_{mk} t} . \tag{A.10}$$
The second-order approximation is now given by

\[ c_m^{(2)}(t) = \frac{1}{i\hbar} \sum_k \int_0^t c_k^{(1)}(t'') \langle m|H_{\text{int}}|k \rangle e^{i\omega_{mk}t''} \, dt'' \]

(A.11)

\[ = \frac{1}{i\hbar} \sum_k \int_0^t \langle m|H_{\text{int}}|k \rangle e^{i\omega_{mk}t''} \int_0^{t''} \frac{1}{i\hbar} \langle k|H_{\text{int}}|l \rangle e^{i\omega_{kl}t'} \, dt' \, dt''. \]

(A.12)

This second-order approximation will be used in our derivation of the single-photon scattering cross-section.

\section*{A.2 Transitions involving a single Photon}

The photon-atom interaction Hamiltonian is given by

\[ H_{\text{int}} = -\frac{e}{m_c} \mathbf{p} \cdot \mathbf{A} + \frac{e^2}{2m_c c^2} A^2, \]

(A.13)

where \( \mathbf{p} \) is the momentum operator, \( \mathbf{A} \) is the vector potential, \( m_c \) is the electron mass and \( e \) is the electric charge of an electron. Second quantisation of the radiation field gives the vector potential to be

\[ A(r,t) = cA_0 \sum_k \frac{1}{\sqrt{\alpha}} \left[ \sum_{\alpha=1}^{2} \left( a_{k,\alpha}(t)e^{(\alpha)}e^{ik \cdot r} + a^+_{k,\alpha}(t)e^{(\alpha)}e^{-ik \cdot r} \right) \right], \]

(A.14)

where the creation and annihilation operators are given by

\[ a^+_{k,\alpha}(t) = a^+_{k,\alpha}(0)e^{i\omega t}, \]

(A.15)

\[ a_{k,\alpha}(t) = a_{k,\alpha}(0)e^{-i\omega t}. \]

(A.16)

\( \mathbf{k} \) refers to the wavevectors of E.M. modes, \( \omega \) to the corresponding photon frequency and \( e^{(\alpha)} \) refers to the polarisation vectors \( (\alpha = 1, 2) \) that are perpendicular to \( \mathbf{k} \) and each other. The \( A^2 \) term involves the terms \( a_{k,\alpha}a_{k',\alpha}, a_{k,\alpha}a^+_{k',\alpha}, a^+_{k,\alpha}a_{k',\alpha} \) and \( a^+_{k,\alpha}a^+_{k',\alpha} \) which results in a change of 0 or \( \pm 2 \) photons.

Various forms of \( A_0 \) have been presented in literature. For example, Sakurai [35] gives \( A_0 = \sqrt{\hbar/2V} \), whilst Band [201] gives \( A_0 = \sqrt{2\pi \hbar/V} \) which is different by a factor of \( \sqrt{4\pi} \). This difference in \( A_0 \) is due to difference in the units used in these references. Sakurai [35] uses Heavyside-Lorentz rationalised units, where the fine-structure constant is \( \alpha = e^2/4\pi \hbar c \). Band [201] uses Gaussian units, where \( \alpha = e^2/\hbar c \). In our derivation we will use SI units, where the fine structure is given by \( \alpha = e^2/4\pi \varepsilon_0 \hbar c \) [35]. Regardless of the system of units, the fine-structure constant is the same value \( (\alpha \approx 1/137) \) as it is dimensionless.

Though the value of the fine-structure constant is the same for all system of units, it is important that the formula is consistent with the system of units. Here I have chosen to use SI units for my derivation, as I felt it was important to include in my derivation all factors \( (\varepsilon_0, \hbar, e) \) which would be equal to 1 in atomic
units and vanish. However, the formulae will be converted to atomic units at the end of each derivation.

We need to ensure that the same units are used throughout our derivation in order to give the correct results. For example, the classical electron radius is given by \( r_e = e^2 / 4\pi m_e c^2 \) in the units used by Sakurai [35], whereas \( r_e = e^2 / m_e c^2 \) in Gaussian units. As our derivation is in SI units, we will use \( A_0 = \sqrt{2\pi \hbar / 4\pi \varepsilon_0 V} \) and \( r_e = e^2 / 4\pi \varepsilon_0 m_e c^2 \). I will convert to atomic units only at the very end of each derivation.

If we consider the absorption of one photon, only the \( \mathbf{p} \cdot \mathbf{A} \) term is relevant because this term describes a process with a net change of \( \pm 1 \) photon. The initial (and final) state is a direct product of the state vector of the atom and the state vector of the photon, \( |A; n_k, \alpha \rangle \) where \( n_k, \alpha \) refers to the number of photons characterised by a specific \( k, \alpha \). The matrix element of a transition for an atom initially in state \( A \) to state \( B \) by absorption of one photon characterised by a specific \( k, \alpha \) is

\[
\langle B; n_{k, \alpha} - 1 | H_{\text{int}} | A; n_{k, \alpha} \rangle = -\frac{e}{m_e c} \langle B; n_{k, \alpha} - 1 | \mathbf{p} \cdot \mathbf{A} | A; n_{k, \alpha} \rangle,
\]

where \( k = \omega / c \).

The \( \mathbf{p} \cdot \mathbf{A} \) term in the interaction Hamiltonian can be written in terms of the electric field \( \mathbf{E} \) and the position operator \( \mathbf{r} \), such that [201]

\[
-\frac{e}{m_e c} \mathbf{p} \cdot \mathbf{A} = -e \mathbf{r} \cdot \mathbf{E}.
\]

since the vector potential is related to the quantised electric field by

\[
-\frac{1}{c} \frac{\partial \mathbf{A}}{\partial t} = \mathbf{E}(\mathbf{r}, t) = iA_0 \sum_k \sqrt{\omega} \left[ \sum_{\alpha = 1}^2 \left( a_{k, \alpha} e^{-i\omega t} e^{i \mathbf{k} \cdot \mathbf{r}^{(\alpha)}} - a_{k, \alpha}^+ e^{i\omega t} e^{-i \mathbf{k} \cdot \mathbf{r}^{(\alpha)}} \right) \right].
\]

The matrix element describing the transition from state \( A \) to state \( B \) through the absorption of a single photon of wavevector \( \mathbf{k} \) (where \( k = \omega / c \)) is now given by

\[
\langle B; n_{k, \alpha} - 1 | H_{\text{int}} | A; n_{k, \alpha} \rangle = iA_0 \sqrt{\omega} \sum_{\alpha} \langle B | e^{i \mathbf{k} \cdot \mathbf{r}^{(\alpha)}} | A \rangle e^{-i\omega t}.
\]

If we assume that the photon wavelength is much larger than the size of the atom, then we can apply the dipole approximation \( e^{i \mathbf{k} \cdot \mathbf{r}} \approx 1 \). The matrix element for transition from atomic state \( A \) to \( B \) through absorption of one photon is thus

\[
\langle B; n_{k, \alpha} - 1 | H_{\text{int}} | A; n_{k, \alpha} \rangle \approx ieA_0 \sqrt{\omega} \sum_{\alpha} \langle B | \mathbf{r}^{(\alpha)} | A \rangle e^{-i\omega t}.
\]

### A.3 Single Photon Absorption Cross-section

In Appendix A.1 expressions were derived for \( c_m^{(1)}(t) \) and \( c_m^{(2)}(t) \) using first-and second-order time-dependent perturbation theory respectively. Here we use the first-order expression to find the cross-section
of single photon absorption by an atom. As this involves the absorption of only a single photon, only the $\frac{e}{m_e c} \mathbf{p} \cdot \mathbf{A}$ term in the interaction Hamiltonian is relevant. The transition matrix element describing the absorption of one photon of energy $\hbar \omega$ and polarisation $\alpha$ is given by

$$\langle B; n_{k, \alpha k} - 1 | - \frac{e}{m_e c} \mathbf{p} \cdot \mathbf{A} | A; n_{k, \alpha k} \rangle \simeq i e A_0 \sqrt{\omega} \langle B | \mathbf{r} \cdot \mathbf{e}(\alpha) | A \rangle e^{-i \omega t}.$$  \hspace{2cm} (A.22)

For simplicity, let us write this transition matrix element as

$$\langle B; n_{k, \alpha k} - 1 | - \frac{e}{m_e c} \mathbf{p} \cdot \mathbf{A} | A; n_{k, \alpha k} \rangle = T_{BA} e^{-i \omega t}.$$  \hspace{2cm} (A.23)

This can then be substituted into Eqn. A.9 to give

$$c_m^{(1)}(t) = \frac{1}{i \hbar} \int_0^t \langle m | H_{ml} | l \rangle e^{i \omega_{ml} t'} dt' = \frac{1}{i \hbar} T_{ml} \int_0^t e^{i(\omega_{ml} - \omega)t'} dt'.$$  \hspace{2cm} (A.24)

The transition probability is given by

$$|c_m^{(1)}(t)|^2 = \frac{1}{\hbar^2} |T_{ml}|^2 \left| \int_0^t e^{i(\omega_{ml} - \omega)t'} dt' \right|^2.$$  \hspace{2cm} (A.25)

The amplitude can be written as

$$\left| \int_0^t e^{i(\omega_{ml} - \omega)t'} dt' \right|^2 \simeq \left| \frac{e^{i(\omega_{ml} - \omega)t}}{i(\omega_{ml} - \omega)} - \frac{1}{i(\omega_{ml} - \omega)} \right|^2 = \left| e^{i(\omega_{ml} - \omega)t/2} \left[ \frac{e^{i(\omega_{ml} - \omega)t/2}}{i(\omega_{ml} - \omega)} - \frac{e^{-i(\omega_{ml} - \omega)t/2}}{i(\omega_{ml} - \omega)} \right] \right|^2$$

$$= \frac{4 \sin^2(\omega_{ml} - \omega)t/2}{(\omega_{ml} - \omega)^2 t},$$  \hspace{2cm} (A.26)

since $\sin(\alpha) = (e^{i\alpha} - e^{-i\alpha})/2i$. Assuming long time $t$, and using $\alpha = t/2\hbar$ and $x = \varepsilon_{ml} - \hbar \omega$, gives

$$\frac{1}{t} \left| \int_0^t e^{i(\omega_{ml} - \omega)t'} dt' \right|^2 \simeq 2\hbar \sin^2(x\alpha/\alpha^2) = 2\hbar \pi \delta(x),$$  \hspace{2cm} (A.28)

given the identity,

$$\lim_{\alpha \to \infty} \frac{\sin^2(\alpha x)}{\alpha^2} = \pi \delta(x).$$  \hspace{2cm} (A.29)

The transition probability for absorption of one photon $\omega$ can now be written as

$$|c_m^{(1)}(t)|^2 = \frac{1}{\hbar^2} |T_{ml}|^2 2\pi \hbar \delta(x) t = \frac{2\pi}{\hbar} |T_{ml}|^2 \delta(\varepsilon_{ml} - \hbar \omega) t.$$  \hspace{2cm} (A.30)
A.3. Single Photon Absorption Cross-section

The transition rate \( w_{ml} \) is given by

\[
w_{ml} = \frac{|c^{(1)}_{ml}(t)|^2}{t} = \frac{2\pi}{\hbar}|T_{ml}|^2 \delta(\varepsilon_{ml} - \hbar \omega),
\]  

(A.31)

which is known as Fermi’s golden rule. Substituting the transition matrix element \( T_{ml} \) for the absorption of a single photon gives

\[
w_{ml} = \frac{2\pi}{\hbar} ieA_0 \sqrt{\omega} \langle m | \mathbf{r} \cdot \mathbf{e}^{(\alpha)} | l \rangle^2 \delta(\varepsilon_{ml} - \hbar \omega) = \frac{2\pi A_0^2}{\hbar^2} \omega e^2 | \langle m | \mathbf{r} \cdot \mathbf{e}^{(\alpha)} | l \rangle|^2 \delta(\varepsilon_{ml} - \hbar \omega),
\]  

(A.32)

which is independent of time \( t \). This transition rate can be converted to a cross-section by dividing by photon flux, \( c/V \), such that

\[
\sigma_{ml} = \frac{\hbar \omega (4\pi^2) \alpha | \langle m | \mathbf{r} \cdot \mathbf{e}^{(\alpha)} | l \rangle|^2 \delta(\varepsilon_{ml} - \hbar \omega)}{V c} = \frac{\omega}{c} \frac{4\pi^2 A_0^2}{\hbar^2} \omega e^2 | \langle m | \mathbf{r} \cdot \mathbf{e}^{(\alpha)} | l \rangle|^2 \delta(\varepsilon_{ml} - \hbar \omega),
\]  

(A.33)

is the absorption cross-section describing the process where the absorption of a single photon results in a transition from state \( l \) to state \( m \). To simplify the expression, let us write it in terms of the fine-structure constant, \( \alpha = \frac{e^2}{(4\pi \varepsilon_0) \hbar c} \), so

\[
\sigma_{ml} = \hbar \omega (4\pi^2) \alpha | \langle m | \mathbf{r} \cdot \mathbf{e}^{(\alpha)} | l \rangle|^2 \delta(\varepsilon_{ml} - \hbar \omega).
\]  

(A.34)

Let us convert \( \sigma_{ml} \) into units of \( a_0^2 \), where \( a_0 = \alpha^2 \hbar/mc \). The cross-section \( \bar{\sigma}_{ml} \) is then given by

\[
\bar{\sigma}_{ml} = \frac{a_0^2}{a_0^2} \times \hbar \omega (4\pi^2) \alpha | \langle m | \mathbf{r} \cdot \mathbf{e}^{(\alpha)} | l \rangle|^2 \delta(\varepsilon_{ml} - \hbar \omega) = a_0^2 \hbar \omega (4\pi^2) \frac{m_e c^2}{\alpha^2 \hbar^2} | \langle m | \mathbf{r} \cdot \mathbf{e}^{(\alpha)} | l \rangle|^2 \delta(\varepsilon_{ml} - \hbar \omega).
\]  

(A.35)

Now let us convert \( \omega \), \( | \langle m | \mathbf{r} \cdot \mathbf{e}^{(\alpha)} | l \rangle| \) and \( \delta(\varepsilon_{ml} - \hbar \omega) \) from SI units to atomic units. \( \hbar \omega \) is in unit of energy, and is related to the frequency in atomic units \( \tilde{\omega} \) by \( \tilde{\omega} = \hbar \omega / E_h \), where the Hartree energy is given by \( E_h = \alpha^2 m_e c^2 \). The delta function \( \delta(\varepsilon_{ml} - \hbar \omega) \) is in units of inverse energy, so in atomic units is given by \( \delta(\tilde{\varepsilon}_{ml} - \tilde{\omega}) = \delta(\varepsilon_{ml} - \hbar \omega) E_h \). Finally, the transition matrix element is given in units of length, which is in atomic units given by \( | \tilde{T}_{ml} |^2 = | \langle m | \mathbf{r} \cdot \mathbf{e}^{(\alpha)} | l \rangle |^2 = | \langle m | \mathbf{r} \cdot \mathbf{e}^{(\alpha)} | l \rangle |^2 / a_0^2 \), where \( a_0 = \alpha^2 \hbar/m_e c \). Converting each term to atomic units gives

\[
\bar{\sigma}_{ml} = 4\pi^2 \frac{m_e c^2}{\alpha^2 \hbar^2} (\tilde{\omega} \alpha^2 m_e c^2) \left( | \tilde{T}_{ml} |^2 \frac{\alpha^6 \hbar^2}{m_e c^2} \right) \left( \frac{\delta(\tilde{\varepsilon}_{ml} - \tilde{\omega})}{\alpha^2 m_e c^2} \right) a_0^2 = 4\pi^2 \alpha \tilde{\omega} | \tilde{T}_{ml} |^2 \delta(\tilde{\varepsilon}_{ml} - \tilde{\omega}) a_0^2.
\]  

(A.36)

This cross-section is best written in terms of the Thomson cross-section,

\[
\sigma_T = \frac{8\pi}{3} \alpha^4 a_0^2,
\]  

(A.37)
so the absorption cross-section from state $|l\rangle$ to state $|m\rangle$ is

$$
\bar{\sigma}_{ml} = \bar{\omega} \frac{3\pi}{2} \frac{1}{\alpha^3} \sigma_T |\langle m | \mathbf{r} \cdot \mathbf{e}^{(\alpha)} | l \rangle|^2 \delta(\bar{\epsilon}_{ml} - \bar{\omega}) = \bar{\omega} \frac{3\pi}{2} c^3 \sigma_T |\langle m | \mathbf{r} \cdot \mathbf{e}^{(\alpha)} | l \rangle|^2 \delta(\bar{\epsilon}_{ml} - \bar{\omega}) .
$$

(A.38)

Note that for the main part of this thesis these bars (indicating atomic units) are implicit and all expressions are in atomic units.

### A.4 Single Photon Ionisation Cross-section

The photoionisation cross-section can be found using a similar derivation as was used for the absorption cross-section in Appendix A.3. The absorption cross-section describes the process where the atom absorbs a photon and ends in a final bound state $m$, whilst the photoionisation cross-section describes the processes where a photon is absorbed and the atom is ionised. To find the total probability per unit time $w_{ij}$ for a transition to all possible final states with energy $\epsilon_j$, we must integrate over the final state energy such that (e.g. see Eqn. 2.138 in Friedrich [200])

$$
w_{ji} = \int_0^\infty \frac{2\pi}{\hbar} |T_{ji}|^2 \rho(\epsilon_j) \delta(\epsilon_{ji} - \hbar\omega) d\epsilon_j ,
$$

(A.39)

where $\rho(\epsilon_j)$ is the density of the final states, where $\rho(\epsilon_j) = 1$ [200]. This then gives a transition probability per unit time as

$$
w_{ji} = \frac{2\pi}{\hbar} |T_{ji}|^2 = \frac{4\pi^2 \omega}{4\pi\epsilon_0 V} e^2 |\langle \epsilon_j | \mathbf{r} \cdot \mathbf{e}^{(\alpha)} | i \rangle|^2 ,
$$

(A.40)

and dividing by photon flux ($c/V$) gives the photoionisation cross-section

$$
\sigma_I(\omega) = \omega \frac{4\pi^2}{4\pi\epsilon_0 c} e^2 |\langle \epsilon_j | \mathbf{r} \cdot \mathbf{e}^{(\alpha)} | i \rangle|^2 ,
$$

(A.41)

which is effectively the same as the absorption cross-section given in Eqn. A.38, but without the delta function.

Let us convert this into atomic units, by first rewriting the cross-section in terms of $a_0^2$,

$$
\bar{\sigma}_I(\omega) = \hbar \omega 4\pi^2 \frac{m_e^2 c^2}{\alpha^5 \hbar^2} |\langle \epsilon_j | \mathbf{r} \cdot \mathbf{e}^{(\alpha)} | i \rangle|^2 a_0^2 .
$$

(A.42)

Note that, due to normalisation of the continuum function, this transition matrix element has dimension of length times inverse square root energy. See Friedrich [200] for more discussion on this. Therefore, the transition matrix element must be converted to atomic units by $|\bar{T}_{\epsilon j}|^2 = |\langle \epsilon_j | \mathbf{r} \cdot \mathbf{e}^{(\alpha)} | i \rangle|^2 = |\langle \epsilon_j | \mathbf{r} \cdot \mathbf{e}^{(\alpha)} | i \rangle|^2 E_{\hbar}/a_0^2 = |\langle \epsilon_j | \mathbf{r} \cdot \mathbf{e}^{(\alpha)} | i \rangle|^2 E_{\hbar} (m_e^2 c^2/\alpha^6 \hbar^2)$. $\bar{\omega}$ is given in atomic units by $\bar{\omega} = \hbar \omega / E_{\hbar} =$
where \( \varepsilon \). Therefore, the cross-section can now be written (in atomic units) as

\[
\bar{\sigma}_{i}(\omega) = 4\pi^{2}\left(\frac{\alpha\langle i|\mathbf{e}(\alpha)|i\rangle}{\omega} \right) \left(\frac{\hat{T}_{\omega,\omega}^{|i\rangle}}{2\hbar m_{c}c} \right)^{2} a_{0}^{2} = 4\pi^{2}\alpha|\langle e_{j}|\mathbf{r} \cdot \mathbf{e}(\alpha)|i\rangle|^{2} a_{0}^{2}, \tag{A.43}
\]

where \( \alpha \) is the fine-structure constant.

The imaginary polarisability \( \text{Im} \left[ \alpha_{ij}(\omega) \right] \) is derived in Section 2.4 and originates from removing the poles in the continuum. This imaginary polarisability is given (in atomic units) by

\[
\text{Im} \left[ \alpha_{ij}(\omega) \right] = \pi |\langle e_{j}|\mathbf{r} \cdot \mathbf{e}(\alpha)|i\rangle|^{2}, \tag{A.44}
\]

where \( \varepsilon_{j} = \varepsilon_{i} + \omega \). Upon comparison of Eqns. A.43 and A.44, we see that \( \text{Im} \left[ \alpha_{ij}(\omega) \right] \) can be related to the photoionisation cross-section by [102]

\[
\bar{\sigma}_{i}(\omega_{j}) = 4\pi\alpha_{ij}\text{Re} \left[ \alpha_{ij}(\omega_{j}) \right] a_{0}^{2} = \frac{3}{2} \alpha^{3} \sigma_{T} \alpha_{ij} \text{Im} \left[ \alpha_{ij}(\omega_{j}) \right], \tag{A.45}
\]

which, in atomic units, is

\[
\bar{\sigma}_{i}(\omega_{j}) = \frac{3}{2} \alpha^{3} \alpha_{ij} \text{Im} \left[ \alpha_{ij}(\omega_{j}) \right]. \tag{A.46}
\]

Note that for the main part of this thesis these bars (indicating atomic units) are implicit and all expressions are in atomic units.

### A.5 Derivation of the Kramers-Heisenberg Formula

Let us now consider the differential cross-section for the process where an atom initially in state \( i \) absorbs then emits a photon (and vice-versa) and ends in state \( j \) (i.e. there is no net change in photon number). The process involves the absorption of photon with frequency \( \omega \) and polarisation \( \mathbf{e}(\alpha) \) and the emission of a photon of frequency \( \omega' \) and polarisation \( \mathbf{e}(\alpha') \). First-order perturbation theory is needed to find the contribution from the \( \mathbf{A} \cdot \mathbf{A} \) term (not considered here), and second-order perturbation theory for the \( \mathbf{p} \cdot \mathbf{A} \) term.

In Appendix A.1, we found that second-order perturbation theory gives us

\[
c^{(2)}_{i}(t) = \frac{1}{\hbar^{2}} \sum_{n} \int_{0}^{t} \langle j|H_{\text{int}}|n\rangle e^{i\omega_{n}t'} \int_{0}^{t'} \frac{1}{\hbar} \langle n|H_{\text{int}}|i\rangle e^{i\omega_{n}t'} dt' dt'', \tag{A.47}
\]

where the transition matrix element has been previously considered in A.2, and gives

\[
c^{(2)}_{i}(t) = \frac{1}{\hbar^{2}} \sum_{n} \left[ \frac{\langle j|H_{\text{int}}|n\rangle e^{i\omega_{n}t'} \langle n|H_{\text{int}}|i\rangle e^{i\omega_{n}t'}}{\alpha_{ij}(\omega_{n})} \right] \int_{0}^{t} e^{i(\omega_{n}+\omega'-\omega)t'} dt'. \tag{A.48}
\]
The transition probability per unit time is then given by

$$\frac{|c_i^{(2)}(t)|^2}{t} = \frac{e^A_0 A_0^4 \omega \omega'}{\hbar^2 t} \sum_n \left[ \frac{\langle j | \ell_j m_j | (r \cdot e^{(\alpha)}) | n \ell_n m_n \rangle \langle n \ell_n m_n | (r \cdot e^{(\alpha')}) | i \ell_i m_i \rangle}{(\varepsilon_n - \varepsilon_i - \hbar \omega)} + \frac{\langle j | \ell_j m_j | (r \cdot e^{(\alpha')}) | n \ell_n m_n \rangle \langle n \ell_n m_n | (r \cdot e^{(\alpha)}) | i \ell_i m_i \rangle}{(\varepsilon_n - \varepsilon_i - \hbar \omega)} \right]^2 \left| \int_0^t e^{i(\omega_j + \omega' - \omega)t'} dt' \right|^2$$

(A.49)

where we can apply the approximation (see Eqn. A.28)

$$\left| \int_0^t e^{i(\omega_j + \omega' - \omega)t'} dt' \right|^2 \approx 2\pi \delta(\varepsilon_j + \hbar \omega' - \hbar \omega)\hbar$$

(A.50)

for long time $t$. The transition probability per unit time from state $i$ to state $j$ is now independent of time and is given by

$$\frac{|c_i^{(2)}(t)|^2}{t} = \frac{e^A_0 A_0^4 \omega \omega'}{\hbar} \sum_n \left[ \frac{\langle j | \ell_j m_j | (r \cdot e^{(\alpha)}) | n \ell_n m_n \rangle \langle n \ell_n m_n | (r \cdot e^{(\alpha')}) | i \ell_i m_i \rangle}{(\varepsilon_n - \varepsilon_i - \hbar \omega)} + \frac{\langle j | \ell_j m_j | (r \cdot e^{(\alpha')}) | n \ell_n m_n \rangle \langle n \ell_n m_n | (r \cdot e^{(\alpha)}) | i \ell_i m_i \rangle}{(\varepsilon_n - \varepsilon_i - \hbar \omega)} \right]^2 2\pi \delta(\omega_j + \omega' - \omega),$$

(A.51)

where the delta function sets $\omega' = \omega - \omega_j$.

In order to take into account the scatter over all possible outgoing photon energies, we must multiply the transition probability by the density of states per unit energy $d^3 \rho(\hbar \omega')/d\omega'$ and integrate over the outgoing energy [201]. The density of states per unit energy is given by [201]

$$\frac{d^3 \rho(\hbar \omega')}{d\omega'} = \frac{V}{(2\pi)^3} \frac{d^3 k'}{d\omega'} = \frac{V k^2 dk d\Omega}{(2\pi)^3 d\omega'} = \frac{V \omega^2}{\hbar(2\pi)^3 c^3} d\Omega,$$

(A.52)

so the transition probability is given by

$$w_{ij} = \int_0^\infty \frac{|c_i^{(2)}(t)|^2}{t} \rho_{\hbar \omega'} d(\hbar \omega')$$

(A.53)

$$= \int_0^\infty e^A_0 A_0^4 \omega \omega' \frac{1}{\hbar} \sum_n \left[ \frac{\langle j | \ell_j m_j | (r \cdot e^{(\alpha)}) | n \ell_n m_n \rangle \langle n \ell_n m_n | (r \cdot e^{(\alpha')}) | i \ell_i m_i \rangle}{(\varepsilon_n - \varepsilon_i - \hbar \omega)} + \frac{\langle j | \ell_j m_j | (r \cdot e^{(\alpha')}) | n \ell_n m_n \rangle \langle n \ell_n m_n | (r \cdot e^{(\alpha)}) | i \ell_i m_i \rangle}{(\varepsilon_n - \varepsilon_i - \hbar \omega)} \right]^2 2\pi \delta(\omega_j + \omega' - \omega) \frac{V \omega^2}{\hbar(2\pi)^3 c^3} d\Omega.$$

(A.54)

As the integral has the delta function $\delta(\omega_j + \omega' - \omega)$, $w_{ij}$ is simply
The transition rate can be converted to cross-section by dividing by the incident photon flux, so the differential cross-section expression can be written as

\[
\frac{d\sigma_{ij}}{d\Omega} = e^4 \frac{\omega \omega'}{(4\pi\varepsilon_0)^2 c^3 V} \left| \sum_n \left[ \frac{\langle j\ell_j m_j | (r \cdot e^{(\alpha)}) | n\ell_n m_n \rangle \langle n\ell_n m_n | (r \cdot e^{(\alpha')}) | i\ell_i m_i \rangle}{\varepsilon_n - \varepsilon_i - \hbar \omega} + \frac{\langle j\ell_j m_j | (r \cdot e^{(\alpha')}) | n\ell_n m_n \rangle \langle n\ell_n m_n | (r \cdot e^{(\alpha)}) | i\ell_i m_i \rangle}{\varepsilon_n - \varepsilon_i + \hbar \omega'} \right] \right|^2 d\Omega ,
\]

where \( \omega' = \omega - \omega_i \). The transition rate per unit solid angle is then

\[
\frac{w_{ij}}{d\Omega} = e^4 \frac{\omega \omega'}{(4\pi\varepsilon_0)^2 c^3 V} \left| \sum_n \left[ \frac{\langle j\ell_j m_j | (r \cdot e^{(\alpha)}) | n\ell_n m_n \rangle \langle n\ell_n m_n | (r \cdot e^{(\alpha')}) | i\ell_i m_i \rangle}{\varepsilon_n - \varepsilon_i - \hbar \omega} + \frac{\langle j\ell_j m_j | (r \cdot e^{(\alpha')}) | n\ell_n m_n \rangle \langle n\ell_n m_n | (r \cdot e^{(\alpha)}) | i\ell_i m_i \rangle}{\varepsilon_n - \varepsilon_i + \hbar \omega'} \right] \right|^2 .
\]

The transition rate can be converted to cross-section by dividing by the incident photon flux \((c/V)\), so

\[
\frac{d\sigma_{ij}}{d\Omega} = e^4 \frac{\omega \omega'}{(4\pi\varepsilon_0)^2 c^4} \left| \sum_n \left[ \frac{\langle j\ell_j m_j | (r \cdot e^{(\alpha)}) | n\ell_n m_n \rangle \langle n\ell_n m_n | (r \cdot e^{(\alpha')}) | i\ell_i m_i \rangle}{\varepsilon_n - \varepsilon_i - \hbar \omega} + \frac{\langle j\ell_j m_j | (r \cdot e^{(\alpha')}) | n\ell_n m_n \rangle \langle n\ell_n m_n | (r \cdot e^{(\alpha)}) | i\ell_i m_i \rangle}{\varepsilon_n - \varepsilon_i + \hbar \omega'} \right] \right|^2 .
\]

The classical electron radius, \( r_e \), is given by

\[
r_e = \frac{e^2}{(4\pi\varepsilon_0)me^2} ,
\]

so the differential cross-section expression can be written as

\[
\frac{d\sigma_{ij}}{d\Omega} = \omega \omega' r_e^2 \left| \sum_n \left[ \frac{\langle j\ell_j m_j | (r \cdot e^{(\alpha)}) | n\ell_n m_n \rangle \langle n\ell_n m_n | (r \cdot e^{(\alpha')}) | i\ell_i m_i \rangle}{\omega_{ni} - \omega} + \frac{\langle j\ell_j m_j | (r \cdot e^{(\alpha')}) | n\ell_n m_n \rangle \langle n\ell_n m_n | (r \cdot e^{(\alpha)}) | i\ell_i m_i \rangle}{\omega_{ni} + \omega'} \right] \right|^2 .
\]

**A.6 Polarisation**

In order to integrate the Kramers-Heisenberg expression (Eqn. A.59) over solid angle, we must consider the polarisation of the incident and emitted photon. The propagation direction of the incident photon is given by \( \mathbf{k} \) and the polarisation by \( e^{(\alpha)} \) where \( \alpha = 1, 2 \) and all three vectors are perpendicular to each other. Here we denote the propagation direction of the outgoing photon by \( \mathbf{k}' \) and the polarisation by \( e^{(\alpha')} \).

The relation between the vectors \( \mathbf{r}, \mathbf{k} \) and \( e^{(\alpha)} \) are depicted in Fig. A.1. The same relation holds for
the vectors $\mathbf{r}$, $\mathbf{k}$ and $\mathbf{e}^{(\alpha)'}$.

Figure A.1: Diagram showing relation between $\mathbf{r}$, $\mathbf{k}$ and $\mathbf{e}^{(\alpha)}$ vectors.

For now let us write the Kramers-Heisenberg expression given in Eqn. A.59 in a more compact form, so

$$
\frac{d\sigma_{ij}}{d\Omega} = \omega \omega' r^2 e \left| \langle j | (\mathbf{r} \cdot \mathbf{e}^{(\alpha)}) \lambda_n (\mathbf{r} \cdot \mathbf{e}^{(\alpha)'}) | i \rangle + \langle j | (\mathbf{r} \cdot \mathbf{e}^{(\alpha)'}) \lambda_{n'} (\mathbf{r} \cdot \mathbf{e}^{(\alpha)}) | i \rangle \right|^2,
$$

(A.60)

where

$$
\lambda_n = \sum_n \frac{|n\ell_n m_n\rangle \langle n\ell_n m_n|}{\varepsilon_n - \varepsilon_i - \hbar \omega},
$$

(A.61)

and

$$
\lambda_{n'} = \sum_n \frac{|n\ell_n m_n\rangle \langle n\ell_n m_n|}{\varepsilon_n - \varepsilon_i + \hbar \omega'}.
$$

(A.62)

From Fig. A.1, we can see that $\mathbf{r} \cdot \mathbf{e}^{(\alpha)}$ is given by

$$
\mathbf{r} \cdot \mathbf{e}^{(1)} = r \sin \theta \cos \phi,
$$

(A.63)

and

$$
\mathbf{r} \cdot \mathbf{e}^{(2)} = r \sin \theta \sin \phi.
$$

(A.64)

When the incident photon polarisation is unknown, we must average over the polarisation and direction of the incident photon, and sum over the polarisation and direction of the emitted photon [202]. We average over the incident polarisation and average over solid angle by

$$
\frac{d\sigma_{ij}}{d\Omega} = \omega \omega'^3 e \frac{1}{4\pi} \int \frac{1}{2} \left| \langle j | (\mathbf{r} \cdot \mathbf{e}^{(1)} \lambda_n (\mathbf{r} \cdot \mathbf{e}^{(1)'} | i \rangle + \langle j | (\mathbf{r} \cdot \mathbf{e}^{(1)'}) \lambda_{n'} (\mathbf{r} \cdot \mathbf{e}^{(1)}) | i \rangle \right|^2 d\Omega (A.65)
$$

$$
= \omega \omega'^3 e \frac{1}{4\pi} \int \frac{1}{2} \left( \langle j | (\mathbf{r} \cdot \mathbf{e}^{(2)} \lambda_n (\mathbf{r} \cdot \mathbf{e}^{(2)'}) | i \rangle + \langle j | (\mathbf{r} \cdot \mathbf{e}^{(2)'}) \lambda_{n'} (\mathbf{r} \cdot \mathbf{e}^{(2)}) | i \rangle \right|^2 d\Omega (A.66)
$$

$$
+ \langle j | (\mathbf{r} \cdot \mathbf{e}^{(2)}) \lambda_n (\mathbf{r} \cdot \mathbf{e}^{(2)'}) | i \rangle + \langle j | (\mathbf{r} \cdot \mathbf{e}^{(2)'}) \lambda_{n'} (\mathbf{r} \cdot \mathbf{e}^{(2)}) | i \rangle \right|^2 d\Omega.
$$
Substituting in Eqns. A.63 and A.64 then gives us

\[
\frac{d\sigma_{ij}}{d\Omega} = \omega \omega' r_c^2 \frac{1}{4\pi} \int \left( |\langle j | r \lambda_n (r \cdot e^{(\alpha)')} | i \rangle + |\langle j | (r \cdot e^{(\alpha)')} \lambda_{n'} r | i \rangle |^2 \right) \left( \sin^2 \theta \cos^2 \phi + \sin^2 \theta \sin^2 \phi \right) d\Omega \quad (A.67)
\]

\[
= \omega \omega' r_c^2 \left( |\langle j | r \lambda_n (r \cdot e^{(\alpha)')} | i \rangle + |\langle j | (r \cdot e^{(\alpha)')} \lambda_{n'} r | i \rangle |^2 \right) \int \frac{1}{2} \sin^2 \theta d\Omega \quad (A.68)
\]

\[
= \omega \omega' r_c^2 \left( |\langle j | r \lambda_n (r \cdot e^{(\alpha)')} | i \rangle + |\langle j | (r \cdot e^{(\alpha)')} \lambda_{n'} r | i \rangle |^2 \right) \frac{1}{3}. \quad (A.69)
\]

Then to find the total cross-section we must sum over the polarisation and integrate over the solid angle of the emitted photon, such that

\[
\sigma_{ij} = \omega \omega' r_c^2 \frac{1}{3} \int \sum_{\alpha'} \left( |\langle j | r \lambda_n (r \cdot e^{(\alpha)')} | i \rangle + |\langle j | (r \cdot e^{(\alpha)')} \lambda_{n'} r | i \rangle |^2 \right) d\Omega \quad (A.70)
\]

\[
= \omega \omega' r_c^2 \frac{1}{3} \int \left( \left( |\langle j | r \lambda_n (r \cdot e^{(1)')} | i \rangle + |\langle j | (r \cdot e^{(1)')} \lambda_{n'} r | i \rangle |^2 \right)^2 \right) d\Omega \quad (A.71)
\]

\[
= \omega \omega' r_c^2 \frac{1}{3} \int \left( |\langle j | r \lambda_n r | i \rangle + |\langle j | r \lambda_{n'} r | i \rangle |^2 \right)^2 \left( \sin^2 \theta' \cos^2 \phi' + \sin^2 \theta' \sin^2 \phi' \right) d\Omega \quad (A.72)
\]

\[
= \omega \omega' r_c^2 \frac{1}{3} \int \left( |\langle j | r \lambda_n r | i \rangle + |\langle j | r \lambda_{n'} r | i \rangle |^2 \right)^2, \quad (A.73)
\]

and in terms of Thomson cross-section,

\[
\sigma_{ij}(\omega) = \omega \omega' r_c^2 \frac{1}{3} \sigma_T \left( \sum_n \left[ \frac{\langle j \ell j m_j | r | n \ell m_n \rangle \langle n \ell m_n | r | i \ell m_i \rangle}{\epsilon_n - \epsilon_i - \hbar \omega} + \frac{\langle j \ell j m_j | r | n \ell m_n \rangle \langle n \ell m_n | r | i \ell m_i \rangle}{\epsilon_n - \epsilon_i + \hbar \omega} \right] \right)^2. \quad (A.74)
\]

We now have an expression for the cross-section for a transition from state \( i \) to state \( j \), though the transition matrix elements are still dependent on the magnetic quantum numbers. This dependence can be removed by applying the Wigner-Eckart theorem and writing the cross-section in terms of reduced matrix elements.

### A.7 Tensor Operators

Alternatively, since the dipole moment operator is a spherical tensor, the properties of spherical tensor operators can be used in the derivation of the polarisability. Throughout this thesis I have used the
polarisability expressions given by Delserieys et al. [48], which I have validated by comparing with previous data for the Rayleigh and Raman scattering cross-sections of hydrogen (see Chapter 4). For completeness, I have attempted to derive the coefficients of the polarisability in this section. However, the coefficients given by this derivation do not agree with the coefficients presented by Delserieys et al. [48].

Here we use the notation given by Zare [85] for spherical tensor operators. We can rewrite the operators in an alternative form, with the property [20, 85]

\[
\sum_{K,q} (-1)^{K+q} [r^{(1)} \otimes \lambda_n r^{(1)}]_{-q} [e^{(1)} \otimes e^{1(1)}]_q (K),
\]

where \( e = e^{(\alpha)} \) and \( e' = e^{(\alpha')} \) and \( \lambda_n = |n \ell_n m_n \rangle \langle n \ell_n m_n |. [e^{(1)} \otimes e^{1(1)}]_q (K) \) is referred to as the polarisation vector. Additionally, \([r^{(1)} \otimes \lambda_n r^{(1)}]_{-q} (K) \) can be written as [85]

\[
[r^{(1)} \otimes \lambda_n r^{(1)}]_{-q} (K) = \sum_{\mu} (-1)^q \sqrt{2K+1} r_{\mu} \lambda_n r_{-\mu-q} \left( \begin{array}{ccc} 1 & 1 & K \\ \mu & q - \mu & -q \end{array} \right).
\]

Therefore, the polarisability can now be written as

\[
\alpha_{ij}(\omega) = \sum_{n, K,q} (-1)^{K+q} [e^{(1)} \otimes e^{1(1)}]_{q} (K) \sum_{\mu} (-1)^q \sqrt{2K+1} \left( \begin{array}{ccc} 1 & 1 & K \\ \mu & q - \mu & -q \end{array} \right) \left[ \frac{\langle j \ell_m | r_{\mu} \lambda_n r_{-\mu-q} | i \ell_i m_i \rangle}{\epsilon_n - \epsilon_i - \omega} + \frac{\langle j \ell_m | r_{\mu} \lambda_n r_{-\mu-q} | i \ell_i m_i \rangle}{\epsilon_n - \epsilon_i + \omega'} \right],
\]

and applying the Wigner-Eckart theorem gives

\[
\alpha_{ij}(\omega) = \sum_{n} (-1)^{\ell_j + \ell_n - m_j - m_n} \sqrt{(2\ell_n + 1)(2\ell_j + 1)} \sum_{K,q} (-1)^{K+2q} [e^{(1)} \otimes e^{1(1)}]_{q} (K) \sqrt{2K+1} \left[ \frac{\langle j \ell_m | n \ell_n | r_{\mu} \lambda_n r_{-\mu-q} | i \ell_i m_i \rangle}{\epsilon_n - \epsilon_i - \omega} + \frac{\langle j \ell_m | n \ell_n | r_{\mu} \lambda_n r_{-\mu-q} | i \ell_i m_i \rangle}{\epsilon_n - \epsilon_i + \omega'} \right].
\]

The three Wigner-3j symbols can be combined by using the property [85]

\[
\left\{ \begin{array}{ccc} j_1 & j_2 & j_3 \\ j_4 & j_5 & j_6 \end{array} \right\} \left( \begin{array}{ccc} j_5 & j_1 & j_6 \\ m_5 & m_1 & m_6 \end{array} \right) = \sum_{m_2,m_3,m_4} (-1)^{j_1+j_2-j_3+j_4+j_5+j_6-m_1-m_4} \times \left( \begin{array}{ccc} j_1 & j_2 & j_3 \\ m_1 & m_2 & -m_3 \end{array} \right) \left( \begin{array}{ccc} j_4 & j_5 & j_3 \\ m_4 & m_5 & m_3 \end{array} \right) \left( \begin{array}{ccc} j_2 & j_4 & j_6 \\ m_2 & m_4 & -m_6 \end{array} \right).
\]

(A.78)
Given that
\[
\begin{pmatrix}
\ell_n & 1 & \ell_i \\
m_n & q-\mu & -m_i
\end{pmatrix}
= \begin{pmatrix}
1 & \ell_i \\
q-\mu & -m_i
\end{pmatrix},
\] (A.81)
then
\[
\left\{ \ell_j & 1 & \ell_n \\
1 & \ell_i & K
\right\}
\begin{pmatrix}
\ell_i & \ell_j & K \\
-m_i & m_j & q
\end{pmatrix}
= \sum_{\mu, m_n, q-\mu} (-1)^{\ell_j+1-\ell_n+1+\ell_i+K-m_j-q+\mu} \begin{pmatrix}
\ell_j & 1 & \ell_n \\
m_j & \mu & -m_n
\end{pmatrix}
\begin{pmatrix}
1 & \ell_i & \ell_n \\
1 & q-\mu & -m_i
\end{pmatrix}
\begin{pmatrix}
1 & \ell_i & K \\
\mu & q-\mu & -q
\end{pmatrix}
\] (A.82)
\[
= (-1)^{\ell_j+1-\ell_n+1+\ell_i+K} \sum_{\mu, m_n, q-\mu} (-1)^{-m_n-q+2\mu} \begin{pmatrix}
\ell_j & 1 & \ell_n \\
m_j & \mu & -m_n
\end{pmatrix}
\begin{pmatrix}
1 & \ell_i & \ell_n \\
1 & q-\mu & -m_i
\end{pmatrix}
\begin{pmatrix}
1 & \ell_i & K \\
\mu & q-\mu & -q
\end{pmatrix},
\] (A.83)
so
\[
\alpha_{ij}(\omega) = \sum_{n, K, q_1} (-1)^{\ell_i-m_j} \sqrt{(2K+1)(2\ell_n+1)(2\ell_j+1)} [e^{(1)}_q \otimes e'^{(1)}_q]_{\ell} \left\{ \ell_j & 1 & \ell_n \\
1 & \ell_i & K
\right\}
\begin{pmatrix}
\ell_i & \ell_j & K \\
-m_i & m_j & q
\end{pmatrix}
\frac{\langle j\ell_j|n\ell_n|\ell_c\ell_i|l\ell_i \rangle}{\epsilon_n-\epsilon_i-\omega}
+ \frac{\langle j\ell_j|n\ell_n|\ell_c\ell_i|l\ell_i \rangle}{\epsilon_n-\epsilon_i+\omega'}
\] (A.84).

Now let us consider the polarisation tensor, \( E^K_q(e, e') = [e^{(1)}_q \otimes e'^{(1)}_q]_{\ell} \) where \( e \) is the polarisation of the incident light and \( e' \) of the scattered light. This can be rewritten as
\[
E^K_q(e, e') = \sum_{q_1} (-1)^q \sqrt{2K+1} e_{q_1}^1 e_{q-q_1}^1 \begin{pmatrix}
1 & 1 & K \\
q_1 & q-q_1 & -q
\end{pmatrix},
\] (A.85)
If we assume that the incident light is polarised along the z-axis, then \( q = 0 \) and the polarisation tensor is given by
\[
E^K_0(e, e') = \sum_{q_1} \sqrt{2K+1} e_{q_1}^1 e_{-q_1}^1 \begin{pmatrix}
1 & 1 & K \\
q_1 & -q_1 & 0
\end{pmatrix},
\] (A.86)
which becomes [20]
\[
E^K_0(e, e') = \sqrt{2K+1} e_{0}^1 e_{0}^1 \begin{pmatrix}
1 & 1 & K \\
0 & 0 & 0
\end{pmatrix}.
\] (A.87)
Therefore, for incident light polarised along the $z$-axis, the polarisability is given by [20]

\[
\alpha_{ij}(\omega) = \sum_{n,K} (-1)^{-\ell_i-m_i}(2K+1)\sqrt{(2\ell_n+1)(2\ell_j+1)} \left\{ \begin{array}{ccc} \ell_j & 1 & \ell_n \\ 0 & 1 & \ell_i \end{array} \right\} \left\{ \begin{array}{ccc} \ell_i & \ell_j & K \\ -m_i & m_j & 0 \end{array} \right\} \\
\times \frac{\langle j \ell_j | z | n \ell_n \rangle \langle n \ell_n | z | i \ell_i \rangle}{\epsilon_n - \epsilon_i - \omega} \frac{\langle j \ell_j | z | n \ell_n \rangle \langle n \ell_n | z | i \ell_i \rangle}{\epsilon_n - \epsilon_i + \omega'} \right].
\] (A.88)

Delserieys et al. [48] have derived expressions for the single-photon scattering cross-sections with and without fine-structure. From their expressions, the Raman scattering cross-section is given by

\[
\sigma_{ij} = \sigma_T \omega \omega' |\alpha_{ij}(\omega)|^2,
\] (A.89)

where the transition polarisability, in terms of reduced matrix elements, is given by

\[
\alpha_{ij}(\omega) = \sum_n C_{i,n,j} \left[ \frac{\langle j \ell_j | z | n \ell_n \rangle \langle n \ell_n | z | i \ell_i \rangle}{\epsilon_n - \epsilon_i - \omega} + \frac{\langle j \ell_j | z | n \ell_n \rangle \langle n \ell_n | z | i \ell_i \rangle}{\epsilon_n - \epsilon_i + \omega'} \right].
\] (A.90)

Evaluating their expressions gives $C_{i,n,j} = 1/3$ for angular momenta $\ell_i = 0$, $\ell_n = 1$ and $\ell_j = 0$ or 2. See Section 2.2 for more details.

However, the equivalent coefficient given by my derivation in Eqn. A.88 gives coefficients $C_{i,n,j} = 1/\sqrt{3}$ for $\ell_j = 0$ and $C_{i,n,j} = \sqrt{2}/3$ for $\ell_j = 2$. For this reason there must be a mistake in my derivation above, though I have not been able to determine where. Throughout this thesis I will use the correct scattering cross-section expressions that were presented by Delserieys et al. [48]. I have validated these in Chapter 4 against data from previous calculations of Rayleigh and Raman scattering cross-sections of hydrogen.
Appendix B

Small Basis Set Calculation

The energies for states with angular momentum $\ell = 0, 1, 2, 3$ are given for a basis set of $N_\ell = 10$ and $\lambda_\ell = 0.5$ in Table B.1. The oscillator strengths presented here can be used to do some test example calculations of Rayleigh and Raman scattering cross-sections, e.g. $\sigma_{1s,1s},\sigma_{1s,2s},\sigma_{1s,3s},\sigma_{1s,3d},\sigma_{2s,2s}$ and $\sigma_{3d,3d}$. The oscillator strengths in the small basis set calculation are also shown to obey the Thomas-Reiche-Kuhn sum rule. Test calculations can also be done with the effective oscillator strengths provided by Jiang et al. [83], though these are only for the ground states of atoms.
Table B.1: Table of energies (in atomic units) and oscillator strengths for a $N_{\ell} = 10$ and $\lambda_{\ell} = 0.5$ Laguerre basis set, as well as the sum of the oscillator strengths for initial states $1s$, $2s$, $3s$ and $3d$. The numbers in brackets ($\times$) denote ($\times 10^{x}$).

<table>
<thead>
<tr>
<th>$j$</th>
<th>$\ell_{j}$</th>
<th>$\epsilon$</th>
<th>$f_{1s,j}$</th>
<th>$f_{2s,j}$</th>
<th>$f_{3s,j}$</th>
<th>$f_{3d,j}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>-0.499999976</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>-0.125000000</td>
<td>4.16196579(-1)</td>
<td>-2.72507505(-12)</td>
<td>-4.07688051(-2)</td>
<td>-4.17470823(-1)</td>
</tr>
<tr>
<td>3</td>
<td>0</td>
<td>-0.125000000</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>2</td>
<td>-0.055555556</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>1</td>
<td>-0.055555555</td>
<td>7.91024747(-2)</td>
<td>4.34865532(-1)</td>
<td>-1.05138613(-6)</td>
<td>1.20669385(-8)</td>
</tr>
<tr>
<td>6</td>
<td>0</td>
<td>-0.055555545</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>3</td>
<td>-0.031249699</td>
<td></td>
<td></td>
<td></td>
<td>1.017675400</td>
</tr>
<tr>
<td>8</td>
<td>2</td>
<td>-0.03124884</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>1</td>
<td>-0.031210784</td>
<td>2.94008148(-2)</td>
<td>1.04388614(-1)</td>
<td>4.91004189(-1)</td>
<td>1.11353326(-2)</td>
</tr>
<tr>
<td>10</td>
<td>0</td>
<td>-0.031068302</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>3</td>
<td>-0.019750063</td>
<td></td>
<td></td>
<td></td>
<td>1.73053585(-1)</td>
</tr>
<tr>
<td>12</td>
<td>2</td>
<td>-0.019012621</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>1</td>
<td>-0.017280784</td>
<td>2.61553414(-2)</td>
<td>7.50168448(-2)</td>
<td>1.98445203(-1)</td>
<td>3.42987144(-3)</td>
</tr>
<tr>
<td>14</td>
<td>0</td>
<td>-0.013978236</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>3</td>
<td>-0.009753707</td>
<td></td>
<td></td>
<td></td>
<td>1.04071676(-1)</td>
</tr>
<tr>
<td>16</td>
<td>2</td>
<td>-0.004901114</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>17</td>
<td>1</td>
<td>0.003285914</td>
<td>4.15467715(-2)</td>
<td>9.50954937(-2)</td>
<td>1.51227735(-1)</td>
<td>1.89832746(-3)</td>
</tr>
<tr>
<td>18</td>
<td>3</td>
<td>0.006169448</td>
<td></td>
<td></td>
<td></td>
<td>6.14159886(-2)</td>
</tr>
<tr>
<td>19</td>
<td>0</td>
<td>0.016614284</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>2</td>
<td>0.019091111</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>21</td>
<td>3</td>
<td>0.031818523</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>22</td>
<td>1</td>
<td>0.040831602</td>
<td>6.42255192(-2)</td>
<td>1.00642900(-1)</td>
<td>9.97293021(-2)</td>
<td>7.41771964(-4)</td>
</tr>
<tr>
<td>23</td>
<td>2</td>
<td>0.059792285</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>24</td>
<td>3</td>
<td>0.073392906</td>
<td></td>
<td></td>
<td></td>
<td>1.09359017(-2)</td>
</tr>
<tr>
<td>25</td>
<td>0</td>
<td>0.079082753</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>26</td>
<td>3</td>
<td>0.111899984</td>
<td>8.88756248(-2)</td>
<td>8.90273295(-2)</td>
<td>5.73526183(-2)</td>
<td>2.21635695(-4)</td>
</tr>
<tr>
<td>27</td>
<td>2</td>
<td>0.132226925</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>28</td>
<td>3</td>
<td>0.144270800</td>
<td></td>
<td></td>
<td></td>
<td>3.45513579(-3)</td>
</tr>
<tr>
<td>29</td>
<td>0</td>
<td>0.223962191</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>1</td>
<td>0.263022168</td>
<td>1.12221784(-1)</td>
<td>6.30673337(-2)</td>
<td>2.94786907(-2)</td>
<td>3.91802106(-5)</td>
</tr>
<tr>
<td>31</td>
<td>2</td>
<td>0.275345914</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>32</td>
<td>3</td>
<td>0.277000421</td>
<td></td>
<td></td>
<td></td>
<td>8.36525017(-4)</td>
</tr>
<tr>
<td>33</td>
<td>0</td>
<td>0.569233010</td>
<td></td>
<td></td>
<td></td>
<td>1.29563478(-4)</td>
</tr>
<tr>
<td>34</td>
<td>3</td>
<td>0.616203362</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>35</td>
<td>1</td>
<td>0.665115659</td>
<td>1.02378003(-1)</td>
<td>3.10326841(-2)</td>
<td>1.13362706(-2)</td>
<td>5.19757532(-6)</td>
</tr>
<tr>
<td>36</td>
<td>0</td>
<td>0.673735255</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>37</td>
<td>3</td>
<td>1.458868360</td>
<td></td>
<td></td>
<td></td>
<td>8.09124194(-6)</td>
</tr>
<tr>
<td>38</td>
<td>2</td>
<td>1.805673625</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>39</td>
<td>1</td>
<td>2.394891797</td>
<td>3.99018281(-2)</td>
<td>6.86326898(-3)</td>
<td>2.17601491(-3)</td>
<td>5.73509373(-8)</td>
</tr>
<tr>
<td>40</td>
<td>0</td>
<td>3.482207576</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Oscillator Strength Sum:

| $\sum_{j} f_{i,j}$ | 1.000004741 | 1.000000000 | 0.999980168 | 1.000000547 |
Appendix C

Pseudostate Packing

The pseudostate method that I developed in Chapter 3 allows us to compute the complex transition polarisability at frequencies both below and above threshold. A consequence of our pseudostate method is that we are only able to compute the polarisability above threshold at frequencies that correspond to the energy difference between the initial state and a ground state, i.e. \( \omega = \omega_t \) where state \( t \) is a pseudostate and \( i \) is the initial state. The energy gap between successive pseudostates becomes larger the higher a state is in energy, which results in a very sparse frequency grid at higher energies.

When the polarisability is a smooth function above threshold, a good approximation of the polarisability at a specific frequency \( \omega \neq \omega_t \) is given simply by interpolating from the closest points. However, a preferable method would be to add pseudostates to our calculation, especially if the polarisability has structure above threshold. Adding pseudostates to our calculation will give a better description of the structure above threshold, and would also be very useful in our hyperpolarisability calculation. The hyperpolarisability calculation is discussed in detail in Chapter 5.

I have attempted to extend our pseudostate method to more frequencies by a technique we call pseudostate packing. Unfortunately I have so far been unable to apply this pseudostate packing method to transitions between two free states. In this method I attempt to add or ‘pack’ more pseudostates between existing pseudostates, hence the name pseudostate packing.

Previously similar methods have been considered, but rather than adding more states the aim had been to remove pseudostates from the set by making a set of “effective” oscillator strengths [46, 83, 90, 103]. In the paper by Jiang et al. [83] the effective oscillator strengths have been used to compute the polarisabilities of noble gases, alkali atoms, atomic hydrogen, as well as singly-charged alkaline-earth ions and alkaline-earth atoms. This method relies on solving the set of nonlinear equations given by the sum-rules

\[
S^{(\ell)}(-k) = \sum_j \frac{f_{ij}^{(\ell)}}{(\epsilon_{ij})^k},
\]

since the sum-rules given by the effective transitions should approximate the original distribution. In Eqn. C.1 \( (\ell) \) refers to the multipole, and \( k \) to the moment. Similarly, Langhoff et al. [46, 90, 103] also
consider the oscillator strengths and energies as a set of moments that can be used to build an effective oscillator strength distribution (with fewer number of pseudostates than the original set) using the Stieltjes imaging technique.

Our attempt at a pseudostate packing method for the polarisability is very simple because the normalisation of the bound-to-free oscillator strengths is known. There are two criteria that the new set of oscillator strengths must fulfill:

1. The unnormalised pseudostate oscillator strengths \( f_j \) should add to 1, given that the initial state is a bound state.

\[
S^{(1)}(0) \equiv \sum_{j}^{N_B} f_j + \sum_{j}^{N_P} f_j = 1.
\]

As we add new pseudostates to the calculation, the oscillator strengths must decrease in magnitude in order to still give the correct sum.

2. The oscillator strengths should give the correct polarisability, \( S^{(1)}(−2) \).

In order to add new states, we must first find the normalised oscillator strengths. The pseudostate oscillator strengths (for a transition to a free state with energy \( \epsilon_j \)) are normalised by the energy density \( \rho(\epsilon_j) \),

\[
g_j = \frac{f_j}{\rho(\epsilon_j)},
\]

where \( g_j \) is the normalised oscillator strength. We can then add normalised oscillator strengths at new frequencies by interpolating from the known values. Here I will use linear interpolation, though for a more accurate description of the continuum more sophisticated interpolation methods should be used.

Let us first approach this problem by adding two states at equal distances between the original pseudostates, as shown in Fig. C.1. Fig. C.1 shows the normalised oscillator strength from the initial 1s state of hydrogen with a new set of states added to the existing pseudostates. Given that we now have a new set of pseudostates of energy \( \epsilon_i \) and with normalised oscillator strength \( f_i \), we can find the unnormalised oscillator strengths by

\[
f_i(\epsilon_{i+1} - \epsilon_{i-1})/2 = f_i^P.
\]
Figure C.1: Plot of the normalised oscillator strengths for initial 1s state with new states added between the existing pseudostates using linear interpolation.

The unnormalised oscillator strengths are given in Fig. C.2 for the case where I have added two new pseudostates between each existing pseudostate. Since the new pseudostates are added at equal distances between the original states, the unnormalised oscillator strengths and energy density are no longer smooth (shown in Figs. C.2 and C.3). However, this could be easily fixed by using an interpolation that is not linear.

Figure C.2: Plot comparing the unnormalised oscillator strengths from the old set and new set of states, where two new states are added in between each existing pseudostate.
Since the energy density cancels out in our polarisability calculation, these new oscillator strengths should still give the correct polarisability, as shown in Fig. C.4.

The real 1s-1s polarisability for the calculation with and without pseudostate packing is given in Fig C.4. Though I have considered the possibility of pseudostate packing here, we have not yet been able to develop a method that successfully applies pseudostate packing to transitions involving two free states. As such, this work has been only included in the Appendix, with the view that more work must be done before it can be used in calculations of hyperpolarisability and two-photon ionisation.
Appendix D

Convergence Data

Although I have attempted to validate my calculations against literature values where possible, to have confidence in our calculations we must also perform some convergence studies. If we find that our calculations diverge when increasing basis set size or box size, it is usually a good indicator that there is an error in our calculation. Here I present some convergence data for the various calculations in this thesis using our pseudostate method.

The static polarisability and hyperpolarisability are well-known for atomic hydrogen and were computed in Chapters 3 and 5 respectively. Table D.1 demonstrates that our pseudostate calculation of these values is completely converged with respect to basis set size.

Table D.1: Convergence of the static polarisability $\alpha$ and hyperpolarisability $\gamma$ of atomic hydrogen (in atomic units) given by our pseudostate calculation with increasing basis set size $N_\ell$. The contribution from $\ell = 0$ intermediate states ($\gamma_{0101}$) and $\ell = 2$ intermediate states ($\gamma_{0121}$) to the hyperpolarisability $\gamma = \gamma_{0101} + \gamma_{0121}$ is also presented.

<table>
<thead>
<tr>
<th>$N_\ell$</th>
<th>$\alpha$</th>
<th>$\gamma_{0101}$</th>
<th>$\gamma_{0121}$</th>
<th>$\gamma$</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>4.50000618797</td>
<td>621.514973344</td>
<td>711.949079983</td>
<td>1333.464053327</td>
</tr>
<tr>
<td>12</td>
<td>4.4999972466</td>
<td>621.381120103</td>
<td>711.756219485</td>
<td>1333.137339588</td>
</tr>
<tr>
<td>14</td>
<td>4.4999997826</td>
<td>621.375215882</td>
<td>711.750160176</td>
<td>1333.125376058</td>
</tr>
<tr>
<td>16</td>
<td>4.4999999907</td>
<td>621.375004240</td>
<td>711.750003173</td>
<td>1333.125007413</td>
</tr>
<tr>
<td>18</td>
<td>4.4999999994</td>
<td>621.374999905</td>
<td>711.750000018</td>
<td>1333.124999923</td>
</tr>
<tr>
<td>20</td>
<td>4.4999999997</td>
<td>621.374999976</td>
<td>711.749999987</td>
<td>1333.124999963</td>
</tr>
</tbody>
</table>

In Chapter 3 the complex polarisability was computed using our pseudostate method. The convergence of $\text{Re}[\alpha_{ii}(\omega)]$ for ground state atomic hydrogen at frequencies below threshold is presented in Table D.2, whilst the convergence of the $\text{Im}_0[\alpha_{ii}(\omega)]$ is given in Table D.3 using different functions for the decay rate. From these tables we can see that the complex polarisability is completely converged at frequencies below threshold. Though converged, there is some variation between the methods which is due to the choice of decay. For example, the calculation using Eqn. 3.21 for the decay rates gives $\text{Im}_0[\alpha_{1s,1s}(\omega)] = 0$ at $\omega = 0.0, 0.1$ and 0.2 a.u., since the decay is chosen to be zero at these frequencies.
Table D.2: Convergence of the real polarisability Re[α_{1s,1s}(ω)] (in atomic units) of atomic hydrogen at several frequencies below threshold with respect to increasing the size of the basis set in the pseudostate calculation. The matrix elements calculated by Gavrila [1] are presented here as polarisability.

<table>
<thead>
<tr>
<th>N_ℓ</th>
<th>ω = 0.0 a.u.</th>
<th>ω = 0.1 a.u.</th>
<th>ω = 0.2 a.u.</th>
<th>ω = 0.3 a.u.</th>
<th>ω = 0.4 a.u.</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>4.50000618797</td>
<td>4.7843069983</td>
<td>5.9416832288</td>
<td>10.5639027732</td>
<td>-16.8225861385</td>
</tr>
<tr>
<td>12</td>
<td>4.4999972466</td>
<td>4.7843000419</td>
<td>5.9416745005</td>
<td>10.5638884922</td>
<td>-16.8226449232</td>
</tr>
<tr>
<td>14</td>
<td>4.49999997826</td>
<td>4.7843003187</td>
<td>5.9416748296</td>
<td>10.5638888253</td>
<td>-16.8226453959</td>
</tr>
<tr>
<td>16</td>
<td>4.49999999907</td>
<td>4.7843003419</td>
<td>5.9416748595</td>
<td>10.5638888647</td>
<td>-16.8226453590</td>
</tr>
<tr>
<td>18</td>
<td>4.49999999994</td>
<td>4.7843003429</td>
<td>5.9416748609</td>
<td>10.5638888669</td>
<td>-16.8226453558</td>
</tr>
<tr>
<td>20</td>
<td>4.49999999997</td>
<td>4.7843003430</td>
<td>5.9416748609</td>
<td>10.5638888670</td>
<td>-16.8226453557</td>
</tr>
</tbody>
</table>

Gavrila

Table D.3: Convergence of the Im[α_{1s,1s}(ω)] pseudostate calculation (in atomic units) at several frequencies below threshold for atomic hydrogen with respect to basis set size. The Im[α_{1s,1s}(ω)] calculation is presented for the different functions of frequency-dependent decay rate - my own frequency-dependent function given in Eqn. 3.21, the frequency-dependence given by Wijer’s et al. [110] in Eqn. 3.18 and using a constant decay rate independent of frequency. The numbers in brackets (x) denote (×10^x).

<table>
<thead>
<tr>
<th>N_ℓ</th>
<th>ω = 0.1 a.u.</th>
<th>ω = 0.2 a.u.</th>
<th>ω = 0.3 a.u.</th>
<th>ω = 0.4 a.u.</th>
</tr>
</thead>
<tbody>
<tr>
<td>120</td>
<td>0.00</td>
<td>0.00</td>
<td>3.101270(-7)</td>
<td>6.223381(-6)</td>
</tr>
<tr>
<td>100</td>
<td>0.00</td>
<td>0.00</td>
<td>3.101270(-7)</td>
<td>6.223381(-6)</td>
</tr>
<tr>
<td>80</td>
<td>0.00</td>
<td>0.00</td>
<td>3.101270(-7)</td>
<td>6.223381(-6)</td>
</tr>
</tbody>
</table>

Decay rate given by Eqn. 3.21

<table>
<thead>
<tr>
<th>N_ℓ</th>
<th>ω = 0.1 a.u.</th>
<th>ω = 0.2 a.u.</th>
<th>ω = 0.3 a.u.</th>
<th>ω = 0.4 a.u.</th>
</tr>
</thead>
<tbody>
<tr>
<td>120</td>
<td>1.079251(-8)</td>
<td>8.07465(-8)</td>
<td>6.962292(-7)</td>
<td>6.791663(-6)</td>
</tr>
<tr>
<td>100</td>
<td>1.079250(-8)</td>
<td>8.07464(-8)</td>
<td>6.962290(-7)</td>
<td>6.791662(-6)</td>
</tr>
<tr>
<td>80</td>
<td>1.079246(-8)</td>
<td>8.07462(-8)</td>
<td>6.962280(-7)</td>
<td>6.791657(-6)</td>
</tr>
</tbody>
</table>

Decay rate given by Eqn. 3.18

<table>
<thead>
<tr>
<th>N_ℓ</th>
<th>ω = 0.1 a.u.</th>
<th>ω = 0.2 a.u.</th>
<th>ω = 0.3 a.u.</th>
<th>ω = 0.4 a.u.</th>
</tr>
</thead>
<tbody>
<tr>
<td>120</td>
<td>7.71171(-8)</td>
<td>1.546645(-7)</td>
<td>7.687885(-7)</td>
<td>6.850095(-6)</td>
</tr>
<tr>
<td>100</td>
<td>7.71169(-8)</td>
<td>1.546643(-7)</td>
<td>7.687881(-7)</td>
<td>6.850094(-6)</td>
</tr>
<tr>
<td>80</td>
<td>7.71164(-8)</td>
<td>1.546636(-7)</td>
<td>7.687865(-7)</td>
<td>6.850088(-6)</td>
</tr>
</tbody>
</table>

Constant decay rate

I have also studied the convergence of the complex hyperpolarisability of atomic hydrogen at non-zero frequencies below threshold, as shown in tables D.4 and D.5. These tables demonstrate that our pseudostate hyperpolarisability calculation is converged with respect to basis set size at frequencies below threshold. Table D.5 considers the convergence of Im[γ(ω)] at frequency ω = 0.2 a.u. Comparison of tables D.4 and D.5 show that Im[γ(ω)] is much smaller than Re[γ(ω)] at this frequency. Im[γ(ω)] and Re[γ(ω)] are only expected to be comparable near resonance.
Table D.4: Convergence of real hyperpolarisability \( \text{Re}[\gamma(\omega)] \) (in atomic units) of atomic hydrogen at below threshold frequencies for pseudostate calculations with increasing basis set size \( N_\ell \).

<table>
<thead>
<tr>
<th>( N_\ell )</th>
<th>( \omega = 0.05 ) a.u.</th>
<th>( \omega = 0.10 ) a.u.</th>
<th>( \omega = 0.15 ) a.u.</th>
<th>( \omega = 0.20 ) a.u.</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>1473.08641667</td>
<td>2055.33588724</td>
<td>4408.51937208</td>
<td>-5442.65709235</td>
</tr>
<tr>
<td>12</td>
<td>1472.73855754</td>
<td>2054.91228258</td>
<td>4407.90639724</td>
<td>-5443.89490231</td>
</tr>
<tr>
<td>14</td>
<td>1472.72589321</td>
<td>2054.89713461</td>
<td>4407.88511172</td>
<td>-5443.93620946</td>
</tr>
<tr>
<td>16</td>
<td>1472.7250402</td>
<td>2054.89667282</td>
<td>4407.88447137</td>
<td>-5443.93741995</td>
</tr>
<tr>
<td>18</td>
<td>1472.72549591</td>
<td>2054.89666256</td>
<td>4407.88445610</td>
<td>-5443.93745023</td>
</tr>
<tr>
<td>20</td>
<td>1472.72549593</td>
<td>2054.89666254</td>
<td>4407.88445598</td>
<td>-5443.93745071</td>
</tr>
</tbody>
</table>

Table D.5: Convergence of \( \text{Im}[\gamma(\omega)] \) (in atomic units) at below threshold frequency \( \omega = 0.2 \) a.u. for pseudostate calculations with increasing basis set size \( N_\ell \). The numbers in brackets \((\times)\) denote \((\times10^x)\).

<table>
<thead>
<tr>
<th>( N_\ell )</th>
<th>( \omega = 0.2 ) a.u.</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>5.065047698((-6))</td>
</tr>
<tr>
<td>12</td>
<td>5.065218522((-6))</td>
</tr>
<tr>
<td>14</td>
<td>5.065220792((-6))</td>
</tr>
<tr>
<td>16</td>
<td>5.065220816((-6))</td>
</tr>
<tr>
<td>18</td>
<td>5.065220817((-6))</td>
</tr>
<tr>
<td>20</td>
<td>5.065220817((-6))</td>
</tr>
</tbody>
</table>

In Chapter 4 our pseudostate method was used to compute single photon scattering cross-sections using transition polarisabilities. The Rayleigh scattering cross-section is given by the transition polarisability \( \alpha_{ij}(\omega) \) where \( i = j \), which was computed in Chapter 3. Since we know that this polarisability of ground state atomic hydrogen converges, the Rayleigh scattering cross-sections given by our calculation must also be converged.

In Chapter 4 I present my pseudostate calculation of the cross-sections for the \( 1s-2s \) and \( 3s-3d \) transitions as these can be compared with literature values. The convergence of these cross-sections is studied in Tables D.6 and D.7. These tables give the cross-sections computed with our pseudostate method for different basis set sizes \((N_\ell = 80, 100 \text{ and } 120)\) at frequencies both below and above threshold.

Evidently the cross-sections are converged to many significant figures at frequencies below threshold. For example, the \( 1s-2s \) cross-section is converged to 10 significant figures at \( \omega = 0.4 \) a.u. Similarly, the \( 3s-3d \) transition is converged to 10 significant figures at \( \omega = 0.05 \) a.u. Threshold occurs at \( \omega = 0.5 \) a.u. in the \( 1s-2s \) cross-section and at \( \omega = 0.556 \) in the \( 3s-3d \) cross-section. There is some uncertainty in these results as our pseudostate method gives cross-sections only at certain frequencies above threshold, which varies as we change the basis set. In these tables I have used linear interpolation to compare the different basis set calculations at a common frequency. We can see that the cross-sections have much slower convergence at frequencies above the threshold, with lack of convergence but similar order-of-magnitudes.
Table D.6: Raman 1s-2s scattering cross-section (in units of $\sigma_T$) in atomic hydrogen given by our pseudostate method using basis set sizes $N_\ell = 80, 100$ and 120. 1s-2s cross-sections are presented for frequencies both below and above threshold. The cross-sections at frequencies above threshold are interpolated from the nearest datapoints. The numbers in brackets ($x$) denote ($\times 10^x$).

<table>
<thead>
<tr>
<th>$\omega$ (a.u.)</th>
<th>$N_\ell = 120$</th>
<th>$N_\ell = 100$</th>
<th>$N_\ell = 80$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.38</td>
<td>9.9092334774(-3)</td>
<td>9.9092334774(-3)</td>
<td>9.9092334737(-3)</td>
</tr>
<tr>
<td>0.39</td>
<td>3.4050630542(-2)</td>
<td>3.4050630542(-2)</td>
<td>3.4050630537(-2)</td>
</tr>
<tr>
<td>0.40</td>
<td>6.7720825864(-2)</td>
<td>6.7720825864(-2)</td>
<td>6.7720825858(-2)</td>
</tr>
<tr>
<td>0.42</td>
<td>2.2068746084(-1)</td>
<td>2.2068746084(-1)</td>
<td>2.2068746082(-1)</td>
</tr>
<tr>
<td>0.44</td>
<td>3.1465462347</td>
<td>3.1465462347</td>
<td>3.1465462332</td>
</tr>
<tr>
<td>0.45</td>
<td>5.3770506693(-1)</td>
<td>5.3770506693(-1)</td>
<td>5.3770506736(-1)</td>
</tr>
<tr>
<td>0.46</td>
<td>5.9511617700(-2)</td>
<td>5.9511617700(-2)</td>
<td>5.9511617655(-2)</td>
</tr>
<tr>
<td>0.48</td>
<td>6.2252736942(12)</td>
<td>6.2252736942(12)</td>
<td>6.2252313269(12)</td>
</tr>
<tr>
<td>0.49</td>
<td>4.1754768379</td>
<td>4.1754768379</td>
<td>4.1754769218</td>
</tr>
<tr>
<td>0.51</td>
<td>2.108(-3)</td>
<td>2.103(-3)</td>
<td>2.101(-3)</td>
</tr>
<tr>
<td>0.52</td>
<td>9.427(-4)</td>
<td>9.530(-4)</td>
<td>9.709(-4)</td>
</tr>
<tr>
<td>0.53</td>
<td>2.965(-4)</td>
<td>3.078(-4)</td>
<td>3.270(-4)</td>
</tr>
<tr>
<td>0.54</td>
<td>3.025(-5)</td>
<td>3.456(-5)</td>
<td>4.018(-5)</td>
</tr>
<tr>
<td>0.55</td>
<td>2.694(-5)</td>
<td>2.482(-5)</td>
<td>1.809(-5)</td>
</tr>
<tr>
<td>0.60</td>
<td>1.702(-3)</td>
<td>1.637(-3)</td>
<td>1.541(-3)</td>
</tr>
<tr>
<td>0.80</td>
<td>6.106(-3)</td>
<td>5.929(-3)</td>
<td>5.664(-3)</td>
</tr>
<tr>
<td>1.00</td>
<td>5.361(-3)</td>
<td>5.203(-3)</td>
<td>4.969(-3)</td>
</tr>
<tr>
<td>2.00</td>
<td>1.196(-3)</td>
<td>1.149(-3)</td>
<td>1.104(-3)</td>
</tr>
<tr>
<td>5.00</td>
<td>7.366(-5)</td>
<td>7.190(-5)</td>
<td>6.950(-5)</td>
</tr>
<tr>
<td>10.0</td>
<td>7.188(-6)</td>
<td>7.292(-6)</td>
<td>7.347(-6)</td>
</tr>
</tbody>
</table>
Table D.7: Cross-section (in units of $\sigma_T$) of (Rayleigh-like) Raman $3s-3d$ transition in atomic hydrogen given by our pseudostate method using basis set sizes $N_\ell = 80$, 100 and 120. $3s-3d$ cross-sections are presented for frequencies both below and above threshold. The cross-sections at frequencies above threshold are interpolated from the nearest datapoints. The cross-sections given by Florescu et al. [7] are also shown. The numbers in brackets ($\times$) denote ($\times 10^x$).

<table>
<thead>
<tr>
<th>$\omega$ (a.u.)</th>
<th>$N_\ell = 120$</th>
<th>$N_\ell = 100$</th>
<th>$N_\ell = 80$</th>
<th>Florescu et al.</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01</td>
<td>1.091236196 (-3)</td>
<td>1.091236196 (-3)</td>
<td>1.091236196 (-3)</td>
<td>9.8211 (-4)</td>
</tr>
<tr>
<td>0.02</td>
<td>1.195398021 (-1)</td>
<td>1.195398021 (-1)</td>
<td>1.195398021 (-1)</td>
<td>1.0759 (-1)</td>
</tr>
<tr>
<td>0.03</td>
<td>1.692523621 (-1)</td>
<td>1.692523621 (-1)</td>
<td>1.692523620 (-1)</td>
<td>1.5233 (-1)</td>
</tr>
<tr>
<td>0.04</td>
<td>1.078035887 (-1)</td>
<td>1.078035887 (-1)</td>
<td>1.078035886 (-1)</td>
<td>9.7023 (-2)</td>
</tr>
<tr>
<td>0.05</td>
<td>4.209758654 (-1)</td>
<td>4.209758654 (-1)</td>
<td>4.209758586 (-1)</td>
<td>3.7890 (-1)</td>
</tr>
<tr>
<td>0.055</td>
<td>5.320628901 (-1)</td>
<td>5.320628901 (-1)</td>
<td>5.320628901 (-1)</td>
<td>6.604907344 (-1)</td>
</tr>
<tr>
<td>0.06</td>
<td>1.423</td>
<td>1.429</td>
<td>1.437</td>
<td>1.2918</td>
</tr>
<tr>
<td>0.07</td>
<td>2.108 (3)</td>
<td>1.102 (2)</td>
<td>5.604 (3)</td>
<td>2.9547 (2)</td>
</tr>
<tr>
<td>0.08</td>
<td>7.364 (-1)</td>
<td>7.612 (-1)</td>
<td>7.824 (-1)</td>
<td>6.5961 (-1)</td>
</tr>
<tr>
<td>0.09</td>
<td>1.572 (-1)</td>
<td>1.559 (-1)</td>
<td>1.612 (-1)</td>
<td>1.4224 (-1)</td>
</tr>
<tr>
<td>0.10</td>
<td>5.719 (-2)</td>
<td>5.737 (-2)</td>
<td>5.743 (-2)</td>
<td>5.3289 (-2)</td>
</tr>
<tr>
<td>0.15</td>
<td>3.243 (-3)</td>
<td>3.276 (-3)</td>
<td>3.297 (-3)</td>
<td>3.4143 (-3)</td>
</tr>
<tr>
<td>0.20</td>
<td>5.654 (-4)</td>
<td>5.754 (-4)</td>
<td>5.804 (-4)</td>
<td>6.7665 (-4)</td>
</tr>
<tr>
<td>0.25</td>
<td>1.525 (-4)</td>
<td>1.536 (-4)</td>
<td>1.604 (-4)</td>
<td>2.0403 (-4)</td>
</tr>
<tr>
<td>0.30</td>
<td>5.230 (-5)</td>
<td>5.346 (-5)</td>
<td>5.487 (-5)</td>
<td>7.6749 (-5)</td>
</tr>
<tr>
<td>0.40</td>
<td>9.469 (-6)</td>
<td>9.685 (-6)</td>
<td>1.015 (-5)</td>
<td>1.6690 (-5)</td>
</tr>
<tr>
<td>0.50</td>
<td>2.461 (-6)</td>
<td>2.578 (-6)</td>
<td>2.761 (-6)</td>
<td>5.1699 (-6)</td>
</tr>
<tr>
<td>0.80</td>
<td>1.329 (-7)</td>
<td>1.425 (-7)</td>
<td>1.572 (-7)</td>
<td>1.1783 (-7)</td>
</tr>
<tr>
<td>1.00</td>
<td>3.163 (-8)</td>
<td>3.389 (-8)</td>
<td>3.884 (-8)</td>
<td>2.2719 (-9)</td>
</tr>
<tr>
<td>2.00</td>
<td>2.917 (-10)</td>
<td>3.372 (-10)</td>
<td>4.496 (-10)</td>
<td>2.0881 (-10)</td>
</tr>
<tr>
<td>3.00</td>
<td>1.748 (-11)</td>
<td>2.368 (-11)</td>
<td>3.572 (-11)</td>
<td>2.3179 (-11)</td>
</tr>
<tr>
<td>4.00</td>
<td>2.281 (-12)</td>
<td>3.583 (-12)</td>
<td>6.067 (-12)</td>
<td>5.1538 (-12)</td>
</tr>
<tr>
<td>5.00</td>
<td>5.042 (-13)</td>
<td>8.308 (-13)</td>
<td>1.551 (-12)</td>
<td>9.5838 (-12)</td>
</tr>
<tr>
<td>8.00</td>
<td>1.594 (-14)</td>
<td>4.155 (-14)</td>
<td>7.495 (-14)</td>
<td>5.2665 (-13)</td>
</tr>
<tr>
<td>10.0</td>
<td>3.502 (-15)</td>
<td>1.036 (-14)</td>
<td>2.320 (-14)</td>
<td>1.3024 (-13)</td>
</tr>
<tr>
<td>20.0</td>
<td>7.659 (-17)</td>
<td>2.206 (-16)</td>
<td>6.758 (-16)</td>
<td>6.758 (-16)</td>
</tr>
<tr>
<td>50.0</td>
<td>9.678 (-19)</td>
<td>1.871 (-18)</td>
<td>8.455 (-18)</td>
<td>8.455 (-18)</td>
</tr>
<tr>
<td>100</td>
<td>5.432 (-20)</td>
<td>5.301 (-20)</td>
<td>7.984 (-19)</td>
<td>7.984 (-19)</td>
</tr>
</tbody>
</table>
We are also able to estimate the total Raman scattering cross-section \( \sum_{n}^{N_b} \sigma_{1,s,ns} + \sigma_{1,s,nd} \), as discussed in Chapter 4. It is important to do convergence studies, especially since we have no data to compare against for the total Raman scattering cross-sections. Table D.8 gives the total Raman scattering cross-section for ground state atomic hydrogen computed with our pseudostate method using different basis set sizes. The cross-section is presented at frequencies below threshold and several frequencies just above threshold. Evidently the total Raman scattering cross-section is converged to many significant figures at frequencies below threshold, and converges slowly at frequencies above threshold.

Table D.8: Total Raman scattering cross-section (in units of \( \sigma_T \)) of ground state atomic hydrogen given by our pseudostate method for basis set sizes \( N_\ell = 80, 100 \) and 120. The cross-sections are presented for photon frequencies both below and above ionisation threshold. The numbers in brackets (\( \times 10^x \)) denote \( (\times 10^x) \).

<table>
<thead>
<tr>
<th>( \omega ) (a.u.)</th>
<th>( N_\ell = 120 )</th>
<th>( N_\ell = 100 )</th>
<th>( N_\ell = 80 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.38</td>
<td>9.9092334774 (-3)</td>
<td>9.9092334774 (-3)</td>
<td>9.9092334737 (-3)</td>
</tr>
<tr>
<td>0.39</td>
<td>3.4050630542 (-2)</td>
<td>3.4050630542 (-2)</td>
<td>3.4050630537 (-2)</td>
</tr>
<tr>
<td>0.40</td>
<td>6.7720825864 (-2)</td>
<td>6.7720825864 (-2)</td>
<td>6.7720825858 (-2)</td>
</tr>
<tr>
<td>0.42</td>
<td>2.2068746084 (-1)</td>
<td>2.2068746084 (-1)</td>
<td>2.2068746082 (-1)</td>
</tr>
<tr>
<td>0.44</td>
<td>3.1465462347</td>
<td>3.1465462347</td>
<td>3.1465462332</td>
</tr>
<tr>
<td>0.45</td>
<td>5.6578045200 (-1)</td>
<td>5.6578045200 (-1)</td>
<td>5.6578045242 (-1)</td>
</tr>
<tr>
<td>0.46</td>
<td>1.8346572124 (-1)</td>
<td>1.8346572124 (-1)</td>
<td>1.8346572116 (-1)</td>
</tr>
<tr>
<td>0.48</td>
<td>1.7527507391 (-1)</td>
<td>1.7527507391 (-1)</td>
<td>1.7527507382 (-1)</td>
</tr>
<tr>
<td>0.49</td>
<td>6.8022603625</td>
<td>6.8022603625</td>
<td>6.8022604995</td>
</tr>
<tr>
<td>0.51</td>
<td>5.87 (-2)</td>
<td>5.86 (-2)</td>
<td>5.75 (-2)</td>
</tr>
<tr>
<td>0.52</td>
<td>4.56 (-2)</td>
<td>4.56 (-2)</td>
<td>4.48 (-2)</td>
</tr>
<tr>
<td>0.53</td>
<td>3.71 (-2)</td>
<td>3.70 (-2)</td>
<td>3.64 (-2)</td>
</tr>
<tr>
<td>0.54</td>
<td>3.11 (-2)</td>
<td>3.10 (-2)</td>
<td>3.05 (-2)</td>
</tr>
<tr>
<td>0.55</td>
<td>2.69 (-2)</td>
<td>2.68 (-2)</td>
<td>2.63 (-2)</td>
</tr>
<tr>
<td>0.60</td>
<td>1.75 (-2)</td>
<td>1.73 (-2)</td>
<td>1.69 (-2)</td>
</tr>
</tbody>
</table>

Table D.9 studies the convergence of the total Raman, as well as photoionisation and Rayleigh scattering cross-sections at frequencies further above threshold. In this table I have presented not only the cross-sections for varying basis size \( N_\ell \), but also for varying box size (by varying \( \lambda_\ell \)). As I decrease \( \lambda_\ell \) the box radius becomes larger. From table D.9 it is evident that the Rayleigh scattering cross-section is converged even at \( \omega = 100 \) a.u. On the other hand, the photoionisation cross-section no longer shows convergence at \( \omega = 100 \) a.u. This is not surprising, as I have shown in Chapter 4 that our photoionisation cross-sections are no longer as accurate at higher frequencies.

Finally, Table D.9 indicates that the total Raman scattering cross-section does not converge at frequencies above threshold. This is also not surprising, as we have found in Chapter 4 that the total Raman scattering cross-section is heavily influenced by the Rydberg states. Since primarily the higher-lying states are effected by changing basis, it is not surprising that this results in differing total Raman scattering cross-sections. In my discussion in Chapter 4 I mentioned that a better convergence study would be...
considering Raman + Compton. However, since the Raman scattering cross-sections are much smaller than the Compton scattering cross-sections, we consider the convergence of solely the Compton scattering cross-sections in Table 4.5.

Table D.9: Rayleigh, photoionisation and total Raman scattering cross-sections (in units of $\sigma_T$) calculated for ground state atomic hydrogen at several frequencies above threshold using our pseudostate method with basis set sizes $N_\ell = 80, 100$ and 120, and $\lambda_\ell = 0.49, 0.50$ and 0.51.

<table>
<thead>
<tr>
<th>$\omega$ (a.u.)</th>
<th>$N_\ell$</th>
<th>$\lambda_\ell$</th>
<th>Rayleigh</th>
<th>Photoionisation</th>
<th>Raman</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.80</td>
<td>80</td>
<td>0.49</td>
<td>1.4711</td>
<td>2.6213 (6)</td>
<td>1.2086 (-2)</td>
</tr>
<tr>
<td>0.80</td>
<td>80</td>
<td>0.50</td>
<td>1.4711</td>
<td>2.6239 (6)</td>
<td>1.2117 (-2)</td>
</tr>
<tr>
<td>0.80</td>
<td>80</td>
<td>0.51</td>
<td>1.4714</td>
<td>2.6210 (6)</td>
<td>1.2154 (-2)</td>
</tr>
<tr>
<td>0.80</td>
<td>100</td>
<td>0.49</td>
<td>1.4778</td>
<td>2.6240 (6)</td>
<td>1.2681 (-2)</td>
</tr>
<tr>
<td>0.80</td>
<td>100</td>
<td>0.51</td>
<td>1.4779</td>
<td>2.6249 (6)</td>
<td>1.2619 (-2)</td>
</tr>
<tr>
<td>0.80</td>
<td>100</td>
<td>0.50</td>
<td>1.4779</td>
<td>2.6242 (6)</td>
<td>1.2652 (-2)</td>
</tr>
<tr>
<td>0.80</td>
<td>120</td>
<td>0.49</td>
<td>1.4822</td>
<td>2.6252 (6)</td>
<td>1.3052 (-2)</td>
</tr>
<tr>
<td>0.80</td>
<td>120</td>
<td>0.50</td>
<td>1.4823</td>
<td>2.6239 (6)</td>
<td>1.3164 (-2)</td>
</tr>
<tr>
<td>0.80</td>
<td>120</td>
<td>0.51</td>
<td>1.4823</td>
<td>2.6253 (6)</td>
<td>1.3020 (-2)</td>
</tr>
<tr>
<td>4.00</td>
<td>80</td>
<td>0.49</td>
<td>1.0663</td>
<td>2.3060 (4)</td>
<td>2.4075 (-4)</td>
</tr>
<tr>
<td>4.00</td>
<td>80</td>
<td>0.50</td>
<td>1.0660</td>
<td>2.2556 (4)</td>
<td>2.4373 (-4)</td>
</tr>
<tr>
<td>4.00</td>
<td>80</td>
<td>0.51</td>
<td>1.0656</td>
<td>2.1925 (4)</td>
<td>2.4912 (-4)</td>
</tr>
<tr>
<td>4.00</td>
<td>100</td>
<td>0.49</td>
<td>1.0674</td>
<td>2.2217 (4)</td>
<td>3.1680 (-4)</td>
</tr>
<tr>
<td>4.00</td>
<td>100</td>
<td>0.50</td>
<td>1.0678</td>
<td>2.2563 (4)</td>
<td>3.6477 (-4)</td>
</tr>
<tr>
<td>4.00</td>
<td>100</td>
<td>0.51</td>
<td>1.0682</td>
<td>2.2859 (4)</td>
<td>2.4632 (-4)</td>
</tr>
<tr>
<td>4.00</td>
<td>120</td>
<td>0.49</td>
<td>1.0689</td>
<td>2.2610 (4)</td>
<td>6.7804 (-4)</td>
</tr>
<tr>
<td>4.00</td>
<td>120</td>
<td>0.50</td>
<td>1.0692</td>
<td>2.2724 (4)</td>
<td>8.1777 (-4)</td>
</tr>
<tr>
<td>4.00</td>
<td>120</td>
<td>0.51</td>
<td>1.0691</td>
<td>2.2483 (4)</td>
<td>2.9718 (-4)</td>
</tr>
<tr>
<td>20.0</td>
<td>80</td>
<td>0.49</td>
<td>1.0046</td>
<td>1.6958 (2)</td>
<td>7.3317 (-6)</td>
</tr>
<tr>
<td>20.0</td>
<td>80</td>
<td>0.50</td>
<td>1.0046</td>
<td>1.6338 (2)</td>
<td>1.1366 (-5)</td>
</tr>
<tr>
<td>20.0</td>
<td>80</td>
<td>0.51</td>
<td>1.0045</td>
<td>1.5571 (2)</td>
<td>1.7407 (-5)</td>
</tr>
<tr>
<td>20.0</td>
<td>100</td>
<td>0.49</td>
<td>1.0045</td>
<td>1.5521 (2)</td>
<td>4.6174 (-5)</td>
</tr>
<tr>
<td>20.0</td>
<td>100</td>
<td>0.50</td>
<td>1.0045</td>
<td>1.5141 (2)</td>
<td>6.8742 (-5)</td>
</tr>
<tr>
<td>20.0</td>
<td>100</td>
<td>0.51</td>
<td>1.0045</td>
<td>1.4573 (2)</td>
<td>2.8236 (-6)</td>
</tr>
<tr>
<td>20.0</td>
<td>120</td>
<td>0.49</td>
<td>1.0045</td>
<td>1.4712 (2)</td>
<td>2.3118 (-4)</td>
</tr>
<tr>
<td>20.0</td>
<td>120</td>
<td>0.50</td>
<td>1.0045</td>
<td>1.4461 (2)</td>
<td>3.0248 (-4)</td>
</tr>
<tr>
<td>20.0</td>
<td>120</td>
<td>0.51</td>
<td>1.0045</td>
<td>1.4001 (2)</td>
<td>2.7541 (-5)</td>
</tr>
<tr>
<td>100</td>
<td>80</td>
<td>0.49</td>
<td>1.0004</td>
<td>2.3956</td>
<td>2.0975 (-6)</td>
</tr>
<tr>
<td>100</td>
<td>80</td>
<td>0.50</td>
<td>1.0004</td>
<td>2.1825</td>
<td>3.5048 (-6)</td>
</tr>
<tr>
<td>100</td>
<td>80</td>
<td>0.51</td>
<td>1.0004</td>
<td>1.9849</td>
<td>5.6066 (-6)</td>
</tr>
<tr>
<td>100</td>
<td>100</td>
<td>0.49</td>
<td>1.0003</td>
<td>7.5498 (-1)</td>
<td>1.4271 (-5)</td>
</tr>
<tr>
<td>100</td>
<td>100</td>
<td>0.50</td>
<td>1.0003</td>
<td>6.7080 (-1)</td>
<td>2.1068 (-5)</td>
</tr>
<tr>
<td>100</td>
<td>100</td>
<td>0.51</td>
<td>1.0002</td>
<td>5.9666 (-1)</td>
<td>5.2928 (-7)</td>
</tr>
<tr>
<td>100</td>
<td>120</td>
<td>0.49</td>
<td>1.0003</td>
<td>1.0165</td>
<td>7.0447 (-5)</td>
</tr>
<tr>
<td>100</td>
<td>120</td>
<td>0.50</td>
<td>1.0003</td>
<td>1.0603</td>
<td>9.3125 (-5)</td>
</tr>
<tr>
<td>100</td>
<td>120</td>
<td>0.51</td>
<td>1.0003</td>
<td>1.0697</td>
<td>8.2569 (-6)</td>
</tr>
</tbody>
</table>