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# Investigation of Theoretical Approaches for Computing Relativistic Atomic Form Factors

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## **Abstract**

The calculation of accurate atomic form factors is of great importance in fields such as crystallography and medicine, as they provide valuable information about how photons (especially in the X-ray regime) interact with matter. Theoretical methods for calculating relativistic atomic form factors are investigated with an emphasis on the Hydrogen atom. New results and comparisons with other theories for relativistic normal form factors for hydrogenic atoms are presented. Anomalous form factor calculations using a relativistic S-matrix approach are also computed for hydrogen using an “all-poles” and the electric dipole approximation.

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# 1 PROJECT OVERVIEW AND ATOMIC FORM FACTOR THEORY

## 1.1 Introduction

The use of high energy radiation has many wide spread uses. In particular, the understanding of how radiation in the X ray regime interacts with matter has applications in areas such as astronomy, medicine and in the study of the structure of materials such as in the field of crystallography.

In order to be able to interpret results of experiments which make use of X rays or other high energy photons we must understand how such photons interact with matter. The most fundamental process that can be considered is the interaction of a single photon with a single isolated atom. This can include the study of coherent and incoherent scattering processes, photoionisation, photoabsorption and pair production.

In particular, the theoretical calculation of atomic form factors allows the determination of quantities such as cross sections and attenuation coefficients which are valuable in obtaining information about the atom-photon interaction process.

The study of atom-photon interactions through the calculation of atomic form factors covering all elements has been the subject of decades of experimental and theoretical research. This work includes the synthesis by Henke [13] of experimental and theoretical results, theoretical results using the relativistic dipole approximation of Cromer and Libermann [9, 11, 10], theoretical results of Kane et al. based on S-matrix theory [15], recent theoretical tabulations by Chantler [5], the results of Saloman, Hubbell and Scofield [23] and the results of Creagh [7, 8].

## 1.2 Project Aims

Major improvements on current results [4] would also involve many years of additional research. However, a detailed comprehension of the assumptions made in research to date may be made by a detailed and critical study of form factor calculations for hydrogen; in particular looking at the different assumptions and methods used to compute atomic form factors. This study of hydrogen allows us to show new results for:

1. Analytic forms for the relativistic normal form factor for hydrogenic atoms.
2. Numerical results for imaginary component of the anomalous form factor for hydrogen using a relativistic S-matrix approach.
3. The angular dependence of the photionisation differential cross sections at selected energies.
4. Semi-analytic results for hydrogenic bound-bound transition matrix elements.

## 1.3 Atomic Form Factor Theory

The atomic form factor is given by the x-ray scattering amplitude  $f$  which by convention separated into a number of components. It is commonly written as [4]

$$f = f_0 + f' + if'' \quad (1.1)$$

where  $f_0 = f_0(q, Z)$  is known as the normal or coherent scattering amplitude and is a function of momentum transfer  $q$  and atomic number  $Z$ . The anomalous scattering component (also known as

the anomalous dispersion or resonant scattering component) has real and imaginary parts given by  $f'$  and  $f''$ . The anomalous component is a function of the incident photon energy. In the literature  $f'$  and  $f''$  are also known as  $f_1$  and  $f_2$ .

### 1.3.1 Normal Component

The normal component of the atomic form factor is defined as the Fourier transform of an atom's electronic charge density [6]. The expression for  $f_0(q)$  with an atom with electronic charge density  $\rho(\mathbf{r})$ , is given below with the second equation being valid for the case of a spherically symmetric atom [4].

$$f_0(q) = \int \rho(\mathbf{r}) e^{i\mathbf{q}\cdot\mathbf{r}} d\mathbf{r} = \int_0^\infty \rho(r) \frac{\sin(qr)}{qr} r^2 dr \quad (1.2)$$

The momentum transfer is defined as

$$q = |\mathbf{k}_{\text{final}} - \mathbf{k}_{\text{initial}}| = \frac{4\pi \sin(\theta/2)}{\lambda} \quad (1.3)$$

where  $\lambda$  is the wavelength of the incident photon and  $\theta$  is the scattering angle. It is conventional to measure the momentum transfer  $q$  in inverse Angstroms ( $\text{\AA}^{-1}$ ).

### 1.3.2 Anomalous Component

The imaginary part of the anomalous form factor is related to the total photoionisation cross section.

$$f''(\omega) = \frac{\omega}{4\pi c r_0} \sigma(\omega) \quad (1.4)$$

The photon energy is given by  $\hbar\omega$ ,  $c$  is the speed of light and  $r_0$  is the classical electron radius. The photionisation cross section  $\sigma(\omega)$  may also include cross sections from bound-bound transitions.

The  $f'$  component may be computed from the  $f''$  component using a dispersion relation.

$$f'(\omega) = f'(\infty) - \frac{2}{\pi} P \int_0^\infty \frac{\omega' f''(\omega')}{\omega^2 - \omega'^2} d\omega' \quad (1.5)$$

### 1.3.3 Theoretical Limitations and Assumptions

The theoretical calculations of atomic form factors are usually made with a number of limitations and/or assumptions. These fall into a number of different categories. Improvements to existing theories attempt to eliminate one or more of these assumptions or limitations.

1. **ATOMIC STRUCTURE** : For a simple atom such as hydrogen, the quantum mechanical wave-functions of an atom may be either non relativistic (standard Schrödinger wave-functions), or relativistic (four component Dirac spinors). For many-electron atoms there is still a choice between non relativistic and relativistic wave-functions but additional choices have to be made as how to compute these wave-functions as analytic solutions are not available. Methods for computing many electron wave-functions include Hartree-Fock (HF), Dirac-Hartree-Fock (DHF), Hartree-Slater (HS), Multi-Configuration-Dirac-Fock (MCDF) and all orders methods which include quantum electrodynamic corrections [24]. Although issues such as the suitability of the independent particle approximation (IPA) and the computational methods used to determine atomic structure are important in the areas of atomic physics, many body perturbation theory and computational chemistry, they are also of relevance to form factor theory due to the reliance on accurate computed wave-functions.



2. *ELECTROMAGNETIC FIELD* : The incident photon is modeled as either a classical or quantised electromagnetic field. The simpler approach of using a classical electromagnetic field is more common and approximations to this model involve considering only the electric dipole (E1) and/or electric quadrupole (E2) approximations. Alternatives includes using a relativistic multipole (RMP) or an “all-poles” approach can be taken in which no approximations to the classical electromagnetic field are made.
3. *ISOLATED ATOM* : Most form factor calculations are done for a single isolated atom. However, experimentally it is extremely difficult if not impossible to obtain results from an isolated atom. As a result, there are inherent limitations in theories which consider only the case of an isolated atom. Experimentally, effects such as XAFS (X-ray Anomalous Fine Structure) arise from multiple scattering processes off multiple atoms.
4. *PERTURBATION THEORY* : Models of atom-photon interactions usually treat the electromagnetic field model of the photon as a small perturbation, and such there are a number of approaches in computing the required matrix elements and relevant scattering amplitudes. The main issue involves the order of the perturbation theory (usually first or second order) and the type of perturbation theory used - standard (time dependent or time independent), relativistic perturbation theory and second order S-matrix theory which is obtained from covariant perturbation theory.
5. *ADDITIONAL PROCESSES* : A number of processes can occur when a photon interacts with an atom. An atomic form factor calculation usually includes one or more of these processes. These processes include:
  - Photoionisation
  - Bound-Bound Transitions
  - Rayleigh (Coherent) Scattering
  - Compton (Incoherent) Scattering
  - Delbrück Scattering
  - Pair Production
  - Nuclear Thomson Scattering
6. *NUMERICAL AND COMPUTATIONAL* : Form factor calculations require considerable computational work. Therefore a number of numerical computation issues need to be considered. These includes choices for integration and interpolation methods, numerical precision, convergence and computation time.

## 2 REVIEW OF ATOMIC STRUCTURE

This section describes the atomic structure information required for the form factor calculations such as physical constants, definitions, atomic energy levels and atomic wave functions.

### 2.1 Constants and Definitions

We first need to define the usual symbols which are common in atomic physics.

Symbol	Meaning
$c$	Speed Of Light
$e$	Electron Charge
$m$	Electron Mass
$a_0$	Bohr Radius
$\alpha$	Fine Structure Constant
$\hbar$	Planck's Constant/ $2\pi$
$r_0$	Classical Electron Radius
$Z$	Atomic Number
$Y_{lm}(\theta, \phi)$	Spherical Harmonics

We will use  $\mathbf{k} = (k_x, k_y, k_z)$  to represent the photon wave propagation vector, and in the case of photoionisation, we will use  $\mathbf{k}' = (k'_x, k'_y, k'_z)$  for the wave-vector of the ejected electron. Electronic coordinates with respect to the nucleus will be denoted by  $\mathbf{r} = (r, \theta, \phi)$  whereas the ejection angles of a photo-electron will be denoted by  $\Omega = (\Theta, \Phi)$ . In order to avoid confusion with the fine structure constant  $\alpha$ , the Dirac alpha matrix will be denoted by  $\bar{\alpha}$  where

$$\bar{\alpha} = \begin{pmatrix} 0 & \boldsymbol{\sigma} \\ \boldsymbol{\sigma} & 0 \end{pmatrix} \quad (2.1)$$

and where  $\boldsymbol{\sigma}$  are the Pauli spin matrices.

When dealing with four component spinors the following definitions have been adopted.

- $|i\rangle$  denotes the  $i^{\text{th}}$  state of an atom. For example,  $|0\rangle$  denotes the ground state,  $|1\rangle$  denotes the first excited state etc.  $|c\rangle$  denotes the continuum or free electron state. The state  $|i\rangle$  may also be written as  $\psi_i$ .
- $\psi_{ij}$  denotes the  $j^{\text{th}}$  component of the  $i^{\text{th}}$  atomic state.
- $g_i(r)$  and  $h_i(r)$  denote the radial components of the  $i^{\text{th}}$  atomic state.
- $A_{ij}(\theta, \phi)$  denotes the  $j^{\text{th}}$  angular component of the  $i^{\text{th}}$  atomic state.

$$\gamma_1 = \sqrt{1 - (\alpha Z)^2} \quad \gamma_2 = \sqrt{4 - (\alpha Z)^2} \quad (2.2)$$

$$N_1 = 1; \quad N_2 = \sqrt{2(1 + \gamma_1)}; \quad N_3 = 2; \quad \sigma_1 = \left( \frac{2Z}{N_1 a_0} \right) \quad (2.3)$$

$$\epsilon_1 = \left[ 1 + \left( \frac{\alpha Z}{\gamma_1} \right)^2 \right]^{-1/2} \quad \epsilon_2 = \left[ 1 + \left( \frac{\alpha Z}{1 + \gamma_1} \right)^2 \right]^{-1/2} \quad \epsilon_3 = \left[ 1 + \left( \frac{\alpha Z}{\gamma_2} \right)^2 \right]^{-1/2} \quad (2.4)$$

## 2.2 The Schrödinger Equation and Non Relativistic Wave-functions

The Schrödinger equation for an electron in a Coulomb potential describes the non relativistic structure of a hydrogen atom. Ignoring fine structure corrections, the equation can be written as:

$$\left[ -\frac{\hbar^2}{2m} \nabla^2 - \frac{Ze}{r} \right] \psi(\mathbf{r}) = E\psi(\mathbf{r}) \quad (2.5)$$

Solutions to this equation [3] give the energy levels of the hydrogen atom as a function of the principal quantum number  $n$

$$E_n = -\frac{e^2}{4\pi\epsilon_0 a_0} \frac{Z^2}{2n^2} \quad (2.6)$$

and wave functions as a function of the three space variables  $r$ ,  $\theta$  and  $\phi$  and the three quantum numbers  $n, l$  and  $m$ .

$$\psi_{nlm}(r, \theta, \phi) = R_{nl}(r)Y_{lm}(\theta, \phi) = -\sqrt{\left(\frac{2Z}{na_0}\right)^3 \frac{(n-l-1)!}{2n[(n+l)!]^3}} e^{-\rho/2} \rho^l L_{n+l}^{2l+1}(\rho) Y_{lm}(\theta, \phi) \quad (2.7)$$

where  $\rho = 2Zr/na_0$ ,  $a_0 = 4\pi\epsilon_0\hbar^2/e^2m$ ,  $Y_{lm}(\theta, \phi)$  are the spherical harmonics and  $L_{n+l}^{2l+1}(\rho)$  are the associated Laguerre polynomials [3].

For example, the ground state wave-function of hydrogen ( $\psi_{1s}$  or  $\psi_{100}$ ) is defined as:

$$\psi_{1s}(r, \theta, \phi) = \frac{1}{\sqrt{\pi}} \left(\frac{Z}{a_0}\right)^{3/2} e^{-Zr/a_0}. \quad (2.8)$$

## 2.3 The Dirac Equation and Relativistic Wave-functions

In order to obtain more accurate energy levels and wave-functions for hydrogen, the effects of special relativity which give rise to the fine structure in the hydrogen spectrum need to be considered. and as such the solutions to the Dirac equation for an electron in a central coulombic field need to be used. The Dirac equation is shown here (where  $\psi$  is a four component spinor wave-functions) together with its energy eigenvalue  $E_{nj}$  for hydrogenic atoms.

$$\left[ e\vec{\alpha} \cdot \mathbf{p} + \beta mc^2 - \frac{Ze^2}{r} \right] \psi = E_{nj}\psi \quad ; \quad E_{nj} = \frac{mc^2}{\sqrt{1 + \frac{(Z\alpha)^2}{n-j-\frac{1}{2} + \sqrt{(j+\frac{1}{2})^2 - (Z\alpha)^2}}}} \quad (2.9)$$

Solutions to the Dirac equation for hydrogenic atoms are written in terms of four component spinors, separated in radial and angular components as defined in [2]. There are two general spinor solutions  $\psi_a$  corresponding to the case when  $j = l + 1/2$  and  $\psi_b$  for the case when  $j = l - 1/2$ . Note, also that the large and small components of the radial wave-functions are denoted by  $g(r)$  and  $h(r)$  instead of the more traditional  $g(r)$  and  $f(r)$ , so as to avoid confusion with equation for the form factor which uses the symbol  $f$ .

$$\psi_a = \begin{pmatrix} g(r)\sqrt{\frac{l+m+1/2}{2l+1}}Y_{l,m-1/2}(\theta, \phi) \\ -g(r)\sqrt{\frac{l-m+1/2}{2l+1}}Y_{l,m+1/2}(\theta, \phi) \\ -ih(r)\sqrt{\frac{l-m+3/2}{2l+3}}Y_{l+1,m-1/2}(\theta, \phi) \\ -ih(r)\sqrt{\frac{l+m+3/2}{2l+3}}Y_{l+1,m+1/2}(\theta, \phi) \end{pmatrix} \quad \psi_b = \begin{pmatrix} g(r)\sqrt{\frac{l-m+1/2}{2l+1}}Y_{l,m-1/2}(\theta, \phi) \\ g(r)\sqrt{\frac{l+m+1/2}{2l+1}}Y_{l,m+1/2}(\theta, \phi) \\ -ih(r)\sqrt{\frac{l+m-1/2}{2l-1}}Y_{l-1,m-1/2}(\theta, \phi) \\ ih(r)\sqrt{\frac{l-m-1/2}{2l-1}}Y_{l-1,m+1/2}(\theta, \phi) \end{pmatrix} \quad (2.10)$$

The radial components  $g(r)$  and  $f(r)$  of the spinors can be written in general in terms of the hypergeometric function  $F(a, b, x)$ .

$$g(r) = -\frac{\sqrt{\Gamma(2\gamma + n' + 1)}}{\Gamma(2\gamma + 1)\sqrt{n'!}} \sqrt{\frac{1 + \epsilon}{4N(N - x)}} \left(\frac{2Z}{Na_0}\right)^{3/2} e^{-Zr/a_0} \left(\frac{2Zr}{Na_0}\right)^{\gamma-1} \times \left[ -n'F(-n' + 1, 2\gamma + 1, \frac{2Zr}{Na_0}) + (N - x)F(-n', 2\gamma + 1, \frac{2Zr}{Na_0}) \right] \quad (2.11)$$

$$h(r) = -\frac{\sqrt{\Gamma(2\gamma + n' + 1)}}{\Gamma(2\gamma + 1)\sqrt{n'!}} \sqrt{\frac{1 - \epsilon}{4N(N - x)}} \left(\frac{2Z}{Na_0}\right)^{3/2} e^{-\frac{Zr}{Na_0}} \left(\frac{2Zr}{Na_0}\right)^{\gamma-1} \times \left[ n'F(-n' + 1, 2\gamma + 1, \frac{2Zr}{Na_0}) + (N - x)F(-n', 2\gamma + 1, \frac{2Zr}{Na_0}) \right] \quad (2.12)$$

Where we have  $x = -(j + 1/2) = -(l + 1)$  if  $j = l + 1/2$ ,  $x = j + 1/2 = +l$  if  $j = l - 1/2$ ,  $\gamma = \pm\sqrt{x^2 - (Z\alpha)^2}$ ,  $\epsilon = E/E_0$  (energy/rest mass energy),  $n' = \alpha Z\epsilon/\sqrt{1 - \epsilon^2} - \gamma$ ,  $N = \sqrt{n^2 - 2n'(k - \sqrt{k^2 - \alpha^2 Z^2})}$ ,  $k = |x|$ , and  $m = \pm(l + 1/2)^1$ .

### 2.3.1 The Ground State

The ground state (or  $1S_{\frac{1}{2}}$ ) of the hydrogen atom corresponds to the quantum numbers  $n = 1$ ,  $l = 0$  and  $j = \frac{1}{2}$ . This corresponds to the  $j = l + \frac{1}{2}$  spinor.

$$|1S_{\frac{1}{2}}\rangle = |0\rangle = \begin{pmatrix} A_{01}(\theta, \phi) g_0(r) \\ A_{02}(\theta, \phi) g_0(r) \\ A_{03}(\theta, \phi) h_0(r) \\ A_{04}(\theta, \phi) h_0(r) \end{pmatrix} = \begin{pmatrix} Y_{00}g_0(r) \\ 0 \\ -i\sqrt{\frac{1}{3}}Y_{10}h_0(r) \\ -i\sqrt{\frac{2}{3}}Y_{11}h_0(r) \end{pmatrix} \quad (2.13)$$

$$g_0(r) = G_0 e^{-\frac{1}{2}\sigma_1 r} r^{\gamma_1 - 1} \quad h_0(r) = H_0 g_0(r) \quad (2.14)$$

$$H_0 = -\sqrt{\frac{1 - \epsilon_1}{1 + \epsilon_1}} \quad G_0 = \left(\frac{2Z}{a_0}\right)^{3/2} \sqrt{\frac{1 + \epsilon_1}{2\Gamma(2\gamma_1 + 1)}}$$

### 2.3.2 The First Excited State

$$|2S_{1/2}\rangle = |1\rangle = \begin{pmatrix} A_{11}(\theta, \phi) g_1(r) \\ A_{12}(\theta, \phi) g_1(r) \\ A_{13}(\theta, \phi) h_1(r) \\ A_{14}(\theta, \phi) h_1(r) \end{pmatrix} = \begin{pmatrix} Y_{00}g_1(r) \\ 0 \\ -i\sqrt{\frac{1}{3}}Y_{10}h_1(r) \\ -i\sqrt{\frac{2}{3}}Y_{11}h_1(r) \end{pmatrix} \quad (2.15)$$

$$g_1(r) = e^{-\frac{1}{2}\sigma_2 r} r^{\gamma_1} \left(G'_1 \frac{1}{r} - G''_1\right) \quad h_1(r) = H_1 \left(\frac{H'_1 - H''_1 r}{H'_1 r - H'''_1 r}\right) g_1(r) \quad (2.16)$$

$$G_1 = \left(\frac{2Z}{Na_0}\right)^{3/2} \sqrt{\frac{2\gamma_1 + 1}{\Gamma(2\gamma_1 + 1)}} \sqrt{\frac{1 + \epsilon_2}{4N_2(N_2 + 1)}}; \quad G'_1 = N_2 G_1 \sigma_2^{\gamma_1 - 1}; \quad G''_1 = \left(\frac{N_2 + 1}{2\gamma_1 + 1}\right) G_1 \sigma_2^{\gamma_1}$$

$$H_1 = -\sqrt{\frac{1 - \epsilon_2}{1 + \epsilon_2}}; \quad H'_1 = (2\gamma_1 + 1)(N_2 + 2); \quad H''_1 = (N_2 + 1)\sigma_2$$

$$H'''_1 = (2\gamma_1 + 1)N_2; \quad H''''_1 = (N_2 + 1)\sigma_2$$

<sup>1</sup>See Bethe and Salpeter [2] for a detailed explanation of all these constants and definitions

## 2.3.3 The Second Excited State

$$|2P_{1/2}\rangle = |2\rangle = \begin{pmatrix} A_{21}(\theta, \phi)g_2(r) \\ A_{22}(\theta, \phi)g_2(r) \\ A_{23}(\theta, \phi)h_2(r) \\ A_{24}(\theta, \phi)h_2(r) \end{pmatrix} = \begin{pmatrix} \sqrt{\frac{1}{3}}Y_{10}g_2(r) \\ \sqrt{\frac{2}{3}}Y_{11}g_2(r) \\ -iY_{00}h_2(r) \\ 0 \end{pmatrix} \quad (2.17)$$

$$g_2(r) = e^{-\frac{1}{2}\sigma_2 r} r^{\gamma_1} (G_2' \frac{1}{r} - G_2'') ; \quad h_2(r) = H_2 \left( \frac{H_2' - H_2'' r}{H_2''' - H_2'''' r} \right) g_2(r) \quad (2.18)$$

$$G_2 = \left( \frac{2Z}{N_2 a_0} \right)^{3/2} \sqrt{\frac{2\gamma_1+1}{\Gamma(2\gamma_1+1)}} \sqrt{\frac{1+\epsilon_2}{4N_2(N_2-1)}} ; \quad G_2' = (N_2 - 2)\sigma_2^{\gamma_1-1} G_2 ; \quad G_2'' = \left( \frac{N_2-1}{2\gamma_1+1} \right) \sigma_2^{\gamma_1} G_2$$

$$H_2 = -\sqrt{\frac{1-\epsilon_2}{1+\epsilon_2}} \quad H_2' = (2\gamma_1 + 1)N_2$$

$$H_2'' = (N_2 - 1)\sigma_2 \quad H_2''' = (2\gamma_1 + 1)(N_2 - 2) \quad H_2'''' = (N_2 - 1)\sigma_2$$

## 2.3.4 The Third Excited State

$$|2P_{3/2}\rangle = |3\rangle = \begin{pmatrix} A_{31}(\theta, \phi)g_3(r) \\ A_{32}(\theta, \phi)g_3(r) \\ A_{33}(\theta, \phi)h_3(r) \\ A_{34}(\theta, \phi)h_3(r) \end{pmatrix} = \begin{pmatrix} \sqrt{\frac{2}{3}}Y_{10}g_3(r) \\ -\sqrt{\frac{1}{3}}Y_{11}g_3(r) \\ -i\sqrt{\frac{2}{5}}Y_{20}h_3(r) \\ -i\sqrt{\frac{3}{5}}Y_{21}h_3(r) \end{pmatrix} \quad (2.19)$$

$$g_3(r) = G_3 e^{-\frac{1}{2}\sigma_3 r} r^{\gamma_2-1} ; \quad h_3(r) = H_3 g_3(r) \quad (2.20)$$

$$G_3 = \left( \frac{Z}{a_0} \right)^{3/2} \sqrt{\frac{1+\epsilon_3}{2\Gamma(2\gamma_2+1)}} \sigma_3^{\gamma_2-1} ; \quad H_3 = -\sqrt{\frac{1-\epsilon_3}{1+\epsilon_3}}$$

## 2.3.5 The Free Dirac Electron

The continuum state is described by a free Dirac electron state with energy  $E$  and momentum wave-vector  $\mathbf{k}' = (k'_x, k'_y, k'_z)$ . Such a state, can be represented by one of the two four-component spinors below.

$$|\psi_c\rangle_{\uparrow} = \begin{pmatrix} 1 \\ 0 \\ \xi k'_z \\ \xi(k'_x + ik'_y) \end{pmatrix} ; \quad |\psi_c\rangle_{\downarrow} = \begin{pmatrix} 0 \\ 1 \\ \xi(k'_x - ik'_y) \\ -\xi k'_z \end{pmatrix} ; \quad \xi = \frac{c\hbar}{E+E_0} \quad (2.21)$$

Where we have  $E$  and  $E_0$  as the electron's kinetic and rest mass energy respectively. The  $|\psi_c\rangle_{\uparrow}$  represents the electron in the spin up state, whereas the  $|\psi_c\rangle_{\downarrow}$  represents the electron in the spin down state.

### 3 NORMAL FORM FACTOR FOR HYDROGENIC ATOMS

#### 3.1 Non Relativistic Theory

Using the non relativistic Schrödinger equation, the ground state wave-function for a hydrogenic atom is given by equation 2.8. The corresponding electron density for the ground state is given by  $\rho(\mathbf{r}) = \psi_{1s}^* \psi_{1s} = \frac{1}{\pi a_0^3} e^{-2Zr/a_0}$ . We know that for a hydrogenic atom we can assume spherical symmetry, and therefore by substituting the charge density into equation 1.2 we get the non relativistic normal form factor for hydrogenic atoms.

$$f_0(q) = \frac{4}{q} \left( \frac{Z}{a_0} \right)^3 \int_0^\infty e^{-2Zr/a_0} \sin(qr) r \, dr$$

$$\boxed{f_0(q) = \left( \frac{2Z}{a_0} \right)^4 \left[ \left( \frac{2Z}{a_0} \right)^2 + q^2 \right]^{-2}} \quad (3.1)$$

Here we have  $q = 4\pi \sin(\theta/2)/\lambda \text{ \AA}^{-1}$  as stated earlier. This result was also obtained by Hubbell [14] and Pirenne [19], however in a slightly modified form due to a different definition of  $q$  which does not include the factor of  $4\pi$ .

#### 3.2 New Results from Relativistic Theory

To compute the relativistic version of the normal form factor, we need to use the Dirac four component spinors. As for the non relativistic case we need to determine the electronic charge density given by:  $\rho(\mathbf{r}) = \psi^\dagger \psi = |\psi_1|^2 + |\psi_2|^2 + |\psi_3|^2 + |\psi_4|^2$

Using the ground state solution to the Dirac equation for hydrogenic atoms given by equation 2.13, the electron density is given by:

$$\begin{aligned} \rho(\mathbf{r}) &= |g_0(r)Y_{00}|^2 + \frac{1}{3}|ih_0(r)Y_{10}|^2 + \frac{2}{3}|ih_0(r)Y_{11}|^2 \\ \rho(\mathbf{r}) &= \frac{1}{4\pi} (|g_0(r)|^2 + |h_0(r) \cos \theta|^2 + |h_0(r) \sin \theta e^{i\phi}|^2) = \frac{1}{4\pi} (|g_0(r)|^2 + |h_0(r)|^2) \end{aligned}$$

The radial function  $g_0(r)$  and  $h_0(r)$  are defined by equation 2.14. Once again using the assumption that a hydrogenic atom is spherically symmetric we substitute the electron density  $\rho$  into the normal form factor equation given by 1.2.

$$\begin{aligned} f_0(q) &= \frac{1}{q} \int_0^\infty \sin(qr) r (|g_0(r)|^2 + |h_0(r)|^2) \, dr = \frac{2}{q(1 + \epsilon_1)} \int_0^\infty r |g_0(r)|^2 \sin(qr) \, dr \\ &= \frac{1}{q \Gamma(2\gamma_1 + 1)} \left( \frac{2Z}{a_0} \right)^{2\gamma_1 + 1} \int_0^\infty r^{2\gamma_1 - 1} e^{-2Zr/a_0} \sin(qr) \, dr \\ &= \frac{1}{2iq \Gamma(2\gamma_1 + 1)} \left( \frac{2Z}{a_0} \right)^{2\gamma_1 + 1} \left[ \int_0^\infty r^{2\gamma_1 - 1} e^{-(2Z/a_0 - iq)r} \, dr - \int_0^\infty r^{2\gamma_1 - 1} e^{-(2Z/a_0 + iq)r} \, dr \right] \end{aligned}$$

Making use of the standard integral  $\int_0^\infty x^n e^{-ax} \, dx = \frac{\Gamma(n+1)}{a^{n+1}}$ , and after some algebraic manipulation, we obtain equation 3.2. Equation 3.2 is a *new* result, providing an explicit analytic solution

for the relativistic normal form factor for hydrogenic atoms.

$$f_0(q) = \frac{\Gamma(2\gamma_1)}{2iq\Gamma(2\gamma_1 + 1)} \left(\frac{2Z}{a_0}\right)^{2\gamma_1+1} \left[ \frac{\left(\frac{2Z}{a_0} + iq\right)^{2\gamma_1} - \left(\frac{2Z}{a_0} - iq\right)^{2\gamma_1}}{\left[\left(\frac{2Z}{a_0}\right)^2 + q^2\right]^{2\gamma_1}} \right] \quad (3.2)$$

This equation cannot be simplified any further because  $\gamma_1$  is not an integer. Although the equation has expression containing the complex number  $i$ , when it is evaluated  $f_0(q)$  is real valued as expected.

Previous work in this area include the analytic atomic form factor for two electrons in the ground state (K shell) for a helium like atom by Bethe and Levinger [18] and Smend and Schumacher [26]. The normal form factor for two electrons in the K shell as quote in Schaupp et al. [25] is

$$f_0(q) = \frac{(2Z\alpha)^{2\gamma_1+1}}{\gamma_1 q} \frac{\sin[2\gamma_1 \arctan(\frac{q}{2Z\alpha})]}{[(2Z\alpha)^2 + q^2]^{\gamma_1}}. \quad (3.3)$$

### 3.3 Comparing the Non Relativistic and Relativistic Results

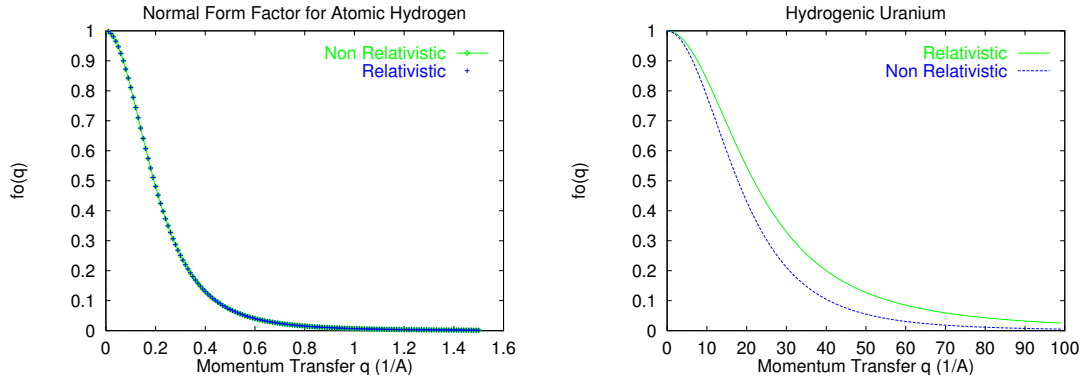


Figure 3.1: Normal Form Factor for Single Electron Hydrogen and Uranium

The relativistic normal form factor in equation 3.2 can be compared to the non relativistic case by considering the small values of  $Z$  in which the parameter  $\gamma_1 = \sqrt{1 - \alpha^2 Z^2} \approx 1$ . In this case equation 3.2 becomes:

$$f_0(q) \approx 2 \frac{\Gamma(2)}{\Gamma(3)} \left(\frac{2Z}{a_0}\right)^4 \left[ \left(\frac{2Z}{a_0}\right)^2 + q^2 \right]^{-2} = \left(\frac{2Z}{a_0}\right)^4 \left[ \left(\frac{2Z}{a_0}\right)^2 + q^2 \right]^{-2} \quad (3.4)$$

which is in agreement with equation 3.1. In figure 3.1 we see plots for  $f_0(q)$  comparing the non relativistic and relativistic results for standard atomic hydrogen and hydrogenic uranium. We can see that in the case of atomic hydrogen ( $Z = 1$ ), there is excellent agreement between the two results. In the case of hydrogenic uranium ( $Z = 92$ ) we can see that there is a significant difference over a range of momentum transfers between the relativistic and non relativistic results. This shows the need for using relativistic Dirac wave functions as opposed to the Schrödinger wave functions when computing atomic form factors especially for heavier atoms. In figure 3.1 it is difficult to make out difference between relativistic and non relativistic values for atomic hydrogen, since there seems to be quite good agreement between the two. However, if we plot the difference between the two results as is done in figure 3.2, we can clear identify the regions

of momentum transfer where the relativistic theory is better even though the difference is of the order of  $10^{-6}$  or less. We can see that the maximum difference between the two theories is at approximately  $q = 0.3 \text{ \AA}^{-1}$  and it gets smaller at higher values of  $q$ .

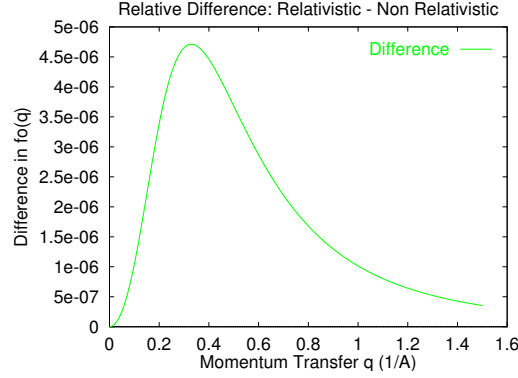


Figure 3.2: Difference ( $\Delta f_0(q)$ ) between relativistic and non relativistic theory

### 3.4 Comparison with other theoretical results

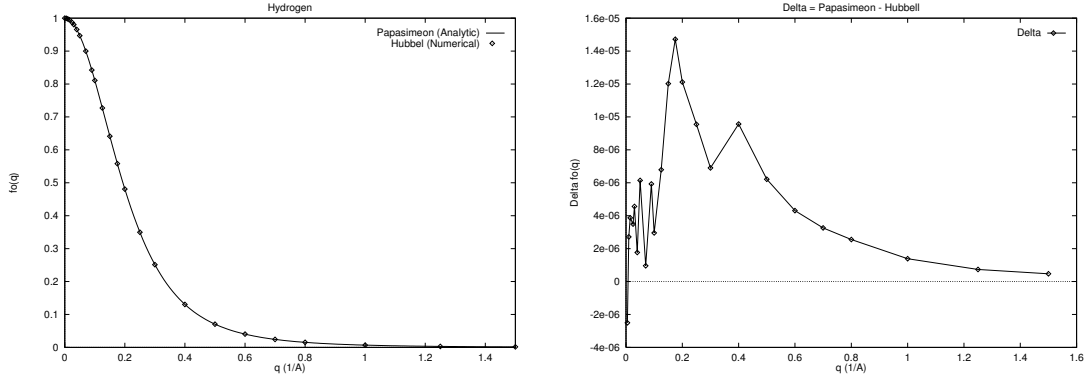


Figure 3.3: Normal Form Factor for Hydrogen – Comparison With Hubbell's Theoretical Results

We can make a comparison between the results obtained using equation 3.2 and other theoretical results which have used relativistic wave functions in computing  $f_0(q)$ . Tabulations of atomic form factors, incoherent scattering function and photon scattering cross sections were published by Hubbel et. al. [14]. The tabulations for the normal form factor for hydrogen used non relativistic wave functions. Figure 3.3 shows two plots comparing the analytic result of equation 3.2 with Hubbell's tabulated results. The plot on the left shows good agreement, but looking at the difference between the two theories on the plot on the right shows the differences more clearly. The shape is similar to that shown in figure 3.2 but the maximum difference is of the order of  $10^{-5}$ .



## 4 ANOMALOUS FORM FACTOR FOR HYDROGENIC ATOMS

### 4.1 Computing $f''(\omega)$

From equation 1.4 we see that in order to determine the imaginary component of the anomalous form factor  $f''$  we need to know the total photoionisation cross section. Therefore the basic tool that is required is the computation of the photo-electric matrix element which will give as the photoionisation amplitude. This matrix element can then be used in two approaches to computing  $f''$  such as:

- Relativistic First Order Perturbation Theory
- Second Order S-Matrix Theory

We have concentrated on obtaining results for the form factor using second order S-Matrix theory. The purpose is to attempt to obtain analytic solutions to these problems. Numerical techniques will be used when it is no longer possible to solve a problem analytically.

### 4.2 Amplitude for Photoionisation

The relativistic photon absorption and emission operators for many electron atoms are defined [20] as:

$$\mathcal{A}_i = \sum_j \bar{\alpha} \cdot \hat{\epsilon}_j e^{i\mathbf{k}_i \cdot \mathbf{r}_j} \quad (4.1)$$

$$\mathcal{A}_f^\dagger = \sum_j \bar{\alpha} \cdot \hat{\epsilon}_j e^{-i\mathbf{k}_f \cdot \mathbf{r}_j} \quad (4.2)$$

where the sum is over all the electrons in an atom,  $\bar{\alpha}$  is the Dirac alpha matrix,  $\mathbf{r}_j$  is the position of the  $j$ -th electron,  $\hat{\epsilon}_j$  is the polarisation of the photon and  $\mathbf{k}$  is the wave vector of the photon. The subscripts  $i$  and  $f$  indicate initial and final states respectively. This is needed if we are considering for example Compton (inelastic) scattering where the momentum of the photon changes in a scattering process. However, for the case of Rayleigh scattering the photon momentum is unchanged ( $\hbar\omega_i = \hbar\omega_f$ ) and as such in this case we drop the subscripts and just use the symbols  $\omega$  and  $\mathbf{k}$ .

We also need to define the coordinate system to be used to describe photoionisation. The coordinate system setup is shown in figure 4.1. The small case angles  $(\theta, \phi)$  are used to describe the angular position of an electron bound to an atom, whereas the angles  $(\Theta, \Phi)$  are used to describe the electron ejected angle. We make the following assumptions:

- The incident photon has energy  $\hbar\omega$  and is traveling in the  $+Z$  direction with a momentum wave-vector  $\mathbf{k} = (k_x, k_y, k_z)$ .
- The photon has a constant well defined polarisation. We will consider photon polarisations in the  $x$  and  $y$  directions.
- The ejected electron has a wave-vector  $\mathbf{k}' = k'_x, k'_y, k'_z$  which defines its linear momentum and ejection direction/angles since:

$$\begin{aligned} k'_x &= |k'| \sin(\Theta) \cos(\Phi) \\ k'_y &= |k'| \sin(\Theta) \sin(\Phi) \\ k'_z &= |k'| \cos(\Theta) \end{aligned} \quad (4.3)$$

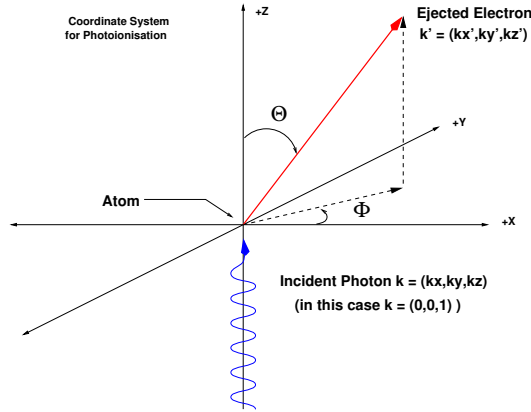


Figure 4.1: Coordinate System for Photoionisation [3]

- The atom is initially in its ground state, and is represented by a  $|1S_{1/2}\rangle$  (or  $|0\rangle$  or  $\psi_0$ ) wave-function (non relativistic or relativistic).
- After photoionisation the ejected electron will be represented by a continuum (or free electron) state  $|c\rangle$  (or  $\psi_c$ ), (non relativistic or relativistic).

#### 4.2.1 Photoionisation to a Continuum State

We first consider the first order photo-electric matrix element for a single electron atom using 4.1:  $A_1 = \langle \psi_c | \mathcal{A} | \psi_0 \rangle = \langle \psi_c | e^{i\mathbf{k}\cdot\mathbf{r}} \bar{\alpha}_j | \psi_0 \rangle$ . In the case that the incident photon is polarised either in the  $x$  or  $y$  direction, and knowing that the second components of the ground state and continuum states are both zero ( $\psi_{02} = 0$  and  $\psi_{c2} = 0$ ) results in the following form for  $A_1$ :

$$A_1 = \langle \psi_c | e^{i\mathbf{k}\cdot\mathbf{r}} \bar{\alpha}_j | \psi_0 \rangle = \begin{cases} \int \psi_{c1}^* e^{i\mathbf{k}\cdot\mathbf{r}} \psi_{04} d^3\mathbf{r} & + \int \psi_{c4}^* e^{i\mathbf{k}\cdot\mathbf{r}} \psi_{01} d^3\mathbf{r} = m_1 + m_2 & , \text{ if } j = x \\ -i \int \psi_{c1}^* e^{i\mathbf{k}\cdot\mathbf{r}} \psi_{04} d^3\mathbf{r} & + i \int \psi_{c4}^* e^{i\mathbf{k}\cdot\mathbf{r}} \psi_{01} d^3\mathbf{r} = -im_1 + im_2 & , \text{ if } j = y \end{cases}$$

With known values for the spinor components  $\psi_{c1}$ ,  $\psi_{c4}$ ,  $\psi_{01}$  and  $\psi_{04}$  we can determine the integrals  $m_1$  and  $m_2$ .

With  $\psi_{c1}^* = e^{-i\mathbf{k}'\cdot\mathbf{r}}$  and  $\psi_{04} = -i\sqrt{\frac{2}{3}}Y_{11}(\theta, \phi)f_0(r) = \frac{i}{\sqrt{4\pi}}\sin(\theta)e^{i\phi}f_0(r)$  we obtain for the  $m_1$  integral:

$$m_1 = \frac{i}{\sqrt{4\pi}} \int \sin(\theta)e^{i\phi}e^{i\mathbf{k}\cdot\mathbf{r}}e^{-i\mathbf{k}'\cdot\mathbf{r}}f_0(r) d^3\mathbf{r}$$

To do the integration we change to spherical polar coordinates,  $\mathbf{r} = r(\sin\phi\cos\theta, \sin\phi\sin\theta, \cos\phi)$ , and we define

$$\mu(\mathbf{q}, \theta, \phi) = q_x \sin\phi\cos\theta + q_y \sin\phi\sin\theta + q_z \cos\phi \quad (4.4)$$

where  $\mathbf{q} = \mathbf{k} - \mathbf{k}' = (q_x, q_y, q_z)$ . Using the definition of  $\mu(\mathbf{q}, \theta, \phi)$  and using  $f_0(r) = F_0 G_0 r^{\gamma_1-1} e^{-\frac{1}{2}\sigma_1 r}$ ,  $m_1$  becomes:

$$m_1 = F_0 G_0 \frac{i}{\sqrt{4\pi}} \int \sin(\theta)e^{i\phi}e^{i\mu(\mathbf{q}, \theta, \phi)}r^{\gamma_1-1}e^{-\frac{1}{2}\sigma_1 r} d^3\mathbf{r}$$

We can now convert the integral over all space into one using spherical polar coordinates.

$$m_1 = F_0 G_0 \frac{i}{\sqrt{4\pi}} \int_0^{2\pi} \int_0^\pi \int_0^\infty \sin^2(\theta)e^{i\phi}r^{\gamma_1+1}e^{-[\frac{1}{2}\sigma_1 - i\mu(\mathbf{q}, \theta, \phi)]r} dr d\theta d\phi$$

The angular integrations over  $\theta$  and  $\phi$  cannot be solved analytically due to the fact that  $\mu(\mathbf{q}, \theta, \phi)$  is a non simple function of  $\theta$  and  $\phi$ . However, using the fact that  $\int_0^\infty e^{-ax} dx = \Gamma(n+1)/a^{n+1}$  the radial integral can be solved.

$$m_1 = \frac{i}{\sqrt{4\pi}} F_0 G_0 \Gamma(\gamma_1 + 2) \int_0^{2\pi} \int_0^\pi \left[ \frac{\sin^2(\theta) e^{i\phi}}{(\frac{1}{2}\sigma_1 - i\mu(\mathbf{q}, \theta, \phi))^{\gamma_1+2}} \right] d\theta d\phi$$

We can determine the integral  $m_2$  following a similar process to that used to determine  $m_1$ . In the case of  $m_2$  the spinor components are given by  $\psi_{c4}^* = \xi(k'_x - ik'_y) e^{-i\mathbf{k}' \cdot \mathbf{r}}$  and  $\psi_{01} = Y_{00} g_0(r) = \frac{1}{\sqrt{4\pi}} G_0 e^{-\frac{1}{2}\sigma_1 r} r^{\gamma_1-1}$  we obtain for  $m_2$ :

$$m_2 = \frac{\xi(k'_x - ik'_y)}{\sqrt{4\pi}} G_0 \Gamma(\gamma_1 + 2) \int_0^{2\pi} \int_0^\pi \left[ \frac{\sin(\theta)}{(\frac{1}{2}\sigma_1 - i\mu(\mathbf{q}, \theta, \phi))^{\gamma_1+2}} \right] d\theta d\phi$$

Using  $m_1$  and  $m_2$  we can obtain an equation for the first order photo-electric amplitude  $A_1(\mathbf{k}, \mathbf{k}')_j$ , where  $j$  denotes the polarisation direction.

$$A_1(\mathbf{k}, \mathbf{k}')_x = \frac{G_0 \Gamma(\gamma_1 + 2)}{\sqrt{4\pi}} \int_0^{2\pi} \int_0^\pi \left[ \frac{\sin(\theta) [\xi(k'_x - ik'_y) + iF_0 \sin(\theta) e^{i\phi}]}{(\frac{1}{2}\sigma_1 - i\mu(\mathbf{q}, \theta, \phi))^{\gamma_1+2}} \right] d\theta d\phi \quad (4.5)$$

$$A_1(\mathbf{k}, \mathbf{k}')_y = \frac{G_0 \Gamma(\gamma_1 + 2)}{\sqrt{4\pi}} \int_0^{2\pi} \int_0^\pi \left[ \frac{i \sin(\theta) [\xi(k'_x - ik'_y) - iF_0 \sin(\theta) e^{i\phi}]}{(\frac{1}{2}\sigma_1 - i\mu(\mathbf{q}, \theta, \phi))^{\gamma_1+2}} \right] d\theta d\phi \quad (4.6)$$

These results have been derived without any approximations to the plane wave form of the electromagnetic field ( $e^{i\mathbf{k} \cdot \mathbf{r}}$ ) in the absorption and emission operators. This is the “all poles” approach. In the electric dipole (E1) approximation we have  $e^{i\mathbf{k} \cdot \mathbf{r}} \approx 1$ . We can interpret this as having no information about the propagation direction of the incident photon and hence in the electric dipole approximation  $\mathbf{k} = 0$ . Therefore to obtain results for the electric dipole approximation from equations 4.5 and 4.6 it is simply a matter of setting  $\mathbf{k} = 0$ .

$$A_1^{E1}(\mathbf{k}, \mathbf{k}')_j = A_1(0, \mathbf{k}')_j \quad (4.7)$$

#### 4.2.2 Photoionisation in the Forward Scattering Direction

The integrals  $m_1$  and  $m_2$  defined in the previous section cannot be solved analytically in general. However, it is possible to obtain an analytic solution for some special cases. One such case is when the incident photon is traveling in the  $+z$ -direction with a propagation vector  $k\hat{\mathbf{n}} = (0, 0, k)$  and the electron is ejected in the  $\Theta = 0$  (or forward scattering direction). In this case, the propagation vector for the ejected electron is  $k'\hat{\mathbf{n}}' = (0, 0, k')$ .

We note from these assumptions that the integral  $m_2 = 0$  because it is multiplied by the factor  $\xi(k'_x - ik'_y)$  and in the forward scattering direction  $k'_x = 0$  and  $k'_y = 0$ . We also note that the function  $\mu(\mathbf{q}, \theta, \phi)$  is simplified to  $\mu(\mathbf{q}, \theta, \phi) = q_z \cos(\theta)$ . We these new assumption we can rewrite the integral for  $m_1$  and attempt an analytic solution.

$$m_1 = \frac{i}{\sqrt{4\pi}} \int_0^\infty \int_0^{2\pi} \int_0^\pi \sin^2(\theta) e^{iq_z \cos(\theta)} e^{i\phi} r^2 f_0(r) d\theta d\phi dr$$

Integrating over  $\phi$  gives  $2i$  and making use of the trigonometric identity  $2\sin^2(\theta) = 1 - \cos(\theta)$ ,  $m_1$

can be written as:

$$\begin{aligned}
m_1 &= \frac{-2}{\sqrt{4\pi}} \int_0^\infty f_0(r) r^2 \left[ \frac{1}{2} \int_0^\pi e^{iq_z r \cos(\theta)} d\theta + \frac{1}{2} \int_0^\pi \cos(2\theta) e^{iq_z r \cos(\theta)} d\theta \right] dr \\
&= \frac{-2}{\sqrt{4\pi}} \int_0^\infty f_0(r) r^2 \left[ \frac{1}{2} (\pi J_0(q_z r) + \pi J_2(q_z r)) \right] dr \\
&= \frac{-\pi F_0 G_0}{\sqrt{4\pi}} \left[ \int_0^\infty J_0(q_z r) r^{\gamma_1+1} e^{-\frac{1}{2}\sigma_1 r} dr + \int_0^\infty J_2(q_z r) r^{\gamma_1+1} e^{-\frac{1}{2}\sigma_1 r} dr \right]
\end{aligned}$$

where  $J_n(x)$  is a Bessel function of the first kind of order  $n$ . The integrals involving the Bessel functions can be solved in terms of the hypergeometric function  ${}_2F_1(a, b; c; z)$ <sup>1</sup>. Since  $m_2$  is zero, the first order amplitude is given in terms of  $m_1$ , where we have  $A(k, k')_x = m_1$  and  $A(k, k')_y = -im_1$ , for photon polarisations in the  $x$  and  $y$  directions respectively. Using this information, and substituting in the for the constants  $F_0$ ,  $G_0$  and  $\sigma_1$  which were defined earlier, the analytic solutions for the first order photo-electric matrix elements in the forward scattering direction are given by:

$$\begin{aligned}
A_1(k, k')_x &= \frac{\pi}{\sqrt{\pi}} \left( \frac{2Z}{a_0} \right)^{3/2} \sqrt{\frac{1 - \epsilon_1}{2\Gamma(2\gamma_1 + 1)}} \times \\
&\left\{ \left( \frac{Z}{a_0} \right)^{-(\gamma_1+2)} \Gamma(\gamma_1 + 2) {}_2F_1 \left( \frac{\gamma_1 + 2}{2}, \frac{\gamma_1 + 3}{2}; 1; - \left( \frac{2a_0}{Z} \right)^2 (k - k')^2 \right) + \right. \\
&\left. \frac{1}{8} (k - k')^2 \left( \frac{Z}{a_0} \right)^{-(\gamma_1+4)} \Gamma(\gamma_1 + 4) {}_2F_1 \left( \frac{\gamma_1 + 4}{2}, \frac{\gamma_1 + 5}{2}; 1; - \left( \frac{2a_0}{Z} \right)^2 (k - k')^2 \right) \right\}
\end{aligned} \tag{4.8}$$

$$A_1(k, k')_y = -iA_1(k, k')_x \tag{4.9}$$

This implies that in the forward scattering direction, the probability of photoionisation is the same for a photon polarised in the  $x$  or  $y$  direction, because  $|A_1(k, k')_x|^2 = |A_1(k, k')_y|^2$ .

### 4.3 S-Matrix Theory

S-matrix theory as developed in covariant perturbation theory (or quantum field theory) is used to solve a large number of scattering problems in quantum mechanics [21, 12, 28, 1, 27]. The use of S-matrix theory to compute atomic form factors has been applied by Kissel and Pratt [20]. For a given photon of energy  $\hbar\omega$  the second order S-matrix (scattering) amplitude  $A_2(\omega)$  is related to the imaginary component of the form factor  $f''(\omega)$  and to the total cross section  $\sigma^{TOT}(\omega)$  through the following relation:

$$\text{Im}A_2(\omega) = r_0 f''(\omega) = \frac{\omega}{4\pi c} \sigma^{TOT}(\omega) \tag{4.10}$$

The relationship between the total cross section and  $f''(\omega)$  is the same as equation 1.4. Although here we will only be considering the photoionisation cross section,  $\sigma^{TOT}(\omega)$  may also include partial cross section contributions from other process such as bound-bound transitions. In addition to this we also have that:

- The second order amplitude considers only the forward scattering direction.  
 $A_2(\omega) = A_2(\omega, \Theta = 0)$ .
- The sign of  $f''$  as define by Kissel and Pratt [20] is opposite of that used in the crystallography literature ( $f''_{Kissel} = -f''_{cl}$ ). We will follow the convention of the crystallography community. literature.

<sup>1</sup>These integrals were solved using Mathematica 3.0

The second order S-matrix amplitude is defined as follows:

$$A_2 = -r_0 mc^2 \sum_p \left[ \frac{\langle m | \mathcal{A}_f^\dagger | p \rangle \langle p | \mathcal{A}_i | n \rangle}{E_n - E_p + \hbar\omega_f + i0_+} + \frac{\langle m | \mathcal{A}_i | p \rangle \langle p | \mathcal{A}_f^\dagger | n \rangle}{E_n - E_p - \hbar\omega_i + i0_+} \right] \quad (4.11)$$

where the state  $|\psi\rangle$  is a four component relativistic spinor which satisfies the Dirac equation (equation 2.9). The equation describes a second order scattering process with the subscript  $i$  denoting the initial situation and  $f$  denoting the final situation. The two components correspond to the processes of photoabsorption followed by photoemission, and photoemission followed by photoabsorption, as shown in the Feynmann diagrams in figure 4.2.

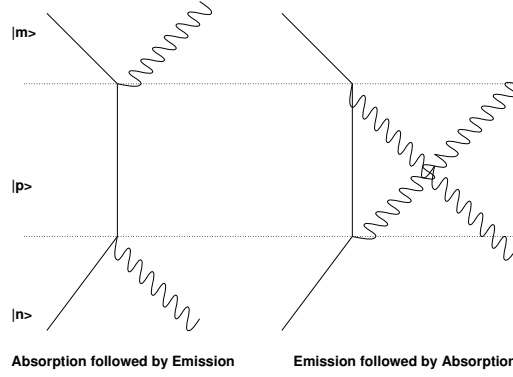


Figure 4.2: Second Order Photon Scattering

The initial state of the atom (which we will make the ground state) is  $|n\rangle$ , the final state is  $|m\rangle$  and we have a sum of all intermediate states  $|p\rangle$ . The energy of the initial state is  $E_n$ , the energy of the intermediate states is  $E_p$ , and initial and final energy of the photon are  $\hbar\omega_i$  and  $\hbar\omega_f$  respectively. The denominator of both components of  $A_2(\omega)$  includes a small complex positive value  $i0_+$ .

For the case of Rayleigh scattering,  $\hbar\omega_i = \hbar\omega_f = \hbar\omega$ , and the final atomic state is the same as the initial atomic state ( $|n\rangle = |m\rangle$ ). We can then define the form factor  $f''$  in terms of the second order elastic (Rayleigh) S-matrix  $\text{Im}A_2^R(\omega)$ .

$$f''(\omega) = \frac{\text{Im}A_2^R(\omega)}{r_0} = \frac{\omega}{4\pi cr_0} \sigma^{TOT}(\omega) \quad (4.12)$$

If the initial state is the ground state of the hydrogen atom  $|\psi_0\rangle$ , and we substitute in for the emission and absorption operators previously defined (without the summation since we only have a single electron) we obtain:

$$A_2^R(\omega) = -r_0 mc^2 \sum_p \left[ \frac{\langle \psi_0 | e^{-i\mathbf{k}\cdot\mathbf{r}} \bar{\alpha}_j | \psi_p \rangle \langle \psi_p | e^{i\mathbf{k}\cdot\mathbf{r}} \bar{\alpha}_j | \psi_0 \rangle}{E_0 - E_p + \hbar\omega + i0_+} + \frac{\langle \psi_0 | e^{i\mathbf{k}\cdot\mathbf{r}} \bar{\alpha}_j | \psi_p \rangle \langle \psi_p | e^{-i\mathbf{k}\cdot\mathbf{r}} \bar{\alpha}_j | \psi_0 \rangle}{E_0 - E_p - \hbar\omega - i0_+} \right] \quad (4.13)$$

Making use of  $\langle a | X^\dagger | b \rangle \langle b | X | a \rangle = \langle b | X | a \rangle^* \langle b | X | a \rangle = |\langle b | X | a \rangle|^2$  and splitting the sum into a sum over discrete states (bound excited states of the hydrogen atom) and an integral over continuum states ( $|\psi_c\rangle$  is the free electron continuum state) we obtain:

$$A_2^R(\omega) = -r_0 mc^2 \int_0^\infty \left[ \frac{|\langle \psi_c | e^{i\mathbf{k}\cdot\mathbf{r}} \bar{\alpha}_j | \psi_0 \rangle|^2}{E_0 - E_c + \hbar\omega + i0_+} + \frac{|\langle \psi_c | e^{-i\mathbf{k}\cdot\mathbf{r}} \bar{\alpha}_j | \psi_0 \rangle|^2}{E_0 - E_c - \hbar\omega - i0_+} \right] dE_c \\ - r_0 mc^2 \sum_p \left[ \frac{|\langle \psi_p | e^{i\mathbf{k}\cdot\mathbf{r}} \bar{\alpha}_j | \psi_0 \rangle|^2}{E_0 - E_p + \hbar\omega + i0_+} + \frac{|\langle \psi_p | e^{-i\mathbf{k}\cdot\mathbf{r}} \bar{\alpha}_j | \psi_0 \rangle|^2}{E_0 - E_p - \hbar\omega - i0_+} \right] \quad (4.14)$$

Ideally both continuum and bound-bound components would be included in a calculation of the S-matrix amplitude. However, due to time constraints the calculations focused on the continuum component. From the standard non relativistic understanding of the photo-electric effect [22, 20, 4] we know that the ground state to continuum amplitude dominates over the bound-bound transition amplitudes. However Chapter 5 of this report contains some results for bound-bound, transitions which may be used as a basis for determining atomic form factors.

Therefore, we can now write down the second order S-matrix amplitude which needs be calculated. We see that the matrix elements in the numerators are simply the first order photoionisation matrix elements (equations 4.5, 4.6, 4.8) so we can write the second order amplitude in terms of first order amplitudes. ( $\omega = kc$ ).

$$A_2^R(\omega) = A_2(\mathbf{k}, \mathbf{k}')_j = -r_0 mc^2 \left[ \int_0^\infty \frac{|A_1(\mathbf{k}, \mathbf{k}')_j|^2}{E_0 - E_c + \hbar\omega + i0_+} dEc + \int_0^\infty \frac{|A_1(-\mathbf{k}, \mathbf{k}')_j|^2}{E_0 - E_c - \hbar\omega - i0_+} dEc \right] \quad (4.15)$$

The second order amplitude for the electric dipole approximation, as for the first order matrix elements is simply given by setting  $\mathbf{k} = 0$ .

$$A_2^{E1}(\mathbf{k}, \mathbf{k}')_j = A_2(0, \mathbf{k}')_j \quad (4.16)$$

### 4.3.1 Computational Method

To compute  $f''$ , we need to compute the value of equation 4.15 over a range of photon energies ( $\hbar\omega$ ), take the imaginary component and then divide by  $r_0$ . This was done by developing a computer program in the C++ language to perform the computations using numerical integration methods to solve the integrals in equations 4.5 and 4.6 and the integral over the continuum state (ejected electron energies).

- One of the main computation issues faced was the problem of multi dimensional integrals. Although there was a single outer integral over continuum energies to compute the first order matrix element required the numerical computation of a two dimensional angular integral.
- The integration methods used originally elementary algorithms based on the Simpson's and Trapezoidal rules. The main problem with these methods was computation speed and accuracy. Performance and accuracy of results improved when the integration routines were changed to a 10-point Gauss-Legendre integration method [16].
- The integration method used for the integral over continuum states had to handle integrating over a singularity. This was handled by implementing a numerical version of the Cauchy principal value technique [17]. The integral was split into three regions, below the singularity, near the singularity and above the singularity to infinity. The integral to infinity was numerically by making an appropriate change of variable, changing the integral from one that was over an open interval to one that was over a closed interval.
- All the computations were done in atomic units (a.u.) giving the standard units of electrons/atom for  $f''$ . The energy axes in keV were converted after the computation was performed.
- Since  $f''(\omega)$  is calculated using the imaginary component of the second order S-matrix amplitude the size of the small positive complex value  $i0_+$  was expected to effect the results. The pseudo-code below gives an outline of the depth level of all the numerical integrations involved in the calculation, showing why computation speed was an issue.

PROGRAM

```

{
  For E = Min_Photon_Energy To Max_Photon_Energy With Step=EnergyStep
    Compute 2nd Order Matrix Element
      Integrate A2 Over All Continuum Energies
    Compute 1st Order Matrix Element
      Integrate Over Phi From 0 To 2Pi
      Integrate Over Theta From 0 To Pi
  }

```

#### 4.3.2 Results for $f''(\omega)$ and Possible Problems With S-Matrix Theory as Currently Implemented

Figure 4.3 shows a logplot the form factor ( $\log_{10}(f'')$ ) for a range of photon energies to 100 keV. The plot compares the result obtained using the all poles approach with that obtained for  $f''$  using the electric dipole approximation. As can be seen, the all pole and electric dipole approach are closer in agreement at lower energies. We expect that the electric dipole approximation breaks down the higher the photon energy we have and this is indeed the case in the results obtained. This is because the electric dipole approximation makes the assumption that the wavelength of the photon is much larger than the size of the atom it is interacting with. At higher energies, and hence shorter wavelengths, this approximation begins to break down as is evident in figure 4.3.

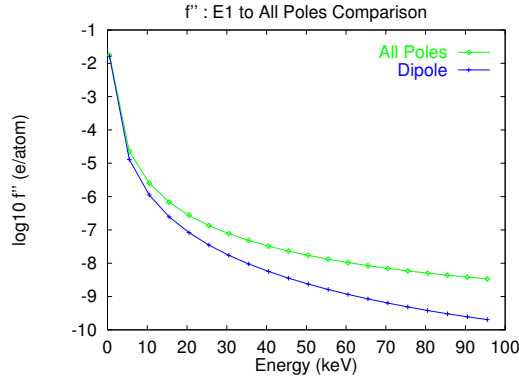


Figure 4.3: Relativistic Form Factor  $f''$  – Comparing Electric Dipole to All Poles Result

Figure 4.4 shows three plots of  $f''(\omega)$  at an energy range encompassing an edge (in this case the ionisation energy of the hydrogen atom  $E_0 = 13.6$  eV). The plots contain comparisons between these new results, the S-matrix results of Kissel and Pratt [20], and the recent results of Chantler [5]. The three plots show the new results for three different values of the small complex value  $i0_+ = 7 \times 10^{-8}, 8 \times 10^{-8}, 9 \times 10^{-8}$ . Clearly, the results are affected by the change in size of  $i0_+$ . All three theories predict the correct edge at 13.6 eV, all qualitatively have a similar shape, but there is disagreement between all three.

With regards to the new results, there clearly are some issues that need to be addressed. The main one is the dependence on  $i0_+$ . One way to attempt to solve this problem would be to try to change the integration scheme used from a non-convergent method (Gauss-Legendre) used to obtain the current results to a method such as a form of Romberg integration which converges to a result. This may or may not fix the problem with regard to the size of  $i0_+$ . If the problem still persists, then it could possibly suggest there are still some problems with S-matrix theory as currently implemented in the area of calculating atomic form factors.

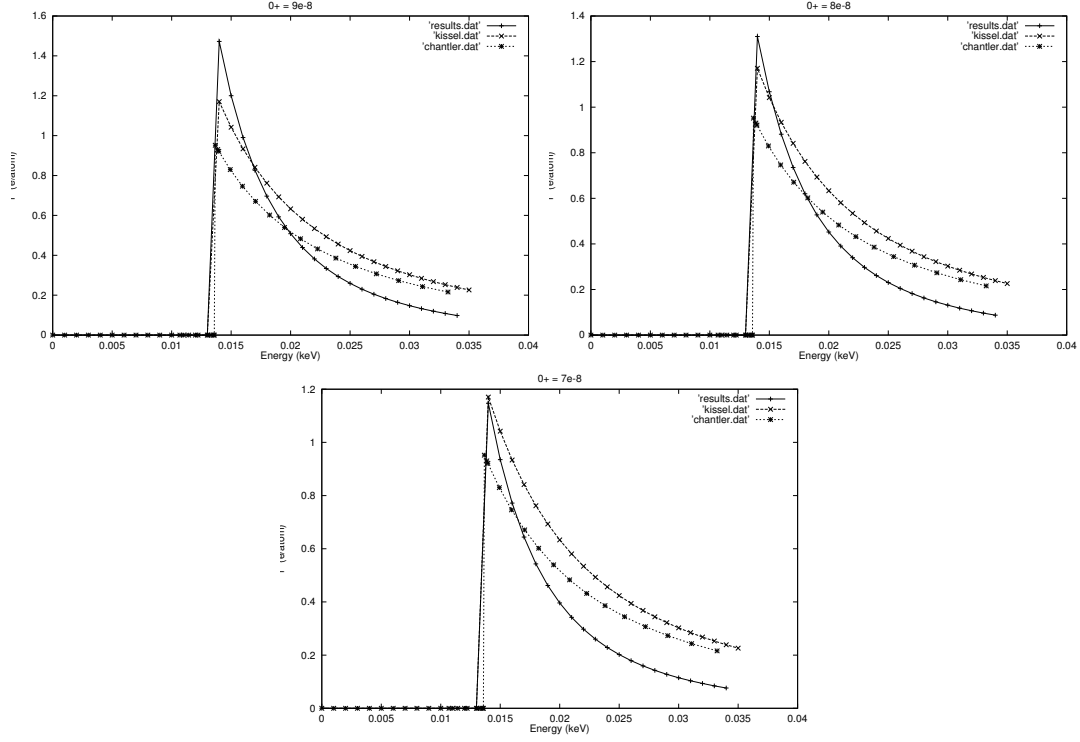


Figure 4.4: Comparing Current Results for  $f''$  with those of Chantler and those of Kissel and Pratt

#### 4.3.3 Results for Angular Dependence

The mod-squared of the second order S-matrix element  $|A_2(\mathbf{k}, \mathbf{k}')_j|$  cannot also be used to study the angular distribution of the ejected electron (or photoelectrons) at selected energies. We keep the direction of the photon wave-vector the same ( $\mathbf{k} = k(0, 0, 1)$ ) as when calculating  $f''$ , just changing the magnitude for different photon energies. However the ejected electron wave vector is described by the ejection angles  $(\Theta, \Phi)$  (see equation 4.3). In the  $f''$  case we were interested in the forward scattering direction so we set  $\Theta = 0$ . Alternatively, we can set  $\Phi = 0$  and vary  $\Theta$  over a range from 0 to  $2\pi$ . This gives as an ejected electron angular distribution for all values of  $\Theta$  in the  $\Phi = 0$  plane.

The results for  $|A_2(\mathbf{k}, \mathbf{k}')_j|$  at photon energies of 100 eV, 200 eV, 500 eV and 1 keV are shown in figure 4.5. The top left plot for a photon energy of 100 eV also shows the distribution for the electric dipole approximation. At the lower energies we see that the plots exhibit a  $\sin^2(\Theta)$  distribution. As the energy is increased we see finer definition of the ejection lobes in all directions, indicating the very precise directions of electron ejection.



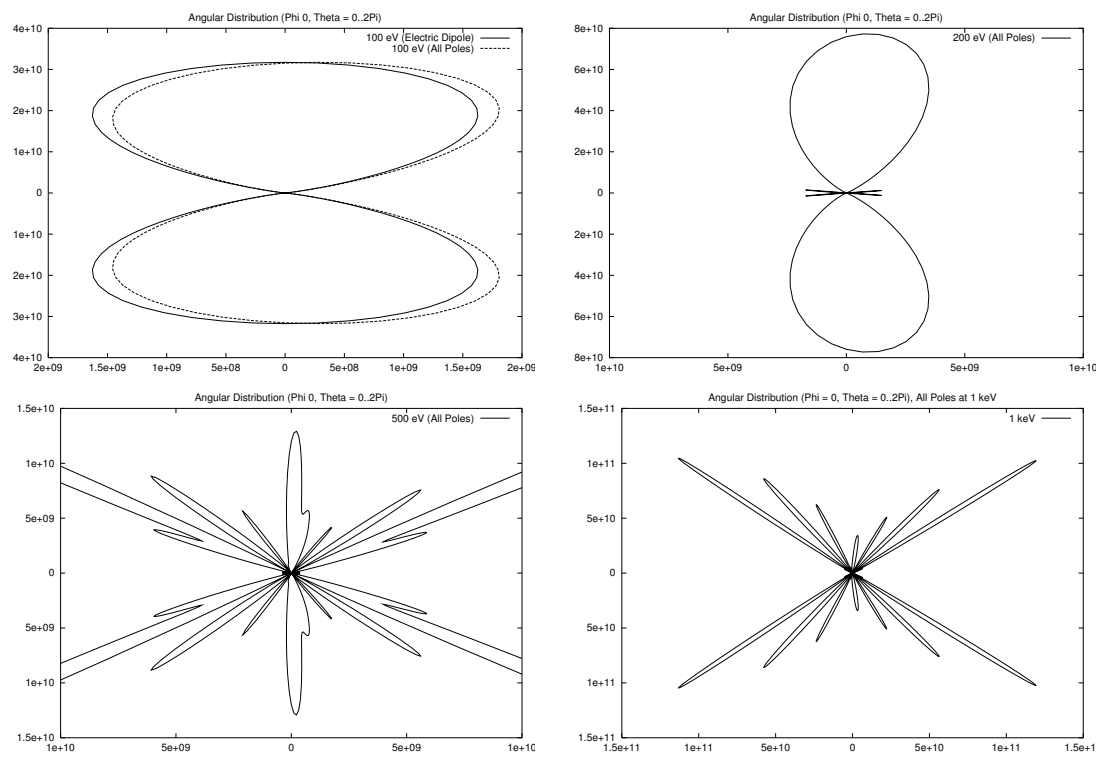


Figure 4.5: Ejected Electron Angular Distributions at Photon Energies of 100 eV, 200 eV, 500 eV and 1 keV

## 5 ATOMIC BOUND-BOUND TRANSITIONS

### 5.1 Ground State to an Excited Bound State

We mentioned in Chapter 5 that ideally the total cross section would have both amplitudes corresponding to ground-continuum transitions and bound-bound transitions. The first step that is required is to calculate a photoabsorption matrix element from the ground state to one of the excited bound states of hydrogen.

This chapter provides semi analytic results for photoabsorption matrix elements from the ground state to the first three excited states of hydrogen. We will consider the relativistic absorption operator  $\mathcal{A} = \bar{\alpha}_x e^{i\mathbf{k}\cdot\mathbf{r}} = \bar{\alpha}_x e^{i\eta(\mathbf{k},\theta,\phi)r}$  for a photon polarised in the  $x$  direction and we define  $\eta$  as:

$$\eta(\mathbf{k}, \theta, \phi) = k_x \sin \phi \cos \phi + k_y \sin \phi \sin \theta + k_z \cos \phi \quad (5.1)$$

In the electric dipole approximation  $\mathbf{k} = 0$  and hence  $\eta = 0$ . The use of  $\eta$  allows us to separate the angular and radial integrals therefore writing the photoabsorption matrix element from the ground state  $|\psi_0\rangle$  to an excited bound state  $|\psi_i\rangle$  as:

$$\langle \psi_i | X | \psi_0 \rangle = \int (A_{i1}A_{01} + A_{ii}A_{0i})R_{0i}^g d\Omega + \int (A_{i3}A_{03} + A_{i4}A_{04})R_{0i}^h d\Omega \quad (5.2)$$

where  $A_{ij}(\theta, \phi)$  are the angular components of the excited state Dirac spinors as defined in Chapter 2.  $R_{0i}^g$  and  $R_{0i}^h$  are the large and small component radial integrals which are defined in the sections below for each excited state. Some of the radial integrals are analytic while others have to be solved numerically. The final integration over all angles  $d\Omega$  has to be performed numerically.

All the radial integrals are written in terms of the constants defined in Chapter 2 and in terms of the integrals  $\mathcal{J}$  and  $\mathcal{K}$  defined below.

$$\mathcal{J}[a, n] = \int_0^\infty e^{-ar} r^n dr \quad (5.3)$$

$$\mathcal{K}[a, n, A, B, C, D] = \int_0^\infty \left( \frac{A - Br}{C - Dr} \right) e^{-ar} r^n dr \quad (5.4)$$

### 5.2 Ground State to First Excited State

$$R_{01}^g = G_0 G_1' \mathcal{J}[\frac{1}{2}(\sigma_1 + \sigma_2) - i\eta, 2\gamma_1] - G_0 G_1'' \mathcal{J}[\frac{1}{2}(\sigma_1 + \sigma_2) - i\eta, 2\gamma_1 + 1] \quad (5.5)$$

$$\begin{aligned} R_{01}^h = & H_0 G_0 H_1 G_1' \mathcal{K}[\frac{1}{2}(\sigma_1 + \sigma_2) - i\eta, 2\gamma_1, H_1', H_1'', H_1''', H_1'''] \\ & - H_0 G_0 H_1 G_1'' \mathcal{K}[\frac{1}{2}(\sigma_1 + \sigma_2) - i\eta, 2\gamma_1, 1H_1', H_1'', H_1''', H_1'''] \end{aligned} \quad (5.6)$$

### 5.3 Ground State to Second Excited State

$$R_{02}^g = G_0 G_2' \mathcal{J}[\frac{1}{2}(\sigma_1 + \sigma_2) - i\eta, 2\gamma_1] - G_0 G_2'' \mathcal{J}[\frac{1}{2}(\sigma_1 + \sigma_2) - i\eta, 2\gamma_1 + 1] \quad (5.7)$$

$$\begin{aligned}
R_{02}^h = & H_0 G_0 H_2 G_1' \mathcal{K} \left[ \frac{1}{2}(\sigma_1 + \sigma_2) - i\eta, 2\gamma_1, H_2', H_2'', H_2''', H_2'''' \right] \\
& - H_0 G_0 H_2 G_1'' \mathcal{K} \left[ \frac{1}{2}(\sigma_1 + \sigma_2) - i\eta, 2\gamma_1, 1H_2', H_2'', H_2''', H_2'''' \right]
\end{aligned} \tag{5.8}$$

#### 5.4 Ground State to Third Excited State

$$R_{03}^g = G_0 G_3 \mathcal{J} \left[ \frac{1}{2}(\sigma_1 + \sigma_3) - i\eta, \gamma_1 + \gamma_2 \right] \tag{5.9}$$

$$R_{03}^h = H_0 G_0 H_3 G_3 \mathcal{J} \left[ \frac{1}{2}(\sigma_1 + \sigma_3) - i\eta, \gamma_1 + \gamma_2 \right] \tag{5.10}$$

## 6 SUMMARY OF NEW RESULTS

### 6.1 New Results

- We show a new result for the relativistic normal form factor for hydrogenic atoms in equation 3.2.
- We show that for low  $Z$  atoms (non-relativistic limit) the relativistic normal form factor reduces to the non relativistic normal form factor for hydrogen in equation 3.4.
- We compare and look at the differences between the new relativistic form factor and the non relativistic theory 3.1 and an alternate theory (Hubbell) and graphically show the differences in figures 3.2 and 3.3
- We show semi-analytic results for the first order relativistic photoabsorption amplitude for photons polarised in both the  $x$  and  $y$  directions for the all poles approach (equations 4.5 and 4.6) and for the electric dipole approximation (equation 4.7).
- We show a new complete analytic result for the first order photoabsorption amplitude in the forward scattering direction (equation 4.8).
- We show a result for the second order S-matrix amplitude for the all poles (equation 4.15) and electric dipole approximation (equation 4.16).
- We present a result in figure 4.3 for the normal form factor  $f''$  in both the all poles approach and the electric dipole approximation over a range of energies.
- We compare the results obtained for  $f''$  near an absorption edge for hydrogen with other theories (see figure 4.4).
- We show results for angular the angular distribution of ejected photoelectrons at selected energies (see figure 4.5).

### 6.2 Further Work In This Area

The work presented in this thesis can be expanded in a number of different ways. Firstly, the integration techniques used in the S-matrix theory can be improved to hopefully provide more accurate results. Secondly, the first order photoionisation amplitudes can be used to calculate a first order photo-electric cross section which can then be used to calculate  $f''$ , which may then be compared to the results obtained with the second order S-matrix theory. Thirdly, the cross section components due to bound-bound transitions, and other effect such as Delbrück and Compton scattering and pair production should be added to the existing photoionisation cross section.

Longer term research in the area of relativistic atomic form factors can include calculations for molecular hydrogen, bound hydrogen, and a study of the multiple scattering processes which give rise to XAFS (X-Ray Anomalous Fine Structure). Additionally, the development form factor calculations for many electron atoms ranging from Helium to Uranium making use of numerical relativistic Dirac-Hartree-Fock wave-functions is also of great interest.

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