Theoretical cross sections for more accurate calculations of dosimetric quantities



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Abstract

Fundamental interaction cross sections are essential for both experimental and simulation-based determinations of energy deposition in matter from ionizing radiation, at both macroscopic and microscopic scales. In this work, we present investigations of semi-empirical and *ab initio* theoretical cross sections for three different physical interactions of central importance in calculations of dosimetric quantities, namely electron-impact ionization, Compton scattering, and low-energy elastic scattering of electrons and molecules. In particular, the electron-impact ionization and elastic cross sections could lead to improvements in microdosimetric Monte Carlo simulations of DNA damage from low-energy electrons.

We studied the relativistic binary-encounter-dipole (RBED) model for electron-impact ionization, which combines binary-encounter theory and the Bethe dipole limit in a semiempirical fashion. The Bethe asymptote is modelled based on the optical oscillator strength (OOS), a property of the target atom or molecule which can be either approximated by simple analytical expressions or calculated via *ab initio* numerical methods. We computed RBED differential and integrated cross sections for inner-shell ionization of neutral atoms, using first an empirical power-law OOS, then analytical hydrogenic OOSs, and finally OOSs calculated numerically from self-consistent Dirac–Hartree–Fock–Slater potentials. We found that when compared to the state-of-the-art distorted-wave Born approximation results, the RBED with either hydrogenic or numerical OOSs is generally in better agreement than with the power-law OOS. We also noted that the RBED model does not recover the Bethe asymptotic limit at highly-relativistic energies, and proposed an alternative prefactor which does restore the correct Bethe asymptote, but performs more poorly at intermediate energies.

Next we focused on the relativistic impulse approximation (RIA) for Compton scattering, which assumes a fixed momentum distribution for each target electron throughout the scattering process. By incorporating the momentum distribution through the Compton profile (CP), the RIA is able to account appropriately for both binding effects and Doppler broadening, unlike

simpler theories such as the Klein–Nishina (KN) or the Waller–Hartree (WH) models. We calculated RIA cross sections using molecular as opposed to atomic CPs for air, water, and graphite, as well as photon mass attenuation, energy-transfer, and energy-absorption coefficients. We found small differences resulting from the use of molecular rather than atomic CPs within the RIA, but unexpectedly found significant discrepancies between the WH and RIA Compton mass energy-transfer coefficient (for the Compton interaction only), which grow with decreasing energy up to about one order of magnitude at 1 keV. Ultimately, the overall impact of these discrepancies on the mass energy-absorption coefficient is limited to within 0.4%, since energy-transfer from photon interactions is dominated by the photoeffect at low energies where the choice of CP or Compton model matters most. However, this finding has not been widely reported despite the WH model remaining among the most frequently used and cited in the field.

Finally, we investigated the modified independent-atom model for elastic scattering of electrons by molecules, which is based on multiple scattering with the atoms in the molecule within the Born approximation, and does not contain any empirical or semi-empirical factors. We found that the differential cross section seemed to be negative over certain energy and angle ranges, as well as several other inconsistencies in the initial publications, and proceeded to rederive the expressions. We identified one potential mathematical error, namely an inconsistent choice of coordinate systems when carrying out the spherical averaging, and emphasize that a few higher-order terms (which were not explicitly derived by the original authors) would need to be included to guarantee positive cross sections. We further report that except at small scattering angles, the agreement with experiments can be excellent, although the choice of cordinate model to potential can be as important as the choice of theoretical model for scattering with molecules.

Résumé

Les sections efficaces des interactions physiques fondamentales sont essentielles pour la détermination du dépôt d'énergie dans la matière provenant des rayonnements ionisants, à l'échelle macroscopique ainsi que microscopique. Dans cette thèse, nous présentons des études de sections efficaces semi-empiriques et *ab initio* pour trois interactions différentes de grande importance pour les calculs de quantités dosimétriques, à savoir l'ionisation par impact d'électrons, la diffusion Compton et la diffusion élastique à faible énergie des électrons par les molécules. En particulier, l'ionisation par impact d'électrons et les sections efficaces élastiques pourraient permettre d'améliorer les codes microdosimétriques de Monte Carlo, qui simulent les dommages causés à l'ADN par des électrons de faible énergie.

Nous avons étudié le modèle RBED (*relativistic binary-encounter-dipole*) pour l'ionisation par impact d'électrons, qui combine la théorie de *binary encounter* et la limite asymptotique de Bethe de manière semi-empirique. L'asymptote de Bethe est modélisée à partir de la puissance d'oscillateur optique (OOS), une propriété de l'atome ou de la molécule cible qui peut être soit approximée par de simples expressions analytiques, soit calculée par des méthodes numériques *ab initio*. Nous avons calculé les sections efficaces RBED différentielles et intégrées pour l'ionisation des couches internes électroniques des atomes neutres, en utilisant d'abord un OOS empirique basé sur la loi de puissance, puis des OOS hydrogéniques analytiques, et enfin des OOS calculés numériquement à partir de potentiels Dirac–Hartree–Fock–Slater. Nous avons constaté que, par rapport aux résultats de l'approximation de Born à ondes déformées (DWBA), le modèle RBED avec des OOS hydrogéniques ou numériques est généralement en meilleur accord que les OOS à loi de puissance. Nous avons également noté que le modèle RBED ne récupère pas la limite asymptotique de Bethe aux énergies extrêmes relativistes, et nous avons considéré un préfactoriel alternatif qui restaure l'asymptote de Bethe, mais dont la performance est plus faible aux énergies intermédiaires.

Ensuite, nous nous sommes concentrés sur l'approximation relativiste de l'impulsion (RIA) pour la diffusion Compton, qui assume une distribution du moment linéaire fixe pour chaque électron cible tout au long du processus de diffusion. En incorporant la distribution du moment linéaire à travers le profil Compton (CP), le modèle RIA est capable de prendre en compte de manière appropriée les effets de liaison et l'élargissement Doppler, contrairement aux théories plus simples telles que les modèles Klein-Nishina (KN) ou Waller-Hartree (WH). Nous avons calculé les sections efficaces du RIA en utilisant des CP moléculaires plutôt qu'atomiques pour l'air, l'eau et le graphite, ainsi que des coefficients d'atténuation, de transfert d'énergie et d'absorption d'énergie de photons. Nous avons trouvé des différences minimes entre l'utilisation de PC moléculaires et atomiques dans le RIA, mais nous avons été surpris de constater des écarts significatifs entre les coefficients de transfert d'énergie du WH et du RIA (pour l'interaction de Compton uniquement), qui augmentent avec la décroissance de l'énergie jusqu'à environ un ordre de grandeur à 1 keV. En fin de compte, l'impact global de ces écarts sur le coefficient d'absorption d'énergie est limité à 0,4 %, car le transfert d'énergie des interactions de photons à basse énergie est dominé par l'effet photoélectrique. Cependant, ce résultat n'a pas été largement diffusé, bien que le modèle WH reste parmi les plus fréquemment utilisés et cités dans le domaine.

Enfin, nous avons étudié le modèle de l'atome indépendant modifié pour la diffusion élastique des électrons par les molécules, qui est basé sur la diffusion multiple avec les atomes de la molécule dans l'approximation de Born, et qui ne contient aucun facteur empirique ou semi-empirique. Nous avons constaté que la section efficace différentielle semblait être négative sur certaines gammes d'énergie et d'angle de diffusion, ainsi que plusieurs autres incohérences dans les publications initiales, et nous avons procédé à une nouvelle dérivation des expressions. Nous avons identifié une erreur mathématique potentielle, à savoir un choix incohérent de systèmes de coordonnées lors de la réalisation de la moyenne sphérique, et nous avons souligné que quelques termes d'ordre supérieur (qui n'ont pas été explicitement dérivés par les auteurs originaux) devraient être inclus pour garantir des sections efficaces positives. Nous signalons en outre que, sauf pour les petits angles de diffusion, l'accord avec les données expérimentales peut être excellent, bien que le choix de certains paramètres du potentiel atomique puisse être aussi important que le choix du modèle théorique de diffusion par les molécules.

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Preface

Contribution to original knowledge

This thesis contains two published manuscripts and a third one in preparation, all of which represent original contributions to research. This work presents improvements to two semiempirical theoretical models for electron-impact ionization and Compton scattering, respectively, through the use of more accurate ingredients in the models. Furthermore, we also investigate an *ab initio* model for low-energy elastic scattering of electrons and molecules, and propose potential corrections which would prevent the occurrence of unphysical negative cross sections.

Contribution of Authors

Chapters 1-3 provide the necessary theoretical background as well as the context for understanding the impact of the work in this thesis. These chapters were written by myself, and include revisions suggested by José M. Fernàndez-Varea and Jan Seuntjens. The contributions of the authors to the three manuscripts are described below.

 Xiaoya Judy Wang, Jan Seuntjens, and José M. Fernàndez-Varea, "RBED cross sections for the ionization of atomic inner shells by electron-impact", Journal of Physics B, vol. 51, no. 14, pp. 145201, 2018. (Chapter 4)

I wrote the Python script to compute all differential and integrated cross sections, generated all the figures, and wrote the manuscript. José M. Fernàndez-Varea proposed this study, provided the numerical OOS, and gave crucial guidance in outlining the context and in discussions surrounding the selection of relevant figures to present in the results section. José M. Fernàndez-Varea also suggested many revisions which improved the clarity of the manuscript. Jan Seuntjens provided further context and feedback to the manuscript, especially for the selection of results which most succinctly capture the main messages of the article. 2. Xiaoya Judy Wang, Beatriz Miguel, Jan Seuntjens, and José M. Fernàndez-Varea, "On the relativistic impulse approximation for the calculation of Compton scattering cross sections and photon interaction coefficients used in kV dosimetry", Physics in Medicine and Biology, vol. 65, no. 12, 2020. (Chapter 5)

I wrote the Python script used to calculate the differential and integrated cross sections, generated the figures, and wrote the manuscript, including the exploration of the full RIA and the origins of divergences in QED. Beatriz Miguel provided the numerical molecular OOSs, and wrote the paragraph describing the framework for calculating these OOSs. José M. Fernàndez-Varea proposed this study, and played a central role in discussions regarding the full background and history of Compton scattering theories, as well as decisions on the key figures to present as part of the results. Jan Seuntjens provided essential insight and context for the dosimetric impact of the work, and also played a key role in discussing the results.

3. Xiaoya Judy Wang, Jan Seuntjens, and José M. Fernàndez-Varea, "On the modified independent-atom model (MIAM) for elastic scattering of electrons in molecules", in preparation, 2020. (Chapter 6)

I wrote the Python script to compute the DCS expressions published by the initial authors of the MIAM, and discovered the negative DCSs as well as the other inconsistencies in their early publications. I fully re-derived the expressions, including the higher-order subterms which should be included to guarantee positive DCSs, generated the figures, and wrote the draft of the manuscript. José M. Fernàndez-Varea and Jan Seuntjens have provided big-picture guidance and suggestions regarding the specific directions to explore, and also whenever I hit a significant roadblock. They have also reviewed and commented on the manuscript.

Chapter 1

Introduction

1.1 Radiation dosimetry

Dosimetry is the branch of medical physics and related disciplines which deals with the accurate determination of energy deposition by ionizing radiation in matter, and is of central importance in radiology, radiation therapy, radiation protection, and industry applications involving ionizing radiation. In the medical context, the overwhelming majority of ionizing radiation consists of photons and electrons in the energy range from 10 keV to 25 MeV, although some more exotic treatment modalities make use of protons and other light ions [1]. The materials of interest include liquid water, air, graphite, and biological materials (e.g. muscle, fat and bone) whose atomic composition and mass density are not uniquely defined, but which are often assigned an effective atomic number and density.

Although energy deposition at the microscopic level is a stochastic process, most quantities which are of interest in dosimetry are macroscopic, and are the results of averaging over a large number of individual physical interactions. As shown in the schematic diagram in fig. 1.1, the concept of absorbed dose is an idealization in the limit of large mass m of the interacting medium [1]. As the mass or the volume is reduced, the stochastic and random nature of energy deposition becomes apparent. We define the absorbed dose D as a non-stochastic, continuous quantity,

$$D = \frac{d\overline{\varepsilon}}{dm},\tag{1.1}$$

where $\overline{\epsilon}$ is the mean energy imparted in a volume of mass *m*. We note that even though absorbed dose is defined mathematically in terms of infinitesimal energy depositions and masses, in reality



Figure 1.1 Schematic diagram of energy depositions as a function of the mass of the volume in which the energy deposition is scored.

it is physically impossible to know the true dose to a point, due to the inherent randomness at microscopic length scales.

Absorbed dose measurements can be performed using detectors called dosimeters, whose measured signal must be proportional to the mean absorbed dose in its sensitive volume. As an example, one of the most common types of dosimeters is an air-filled ionization chamber, for which the mean absorbed dose D_{det} is

$$D_{\rm det} = \frac{q_{\rm air}}{m_{\rm air}} \left(\frac{W_{\rm air}}{e}\right),\tag{1.2}$$

where q_{air} and m_{air} are respectively the charge created and the mass of air in the sensitive volume, and (W_{air}/e) is the mean energy required to produce an ion pair in air. The accuracy of the value of (W_{air}/e) is clearly of central importance in dose measurements for ionization chambers. Its determination is mainly achieved through measurements because the uncertainties in fundamental interaction cross section data are currently too large for first-principles calculations to be used for metrological purposes [2]. However, its value does depend partly on stopping powers for graphite and air, which are required in measurements using graphite-walled ionization chambers, and which do rely on theoretical calculations [3]. Recently, there have been a number of new measurements and re-evaluations of experimental data which have identified important corrections to the value of (W_{air}/e) [2, 4, 5].

Once the absorbed dose to the detector is known, it must be converted into the absorbed dose to the medium D_{med} , which is the actual quantity of interest. The detector can be thought

of as a cavity inside the medium, and so-called cavity theories have been developed to find the ratio

$$f_Q = \left(\frac{D_{\text{med}}}{D_{\text{det}}}\right)_Q \tag{1.3}$$

for a beam of quality Q. The radiation quality Q is a set of parameters which characterize the beam in a given medium, such as the half-value layer (the thickness of material required to attenuate the x-ray beam intensity by a half) or the absorbed dose at certain reference depths. These parameters are typically measured, since they generally depend not only on the nominal or maximum energy of the radiation, but also on the beam filtration settings, scatter distributions, and other machine-specific and usage-specific properties [1].

Simple relations can be found between the absorbed dose in the medium and the particle fluence and interaction coefficients, under certain assumptions. The most important of these assumptions is charged-particle equilibrium (CPE), which is illustrated in fig. 1.2. In short, CPE exists in a volume v if the number of particles of a given type and energy leaving v is balanced by an equal number of particles of the same type and energy entering the volume.



Figure 1.2 Secondary charged particles are produced uniformly in v through interactions of the primary uncharged particle beam in the medium. If the minimum distance separating the boundaries of v and the smaller internal volume v is greater than the maximum range of charged particles present, then CPE is established in v.

For monoenergetic photons of energy E, under CPE, the dose absorbed in a medium can be expressed as

$$D_{\rm med} = E \,\Phi_{\rm med} \left[\mu_{\rm en}(E) / \rho \right]_{\rm med}, \qquad (1.4)$$

where Φ_{med} is the photon fluence in the medium, and $[\mu_{\text{en}}(E)/\rho]_{\text{med}}$ is the mass energyabsorption coefficient for the medium. Similarly, for charged particles with kinetic energy *E*, the absorbed dose is

$$D_{\rm med} = \Phi_{\rm med} \left[S_{\rm el}(E) / \rho \right]_{\rm med}, \qquad (1.5)$$

where $[S_{\rm el}(E)/\rho]_{\rm med}$ is the mass electronic stopping power for the medium. The interaction coefficients $[\mu_{\rm en}(E)/\rho]$ and $[S_{\rm el}(E)/\rho]$ will be defined in the following section, and their dependence on cross sections will be made clear.

Cavity theory deals with various different limiting situations, depending on the size of the detector and the range of the charged particles involved. In the Bragg–Gray cavity theory, the cavity is small compared to the range of secondary electrons in the medium of interest, similar to what is shown in fig. 1.2. We can assume that the vast majority of charged particles crossing the cavity were generated in the surrounding medium, and thus the cavity does not significantly perturb the fluence of charged particles and we can set $\Phi_{med} \approx \Phi_{det}$. With these assumptions, the ratio of the absorbed doses to the medium and to the detector simplifies to the ratio of their electronic stopping powers,

$$\frac{D_{\text{med}}}{D_{\text{det}}} = \frac{[S_{\text{el}}(E)/\rho]_{\text{med}}}{[S_{\text{el}}(E)/\rho]_{\text{det}}}.$$
(1.6)

On the other hand, for cavities that are large compared to the ranges of secondary charged particles but still small compared to photon mean free paths, the photon energy fluence can be assumed to be undisturbed, and the ratio of absorbed doses becomes

$$\frac{D_{\text{med}}}{D_{\text{det}}} = \frac{\left[\mu_{\text{en}}(E)/\rho\right]_{\text{med}}}{\left[\mu_{\text{en}}(E)/\rho\right]_{\text{det}}}.$$
(1.7)

The above simplified picture needs to be amended by considerations of so-called δ -electrons, charged particles whose energies are too high to deposit dose locally, in defining CPE and also in calculations of stopping powers. Furthermore, since cavity theory deals with an idealized situation involving a uniform cavity inside a uniform medium with no disturbance to the radiation fluence, correction factors have to be incorporated to account for, e.g., the wall of the ionization chamber and fluence perturbations. Regardless of these complications, it is evident that cavity theories rely on accurate physical interaction data, such as photon interaction coefficients and electronic stopping power, which we will discuss in the next section.

In clinical usage, dosimeters need to be calibrated against a reference detector that in turn has been calibrated at a standards laboratory under well-established reference conditions. A primary standard is an instrument that can be used to determine the physical quantity of interest without the need to be calibrated or referenced against another instrument, and its accuracy must be comparable to the highest achievable level. Primary standards are maintained in national laboratories around the world, and consistency between them is ensured through regular international comparisons called key comparisons [6].

Since many dosimetric quantities are impractical or impossible to measure experimentally, computer-based Monte Carlo (MC) particle transport codes have been developed alongside experimental methods, and together they form the basis of accurate dose determination. Fundamental physical data characterizing the interactions of radiation with matter, such as photon cross sections, electron stopping powers, and the average energy to create an ion pair in air, are required for both calculations and measurements of dosimetric quantities. In this chapter we begin by giving a brief overview of the most important fundamental key data relevant in dosimetry, then we discuss their usage in measurements and MC codes, and finally we end with an outline of this thesis.

1.2 Dosimetric quantities

We know from electromagnetic theory that photons in uniform liquids or amorphous materials at the energies relevant for medical applications (on the order of 10 MeV or less) simply attenuate exponentially, thus we are mainly concerned with the mass attenuation coefficient and other closely-related quantities. The mass attenuation coefficient is defined as

$$\frac{\mu}{\rho} = \frac{N_A}{M} \sum_j \sigma_j, \tag{1.8}$$

where ρ is the mass density of the medium, N_A is the Avogadro constant, M is the molar mass of the atoms or molecules that make up the medium, and σ_j is the integrated cross section (ICS) for the interaction of type j. The mass energy-transfer coefficient is

$$\frac{\mu_{\rm tr}}{\rho} = \sum_j f_j \frac{\mu_j}{\rho},\tag{1.9}$$

where f_j is the average fraction of the photon energy transferred to kinetic energy of charged particles, which is defined differently for each interaction type (photoelectric, Compton, and pair production).

The mass energy-absorption coefficient μ_{en}/ρ is defined as

$$\frac{\mu_{\rm en}}{\rho} = (1-g)\frac{\mu_{\rm tr}}{\rho},\tag{1.10}$$

where g is the average fraction of the kinetic energy of secondary charged particles which is subsequently lost to radiative processes. For low-Z materials, 1 - g is usually very small, being typically around 0.2% or 0.3% at E = 1 MeV, and an order of magnitude smaller for energies of a few hundred keV and below [1].

Compared to photons, charged particles undergo a much larger number of interactions per unit length travelled inside matter. For example, a 1 MeV electron will undergo on the order of 10^5 interactions while penetrating to a depth of roughly 0.5 cm, whereas a 1 MeV photon has a mean free path of more than 10 cm. As a result, we describe electron interactions in terms of multiple-scattering theory, and we are interested in the mean value of the distribution of energy losses. We define the energy loss per unit path length *s*, normalized by the mass density ρ of the stopping medium, as the mass electronic stopping power [7, 2]

$$\frac{1}{\rho}S_{\rm el} = \frac{1}{\rho}\left(-\frac{dE}{ds}\right)_{\rm el} = \frac{N_{\rm A}}{M}\int W\frac{d\sigma}{dW}dW,\tag{1.11}$$

where $d\sigma/dW$ is the DCS per atom for inelastic collisions resulting in an energy transfer W.

Inelastic charged-particle collisions are typically classified as being "soft" or "hard", with the former referring to collisions with large impact parameters and small energy transfers, and the latter being used for collisions with small impact parameters and large energy transfers. Bethe [8, 9] has shown that the inelastic cross section can be expressed in terms of the generalized oscillator strength (see section 2.6), a quantity solely dependent on atomic properties and which obeys certain sum rules. Using these sum rules, Bethe was able to derive expressions for both soft and hard inelastic collisions in terms of the mean excitation energy I, and has shown that for an electron travelling at speed v with kinetic energy E, the sum of the two contributions is given by

$$\frac{1}{\rho}S_{\rm el} = \frac{2\pi r_{\rm e}^2 m_{\rm e}c^2}{\rm u} \frac{Z}{A} \frac{1}{\beta^2} \left[\ln(E/I)^2 + \ln(1+\tau/2) + F^-(\tau) - \delta(\beta)\right], \qquad (1.12)$$

where A is the mass number of the target element, $\beta = v/c$, $\tau = E/m_ec^2$, and

$$F^{-}(\tau) = (1 - \beta^{2}) \left[1 + \frac{\tau^{2}}{8} - (2\tau + 1) \ln 2 \right].$$
 (1.13)

The density-effect correction $\delta(\beta)$ accounts for the polarization of atoms and molecules as charged particles pass through the medium. This polarization decreases the strength of the electromagnetic field acting on the projectile, and in turn reduces the stopping power. The density effect increases with the mass density of the medium, and also with the kinetic energy of the projectile. The *I*-value was defined by Bethe as a geometric average of the ionization and excitation energies E_n of the target material weighted by the optical oscillator strengths f_n for all (sub)shells *n*, and can be approximately written as

$$\ln I \approx \frac{\sum_{n} f_n \ln E_n}{\sum_{n} f_n}.$$
(1.14)

As we will show in the next chapter, the optical oscillator strength is proportional to the square of the matrix element of the dipole operator

$$f_n \propto \left| \left\langle n \left| \sum_{i=1}^Z x_i \right| 0 \right\rangle \right|^2.$$
 (1.15)

While *ab initio* calculations of *I* are accurate for atoms, whose electronic structures are well studied, they are not adequate for most materials of practical interest. Instead, the value of *I* is often obtained from measurements of energy loss of heavy charged particles with energies in the range of validity of the Bethe formula [10–12], or from experimentally determined dielectric-response functions from low-energy photon experiments [13–15]. In particular, measurements of I_g for graphite were required to reach the conclusion that the crystalline mass density should be used instead of the bulk density in calculations of electronic stopping powers for graphite [16, 2].

1.3 Cross sections

The simplest way to define a cross section is to consider the experimental setup shown in fig. 1.3.



Figure 1.3 Experimental setup to measure $d^2\sigma/d\Omega dW$ for a scattering experiment [1].

The cross section is a quantity which represents the probability of interaction, and which is essentially a ratio of outgoing to incoming fluxes. More concretely, the differential cross section can be written as

$$d\sigma = \frac{\dot{N}_{\text{out}}}{\dot{N}_{\text{in}} n_T} \, d\Omega \, dW, \tag{1.16}$$

where \dot{N}_{out} is the number of particles per second scattered into $d\Omega$ with energy loss between W and W + dW, and \dot{N}_{in} is the number of incident particles per second per unit area which have interacted with n_T particles in the target. The total probability of the interaction occurring is given by the integrated cross section

$$\sigma = \int \frac{d^2 \sigma}{d\Omega \, dW} \, d\Omega \, dW, \tag{1.17}$$

which has units of area, and can be thought of as the "effective" target area "seen" by the incident beam. In MC simulations, the mean free path is inversely proportional to the sum of σ_i , where the index *i* runs over all relevant interaction types. For instance, for photons in the energy range of interest, we consider the photoelectric effect, Rayleigh scattering, Compton scattering, and pair production.

1.4 Monte Carlo methods for dose calculation in medical applications

In MC absorbed dose calculations, averages of macroscopic quantities such as dose distributions in patients are obtained by transporting a large number of individual particles according to physical models describing their interactions with matter. Interaction probability distributions proportional to cross sections are sampled using a pseudo-random number generator in order to produce a particle track along which energy is deposited [17]. In simulations of patient treatment plans, the dose scoring volume is divided into regions which are typically between 1 mm³ and 1 cm³, in the same range as the spatial resolution of most measurement methods. MC methods are also heavily used for simulations of dosimeters in order to calculate correction factors due to fluence perturbations, in which case the dose scoring regions are chosen to be much smaller than the effective volume of the detector.

Particles are initialised with a position, energy and direction, and the distance to the next interaction is sampled from a probability distribution determined by the inverse of the total cross section of all possible interactions. The probability for each interaction type and secondary particle production is proportional to the relative cross section for that event, while the scattering angles and energy losses are sampled from differential cross sections.

In order to achieve reasonable simulation times and memory usage, the step size needs to be many orders of magnitude larger than the mean free path of electrons, such that multiple-scattering models are required. Particles are transported until their energy falls below a prese-lected threshold, or until they leave the geometry of interest. For non-scattering processes such as characteristic x-ray emission, the cross section is of course not used to determine the mean free path, but it remains proportional to the probability for the process to occur. In general, the statistical uncertainties are proportional to the inverse square root of the total number of particles simulated, and achieving relative uncertainties below 1% in patient dose calculations typically requires millions of particles to be transported.

The most widely used MC codes are developed and maintained by various national laboratories and large research collaborations, including EGSnrc by the National Research Council (NRC) of Canada [18], MCNP by the Oak Ridge National Laboratory [19], GEANT4 by CERN [20], PENELOPE [21] by the University of Barcelona, among others.

1.5 Microdosimetry

In recent decades, proton and light-ion beams have gained popularity [22–24] owing to their sharply peaked dose distribution profile as a function of depth near the end of the tracks, potentially allowing for more precise tumour targeting and sparing of healthy tissue. Ion beams generate a much less uniform density of ionizations in matter compared to conventional MV photon beams, hence they induce tissue responses which depend not only on absorbed dose, but also on radiation quality (which in this context refers to the density of ionization when considering energy deposition on a microscopic scale). In addition, research in concurrent use of chemotherapeutic agents [25, 26] and radiosensitizers such as gold nanoparticles [27–30] during radiotherapy treatments has also proliferated. These novel techniques induce non-trivial dose deposition patterns on microscopic length scales, and uncovering these patterns could lead to a mechanistic understanding of radiation damage in biological structures.

The field of microdosimetry has developed to quantify the inhomogeneities and statistical fluctuations in dose deposition which are averaged out in conventional MV photon dosimetry [31, 32]. The main dosimetric quantities of interest to microdosimetry, which have been formalized in the ICRU Report 36 [33], are distributions of stochastic quantities defined in "sites" whose sizes are chosen based on the biological structures being studied.

The energy imparted in a volume with mass m is defined as

$$\varepsilon = \sum_{i} \varepsilon_i \tag{1.18}$$

where ε_i is the energy deposited in a single interaction, and the sum is over all energy deposition events in that volume. It is important to note that ε is a stochastic quantity, and may be due to one or more statistically independent tracks. The specific energy *z* is the stochastic equivalent of the absorbed dose in macroscopic dosimetry,

$$z = \frac{\varepsilon}{m},\tag{1.19}$$

and its expectation value \bar{z} is given in terms of its probability distribution function f(z),

$$\bar{z} = \int_0^\infty z f(z) \, dz. \tag{1.20}$$

 \bar{z} is also known as the mean specific energy, and is a non-stochastic quantity. The lineal energy y is defined as

$$y = \frac{\varepsilon}{\bar{l}},\tag{1.21}$$

where \bar{l} is the mean length of randomly-oriented chords in the dose-scoring volume, called the mean chord length. For a convex body with volume V and surface area a, $\bar{l} = 4V/a$. Various other useful statistical distributions and expectation values are also commonly defined based on z and y, such as the probability of an energy deposition event having specific energy less than or equal to z or lineal energy less than or equal to y.

MC simulations of these quantities have been validated through experiments using proportional counters or silicon diodes, which have enabled accurate dose measurements on the order of 1 μ m [34, 35], sufficient for resolving sub-cellular structures and organelles.

The concepts of microdosimetry have been applied at even lower energies and length scales in order to directly simulate the effects of radiation on DNA. So-called "track structure" MC code packages such as GEANT4-DNA [36, 37] and PARTRAC [38] have been developed, which simulate every single physical interaction along a particle track [39], down to electron energies of about 10 eV and mean free path lengths on the order of a few nanometers. Typically the medium is taken to be liquid water for simplicity, and the particle tracks are then superimposed on the geometry of DNA in a given configuration in order to localize the energy depositions within the DNA. One of the main objectives is to study different types of strand breaks in order to incorporate information about microscopic DNA damage when determining the relative biological effectiveness (RBE). The RBE is an empirical measure of the biological effectiveness of one type of radiation relative to another given the same absorbed dose, defined with respect to a specific biological endpoint such as cell death.

Owing to the extremely low energies of the simulated particles in nanodosimetry, condensed matter effects become significant and the physical interaction cross sections have large uncertainties. Concerns also arise due to the basic fact that Heisenberg's uncertainty principle predicts large uncertainties in momentum and position for low-energy particles (5% at 1 keV and above 20% below 100 eV in liquid water [40]). Results from these microdosimetry codes are impossible to validate directly since experiments which measure DNA fragmentation after irradiation contain many unknowns which must be modelled explicitly in the simulations, such as the DNA configuration and compactness, which vary depending on cell cycle and cell type [38]. These parameters can alter the number of measured DNA strand breaks by a factor of

order unity or even larger [41], they are interrelated such that many distinct parameters can have compensatory effects on the results, and for now their values in nanodosimetric models are simply chosen so as to reproduce reasonable agreement with experiments [38]. As an example, varying the energy threshold for induction of a single strand break (SSB) or the distance required between two SSBs to be counted as a double strand break (DSB) would result in factors of two and three in the final count of SSBs and DSB [42], respectively, even if one stays within the reasonable range of values for these parameters. Despite these fundamental challenges, improvements in cross sections for low-energy electron interactions could nevertheless have a significant impact on the accuracy of track-structure Monte Carlo simulations.

1.6 Thesis outline

The overview of dosimetry applications discussed above shows that accurate cross sections are a crucial fundamental ingredient in both measurements and MC simulations of dose deposition. This thesis presents three studies of theoretical cross sections which can lead to potential improvements in calculations of dosimetric quantities. We begin by reviewing in chapter 2 some relevant aspects of basic scattering theory within quantum mechanics. Although this material can be found in many standard undergraduate and graduate level textbooks, this knowledge cannot be assumed for a medical physics audience, and it is required to follow the derivation in chapter 6. Chapter 3 consists of a literature review and contextualization for each of the following chapters, as they deal with separate theories for different physics processes. Chapter 4 is a published article on the relativistic binary-encounter-dipole (RBED) theory for electron-impact ionization, which is a semi-empirical model based on the optical oscillator strength, and whose simplicity makes it easier to implement than the current best-available theory. The published article in chapter 5 presents calculations of Compton scattering cross sections within the relativistic impulse approximation (RIA), using molecular instead of atomic Compton profiles, and further explores a significant source of discrepancy between commonly used Compton theories. Finally in chapter 6, we found that the modified independent atom model (MIAM) for elastic scattering of electrons by molecules yielded negative differential cross sections over certain energy and angle ranges, and set out to re-derive the expressions before carrying out a thorough comparison to experimental data.

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Chapter 2

Theoretical calculations of cross sections for electrons and photons

2.1 Introduction

In this chapter, we review basic concepts from scattering theory within quantum mechanics [1, 2], mostly but not exclusively as necessary background for the derivation of the modified independent atom model (MIAM) in chapter 6. Topics relevant to the derivation include the Green's function method of solving the Schrödinger equation (SE), the Born approximation, the partial-wave expansion, and a brief definition of the *T*-matrix. These topics take up the majority of this chapter, since the MIAM chapter is the only one involving a derivation. From the Born approximation, we lead into a section on inelastic electron-atom cross sections, which is relevant for the RBED chapter. Finally, we briefly discuss interactions of charged particles with the EM field, which serves as the basis for introducing the (non-relativistic) impulse approximation and Waller–Hartree model used in calculations of Compton scattering cross sections.

2.2 Scattering in quantum mechanics

Scattering in quantum mechanics describes a process whereby a particle in an initial continuum state transitions into a final continuum state through the interaction with a potential representing

the scatterer. We solve the SE for the projectile particle,

$$i\hbar \frac{\partial}{\partial t} \Psi(\mathbf{r},t) = \left[-\frac{\hbar^2}{2m} \nabla^2 + V(\mathbf{r},t) \right] \Psi(\mathbf{r},t),$$
 (2.1)

while typically considering potentials with spherical symmetry, which leads to solutions involving eigenfunctions of angular momentum operators. Unlike the wavefunctions of bound atomic electrons, however, the solutions we seek are the asymptotic forms of states in the continuum.

Generally it is assumed that the interaction time is short compared to the time scale of the experiment, such that experimentally we measure particles described by steady-state solutions. The incoming wavefunction will be a mono-energetic plane wave, and the scattered wavefunction will be a freely propagating spherical wave of the form $f(k, \theta)e^{ikr}/r$, where the scattering amplitude $f(k, \theta)$ captures the angular dependence of the scattered wave. Therefore we seek solutions of the form

$$\Psi(\mathbf{r}) \xrightarrow[r \to \infty]{} Ae^{ikz} + Af(k,\theta) \frac{e^{ikr}}{r} = \psi_{\rm in} + \psi_{\rm sc}.$$
(2.2)

To relate the wavefunction to the cross section, we start by defining the latter as the ratio of scattered flux to incident flux, with the standard definition for the flux Φ passing through an area element $d\mathbf{A}$

$$\Phi = \mathbf{j} \cdot d\mathbf{A},\tag{2.3}$$

where **j** is the probability current density. The incident flux j_{in} is simply the number of particles per volume, $|\psi_{in}|^2$, times the velocity $v = \hbar k/m$

$$\dot{j}_{\rm in} = \frac{\hbar k}{m} |\psi_{\rm in}|^2 = \frac{\hbar k}{m} |A|^2.$$
 (2.4)

The scattered flux is $\mathbf{j}_{sc} \cdot d\mathbf{A} = \mathbf{j}_{sc} \cdot \hat{\mathbf{r}} r^2 d\Omega$. The cross section is then given by

$$d\boldsymbol{\sigma} = \frac{\mathbf{j}_{\rm sc} \cdot \hat{\mathbf{r}} r^2 d\Omega}{j_{\rm in}}.$$
 (2.5)

The probability current density can be obtained by taking the time derivative of the total probability of finding a particle within a volume V

$$\frac{\partial}{\partial t} \int_{V} |\Psi(\mathbf{r},t)|^{2} d\mathbf{r} = \int_{V} \left(\Psi^{*} \frac{\partial \Psi}{\partial t} + \frac{\partial \Psi^{*}}{\partial t} \Psi \right) d\mathbf{r}$$

$$= \int_{V} \frac{i\hbar}{2m} \left(\Psi^{*} \nabla^{2} \Psi - \nabla^{2} \Psi^{*} \Psi \right) d\mathbf{r}$$

$$= -\int_{V} \nabla \cdot \left[\frac{\hbar}{2mi} \left(\Psi^{*} \nabla \Psi - \nabla \Psi^{*} \Psi \right) \right] d\mathbf{r}$$

$$= -\int_{V} \nabla \cdot \mathbf{j} d\mathbf{r},$$
(2.6)

where on the last line we have defined

$$\mathbf{j} = \frac{\hbar}{2mi} \left(\Psi^* \, \nabla \Psi - \nabla \Psi^* \, \Psi \right). \tag{2.7}$$

Using Gauss's divergence theorem, we can further write

$$\frac{\partial}{\partial t} \int_{V} |\Psi(\mathbf{r},t)|^{2} d\mathbf{r} = -\int_{S} \mathbf{j} \cdot d\mathbf{S}, \qquad (2.8)$$

which says that the rate of change of the total probability is equal to the flux through the surface S which bounds the volume V. Thus we see that **j** can be interpreted as a probability current density, and by analogy to the equation of charge conservation in electromagnetism, we also have the following continuity equation

$$\frac{\partial}{\partial t} |\Psi(\mathbf{r},t)|^2 + \nabla \cdot \mathbf{j} = 0.$$
(2.9)

We wish to calculate the scattered probability current density

$$\mathbf{j}_{\rm sc} = \frac{\hbar}{2mi} \left(\boldsymbol{\psi}_{\rm sc}^* \, \boldsymbol{\nabla} \boldsymbol{\psi}_{\rm sc} - \boldsymbol{\nabla} \boldsymbol{\psi}_{\rm sc}^* \, \boldsymbol{\psi}_{\rm sc} \right), \tag{2.10}$$

for which we recall that the gradient in spherical coordinates is

$$\boldsymbol{\nabla} = \frac{\partial}{\partial r}\,\hat{\mathbf{r}} + \frac{1}{r}\,\frac{\partial}{\partial\theta}\,\hat{\boldsymbol{\theta}} + \frac{1}{r\sin\theta}\,\frac{\partial}{\partial\phi}\,\hat{\boldsymbol{\phi}}.$$
(2.11)

Hence the radial component of \mathbf{j}_{sc} is simply

$$\mathbf{j}_{\rm sc} \cdot \hat{\mathbf{r}} = \frac{\hbar}{2mi} \left(\psi_{\rm sc}^* \frac{\partial \psi_{\rm sc}}{\partial r} - \frac{\partial \psi_{\rm sc}^*}{\partial r} \,\psi_{\rm sc} \right), \tag{2.12}$$

and after carrying out the algebra we obtain

$$\mathbf{j}_{\mathrm{sc}} \cdot \hat{\mathbf{r}} = \frac{\hbar k}{m} |A|^2 |f(k, \boldsymbol{\theta})|^2 \frac{1}{r^2}.$$
(2.13)

Putting everything back into eq. (2.5), we see that the differential cross section is simply given by the modulus squared of the scattering amplitude,

$$\frac{d\sigma}{d\Omega} = |f(k,\theta)|^2.$$
(2.14)

2.3 Born approximation

We can solve the problem of scattering within perturbation theory, with the perturbation turned on in the interaction region and turned off as the scattered particle leaves the region. It can be shown that under typical experimental conditions, and assuming a potential with no explicit time dependence, it is entirely sufficient to solve the time-independent SE for scattering problems,

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{r})\right]\psi(\mathbf{r}) = E\,\psi(\mathbf{r}),\tag{2.15}$$

in order to look for asymptotic steady-state solutions of the form show in eq. (2.2). Suppose there was a Green's function $G(\mathbf{r}, \mathbf{r}')$ that solves the SE for an impulse or delta-function source

$$\left[\frac{\hbar^2}{2m}\nabla^2 + E\right]G(\mathbf{r},\mathbf{r}') = \delta(\mathbf{r}-\mathbf{r}'), \qquad (2.16)$$

then we could recast the SE above as an integral equation,

$$\boldsymbol{\psi}(\mathbf{r}) = \boldsymbol{\psi}_0(\mathbf{r}) + \int G(\mathbf{r}, \mathbf{r}') \, V(\mathbf{r}') \, \boldsymbol{\psi}(\mathbf{r}') \, d^3 r'$$
(2.17)

where $\psi_0(\mathbf{r})$ is the solution to the homogeneous SE with no potential. One can verify that eq. (2.17), which is known as the Lippmann–Schwinger equation, indeed satisfies the SE by plugging eqs. (2.16) and (2.17) back into eq. (2.15).

To simplify the notation, we slightly re-write the SE as

$$(\nabla^2 + k^2) \ \psi(\mathbf{r}) = U(\mathbf{r}) \ \psi(\mathbf{r}), \tag{2.18}$$

where $U(\mathbf{r}) = (2m/\hbar^2) V(\mathbf{r})$, and re-define the Green's function as

$$(\nabla^2 + k^2) G(\mathbf{r}, \mathbf{r}') = \delta(\mathbf{r} - \mathbf{r}').$$
(2.19)

To solve for $G(\mathbf{r}, \mathbf{r}')$, first consider it as the Fourier transform of some function $g(\mathbf{k})$

$$G(\mathbf{r},\mathbf{r}') = \frac{1}{(2\pi)^{3/2}} \int \exp(i\mathbf{k} \cdot (\mathbf{r} - \mathbf{r}'))g(\mathbf{k}) d^3k.$$
(2.20)

Then we have

$$(\nabla^2 + k^2) G(\mathbf{r}, \mathbf{r}') = \frac{1}{(2\pi)^{3/2}} \int (\nabla^2 + k^2) e^{i\mathbf{k}' \cdot (\mathbf{r} - \mathbf{r}')} g(\mathbf{k}') d^3k' = \delta(\mathbf{r} - \mathbf{r}').$$
(2.21)

Recall that the delta function is defined as

$$\delta(\mathbf{r} - \mathbf{r}') = \frac{1}{(2\pi)^3} \int e^{i\mathbf{k}' \cdot (\mathbf{r} - \mathbf{r}')} d^3k', \qquad (2.22)$$

so we see that

$$g(\mathbf{k}') = \frac{1}{(2\pi)^{3/2}} \frac{1}{k^2 - k'^2}.$$
(2.23)

If we plug $g(\mathbf{k}')$ back into $G(\mathbf{r}, \mathbf{r}')$, we get

$$G(\mathbf{r}, \mathbf{r}') = \frac{1}{(2\pi)^3} \int \frac{e^{i\mathbf{k}' \cdot (\mathbf{r} - \mathbf{r}')}}{k^2 - k'^2} \, d^3k'.$$
(2.24)



Figure 2.1 The portion of the contour in the complex plane which is along the real axis, showing the sign of the infinitesimal semi-circles which avoid the singularities.

To perform the angular integral, we can choose coordinates such that $(\mathbf{r} - \mathbf{r}')$ lies along the *z*-axis

$$G(\mathbf{r}, \mathbf{r}') = \frac{1}{(2\pi)^3} \int_0^\infty \frac{k'^2}{k^2 - k'^2} 2\pi \int_0^\pi e^{ik'|\mathbf{r} - \mathbf{r}'|\cos\theta} \sin\theta \, d\theta \, dk'$$
$$= \frac{1}{4\pi^2 |\mathbf{r} - \mathbf{r}'|} \int_{-\infty}^\infty \frac{k' \sin(k'|\mathbf{r} - \mathbf{r}'|)}{k^2 - k'^2} \, dk', \qquad (2.25)$$

where we were able to recast the k' integration from $-\infty$ to ∞ because the integrand is even. This integral requires complex integration due to the singularities at $k' = \pm k$. We can add an infinitesimal imaginary part to the singularities so that they now occur at $k' = \pm (k + i\varepsilon)$, and redefine ε while keeping its sign intact, to write

$$G(\mathbf{r},\mathbf{r}') = \lim_{\varepsilon \to 0} \frac{1}{4\pi^2 |\mathbf{r} - \mathbf{r}'|} \int_{-\infty}^{\infty} \frac{k' \sin(k' |\mathbf{r} - \mathbf{r}'|)}{k^2 - k'^2 + i\varepsilon} dk'.$$
 (2.26)

As we will see below, the sign of ε determines whether one passes over or under each pole when following the integration contour along the real axis, and it is chosen such that the Green's function represents an outgoing wave. Fig. 2.1 shows the contour along the real axis which we will follow in order to satisfy our boundary conditions.

One method for computing the integral is to use Cauchy's integral theorem,

$$\oint_C \frac{f(z)}{z - z_o} \, dz = 2\pi i \, f(z_o), \tag{2.27}$$

for a given pole at z_o lying inside the contour *C* in the complex plane. To see how we should close off the contour, we re-write eq. (2.25) as

$$G(\mathbf{r},\mathbf{r}') = \frac{i}{8\pi^2 |\mathbf{r}-\mathbf{r}'|} \int_{-\infty}^{\infty} \frac{e^{ik'|\mathbf{r}-\mathbf{r}'|} - e^{-ik'|\mathbf{r}-\mathbf{r}'|}}{k^2 - k'^2 + i\varepsilon} \, k' \, dk'.$$
(2.28)

The full contour will consist of the path in fig. 2.1 plus a semicircle at infinity either in the top half or the bottom half of the complex plane. Since we are trying to calculate the portion along the real axis, we would like the semicircle to contribute nothing. For the first term in eq. (2.28), $e^{ik'|\mathbf{r}-\mathbf{r}'|} \rightarrow 0$ when $\text{Im}(k') \rightarrow +\infty$, so we choose the semicircle in the positive half. Likewise, we choose the bottom half-circle for the second term (which picks up a factor of -1 because the contour goes clockwise). Applying Cauchy's integral theorem for both terms, we arrive at the result for the Green's function in position space

$$G(\mathbf{r},\mathbf{r}') = -\frac{e^{ik|\mathbf{r}-\mathbf{r}'|}}{4\pi|\mathbf{r}-\mathbf{r}'|}.$$
(2.29)

One can verify that if we had chosen the sign of ε such that we would skirt around the k' = -k pole below the real axis and the k' = k pole above the real axis, we would get a Green's function which is an incoming wave, i.e. of the form $G(\mathbf{r}, \mathbf{r}') \propto e^{-ik|\mathbf{r}-\mathbf{r}'|}/|\mathbf{r}-\mathbf{r}'|$.

Another way to express the Green's function integral is in terms of the Cauchy principal value, defined as

$$\mathscr{P}\int_{-\infty}^{\infty} \frac{f(x)}{x - x_0} \, dx = \lim_{\delta \to 0} \left[\int_{-\infty}^{x_0 - \delta} \frac{f(x)}{x - x_0} \, dx + \int_{x_0 + \delta}^{\infty} \frac{f(x)}{x - x_0} \, dx \right]. \tag{2.30}$$

If we integrate along the path in fig. 2.1, the Green's function of eq. (2.26) can be written as

$$G(\mathbf{r},\mathbf{r}') = \frac{1}{4\pi^2 |\mathbf{r} - \mathbf{r}'|} \mathscr{P} \int_{-\infty}^{\infty} \frac{k' \sin(k' |\mathbf{r} - \mathbf{r}'|)}{k^2 - k'^2} dk' + \frac{1}{4\pi^2 |\mathbf{r} - \mathbf{r}'|} \left[\int_{c_-} \frac{k' \sin(k' |\mathbf{r} - \mathbf{r}'|)}{k^2 - k'^2} dk' + \int_{c_+} \frac{k' \sin(k' |\mathbf{r} - \mathbf{r}'|)}{k^2 - k'^2} dk' \right], \quad (2.31)$$

where c_{-} and c_{+} are the semicircles that go around the singularities at k' = -k and k' = +k, respectively.

When integrating a function f(z) around a singularity located at $z_0 = x_0 + i\varepsilon$, we can evaluate the portion along the semicircle *c* (with radius δ) as follows

$$\lim_{\delta \to 0} \int_c \frac{f(z)}{z - z_0} dz = \lim_{\delta \to 0} \int_{-\pi}^0 \frac{f(x_0)}{\delta e^{i\phi}} \left(i\phi \,\delta \,e^{i\phi} \,d\phi \right) = i\pi f(x_0), \tag{2.32}$$

which leads to the general relation

$$\int_{-\infty}^{\infty} \frac{f(x)}{x - x_0} \, dx = \mathscr{P} \int_{-\infty}^{\infty} \frac{f(x)}{x - x_0} \, dx + i\pi f(x_0). \tag{2.33}$$

Returning to the second line of eq. (2.31), we can parametrize the semicircles as $k' = \pm k + \delta e^{i\phi}$, with ϕ running from π to 0 near k' = -k, and ϕ running from $-\pi$ to 0 near k' = +k. For the singularity at k' = -k, an expression very similar to eq. (2.33) can be found, and the result for the Green's function is thus

$$G(\mathbf{r},\mathbf{r}') = \frac{1}{4\pi^2 |\mathbf{r}-\mathbf{r}'|} \left[\mathscr{P} \int_{-\infty}^{\infty} \frac{k' \sin(k' |\mathbf{r}-\mathbf{r}'|)}{k^2 - k'^2} \, dk' + i\pi \sin(k|\mathbf{r}-\mathbf{r}'|) \right].$$
(2.34)

We now restore the factor of $(2m/\hbar^2)$ to the Green's function (eq. (2.29))

$$G(\mathbf{r},\mathbf{r}') = -\frac{m}{2\pi\hbar^2} \frac{e^{ik|\mathbf{r}-\mathbf{r}'|}}{|\mathbf{r}-\mathbf{r}'|},$$
(2.35)

and go back to the Lippmann–Schwinger equation, eq. (2.17), which we can expand in an iterative series

$$\psi(\mathbf{r}) = \psi_0(\mathbf{r}) + \int G(\mathbf{r}, \mathbf{r}') V(\mathbf{r}') \psi(\mathbf{r}') \left[\psi_0(\mathbf{r}') + \int G(\mathbf{r}', \mathbf{r}'') V(\mathbf{r}'') \psi(\mathbf{r}'') d^3 r'' \right] d^3 r'. \quad (2.36)$$

If the perturbation $V(\mathbf{r})$ is weak, we would expect the series to converge and that it would be a good approximation to only keep the first few terms. The first Born approximation amounts to keeping only the lowest-order non trivial term

$$\boldsymbol{\psi}(\mathbf{r}) \simeq \boldsymbol{\psi}_0(\mathbf{r}) + \int \boldsymbol{G}(\mathbf{r}, \mathbf{r}') \, \boldsymbol{V}(\mathbf{r}') \, \boldsymbol{\psi}_0(\mathbf{r}') \, d^3 \boldsymbol{r}'. \tag{2.37}$$

2.4 The cross section in terms of the *T*-matrix

To introduce the *T*-matrix, we use a more compact notation to write the Born series, eq. (2.36), as

$$|\psi\rangle = (1 + GV + GVGV + GVGVGV + \dots)|\psi_0\rangle. \tag{2.38}$$

We see that the quantum picture of scattering in the Born approximation consists of successive interaction events with the potential V followed by propagation of free spherical waves as represented by the Green's function. Each higher order term corresponds to a path where the particle undergoes an additional scattering event, and the full wavefunction is the sum of all possible paths. We could define an operator called the *T*-matrix which captures all the effects of scattering (excluding the last free spherical wave propagation) such that

$$|\psi\rangle = (1 + GT) |\psi_0\rangle, \tag{2.39}$$

$$T = V(1 + GV + GVGV + ...) = V + VGT.$$
 (2.40)

One could show from Schrödinger's equation that the Green's function in operator form can be expressed as $(E - H_0 + i\varepsilon)^{-1}$, where as before the $i\varepsilon$ is introduced to deal with the singularity in the denominator, which leads to the relation

$$T = V + V \frac{1}{E - H_0 + i\varepsilon} T.$$
(2.41)

To see how the T-matrix is related to the cross section, we consider the large-r limit of the full wavefunction, since we assume the detector to be sufficiently far away from the scatterer

$$\lim_{r \to \infty} \Psi(\mathbf{r}) = \Psi_0(\mathbf{r}) + \lim_{r \to \infty} \int G(\mathbf{r}, \mathbf{r}') T(\mathbf{r}', \mathbf{r}'') \Psi_0(\mathbf{r}'') d^3 r' d^3 r''$$
$$= e^{ikz} - \frac{m}{2\pi\hbar^2} \lim_{r \to \infty} \int \frac{e^{ik|\mathbf{r} - \mathbf{r}'|}}{|\mathbf{r} - \mathbf{r}'|} T(\mathbf{r}', \mathbf{r}'') e^{ikz''} d^3 r' d^3 r'', \qquad (2.42)$$

One can easily show that

$$\lim_{r \to \infty} |\mathbf{r} - \mathbf{r}'| \approx r - \hat{\mathbf{r}} \cdot \mathbf{r}' \quad \text{and} \quad \lim_{r \to \infty} \frac{1}{|\mathbf{r} - \mathbf{r}'|} \approx \frac{1}{r},$$
(2.43)

which leads to

$$\lim_{r \to \infty} \Psi(\mathbf{r}) = e^{ikz} - \frac{m}{2\pi\hbar^2} \frac{e^{ikr}}{r} \int e^{-ik\hat{\mathbf{r}}\cdot\mathbf{r}'} T(\mathbf{r}',\mathbf{r}'') e^{ikz''} d^3r' d^3r''.$$
(2.44)

Comparison with equation eq. (2.2) shows that

$$f(k,\boldsymbol{\theta}) = -\frac{m}{2\pi\hbar^2} \int e^{-ik\hat{\mathbf{r}}\cdot\mathbf{r}'} T(\mathbf{r}',\mathbf{r}'') e^{ikz''} d^3r' d^3r''.$$
(2.45)

Since the incoming plane wave is associated with $\mathbf{k} = k\hat{\mathbf{z}}$ and the detected wave with $\mathbf{k}' = k\hat{\mathbf{r}}$, we can write a more general expression for the scattering amplitude in terms of *T*-matrix elements

$$f(\mathbf{k}, \mathbf{k}') = -\frac{m}{2\pi\hbar^2} \int e^{-i\mathbf{k}'\cdot\mathbf{r}'} T(\mathbf{r}', \mathbf{r}'') e^{i\mathbf{k}\cdot\mathbf{r}''} d^3r' d^3r''$$
$$= -\frac{(2\pi)^2 m}{\hbar^2} \int \langle \mathbf{k}' | \mathbf{r}' \rangle \langle \mathbf{r}' | T | \mathbf{r}'' \rangle \langle \mathbf{r}'' | \mathbf{k} \rangle d^3r' d^3r''$$
$$= -\frac{(2\pi)^2 m}{\hbar^2} \langle \mathbf{k}' | T | \mathbf{k} \rangle.$$
(2.46)

2.5 Partial-wave series

Generally in scattering problems we consider spherically symmetric potentials such that we can separate the SE into a radial component and an angular component consisting of eigenfunctions of the angular momentum operators L^2 and L_z ,

$$\boldsymbol{\psi}_{lm}(\mathbf{r}) = R_l(r) Y_l^m(\boldsymbol{\theta}, \boldsymbol{\phi}). \tag{2.47}$$

The angular wavefunctions are the spherical harmonics $Y_l^m(\theta, \phi)$, while the radial wavefunctions satisfy the following ordinary differential equation

$$\left[\frac{d^2}{dr^2} + \frac{2}{r}\frac{d}{dr} - \frac{l(l+1)}{r^2} - U(r) + k^2\right]R_l(r) = 0,$$
(2.48)

where $U(r) = (2m/\hbar^2) V(r)$ as before. Defining $u_l(r) = rR_l(r)$, the above equation can be simplified to

$$\left[\frac{d^2}{dr^2} - \frac{l(l+1)}{r^2} - U(r) + k^2\right] u_l(r) = 0.$$
(2.49)

Provided the potential diverges less rapidly than $1/r^2$ as $r \to 0$, this equation can be solved for the small *r* region by expanding the function $u_l(r)$ in a power series, from which we find two solutions

$$u_l(r \to 0) \sim r^{l+1}$$
 and $u_l(r \to 0) \sim r^{-l}$. (2.50)

We see that only the first solution leads to a physical behaviour near the origin.

We now look for the asymptotic large-*r* form of the solutions, where V(r > a) = 0, with *a* being the range of the potential. Details of the procedure can be found in e.g. Bransden & Joachain [3], but the solutions are given by the spherical Bessel functions $j_l(\rho)$ and spherical Neumann functions $n_l(\rho)$, where $\rho = kr$

$$R_l(\rho) = A j_l(\rho) + B n_l(\rho), \qquad (2.51)$$

$$j_l(\rho) = (-1)^l \rho^l \left(\frac{1}{\rho} \frac{\partial}{\partial \rho}\right)^l \frac{\sin \rho}{\rho}, \qquad (2.52)$$

$$n_l(\rho) = -(-1)^l \rho^l \left(\frac{1}{\rho} \frac{\partial}{\partial \rho}\right)^l \frac{\cos \rho}{\rho}.$$
 (2.53)

Near the origin as $\rho \rightarrow 0$, these functions behave as

$$j_l(\boldsymbol{\rho}) \sim \boldsymbol{\rho}^l, \tag{2.54}$$

$$n_l(\rho) \sim \rho^{-(l+1)},$$
 (2.55)

which is consistent with the power series solution, while for large values of ρ they tend toward

$$j_l(\rho) \to \frac{1}{\rho} \sin\left(\rho - \frac{l\pi}{2}\right),$$
 (2.56)

$$n_l(\rho) \to -\frac{1}{\rho} \cos\left(\rho - \frac{l\pi}{2}\right).$$
 (2.57)

We can further examine the general structure of the solution at $r \rightarrow \infty$,

$$R_l(r) = \frac{1}{kr} \left[B_l(k) \sin\left(kr - \frac{l\pi}{2}\right) - C_l(r) \cos\left(kr - \frac{l\pi}{2}\right) \right], \qquad (2.58)$$

by defining

$$A_l(k) = \sqrt{B_l^2(k) + C_l^2(k)}$$
 and $\tan \delta_l(k) = -\frac{B_l(k)}{C_l(k)}$. (2.59)

Using a trigonometric identity, we can express the asymptotic form of $R_l(r)$ as

$$R_l(r) = \frac{A_l(k)}{kr} \sin\left(kr - \frac{l\pi}{2} + \delta_l(k)\right), \qquad (2.60)$$

where the $\delta_l(k)$ is called the phase shift and succinctly captures the effect of the scattering. We see that the radial solution is simply a plane wave characterized by a phase shift. In the absence of any interaction, we would have to set $C_l(k) = 0$ since $n_l(k)$ diverges as $r \to 0$, and thus we would have $\delta_l(k) = 0$.

To relate the phase shifts to the scattering amplitude $f(k, \theta)$, we first note that since plane waves and spherical waves both form complete sets of solutions of the SE in 3D space, a plane wave can be expanded in terms of spherical waves with definite angular momentum

$$e^{i\mathbf{k}\cdot\mathbf{r}} = \sum_{l=0}^{\infty} (2l+1)i^l j_l(kr) P_l(\hat{\mathbf{k}}\cdot\hat{\mathbf{r}}).$$
(2.61)

Since we are assuming azimuthal symmetry, the above simplifies to

$$e^{ikr\cos\theta} = \sum_{l=0}^{\infty} (2l+1)i^l j_l(kr) P_l(\cos\theta).$$
 (2.62)

Similarly, the wavefunction and scattering amplitudes can also be expanded as

$$\psi(\mathbf{r}) = \sum_{l=0}^{\infty} R_l(r) P_l(\cos \theta), \qquad (2.63)$$

$$f(k,\theta) = \sum_{l=0}^{\infty} f_l(k) P_l(\cos\theta).$$
(2.64)

We know that the wavefunction has the asymptotic form

$$\Psi(\mathbf{r}) = e^{ikr\cos\theta} + f(k,\theta)\frac{e^{ikr}}{r},$$
(2.65)

which we can expand using eqs.(2.62) and (2.64), and compare to eq. (2.63). Equating coefficients, we find

$$R_{l}(r) = (2l+1)i^{l}j_{l}(kr) + f_{l}(k)\frac{e^{ikr}}{r}$$

= $(2l+1)i^{l}\frac{\sin(kr-\frac{l\pi}{2})}{kr} + f_{l}(k)\frac{e^{ikr}}{r}.$ (2.66)

If we now equate the above expression with eq. (2.60), we get after some algebra

$$A_l(k) = (2l+1)i^l e^{i\delta_l(k)}, \qquad (2.67)$$

$$f_l(k) = \frac{2l+1}{2ik} \left(e^{2i\delta_l(k)} - 1 \right).$$
(2.68)

Finally, we see that the scattering amplitude is given by

$$f(k,\theta) = \frac{1}{2ik} \sum_{l=0}^{\infty} (2l+1) \left(e^{2i\delta_l(k)} - 1 \right) P_l(\cos\theta),$$
(2.69)

and the integrated cross section is (see eq. (2.14))

$$\sigma = 2\pi \int_0^\pi |f(k,\theta)|^2 \sin\theta \, d\theta = \frac{4\pi}{k^2} \sum_{l=0}^\infty (2l+1) \sin^2 \delta_l(k).$$
(2.70)

We have found the general form of the solution in the region r > a, expressed in terms of the phase shifts $\delta_l(k)$. To compute the phase shifts, we must solve the radial equation, eq. (2.48), in the presence of the interaction potential, for r < a. This is generally carried out numerically, and for boundary conditions we require that both $R_l(r)$ and $dR_l(r)/dr$ be continuous at r = a.

The method of partial waves is most useful at low incident energies, when only a small number of partial waves are needed to accurately describe the scattering. To see why this is the case, we turn back to eq. (2.49) and notice that it looks like the 1D SE with an effective potential

$$U_{\rm eff}(r) = U(r) + \frac{l(l+1)}{r^2},$$
 (2.71)

where the second term acts as a centrifugal barrier. At low incident energies, the particle does not have enough energy to overcome the centrifugal barrier and probe the interaction region if l is large, so that the higher l terms in the partial wave series do not contribute to the scattering

description. At higher incident energies, however, more and more partial waves can overcome the centrifugal repulsion and must be included in the expansion since they can contribute to the scattering process. We therefore see that the Born approximation and the partial wave method are complementary, as the former is typically valid at high energies, whereas the latter is most useful at low energies.

2.6 Inelastic electron-atom scattering

The previous sections have been focused on elastic scattering. We now wish to consider inelastic scattering of an electron by an atom. For the simple treatment we present here, we are ignoring exchange effects and assuming that the projectile is distinguishable from the atomic electrons. The initial state consists of an electron with definite momentum \mathbf{k} and the atom in its ground state, while the final state has the electron with momentum \mathbf{k}' and the atom in an excited state n. We denote this transition by

$$|\mathbf{k},0\rangle \to |\mathbf{k}',n\rangle,$$
 (2.72)

and the corresponding wavefunctions are

$$e^{\mathbf{i}\mathbf{k}\cdot\mathbf{r}} \psi_0(\mathbf{r}_1,\ldots\mathbf{r}_Z) \to e^{\mathbf{i}\mathbf{k}'\cdot\mathbf{r}} \psi_n(\mathbf{r}_1,\ldots\mathbf{r}_Z),$$
 (2.73)

with the incoming electron coordinates denoted by \mathbf{r} and the atomic electrons' coordinates denoted by \mathbf{r}_i .

Taking T = V in the first Born approximation (see eqs. (2.36)-(2.40)), it is straightforward to write down the cross section from eq. (2.46), except with one important difference. If we go back to the initial definition of the cross section in eq. (2.5), we see that in the case of inelastic scattering $|\mathbf{k}'| \neq |\mathbf{k}|$, so there would be an additional factor of k'/k

$$\frac{d\sigma}{d\Omega} = \frac{(2\pi)^4 m_{\rm e}^2}{\hbar^4} \frac{k'}{k} \left| \langle \mathbf{k}', n | V | \mathbf{k}, 0 \rangle \right|^2$$

$$= \frac{m_{\rm e}^2}{(2\pi)^2 \hbar^4} \frac{k'}{k} \left| \int e^{i\mathbf{q}\cdot\mathbf{r}} \psi_n^*(\mathbf{r}_1, \dots, \mathbf{r}_Z) V \psi_0(\mathbf{r}_1, \dots, \mathbf{r}_Z) d^3 r_1 \dots d^3 r_n d^3 r \right|^2, \quad (2.74)$$

where $\mathbf{q} = \mathbf{k} - \mathbf{k}'$ is the momentum transfer.

The Coulomb interaction between the incoming electron and the electrons and nucleus of the atom gives rise to the potential

$$V = -\frac{Ze^2}{r} + \sum_{i=1}^{Z} \frac{e^2}{|\mathbf{r} - \mathbf{r}_i|},$$
(2.75)

where we have set the nucleus at the origin. Plugging the potential into eq. (2.74), we see that the first term (the interaction with the nucleus) does not depend on atomic electron coordinates, and thus the integration over the atomic electron coordinates $\mathbf{r}_1 \dots \mathbf{r}_Z$ simply amounts to

$$\langle n|0\rangle = \delta_{n0}, \qquad (2.76)$$

which means that this term only contributes to elastic scattering. For the second term, it is easier to first perform the integration over **r** by shifting $\mathbf{r} \rightarrow \mathbf{r} + \mathbf{r}_i$ and then using the Fourier transform of the Coulomb potential to obtain

$$\int \frac{e^{\mathbf{i}\mathbf{q}\cdot\mathbf{r}}}{|\mathbf{r}-\mathbf{r}_i|} d^3r = \int \frac{e^{\mathbf{i}\mathbf{q}\cdot(\mathbf{r}+\mathbf{r}_i)}}{|\mathbf{r}|} d^3r = \frac{4\pi}{q^2} e^{\mathbf{i}\mathbf{q}\cdot\mathbf{r}_i}.$$
(2.77)

The cross section can then be re-written as

$$\frac{d\sigma}{d\Omega} = \left(\frac{2m_{\rm e}e^2}{\hbar^2q^2}\right)^2 \frac{k'}{k} \left| \left\langle n \left| \sum_{i=1}^{Z} e^{i\mathbf{q}\cdot\mathbf{r}_i} \right| 0 \right\rangle \right|^2, \qquad (2.78)$$

and we see that it can be thought of as the product of a factor containing only kinematic observable quantities and a factor which only describes a property of the atom. The latter gives the probability that the atom undergoes the transition $0 \rightarrow n$ when given a momentum transfer of $\hbar \mathbf{q}$, and the matrix element

$$F_n(\mathbf{q}) = \left| \left\langle n \left| \sum_{i=1}^{Z} e^{i\mathbf{q} \cdot \mathbf{r}_i} \right| 0 \right\rangle \right|^2$$
(2.79)

is commonly called the inelastic form factor.

Typically in an experiment one considers the atoms to be randomly oriented, so that an orientational average is usually implied. Additionally, a sum over all degenerate states of energy E_n is also implied, such that the state $|n\rangle$ refers to the set of all states with energy E_n . Under

these assumptions, $F_n(\mathbf{q})$ becomes $F_n(q)$, a function which only depends on the magnitude of the momentum transfer.

In atomic physics, a slightly different quantity called the generalized oscillator strength is more often used

$$f_n(q) = \frac{E_n}{Q} F_n(q), \qquad (2.80)$$

where $Q = (\hbar q)^2 / 2m_e$ so that $f_n(q)$ is still dimensionless. It is a generalization of the optical oscillator strength

$$f_n = \frac{E_n}{R} M_n^2, \tag{2.81}$$

where

$$M_n^2 = \frac{1}{a_0^2} \left| \left\langle n \left| \sum_{i=1}^Z x_i \right| 0 \right\rangle \right|^2, \qquad (2.82)$$

and x_i is a component of \mathbf{r}_i . In the optical (dipole) approximation, one can show that

$$\lim_{q \to 0} f_n(q) = f_n,$$
 (2.83)

a limit which is approached for forward scattering at high velocities, and where the above relationship can be used to connect the collision of fast charged particles to photoabsorption.

We can perform a change of variables and replace $d\Omega$ by $2\pi \sin\theta d\theta = \pi d(q^2)/kk'$ in eq. (2.78) to obtain

$$d\sigma = \frac{2\pi e^4}{m_e v^2} \frac{1}{E_n Q} f_n(Q) dQ, \qquad (2.84)$$

which is more convenient in practical applications. In the case of ionization where the final state is in the continuum, the generalized oscillator strength is differential in the energy loss W and is denoted by df(Q,W)/dW. The cross section is then

$$\frac{d^2\sigma}{dW\,dQ} = \frac{2\pi e^4}{m_{\rm e}v^2} \frac{1}{WQ} \frac{df(Q,W)}{dW}$$
(2.85)

Moving to the relativistic framework, Fano has shown that in the Coulomb gauge the interaction between the projectile and target electrons is divided into a term representing the instantaneous static Coulomb interaction and a term describing the process of absorption and emission of virtual photons [4]. They are typically referred to as the longitudinal and transverse interactions, respectively. The transverse contribution becomes significant when both the

projectile and target electrons are relativistic, in which case the relativistic form of eq. (2.84) is given by [4]

$$\frac{d^2\sigma}{dW\,dQ} = \frac{2\pi e^4}{m_{\rm e}v^2} \left(\frac{2m_{\rm e}c^2}{WQ(Q+2m_{\rm e}c^2)} + \frac{\beta^2\sin^2\theta_r W\,2m_{\rm e}c^2}{[Q(Q+2m_{\rm e}c^2)-W^2]^2}\right) \frac{df(Q,W)}{dW},\tag{2.86}$$

where $\beta = v/c$, and θ_r is the angle between the initial momentum of the projectile and the momentum transfer.

2.7 Fermi's golden rule

Another useful tool when studying scattering problems is Fermi's golden rule, which describes the transition rate from an initial eigenstate of a system (e.g. an atom) to continuum eigenstates under the effect of a weak time-dependent perturbation. In time-dependent perturbation theory, we assume that the Hamiltonian can be written as

$$H = H_0 + H_1, (2.87)$$

where the eigenstates of H_0 are known, and H_1 is a small perturbation. We proceed by expanding a perturbed state at a later time *t* in terms of the eigenstates $|n\rangle$ of the unperturbed Hamiltonian,

$$|\psi(t)\rangle = \sum_{n} a_n(t) e^{-iE_n t/\hbar} |n\rangle.$$
(2.88)

Using the SE we can solve for the coefficients $a_n(t)$, with $n \neq i$, and find that to first order in the perturbation,

$$a_n(t) = \frac{2}{i\hbar} \langle n|H_1|i\rangle e^{i\omega t/2} \frac{\sin \omega t/2}{\omega}, \qquad (2.89)$$

where $\omega = (E_n - E_i)/\hbar$. The transition rate is given by

$$\Gamma_{i\to n} = \frac{d}{dt} |a_n(t)|^2 = \frac{2|\langle n|H_1|i\rangle|^2}{\hbar^2} \frac{\sin \omega t}{\omega},$$
(2.90)

which seems to predict the surprising result that as $\omega \to 0$, when the initial and final states are infinitesimally close to one another, $\sin(\omega t)/\omega \to t$, and the transition rate grows linearly with *t*. However, when we account for the density of states $\rho(E)$, we must integrate over an energy

interval,

$$\Gamma_{i\to f} = \frac{2}{\hbar} \int_{-\infty}^{\infty} \rho(\omega) |\langle f|H_1|i\rangle|^2 \frac{\sin \omega t}{\omega} d\omega.$$
(2.91)

We are looking for steady-state solutions, so we can take the large t limit, where the sinc function $\operatorname{sinc}(\omega t) = \sin \omega t / (\omega t)$ is sharply peaked at $\omega = 0$, and the density of states can be taken outside the integral. The rate is then given by the well-known Fermi's golden rule

$$\Gamma_{i \to f} = \frac{2\pi}{\hbar} |\langle f|H_1|i\rangle|^2 \rho(E_f).$$
(2.92)

2.8 Interactions of charged particles with the EM field

By writing out the Lagrangian for a charged particle interacting with an electromagnetic field, one can show that the non-relativistic Hamiltonian for such a system is given by (see e.g. appendix E of [1])

$$H = \frac{(\mathbf{p} + e\mathbf{A}/c)^2}{2m_{\rm e}} - e\phi, \qquad (2.93)$$

where **A** and ϕ are the vector and scalar potentials. In the Coulomb gauge, $\nabla \cdot \mathbf{A} = 0$, so that we can write the Hamiltonian as

$$H = H_0 + H_1, (2.94)$$

with the unperturbed Hamiltonian

$$H_0 = \frac{p^2}{2m_{\rm e}} - e\phi,$$
 (2.95)

and the interaction term

$$H_1 = \frac{e\mathbf{A} \cdot \mathbf{p}}{m_e c} + \frac{e^2 A^2}{2m_e c^2}.$$
(2.96)

Equivalently, in operator notation we have

$$H_1 = \frac{e}{m_{\rm e}c} \mathbf{A} \cdot \frac{\hbar}{i} \nabla + \frac{e^2}{2m_{\rm e}c^2} \mathbf{A}^2.$$
(2.97)

In the non-relativistic limit, we can quantize the electromagnetic field by considering it as a collection of independent harmonic oscillators and by introducing creation and annihilation operators which act on Fock states (representing the number of photons with a given wave vector and polarization). In this picture, the vector potential is made up of terms which are first order in creation and annihilation operators. Since Compton scattering involves an incoming and an outgoing photon of different energies, to lowest order it is described by the A^2 term in the Hamiltonian. For photon-atom Compton scattering, the A^2 term treated in first-order time-dependent perturbation theory yields

$$\frac{d^2\sigma}{d\Omega d\omega} = \left(\frac{d\sigma}{d\Omega}\right)_{\rm T} \frac{\omega_2}{\omega_1} \sum_f \left| \left\langle f \left| \sum_j \exp(i\mathbf{k} \cdot \mathbf{r}_j) \right| i \right\rangle \right|^2 \delta(E_f - E_i - \omega), \quad (2.98)$$

where ω_1 and ω_2 are the incoming and scattered photon energies with $\omega = \omega_1 - \omega_2$, the momentum transfer is $\mathbf{k} = \mathbf{k}_1 - \mathbf{k}_2$ with \mathbf{k}_1 and \mathbf{k}_2 the incoming and scattered photon wave vectors, \mathbf{r}_j is the coordinate of the *j*-th electron in the atom, and $(\frac{d\sigma}{d\Omega})_T$ is the Thomson DCS. The prefactor ω_2/ω_1 is related to the photon flux, which has been chosen to be linear in order to be consistent with the relativistic treatment [5, 6]. The Waller–Hartree model for (relativistic) Compton scattering with bound electrons, which will be covered in section 5.3.2, arises from the replacement of the Thomson DCS by the Klein–Nishina DCS.

In the impulse approximation, only one target electron is involved in the scattering process, and the remaining electrons act as mere spectators which contribute only to determining the target electron's initial momentum distribution. The scattering interaction itself is assumed to occur over a short enough time scale that the spectator electron distributions are fixed and do not relax before the recoiling electron has escaped, an assumption which is valid when the energy transfer greatly exceeds the binding energy of the target electron. Adopting the impulse approximation, the initial and final states in eq. (2.98) simplify to single-electron states, and furthermore the outgoing electron state can be represented by a plane wave. The matrix element thus becomes a Fourier transform of the bound target electron wavefunction [6, 7], and by considering an integral of continuum final states rather than the discrete sum in eq. (2.98), the DDCS becomes proportional to an integral of the bound electron momentum density known as the Compton profile. In the relativistic case, one also recovers a DDCS proportional to the Compton profile, after neglecting some additional terms which can be shown to be small [8]. The derivation is based in quantum electrodynamics, which is beyond the scope of this thesis and shall not be discussed presently.

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Chapter 3

Currently used theories and models for relevant interactions

3.1 Theoretical models for electron-impact ionization

Empirical and semi-empirical models for electron-impact ionization of atoms and molecules rely on simple theories and analytical expressions to accurately capture the behaviour in different limiting regimes (e.g. low/high incident or ejected electron energies, small/large momentum transfers, etc.) [1]. Generally speaking, hard collisions refer to scattering events with small impact parameters and large momentum transfers, which dominate at lower incident energies (and vice versa for soft collisions). The Mott theory, which offers an adequate description of hard collisions, represents the scattering of two free electrons and was generalized from the Rutherford cross section by taking into account the exchange of two indistinguishable particles [2]. Its accuracy has been extended via the binary-encounter theory, whereby the bound electrons are assigned a velocity or momentum distribution [3]. On the other hand, soft collisions are well described by the Bethe theory, which in its simplest form involves calculating matrix elements of the optical dipole operator between the incident particle and the target electron [4].

The binary-encounter-dipole (BED) model for electron-impact ionization is a semi-empirical attempt to combine theories for hard and soft collisions into a single expression without the need for free adjustable parameters [5]. In the BED model, the asymptotic forms of the differential and integrated cross sections are chosen to match the corresponding behaviours derived by

Bethe within the first Born approximation [5]. Thus, the cross section differential in the energy of the ejected electron is proportional to the optical oscillator strength (OOS) distribution of the active atomic (sub)shell in the asymptotic limit of large incident electron energies. The authors also proposed the more compact binary-encounter-Bethe (BEB) model, in which a simple analytical function is used instead of the exact numerical OOS. In a subsequent publication, relativistic kinematic variables were introduced in order to extend the BED and BEB models to the relativistic regime [6], resulting in the RBED and RBEB models. Their use has also been applied to molecules, with experimental OOS values from photoionization studies where available [7, 8].

The plane-wave Born approximation (PWBA) [9, 10] allows for semi-empirical or ab initio numerical calculations of electron-impact ionization cross sections. As shown in the previous chapter (section 2.6), the differential cross section is simply the product of a kinematic factor which depends only on the incident charged particle, and the generalized oscillator strength (GOS) characterizing the target's response under a given momentum transfer and energy transfer. The PWBA is accurate for incident energies typically much higher than the ionization threshold [11], since at energies near threshold the assumption of plane waves for the incident and scattered projectile wavefunctions breaks down as the latter are distorted by the nuclear field of the target. Numerous semi-empirical corrections and modifications to the PWBA have been introduced, and experimental measurements are incorporated where available [11], although they are scarce and contain large uncertainties. In particular, the Hippler model [12, 13] is based on the PWBA and resorts to the analytical GOSs from non-relativistic hydrogenic wavefunctions. Hippler made use of the Ochkur approximation to account for exchange, and further shows that by including a simple Coulomb correction for the acceleration of the incident electron in the nuclear field, excellent agreement was found with experiments, even at lower near-threshold energies [12].

At the other end of the spectrum, the most sophisticated *ab initio* calculations are based on the distorted-wave Born approximation (DWBA) [14–16]. As the name implies, the incident and scattered wavefunctions are distorted by the nuclear field, which is achieved by adding a central potential $V_p(r)$ depending only on the projectile coordinates to the unperturbed Hamiltonian for the projectile (and subtracting the same term from the interaction Hamiltonian) [16]. It is assumed that with a judicious choice of $V_p(r)$, the remaining interaction Hamiltonian can be made small enough for first-order perturbation theory to be valid. Numerical DWBA calculations for neutral atoms suffer from very slow convergence of the partial-wave series as the projectile energy is increased to about ten times the ionization energy [16], thus at higher energies the DWBA results are smoothly matched to the PWBA.

The calculations of integrated cross sections by Bote and Salvat [16] have been tabulated by NIST [17] and are generally considered to be the gold standard for electron-impact ionization of neutral atoms. However, although the calculation is fully relativistic, only the longitudinal term is evaluated using distorted waves for the initial and final wave functions of the projectile and target electrons, while the transverse term is described with plane waves in order to simplify the numerical procedure (the authors work within the Coulomb gauge where the electromagnetic interaction is divided into longitudinal and transverse components). Very recently, Santos et al. [18] presented experimental data as well as calculations using the subconfiguration average distorted-wave (SCADW) method, which has mainly been applied to study the ionization of ions [19] but has since been adapted to neutral atoms [20]. The SCADW formalism is based on first-order perturbation theory within the Lorentz gauge, and adopts distorted waves for all continuum electron states. They found discrepancies between the SCADW and the DWBA which grow with Z and become substantial for high Z elements (25% for Bi), and found much better agreement between the SCADW and experiments. Despite the recent interest and activity for these *ab initio* methods, due to the intense numerical resources required for these calculations, differential cross sections necessary for Monte Carlo simulations have not yet been systematically tabulated and made available for implementation.

The far greater simplicity and ease of implementation of semi-empirical models, as compared to numerical calculations like the DWBA and SCADW, has spurred interest in their applications. The availability of both differential and integrated cross sections is another major advantage. In particular, the validity of the RBEB has been studied through comparisons with other theories and recent experiments. Santos *et al* [21] found reasonable agreement with existing experimental and theoretical results for the RBEB TCSs for K-shell ionization of low and intermediate atomic numbers. Guerra *et al* [22, 23] proposed several minor modifications to improve the RBEB model, especially for weakly-bound shells. For a few high-Z elements, the RBEB cross sections are less consistent with measurements than the Hippler model [24].

In chapter 4, we study the potential improvement of using an exact numerical OOS in the RBED expressions as opposed to the simpler RBEB model. The OOSs were calculated numerically from self-consistent Dirac–Hartree–Fock–Slater (DHFS) potentials, within the framework described in [16]. We compare our results to the DWBA calculation by Bote and

Salvat [16], which has been shown to be in overall excellent agreement with experiments through a systematic comparison with measured inner-shell ionization cross sections [25].

3.2 Compton scattering

The Klein–Nishina (KN) DCS assumes the photon is scattered by a free electron at rest [26, 27] and has historically played a central role in calculations of atomic Compton scattering cross sections. To account for binding effects, a simple and widely-used approximation called the Waller–Hartree (WH) model [28] consists of multiplying the KN DCS by the incoherent scattering function [29, 30] for a whole atom. Seltzer calculated and tabulated mass energy-absorption coefficients for elements and compounds using the WH model for the Compton interaction, which to this day is still considered an important source of photon interaction data [31]. Other well-known photon interaction data sets, including the XCOM [32] and EPDL'97 [33, 34] compilations, also make use of the WH theory to describe Compton scattering.

However, the WH approximation neglects the spread in energy of photons scattered at any given angle by the moving target electrons [35, 36], also known as Doppler broadening. This effect implies that the fundamental quantity is the DDCS differential in both outgoing photon energy and angle, which displays a broadened peak centered at the outgoing photon energy given by the usual Compton relation (eq. (5.2) below). For low-Z materials of dosimetric interest, Doppler broadening can be responsible for corrections in mass energy-absorption coefficients of up to a few percent [37]. The relativistic impulse approximation (RIA) is the simplest approach which is able to incorporate both binding effects and Doppler broadening [38, 39], and which yields a DDCS. The derivation of the RIA DDCS follows closely that of the KN cross section in assuming a free target electron, except with the same momentum distribution as that of a bound electron (instead of zero momentum) [38]. The insertion of a predetermined electron momentum distribution, rather than incorporating the full target potential while solving the scattering problem, is an impulse-type approximation. After further approximations whereby a few small terms are shown to be negligible, the RIA DDCS can be expressed as a relatively simple expression which is analytical except for an integral of the electron momentum distribution known as the Compton profile (CP).

The *S*-matrix formalism [40–42] refers to a full QED calculation of the scattering process in the presence of the external electromagnetic field of the atom (without making any impulse-type approximations), and is currently the most accurate and sophisticated theory for describing

Compton scattering. It evidently accounts for the broadening of the main peak in the DDCS, but also predicts infrared divergences in the limit of low scattered photon energies due to the presence of experimentally undetectable low-energy photons [27]. In order to cancel out these divergences, the process with one fewer photon in the final state, in this case the photoelectric effect, needs to be included in the CS as well [43, 44]. Furthermore, *S*-matrix theory predicts a small shift of the DDCS peak known as the Compton defect, as well as resonances when scattered photon energies coincide with atomic fluorescence lines [40, 41]. These complications, in addition to the considerable numerical complexity of the calculations, have held back efforts to implement and tabulate *S*-matrix results for a wide range of elements and materials of interest and covering the entire energy ranges for various applications.

Comparisons of RIA and S-matrix DDCSs have shown excellent agreement in the main Compton peak region, especially when the incident energy and the energy transfer are large compared to the binding energy [40]. Although the RIA does not predict infrared divergences or resonances, these features are not expected to be important given the low-Z materials and energy interval considered in this work. Because of its simplicity and reasonably good agreement with both experiments and the S-matrix theory, the latest updated Compton scattering cross sections in the MC codes PENELOPE [45] and EGSNRC [46] are based on the RIA. Photon interaction coefficients for molecules and compounds of biological interest have been modeled either by a simple sum of atomic contributions or by building molecular orbitals from atomic shells according to weights calculated from a linear combination of atomic orbitals (LCAO) approach [47, 48]. In both cases the CPs used are atomic and are typically taken from the classic tabulation by Biggs, Mendelsohn and Mann [49], which had been calculated numerically using Hartree–Fock wavefunctions for all atomic (sub)shells.

More recently, an algorithm for inelastic scattering based on the RIA was used in MC evaluations of the relative contributions of scattered to primary radiation in mammography [50]. The RIA has also been applied to calculations of background x-ray and gamma-ray Compton processes in the context of direct detection of dark matter particles [51, 52]. The authors studied the exact numerical RIA without the approximations which allow the DDCS to be written as a product of the Compton profile and a simple analytical expression, and found that while both versions of the RIA yield similar and accurate results in the Compton peak, neither can accurately reproduce *S*-matrix results far from the Compton peak.

In chapter 5 we present RIA calculations of Compton scattering cross sections with molecular CPs calculated by assuming Gaussian-type orbitals within an unrestricted Hartree–Fock formalism, in order to investigate the effect of using more accurate CPs. Ultimately we wish to determine the overall uncertainty in photon mass energy-absorption coefficients from choosing different theoretical models and their inputs, for various low-Z materials of biological interest and in the energy range of 1 keV to 1 MeV. In the most recent update on recommendations of key data for dosimetry (fundamental interaction cross sections, stopping powers, etc.), the ICRU Report 90 [48], $\mu^{\rm C}/\rho$ has been tabulated for the models studied in this work for water, air and graphite, using atomic CPs for the RIA data. However, systematic comparisons of $\mu_{\rm tr}^{\rm C}/\rho$ and $\mu_{\rm en}/\rho$ have not been carried out, and a definitive recommendation has not been made. Following the example of Andreo *et al.* [53], who attempted to establish an envelope of uncertainty for mass energy-absorption coefficients while considering different photoelectric cross section models, we wish to quantify the uncertainty from Compton scattering theories.

3.3 Elastic scattering of electrons by molecules

Elastic scattering of electrons by molecules are typically calculated by either a simple sum of atomic cross sections, or a coherent sum of atomic scattering amplitudes taking into account the relative atomic positions[54]. Ignoring spin, the (non-relativistic) coherent sum, which is also known as the independent atom model (IAM), is given by

$$\frac{d\sigma}{d\Omega} = |F(\theta)|^2 = \left|\sum_{i} \exp(i\mathbf{q} \cdot \mathbf{r}_i) f_i(\theta)\right|^2 = \sum_{i,j} \exp(i\mathbf{q} \cdot \mathbf{r}_{ij}) f_i(\theta) f_j^*(\theta), \quad (3.1)$$

where $f_i(\theta)$ are the atomic scattering amplitudes, and \mathbf{r}_i the atomic positions, with $\mathbf{r}_{ij} = \mathbf{r}_i - \mathbf{r}_j$. Typically, molecules in experiments are randomly oriented, so we can perform a spherical average to obtain

$$\frac{d\sigma}{d\Omega} = \sum_{i,j} \frac{\sin(qr_{ij})}{qr_{ij}} f_i(\theta) f_j^*(\theta).$$
(3.2)

The IAM has been shown to be in good agreement with experiments above energies of hundreds of eV [54]. However, given the recent interest and activity in the field of Monte Carlo microdosimetric calculations of DNA damage from ionizing radiation, there is a need for more accurate models valid at lower energies, especially applied to DNA molecules or surrogates.

A more sophisticated model was introduced within the optical-potential formalism, whereby the elastic interaction is divided into a short-range potential describing multiple scattering of the electron by individual atoms, and a long-range potential which can account for non-spherical effects such as polarization [55]. This multi-center process was described within the Born approximation, with higher-order terms representing successive scattering events off of different atoms within the molecule, and does not make use of empirical correction factors. Once again, an orientational average is necessary for comparison with experiments. The long-range potential is expected to be a small correction to the spherically-averaged short-range potential, and is mostly significant for polar molecules [55, 56]. This model has been used in many studies and compared to experimental data [57, 58, 56, 59, 60], although we have found that it yields negative differential cross sections over certain angle ranges at energies of about 100 eV and less. We elaborate on this issue in chapter 6, and re-derive the expressions to correct potential mistakes made in the original derivation, and ensure positive cross sections.

An alternative semi-empirical model has been proposed by Blanco and García [61, 62], who formulate the electron-molecule elastic scattering potential in terms of atoms screening each other, thus reducing the cross section. The screening effect is simply calculated as a geometric overlap of atomic cross sections, with the atoms at specified positions within the molecule. The authors describe a simple mathematical model to recursively account for the screening of each additional atom [61]. This model was initially introduced for integrated elastic cross sections, while a very approximate procedure for calculating DCSs was later proposed [62].

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Chapter 4

RBED cross sections for the ionization of atomic inner shells by electron impact

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4.1 Abstract

The RBED (relativistic binary-encounter-dipole) model for electron-impact ionization of atoms combines classical binary-encounter theory and the asymptotic dipole interaction, which is based on the plane-wave Born approximation (PWBA), with the only non-trivial ingredient being the optical oscillator strength (OOS). Due to the difficulty of obtaining accurate OOSs, the performance of the RBED model has so far not been fully assessed. In the present work we compare RBED inner-shell ionization cross sections (total and differential) of neutral atoms evaluated using three types of OOSs, namely an empirical power-law OOS, analytical hydrogenic OOSs and *ab initio* OOSs calculated numerically from self-consistent atomic potentials. We find that, compared to the distorted-wave Born approximation (DWBA), the RBED with either hydrogenic or numerical OOSs generally yields more accurate total cross sections (TCSs) than the RBED with the power-law OOS, especially for the most tightly-bound shells. In the highly-relativistic limit the RBED model does not recover the Bethe asymptotic behaviour because of its different energy-dependent prefactor, hence we investigate an alternative prefactor which restores the correct Bethe asymptote. Finally, we suggest

multiplying the RBED differential cross sections (DCSs) by the ratio of DWBA to RBED TCSs and verify that this renormalization improves the agreement with the DWBA DCSs.

4.2 Introduction

Electron-impact ionization cross sections contribute to our understanding of fundamental atomic and molecular physics and are essential for modelling radiation effects in all states of matter. There is a need for accurate, comprehensive cross section databases (both total and differential) which cover a wide energy range. Such data sets could be incorporated in Monte Carlo simulation codes and find a vast number of applications in materials science, medical physics and many other fields.

Cross sections for the *direct* ionization of atoms by charged particles¹ can be calculated either with numerical ab initio methods or semi-empirical models. In recent decades, the increase in available computing resources has enabled sophisticated *ab initio* calculations using more accurate atomic and molecular electron wave functions. The plane-wave Born approximation (PWBA) [2, 3] is a convenient starting point for many applications in radiation physics. In this formalism, the doubly differential cross section naturally factorizes into a kinematic factor which depends only on the incident charged particle, and a second factor known as the generalized oscillator strength (GOS) which describes how the target responds to a given momentum and energy transfer. The PWBA is accurate for incident energies typically much higher than the ionization threshold. In turn, the distorted-wave Born approximation (DWBA) [4-7] accounts consistently for exchange effects as well as the distortion of the projectile wave functions by the field of the target atom, thus being a state-of-the-art improvement upon the PWBA. On the very low energy end, R-matrix theory and convergent close coupling methods involve very large basis sets, complicated coupled equations, and integration out to large radial distances[8]. Despite their accuracy, these elaborate numerical calculations can be extremely slow to converge and they are impractical for large-scale implementation in Monte Carlo codes. Moreover, currently DWBA results have only been tabulated for total (integrated) cross sections, whereas differential cross sections are also needed for electron-track Monte Carlo simulations.

¹Besides direct ionization, which is a one-step process, two-step (i.e. indirect) channels such as excitationautoionization and resonant excitation double autoionization also increase the charge state of the target atom or ion by one. All of the aforementioned ionization pathways contribute in an additive way to the impact ionization cross section, see e.g. [1]. The indirect processes play a major role for highly-charged ions but are of lesser importance in the case of neutral atoms, and they are beyond the scope of the present article.

The appeal of semi-empirical models lies in their computational simplicity and ease of implementation for calculating cross sections which have not yet been tabulated using *ab initio* methods. For instance, the Hippler model [9–11] is based on the PWBA formalism with hydrogenic generalized oscillator strengths (GOSs) and includes Coulomb, relativistic, and exchange corrections, as well as the transverse interaction mediated by virtual photons. Another approach is the binary-encounter-dipole (BED) model proposed by Kim and Rudd [12], which attempts to combine binary-encounter cross sections with Bethe's asymptotic PWBA-based dipole interaction. Binary-encounter descriptions of electron-atom collision are based on classical billiard-ball-type collisions, with modifications to account for electron exchange (e.g. Møller) and the linear momentum distribution of bound atomic electrons. Thus, they are well-suited to describe slow collisions with high momentum transfer.

The BED model combines binary-encounter theory with Bethe's dipole interaction by finding an appropriate mixing ratio without introducing adjustable or empirical parameters. It yields singly differential (in energy) cross sections and requires as input only the binding energy, average kinetic energy, and optical oscillator strength (OOS) of the active atomic (sub)shell. Since the OOS is not always known or easily obtainable, Kim and Rudd also developed a simplified version of the BED known as the binary-encounter-Bethe (BEB) model, in which a simple analytical function is used instead of the exact numerical OOS. BED and BEB have subsequently been extended to the relativistic regime by Kim *et al* [13], yielding the RBED and RBEB counterparts.

Due to their simplicity, BEB and RBEB total cross sections (TCSs) have been employed almost exclusively in subsequent studies. Santos *et al* [14] showed that the RBEB TCSs for K-shell ionization are in reasonable agreement with experiments and other theories for low and intermediate atomic numbers ($Z \leq 50$). However, for Au and Bi close to threshold the RBEB is less consistent with measurements than the Hippler model [15]. Guerra *et al* [16, 17] proposed several minor modifications to improve the RBEB model, especially for weakly-bound shells.

Here we focus instead on the RBED formalism applied to inner shells of neutral atoms. To this end, we calculate the required OOSs numerically within the framework described in [6], adopting self-consistent Dirac–Hartree–Fock–Slater (DHFS) potentials. In principle we ought to compare our results directly to experimental data. However, measured cross sections are affected by large uncertainties and the existing data are often discrepant. Recently, Llovet and co-workers [18] found an overall excellent agreement in a thorough comparison of measured inner-shell ionization cross sections to the predictions of the DWBA_{L+T} calculation by Bote

and Salvat [6], where the subindex L+T indicates that both the longitudinal and transverse interactions were included in the calculation (albeit the transverse part was calculated within the PWBA). We therefore deem more pragmatic for the present purposes to benchmark the computed RBED TCSs directly against the DWBA_{L+T}, considering a selection of atoms spanning the periodic table. The DWBA_{L+T} TCSs were taken from the database published by the National Institute of Standards and Technology (NIST) [19]. We highlight the limitations of the RBED TCSs in the asymptotic relativistic region, discussing the possibility of improving its performance in this limit. Meanwhile, the DWBA differential cross sections (DCSs) were calculated with the code developed by Segui *et al* [4], which neglects the transverse interaction and which we will denote by DWBA_L, and finally we propose a renormalization of the RBED DCSs such that the corresponding TCSs match the DWBA_{L+T} TCSs.

4.3 Theory

In this section we give an overview of the RBED model and of the different OOSs which have been explored in this work. We follow for the most part the notation of Kim, Santos and Parente [13].

4.3.1 The RBED model

The starting point for the original (non-relativistic) BED model is the following DCS, written as a sum of three contributions [12]

$$\frac{\mathrm{d}\sigma}{\mathrm{d}w} \propto \sum_{n=1}^{3} F_n(t) \left[\frac{1}{(w+1)^n} + \frac{1}{(t-w)^n} \right],\tag{4.1}$$

where t = T/B and w = W/B are dimensionless quantities representing, respectively, the kinetic energies of the incident and ionized electron normalized by the binding energy *B*. This expression was motivated by the functional form of the Mott and binary-encounter DCSs. The n = 2 term refers to close collisions, the n = 1 term describes interference between the primary and secondary electrons, and the n = 3 term accounts for the target electron having an intrinsic velocity distribution (as opposed to being at rest). All three terms are symmetric under exchange of the outgoing projectile and ionized electrons because they are indistinguishable. The $F_n(t)$ functions also depend on the average kinetic energy U of the active atomic (sub)shell

and are to be determined so as to combine binary-encounter theory with Bethe's asymptotic dipole interaction while preserving the correct high-energy limit for both the total and stopping cross sections. In order to enforce the correct behaviour in the limit of $t \rightarrow \infty$, the n = 3 term was made to represent the asymptotic Bethe equation for ionization by fast incident charged particles [12]. However, the $(t - w)^{-3}$ term had to be omitted because it was not clear how to write down a symmetric form of the Bethe equation. To generalize to the relativistic form of the BED, Kim *et al* [13] considered the Møller instead of the Mott DCS, used the relativistic form of the RBED DCS

$$\left(\frac{\mathrm{d}\sigma}{\mathrm{d}w}\right)_{\mathrm{RBED}} = \frac{4\pi a_0^2 \alpha^4 N}{(\beta_t^2 + \beta_u^2 + \beta_b^2) 2b'} \left\{ \frac{(N_i/N) - 2}{t+1} \left(\frac{1}{w+1} + \frac{1}{t-w} \right) \frac{1+2t'}{(1+t'/2)^2} \right. \\ \left. + \left(2 - \frac{N_i}{N} \right) \left[\frac{1}{(w+1)^2} + \frac{1}{(t-w)^2} + \frac{b'^2}{(1+t'/2)^2} \right] \right. \\ \left. + \frac{1}{N(w+1)} \frac{\mathrm{d}f}{\mathrm{d}w} \left[\ln \frac{\beta_t^2}{1-\beta_t^2} - \beta_t^2 - \ln(2b') \right] \right\},$$
(4.2)

where a_0 is the Bohr radius, α is the fine-structure constant, N is the occupation number of the considered (sub)shell, and the relativistic parameters have the usual definitions

$$\beta_t^2 = 1 - \frac{1}{(1+t')^2}, \qquad t' = T/m_{\rm e}c^2,$$
(4.3)

$$\beta_b^2 = 1 - \frac{1}{(1+b')^2}, \qquad b' = B/m_e c^2,$$
(4.4)

$$\beta_u^2 = 1 - \frac{1}{(1+u')^2}, \qquad u' = U/m_e c^2.$$
 (4.5)

The OOS distribution of the (sub)shell, df/dw, quantifies the probability of excitation to states in the continuum. Its integral,

$$N_i = \int_0^\infty \frac{\mathrm{d}f}{\mathrm{d}w} \,\mathrm{d}w,\tag{4.6}$$

may be regarded as an "effective" number of electrons. In a real atom, inner-shell electrons cannot excite to occupied orbitals with higher energy owing to the Pauli exclusion principle,

thus resulting in $N_i < N$. Similarly, outer-shell electrons cannot de-excite to lower orbitals and in general will have $N_i > N$. This transfer of oscillator strength from inner to outer shells is consistent with the fact that the Thomas–Reiche–Kuhn sum rule applies to the OOS of the whole atom but not to the OOS of individual (sub)shells.

The TCS for ionization is obtained by integrating the DCS, equation (4.2), over *w* from 0 to $w_{\text{max}} = (t-1)/2$, which yields

$$\sigma_{\text{RBED}} = \frac{4\pi a_0^2 \alpha^4 N}{(\beta_t^2 + \beta_u^2 + \beta_b^2) 2b'} \left\{ D(t) \left[\ln \frac{\beta_t^2}{1 - \beta_t^2} - \beta_t^2 - \ln(2b') \right] + \left(2 - \frac{N_i}{N} \right) \left[1 - \frac{1}{t} - \frac{\ln t}{t + 1} \frac{1 + 2t'}{(1 + t'/2)^2} + \frac{b'^2}{(1 + t'/2)^2} \frac{t - 1}{2} \right] \right\}, \quad (4.7)$$

where

$$D(t) = \frac{1}{N} \int_0^{(t-1)/2} \frac{1}{w+1} \frac{\mathrm{d}f}{\mathrm{d}w} \,\mathrm{d}w.$$
(4.8)

The asymptotic limit of D(t) is closely related to the dipole matrix constant M^2 through (following equation (53) of [18])

$$M^2 = \frac{1}{B} \int_0^\infty \frac{1}{w+1} \frac{\mathrm{d}f}{\mathrm{d}w} \,\mathrm{d}w \equiv \frac{N}{B} D(\infty). \tag{4.9}$$

4.3.2 Simple analytical OOS: the RBEB model

In the simplified RBEB model, the OOS is approximated by

$$\left(\frac{\mathrm{d}f}{\mathrm{d}w}\right)_{\mathrm{RBEB}} = \frac{N_i}{(w+1)^2}.\tag{4.10}$$

Without any information about the OOS and its integrals, N_i is usually set equal to N, which results in $D(\infty) = 1/2$ and the RBEB DCS

$$\left(\frac{\mathrm{d}\sigma}{\mathrm{d}w}\right)_{\mathrm{RBEB}} = \frac{4\pi a_0^2 \alpha^4 N}{(\beta_t^2 + \beta_u^2 + \beta_b^2) 2b'} \left\{ -\frac{1}{t+1} \left(\frac{1}{w+1} + \frac{1}{t-w}\right) \frac{1+2t'}{(1+t'/2)^2} + \frac{1}{(w+1)^2} + \frac{1}{(t-w)^2} + \frac{b'^2}{(1+t'/2)^2} + \left[\ln\frac{\beta_t^2}{1-\beta_t^2} - \beta_t^2 - \ln(2b')\right] \left[\frac{1}{(w+1)^3} + \frac{1}{(t-w)^3}\right] \right\}.$$
(4.11)

We note that the simple form of the OOS did enable the $(t - w)^{-3}$ term to be restored. The ensuing RBEB TCS is

$$\sigma_{\text{RBEB}} = \frac{4\pi a_0^2 \alpha^4 N}{(\beta_t^2 + \beta_u^2 + \beta_b^2) 2b'} \left\{ \frac{1}{2} \left[\ln \frac{\beta_t^2}{1 - \beta_t^2} - \beta_t^2 - \ln(2b') \right] \left(1 - \frac{1}{t^2} \right) + 1 - \frac{1}{t} - \frac{\ln t}{t + 1} \frac{1 + 2t'}{(1 + t'/2)^2} + \frac{b'^2}{(1 + t'/2)^2} \frac{t - 1}{2} \right\}.$$
(4.12)

Unlike equation (4.7), which involves a numerical integration, equation (4.12) is fully analytical. The simplicity of the RBEB model has lead to its wider implementation and much greater popularity over the RBED model.

4.3.3 Hydrogenic OOS

We start from the analytical expressions for the non-relativistic GOS of the H atom (Coulomb potential) as summarized in the appendix of [20]. Since the OOS is the optical limit of the GOS, i.e. the GOS evaluated at zero momentum transfer, we simply set Q = 0 in the GOS expressions. Electrons in the inner (sub)shells of many-electron atoms are subject to a potential that is approximately Coulombic with an "effective charge" $Z_{n\ell}$ typically estimated with the help of Slater's rules [21]. It is customary to introduce the reduced energy transfer

$$\mathscr{W} = \frac{B(1+w)}{Z_{n\ell}^2 R},\tag{4.13}$$

where *R* is the Rydberg energy. The non-relativistic hydrogenic OOS for a (sub)shell with quantum numbers (n, ℓ) is then given by [20]

$$\frac{\mathrm{d}f_{n\ell}(\mathscr{W})}{\mathrm{d}\mathscr{W}} = A_n(\mathscr{W})B_n(\mathscr{W})C_{n\ell}(\mathscr{W}). \tag{4.14}$$

The factor $A_n(\mathcal{W})$ takes on different functional forms depending on whether \mathcal{W} is larger or smaller than the binding energy of the (n, ℓ) (sub)shell in a hydrogenic atom with atomic number $Z_{n\ell}$, $B_n(\mathcal{W})$ reduces to a simple power of \mathcal{W} , and $C_{n\ell}(\mathcal{W})$ are polynomials in \mathcal{W} whose coefficients have been tabulated e.g. in [22] (a few typos were pointed out and corrected in [20]).

4.3.4 Numerical OOS

We calculate *ab initio* OOSs in the relativistic PWBA using DHFS potentials. The OOS of a closed atomic (sub)shell with principal quantum number *n* and relativistic angular momentum κ is given by [6]

$$\frac{\mathrm{d}f_{n\kappa}}{\mathrm{d}w} = \frac{2m_{\mathrm{e}}}{3\hbar^2} B^2 (1+w) A_w^2 \sum_{\kappa'} \left\langle \ell \frac{1}{2} j \left\| \mathbf{C}^{(1)} \right\| \ell' \frac{1}{2} j' \right\rangle^2 D_{W\kappa',n\kappa}^2, \tag{4.15}$$

where $\langle \dots \| \mathbf{C}^{(1)} \| \dots \rangle$ is the reduced matrix element of the Racah tensor of order 1 in the coupled representation. The radial integral is defined as

$$D_{W\kappa',n\kappa} \equiv \int_0^\infty \left[P_{W\kappa'}(r) P_{n\kappa}(r) + Q_{W\kappa'}(r) Q_{n\kappa}(r) \right] r \,\mathrm{d}r, \tag{4.16}$$

being P(r) and Q(r) the large and small reduced radial wave functions. These were computed numerically employing the RADIAL subroutine package [23]. Notice that RADIAL delivers $P_{W\kappa'}(r)$ normalized to unit amplitude at large r. Hence, to get the free states normalized on the energy scale we introduce the factor A_w . In the sum, the only allowed values for the relativistic angular-momentum quantum number κ' are $\kappa - 1$, $\kappa + 1$ and $-\kappa$.

The self-consistent DHFS method is a convenient starting point for many applications in radiation physics because it produces rather realistic electron densities and eigenvalues which are close to the experimental binding energies B_{exp} [24, 25]. To correct for the small difference (typically less than a few tens of eV) between DHFS and experimental values, we shift the numerical OOS distributions by an amount $B_{DHFS} - B_{exp}$ such that the RBED plots in the results

section below assume the experimental binding energies. This procedure was adopted e.g. in [6, 26]. Theoretical binding energies can only match the experimental values at the few eV level if nuclear size, many-body effects (correlation, Auger shift) and radiative corrections are included in a rigorous way, see e.g. [27]. However, aside from a marginal (for our purposes) improvement in the theoretical binding energies, the more sophisticated atomic potentials would barely depart from the DHFS potentials at intermediate and large r, thus yielding essentially the same OOSs.

4.4 **Results and discussions**

We computed OOSs, DCSs and TCSs for the (sub)shells of noble gas atoms Ne, Ar, Kr, Xe and Rn, which span the periodic table. Additional calculations were carried out for Zn, Pd and Au. The electronic configuration of most of these atoms consists of only closed (sub)shells so that each atomic wave function can be modelled as a single Slater determinant, thus making the DHFS method especially accurate. Only inner shells having binding energies greater than 200 eV are considered in the present study.

The RBED prefactor departs from the usual factor $1/\beta_t^2$ in the PWBA, and is an *ad hoc* modification to account for Coulomb effects whereby the projectile electron gains kinetic energy at the moment of collision due to the attractive atomic potential. It is the only degree of freedom of the model. Santos *et al* [14] proposed the following average of the standard PWBA and the RBED prefactors,

$$\frac{1}{2} \left(\frac{1}{\beta_t^2} + \frac{1}{\beta_t^2 + \beta_u^2 + \beta_b^2} \right).$$
(4.17)

This expression fits the DWBA better than the RBED (also known as Burgess) prefactor for tightly-bound shells. Thus, unless specified otherwise, in all graphs below we display RBED and RBEB TCSs and DCSs computed with the averaged prefactor.

4.4.1 OOS and associated quantities

In figure 4.1 we depict the RBEB, hydrogenic and numerical OOSs for the $1s_{1/2}$, $2s_{1/2}$ and $2p_{3/2}$ (sub)shells of Ar and Kr. As expected, close to the ionization threshold the hydrogenic OOS is a good approximation when the potential is more Coulombic, as is the case for the tightly-bound $1s_{1/2}$ shells. For higher shells, the discrepancies near threshold between the three

OOSs can be as large as factors of order unity. Farther from the threshold, the hydrogenic OOS departs from the numerical OOS because it does not account for relativistic effects. This is more pronounced for shells with larger binding energies. Since the RBEB OOS has a very crude energy dependence, it diverges greatly from both the DHFS and hydrogenic OOSs the farther we go away from threshold.

Due to the simple logarithmic shape of the asymptotic Bethe equation (see section 4.4.2 below) for the high-energy ionization TCS (both non-relativistic and relativistic), so-called Fano plots can be made which display a linear region in the relativistic asymptote [28]. The slope of this linear region is given by the dimensionless parameter²

$$b_i = BM^2/N = D(\infty), \tag{4.18}$$

see equation (4.9). In the RBEB approximation to the OOS we have $b_{i,RBEB} = \frac{1}{2}$ for all (sub)shells regardless of Z. The b_K values resulting from the hydrogenic and numerical OOSs are summarized in table 4.1. These OOSs yield the same decreasing trend of b_K with increasing Z as reported by Powell *et al* [28]. In particular, the DHFS values are very close to the experimentally fitted results tabulated in [28].

Table 4.1 Parameter $b_{\rm K}$ calculated from hydrogenic and numerical OOSs, and fitted to experimental data by means of Fano plots [28].

Z		b_{K}	
	hydrogenic	DHFS	exp. [28]
10	0.561	0.516	0.524
18	0.470	0.445	0.449
30	0.415	0.398	0.400
46	0.371	0.355	0.357
79	0.304	0.287	0.288

In table 4.2, we list N_i/N ratios calculated with hydrogenic and numerical OOSs, for the $1s_{1/2}$, $2s_{1/2}$, $2p_{1/2}$ and $2p_{3/2}$ (sub)shells. For a given orbital angular momentum ℓ , the two subshells with total angular momentum $j = \ell \pm \frac{1}{2}$ have quite similar OOSs as long as Z is not

²In reality, the Fano plot further shows another linear region near threshold with a different b_i [28], but it is not relevant to the results and discussions in this work.



Figure 4.1 OOSs of the $1s_{1/2}$, $2s_{1/2}$ and $2p_{3/2}$ (sub)shells of Ar and Kr. The (blue) dot-dashed, (green) dotted and (red) dashed curves correspond to the RBEB, hydrogenic and numerical OOSs, respectively.

too large, once we account for the respective number of electrons in the subshells. Table 4.2 also includes the corresponding values of b_i . The hydrogenic OOS becomes less reliable for higher shells, thus we do not give data for $n \ge 3$.

4.4.2 Total ionization cross sections

Figures 4.2–4.7 show comparisons of RBED and RBEB to DWBA_{L+T} TCSs from the NIST database[19] for the K, L and M (sub)shells of some noble gas atoms. To give a quantitative measure of the accuracy of each TCS model, we have chosen three representative energies at which we calculated the percent difference between the RBED/RBEB models and the DWBA_{L+T}: at T = 3B near the low-energy maximum, T = 1 MeV near the local minimum, and T = 1 GeV in the ultra-relativistic region. For a given (sub)shell and energy, we calculated the magnitude of the percent difference for all the elements considered here (five noble gases plus Zn, Pd and Au) and are reporting the average as well as the range of the percent difference values in table 4.3. We observe that there is general improvement from using the RBED model with either OOS instead the RBEB, except in the low-energy peak region of the $2s_{1/2}$ subshell. The magnitude of the low-energy maximum depends strongly on the RBED prefactor, which is the only *ad hoc* element in the model, and which seems to lead to less consistent results for higher shells.

For the $1s_{1/2}$ shells of low- and intermediate-*Z* elements, both RBED models match almost perfectly with the DWBA_{L+T}, whereas for high *Z* neither RBED nor RBEB captures the proper behaviour at high energies. This discrepancy originates in the differences between the RBED and Bethe analytical forms in the relativistic asymptotic limit. Adopting the same notation as above, the relativistic Bethe equation for ionization in the high-energy limit is given by (see e.g. [28])

$$\sigma^{\text{Bethe}} = \frac{4\pi a_0^2 \alpha^4 N}{\beta_t^2 2b'} b_i \left[\ln \frac{1}{1 - \beta_t^2} - \beta_t^2 - \ln \frac{2b'}{c_i \beta_t^2} \right].$$
(4.19)

The first two terms in equation (4.19) are the transverse contribution to the asymptotic TCS whereas the third one is the longitudinal term. The Bethe parameter c_i is related to M^2 and a complicated integral of the GOS that can also be fitted experimentally as done in [28]. In contrast, the asymptotic limit of equation (4.7) is

$$\sigma_{\text{RBED}} \sim \frac{4\pi a_0^2 \alpha^4 N}{(\beta_t^2 + \beta_u^2 + \beta_b^2) 2b'} \left\{ b_i \left[\ln \frac{1}{1 - \beta_t^2} - \beta_t^2 - \ln \frac{2b'}{\beta_t^2} \right] + \left(2 - \frac{N_i}{N} \right) \right\}.$$
(4.20)

(Sub)shell	Ζ	N_i/N		b_i	
		hydrogenic	DHFS	hydrogenic	DHFS
$1s_{1/2}$	10	0.876	0.822	0.561	0.516
1	18	0.730	0.695	0.470	0.445
	30	0.643	0.612	0.415	0.398
	36	0.614	0.581	0.397	0.380
	46	0.573	0.536	0.371	0.355
	54	0.545	0.503	0.354	0.337
	79	0.467	0.419	0.304	0.287
	86	0.444	0.397	0.289	0.272
$2s_{1/2}$	18	0.845	0.680	0.464	0.321
,	30	0.773	0.678	0.427	0.348
	36	0.725	0.649	0.404	0.340
	46	0.656	0.603	0.368	0.323
	54	0.610	0.568	0.344	0.309
	79	0.503	0.487	0.288	0.271
_	86	0.472	0.460	0.271	0.257
2p _{1/2}	18	1.371	1.143	0.914	0.701
,	30	0.950	0.905	0.640	0.582
	36	0.811	0.807	0.548	0.526
	46	0.648	0.688	0.440	0.453
	54	0.556	0.626	0.379	0.415
	79	0.383	0.548	0.263	0.364
	86	0.342	0.535	0.235	0.355
2p _{3/2}	18	1.396	1.145	0.931	0.703
,	30	0.995	0.907	0.669	0.584
	36	0.865	0.804	0.583	0.526
	46	0.717	0.679	0.486	0.450
	54	0.637	0.610	0.433	0.408
	79	0.518	0.507	0.353	0.344
	86	0.492	0.483	0.336	0.330

Table 4.2 N_i/N and b_i as defined in equations (4.6) and (4.18), respectively, computed from hydrogenic and numerical DHFS OOSs.



Figure 4.2 TCSs for the $1s_{1/2}$ shells of Ne, Ar, Kr, Xe and Rn. The (blue) dot-dashed, (green) dotted and (red) dashed curves correspond to TCSs evaluated with the RBEB, hydrogenic and numerical OOSs, respectively. The (black) solid curves are the predictions of the DWBA_{L+T}.



Figure 4.3 Same as figure 4.2 but for the $2s_{1/2}$ subshells of Ar, Kr, Xe and Rn.



Figure 4.4 Same as figure 4.2 but for the $2p_{3/2}$ subshells of Ar, Kr, Xe and Rn.



Figure 4.5 Same as figure 4.2 but for the $3s_{1/2}$ subshells of Kr, Xe and Rn.



Figure 4.6 Same as figure 4.2 but for the $3p_{3/2}$ subshells of Kr, Xe and Rn.



Figure 4.7 Same as figure 4.2 but for the $3d_{5/2}$ subshells of Xe and Rn.

Table 4.3 Magnitude of the percent difference between the TCS of each model and the DWBA_{L+T} TCS, averaged over *Z* for each K and L (sub)shell and at T = 3B, 1 MeV and 1 GeV. In parenthesis is the range (min – max) of the percent difference values which were averaged.

(Sub)shell	TCS model	Percent difference (range)			
		T = 3B	T = 1 MeV	T = 1 GeV	
1s _{1/2}	RBED _{DHFS}	8.5 (1.0 - 14.9)	3.3 (0.2 - 5.4)	6.5 (0.9 - 16.9)	
	RBED _H	8.9 (1.9 – 16.2)	4.9 (0.2 – 10.0)	6.3 (0.2 – 14.0)	
	RBEB	13.6 (7.1 – 20.7)	5.8 (2.0 - 8.5)	16.3 (3.0 – 24.2)	
$2s_{1/2}$	RBED _{DHFS}	10.6 (8.4 - 13.0)	12.7 (10.0 – 15.0)	3.2 (0.9 - 4.4)	
,	RBED _H	7.1 (1.9 – 11.5)	22.4 (16.9 - 37.3)	17.3 (4.9 - 40.8)	
	RBEB	4.4 (0.7 - 8.3)	35.1 (31.3 - 41.0)	48.5 (37.7 - 62.1)	
2p _{3/2}	RBED _{DHFS}	21.4 (16.7 – 26.2)	1.7 (0.7 – 2.4)	1.4 (0.1 – 4.3)	
,	RBED _H	17.7 (3.2 – 25.9)	8.9 (1.3 – 26.2)	9.5 (1.5 – 29.6)	
	RBEB	27.2 (24.4 - 29.7)	9.0 (1.3 – 21.7)	16.9 (5.9 – 27.6)	

As we can see from the above equations, the RBED expression has the Burgess prefactor whereas the Bethe equation has the standard PWBA prefactor, which are quite different when $\beta_u \sim \beta_b \sim 1$. If we wish to correct for this deficiency at high energies for the $1s_{1/2}$ shell of high-Z atoms, we can restore the $1/\beta_t^2$ factor in the Bethe (or dipole) part of the RBED expression while keeping the Burgess prefactor in the binary-encounter part:

$$\sigma_{\text{RBED}}^{\text{Bethe}} = \frac{4\pi a_0^2 \alpha^4 N}{\beta_t^2 2b'} \left\{ D(t) \left[\ln \frac{1}{1 - \beta_t^2} - \beta_t^2 - \ln \frac{2b'}{\beta_t^2} \right] + \frac{\beta_t^2}{\beta_t^2 + \beta_u^2 + \beta_b^2} \left(2 - \frac{N_i}{N} \right) \right. \\ \left. \times \left[1 - \frac{1}{t} - \frac{\ln t}{t + 1} \frac{1 + 2t'}{(1 + t'/2)^2} + \frac{b'^2}{(1 + t'/2)^2} \frac{t - 1}{2} \right] \right\}.$$
(4.21)



Figure 4.8 TCS of the RBED model with DHFS OOSs for the $1s_{1/2}$ shell of Pd and Au, calculated using the (averaged) Burgess prefactor (red long dashed curves), and after restoring the PWBA prefactor to the Bethe/dipole part of the RBED model (green dashed curves), as in equation (4.21). The green dash-dotted curves represent the longitudinal and transverse parts of the RBED with restored PWBA prefactor. The Bethe asymptotic expression is shown by violet dots, and the DWBA_{L+T} TCSs are in black full curve.

As can be seen in figure 4.8, using equation (4.21) we now get almost perfect agreement with $DWBA_{L+T}$ and the Bethe expression at very high energies, although at intermediate energies

the agreement is worse. This highlights the limitations of a model which attempts to combine two disparate theories and which allows the tuning of empirical prefactors.

The remaining discrepancies between the RBED and $DWBA_{L+T}$ cross sections near the ionization threshold are caused by Coulomb and exchange effects, and the limitations of using semi-empirical scaling factors. As anticipated, these disagreements are greater for higher shells, which are less hydrogenic.

4.4.3 Differential ionization cross sections

In figures 4.9–4.11 we plot the DCSs $d\sigma/dw$ for the $1s_{1/2}$, $2s_{1/2}$ and $2p_{3/2}$ (sub)shells of selected atoms at three values of the projectile kinetic energy *T*, namely 1.5*B*, 3*B* and 10*B*. These energies were chosen because they are typically located below, near and above, respectively, the maximum or shoulder of the ionization TCS curves. The maximum secondary electron energy is $w_{\text{max}} = (t-1)/2$. The DWBA_L data were calculated using the code developed by Segui *et al* [4]. Since the DWBA formalism implemented in this code does not include the transverse interaction, it is expected to underestimate the cross sections whenever the contribution of the transverse term is significant (e.g. high energy and high *Z*); hence we restrict the highest kinetic energy to T = 10B. We note that to leading order there is a 1/w dependence, consistent with the Møller DCS for electron-electron inelastic scattering.

As expected, we find that the hydrogenic OOSs yield DCSs very close to the ones obtained with numerical OOSs for tightly-bound shells, and near threshold the hydrogenic DCS gets closer to the DHFS DCS as Z increases and the atomic potential becomes more Coulombic. For the $1s_{1/2}$ shell, both the hydrogenic and numerical OOSs yield RBED DCSs which are an improvement upon the RBEB in terms of agreement with the DWBA_L. As the incident energy T increases, the agreement with the DWBA_L improves significantly for all three OOS models.

Despite the large differences between RBED/RBEB and DWBA_L DCSs at low projectile energies, we see that the overall shapes of the curves are similar. Indeed, if one scales the RBED/RBEB DCSs so that their TCSs are equal to the DWBA_L TCSs, reasonable agreement is achieved, as shown in figure 4.12. Such a procedure could be implemented in Monte Carlo electron transport codes where DWBA TCSs are already incorporated, but DCS data are not yet available, and would ensure consistency between TCS and DCS data.

For the $2s_{1/2}$ and $2p_{3/2}$ subshells, we see similar trends as in the case of the $1s_{1/2}$ shell. However, here the improvement from using either RBED model over the RBEB model is much



Figure 4.9 DCSs at t = 1.5, 3 and 10 for the $1s_{1/2}$ shells of Ne and Kr. The (blue) dotdashed, (green) dotted and (red) dashed curves correspond to TCSs evaluated with the RBEB, hydrogenic and numerical OOSs, respectively. The (black) dots are the predictions of the DWBA_L. The units of the DCSs are kb because *w* is dimensionless.



Figure 4.10 Same as figure 4.9 but for the $2s_{1/2}$ subshells of Ar and Xe.



Figure 4.11 Same as figure 4.9 but for the $2p_{3/2}$ subshells of Ar and Kr.

less clear. Since electrons in these higher shells experience a less Coulombic potential, the hydrogenic OOS is no longer a very good approximation and thus the discrepancies between the hydrogenic and numerical DCSs are much larger. Interestingly, the $2s_{1/2}$ subshell displays an odd behaviour whereby the hydrogenic DCS near threshold is much closer to the RBEB DCS than the DHFS DCS, even though at higher energies the hydrogenic and DHFS DCSs become close once again.

4.5 Conclusions

The RBEB/RBED family of semi-empirical models is of particular interest to Monte Carlo electron transport codes due to their simplicity and ease of implementation, despite the existence of *ab initio* numerical calculations such as the DWBA, which is the current gold standard. We have considered three different OOS models and compared the RBED electron-impact ionization cross sections calculated using these OOSs to DWBA results. By far the simplest of the three is the RBEB model, in which the OOS is assumed to take on a simple functional form. The non-relativistic hydrogenic OOS is also fully analytical, and it can be applied to any atomic (sub)shell with an effective *Z* given by Slater's rules. Finally, the *ab initio* OOSs were calculated out for tightly-bound inner shells (K, L and M) with binding energies larger than 200 eV for a series of atoms spanning the periodic table. A comprehensive database (or parameterization) of numerical OOSs would greatly facilitate the calculation of TCSs and DCSs for electron-impact ionization of neutral atoms with the RBED formalism, and will be made available in the future.

We find that for most atomic (sub)shells the numerical and hydrogenic OOSs yield cross sections (both differential and total) which agree better with each other as well as with the DWBA. In the case of the most tightly bound (sub)shells of low- and intermediate-*Z* elements, the RBED TCSs of all three OOS models show good agreement with the DWBA in the near-threshold region, while in the relativistic asymptote the RBEB deviates substantially from all other curves. For more loosely-bound shells, the near-threshold TCS behaviour of all RBED models is less consistent, although the numerical OOS-based TCSs overlap almost perfectly with the DWBA_{L+T} TCSs in the relativistic limit.

In the ultra-relativistic regime of high-Z elements, the three RBED/RBEB models deviate greatly from the DWBA, which was initially surprising given that one would expect the RBED theory to reproduce Bethe's asymptotic formula in this region. In fact, the choice of the averaged



Figure 4.12 DCSs at t = 1.5 for various (sub)shells and atoms. Each DCS was renormalized so that the ensuing TCS matches the DWBA_L TCS at that energy.

RBED prefactor, which differs from the usual PWBA prefactor, results in a mismatch in the highenergy region of highly-relativistic shells. This deficiency may be corrected for at the cost of worse agreement in the intermediate-energy region, which highlights the lack of generalizability and flexibility of semi-empirical models which attempt to combine vastly different theories. Owing to these limitations, it would be of interest in the future to assess models that start from the doubly differential cross section (DDCS) in the PWBA, with corrections for Coulomb and exchange effects, where the physical basis behind modifications to the PWBA is more clearly understood [9–11]. Moreover, DDCSs are differential in both outgoing electron energy and angle of deflection, the latter of which is also relevant for Monte Carlo simulations but is not provided by the RBED formalism.

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Chapter 5

On the relativistic impulse approximation for the calculation of Compton scattering cross sections and photon interaction coefficients used in kV dosimetry

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5.1 Abstract

We calculate differential and integrated cross sections for the Compton interaction as well as mass attenuation (μ^C/ρ) , mass energy-transfer (μ_{tr}^C/ρ) , and mass energy-absorption (μ_{en}/ρ) coefficients, within the relativistic impulse approximation (RIA) using Compton profiles (CPs) obtained from unrestricted Hartree–Fock electron densities. We investigate the impact of using molecular as opposed to atomic CPs on dosimetric photon interaction coefficients for air, water and graphite, and compare our cross sections to the simpler Waller–Hartree (WH) and Klein–Nishina (KN) formalisms. We find that differences in μ^C/ρ and μ_{tr}^C/ρ resulting from the choice of CPs within the RIA are small relative to the differences between the RIA, WH,

and KN calculations. Surprisingly, although the WH binding corrections seem accurate when considering μ^{C}/ρ , there are significant discrepancies between the WH and RIA results when we look at μ_{tr}^{C}/ρ . The WH theory can differ substantially from the predictions of KN and the RIA in the tens of keV range (e.g., 6–10% at 20 keV), when Compton scattering becomes the dominant interaction mechanism. For lower energies, the disagreement further grows to about one order of magnitude at 1 keV. However, since the photoelectric effect transfers more energy than the Compton interaction in the tens of keV range and below, the differences in the total μ_{en}/ρ values resulting from the choice of Compton models (KN, WH, or RIA) are not larger than 0.4%, and the differences between WH and the other two theories are no longer prominent.

5.2 Introduction

Photon interaction data and electron stopping powers form the basis of most dosimetric standards and radiation interaction applications in medical physics, both for therapy and for imaging. In radiation dosimetry these data play a crucial role in the conversion of detector readings to absorbed dose either through cavity theory or via Monte Carlo (MC) radiation transport calculations [1, 2], and as such these data affect primary radiation standards. More clinically-oriented applications include backscatter factors and mass energy-absorption coefficient ratios used in kV dosimetry protocols for radiotherapy and radiobiology and in diagnostic radiology applications [3–5] as well as in x-ray fluorescence calculations and measurements [6]. Another area of application where the actual Compton angular distribution is critical is x-ray imaging of scattered photons for the characterization of biological samples in which Compton differential cross sections (DCSs) are needed for modelling the backscatter distribution [7]. Compton DCSs also play a key role in the determination of photon energy distributions produced by x-ray tubes from spectra acquired with a Compton spectrometer. The early developments of this technique were reviewed by Alm Carlsson and her co-workers [8]. A state-of the-art implementation has been described e.g. in [9].

For photons, mass attenuation coefficients and mass energy-absorption coefficients are most often based on the tabulations by [10], [11], and [12]. Other photon data include the commonly-used EPDL'97 [13, 14] and the older [15] data sets. A recent publication by Andreo and his co-workers aimed to establish an envelope of uncertainty for mass energy-absorption coefficients, but focused on the photoelectric cross sections [16]. Here we study the uncertainties introduced by using different theoretical formalisms and their inputs for the Compton interaction

in the low- to intermediate-energy range of 1 keV to 1 MeV. While $\mu^{\rm C}/\rho$ has been tabulated in ICRU Report 90 [17] for the same models, a systematic comparison for $\mu_{\rm tr}^{\rm C}/\rho$ has not been made, and the effect on the total $\mu_{\rm en}/\rho$ has not been reported.

The simplest approach for calculating incoherent scattering cross sections is the Klein– Nishina (KN) DCS, in which the photon is assumed to be scattered by a free electron at rest [18, 19]. As an improvement on KN, a well-known and frequently-used approximation is the Waller–Hartree (WH) theory [20] which accounts for binding effects approximately through the incoherent scattering function [21, 22], but which neglects the spread in energy of photons scattered at a given angle (Doppler broadening) [12, 23]. An important source of photon interaction data is from [11], who derived mass energy-absorption coefficients for elements and compounds using the WH model.

On the other hand, the most sophisticated method for calculating Compton scattering cross sections is the *S*-matrix formalism [24–26]. While the KN formula is derived within quantum electrodynamics (QED) assuming a free electron, the full *S*-matrix treatment consists of QED calculations in an external electromagnetic field (also called the Furry or bound-state interaction picture), which increases the complexity of the mathematical procedures. This theory represents the most accurate understanding of fundamental physics, although it is not suitable for tabulation of data for widespread implementation for all elements and covering the entire energy range of interest. In addition to the main Compton peak in the doubly differential cross section (DDCS), it predicts infrared divergences in the limit of low scattered photon energies due to the presence of any number of undetectable low-energy photons [19], and these divergences need to be cancelled out by considering the photoelectric DCS [27, 28]. *S*-matrix calculations also deal with resonances which occur when scattered photon energies correspond to atomic fluorescence lines, and poles appear in the amplitude of one of the diagrams [24, 25].

Owing to the difficulties described above, the relativistic impulse approximation (RIA) has been the model which has been implemented in the MC codes PENELOPE [29] and EGSNRC [30]. The RIA incorporates both binding effects and Doppler broadening and yields an expression for the DDCS differential in the outgoing photon angle and energy [31, 32]. Accounting for the Doppler broadening has been shown to lead to corrections in mass energy-absorption coefficients of up to a few percent for low-Z materials of dosimetric interest [33]. The key ingredient to the calculation of the RIA cross sections is the Compton profile (CP) of each atomic or molecular orbital, which is computed from the corresponding linear momentum distribution. Photon interaction coefficients for compounds used in dosimetry are modeled by adopting an independent-atom approach [34, 35], with the atomic CPs typically taken from the classical tabulation of [36].

Extensive comparisons of RIA with S-matrix theory have been discussed in [24], where excellent agreement was found in the main Compton peak region of the DDCS when the incident energy and the energy transfer are large compared to the binding energy. Comparisons of DCSs are difficult since the RIA does not account for infrared divergences or resonances, and the S-matrix results can vary depending on the low-energy cutoffs applied to the integration of the DDCSs [24]. However, given the low-Z materials and energy interval considered in this work, the additional features predicted by the S-matrix theory are not expected to play a significant role, and we are well within the range where there is good agreement between the RIA and the S-matrix theory.

In this article we investigated for three materials of dosimetric interest (air, water, and graphite) the impact of using more realistic CPs on the Compton cross sections and interaction coefficients derived within the RIA, in the low- and intermediate-energy interval of 1 keV to 1 MeV. By also looking at DCSs, we discuss the differences between the RIA and the WH approach to modelling binding effects, and highlight the limitations of the WH theory. Finally, we calculate the effect of using different Compton models on the total mass energy-absorption coefficient, including the photoelectric effect.

5.3 Background

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In this section we give an overview of the three theoretical frameworks for Compton scattering considered in the present work, namely KN, WH, and RIA. We then briefly describe the unrestricted Hartree–Fock formalism from which we calculated the electron densities in momentum space and the CPs, and finally we review the basic definitions of photon interaction coefficients. We note that all the DDCSs and DCSs we calculate are independent of the azimuthal scattering angle ϕ because we only consider unpolarized photon beams.

5.3.1 Klein–Nishina approximation

A consistent theory for Compton scattering, in which a photon is scattered inelastically by an electron, requires a quantized description of the radiation field. In classical electrodynamics and at non-relativistic energies, Thomson scattering predicts no change in the scattered photon's

wavelength and the collision is thus elastic. High-energy modifications to Thomson can describe light accelerating an electron to relativistic speeds, leading to a recoil of the electron and an associated Doppler shift of the scattered light, however this effect becomes arbitrarily small at low light intensities. Therefore, classical electrodynamics cannot explain general Compton phenomena, and quantization of the electromagnetic field is required.

In QED, the interaction between a photon and an electron is expressed as a perturbative series expansion, where each higher-order term is represented by a Feynman diagram having an additional vertex. Higher-order terms are called radiative corrections since they involve more virtual photons which mediate the interactions between vertices. After further assuming that the electron is free and at rest, the cross section calculated from the lowest-order term results in the well-known KN formula for the DCS per electron

$$\left(\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega}\right)_{\mathrm{KN}} = \frac{r_{\mathrm{e}}^2}{2} \left(\frac{E'}{E}\right)^2 \left(\frac{E'}{E} + \frac{E}{E'} - \sin^2\theta\right). \tag{5.1}$$

In the above, $r_e \equiv e^2/m_ec^2$ is the classical electron radius (*e* is the elementary charge, m_e is the electron rest mass, *c* is the speed of light in vacuum) whereas *E* and *E'* are, respectively, the initial and final photon energies, which are related to the polar scattering angle θ by the famous Compton relation

$$E' = E_{\rm C} \equiv \frac{E}{1 + \frac{E}{m_{\rm c}c^2}(1 - \cos\theta)}.$$
 (5.2)

When the incoming photon energy is much higher than the electron's kinetic and binding energies, the assumptions made in the KN model are approximately valid, and the KN DCS is expected to be realistic. The atomic DCS is obtained by simply multiplying the one-electron DCS of Eq. (5.1) with the atomic number Z.

5.3.2 Waller–Hartree approximation

The simplest model for Compton scattering off of bound atomic electrons is known as the Waller–Hartree (WH) approximation, in which binding effects are incorporated by multiplying the KN DCS with the incoherent scattering function S(q,Z) [21, 22], leading to the following

atomic DCS¹

$$\left(\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega}\right)_{\mathrm{WH}} = \left(\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega}\right)_{\mathrm{KN}} S(q,Z) \tag{5.3}$$

with

$$S(q,Z) = \sum_{\varepsilon > 0} \left| \left\langle \varepsilon \left| \sum_{j=1}^{Z} e^{i\mathbf{q} \cdot \mathbf{r}_j/\hbar} \right| 0 \right\rangle \right|^2,$$
(5.4)

where \mathbf{r}_j is the position of the *j*-th atomic electron, $\mathbf{q} = \mathbf{k} - \mathbf{k}'$ is the momentum transfer vector, being \mathbf{k} and \mathbf{k}' the initial and final photon linear momenta, and *q* is its magnitude

$$q = \frac{1}{c}\sqrt{E^2 + E'^2 - 2EE'\cos\theta}.$$
 (5.5)

 $|0\rangle$ denotes the ground state of the atom, and $|\varepsilon\rangle$ denotes an excited (bound) or ionized (free) state. Adding and subtracting the contribution of the ground state to the right-hand side of Eq. (5.4) and invoking the completeness of atomic states, the incoherent scattering function can be expressed in terms of only the ground-state wave function [21, 22]

$$S(q,Z) = \left\langle 0 \left| \sum_{i=1}^{Z} \sum_{j=1}^{Z} e^{i\mathbf{q} \cdot (\mathbf{r}_{i} - \mathbf{r}_{j})/\hbar} \right| 0 \right\rangle - \left\langle 0 \left| \sum_{j=1}^{Z} e^{i\mathbf{q} \cdot \mathbf{r}_{j}/\hbar} \right| 0 \right\rangle^{2}.$$
(5.6)

The second term is the square of the atomic form factor, which the reader may recognize from the atomic DCS for Rayleigh (i.e. elastic) scattering of photons.

The incoherent scattering function increases monotonically from zero at low momentum transfers to Z at high momentum transfers, at which point the WH and KN approximations are in agreement. [37] summarized the information prior to 1997 on the validity of the WH theory.

5.3.3 Relativistic impulse approximation

In general terms, the impulse approximation can be useful whenever a scattering problem involves a composite target consisting of many particles bound together. At its core, the impulse approximation relies on the assumption that the interaction time is short enough that the state of

$$\left(\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega}\right)_{\rm WH} = \left(\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega}\right)_{\rm T} S(q,Z).$$

¹Eq. (5.3) results from the *ad hoc* replacement of the Thomson DCS with the KN DCS in the DCS for incoherent scattering derived within non-relativistic quantum mechanics,
the target does not change, i.e. any dynamics caused by binding forces can be neglected, and the full target potential only serves to create a momentum distribution for the bound particles. An accompanying assumption is typically made, namely that the scattered projectile only interacts with one of the particles in the target, and that this interaction does not involve the rest of the spectator particles. More specifically, the assumptions of the impulse approximation break down when the energy transfer is not much larger than the binding energy, which is most important for low incident energies and at small scattering angles. One could define a critical scattering angle θ^* or a critical incident energy E^* below which the impulse approximation might be expected to fail [35], and indeed this was formulated by [38]. Nevertheless, these validity conditions are likely to be too restrictive and are not meant to be taken as hard cutoffs [38, 35].

An example of the improvement in accuracy of the RIA over the KN formula can be seen in Fig. 5.1, where the three theoretical DCSs are compared to experiments carried out at 59.54 keV for intermediate-*Z* elements [39–42]. The agreement between WH and the RIA is very close. However, as will be discussed below, WH performs poorly for DCSs differential in outgoing photon energy, which are relevant for quantifying energy transfer and deposition.

For Compton scattering, Ribberfors' derivation of the RIA starts from the same lowestorder Feynman diagram as the one which yielded KN, except that the electron momentum is not taken to be zero or a constant vector. Instead, the momentum distribution of the active electron is inserted into the DCS, and an integral is performed over the angular components of the momentum distribution while assuming the latter is isotropic [31]. The presence of a momentum distribution introduces Doppler broadening, such that for a given scattering angle the outgoing photon energy spectrum is no longer a delta function at the energy given by Eq. (5.2), but rather is a peak that has a finite width centered at that value. Consequently, the theory predicts a cross section doubly differential in both the scattered photon angle and energy, which are treated as independent variables.

Initially the RIA expression for the DDCS of the *i*-th atomic (sub)shell or molecular orbital was derived to be [31]

$$\frac{\mathrm{d}^2 \sigma_i}{\mathrm{d}E' \mathrm{d}\Omega} = N_i \pi r_\mathrm{e}^2 \frac{E'}{E} \frac{(m_\mathrm{e}c)^2}{q} \int_{p_\mathrm{min}}^{\infty} \frac{p \rho_i(p) \bar{X}_\mathrm{int}(p)}{E(p)} \mathrm{d}p, \qquad (5.7)$$

where N_i is the number of electrons in the atomic or molecular orbital, $\rho_i(p)$ is the radial electron density in momentum space, and E(p) is the usual relativistic energy of an electron



Figure 5.1 Whole-atom DCSs of ${}_{22}$ Ti, ${}_{29}$ Cu, and ${}_{42}$ Mo. The predictions of the KN, WH, and RIA formalisms are compared to four sets of experimental data: (1) [41] (purple diamonds); (2) [42] (black circles); (3) [39] (red squares); (4) [40] (grey triangles). The measurements were done using the 59.54 keV γ -rays emitted during the decay of 241 Am.

with momentum p

$$E(p) = \left[(m_{\rm e}c^2)^2 + (pc)^2 \right]^{1/2}.$$
(5.8)

The expression for the cross-section factor $\bar{X}_{int}(p)$ is fairly involved [31] and shall not be reproduced here. Ribberfors suggested as a simple but acceptable approximation to use $p_{min} = p_z$, where p_z is the projection of the electron's initial momentum **p** on the direction of the scattering vector $-\mathbf{q}$, i.e.

$$p_{z} = -\frac{\mathbf{p} \cdot \mathbf{q}}{q} = \frac{EE'(1 - \cos\theta) - m_{e}c^{2}(E - E')}{c^{2}q}.$$
(5.9)

An exact analytical expression for p_{min} was later explicitly given by [43], but we have employed Ribberfors' approximation because the resulting differences in the DDCSs were negligible.

In calculations of integrated cross sections (ICS) where the DDCS is integrated over E' and Ω , the additional momentum integral in Eq. (5.7) increases enormously the computing times. A simplification was further proposed by Ribberfors which enables the integration over p to be performed independently of the DDCS calculation. Eq. (5.7) was integrated by parts, and by far the largest term was found to be proportional to $J_i(p_z)\bar{X}_{int}(p_z)/E(p_z)$, where $J_i(p_z)$ is the CP (see following subsection). The simplification consists in dropping the small remaining terms in the integration by parts, which enables to factor out the initial electron momentum dependence from the kinematics of the scattering process. Then

$$\frac{d^2 \sigma_i}{dE' d\Omega} = N_i \frac{r_e^2}{2} \frac{E'}{E} \frac{(m_e c)^2}{q} \frac{\bar{X}(R, R')}{E(p_z)} J_i(p_z) \Theta(E - E' - U_i),$$
(5.10)

where U_i is the binding energy of the *i*-th atomic or molecular orbital, and the Heaviside step function $\Theta(E - E' - U_i)$ ensures that the DDCS drops to zero when the energy transfer E - E'is less than U_i . The now simplified cross-section factor $\bar{X}(R, R')$ is given by

$$\bar{X}(R,R') = \frac{R}{R'} + \frac{R'}{R} + 2\left(\frac{1}{R} - \frac{1}{R'}\right) + \left(\frac{1}{R} - \frac{1}{R'}\right)^2,$$
(5.11)

where

$$R = \frac{E}{m_{\rm e}c^2} \left\{ \left[1 + \left(\frac{p_z}{m_{\rm e}c}\right)^2 \right]^{1/2} + \frac{E - E'\cos\theta}{cq} \frac{p_z}{m_{\rm e}c} \right\}$$
(5.12)

and

$$R' = R - \frac{EE'}{(m_{\rm e}c^2)^2} (1 - \cos\theta).$$
(5.13)

We have calculated DDCSs using the full (Eq. (5.7)) and simplified (Eq. (5.10)) forms of the RIA for various θ and E which cover the entire range of interest. Unexpectedly, we found that the full RIA seems to display the so-called infrared divergences, whereby for small θ the DDCS diverges as $E' \rightarrow 0$. This effect is much more pronounced when the primary photon energy E is low.

Although their effects have not yet been experimentally confirmed for the Compton interaction (see the review article [25]), infrared divergences are well understood within QED and are predicted whenever there is a pair of processes which would be the same except for one of them having an additional photon in the final state [19]. In the limit of low outgoing photon energy, a detector (which necessarily has a finite energy resolution) cannot distinguish between the two processes, due to the potential presence of undetected low-energy photons. It is therefore artificial and unphysical to treat these indistinguishable events as different types of interactions, and doing so leads to divergences at low scattered photon energies [19]. In the *S*-matrix approach where the Compton interaction occurs in the field of an atom, the associated process which has one fewer photon in the final state is the photoelectric effect. It turns out that the lowest-order diagram for the Compton interaction is directly related to the first-order radiative corrections to atomic photoeffect, and the infrared divergences from these two terms have been shown to (partially) cancel [27, 28] so that their sum is finite.

However, while the above is relevant for Compton scattering with bound electrons, the RIA is based upon the assumption of free electrons (which nevertheless have the momentum distribution of bound electrons). For Compton scattering involving free electrons there is no corresponding process with one fewer photon in the final state. One might then expect the RIA to not exhibit infrared divergences, and in fact it has been stated previously that the RIA should in principle not be able to account for such divergences [25, 44, 26].

We have integrated the full and simplified RIA DDCSs in the Compton peak range near $E' = E_{\rm C}$ (which contains no divergences), and found differences of 0.3% or less in the DCSs, which are smaller than the differences resulting from using atomic vs. molecular Compton profiles (as can be seen in Figs. 5.3 and 5.4 below). We have thus opted to compute all results within this paper using the simplified RIA, Eq. (5.10), also because it is not possible to directly integrate the full RIA over the entire scattered energy and angle ranges for ICS calculations.

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Besides, the simplified expression for the RIA DDCS is the one that has been exclusively used in calculations of Compton cross sections in the literature [35, 34, 17, 45, 46]. The divergences observed in the full RIA call for further investigation, but such an undertaking is beyond the scope of the present work.

5.3.4 Compton profiles

The (isotropic) CP is an integral of the spherically-averaged electron momentum density $\rho_i(p)$ of the considered atomic or molecular orbital,

$$J_i(p_z) = 2\pi \int_{|p_z|}^{\infty} \rho_i(p) \, p \, \mathrm{d}p.$$
 (5.14)

By definition, the CP is symmetric and the following normalization condition is satisfied,

$$\int_{-\infty}^{+\infty} J_i(p_z) \, \mathrm{d}p_z = 1.$$
 (5.15)

Simple analytical forms for the CPs have been proposed in the past, e.g. by [32], where the integration over CPs is approximated by an elementary linear function. [47] also introduced analytical functions for the CPs in order to simplify the random sampling in Monte Carlo codes. A comparison of RIA results with and without CP simplifications has found that deviations can be significant, especially at low incident photon energies and large scattering angles [35].

When such approximations are not necessary, data for CPs of atomic (sub)shells are typically taken from the comprehensive tabulation by [36], which were calculated using non-relativistic $(1 \le Z \le 36)$ and relativistic $(36 \le Z \le 102)$ Hartree–Fock wavefunctions. However, the sparse tabulation and small number of significant figures in the data means that errors of up to 1% can occur in the interpolation procedure alone (although for most subshells the error is closer to 0.1%). Therefore, in this work we do not use the Biggs *et al.* tabulation of CPs for atomic (sub)shells, but instead we calculate CPs for both atomic and molecular orbitals within the Hartree–Fock framework outlined below.

Adopting the unrestricted Hartree–Fock description, the wave function of an atomic or molecular system with *N* electrons is expressed as a Slater determinant constructed with a set $\{\Phi_i\}_{i=1,...,N}$ of one-electron atomic or molecular spin-orbitals. The Fourier transforms of the

corresponding space orbitals are

$$\widetilde{\Phi}_{i}(\mathbf{p}) = \frac{1}{(2\pi\hbar)^{3/2}} \int d^{3}\mathbf{r} \, \mathrm{e}^{-\mathrm{i}\mathbf{p}\cdot\mathbf{r}/\hbar} \Phi_{i}(\mathbf{r}), \qquad (5.16)$$

so that the spherically-averaged momentum distribution can be written as

$$\rho_i(p) = p^2 \int_{4\pi} \mathrm{d}\hat{\mathbf{p}} \left| \widetilde{\Phi}_i(\mathbf{p}) \right|^2.$$
(5.17)

Under the linear combination of atomic orbitals approximation, the space orbitals are expanded in a non-complete basis set $\{\varphi_s\}_{s=1,...,M}$. Then $\rho_i(p)$ can be computed as a sum of contributions from the basis functions. Here we have chosen the Cartesian Gaussian-type orbitals [48], whose Fourier transform was derived by [49]. The size of the adopted basis set was cc-pVTZ [50, 51]. The contributions to $\rho_i(p)$ are given by integrals that can be found in [48]. For the ground state of molecules the optimized equilibrium distance was selected. The calculations have been carried out employing the GAUSSIAN03 program [52].

The momentum distributions ensuing from these self-consistent calculations are tabulated on a very dense grid of p values, with at least 100 times more points than the tabulation of [36] and with 9 significant figures. Since the spin of the electrons was taken into account, the CP was slightly different for spin up and spin down electrons in the same atomic or molecular space orbital. In our cross section calculations, we simply added the contribution from all electrons (spin up and down) within a given space orbital.

In the case of graphite, we differentiate the latter from atomic carbon by considering, as was done in ICRU Report 90 [17], that one of the 2p electrons is a conduction electron. We further assume that these conduction electrons form a degenerate free-electron gas (feg), whose CP is given by [53]

$$J^{\text{feg}}(p_z) = \frac{3}{4p_{\text{F}}} \left(1 - \frac{p_z^2}{p_{\text{F}}^2} \right) \Theta(p_{\text{F}} - |p_z|),$$
(5.18)

where $p_{\rm F} \equiv \hbar (3\pi^2 \rho_{\rm e})^{1/3}$ is the Fermi momentum, and $\rho_{\rm e}$ is the number of electrons per unit volume, which is proportional to the mass density of the material (for graphite we took the grain density of 2.265 g/cm³ [17]). The remaining five electrons in graphite are treated as being identical to the corresponding electrons in the carbon atom.

In Fig. 5.2 we show the unrestricted Hartree–Fock CPs for the occupied (sub)shells of graphite, including the conduction band. We see that more tightly bound shells have a broader



Figure 5.2 CPs for the three occupied (sub)shells of the carbon atom, calculated from unrestricted Hartree–Fock wavefunctions, and for the conduction electron (feg). All quantities are in atomic units.

momentum distribution, as would be expected since the electrons in these shells move faster, and also because the probability distribution in position space (which is the inverse Fourier transform of the momentum distribution) is more sharply peaked for inner shells.

5.3.5 Dosimetric quantities

In this subsection we review the fundamental dosimetric quantities of interest, following standard definitions and conventions [11, 54]. The mass attenuation coefficient is defined as

$$\frac{\mu}{\rho} = \frac{N_{\rm A}}{\mathscr{M}} \sum_{j} \sigma_j, \tag{5.19}$$

where ρ is the mass density of the medium, N_A is the Avogadro constant, \mathcal{M} is the molar mass of the atoms or molecules that make up the medium, and σ_j is the ICS for the interaction of type *j*. The mass energy-transfer coefficient is

$$\frac{\mu_{\rm tr}}{\rho} = \sum_j f_j \frac{\mu_j}{\rho},\tag{5.20}$$

where f_j is the average fraction of the photon energy transferred to kinetic energy of the charged particles, which is defined differently for each interaction type. For the Compton interaction

$$f_{\rm C} = 1 - \frac{\langle E' \rangle + \mathscr{X}}{E},\tag{5.21}$$

where $\langle E' \rangle$ is the average energy of the scattered photons

$$\langle E' \rangle = \frac{1}{\sigma_{\rm C}} \int_{E_{\rm min}}^{E_{\rm max}} E' \frac{{\rm d}\sigma_{\rm C}}{{\rm d}E'} {\rm d}E', \qquad (5.22)$$

with E_{\min} and E_{\max} being different for different theories depending on the allowed range of scattered photon energies, and \mathscr{X} is the average energy of the fluorescence radiation emitted per absorbed photon. In principle, the calculation of \mathscr{X} involves following the entire cascade of x-rays emitted in radiative transitions resulting from the initial vacancy. However, since here we are only dealing with biologically relevant materials which are made of low-Z elements, $\mathscr{X} \ll \langle E' \rangle < E$ and only the x-ray energy emitted directly from the filling of the initial vacancy needs to be considered. We therefore approximate \mathscr{X} as [11]

$$\mathscr{X}(E) = \sum_{n} p_n(E) \,\mathscr{X}_n^{\text{cascade}} \approx \sum_{n} p_n(E) \,\mathscr{X}_n^{\text{direct}},\tag{5.23}$$

where (sub)shell *n* is where the initial vacancy was created, $p_n(E) = \sigma_n(E)/\sigma(E)$ is the probability of Compton interaction for this (sub)shell, and

$$\mathscr{X}_{n}^{\text{direct}} = \omega_{n} \sum_{m} \frac{\Gamma_{nm}}{\Gamma_{n,\text{total}}} E_{nm}, \qquad (5.24)$$

where ω_n is the fluorescence yield, the sum extends over the higher shells involved in the radiative transitions, Γ_{nm} is the emission rate for radiative transitions between (sub)shells *n* and *m*, and the x-ray energy E_{nm} is to a good approximation equal to the difference in binding energies of the two (sub)shells. Furthermore, due to the low fluorescence yields and emission rates of the L subshells, we ultimately only included the contribution from an initial K-shell vacancy. The fluorescence yields and emission rates were taken from the tables of [55] and [56], respectively.

Given the energy interval of present concern (1 keV–1 MeV), the other relevant interaction mechanism is the photoelectric effect (pe), for which the energy-transfer fraction is

$$f_{\rm pe} = 1 - \frac{\mathscr{X}}{E}.\tag{5.25}$$

The pe ICSs were taken from the PENELOPE database [29], which was calculated resorting to standard first-order perturbation theory but with the normalization screening correction included [57].

Finally, we calculate the effect on the total mass energy-absorption coefficient μ_{en}/ρ , defined as

$$\frac{\mu_{\rm en}}{\rho} = (1-g)\frac{\mu_{\rm tr}}{\rho},\tag{5.26}$$

where g is the average fraction of the kinetic energy of secondary charged particles which is subsequently lost to radiative processes. Instead of defining a g_i for each type of interaction, as done in [11], we employed the user code g of the EGSnrc system [30] to compute a value for g for a given material at each photon energy E. For low-Z materials, g has a very small effect on μ_{en}/ρ , being typically around 0.2% or 0.3% at E = 1 MeV, and an order of magnitude smaller for energies of a few hundred keV and below [58].

5.4 Results

5.4.1 Differential cross sections

The RIA DDCS, Eq. (5.10), was computed with a simple Python script, while the CP was interpolated using the interpolation package from SciPy [59]. Integration of the DDCS and DCS were performed with the simps function of the SciPy integration package [59], which implements Simpson's rule. Given the dense interpolation and integration grids we used, and that we are dealing with slowly-varying functions, errors from the above numerical procedures are entirely negligible.

In computing the RIA cross sections using atomic CPs for graphite and the molecules of air, we simply simply added up the contribution of each atomic subshell. However, for water we followed the procedure for the "molecular IA" calculation described in the ICRU Report 90, whereby we constructed molecular orbitals from linear combinations of atomic orbitals, with coefficients taken from [60]. This provides a more stringent evaluation of the effect of

using molecular CPs as opposed to linear combinations of atomic CPs. The atomic binding energies we used are those recommended by [61], and the molecular orbital binding energies are the experimental values tabulated by [62]. For the molecular composition of air, we used the fractions by weight found in the NIST database [63].

In Fig. 5.3, we plot the DCS differential in scattering angle for graphite and water at 2, 10, and 50 keV. As expected, we observe that the DCS becomes more forward peaked at higher energies as backscattering is suppressed. Another well-known feature is that accounting for binding effects forces the DCS to go to zero at $\theta = 0$. Indeed, since we model graphite as having one conduction electron which is free, its atomic DCS does not go to zero at $\theta = 0$, same as for the KN DCS. One could expect the conduction electron's DCS at $\theta = 0$ to go to the same value as predicted by the Thomson DCS for elastic scattering of photons by free electrons. However, an unintended consequence of the RIA is that the DCS at $\theta = 0$ actually goes to one half of the Thomson DCS, due to the CP (and hence, the DDCS) being peaked at the maximum value of E' = E, and thus the integral over E' only covering half of the symmetric Compton peak. At low incident photon energies of about 1 keV, the KN DCS is an order of magnitude larger than the other DCSs, but this gap diminishes as the energy increases. The WH DCS is in excellent agreement with the atomic RIA DCS, which is in turn is very close to the molecular RIA except when a conduction electron is present. The DCS for air displays the same behaviour as described above, and the plots are qualitatively very similar to water and atomic carbon (results not shown).

If we now look at the DCS differential in scattered photon energy for graphite in Fig. 5.4, we first note that both KN and WH predict a minimum E' corresponding to 180° backscattering, whereas the RIA does not. We also note that since the RIA accounts for the binding energy, there is a maximum $E'_{\text{max}} = E - U_i$ for each (sub)shell, leading to the discontinuities clearly visible in the upper two subfigures.

At low energies, the KN DCS is many times larger than the other DCSs. Therefore, we decided not to show the KN DCS in the first panel at 1 keV, since the other DCSs would be scaled down along the y-axis and their detailed features would not be as visible. Despite the vast differences in shape between the WH and the RIA, due to the incoherent scattering function suppressing the DCS when E' approaches E, the two theories have similar ICSs. However, as we shall see below, the integrated energy-transfer CSs are quite different.



Figure 5.3 KN, WH, and RIA DCSs for water and graphite at three incident photon energies (2, 10, and 50 keV). For water, we compare RIA DCSs calculated using both atomic and molecular CPs from unrestricted Hartree–Fock wavefunctions. In the case of graphite we compare the RIA DCSs assuming 1 conduction electron with the RIA DCSs pertaining to atomic carbon.



Figure 5.4 KN, WH, and RIA DCSs differential in scattered photon energy for graphite at four incident photon energies. The RIA DCSs were calculated for graphite with 1 conduction electron as well as for atomic carbon. Note that E' is normalized by E for a clearer presentation of the figures.

5.4.2 Photon interaction coefficients

Same as for the DCS in Fig. 5.3, we see from Figs. 5.5 and 5.6 that the choice of CPs (molecular vs atomic) has a minimal impact on μ^C/ρ and μ_{tr}^C/ρ . Once again, the only exception is graphite, whose μ^C/ρ is almost three times higher than the atomic RIA at 1 keV owing to the presence of the conduction electron. When comparing our RIA results with the ICRU 90 tables for μ^C/ρ , we find that our calculations differ by at most a few percent from the XCOM and the *S*-matrix (mislabeled as '*ab initio* RIA') values for all three materials, and tend to fall somewhere between the two data sets. The only exception is at 1 keV, where differences can be closer to 10%, but above 10 keV the values are within 1% of each other. For water, our molecular RIA results are closest to the 'Molecular IA' column of Rao *et al.*, where discrepancies are within 2%,

even in the low keV range. For graphite with one conduction electron, our values differ by about 1% or less from the PENELOPE tabulation. However, although we have carried out fully atomic calculations (direct sum of atomic orbital contributions) of μ^{C}/ρ , we were not able to reproduce the Rao *et al.* values for atomic carbon and 'Atomic IA' of water. In fact, our fully atomic calculations are at most 5% larger than our molecular results, while Rao *et al.*'s atomic values are higher by up to a factor of two in the low keV range. Furthermore, we could not identify a literature source supporting Rao *et al.*'s atomic IA data below 5 keV for graphite and water.

On the other hand, the choice of theoretical formalism does have an impact on the Compton interaction coefficients. When looking at μ^{C}/ρ , WH binding corrections seem to be in excellent agreement with the RIA, unlike the KN approach which is off by up to an order of magnitude. However, when considering μ_{tr}^{C}/ρ , the WH theory actually agrees less with the RIA than the KN approximation does. This can be better understood by returning to Fig. 5.4, where we see that even though the areas under the WH and RIA curves are the same, the WH energy-transfer cross section would clearly be much smaller for low incident energies. The WH μ_{tr}^{C}/ρ can differ by a large amount from the predictions of the other models in the tens of keV range (e.g. 6–10% at 20 keV), when Compton scattering becomes the dominant interaction mechanism. Our calculated WH μ_{tr}^{C}/ρ values reproduce with high accuracy the data from [11], and our RIA calculations are also in good agreement with previously published results [35, 47]. To our knowledge, the appreciable differences between the WH and RIA predictions for energy transfer were noticed by [33] but have not been widely reported in the literature.

Ultimately, with decreasing photon energy the energy transfer resulting from the photoelectric effect (pe) will overwhelm the diminishing energy transfer from the Compton interaction in the low tens of keV range, hence the differences in the total μ_{en}/ρ resulting from the choice of theoretical Compton model are no larger than 0.4%, and the differences between WH and the other two formalisms are no longer prominent. In Fig. 5.7 we have only considered the μ_{en}/ρ which uses the molecular RIA since the one with the atomic RIA would be indistinguishable when plotted in the figure. Therefore, the uncertainty in μ_{en}/ρ introduced by using different Compton models is significantly smaller than the uncertainty from the pe [16].



Figure 5.5 Partial mass attenuation coefficient μ^{C}/ρ for air, water, and graphite.



Figure 5.6 Partial mass energy-transfer coefficient μ_{tr}^C / ρ for air, water, and graphite, calculated within the KN, WH, and RIA (with molecular and atomic CP) models. The insets show, above 10 keV, the WH and RIA curves normalized by the KN data, with a linear *y*-axis to better visualize the percent differences between the models.



Figure 5.7 Percent difference in mass energy-absorption coefficients, μ_{en}/ρ , including the photoelectric effect, between pairs of Compton models.

5.5 Conclusions

In summary, we calculated differential and integrated cross sections for the Compton interaction within the KN, WH, and RIA formalisms, for three materials of dosimetric interest in the 1 keV to 1 MeV interval. We compared using molecular versus atomic CPs in the RIA, but found no significant differences in the DCS. However, assuming one conduction electron in graphite does result in significant deviations at low energies from calculations for the carbon atom, since we are essentially treating one of the electrons as free, with a momentum distribution corresponding to that of a degenerate free-electron gas.

We then calculated mass energy-transfer coefficients, and surprisingly found the WH theory to differ from the other models by up to an order of magnitude at low energies. This is due to the large differences in the shape of the WH and RIA DCSs differential in outgoing photon energy, despite their integrated cross sections being very close. We therefore conclude that while the approach of multiplying the KN DCS by the incoherent scattering function seems accurate for calculating the DCS and the ICS, it does not seem appropriate for calculating the energy-transfer cross section. Fortunately, when considering the total (Compton + pe) μ_{en}/ρ , the pe contribution dominates in the energy interval where the WH prediction fails, so that the overall differences in μ_{en}/ρ from using different Compton models are within 0.4%.

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Chapter 6

On the modified independent-atom model (MIAM) for elastic scattering of electrons in molecules

As introduced in section 3.3, we investigated the modified independent-atom model (MIAM) proposed by Hayashi and Kuchitsu [1], which describes electron-molecule elastic scattering using a multicenter potential within the Born approximation. The potential is written as

$$V = V_S + V_L, \tag{6.1}$$

the sum of a short-range potential representing multiple scattering of the electron by individual atoms, and a long-range potential to account for polarization of the molecule. The initial authors show that the effects of the long-range potential are small compared to the short-range potential, being significant only at small angles, hence we will leave the study of the former for a future project and focus solely on V_S in the present work.

In section 6.2 we express the short-range contribution as a series expansion consisting of successively higher-order terms involving more scattering events, analogous to the Born approximation. We consider up to two scattering events in the short-range scattering amplitude $f_{\rm S}(\mathbf{k}_f, \mathbf{k}_i)$, and write the DCS as the sum of terms representing different combinations of single

and double scatterings following the notation used by the original authors,

$$\left(\frac{d\sigma}{d\Omega}\right)_{S} = \ll |f_{S}(\mathbf{k}_{f}, \mathbf{k}_{i})|^{2} \gg$$

$$= I_{S} + I_{SS} + I_{SD} + I_{DD}$$

$$= I_{S} + I_{SS} + I_{SD}^{(1)} + I_{SD}^{(2)} + I_{DD}^{(0)} + I_{DD}^{(1)} + I_{DD}^{(2)} + I_{DD}^{(3)},$$

$$(6.2)$$

where the double angle brackets $\ll ... \gg$ indicate an orientational average. I_S is the incoherent sum of individual atomic DCSs, and I_{SS} is the interference between single scattering events (see eqs.[6.23] and [6.24]), such that together they add up to the regular IAM, eq. (3.2). I_{SD} and its subterms $I_{SD}^{(1)}$ and $I_{SD}^{(2)}$ represent interference between an amplitude arising from single scattering and an amplitude arising from double scattering. Finally, I_{DD} is the interference between two amplitudes which each resulted from double scattering events. As will be elaborated on later, figure 6.4 shows all the various subterms and how they are defined based on the number of scattering events with distinct atoms in each scattering amplitude.

We begin in section 6.1 by highlighting a few inconsistencies between the initial authors' published expressions (which are the same across all their articles) and other parts of the publication [2]. This will serve as the motivation for re-deriving the short-range contribution to the cross section, which will be the main goal of the remainder of this chapter.

6.1 Inconsistencies in Hayashi and Kuchitsu, Chem. Phys. Lett. (1976)

The explicit expressions for the subterms in the DCS were initially derived in [1], and are consistently reproduced in a follow-up paper [2], in which they compute DCSs for N₂ and P₄. Equation (16) in [2] and the surrounding text claim that for the tetrahedral P₄ molecule, when the scattering angle θ_{fi} is zero, we have

$$I_{\rm SD}^{(1)}(\theta_{fi}=0) = I_{\rm SD}^{(2)}(\theta_{fi}=0).$$
(6.3)

This relation is in agreement with figure 6.1 (their figure 2), which plots each term up to $I_{DD}^{(0)}$, normalized by I_S (this is a convenient way to graphically show the contribution of each term,

since the y-values cover many orders of magnitude, but a logarithmic y-axis cannot be used because all terms except I_S can be negative). The momentum transfer Δp is related to θ_{fi} through $\Delta p = 2p \sin(\theta_{fi}/2)$.



Fig. 2. Contributions of the terms in the multiple scattering series (relative to $I_{\rm S}$) to $e-P_4$ elastic scattering at an incident energy of 100 eV. (a) $I_{\rm SD}^{(1)}$ (NFES); (b) $I_{\rm SD}^{(2)}$ (NFES); (c) $I_{\rm DD}^{(0)}$ (NFES); (d) $I_{\rm SS}$.

Figure 6.1 Contributions to the DCS due to short-range potentials, normalized to the leading term I_S . Note that the (short-range) DCS becomes negative if the sum of the plotted terms is < -1. NFES refers to the approximation which sets Q = 0 (see eqs.[6.4, 6.6] below), where energy-nonconserving virtual processes are neglected.

More details of the derivation will be given in the following section, but in short, to obtain explicit expressions for $I_{SD}^{(1)}$ and $I_{SD}^{(2)}$ which can be computed, one would start from eq. (6.25). The sum over atomic indices can be divided into a sum involving 2 different atoms and a sum involving 3 different atoms, which are called $I_{SD}^{(1)}$ and $I_{SD}^{(2)}$, respectively. The *p*-integration is carried out partially using complex integration, and the orientational average is performed using well-known angular momentum relations (see appendix to chapter 6).

The resulting expression for $I_{SD}^{(1)}$ published by the original authors is given by

$$I_{\text{SD}}^{(1)} = \frac{i}{k} \sum_{A \neq B}^{N} \left[f_A^*(\mathbf{k}_f, \mathbf{k}_i) + f_B^*(\mathbf{k}_f, \mathbf{k}_i) \right] \sum_{l_1 l_2 l_3} (2l_1 + 1)(2l_2 + 1)(2l_3 + 1) \begin{pmatrix} l_1 & l_2 & l_3 \\ 0 & 0 & 0 \end{pmatrix}^2 \times P_{l_2}(\cos \theta_{fi}) j_{l_3}(kx_{AB}) \left[a_{l_1}(k; B) a_{l_2}(k; A) j_{l_3}(kx_{AB}) + iQ(l_1, l_2, l_3; B, A) \right] + \text{c.c.}, \quad (6.4)$$

where *A* and *B* are indices run over all atoms in the molecule, $x_{AB} = |\mathbf{x}_A - \mathbf{x}_B|$ is the distance between atoms *A* and *B*, $\begin{pmatrix} l_1 & l_2 & l_3 \\ 0 & 0 & 0 \end{pmatrix}$ is the Wigner 3-j symbol, $P_l(x)$ are Legendre polynomials, $j_l(x)$ are spherical Bessel functions, $a_l(k;A)$ is given by eq. (6.30) for atom *A*, and

$$Q(l_1, l_2, l_3; B, A) = \frac{2}{\pi k} \mathscr{P} \int \frac{p^2 dp}{k^2 - p^2} a_{l_1}(k, p; B) a_{l_2}(p, k; A) j_{l_3}(p x_{AB})$$
(6.5)

is a Cauchy principal value integral which represents the off-the-energy-shell *p*-integral (see eq. (6.33)), for which the initial authors discuss various approximation methods, but ultimately neglect in their computations of the expressions. In this energy non-conserving integral, $a_l(k,k';A)$ is given by eq. (6.28). $I_{SD}^{(2)}$ was found to be given by

$$I_{\rm SD}^{(2)} = \frac{4\pi i}{k} \sum_{A \neq B \neq C}^{N} f_{C}^{*}(\mathbf{k}_{f}, \mathbf{k}_{i}) \sum_{\substack{l_{1}l_{2}l_{3} \\ l_{4}l_{5}m_{3}}} i^{l_{3}-l_{4}+l_{5}}(-1)^{m_{3}}(2l_{1}+1)(2l_{2}+1)^{1/2}(2l_{3}+1)(2l_{4}+1)(2l_{5}+1)^{1/2} \\ \times \begin{pmatrix} l_{1} & l_{2} & l_{3} \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l_{1} & l_{2} & l_{3} \\ 0 & -m_{3} & m_{3} \end{pmatrix} \begin{pmatrix} l_{4} & l_{5} & l_{3} \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l_{4} & l_{5} & l_{3} \\ 0 & -m_{3} & m_{3} \end{pmatrix} j_{l_{3}}(kx_{AB}) j_{l_{4}}(kx_{AB}) j_{l_{5}} \begin{pmatrix} 2kx_{AB}\sin\frac{\theta_{fi}}{2} \end{pmatrix} \\ \times Y_{l_{2}}^{-m_{3}}(\theta_{fi}, 0) P_{l_{5}}(\cos\varphi_{BAC}) Y_{l_{5}}^{-m_{3}} \begin{pmatrix} \pi - \theta_{fi} \\ 2 \end{pmatrix} \left[a_{l_{1}}(k;B) a_{l_{2}}(k;A) j_{l_{3}}(kx_{AB}) + i Q(l_{1}, l_{2}, l_{3};B,A) \right] \\ + \text{c.c.}$$

$$(6.6)$$

Let us attempt to check eq. (6.3) for the P₄ molecule, where $f_A = f_B = f_C = f_P$. The summation over the atoms is the same in both $I_{SD}^{(1)}$ and $I_{SD}^{(2)}$, since for $I_{SD}^{(2)}$

$$\sum_{A \neq B \neq C}^{N} f_{C}^{*}(\mathbf{k}_{f}, \mathbf{k}_{i}) (\cdots) = \sum_{A \neq B}^{4} 2 f_{P}^{*}(\mathbf{k}_{f}, \mathbf{k}_{i}) (\cdots) = 24 f_{P}^{*}(\mathbf{k}_{f}, \mathbf{k}_{i}) (\cdots)$$
(6.7)

and similarly for $I_{SD}^{(1)}$,

$$\sum_{A\neq B}^{N} \left[f_A^*(\mathbf{k}_f, \mathbf{k}_i) + f_B^*(\mathbf{k}_f, \mathbf{k}_i) \right] (\cdots) = 24 f_P^*(\mathbf{k}_f, \mathbf{k}_i) (\cdots)$$
(6.8)

Therefore, we have to show that what's inside the sum over atoms is the same in both terms.

We can relabel x_{AB} as simply *x* since the 4 atoms are equidistant, and we also know that $\varphi_{BAC} = \pi/3$, which we can simply call φ . When $\theta_{fi} = 0$, $P_{l_2}(\cos \theta_{fi}) = 1$ and $I_{SD}^{(1)}$ simplifies to

$$I_{\text{SD}}^{(1)}(\theta_{fi}=0) = \frac{i}{k} 24 f_{\text{P}}^{*}(\mathbf{k}_{f},\mathbf{k}_{i}) \sum_{l_{1}l_{2}l_{3}} (2l_{1}+1)(2l_{2}+1)(2l_{3}+1) \begin{pmatrix} l_{1} & l_{2} & l_{3} \\ 0 & 0 & 0 \end{pmatrix}^{2} j_{l_{3}}(kx) \\ \times \left[a_{l_{1}}(k) a_{l_{2}}(k) j_{l_{3}}(kx) + iQ(l_{1},l_{2},l_{3}) \right] + \text{c.c.}$$
(6.9)

As for $I_{SD}^{(2)}$, we first note that

$$j_{l_5}\left(2kx_{AB}\sin\frac{\theta_{fi}}{2}\right) = j_{l_5}(0) = \begin{cases} 1 & \text{if } l_5 = 0\\ 0 & \text{otherwise} \end{cases} = \delta_{l_5,0}.$$
 (6.10)

This brings about a number of simplifications. The Wigner 3-j symbol is related to Clebsh-Gordan coefficients through

$$\begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} = \frac{(-1)^{j_1 - j_2 - m_3}}{\sqrt{2j_3 + 1}} \langle j_1 m_1 j_2 m_2 \mid j_3 (-m_3) \rangle,$$
(6.11)

and when $j_2 = 0$,

$$\langle j_1 m_1 j_2 m_2 | j_3 m_3 \rangle = \delta_{j_3, j_1} \delta_{m_3, m_1}$$
 (6.12)

so that

$$\begin{pmatrix} l_4 & l_5 & l_3 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l_4 & l_5 & l_3 \\ 0 & -m_3 & m_3 \end{pmatrix} = \frac{(-1)^{-m_3}}{2l_3 + 1} \,\delta_{l_3, l_4} \,\delta_{m_3, 0}.$$
(6.13)

Furthermore, we also have

$$Y_{l_2}^{-m_3}(0,0) = \sqrt{\frac{2l_2+1}{4\pi}},\tag{6.14}$$

$$P_{l_5}(\cos \varphi_{BAC}) = P_0(\cos \varphi_{BAC}) = 1$$
 (6.15)

and

$$Y_{l_5}^{-m_3}(\pi/2,0) = Y_0^0(\pi/2,0) = \sqrt{\frac{1}{4\pi}} .$$
 (6.16)

Inserting the above into eq. (6.6), we get

$$\begin{split} I_{\rm SD}^{(2)}(\theta_{fi}=0) &= \frac{4\pi i}{k} \, 24 \, f_{\rm P}^*(\mathbf{k}_f,\mathbf{k}_i) \sum_{\substack{l_1l_2l_3\\l_4l_5m_3}} i^{l_3-l_4+l_5}(-1)^{m_3}(2l_1+1)(2l_2+1)^{1/2}(2l_3+1)(2l_4+1)(2l_5+1)^{1/2} \\ &\times \begin{pmatrix} l_1 & l_2 & l_3\\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l_1 & l_2 & l_3\\ 0 & -m_3 & m_3 \end{pmatrix} \frac{1}{2l_3+1} \, \delta_{l_3,l_4} \, \delta_{m_3,0} \, j_{l_3}(kx) \, j_{l_4}(kx) \, \delta_{l_5,0} \\ &\times \sqrt{\frac{2l_2+1}{4\pi}} \sqrt{\frac{1}{4\pi}} \left[a_{l_1}(k;B) \, a_{l_2}(k;A) \, j_{l_3}(kx_{AB}) + i \, Q(l_1,l_2,l_3;B,A) \right] + {\rm c.c.} \\ &= \frac{i}{k} \, 24 \, f_{\rm P}^*(\mathbf{k}_f,\mathbf{k}_i) \sum_{l_1l_2l_3} (2l_1+1)(2l_2+1)(2l_3+1) \begin{pmatrix} l_1 & l_2 & l_3\\ 0 & 0 & 0 \end{pmatrix}^2 j_{l_3}^2(kx) \\ &\times \left[a_{l_1}(k) \, a_{l_2}(k) \, j_{l_3}(kx) + i \, Q(l_1,l_2,l_3) \right] + {\rm c.c.} \end{split}$$
(6.17)

Comparing eqs. (6.9) and (6.17), we see that there is an extra factor of $j_{l_3}(kx)$ in $I_{SD}^{(2)}$. Indeed, when we compute and plot $I_{SD}^{(2)}$ after removing a Bessel function from the published expression, we obtain fig. 6.2 below. Note that the atomic potential we adopted is very different from the one used by Hayashi and Kuchitsu. Despite this, qualitatively figs. 6.1 and 6.2 have the same broad features.

If instead we plot the original expression for $I_{SD}^{(2)}$ given by eq. (6.6), we would get fig. 6.3. We note how $I_{SD}^{(2)}$ is no longer large enough in magnitude that it could potentially make the cross section positive near $\Delta p = 1$, and also that $I_{SD}^{(1)}$ shows a large resonance dip just outside of the range plotted by Hayashi and Kuchitsu.

Given these potential errors/inconsistencies, we will try to re-derive the expressions to investigate the origins of the negative DCSs.

6.2 Derivation of the MIAM expressions

In keeping with the original notation, the short-range scattering cross section is given by

$$\left(\frac{d\sigma}{d\Omega}\right)_{S} = (2\pi)^{4} \ll |\langle \mathbf{k}_{f} | T_{S} | \mathbf{k}_{i} \rangle|^{2} \gg, \qquad (6.18)$$



Figure 6.2 Contributions to the e-P₄ DCS at 100 eV, normalized to I_S , after intentionally introducing the mistake of removing a factor of $j_{l_3}(kx)$ in $I_{SD}^{(2)}$.

where the *T*-matrix T_S can be expanded as a multiple-scattering series within the Born approximation, with different atoms acting as scatterers for each scattering event occurring within the range of the potential, i.e.

$$T_{S} = \sum_{A=1}^{N} t_{A} + \sum_{A \neq B}^{N} t_{A} (E - K + i\varepsilon)^{-1} t_{B} + \dots$$
(6.19)

The *T*-matrix t_A for a single scattering event with atom *A* is defined as usual by (see eq. (2.41))

$$t_A = V_A + V_A (E - K + i\varepsilon)^{-1} t_A.$$
(6.20)

Using the relation

$$(2\pi)^2 \langle \mathbf{k}_f | t_A | \mathbf{k}_i \rangle = -\exp[i(\mathbf{k}_i - \mathbf{k}_f) \cdot \mathbf{x}_A] f_A(\mathbf{k}_f, \mathbf{k}_i), \qquad (6.21)$$

which takes into account the phase factors arising from atomic spatial positions, we obtain as before

$$\left(\frac{d\sigma}{d\Omega}\right)_{\rm S} = \ll |f_{\rm S}(\mathbf{k}_f, \mathbf{k}_i)|^2 \gg = I_{\rm S} + I_{\rm SS} + I_{\rm DD} + I_{\rm DD}, \tag{6.22}$$



Figure 6.3 Contributions to the e- P_4 DCS at 100 eV, normalized to I_S , using the original published expressions and over the entire 180° range.

with

$$I_{\rm S} = \sum_{A=1}^{N} |f_A(\mathbf{k}_f, \mathbf{k}_i)|^2$$
(6.23)

$$I_{\rm SS} = \sum_{A \neq B} f_A^*(\mathbf{k}_f, \mathbf{k}_i) f_B(\mathbf{k}_f, \mathbf{k}_i) \frac{\sin(kx_{AB})}{kx_{AB}}$$
(6.24)

$$I_{\text{SD}} = -\frac{1}{(2\pi)^2} \sum_{C=1}^{N} \sum_{B\neq A}^{N} \ll f_C^*(\mathbf{k}_f, \mathbf{k}_i) \exp[i\mathbf{k}_f \cdot (\mathbf{x}_C - \mathbf{x}_B) + i\mathbf{k}_i \cdot (\mathbf{x}_A - \mathbf{x}_C)]$$
$$\times \int d^3 p \exp[i\mathbf{p} \cdot (\mathbf{x}_B - \mathbf{x}_A)] \frac{f_B(\mathbf{k}_f, \mathbf{p}) f_A(\mathbf{p}, \mathbf{k}_i)}{k^2 - p^2 + i\varepsilon} \gg + \text{c.c.}$$
(6.25)

$$I_{\rm DD} = \frac{1}{(2\pi)^4} \sum_{C \neq D}^{N} \sum_{B \neq A}^{N} \ll \exp[i\mathbf{k}_f \cdot (\mathbf{x}_D - \mathbf{x}_B) + i\mathbf{k}_i \cdot (\mathbf{x}_A - \mathbf{x}_C)]$$

$$\times \left\{ \int d^3 p' \exp[i\mathbf{p}' \cdot (\mathbf{x}_D - \mathbf{x}_C)] \frac{f_D(\mathbf{k}_f, \mathbf{p}') f_C(\mathbf{p}', \mathbf{k}_i)}{k^2 - p'^2 + i\varepsilon} \right\}^*$$

$$\times \int d^3 p \exp[i\mathbf{p} \cdot (\mathbf{x}_B - \mathbf{x}_A)] \frac{f_B(\mathbf{k}_f, \mathbf{p}) f_A(\mathbf{p}, \mathbf{k}_i)}{k^2 - p^2 + i\varepsilon} \gg .$$
(6.26)

Here we would like to point out that in order to guarantee a positive cross section, the complete terms on the RHS of eq. (6.22) must be included, which the original authors could not achieve due to the prohibitively large computational complexity of the I_{DD} subterms.

In order to carry out the orientational average, we expand the scattering amplitude in a partial-wave series with terms having definite angular momentum

$$f(\mathbf{k}', \mathbf{k}) = \frac{1}{k} \sum_{l} (2l+1) a_{l}(k', k) P_{l}(\hat{\mathbf{k}}', \hat{\mathbf{k}}), \qquad (6.27)$$

where

$$a_{l}(k',k) = -2k \int_{0}^{\infty} dr \ r^{2} \ j_{l}(k'r) V(r) \ u_{l,k}^{(+)}(r), \qquad (6.28)$$

with the radial wavefunction $u_{l,k}^{(+)}(r)$ satisfying the boundary condition

$$u_{l,k}^{(+)}(r) \to \exp(i\delta_l) \left[\cos \delta_l j_l(kr) + \sin \delta_l j_l(kr)\right] \quad \text{when} \quad r \to \infty.$$
 (6.29)

On the energy shell, where k' = k, $a_l(k', k)$ can be reduced to

$$a_l(k) = \exp(i\delta_l)\sin\delta_l. \tag{6.30}$$

In I_{SD} , the terms for which $C = B \neq A$ or $C = A \neq B$ are defined as $I_{SD}^{(1)}$ and the terms for which $C \neq B \neq A$ are defined as $I_{SD}^{(2)}$, which may be graphically represented as shown in figure 6.4. Our goal is to re-write $I_{SD}^{(1)}$ and $I_{SD}^{(2)}$ in a form which can be computed. We will make use of various well-known relations which can be found in the appendix to the current chapter, including many angular momentum relations involved in carrying out the spherical averaging.

The first step is to expand the p-integral in eq. (6.25)

$$\begin{split} I_{p} &= \int d^{3}p \exp\left(i\mathbf{p} \cdot \mathbf{x}_{BA}\right) \frac{f_{B}(\mathbf{k}_{f},\mathbf{p})f_{A}(\mathbf{p},\mathbf{k}_{i})}{k^{2}-p^{2}+i\varepsilon} \\ &= \int d\Omega \frac{p^{2}dp}{k^{2}-p^{2}+i\varepsilon} \sum_{l_{1}} \left(2l_{1}+1\right)i^{l_{1}}j_{l_{1}}(p\,x_{BA})P_{l_{1}}(\hat{\mathbf{p}}\cdot\hat{\mathbf{x}}_{BA}) \\ &\times \frac{1}{k^{2}} \sum_{l_{A},l_{B}} \left(2l_{A}+1\right)\left(2l_{B}+1\right)P_{l_{A}}(\hat{\mathbf{p}}\cdot\hat{\mathbf{k}}_{i})P_{l_{B}}(\hat{\mathbf{k}}_{f}\cdot\hat{\mathbf{p}})a_{l_{A}}(p,k)a_{l_{B}}(k,p) \\ &= \int d\Omega \sum_{l_{1}} \left(2l_{1}+1\right)i^{l_{1}}P_{l_{1}}(\hat{\mathbf{p}}\cdot\hat{\mathbf{x}}_{BA})\sum_{l_{A},l_{B}} \left(2l_{A}+1\right)\left(2l_{B}+1\right)P_{l_{A}}(\hat{\mathbf{p}}\cdot\hat{\mathbf{k}}_{i})P_{l_{B}}(\hat{\mathbf{k}}_{f}\cdot\hat{\mathbf{p}}) \\ &\times \frac{1}{k^{2}} \int \frac{p^{2}dp}{k^{2}-p^{2}+i\varepsilon} j_{l_{1}}(p\,x_{AB})a_{l_{A}}(p,k)a_{l_{B}}(k,p) \end{split}$$
(6.31)
$$&= I_{p\Omega} \times I_{pp}, \end{split}$$

where $\mathbf{x}_{BA} = \mathbf{x}_B - \mathbf{x}_A$, and we have broken I_p down into its angular and radial integrals, which we denote by $I_{p\Omega}$ and I_{pp} , respectively.

Let us rewrite the angular integral using spherical harmonics, and then make use of angular momentum addition to simplify the expression

$$\begin{split} I_{p\Omega} &= \sum_{\substack{l_{A}l_{B}l_{1}\\m_{A}m_{B}m_{1}}} (4\pi)^{3} i^{l_{1}} \int d\Omega \ Y_{l_{1}}^{m_{1}}(\Omega) \ Y_{l_{1}}^{m_{1}}(\hat{\mathbf{x}}_{BA}) \ Y_{l_{A}}^{m_{A}}(\Omega) \ Y_{l_{A}}^{m_{A}}(\hat{\mathbf{z}}) \ Y_{l_{B}}^{m_{B}}(\Omega) \ Y_{l_{B}}^{m_{B}}(\theta_{fi},0) \\ &= \sum_{\substack{l_{A}l_{B}l_{1}\\m_{A}m_{B}m_{1}}} (4\pi)^{3} i^{l_{1}} \ Y_{l_{1}}^{m_{1}}(\hat{\mathbf{x}}_{BA}) \ Y_{l_{B}}^{m_{B}*}(\theta_{fi},0) \sqrt{\frac{2l_{A}+1}{4\pi}} \ \delta_{m_{A},0} \int d\Omega \ Y_{l_{1}}^{m_{1}*}(\Omega) \ Y_{l_{A}}^{m_{A}}(\Omega) \ Y_{l_{B}}^{m_{B}}(\Omega) \\ &= \sum_{\substack{l_{A}l_{B}l_{1}\\m_{1}}} (4\pi)^{3} i^{l_{1}} \ Y_{l_{1}}^{m_{1}}(\hat{\mathbf{x}}_{BA}) \ Y_{l_{B}}^{m_{1}*}(\theta_{fi},0) \sqrt{\frac{2l_{A}+1}{4\pi}} \\ &\times (-1)^{m_{1}} \sqrt{\frac{(2l_{A}+1)(2l_{B}+1)(2l_{1}+1)}{4\pi}} \left(\begin{matrix} l_{A} \ l_{B} \ l_{1}\\0 \ -m_{1} \ m_{1} \end{matrix} \right) \left(\begin{matrix} l_{A} \ l_{B} \ l_{1}\\0 \ 0 \ 0 \end{matrix} \right) \\ &= (4\pi)^{2} \sum_{\substack{l_{A}l_{B}l_{1}\\m_{1}}} i^{l_{1}} (-1)^{m_{1}} (2l_{A}+1) \sqrt{(2l_{B}+1)(2l_{1}+1)} \ Y_{l_{1}}^{m_{1}}(\hat{\mathbf{x}}_{BA}) \ Y_{l_{B}}^{-m_{1}}(\theta_{fi},0) \left(\begin{matrix} l_{A} \ l_{B} \ l_{1}\\0 \ -m_{1} \ m_{1} \end{matrix} \right) \left(\begin{matrix} l_{A} \ l_{B} \ l_{1}\\0 \ 0 \ 0 \end{matrix} \right) \\ &= (6.32) \end{split}$$

The radial integral is

$$\begin{split} I_{pp} &= \frac{1}{k^2} \int \frac{p^2 dp}{k^2 - p^2 + i\epsilon} \, j_{l_1}(p \, x_{AB}) \, a_{l_A}(p, k) \, a_{l_B}(k, p) \\ &= -\frac{1}{k^2} \int \frac{p^2 dp}{(p - k - i\epsilon)(p + k)} \, j_{l_1}(p \, x_{AB}) \, a_{l_A}(p, k) a_{l_B}(k, p) \\ &= \frac{1}{k^2} \left[\mathscr{P} \int \frac{p^2 dp}{k^2 - p^2} \, j_{l_1}(p \, x_{AB}) \, a_{l_A}(p, k) \, a_{l_B}(k, p) - \frac{i\pi k}{2} \, j_{l_1}(k \, x_{AB}) \, a_{l_A}(k, k) \, a_{l_B}(k, k) \right]. \end{split}$$

$$(6.33)$$

The simplest form we can take for I_{pp} is to set the off-shell integral over p to be zero, in which case we can write

$$I_{p} = -i \frac{(2\pi)^{3}}{k} \sum_{\substack{l_{A} l_{B} \\ l_{1} m_{1}}} i^{l_{1}} (-1)^{m_{1}} (2l_{A} + 1) \sqrt{(2l_{B} + 1)(2l_{1} + 1)} j_{l_{1}}(kx_{AB}) Y_{l_{1}}^{m_{1}}(\hat{\mathbf{x}}_{BA}) Y_{l_{B}}^{-m_{1}}(\theta_{fi}, 0)$$

$$\times \begin{pmatrix} l_{A} & l_{B} & l_{1} \\ 0 & -m_{1} & m_{1} \end{pmatrix} \begin{pmatrix} l_{A} & l_{B} & l_{1} \\ 0 & 0 & 0 \end{pmatrix} a_{l_{A}}(k, k) a_{l_{B}}(k, k).$$
(6.34)

 $I_{\text{SD}}^{(1)}$ contains the contributions where $C = A \neq B$ or $C = B \neq A$. In other words, eq. (6.25) becomes

$$I_{\text{SD}}^{(1)} = -\frac{1}{(2\pi)^2} \sum_{B \neq A}^{N} \left[\ll f_A^*(\mathbf{k}_f, \mathbf{k}_i) \exp(i\mathbf{k}_f \cdot \mathbf{x}_{AB}) \times I_p \gg + \ll f_B^*(\mathbf{k}_f, \mathbf{k}_i) \exp(i\mathbf{k}_i \cdot \mathbf{x}_{AB}) \times I_p \gg \right] + \text{c.c.}$$
(6.35)

Since the only factor in I_p which depends on the positions of the atoms is $Y_{l_1}^{m_1}(\hat{\mathbf{x}}_{BA})$ from eq. (6.32), only this factor participates in the orientational averaging. Therefore we need to calculate the orientational averages

$$\ll \exp(i\mathbf{k}_f \cdot \mathbf{x}_{AB}) Y_{l_1}^{m_1}(\hat{\mathbf{x}}_{BA}) \gg \quad \text{and} \quad \ll \exp(i\mathbf{k}_i \cdot \mathbf{x}_{AB}) Y_{l_1}^{m_1}(\hat{\mathbf{x}}_{BA}) \gg .$$
(6.36)



Figure 6.4 Schematic representation of terms arising from the multiple scattering expansion for the short-range potential. The lines correspond to scattering amplitudes, wavy lines indicate integration over **p**, and an atom overlapping two lines implies that both amplitudes have the same phase. The diagrams represent (a) $I_{\rm SD}$, single scattering; (b) $I_{\rm SS}$, interference between two single scatterings; (c) $I_{\rm SD}^{(1)}$, and (d) $I_{\rm SD}^{(2)}$, interference between single and double scattering involving two and three distinct atoms, respectively; (e) $I_{\rm DD}^{(0)}$, pure double scattering; and (f)–(h) $I_{\rm DD}^{(1)}-I_{\rm SD}^{(3)}$, interference between double scatterings involving two, three, and four distinct atoms.

$$\ll \exp(i\mathbf{k}_{f} \cdot \mathbf{x}_{AB}) Y_{l_{1}}^{m_{1}}(\hat{\mathbf{x}}_{BA}) \gg$$

$$= 4\pi \sum_{l_{2}m_{2}} i^{l_{2}} j_{l_{2}}(kx_{AB}) Y_{l_{2}}^{m_{2}}(\theta_{fi}, 0) (-1)^{l_{2}} \left(\frac{1}{4\pi} \int Y_{l_{2}}^{m_{2}*}(\Omega) Y_{l_{1}}^{m_{1}}(\Omega) d\Omega\right)$$

$$= (-i)^{l_{1}} j_{l_{1}}(kx_{AB}) Y_{l_{1}}^{m_{1}}(\theta_{fi}, 0).$$
(6.37)

Likewise,

$$\ll \exp(i\mathbf{k}_{i}\cdot\mathbf{x}_{AB})Y_{l_{1}}^{m_{1}}(\hat{\mathbf{x}}_{BA}) \gg = (-i)^{l_{1}}j_{l_{1}}(kx_{AB})\sqrt{\frac{2l_{1}+1}{4\pi}}\,\delta_{m_{1},0}.$$
(6.38)
Adding up the two contributions, we have

$$I_{\text{SD}}^{(1)} = \frac{2\pi i}{k} \sum_{B \neq A} f_A^*(\mathbf{k}_f, \mathbf{k}_i) \sum_{\substack{l_1 m_1 \\ l_A l_B}} (-1)^{m_1} (2l_A + 1) \sqrt{(2l_B + 1)(2l_1 + 1)} j_{l_1}^2(kx_{AB}) Y_{l_1}^{m_1}(\theta_{fi}, 0) Y_{l_B}^{-m_1}(\theta_{fi}, 0) \times \begin{pmatrix} l_A & l_B & l_1 \\ 0 & -m_1 & m_1 \end{pmatrix} \begin{pmatrix} l_A & l_B & l_1 \\ 0 & 0 & 0 \end{pmatrix} a_{l_A}(k, k) a_{l_B}(k, k) + \text{c.c.} + \frac{i}{2k} \sum_{B \neq A} f_B^*(\mathbf{k}_f, \mathbf{k}_i) \sum_{l_1 l_A l_B} (2l_A + 1)(2l_B + 1)(2l_1 + 1) j_{l_1}^2(kx_{AB}) P_{l_B}(\cos \theta_{fi}) \times \begin{pmatrix} l_A & l_B & l_1 \\ 0 & 0 & 0 \end{pmatrix}^2 a_{l_A}(k, k) a_{l_B}(k, k) + \text{c.c.}$$
(6.39)

When $A \neq B \neq C$, I_p for $I_{SD}^{(2)}$ is the same as in equations eqs.(6.31)-(6.33), but the orientational average now involves

$$\ll \exp(i\mathbf{k}_{f} \cdot \mathbf{x}_{CB} + i\mathbf{k}_{i} \cdot \mathbf{x}_{AC}) Y_{l_{1}}^{m_{1}}(\hat{\mathbf{x}}_{BA}) \gg$$

$$= (4\pi)^{2} \sum_{\substack{l_{2}m_{2} \\ l_{3}m_{3}}} i^{l_{2}+l_{3}} j_{l_{2}}(kx_{AC}) j_{l_{3}}(kx_{CB}) Y_{l_{2}}^{m_{2}}(\hat{\mathbf{z}}) Y_{l_{3}}^{m_{3}}(\boldsymbol{\theta}_{fi}, 0) \ll Y_{l_{2}}^{m_{2}*}(\hat{\mathbf{x}}_{AC}) Y_{l_{3}}^{m_{3}*}(\hat{\mathbf{x}}_{CB}) Y_{l_{1}}^{m_{1}}(\hat{\mathbf{x}}_{BA}) \gg,$$

$$(6.40)$$

and the orientational average of the spherical harmonics is

$$\ll Y_{l_{2}}^{m_{2}*}(\hat{\mathbf{x}}_{AC})Y_{l_{3}}^{m_{3}*}(\hat{\mathbf{x}}_{CB})Y_{l_{1}}^{m_{1}}(\hat{\mathbf{x}}_{BA}) \gg$$

$$= \sum_{m_{1}'m_{2}'m_{3}'} \frac{1}{8\pi^{2}} \int \mathscr{D}_{m_{1}m_{1}'}^{l_{1}*}(\Omega)\mathscr{D}_{m_{2}m_{2}'}^{l_{2}}(\Omega)\mathscr{D}_{m_{3}m_{3}'}^{l_{3}}(\Omega) d\Omega Y_{l_{1}}^{m_{1}'}(\hat{\mathbf{x}}_{BA}')Y_{l_{2}}^{m_{2}'*}(\hat{\mathbf{x}}_{AC}')Y_{l_{3}}^{m_{3}'*}(\hat{\mathbf{x}}_{CB}'). \quad (6.41)$$

Using eq. (6.67), and noting that $m_2 = 0$ and $m'_1 = 0$ since $Y_l^m(\hat{\mathbf{z}}) = \sqrt{(2l+1)/(4\pi)} \delta_{m,0}$,

$$\ll Y_{l_{2}}^{m_{2}*}(\hat{\mathbf{x}}_{AC})Y_{l_{3}}^{m_{3}*}(\hat{\mathbf{x}}_{CB})Y_{l_{1}}^{m_{1}}(\hat{\mathbf{x}}_{BA}) \gg$$

$$= \sum_{m_{2}'} (-1)^{m_{1}} \begin{pmatrix} l_{2} \quad l_{3} \quad l_{1} \\ 0 \quad m_{1} \quad -m_{1} \end{pmatrix} \begin{pmatrix} l_{2} \quad l_{3} \quad l_{1} \\ m_{2}' \quad -m_{2}' \quad 0 \end{pmatrix} \sqrt{\frac{2l_{1}+1}{4\pi}} Y_{l_{2}}^{m_{2}'*}(\hat{\mathbf{x}}_{AC}')Y_{l_{3}}^{-m_{2}'*}(\hat{\mathbf{x}}_{CB}')\delta_{m_{1},m_{3}}.$$

$$(6.42)$$

Putting everything together, and reassigning $m'_2 \rightarrow m_2$, we get

$$I_{\text{SD}}^{(2)} = \frac{8\pi^{2}i}{k} \sum_{A \neq B \neq C} f_{C}^{*}(\mathbf{k}_{f}, \mathbf{k}_{i}) \sum_{\substack{l_{1}l_{2}l_{3} \\ m_{1}m_{2}}} i^{l_{1}+l_{2}+l_{3}} (2l_{1}+1)\sqrt{2l_{2}+1} j_{l_{1}}(kx_{AB}) j_{l_{2}}(kx_{AC}) j_{l_{3}}(kx_{BC})$$

$$\times Y_{l_{3}}^{m_{1}}(\theta_{fi}, 0) Y_{l_{2}}^{m_{2}^{\prime}*}(\hat{\mathbf{x}}_{AC}') Y_{l_{3}}^{-m_{2}^{\prime}*}(\hat{\mathbf{x}}_{CB}') \begin{pmatrix} l_{2} & l_{3} & l_{1} \\ 0 & m_{1} & -m_{1} \end{pmatrix} \begin{pmatrix} l_{2} & l_{3} & l_{1} \\ m_{2}^{\prime} & -m_{2}^{\prime} & 0 \end{pmatrix}$$

$$\times \sum_{l_{A}l_{B}} (2l_{A}+1)\sqrt{2l_{B}+1} a_{l_{A}}(k,k) a_{l_{B}}(k,k) Y_{l_{B}}^{-m_{1}}(\theta_{fi}, 0) \begin{pmatrix} l_{A} & l_{B} & l_{1} \\ 0 & -m_{1} & m_{1} \end{pmatrix} \begin{pmatrix} l_{A} & l_{B} & l_{1} \\ 0 & 0 & 0 \end{pmatrix}$$

$$+ \text{c.c.} \qquad (6.43)$$

We found an inconsistency in the derivation from Hayashi & Kuchitsu (1976) in the way that the coordinate systems were handled. To obtain a simpler expression for $I_{SD}^{(2)}$, they redefined the *z*-axis in the lab frame to be along \mathbf{k}_f , but only within the orientational average part of the calculation. In the remainder of the calculation, they used the standard convention of aligning \mathbf{k}_i along $\hat{\mathbf{z}}$. This inconsistency is not justified, and the expressions we obtain are different from those derived in Hayashi & Kuchitsu because we kept the coordinate systems in both the lab and molecule frames consistent throughout the calculations for each term and also between terms.

We now turn to eq. (6.26), which captures the terms involving two double scatterings. There are four distinct possibilities as shown in fig. 6.4. The first, $I_{DD}^{(0)}$, corresponds to the case where $A = C \neq B = D$, and is given by

$$I_{\text{DD}}^{(0)} = \frac{\pi}{k^2} \sum_{A \neq B} \sum_{l_3 m_3} (2l_3 + 1) j_{l_3}^2(kx_{AB})$$

$$\times \left| \sum_{l_1 l_2} (2l_1 + 1) \sqrt{2l_2 + 1} Y_{l_2}^{-m_3}(\theta_{fi}, 0) \begin{pmatrix} l_A & l_B & l_1 \\ 0 & -m_3 & m_3 \end{pmatrix} \begin{pmatrix} l_A & l_B & l_1 \\ 0 & 0 & 0 \end{pmatrix} a_{l_A}(k, k) a_{l_B}(k, k) \right|^2$$
(6.44)

Next, $I_{DD}^{(1)}$ represents the situation when $D = A \neq C = B$, which becomes

$$I_{\text{DD}}^{(1)} = \frac{1}{(2\pi)^4} \sum_{A \neq B} \ll \exp[-i(\mathbf{k}_i + \mathbf{k}_f) \cdot \mathbf{x}_{BA}] \times I_p^{\prime *} \times I_p \gg .$$
(6.45)

For convenience we define a new vector which is the sum of \mathbf{k}_i and \mathbf{k}_f

$$\mathbf{k}_{if} = \mathbf{k}_i + \mathbf{k}_f$$

$$k_{if} = 2k\cos(\theta_{fi}/2), \qquad (6.46)$$

and after carrying out the calculation, we get

$$\begin{split} I_{\text{DD}}^{(1)} &= \frac{1}{\sqrt{4\pi}} \left(\frac{2\pi}{k}\right)^2 \sum_{A \neq B} \sum_{\substack{l_1 l_2 l_3 \\ m_1 m_2 m_3}} i^{l_1 + l_2 + l_3} (-1)^{m_1 + m_3 + l_3} (2l_1 + 1)(2l_2 + 1)\sqrt{2l_3 + 1} \\ &\times j_{l_1}(kx_{AB}) j_{l_2}(kx_{AB}) j_{l_3}(k_{if} x_{AB}) Y_{l_3}^{m_3}(\hat{\mathbf{k}}_{if}) \begin{pmatrix} l_1 & l_2 & l_3 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l_1 & l_2 & l_3 \\ m_1 & -m_2 & -m_3 \end{pmatrix} \\ &\times \sum_{l_A l_B} (2l_A + 1)\sqrt{2l_B + 1} Y_{l_B}^{-m_1}(\boldsymbol{\theta}_{fi}, 0) \begin{pmatrix} l_A & l_B & l_1 \\ 0 & -m_1 & m_1 \end{pmatrix} \begin{pmatrix} l_A & l_B & l_1 \\ 0 & 0 & 0 \end{pmatrix} a_{l_A}(k,k) a_{l_B}(k,k) \\ &\times \sum_{l_A' l_B'} (2l_B' + 1)\sqrt{2l_A' + 1} Y_{l_A'}^{-m_2*}(\boldsymbol{\theta}_{fi}, 0) \begin{pmatrix} l_B' & l_A' & l_2 \\ 0 & -m_2 & m_2 \end{pmatrix} \begin{pmatrix} l_B' & l_A' & l_2 \\ 0 & 0 & 0 \end{pmatrix} a_{l_A'}^*(k,k) a_{l_B'}^*(k,k) . \end{split}$$

$$(6.47)$$

For $I_{\text{DD}}^{(2)}$, there are three cases which we shall label $I_{\text{DD}}^{(2a)}$, $I_{\text{DD}}^{(2b)}$, and $I_{\text{DD}}^{(2c)}$. The first corresponds to taking $C \to A, D \to C$; $I_{\text{DD}}^{(2b)}$ corresponds to taking $D \to B$; and $I_{\text{DD}}^{(2c)}$ is when $C \to B, D \to C$.

$$I_{\text{DD}}^{(2a)} = \frac{1}{(2\pi)^4} \sum_{A \neq B \neq C} \ll \exp(i\mathbf{k}_f \cdot \mathbf{x}_{CB}) \times I_{p,CA}^{\prime*} \times I_{p,BA} \gg$$
(6.48)

$$I_{\text{DD}}^{(2b)} = \frac{1}{(2\pi)^4} \sum_{A \neq B \neq C} \ll \exp(i \,\mathbf{k}_f \cdot \mathbf{x}_{AC}) \times I_{p,BC}^{\prime*} \times I_{p,BA} \gg$$
(6.49)

$$I_{\text{DD}}^{(2c)} = \frac{1}{(2\pi)^4} \sum_{A \neq B \neq C} \ll \exp(i\mathbf{k}_f \cdot \mathbf{x}_{CB} + i\mathbf{k}_i \cdot \mathbf{x}_{AB}) \times I_{p,CB}^{\prime*} \times I_{p,BA} \gg, \tag{6.50}$$

where $I_{p,BA}$ is the same as I_p from eq. (6.34), and

$$I_{p,CA}^{\prime*} = i \frac{(2\pi)^3}{k} \sum_{\substack{l_C l'_A \\ l_2 m_2}} (-i)^{l_2} (-1)^{m_2} (2l'_A + 1) \sqrt{(2l_C + 1)(2l_2 + 1)} Y_{l_2}^{m_2*}(\hat{\mathbf{x}}_{CA}) Y_{l_C}^{-m_2*}(\theta_{fi}, 0)$$

$$\times \begin{pmatrix} l'_A & l_C & l_2 \\ 0 & -m_2 & m_2 \end{pmatrix} \begin{pmatrix} l'_A & l_C & l_2 \\ 0 & 0 & 0 \end{pmatrix} j_{l_2}(kx_{CA}) a_{l'_A}^*(k, k) a_{l_C}^*(k, k), \qquad (6.51)$$

$$(2\pi)^3$$

$$I_{p,BC}^{\prime*} = i \frac{(2\pi)^{3}}{k} \sum_{\substack{l'_{B} l_{C} \\ l_{2} m_{2}}} (-i)^{l_{2}} (-1)^{m_{2}} (2l_{C}+1) \sqrt{(2l'_{B}+1)(2l_{2}+1)} Y_{l_{2}}^{m_{2}*}(\hat{\mathbf{x}}_{BC}) Y_{l'_{B}}^{-m_{2}*}(\theta_{fi},0)$$

$$\times \begin{pmatrix} l_{C} & l'_{B} & l_{2} \\ 0 & -m_{2} & m_{2} \end{pmatrix} \begin{pmatrix} l_{C} & l'_{B} & l_{2} \\ 0 & 0 & 0 \end{pmatrix} j_{l_{2}}(kx_{BC}) a_{l'_{B}}^{*}(k,k) a_{l_{C}}^{*}(k,k), \qquad (6.52)$$

$$I_{p,CB}^{\prime*} = i \frac{(2\pi)^{3}}{k} \sum_{\substack{l'_{B} l_{C} \\ l_{2} m_{2}}} (-i)^{l_{2}} (-1)^{m_{2}} (2l'_{B}+1) \sqrt{(2l_{C}+1)(2l_{2}+1)} Y_{l_{2}}^{m_{2}*}(\hat{\mathbf{x}}_{CB}) Y_{l_{C}}^{-m_{2}*}(\theta_{fi},0)$$

$$\times \begin{pmatrix} l'_{B} & l_{C} & l_{2} \\ 0 & -m_{2} & m_{2} \end{pmatrix} \begin{pmatrix} l'_{B} & l_{C} & l_{2} \\ 0 & 0 & 0 \end{pmatrix} j_{l_{2}}(kx_{BC}) a^{*}_{l'_{B}}(k,k) a^{*}_{l_{C}}(k,k).$$
(6.53)

The orientational averages for the three cases are

$$\ll \exp(i\mathbf{k}_{f} \cdot \mathbf{x}_{CB}) Y_{l_{2}}^{m_{2}*}(\hat{\mathbf{x}}_{CA}) Y_{l_{1}}^{m_{1}}(\hat{\mathbf{x}}_{BA}) \gg = \sqrt{4\pi} \sum_{l_{3}m_{3}m'_{3}} i^{l_{3}}(-1)^{m_{2}+m_{3}+m'_{3}} \sqrt{2l_{1}+1}$$

$$\times j_{l_{3}}(kx_{CB}) Y_{l_{3}}^{m_{3}}(\theta_{fi},0) Y_{l_{2}}^{m'_{3}}(\hat{\mathbf{x}}_{CA}') Y_{l_{3}}^{m'_{3}}(\hat{\mathbf{x}}_{CB}') \begin{pmatrix} l_{1} & l_{2} & l_{3} \\ 0 & m'_{3} & -m'_{3} \end{pmatrix} \begin{pmatrix} l_{1} & l_{2} & l_{3} \\ m_{1} & -m_{2} & -m_{3} \end{pmatrix}, \quad (6.54)$$

$$\ll \exp(i\mathbf{k}_{i} \cdot \mathbf{x}_{AC}) Y_{l_{2}}^{m_{2}*}(\hat{\mathbf{x}}_{BC}) Y_{l_{1}}^{m_{1}}(\hat{\mathbf{x}}_{BA}) \gg = \sum_{l_{3}m'_{3}} i^{l_{3}}(-1)^{m_{1}+m'_{3}} \sqrt{(2l_{1}+1)(2l_{3}+1)}$$

$$\times j_{l_{3}}(kx_{AC}) Y_{l_{2}}^{m'_{3}}(\hat{\mathbf{x}}_{BC}') Y_{l_{3}}^{m'_{3}}(\hat{\mathbf{x}}_{AC}') \begin{pmatrix} l_{1} & l_{2} & l_{3} \\ 0 & m'_{3} & -m'_{3} \end{pmatrix} \begin{pmatrix} l_{1} & l_{2} & l_{3} \\ m_{1} & -m_{1} & 0 \end{pmatrix}, \qquad (6.55)$$

$$\ll \exp(i\mathbf{k}_{f} \cdot \mathbf{x}_{CB} + i\mathbf{k}_{i} \cdot \mathbf{x}_{AC}) Y_{l_{2}}^{m_{2}*}(\hat{\mathbf{x}}_{CB}) Y_{l_{1}}^{m_{1}}(\hat{\mathbf{x}}_{BA}) \gg$$

$$= \sqrt{4\pi} \sum_{\substack{l_{3}m_{3} \\ l_{4}l_{5}}} i^{l_{3}+l_{4}}(-1)^{l_{4}-m_{1}+m_{2}+m_{3}} \sqrt{2l_{1}+1}(2l_{4}+1)(2l_{5}+1)$$

$$\times j_{l_{3}}(kx_{CB}) j_{l_{4}}(kx_{AB}) Y_{l_{3}}^{m_{2}-m_{1}}(\theta_{fi},0) Y_{l_{2}}^{m_{3}*}(\hat{\mathbf{x}}_{CB}') Y_{l_{3}}^{m_{3}}(\hat{\mathbf{x}}_{CB}')$$

$$\times \begin{pmatrix} l_{1} & l_{4} & l_{5} \\ -m_{1} & 0 & m_{1} \end{pmatrix} \begin{pmatrix} l_{1} & l_{4} & l_{5} \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l_{5} & l_{2} & l_{3} \\ -m_{1} & m_{2} & m_{1}-m_{2} \end{pmatrix} \begin{pmatrix} l_{5} & l_{2} & l_{3} \\ 0 & m_{3} & -m_{3} \end{pmatrix}. \qquad (6.56)$$

Finally, when $A \neq B \neq C \neq D$, we have $I_{DD}^{(3)}$

$$\begin{split} I_{\text{DD}}^{(3)} &= \frac{16\pi^3}{k^2} \sum_{\substack{A \neq B \\ \neq C \neq D}} \sum_{\substack{\text{all} \\ \text{indices}}} i^{l_1+l_2+l_3+l_4} (-1)^{l_1+m_1+2m_2-m'_2} \\ &\times (2l+1)(2l_A+1)(2l_C+1)\sqrt{(2l_1+1)(2l_2+1)(2l_3+1)(2l_4+1)(2l_B+1)(2l_D+1)} \\ &\times j_{l_1}(kx_{CD}) j_{l_2}(kx_{AB}) j_{l_3}(kx_{AC}) j_{l_4}(kx_{BD}) \\ &\times Y_{l_1}^{m'_1*}(\hat{\mathbf{x}}_{DC}) Y_{l_2}^{m'_2}(\hat{\mathbf{x}}_{BA}) Y_{l_3}^{m_3}(\theta) Y_{l_4}^{m_4*}(\theta_{fi}, 0) Y_{l_D}^{-m_1*}(\theta_{fi}, 0) Y_{l_B}^{-m_2}(\theta_{fi}, 0) \\ &\times \begin{pmatrix} l_1 & l_2 & l \\ m_1 & m_2 & -m_4 \end{pmatrix} \begin{pmatrix} l_1 & l_2 & l \\ m'_1 & m'_2 & -m_3 \end{pmatrix} \begin{pmatrix} l_3 & l_4 & l \\ 0 & m_4 & -m_4 \end{pmatrix} \begin{pmatrix} l_3 & l_4 & l \\ m_3 & 0 & -m_3 \end{pmatrix} \\ &\times \begin{pmatrix} l_A & l_B & l_2 \\ 0 & -m_2 & m_2 \end{pmatrix} \begin{pmatrix} l_A & l_B & l_2 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l_C & l_D & l_1 \\ 0 & -m_1 & m_1 \end{pmatrix} \begin{pmatrix} l_C & l_D & l_1 \\ 0 & 0 & 0 \end{pmatrix} \\ &\times a_{l_A}(k,k) a_{l_B}(k,k) a_{l_C}^*(k,k) a_{l_D}^*(k,k), \end{split}$$
(6.57)

where the indices are $\{l, l_1 - l_4, l_A - l_D, m_1 - m_4, m'_1, m'_2\}$, we have taken $\hat{\mathbf{x}}'_{DB} = \hat{\mathbf{z}}'$ in the frame attached to the molecule, and θ is the angle between $\hat{\mathbf{x}}'_{AC}$ and $\hat{\mathbf{x}}'_{DB}$.

6.3 Numerical results and discussion

We have computed the elastic DCS using the re-derived MIAM for THF at energies of 60 eV, 80 eV, 100 eV, and 200 eV. We were restricted at the lower energy end by the optical-potential model for calculating atomic phase shifts, which is valid down to about 50 eV. As the energy increases, convergence requires more terms in the partial-wave series, which became numerically impractical above 200 eV with our current Python code. The computation of the Wigner matrices was made possible thanks to the WIGXJPF library [3], without which the computational speed of 3-j symbols would have restricted our calculations to very small molecules and very low energies below 50 eV, where convergence occurs within ten or so partial waves. We have not included the final sub-term in I_{DD} , $I_{DD}^{(3)}$, which proved too computationally expensive. It is also a higher-order term than the other terms in I_{DD} , involving scattering by 2 different atoms in each amplitude (see figure 6.4) for a total of 4 scattering events, and thus might be expected to be smaller than terms involving scattering by three atoms.

In figures 6.5 and 6.6, we plot the DCS and their contributions, respectively. We see that the DCS is now always positive, and that the largest term we did compute, $I_{DD}^{(2)}$, plays a significant role in maintaining a positive DCS at angles near $\theta = 180^{\circ}$. We find significant differences in both the magnitude and shape of the DCS between the IAM and the MIAM at lower energies, while above a few hundred eV, these differences become insignificant. As expected, the MIAM is lower than the IAM, due to the I_{SD} contribution being negative, and the I_{DD} being higher order and therefore smaller.

However, the good agreement with experiments is somewhat artificial, as it was partly due to our choice of parameters in the atomic potential. We found that empirical parameters in the absorption potential can have a drastic effect on the DCS, whereby even staying within a reasonable range of values can change the DCS by a factor of order unity, especially at low energies close to 50 eV. In particular, the absorption potential is proportional to a factor called A_{abs} , which should be of order unity [4]. We settled on a value of $A_{abs} = 1.5$, which gives good agreement between the MIAM and experimental data. As an example, when A_{abs} is made smaller, the small angle agreement with experiments improves, however elsewhere the DCS is too large (see figure 6.7).

We also calculated integrated cross sections (ICS), which are shown in table 6.1. The large discrepancies between the IAM, the MIAM, and experiment is almost entirely due to forward scattering, where the theory predicts larger DCS values by a factor of two or more. At larger angles, the DCS is smaller by a few orders of magnitude, and does not contribute significantly to the ICS. Notably, the MIAM does provide a significant improvement over the IAM at small angles, especially when we choose a smaller A_{abs} . Inclusion of the polarization potential would also be expected to improve the accuracy of the model at small scattering angles.

<i>E</i> [eV]	$\sigma_{\rm el} [{\rm cm}^2]$		
	MIAM	IAM	Baek exp. [5]
60	31.94	62.84	17.70 ± 2.48
80	28.30	48.22	15.74 ± 2.20
100	24.71	38.90	15.02 ± 2.07
200	15.53	20.18	7.52 ± 1.04

Table 6.1 Integrated elastic cross sections at various energies for the IAM, MIAM, and experimental data of Baek *et al.* [5].



Figure 6.5 DCS calculated from the MIAM and the IAM for five energies ranging from 40 eV to 200 eV, including all terms except $I_{DD}^{(3)}$, and compared with experimental data by Baek *et al.* [5], Milosavljevic *et al.* [6], Colyer *et al.* [7], and Homem *et al.* [8].

Further work is required to numerically compute the full expression including the last and most computationally intensive subterm. Programming the expressions in a computing language



Figure 6.6 Contribution of every term, normalized by the DCS, for five energies ranging from 40 eV to 200 eV. (Since the DCS is now always positive, we are able to normalize the contributions by the DCS instead of I_S , as was done previously.)

which supports parallel programming could be worth exploring. Another missing element is the polarization potential, whose inclusion was proposed in the original formulation, although the



Figure 6.7 Comparison of the DCS at 60 eV with $A_{abs} = 0.5$ and $A_{abs} = 1.5$, to show the effect of this parameter.

authors showed that its effects are expected to be small, and did not include it in their numerical calculations [1]. Extensive comparisons can also be made for a wide range of other molecules of interest. In particular, $I_{DD}^{(3)}$ is not present for diatomic and triatomic molecules, so for these the DCS can be computed exactly. However, small molecules tend to exhibit stronger polarity, such that the polarization potential should be included.

6.4 Conclusions

In implementing the MIAM proposed initially by Hayashi and Kuchitsu [1], we stumbled upon an unphysical behaviour in the theory, which yielded negative DCSs over certain angle ranges. We have re-derived the expressions in order to find any potential errors, and have identified inconsistencies in the coordinate systems in the original derivation, which we believe to be unjustified (and which were presumably introduced to simplify the mathematical expressions). We also point out that the higher-order terms introduced by the original authors would have to be included to ensure positive DCSs, and derive explicit expressions for these terms.

We computed the new MIAM DCS for THF at various energies between 60 eV and 200 eV, and compared with data from recent experiments. The choice of molecule was guided by the interest from the microdosimetry community in low-energy interaction data for molecules of biological relevance, such as DNA components or closely-related molecules. Since it is much larger than diatomic or triatomic molecules, it also serves as a test for the theory. We find that

by varying the strength of the absorption potential, A_{abs} , the MIAM DCS can be brought in very good agreement with experimental data. Other parameters in the atomic potential (e.g. relating to the nuclear charge, electron density, exchange, etc.) could also have a significant impact on the DCS, but it is beyond the scope of this work to fully explore their effects.

Appendix to chapter 6: Useful identities and relations

Expansion of a plane wave in spherical waves:

$$e^{i\mathbf{k}\cdot\mathbf{r}} = \sum_{l} (2l+1)i^{l} j_{l}(kr) P_{l}(\hat{\mathbf{k}}\cdot\hat{\mathbf{r}}).$$
(6.58)

The Legendre polynomials can be expressed in terms of spherical harmonics:

$$P_l(\hat{\mathbf{r}}\cdot\hat{\mathbf{r}}') = \frac{4\pi}{2l+1} \sum_m Y_l^m(\theta,\phi) Y_l^{m*}(\theta',\phi'), \qquad (6.59)$$

where θ and ϕ (θ' and ϕ') describe the unit vector $\hat{\mathbf{r}}$ ($\hat{\mathbf{r}}'$) in spherical coordinates.

Angular momentum addition

Relation between Clebsh-Gordan coefficients and Wigner-3j symbols:

$$\langle j_1 m_1 \, j_2 m_2 \mid j_3 m_3 \rangle = (-1)^{j_1 - j_2 + m_3} \sqrt{2j_3 + 1} \begin{pmatrix} l_1 & l_2 & l_3 \\ m_1 & m_2 & -m_3 \end{pmatrix}.$$
 (6.60)

Addition of two spherical harmonics:

$$Y_{l_{1}}^{m_{1}}(\theta,\phi)Y_{l_{2}}^{m_{2}}(\theta,\phi) = \frac{\sqrt{(2l_{1}+1)(2l_{2}+1)}}{4\pi} \sum_{l,m} \langle l_{1}m_{1}l_{2}m_{2} \mid lm \rangle \langle l_{1}0l_{2}0 \mid l0 \rangle \sqrt{\frac{4\pi}{2l+1}}Y_{l}^{m}(\theta,\phi)$$
$$= \sqrt{\frac{(2l_{1}+1)(2l_{2}+1)}{4\pi}} \sum_{l,m} (-1)^{m}\sqrt{2l+1} \begin{pmatrix} l_{1} \quad l_{2} \quad l \\ m_{1} \quad m_{2} \quad -m \end{pmatrix} \begin{pmatrix} l_{1} \quad l_{2} \quad l \\ 0 \quad 0 \quad 0 \end{pmatrix} Y_{l}^{m}(\theta,\phi).$$
(6.61)

Using the above and orthonormality:

$$\int d\Omega Y_l^{m*}(\theta,\phi) Y_{l_1}^{m_1}(\theta,\phi) Y_{l_2}^{m_2}(\theta,\phi) = (-1)^m \sqrt{\frac{(2l_1+1)(2l_2+1)(2l+1)}{4\pi}} \begin{pmatrix} l_1 & l_2 & l \\ m_1 & m_2 & -m \end{pmatrix} \begin{pmatrix} l_1 & l_2 & l \\ 0 & 0 & 0 \end{pmatrix}$$
(6.62)

Euler rotations

The orientational average is an integral over all possible orientations of the molecule. The change of basis between the lab frame coordinate system and the internal coordinate system of the molecule is described by an Euler rotation, which is a general way of representing any rotation in 3D using 3 elemental non-commuting rotations. The Euler rotation operator is denoted as $\mathscr{D}(\alpha, \beta, \gamma)$ and by convention (in quantum mechanics) consists of a rotation about *z* followed by a rotation about *y* followed by another rotation about *z*. Its matrix elements are given by

$$\mathscr{D}_{m'm}^{l}(\alpha,\beta,\gamma) = \langle l,m' \mid \mathscr{D}_{z}(\alpha) \mathscr{D}_{y}(\beta) \mathscr{D}_{z}(\gamma) \mid l,m \rangle$$
$$= \langle l,m' \left| \exp\left(\frac{-iL_{z}\alpha}{\hbar}\right) \exp\left(\frac{-iL_{y}\beta}{\hbar}\right) \exp\left(\frac{-iL_{z}\gamma}{\hbar}\right) \right| l,m \rangle.$$
(6.63)

Let **r** be a position vector in the (x, y, z)-coordinate system of the lab frame, and **r'** be the same vector in the (x', y', z')-coordinate system of the frame attached to the body of the molecule. We define the Euler rotation such that

$$|\hat{\mathbf{r}}\rangle = \mathscr{D}|\hat{\mathbf{r}}'\rangle. \tag{6.64}$$

We recall that $\langle l, m | \hat{\mathbf{r}} \rangle = Y_l^{m*}(\hat{\mathbf{r}})$, so that

$$Y_l^{m*}(\hat{\mathbf{r}}) = \sum_m' \mathscr{D}_{mm'}^l(\alpha, \beta, \gamma) Y_l^{m'*}(\hat{\mathbf{r}}').$$
(6.65)

Addition of two Wigner \mathcal{D} -matrix elements (eq. (3.8.69) in Sakurai):

$$\mathscr{D}_{m_1m_1'}^{l_1}(R)\,\mathscr{D}_{m_2m_2'}^{l_2}(R) = \sum_{l,m,m'} \left\langle l_1m_1l_2m_2 \mid lm \right\rangle \left\langle l_1m_1'l_2m_2' \mid lm' \right\rangle \mathscr{D}_{mm'}^{l}(R). \tag{6.66}$$

And again using orthogonality (note that in this case the integration is over 3 angles, hence the total solid angle is $8\pi^2$; also the Wigner \mathscr{D} -matrix elements are not orthonormal, unlike the Y_I^m):

$$\frac{1}{8\pi^2} \int d\Omega \,\mathscr{D}_{mm'}^{l*}(\Omega) \,\mathscr{D}_{m_1m_1'}^{l_1}(\Omega) \,\mathscr{D}_{m_2m_2'}^{l_2}(\Omega) = \frac{1}{2l+1} \sum_{l,m,m'} \langle l_1m_1l_2m_2 \mid lm \rangle \, \langle l_1m_1'l_2m_2' \mid lm' \rangle \,.$$
(6.67)

A spherical harmonic can be expressed as an Euler rotation with $\gamma = 0$, since it is equivalent to rotating a \hat{z} eigenket by θ and ϕ (eq. (3.6.51) in Sakurai):

$$Y_l^{m*}(\boldsymbol{\theta}, \boldsymbol{\phi}) = \sqrt{\frac{2l+1}{4\pi}} \, \mathscr{D}_{m0}^l(\boldsymbol{\alpha} = \boldsymbol{\phi}, \boldsymbol{\beta} = \boldsymbol{\theta}, \boldsymbol{\gamma} = 0).$$
(6.68)

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Chapter 7

Summary and Outlook

In the introductory chapter of the thesis we gave a brief overview of the most important quantities of interest in dosimetry and microdosimetry, while highlighting the essential role of physical interaction cross sections. Accurate dose determination for clinical radiation therapy relies on calibration factors obtained from a standards laboratory, as well as key quantities such as stopping power ratios, photon interaction coefficients, and (W_{air}/e) . Cross sections are fundamental ingredients in both calculations and measurements of these key quantities, and for this thesis we studied three models for different interaction types. Although this work is unlikely to result in changes to clinical practice in the near future, it is nonetheless relevant for fundamental research in microdosimetry and for refining key data necessary for maintaining and updating dosimetric standards.

We investigated potential improvements to the semi-empirical RBED model for electronimpact ionization of atoms, which provides differential as well as integrated cross sections and is analytical and therefore relatively very simple to implement. We have benchmarked this model against the *ab initio* distorted-wave Born approximation (DWBA), which does not yet have tabulated DCSs, and have shown that the RBED would constitute a complete data set with comparable accuracy to the gold standard, and thus enable fast implementation in new generalpurpose Monte Carlo codes. Next we studied the use of potentially more accurate Compton profiles in the relativistic impulse approximation (RIA), and quantified the overall uncertainty in mass energy-absorption coefficients from different theoretical models for calculating Compton cross sections. One particular observation we found was that the Waller-Hartree Compton energy-transfer coefficient seems to differ drastically from the RIA at low energies in the tens of keV range and below, although once we included the photoelectric effect as well, the difference in the total energy-transfer coefficient was no more than 0.4%. Finally, we identified inconsistencies and negative differential cross sections in the modified independent-atom model (MIAM) for elastic scattering of electrons and molecules, and re-derived the expressions to ensure positive cross sections. Although they will not affect energy deposition, the modified cross sections could lead to significant changes in simulated track structures, which could in turn affect the numbers and ratios of various types of DNA damage.

We now conclude with a summary and outlook section for each chapter.

7.1 **RBED** model for electron impact ionization

We studied the semi-empirical RBED model for electron-impact ionization of atoms, which combines classical binary-encounter theory and the Bethe asymptotic dipole behaviour in a simple expression without the need for empirical adjustable parameters. The only non-trivial ingredient is the optical oscillator strength (OOS), which is a property of the target and can be calculated from *ab initio* numerical methods. A simplification known as the RBEB was also proposed along with the original RBED formulation, whereby an analytical function is assumed for the OOS. Because of the additional simplicity of the RBEB, it has been the focus of many studies while the performance of the RBED model has so far not been fully assessed. We calculated RBED inner-shell ionization cross sections (integrated and differential) of neutral atoms evaluated using three types of OOSs, namely an empirical power-law OOS, analytical hydrogenic OOSs and *ab initio* OOSs calculated numerically from self-consistent atomic potentials.

We compared our results to the DWBA, and found that the RBED with either hydrogenic or numerical OOSs is generally in better agreement with DWBA integrated cross sections (ICSs) than the RBEB. Due to the slow convergence of the DWBA calculations, only ICS results have been tabulated, therefore semi-empirical models can provide DCSs which have not yet been tabulated using *ab initio* methods. However, at highly-relativistic energies the RBED model cannot recover the Bethe asymptotic limit because of its different energy-dependent prefactor, hence we considered an alternative prefactor which restores the correct Bethe asymptote.

As a follow-up, we could implement the RBED DCS and ICS in existing Monte Carlo codes, and gauge their performance in microdosimetric energy deposition studies. We could also implement other semi-empirical models, such as the Hippler model, which is based on the PWBA formalism with hydrogenic generalized oscillator strengths (GOSs) and includes

Coulomb, relativistic, and exchange corrections, as well as the transverse interaction mediated by virtual photons.

7.2 Relativistic impulse approximation for Compton scattering

The RIA model for Compton scattering accounts for binding effects and Doppler broadening, and its DDCS is an analytical expression except for the Compton profile (CP) of each atomic or molecular orbital, which is computed from the corresponding momentum distribution. We calculated differential and integrated cross sections for materials of dosimetric relevance using molecular as opposed to atomic CPs in order to study the potential improvements of a more accurate input in the theory. We also calculated mass attenuation (μ^{C}/ρ) and mass energy-transfer (μ_{tr}^{C}/ρ) coefficients for air, water and graphite, comparing our results to the simpler Klein-Nishina and Waller-Hartree theories in order to establish the uncertainty in the mass energy-absorption coefficient (μ_{en}/ρ) resulting from using different models for Compton scattering.

We found that differences in μ^{C}/ρ and μ_{tr}^{C}/ρ between molecular and atomic CPs in the RIA are small relative to the differences between the RIA, WH, and KN models. Although the WH binding corrections seem accurate for μ^{C}/ρ , there are significant discrepancies in μ_{tr}^{C}/ρ between the WH and RIA results due to their vastly different DCS differential in energy loss. For lower energies, the disagreement can grow up to about one order of magnitude at 1 keV. However, the photoelectric effect transfers far more energy than the Compton interaction in the tens of keV range and below, and hence the differences in the total μ_{en}/ρ values resulting from the choice of Compton models (KN, WH, or RIA) are within 0.4%.

To expand upon this work, a complete calculation of photon mass attenuation, energytransfer, and energy-absorption coefficients could be calculated using the RIA with CPs from molecular electron densities, and tabulated for all materials of interest for radiation research and applications. Including the latest data for the photoelectric effect as well, such an effort would amount to an update on the previous work of Seltzer [1]. Another side project could be to calculate and provide tables of CPs for all the occupied atomic (sub)shells, so as to provide an updated version of the Biggs *et al* database [2], but with more tabulated points for interpolation accuracy and more decimal places in the data.

7.3 Modified independent-atom model (MIAM) for elastic scattering of electrons in molecules

The commonly used independent-atom model (IAM) for elastic scattering of electrons in molecules consists of a coherent sum of atomic scattering amplitudes while accounting for atomic positions within the molecule. Here we studied a more sophisticated model known as the modified independent-atom model (MIAM), which includes a long-range polarization potential in addition to the short-range potential. The short-range interaction was described as multiple scattering within the Born approximation, with higher-order terms representing successive scattering events off of different atoms. Many theoretical and experimental studies since then have calculated cross sections using the MIAM [3–5], including recent very work focusing on DNA [6, 7]. However, we have found the DCS to be negative over certain angle ranges and at energies of about 100 eV or less, where this model is expected to perform better than the IAM and which is of particular interest to microdosimetry. After identifying further inconsistencies, we re-derived the expressions and found a potential error in the original authors' handling of coordinate systems. Furthermore, we emphasize that in order to guarantee positive cross sections, additional higher-order terms must be included. We computed our re-derived expressions and carried out comparisons to experiments, where we found excellent agreement given a certain choice of parameters in the atomic potential.

Further work could branch off in many directions, since there are still many open questions. In order to numerically compute the full expression including the last and most computationally expensive subterm, we could explore the use of a computing language which supports parallel programming. Another avenue would be to study the effects of including the polarization potential, which could have a significant impact at small scattering angles and for more polar molecules. We could also explore the effects of varying the different atomic potential parameters, especially the empirical ones such as the absorption potential strength. Finally, extensive comparisons could also be made for a wide range of other molecules of interest, wherever experimental data is available.

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