

# Exchange effects in low energy electron impact ionization of the inner and outer shells of argon

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## Abstract

First order distorted wave Born approximation (DWBA) triple differential cross sections are reported for low-energy electron-impact ionization of the inner 3s and outer 3p shells of argon. Previous DWBA works have demonstrated that experiment and theory are not in accord for low energy ionization of inert gases and here we investigate the importance of exchange scattering. Different approximations for treating exchange scattering are investigated. It is shown that exchange scattering is particularly important for 3s ionization. Even with a proper treatment of exchange, the first order calculations are still not in satisfactory agreement with experiment. Consequently higher order effects will have to be included to achieve a satisfactory description of the low-energy ionization process. We also investigated both the Hartree–Fock and optimized potential methods for calculating atomic wavefunctions and static potentials and found that both methods produced almost the same cross sections.

## 1. Introduction

Experimental measurements of the triple differential cross section (TDCS) for electron impact ionization of atoms (normally referred to as (e, 2e)) can be categorized as asymmetric if the two final state electrons have different energies or symmetric if the energies are the same. Both types of experiments are interesting and tend to probe different types of physical effects. Although there have been numerous measurements of both types made, most of the work has concentrated on hydrogen or helium. Excellent reviews of this work have been given by Weigold and McCarthy (1978), McCarthy and Weigold (1988), Weigold (1990), Lahmam-Bennani (1991), Walters *et al* (1993), Whelan *et al* (1993), Coplan *et al* (1994) and Jones and Madison (2000). For the case of the heavier inert gases, the first order distorted wave Born

approximation (DWBA) normally yields relatively good agreement with the experimental data particularly for energies of about 100 eV or higher (Zhang *et al* 1992, 1993, Avaldi *et al* 1993, Bell *et al* 1995, Cavanagh and Lohmann 1997, Brion *et al* 1998, Cavanagh *et al* 1999, Taouil *et al* 1999).

Surprisingly, it has been only very recently that the first experimental TDCS results for low-energy electron impact ionization of a heavy target in the coplanar asymmetric geometry have been reported for ionization of the 3s and 3p shells of argon (Haynes and Lohmann 2000, 2001a, 2001b). In those works, very poor agreement was found with the DWBA calculations of Madison and Lang (1981) and McCarthy (1995). For the 3s shell, the DWBA calculations predicted incorrect positions for the peaks, incorrect shapes and incorrect ratios of binary to recoil peaks. The DWBA recoil peaks were larger than the binary peaks and apparently significantly larger than the experimental measurements. The experimental binary and recoil peaks were shifted away from the DWBA in the direction that would be expected if there were a strong final state repulsion between the ejected and ionized electrons (often called post-collision interaction—PCI). Since PCI is not included in the DWBA except through first order perturbation theory, it was thought that this might account for some of the discrepancy between experiment and theory. However, one of the standard methods for including PCI which has been relatively successful is to approximate PCI using the Gamov factor (Whelan *et al* 1994) and it was found that the Gamov factor produced much smaller shifts in the peaks than the observed differences between experiment and theory. For the 3p shell, the asymmetric experimental data displayed a double peak structure for the binary peak which was not well reproduced by the DWBA and the shape and position of the recoil peak was also not in agreement with the DWBA. In short, the DWBA, which has typically been fairly successful for higher energy asymmetric collisions, did not produce even qualitative agreement with the asymmetric low-energy data for ionization of argon 3s and 3p shells.

An even more severe test of theory is presented by the symmetric collisions in which both final state electrons have the same energy and are observed at the same scattering angles on opposite sides of the beam direction in the scattering plane. Measurements of this type have been made on the 2s and 2p shells of neon (Rioual *et al* 1995, 1997) and the 3p shell of argon (Bell *et al* 1995, Rouvellou *et al* 1998). DWBA calculations including initial channel polarization and PCI using the Gamov factor were performed for neon and argon (Rioual *et al* 1997, Rouvellou *et al* 1998). It was found that these two effects lead to a small improvement in the overall agreement with experimental data but significant discrepancies between theory and experiment were found particularly for incident energies below 100 eV. More recently, Haynes and Lohmann (2001a) presented the first symmetric measurements for low-energy ionization of the 3s shell of argon. There were no theoretical calculations available to compare with those data. However, the data show a different behaviour than had been previously found for 3p scattering and the data suggest that double scattering may be more important for low-energy scattering from the 3s shell than the 3p shell.

The three primary physical effects that are likely to cause the disagreement between experiment and theory for low energies are PCI, charge cloud polarization and electron exchange. The best currently available method for treating PCI in a first-order calculation is through the Gamov factor and it has already been demonstrated that this factor is not able to describe the current large differences between experiment and theory. Consequently, if PCI is important, it will have to be treated in a higher order approximation. In this paper we will concentrate on electron exchange. Electron exchange enters a calculation in two different ways. The first is through the exchange amplitude in which the roles of the projectile and ejected electron are reversed. Essentially all theories include the calculation of both the direct and exchange amplitudes and this is not the concern for this paper. The second effect of

exchange occurs in the calculation of the continuum electron wavefunction. In the standard distorted wave treatment, the continuum wavefunction is found by solving the Schrödinger equation for some effective static potential representing the atom or ion. This static potential does not take into account the fact that the projectile electron can potentially exchange with any of the atomic electrons. This is the type of exchange that will be examined in this paper.

The importance of this exchange effect has been known for a few years now. It first became apparent through the investigation of (e, 2e) processes for spin polarized electrons. Investigations of spin effects have been performed for inert gases (Duemmler *et al* 1993, Guo *et al* 1996, Dorn *et al* 1997, Granitza *et al* 1996, Mette *et al* 1998) and the alkali atoms (Baum *et al* 1992). When experiment and theory were compared for the inert gases, it was found that the standard first-order DWBA was in good accord with the spin asymmetry measurements in some cases but not others. It was subsequently determined that the discrepancy between experiment and theory lay not in relativistic effects as one might assume but rather in an inadequate treatment of exchange between the projectile electron and atomic electrons (Madison *et al* 1996a, 1996b, 1998, Mazevet *et al* 1998a, 1998b). Whereas a proper treatment of this exchange effect would consist of a Hartree–Fock (HF) treatment for the projectile electron wavefunction, it was found that the discrepancy between experiment and theory could be resolved using the more elementary Furness–McCarthy (1973) local approximation (to be referred to as FM) for exchange between the projectile electron and the target electrons (PTX) and this method has been widely used to approximate exchange.

In this paper we study the effects of electron exchange on low energy electron ionization of the 3s and 3p shells of argon. Both the role of the intra-target exchange (ITX) and the exchange between the PTX are examined. The ITX effect is often treated within the Slater approximation which, up to some overall prefactor, is identical with the local density approximation (LDA) of density functional theory (DFT) (Dreizler and Gross 1990). It is well known, however, that this local type of density functional completely misrepresents the self-interaction component of the exchange energy and, in particular, the exchange potential (see e.g. Engel and Dreizler (1999)). The usefulness of the density functional approach for the description of excitation and ionization processes might thus appear questionable. However, an accurate treatment of exchange within DFT is possible on the basis of the optimized potential method (OPM) (Sharp and Horton 1953, Talman and Shadwick 1976). Starting from the Fock expression for the exchange energy  $E_x$ , the OPM provides the optimum multiplicative exchange potential. If the correlation part of the exchange–correlation functional  $E_{xc}$  of DFT is neglected,  $E_{xc} \approx E_x$  (exchange-only limit), the OPM results for the ground state properties of atoms and molecules are very close to their HF counterparts (Engel and Dreizler 1999, Engel *et al* 2000). This is true not only for total energies, but also for more subtle quantities such as ionization potentials, bond lengths or dissociation energies. In addition, it has been shown that the OPM yields more realistic results than the LDA or Slater approximation in the case of ion–atom collisions (Kirchner *et al* 1997, 1998, Gulyas *et al* 2000). Here, we demonstrate that the exchange-only OPM is equivalent to the HF approximation also for (e, 2e) processes, in spite of the completely different single-particle spectra of the two approaches.

The DWBA calculations reported by Rioual *et al* (1997) and Rouvellou *et al* (1998) for low-energy symmetric ionization of the 3p shell of argon used the FM local approximation for PTX which was thought to be adequate. However, the validity of the FM approximation for the PTX has been challenged by Winkler *et al* (1999) who used projectile wavefunctions calculated by the full HF method. They compared their results with the low-energy symmetric experimental data of Rouvellou *et al* (1998) and found that exchange effects were very important for low energies and that the FM method was not an accurate approximation for the full proper treatment of exchange. However, we shall show here that if the FM approximation is used with a judicious

choice of charge densities, it can lead to more accurate results than previous works would suggest. A detailed discussion of the FM approximation is contained in the theory section.

## 2. Theory

In the present work, we use the DWBA approach to calculate direct and exchange amplitudes. Since the details of this theory can be found elsewhere (Madison *et al* 1996a, 1996b), we will only present those aspects necessary for the present discussion. In the DWBA, the direct scattering amplitude may be expressed as

$$f = \langle \chi_a^- \chi_b^- \psi_I | V - U_i | \psi_A \chi_i^+ \rangle \quad (1)$$

where  $\chi_i$  is the wavefunction for the incoming electron,  $\chi_a$  and  $\chi_b$  are the wavefunctions for the two final state electrons,  $\psi_A$  is the initial atomic wavefunction,  $\psi_I$  is the wavefunction for the final state ion,  $V$  is the full interaction between the incident electron and the atom and  $U_i$  is an initial state spherically symmetric static approximation for  $V$ . In the direct amplitude, the incident electron is finally in  $\chi_a$  and the ejected atomic electron is in  $\chi_b$ . The initial state projectile wavefunction (normally called a distorted wave) is a solution of the Schrödinger equation

$$(T_p + U_i - \varepsilon_i) \chi_i^+ = 0. \quad (2)$$

Here  $T_p$  is the kinetic energy operator for the projectile electron and  $\varepsilon_i$  is the energy. The initial state distorting potential  $U_i$  is asymptotically zero so the initial state distorted wave is a phase shifted plane wave. The two final state distorted waves satisfy a Schrödinger equation similar to (2) except that the final state distorting potential  $U_f$  is a spherically symmetric potential for a positive ion. Consequentially, the final state distorted waves are asymptotically phase shifted Coulomb waves. The same distorting potential is used for both final state continuum electrons.

The exchange amplitude  $g$  is identical in form to equation (1) except that the incident projectile electron is finally in  $\chi_b$  and the ejected atomic electron is in  $\chi_a$ . Exchange enters the theory in two different ways. In addition to the exchange amplitude  $g$ , exchange also plays a role in the calculation of the continuum wavefunctions.

We have examined two different treatments of treating PTX for the continuum wavefunctions. In the first, the full HF approximation (Froese Fischer 1978, Saha 1990, Winkler *et al* 1999) is used to calculate both the bound and continuum wavefunctions. In the HF method, the equation for the initial state continuum electron which must be solved self-consistently can be written as,

$$(T_p + V_i - \varepsilon_i) \chi_i^+(r) = \int V_{ex}(r, r') \chi_i^+(r') dr'. \quad (3)$$

Here  $V_i$  is the direct potential and  $V_{ex}$  is the non-local exchange potential. The method we have used to solve equation (3) is described in Winkler *et al* (1999). An unrestricted HF calculation is performed for the initial state which means that both the atomic wavefunctions are varied as well as the continuum wavefunction in the self consistent method. As a result, the initial state contains the effects of both exchange and polarization. The frozen core approximation is used for the final state which means that the bound state wavefunctions for the ion are fixed the same as the self consistent wavefunctions for the initial state. Using the frozen core approximation implies a final core polarization equivalent to the initial state core polarization. Consequently, polarization is included in the HF approach to the extent of this approximation. Although we are not explicitly investigating polarization in this work, we believe that we have in fact included the most important polarization effects in this HF calculation since the initial state neutral atom is more highly polarizable than the final state ion.

Due to the difficulties involved in obtaining solutions to the integro-differential equation (3), it is often desirable to make simplifying approximations. The second calculation we performed is the standard DWBA (Madison and Lang 1981) in which the non-local exchange potential in equation (3) is assumed to have a delta function behaviour in the coordinates. In this approximation, which is often called the static exchange approximation, the initial state distorted wave is obtained from

$$(T_0 + U_i - \varepsilon_i)\chi_i^+(r) = U_{ex}(r)\chi_i^+(r). \quad (4)$$

Here  $U_i$  is the static potential representing the atom and it is obtained from a HF calculation for an undistorted (unpolarized) isolated atom. For the local exchange potential  $U_{ex}$ , we have used the FM (1973) approximation which will be discussed later in this section. The distorted waves were also orthogonalized to the atomic wavefunctions so that the capture and shake-off amplitudes vanish (Jones *et al* 1992).

An alternative to the HF method for determining initial and final state wavefunctions and static atomic potentials is the exchange-only limit of the OPM (for an overview of the stationary OPM see Engel and Dreizler (1999), a time-dependent version has been introduced in Ullrich *et al* (1995)). As a density functional method the OPM requires the self-consistent solution of the Kohn–Sham (KS) equations,

$$\left\{ -\frac{\nabla^2}{2m} + v_s(\mathbf{r}) \right\} = \varepsilon_k \phi_k(\mathbf{r}) \quad (5)$$

$$v_s(\mathbf{r}) = v_{nuc}(\mathbf{r}) + v_H(\mathbf{r}) + v_{xc}(\mathbf{r}) \quad (6)$$

$$v_H(\mathbf{r}) = e^2 \int d^3r' \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \quad (7)$$

$$v_{xc}(\mathbf{r}) = \frac{\partial E_{xc}[n]}{\partial n(\mathbf{r})} \quad (8)$$

$$n(\mathbf{r}) = \sum_{\varepsilon_k \leq \varepsilon_F} |\phi_k(\mathbf{r})|^2 \quad (9)$$

where  $v_{nuc}$  denotes the nuclear potential,  $E_{xc}[n]$  represents the exchange–correlation (xc) energy functional of DFT (Dreizler and Gross 1990),

$$E_{xc} \equiv T_{\text{total}} - T_s - E_H - \int d^3r v_{nuc}(\mathbf{r})n(\mathbf{r}) \quad (10)$$

$$T_s = \frac{-1}{2m} \sum_{\varepsilon_k \leq \varepsilon_F} \int d^3r \phi_k^+(\mathbf{r}) \nabla^2 \phi_k(\mathbf{r}) \quad (11)$$

$$E_H = \frac{e^2}{2} \int d^3\mathbf{r} \int d^3\mathbf{r}' \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \quad (12)$$

and the density  $n$  is constructed from the  $N$  lowest KS orbitals  $\phi_k$  (the Fermi level  $\varepsilon_F$  separates the occupied from the unoccupied KS states).

In most applications of DFT explicitly  $n$ -dependent expressions such as the Slater approximation are utilized for  $E_{xc}[n]$ . The OPM extends the applicability of equations (5)–(9) to a larger class of xc-functionals, i.e. to expressions which depend on the KS orbitals,  $E_{xc}[\phi_k]$  (note that the  $\phi_k$  are functionals of  $n$  themselves,  $\phi_k[n]$ ). The prototype of such an orbital-dependent functional is the exact exchange  $E_x$  of DFT (Sahni *et al* 1982, Langreth and Mehl 1983).  $E_x$  has the same functional form as the HF exchange, with the HF orbitals replaced by their KS counterparts, i.e. the solutions of equation (5),

$$E_x = -\frac{e^2}{2} \int d^3\mathbf{r} \int d^3\mathbf{r}' \sum_{\varepsilon_k, \varepsilon_l \leq \varepsilon_F} \frac{\phi_k^*(\mathbf{r}) \phi_l(\mathbf{r}) \phi_l^*(\mathbf{r}') \phi_k(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}. \quad (13)$$

For orbital-dependent functionals such as  $E_x$ , the functional derivative  $\frac{\partial E_{xc}}{\partial n}$  required for the equation (8) must be evaluated in an indirect (numerical) manner. A suitable equation which allows one to determine  $v_{xc}$  is obtained by replacing  $\frac{\partial E_{xc}}{\partial n}$  by derivatives of  $E_{xc}$  with respect to the KS orbitals, utilizing the chain rule (Sharp and Horton 1953, Talman and Shadwick 1976). Restricting the explicit formula to the exchange-only limit  $E_{xc} \approx E_x$  (i.e. neglecting all correlation contributions to  $E_{xc}$ ) the resulting OPM equations read

$$v_x(\mathbf{r}) = \int d^3r' \chi_s^{-1}(\mathbf{r}, \mathbf{r}') \Lambda_x(\mathbf{r}') \quad (14)$$

$$\chi_s(\mathbf{r}, \mathbf{r}') = - \sum_{\varepsilon_k \leq \varepsilon_F} \phi_k^*(\mathbf{r}) G_k(\mathbf{r}, \mathbf{r}') \phi_k(\mathbf{r}') + \text{c.c.} \quad (15)$$

$$\Lambda_x(\mathbf{r}) = - \sum_k \int d^3r' \phi_k^*(\mathbf{r}) G_k(\mathbf{r}, \mathbf{r}') \frac{\partial E_x}{\partial \phi_k^*(\mathbf{r}')} + \text{c.c.} \quad (16)$$

$$G_k(\mathbf{r}, \mathbf{r}') = \sum_{l \neq k} \frac{\phi_l(\mathbf{r}) \phi_l^*(\mathbf{r}')}{\varepsilon_l - \varepsilon_k} \quad (17)$$

$$\frac{\partial E_x}{\partial \phi_k^*(\mathbf{r}')} = -e^2 \sum_{\varepsilon_l \leq \varepsilon_F} \phi_l(\mathbf{r}') \int d^3r \frac{\phi_l^*(\mathbf{r}) \phi_k(\mathbf{r})}{|\mathbf{r} - \mathbf{r}'|} \quad (18)$$

(for the explicit form of equations (5)–(15) for closed-shell systems see Engel and Vosko (1993); for the inclusion of correlation see Engel and Dreizler (1999)). Equations (14)–(18) have to be solved self-consistently together with the KS equations. For large  $r$  the resulting multiplicative  $v_x$  behaves as  $-\frac{e^2}{r}$  (Talman and Shadwick 1976), which reflects the exact cancellation of the self-interaction of the most weakly bound electron: any electron that is pulled away from the atom with  $N$  electrons must experience the remaining charge  $[(Z - N) + 1]$ .

As a consequence, the total  $v_s$ , equation (6), of a neutral atom decays as  $\frac{-e^2}{r}$  in the asymptotic regime, so that the OPM spectrum of this system exhibits a Rydberg series (in contrast to the HF spectrum). Once the projectile electron is also taken into account in  $v_H$  and  $v_x$  the net potential decays faster than  $\frac{1}{r}$  (as  $v_s$  no longer contains a monopole component). The asymptotic behaviour of  $v_x$  implies that the wavefunction of a projectile electron which is not included in the self-consistency procedure cannot be calculated from the total KS potential of the neutral atom, as the  $\frac{-e^2}{r}$ -behaviour of this  $v_s$  asymptotically simulates an ion. In the case of the OPM we have thus set up the initial state in the following way: the 3s and 3p target wavefunctions have been obtained from an OPM calculation for the ground state of neutral argon. The wavefunction of the incident electron has been calculated from equations (5), (6) with  $v_H$  taken from neutral argon and either  $v_{xc} = 0$ , so that the incoming electron only experiences the electrostatic potential of the target, or  $v_{xc}$  given by the FM approximation (in direct analogy with equation (4)). An analogous procedure has been applied for the final state, using the KS orbitals and the  $v_H$  obtained for the ground state of  $\text{Ar}^+$ .

### 3. The Furness–McCarthy approximation

The FM potential is frequently used in the static-exchange approximation to account for PTX. The explicit form of the FM exchange potential for the initial channel is

$$U_{ex} = -\frac{1}{2} \left\{ (\varepsilon_i - U_i) - \sqrt{(\varepsilon_i - U_i)^2 - (-)^S 2\rho(r)} \right\}. \quad (19)$$

Here  $\rho$  is the radial charge density for the atomic electrons. The FM potential was derived for electron–hydrogen scattering and as a result, it is the exchange potential for the projectile electron exchanging with one of the atomic electrons. Consequently,  $S$  is the total spin of

a two-electron system (projectile electron plus one of the atomic electrons with which the projectile could exchange) and  $\rho$  is the radial charge density for a single atomic electron. In principle, one would have an exchange potential given by (15) for each of the atomic electrons and the total exchange potential would be the sum of all these individual exchange potentials. However, to a good approximation, one can replace the sum over  $n$ -electrons with a single exchange potential given by (15) where  $\rho$  is the charge density of the  $n$ -electrons. Since  $S$  is the total spin of a two electron system, it must either be singlet or triplet (independent of the spin of the atom or ion). For triplet scattering, the potential is attractive which means that radial wavefunctions are pulled toward the origin and for singlet scattering the potential is repulsive which pushes radial wavefunctions away from the origin. One of the problems associated with this potential lies in the fact that the standard distorted wave approximation partial wave expansion is spin independent which means that the continuum waves depend upon orbital angular momentum and not spin. As a result, there is an ambiguity as to which form of the exchange potential should be used. This is not a problem, however, if the atom is in the ground state with total spin singlet. Since the exchange of the projectile electron with one of the atomic electrons cannot change the spin of the atom, the projectile electron can only exchange with an identical spin atomic electron. For exchanging with identical electrons, the exchange potential must be triplet since the total spin of the two electrons would be triplet. It should be noted, however, that only half the atomic electrons will have spins identical to the projectile so that the atomic density which is used should correspond to half the density for the full atom.

For the final state, the exchange potential could be either a singlet or a triplet for exchange with an open shell electron. However, this ambiguity can be reduced if we assume that direct scattering dominates. Let us consider ionization of the 3s shell. If the ejected electron exchanges with the remaining 3s electron, these two electrons will have to form a singlet state for direct scattering since the initial state pair of 3s electrons were singlet. On the other hand, if the ejected s electron exchanged with an electron from one of the other closed shells, it would have to exchange with only those electrons that have identical spins so that the total spin of the closed shells did not change. Consequently, exchange with a closed shell electron would have to be triplet. As a result, the singlet form of the FM potential would be used for exchange with the 3s electron and the triplet form would be used for exchange with the rest of the closed atomic shell electrons (and one would be able to exchange with only half of the electrons in the closed shells).

For ionization of the 3p shell, the situation is not clear. In the initial state the six 3p electrons were a singlet so the final state of ejected electron plus five 3p atomic electrons must be singlet (for direct scattering). Unfortunately, this does not mean that the spin of the ejected electron plus one of the 3p atomic electrons is necessarily singlet since these two electrons could be either singlet or triplet and still have the total spin of the five atomic electrons plus ejected electron couple to a singlet. It is clear though, that exchange of an ejected p-electron with one of the closed shell electrons must be triplet as above. For this work, we have treated exchange of an ejected 3p electron with a remaining 3p electron as singlet and exchange with any of the closed shell electrons as triplet (same as the 3s electron was treated).

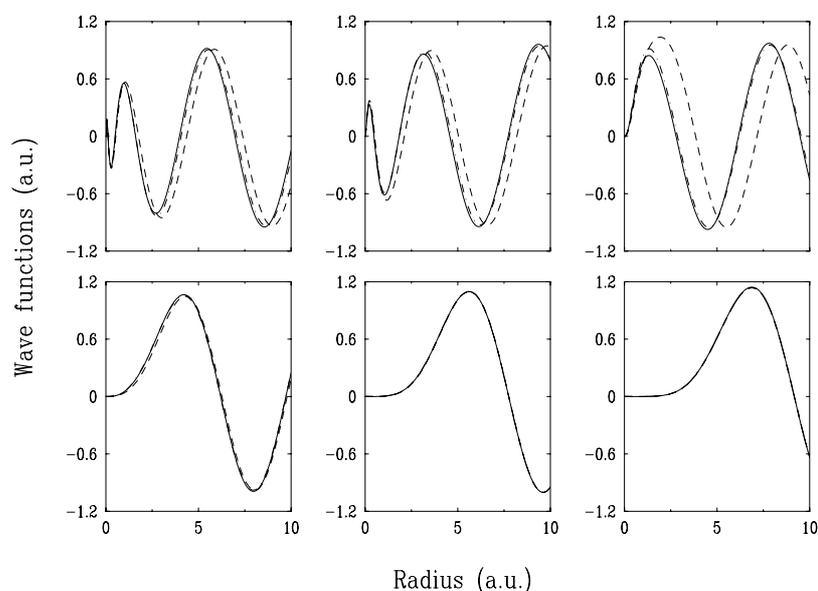
For the final state of the projectile electron, it is also clear that exchange with a closed shell electron must be triplet. Again it is not clear how to handle exchange with the remaining open shell. For this work, we have assumed that exchange with the open shell electrons for the final state of the projectile is triplet in the final channel just as it was in the initial channel where there is no ambiguity. Previous works have used triplet scattering for all shells and all three continuum wavefunctions (Bartschat and Madison 1987a, 1987b, Rouvellou *et al* 1998, Winkler *et al* 1999) instead of making the present distinction between closed and open shells.

#### 4. Results

The accuracy of the FM approximation may be tested by comparing individual partial waves calculated in the HF approximation with the same waves calculated in the FM approximation. Figures 1 and 2 compare HF and FM wavefunctions for 10 eV continuum electrons in the presence of an argon ion with a single vacancy in the 3s shell. Singlet and triplet results are shown for angular momenta from 0 to 5. First it should be noted that exchange only affects the lowest angular momentum and that by an angular momentum of 3–4, the exchange and no-exchange wavefunctions are the same to plotting accuracy. Secondly, for the triplet case, the FM triplet core plus triplet 3s calculation is very close to the HF triplet wavefunction and for the singlet case, the FM triplet core plus singlet 3s is also very close to the HF singlet wavefunction. On the other hand, if one would have naively calculated singlet for the entire core, the resulting wavefunctions are significantly different from the HF. This demonstrates that the FM wavefunctions are relatively accurate (at least for this case) if the closed shells are treated as triplet (using half the charge density) and the open shell is treated as either triplet or singlet. Interestingly, the best mistake that one could make in calculating a singlet wavefunction would be to perform a triplet calculation for all the atomic electrons since the ‘singlet’ is really a triplet for all the electrons except one. In fact, this is clear from figure 2 where it is seen that the HF singlet is pulled toward the origin as compared to the no exchange case instead of being pushed out as one would naively expect for singlet. Consequently, the previous calculations which used the triplet exchange potential for both final state electrons are actually reasonable approximations to the present triplet–singlet model which is better justified. It is also interesting to note that the largest PTX exchange effect occurs for partial wave  $l = 2$ . Comparisons between HF and FM waves were also performed for other energy electrons in the presence of both the ion and neutral atom and the results were always similar to those shown in figures 1 and 2.

The asymmetric TDCS for 113.5 eV electron impact ionization of argon 3s is compared with the experimental data of Haynes and Lohmann (2000) in figure 3. For this case, the faster final state electron is observed at an angle of  $15^\circ$  counterclockwise from the beam direction and the horizontal axis is the observation angle for the slower electron measured clockwise from the beam direction. The energy of the slower electron is indicated on each part of the figure. The experimental data are not absolute so they have been arbitrarily normalized to the theory at the binary peak (near  $60^\circ$ ). In principle, it would have been preferable to normalize the experiment at the recoil peak (near  $230^\circ$ ) since the theories are all similar there. Unfortunately, this is not possible since one cannot tell the location or size of the recoil peak from the data.

We have performed five different calculations. Labelling is a bit troublesome since one has to specify both how exchange is treated within the atom (ITX) as well as between the projectile electron and atomic electrons (PTX). The scheme we have chosen is to specify the treatment within the atom first and the projectile–atomic electrons second. The five calculations are: (1) DWBA using HF wavefunctions for the target bound state wavefunctions and no exchange potential in the calculation of the continuum electron wavefunctions (HF–NE); (2) DWBA using OPM atomic bound state wavefunctions and no exchange potential in the calculation of the continuum electron wavefunctions (OPM–NE); (3) DWBA using HF bound state wavefunctions and FM potential in the calculation of the continuum electron wavefunctions (HF–FM); (4) DWBA using OPM bound state wavefunctions and FM potential in the calculation of the continuum electron wavefunctions (OPM–FM); and (5) DWBA using full HF wavefunctions for both the bound and continuum electrons (HF–HF). For all cases presented here, HF–NE and OPM–NE were sufficiently similar that they could not be distinguished on a journal figure. Consequently, we only present a single result for these two calculations which



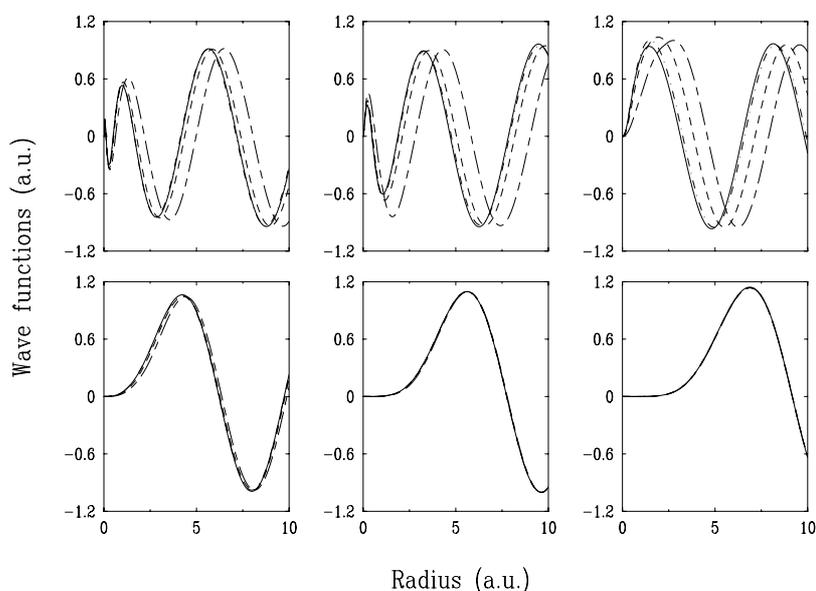
**Figure 1.** Triplet continuum distorted waves for 10 eV electrons in the presence of an argon ion with a 3s vacancy. The different figures correspond to different angular momenta between 0 and 5. The angular momentum increases from left to right with the top left-hand figure corresponding to zero angular momentum and the bottom right-hand figure corresponding to an angular momentum of five. The theoretical curves are: solid—full HF calculation; dashed-dot—FM approximation with triplet for the core plus triplet for the 3s wavefunction; and dashed—exchange ignored.

we label DWNE. Likewise, HF–FM and OPM–FM were also very similar and could not be distinguished on a journal figure. For this case we label the two results as DWFM. To have something like a consistent labelling scheme, the HF–HF results will be called DWHF.

The first issue concerns the accuracy of the FM approximation. From figures 1 and 2, one would expect very little difference between DWFM and DWHF. From figure 3, it is seen that these two results are very similar which means that the FM potential (as calculated here) is a reasonable accurate approximation for full HF exchange. On the other hand, it is also seen that the cross sections are very sensitive to small changes in the continuum wavefunctions since there are larger differences between the cross sections than there are between the wavefunctions. On the more positive side, the present DWFM is a remarkably good approximation for DWHF considering the simplicity of the approximation. Very different results would be obtained, however, if the charge density were treated differently in the FM approximation.

In terms of agreement between theory and experiment, it is clear that the best agreement with experiment is at the highest energy and that the agreement deteriorates significantly with decreasing energy. At 2 eV, the agreement between experiment and theory is pretty bad and the DWFM results are the only ones to be even qualitatively similar to the shape of the experimental binary peak. Although the exchange effects are significant, it is not clear whether or not they produce an improved agreement with experiment. One of the standard methods for evaluating the quality of theory is to look at the ratio of binary to recoil peak. One of the important consequences of exchange is that it significantly changes this ratio but, unfortunately, this ratio cannot be determined from the data.

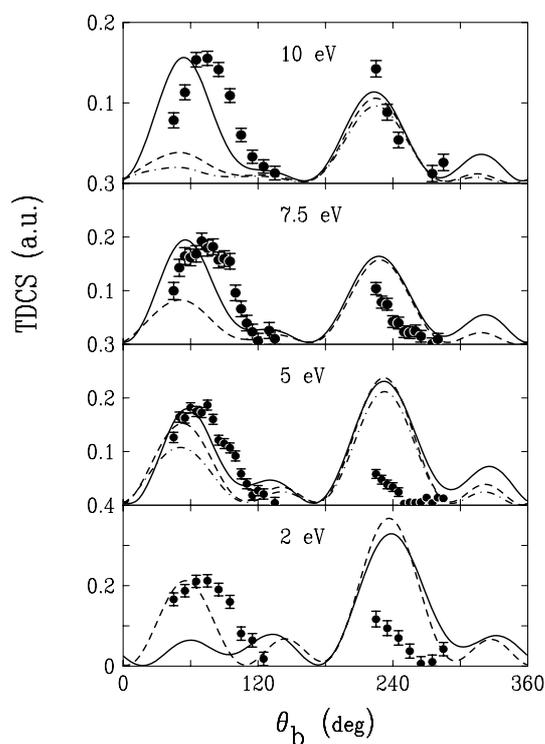
At 10 eV, the effect of exchange in either of the DWHF or DWFM approximations is to significantly reduce the magnitude of the binary peak and significantly decrease the ratio of



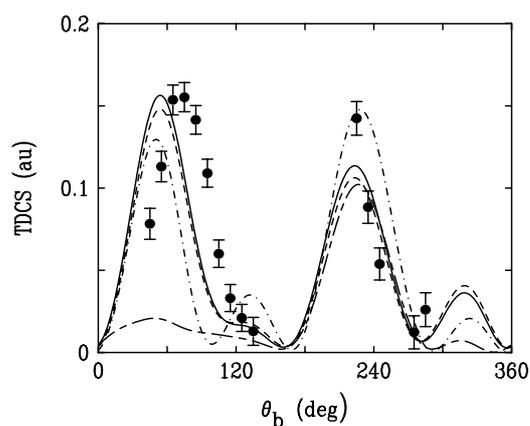
**Figure 2.** Same as figure 1 except for singlet continuum distorted waves. The theoretical curves are: solid—full HF calculation; dashed-dot—FM approximation with triplet for the core plus singlet for the 3s wavefunction; long dash–short dash—FM approximation using singlet for the core plus singlet for the 3s wavefunction; and dashed—exchange ignored.

the binary peak to recoil peak. Since this behaviour seemed unusual and counter intuitive (i.e. we did not believe it), we investigated the source of this phenomenon. Figure 4 shows the individual partial wave contributions to the DWHF TDCS. The starting point is DWNE with no exchange (solid curve). We then changed the partial waves for the 10 eV ejected electron only from no exchange to HF-exchange one wave at a time. It is seen that the  $l = 0$  and 1 waves had a small but noticeable effect. However, when the  $l = 2$  is included, the binary peak is almost eliminated relative to the recoil peak. Adding additional HF partial waves for the 10 eV electron made very little difference. As previously noted, the largest exchange effect was observed for  $l = 2$ . However, from figure 2, it is seen that the difference between the  $l = 2$  no exchange and HF partial waves is not spectacular. Consequently, it is rather amazing that this wave can have such a dramatic effect on the TDCS.

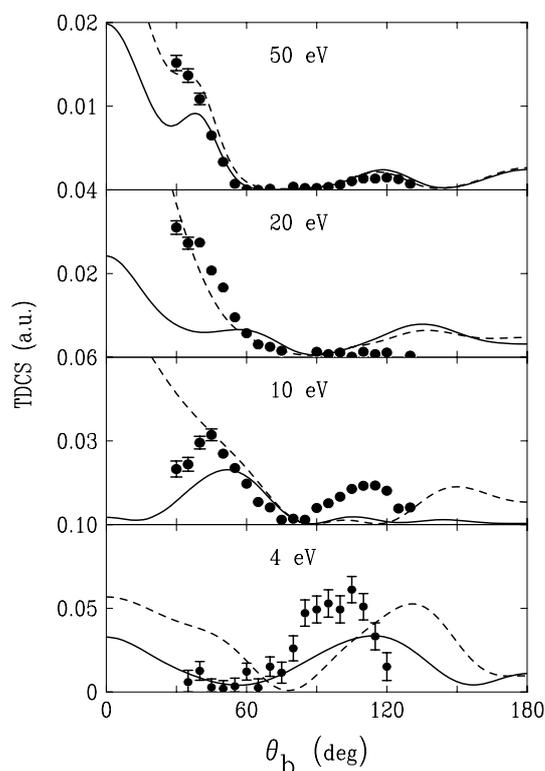
In figure 5, coplanar symmetric results for ionization of the 3s shell are compared with the experimental data of Haynes and Lohmann (2001a). For the coplanar symmetric geometry, both final state electrons are observed at the same angle on opposite sides of the beam direction and the electrons have the same energy. Haynes and Lohmann (2001a) measured cross sections for 37.3, 49.3, 69.3 and 129.3 eV incident electrons which results in 4, 10, 20 and 50 eV final state electrons. Theoretical results are presented for the DWNE and DWFM approximations. Again exchange effects are very important. The experimental data are not absolute so only shapes can be compared. It is clear from figure 5 that the DWFM approximation is in significantly better agreement with the shape of the data for the two higher energies so the data are normalized (arbitrarily) for the best visual agreement with DWFM. As the energy is lowered, the shape of the data changes dramatically. There is a low angle maximum in the data which is not predicted by DWFM at 10 eV. It is clear that the theories are wrong for small scattering angles since the cross section should go to zero for  $0^\circ$  scattering. However, DWNE does have a low angle maximum at 10 eV but at a different angle from that seen in the data.



**Figure 3.** TDCS in atomic units (au) for coplanar asymmetric 113.5 eV electron impact ionization of the 3s shell of argon. The faster final state electron is observed at an angle of  $15^\circ$  counterclockwise from the beam direction and the horizontal axis is the angle of observation for the slower electron measured clockwise relative to the beam direction. The energy of the slower electron is indicated on each part of the figure. The experimental data are those of Haynes and Lohmann (2000). The theoretical calculations are: DWNE—solid; DWFM—dashed; and DWHF—long dash–short dash.



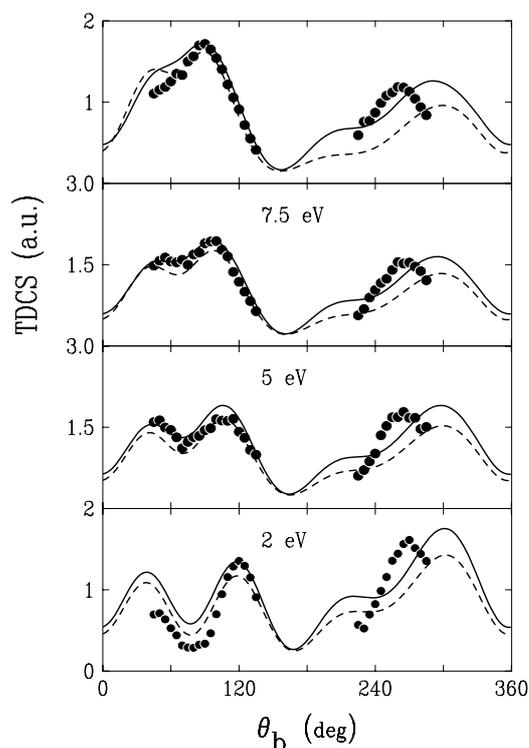
**Figure 4.** TDCS in au for coplanar asymmetric 113.5 eV electron impact ionization of the 3s shell of argon. The faster final state electron is observed at an angle of  $15^\circ$  counterclockwise from the beam direction. The energy of the slower electron is 10 eV and the horizontal axis is the angle of observation for the slower electron measured clockwise relative to the beam direction. The experimental data are those of Haynes and Lohmann (2000). The theoretical calculations are: DWNE—solid; DWNE with 10 eV  $l = 0$  HF—dashed; DWNE with 10 eV  $l = 0, 1$  HF—dash–dot; and DWNE with 10 eV  $l = 0, 1, 2$  HF—long dash–short dash.



**Figure 5.** TDCS in au for coplanar symmetric ionization of the 3s shell of argon. Both final state electrons have the energy indicated in the figure and both electrons are observed at the same angle  $\theta_b$  on opposite sides of the beam direction. The experimental data are those of Haynes and Lohmann (2001a). The theoretical calculations are: DWNE—solid; DWFM—dashes.

One would expect that PCI effects would be most important for the symmetric geometry and further that these effects would become increasingly important for decreasing energy. PCI is treated only to first order in these calculations so it should be underestimated when it becomes important. Since PCI should push the electrons apart, one would expect that PCI would shift the peak positions to larger angles for scattering angles less than  $90^\circ$  and to smaller angles for scattering angles greater than  $90^\circ$ . In most low energy cases, shifts of this type would tend to improve agreement between experiment and theory so we expect that PCI is a major cause for the disagreement between theory and experiment at low ejected electron energies.

The discussion to this point has concentrated on inner shell ionization of the 3s shell. Very recently, Haynes and Lohmann (2001b) have measured ionization of the outer 3p shell in the asymmetric geometry. The faster final state electron energy was adjusted such that the low-energy final state electrons had the same energy as measured for asymmetric ionization of the 3s shell. Comparison of experiment and theory for ionization of the 3p shell is contained in figure 6. Experiment and theory are in noticeably better agreement for 3p ionization than was seen in figure 3 for 3s ionization. The second striking feature of figure 6 is that exchange effects are much less important. For this case, the DWFM calculation for the ejected electron was performed using the triplet potential for closed shells of the core plus a singlet potential for the outer five p-electrons. Both theories tend to predict binary peaks in essentially the same location as the data and a recoil peak at an angle of about  $30^\circ$  too large. Although PCI



**Figure 6.** TDCS in au for coplanar asymmetric 113.5 eV electron impact ionization of the 3p shell of argon. The faster final state electron is observed at an angle of  $15^\circ$  counterclockwise from the beam direction and the horizontal axis is the angle of observation for the slower electron measured clockwise relative to the beam direction. The energy of the slower electron is indicated on each part of the figure. The experimental data are those of Haynes and Lohmann (2001b). The theoretical calculations are: DWNE—solid; DWFM—dashes.

should shift the recoil peak to smaller angles, it seems unlikely that the shift would be this large particularly for the low energy (largest asymmetry) case. Furthermore, if PCI would shift the recoil peak to smaller angles by that much, then one would expect the binary peak to also shift by about the same amount to larger angles which would tend to make the agreement between experiment and theory worse. Consequently, it seems unlikely that PCI can explain the disagreement between experiment and theory for this case.

## 5. Conclusions

We have investigated the effect of electron exchange on low energy inner and outer shell ionization of argon. It was found that PTX exchange effects are very important for ionization of the 3s shell and moderately important for 3p shell ionization. Consequently, exchange effects must be included in any accurate calculation of low energy electron-impact ionization cross sections. We performed a full HF calculation for the continuum wavefunctions and compared these wavefunctions to the much simpler FM approximation. It was found that the FM approximation is an easy, reasonably good approximation for the full HF provided the triplet potential is used for the incident and faster final state electrons and a combination of triplet and singlet potentials is used for the lower energy ejected electron. Although the

exchange approximations tended to improve agreement between experiment and theory in some cases, agreement is far from satisfactory. Consequently, a better treatment of PCI and/or charge cloud polarization will be required to achieve a satisfactory understanding of the experimental data. We also compared the exchange-only OPM and the HF approach for calculating the bound state wavefunctions and static atomic potentials and found that the two methods yielded results which are indistinguishable on a journal figure. The OPM thus appears to be the appropriate DFT method to be used in calculations for scattering processes. In contrast to the Slater approximation, the OPM is parameter-free and allows for the inclusion of correlation effects, thus offering the possibility to go beyond the HF level.

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