Distorted-wave Born and Impulse Approximations for Electron–Atom Ionisation

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Abstract

The distorted-wave Born and impulse approximations set the standard for the calculation of the ionisation of atoms by electrons. The approximations are derived from formal scattering theory. Their computational forms are given and a program for their numerical calculation is described. Input and output data are given for a trial run.

1. Introduction

Electron–atom ionisation provides a very interesting diversity of phenomena because of the wide range of kinematic situations available to a three-body final state. To a very good approximation, which has been verified in detail experimentally, it may be considered as a three-body problem governed by Coulomb forces. The incident electron knocks out an electron from a single-particle orbital, with the remainder of the target atom acting as an inert spectator core. In an experiment the ion is left in a set of states belonging to different symmetry manifolds. The sum of the ionisation cross sections for all the states of a manifold behaves like the cross section for the corresponding orbital in the three-body model (McCarthy and Weigold 1991).

The long-range nature of the Coulomb force provides serious difficulties in obtaining a straightforward method of solution, and in fact no such method has yet been demonstrated that is valid over the whole kinematic range.

Different kinematic arrangements of the final state emphasise different two-body subsystems of the three-body problem. Certain subsystems are treated completely, that is by including their wavefunctions, or equivalently their half-on-shell T-matrix elements, in the calculation. If the two final-state electrons remain close to each other for a relatively long time, methods that include the exact three-body boundary condition for the final state have had some success (e.g. Brauner *et al.* 1989). In essentially all other kinematic situations the standard for relatively simple solutions is set by the distorted-wave Born approximation (DWBA).

The name DWBA is unfortunate as it implies that some feature of the approximation is of first order in a perturbative sense. In fact it is easy to define a formal distorted wave for which the approximation is exact. The approximation lies in choosing a local, central potential for simple calculation of a distorted wave that is as close as possible to the formally exact one. All potentials are

included in the DWBA to all orders of perturbation theory. The approximation assumes weak coupling between the entrance channel and all excited channels.

If the electron–ion potentials are ignored, the ionisation amplitude factorises into the product of a half-on-shell electron–electron T-matrix element and the momentum representation of the bound-state orbital. This is the impulse approximation, which treats the electron–electron subsystem fully. It is valid for small recoil momenta of the ion at high energy (McCarthy and Weigold 1991). At lower energy the electron–ion potentials are included by replacing the plane waves in the momentum representation of the orbital by distorted waves calculated in the potentials used for the DWBA, but retaining the factorisation. This is the distorted-wave impulse approximation (DWIA), which has turned out to be valid (McCarthy and Weigold 1991) for energies above a few hundred eV and final-state kinematics on the Bethe ridge. The condition for the Bethe ridge is that the momentum of the slow electron is equal in magnitude to the momentum transfered from the incident to the fast electron. This condition is trivially satisfied in a two-electron collision and the DWIA is applicable for kinematic conditions that resemble two-electron kinematics in the sense that the reaction is on the Bethe ridge.

The minimum number of kinematic variables defining the final state is five. We take them to be the energies E_f and E_s of the fast and slow electrons, the polar angles θ_f and θ_s of the fast and slow electrons relative to the incident direction, and the relative azimuthal angle $\pi - \phi$. An experiment keeps four kinematic variables constant and varies one. The following three kinematic situations are commonly used.

   (i) *Coplanar asymmetric*: energies fixed and very unequal; polar angle of the fast electron fixed at a small value, generally less than about 30°; relative azimuthal angle π, i.e. three electron directions coplanar; polar angle of the slow electron varied.
   (ii) *Coplanar symmetric*: energies fixed and equal; relative azimuthal angle π; polar angles equal and varied.
   (iii) *Noncoplanar symmetric*: energies fixed and equal; polar angles equal and fixed usually at 45°; relative azimuthal angle varied.

The polar angle of the fast electron in coplanar asymmetric kinematics may be chosen to keep the whole experiment on the Bethe ridge. For relative azimuthal angles less than about 30° from π, the noncoplanar symmetric case is very nearly on the Bethe ridge. Coplanar symmetric kinematics tests approximations very strictly because it involves large variations of both the momentum transfer and the recoil momentum. Both the other cases keep the momentum transfer essentially fixed and vary the recoil momentum. To a good approximation the differential cross section in noncoplanar symmetric kinematics follows the momentum distribution of the electron in the bound orbital. Hence this case is used as a sensitive probe of the target structure, known as electron momentum spectroscopy.

2. Formulation of the Problem

We consider the problem of two electrons, numbered 1 and 2, interacting with an inert core via potentials v_1 and v_2 respectively, which have the long-range form

of attractive Coulomb potentials. The corresponding coordinates are r_1 and r_2. For the purpose of writing an unsymmetrised amplitude we associate the labels 1 and 2 with the fast and slow electrons respectively. The corresponding kinetic energies are E_f and E_s. The corresponding momenta are k_f and k_s. The kinetic energy of the incident electron is E_0. We use atomic units ($\hbar = m_e = e = 1$). Spin and the Pauli exclusion principle are introduced by way of an exchange amplitude obtained by reversing the roles of k_f and k_s in the direct amplitude. Spin–orbit coupling is neglected in v_1 and v_2. The initial-state boundary condition is always satisfied. It describes an electron of momentum k_0 incident on an uncharged system consisting of electron 2 bound to the core in the state α, with separation energy ϵ_α.

The differential cross section is

$$\frac{\mathrm{d}^5\sigma}{\mathrm{d}\Omega_f \mathrm{d}\Omega_s \mathrm{d}E_f} = (2\pi)^4 \frac{k_f k_s}{k_0} \sum_{av} |\langle k_f k_s | T | \alpha k_0 \rangle|^2 \,, \tag{1}$$

where the notation $\sum_{av}$ represents a sum over final and average over initial magnetic and spin degeneracies. The T-matrix element is the ionisation amplitude, which is the object of the approximations.

The Hamiltonian of the problem is partitioned as follows:

$$H = [(K_1 + U_1) + (K_2 + v_2)] + [v_1 + v_3 - U_1]\,. \tag{2}$$

We have added and subtracted a local, central potential $U_1(r_1)$, which defines distorted waves $|\chi^{(\pm)}(k)\rangle$ with outgoing- and ingoing-spherical-wave boundary conditions respectively,

$$[E_{0,f} - K_1 - U_1]|\chi^{(\pm)}(k)\rangle = 0\,. \tag{3}$$

The first of the bracketed terms in (2) is the channel Hamiltonian K, whose eigenstates are separable in the coordinates r_1, r_2. The initial channel state is given by

$$[E - K]|\alpha\chi^{(+)}(k_0)\rangle = 0\,. \tag{4}$$

The final channel state is given by

$$[E - K]|\chi^{(-)}(k_s)\chi^{(-)}(k_f)\rangle = 0\,. \tag{5}$$

Both $|\alpha\rangle$ and $|\chi^{(-)}(k_s)\rangle$ are eigenstates of v_2, while $|\chi^{(-)}(k_f)\rangle$ is an eigenstate of U_1, given by (3). An appropriate form for v_2 in a many-electron atom is the Hartree–Fock potential.

The T-matrix element (Gell-Mann and Goldberger 1953) is

$$\langle k_f k_s | T | \alpha k_0 \rangle = \langle \chi^{(-)}(k_f)\chi^{(-)}(k_s) | v_1 + v_3 - U_1 | \Psi_\alpha^{(+)}(k_0)\rangle, \tag{6}$$

where the three-body collision state $|\Psi_\alpha^{(+)}(k_0)\rangle$ is given by

$$[E - H]|\Psi_\alpha^{(+)}(k_0)\rangle. \tag{7}$$

In the next two sections we derive approximations to (6).

3. Derivation of the Distorted-wave Born Approximation

We may write the collision state $|\Psi_\alpha^{(+)}(\boldsymbol{k}_0)\rangle$ as the product of the orbital $|\alpha\rangle$ with a formal distorted wave $|X^{(+)}(\boldsymbol{k}_0)\rangle$ obtained by projecting $|\alpha\rangle$ from $|\Psi_\alpha^{(+)}(\boldsymbol{k}_0)\rangle$,

$$|X^{(+)}(\boldsymbol{k}_0)\rangle = \langle\alpha|\Psi_\alpha^{(+)}(\boldsymbol{k}_0)\rangle. \tag{8}$$

The DWBA approximates $|X^{(+)}(\boldsymbol{k}_0)\rangle$ by the solution $|\chi^{(+)}(\boldsymbol{k}_0)\rangle$ of the problem of electron scattering by a local, central potential U_1 (3). We choose U_1 so that the approximation is as close as possible.

In the projection (8) we substitute the integral equation corresponding to (7):

$$\langle\alpha|\Psi_\alpha^{(+)}(\boldsymbol{k}_0) = |\chi^{(+)}(\boldsymbol{k}_0)\rangle + \sum_\mu \langle\alpha|\frac{1}{E^{(+)} - K}|\mu\rangle\,\langle\mu|v_1 + v_3 - U_1|\Psi_\alpha^{(+)}(\boldsymbol{k}_0)\rangle. \tag{9}$$

We have introduced the unit operator corresponding to the complete set μ of target orbitals. The approximation requires the second term of (9) to be small. Making the approximation, the second term becomes

$$\frac{1}{E^{(+)} - \epsilon_\alpha - K_1 - U_1}\langle\alpha|v_1 + v_3 - U_1|\alpha\rangle\,|\chi^{(+)}(\boldsymbol{k}_0)\rangle.$$

The approximation is consistent if we choose

$$U_1 = \langle\alpha|v_1 + v_3|\alpha\rangle. \tag{10}$$

The DWBA is

$$\langle\boldsymbol{k}_f\boldsymbol{k}_s|T|\alpha\boldsymbol{k}_0\rangle = \langle\chi^{(-)}(\boldsymbol{k}_f)\chi^{(-)}(\boldsymbol{k}_s)|v_3|\alpha\chi^{(+)}(\boldsymbol{k}_0)\rangle. \tag{11}$$

Note that the central potential $v_1 - U_1$ has no contribution because the states $|\alpha\rangle$ and $|\chi^{(-)}(\boldsymbol{k}_s)\rangle$ of electron 2 are orthogonal. The distorted waves $|\chi^{(+)}(\boldsymbol{k}_0)\rangle$ and $|\chi^{(-)}(\boldsymbol{k}_f)\rangle$ are calculated in the potential U_1. The outgoing target state $|\chi^{(-)}(\boldsymbol{k}_s)\rangle$ is calculated in the potential v_2.

A formulation of the exact T-matrix element that is the time-reversed analogue of (6) is

$$\langle\boldsymbol{k}_f\boldsymbol{k}_s|T|\alpha\boldsymbol{k}_0\rangle = \langle\Psi^{(-)}(\boldsymbol{k}_f, \boldsymbol{k}_s)|v_1 + v_3 - U_1|\alpha\chi^{(+)}(\boldsymbol{k}_0)\rangle, \tag{12}$$

where $|\Psi^{(-)}(\boldsymbol{k}_f, \boldsymbol{k}_s)\rangle$ is the exact collision state with final-state boundary conditions. The exact boundary condition for an unbound state of three charged bodies was first attributed to Redmond by Rosenberg (1973). It was first used in an ionisation calculation by Brauner *et al.* (1989), who approximated $|\Psi^{(-)}(\boldsymbol{k}_f, \boldsymbol{k}_s)\rangle$ by the product of the three two-body states, with appropriate momentum relationships. For kinematic conditions where the two final-state electrons do not interact significantly, an appropriate approximation is the product of two electron–ion

states. This again has the form of the DWBA (11), the only change being that $|\chi^{(-)}(\boldsymbol{k}_f)\rangle$ is calculated in the ion potential v_1, rather than the distorting potential U_1. Note that it is formally necessary to have the correct boundary condition in either the initial or final state, not both. This has been clarified by Klar *et al.* (1993). The state $|\alpha\chi^{(+)}(\boldsymbol{k}_0)\rangle$ has the correct boundary condition.

4. Derivation of the Distorted-wave Impulse Approximation

The potential responsible for ionisation is the electron–electron potential v_3. An approximation with the correct initial-state boundary condition for ionisation is the plane-wave impulse approximation (PWIA),

$$\langle \boldsymbol{k}_f \boldsymbol{k}_s | T | \alpha \boldsymbol{k}_0 \rangle = \langle \boldsymbol{k}_f \boldsymbol{k}_s | t_3 | \alpha \boldsymbol{k}_0 \rangle . \tag{13}$$

This assumes that the energies of the unbound electrons are so high that their interaction with the ion can be neglected. However it treats the electron–electron collision exactly by using the T matrix t_3 for the Coulomb potential v_3. Translational invariance is expressed by

$$\langle \boldsymbol{k}_1' \boldsymbol{k}_2' | t_3 | \boldsymbol{k}_2 \boldsymbol{k}_1 \rangle = \langle \boldsymbol{k}' | t_3 | \boldsymbol{k} \rangle \delta(\boldsymbol{K}' - \boldsymbol{K}) , \tag{14}$$

where the relative and centre-of-mass coordinates $\boldsymbol{k}$, $\boldsymbol{K}$ are related to the particle coordinates $\boldsymbol{k}_1, \boldsymbol{k}_2$ by

$$\boldsymbol{k} = \tfrac{1}{2}(\boldsymbol{k}_1 - \boldsymbol{k}_2), \qquad \boldsymbol{K} = \boldsymbol{k}_1 + \boldsymbol{k}_2 . \tag{15}$$

Primes denote the final state. The Coulomb T matrix is defined by

$$\langle \boldsymbol{k}' | t_3 | \boldsymbol{k} \rangle = \langle \boldsymbol{k}' | v_3 | \psi^{(+)}(\boldsymbol{k}) \rangle , \tag{16}$$

where $|\psi^{(+)}(\boldsymbol{k})\rangle$ is the Coulomb state vector. Strictly this is the half-on-shell T matrix, where the Schrödinger equation for $|\psi^{(+)}(\boldsymbol{k})\rangle$ is solved at the initial-state relative energy corresponding to $\boldsymbol{k}$.

Because of translational invariance (14) the PWIA factorises as follows into collision and structure factors

$$\langle \boldsymbol{k}_f \boldsymbol{k}_s | T | \alpha \boldsymbol{k}_0 \rangle = \int d^3 q \langle \boldsymbol{k}_f \boldsymbol{k}_s | t_3 | \boldsymbol{q} \boldsymbol{k}_0 \rangle \langle \boldsymbol{q} | \alpha \rangle$$

$$= \langle \boldsymbol{k}' | t_3 | \boldsymbol{k} \rangle \langle \boldsymbol{q} | \alpha \rangle , \tag{17}$$

where

$$\boldsymbol{k}' = \tfrac{1}{2}(\boldsymbol{k}_f - \boldsymbol{k}_s), \quad \boldsymbol{q} = \boldsymbol{k}_f + \boldsymbol{k}_s - \boldsymbol{k}_0, \quad \boldsymbol{k} = \tfrac{1}{2}(\boldsymbol{k}_0 - \boldsymbol{q}) . \tag{18}$$

The high-energy condition is relaxed by replacing the plane waves in the structure factor by distorted waves, defined as for the DWBA. The factorisation (17) is retained. The DWIA T-matrix element is

$$\langle \boldsymbol{k}_f \boldsymbol{k}_s | T | \alpha \boldsymbol{k}_0 \rangle = \langle \boldsymbol{k}' | t_3 | \boldsymbol{k} \rangle \langle \chi^{(-)}(\boldsymbol{k}_f) \chi^{(-)}(\boldsymbol{k}_s) | \alpha \chi^{(+)}(\boldsymbol{k}_0) \rangle. \tag{19}$$

After implementing the sum and average over spin projections (1), the DWIA differential cross section is

$$\frac{\mathrm{d}^5 \sigma}{\mathrm{d}\Omega_f \mathrm{d}\Omega_s \mathrm{d}E_f} = (2\pi)^4 \frac{k_f k_s}{k_0} f_{ee} N_\alpha \Sigma_m |\langle \chi^{(-)}(\boldsymbol{k}_f) \chi^{(-)}(\boldsymbol{k}_s) | \alpha \chi^{(+)}(\boldsymbol{k}_0) \rangle|^2, \tag{20}$$

where the number of electrons occupying the orbital $|\alpha\rangle$ is N_α, its orbital-angular-momentum projection quantum number is m, and the collision factor f_{ee} takes the form found by Ford (1964):

$$f_{ee} = (2\pi)^{-2} \frac{2\pi\nu}{e^{2\pi\nu} - 1} \left[\frac{1}{|\boldsymbol{k}_0 - \boldsymbol{k}_f|^4} + \frac{1}{|\boldsymbol{k}_0 - \boldsymbol{k}_s|^4} \right.$$

$$\left. - \frac{1}{|\boldsymbol{k}_0 - \boldsymbol{k}_f|^2} \frac{1}{|\boldsymbol{k}_0 - \boldsymbol{k}_s|^2} \cos\left(\nu \ln \frac{|\boldsymbol{k}_0 - \boldsymbol{k}_s|^2}{|\boldsymbol{k}_0 - \boldsymbol{k}_f|^2} \right) \right], \qquad \nu = 1/k'. \tag{21}$$

The DWIA is computationally easier to implement than the DWBA because it replaces $v_3(\boldsymbol{r}_1 - \boldsymbol{r}_2)$ by $\delta(\boldsymbol{r}_1 - \boldsymbol{r}_2)$, affording considerable simplication to the radial integration.

5. Computational Form of the Approximations

The DWBA T-matrix element (11) and the distorted-wave factor in the DWIA T-matrix element (19) have similar computational forms. For the DWIA the potential $v_3(\boldsymbol{r}_1 - \boldsymbol{r}_2)$ is replaced by $\delta(\boldsymbol{r}_1 - \boldsymbol{r}_2)$. The direct amplitude is

$$\langle \chi^{(-)}(\boldsymbol{k}_f) \chi^{(-)}(\boldsymbol{k}_s) | v_3 | \alpha \chi^{(+)}(\boldsymbol{k}_0) \rangle$$

$$= (2\pi)^{-9/2} (4\pi)^{5/2} (\boldsymbol{k}_f \boldsymbol{k}_s \boldsymbol{k}_0)^{-1}$$

$$\times \sum_{L'L''M''\lambda} (-1)^{M''} \begin{pmatrix} \ell & \lambda & L'' \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} \ell & \lambda & L'' \\ m & M'' - m & -M'' \end{pmatrix}$$

$$\times \sum_l \begin{pmatrix} L' & \lambda & L \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} L' & \lambda & L \\ m - M'' & M'' - m & 0 \end{pmatrix} R^{(\lambda)}_{L'L''L\ell}(k_f, k_s, k_0)$$

$$\times Y_{L'm-M''}(\theta_f, 0) \, Y_{L''M''}(\theta_s, \pi - \phi), \tag{22}$$

where

$$R^{(\lambda)}_{L'L''L\ell}(k_f, k_s, k_0) = i^{L-L'-L''} \exp[i(\sigma_{L'} + \sigma_{L''})]\hat{L}'\hat{L}''\hat{\ell}\hat{L}^2$$
$$\times \int dr_1 \int dr_2 \, u_{L'}(k_f, r_1) \, u_{L''}(k_s, r_2) \, v_\lambda(r_1, r_2) \, u_{n\ell}(r_2)u_L(k_0, r_1) \,. \qquad (23)$$

The partial-wave expansions of the distorted waves are

$$\langle \boldsymbol{r}|\chi^{(+)}(\boldsymbol{k})\rangle = \left(\frac{2}{\pi}\right)^{\frac{1}{2}} \frac{1}{kr} \sum_{LM} i^L \, u_L(k, r) \, Y^*_{LM}(\hat{\boldsymbol{k}}) \, Y_{LM}(\hat{\boldsymbol{r}}),$$

$$\langle \chi^{(-)}(\boldsymbol{k})|\boldsymbol{r}\rangle = \left(\frac{2}{\pi}\right)^{\frac{1}{2}} \frac{1}{kr} \sum_{LM} i^{-L} \, e^{i\sigma_L} \, u_L(k, r) \, Y_{LM}(\hat{\boldsymbol{k}}) \, Y^*_{LM}(\hat{\boldsymbol{r}}) \,. \qquad (24)$$

The coordinate representation of the orbital $|\alpha\rangle$ is

$$\langle \boldsymbol{r}|\alpha\rangle = r^{-1} \, u_{n\ell}(r) \, Y_{\ell m}(\hat{\boldsymbol{r}}) \,. \qquad (25)$$

The notation $\hat{L}$ is defined by

$$\hat{L} = (2L + 1)^{\frac{1}{2}} \,. \qquad (26)$$

The Coulomb phase shift is σ_L.

The multipole expansion of the potential $v_3(\boldsymbol{r}_1, \boldsymbol{r}_2)$ is

$$v_3(\boldsymbol{r}_1, \boldsymbol{r}_2) = \sum_{\lambda\mu} 4\pi\hat{\lambda}^{-2} \, v_\lambda(r_1, r_2) \, Y_{\lambda\mu}(\hat{\boldsymbol{r}}_1) \, Y^*_{\lambda\mu}(\hat{\boldsymbol{r}}_2) \,, \qquad (27)$$

where

$$v_\lambda(r_1, r_2) = r^\lambda_</r^{\lambda+1}_>, \qquad \text{DWBA},$$
$$= \delta(r_1 - r_2)/r_1^2, \qquad \text{DWIA} \,, \qquad (28)$$

and $r_<$ and $r_>$ denote the lesser and greater respectively of r_1 and r_2.

The partial waves $u_L(k, r)$ are obtained by solving the corresponding differential equation for elastic scattering by a short-range potential $v(r)$ and a Coulomb potential $-Z/r$:

$$\left[\frac{d^2}{d\rho^2} - \frac{L(L+1)}{\rho^2} - \frac{\eta}{\rho} - \frac{v(r)}{E} + 1\right] u_L(k, \rho) = 0 \,, \qquad (29)$$

where the Coulomb parameter is

$$\eta = -Z/k \,, \tag{30}$$

and the numerical solution of the equation is made approximately independent of the incident energy

$$E = \tfrac{1}{2}k^2 \tag{31}$$

by using the dimensionless variable

$$\rho = kr \,. \tag{32}$$

The boundary conditions are obtained by the partial-wave solutions of the equation for an external Coulomb potential. They are

$$u_L(k,\rho) = F_L(\rho) + C_L(G_L(\rho) + iF_L(\rho)), \quad \rho \geq \rho_1 \,. \tag{33}$$

where $F_L(\rho)$ and $G_L(\rho)$ are respectively the regular and irregular Coulomb functions. The internal and external solutions are matched at two points ρ_0, ρ_1 in the region where $v(r)$ is negligible. The matching determines the complex number C_L, which is the partial scattering amplitude.

The program is at present restricted to real distorting potentials. This reduces the storage required for partial waves u_L, since they are then represented by real numbers v_L and ϕ_L, where

$$u_L(k,r) = v_L(k,r)\exp(i\phi_L(k)) \,. \tag{34}$$

The position-independent phase factor is given by

$$\exp(i\phi_L(k)) = [F_L(\rho_0) + C_L(G_L(\rho_0) + iF_L(\rho_0))]/v_L(k,r_0) \,. \tag{35}$$

The real differential equation (29) is solved for $v_L(k,r)$ up to r_0.

The direct distorting potentials are obtained from the target radial orbitals $u_{n\ell}(r)$ by

$$V_D(r) = \sum_{n\ell} N_{n\ell} \int \mathrm{d}r' [u_{n\ell}(r')]^2/r_> \,, \tag{36}$$

where $r_>$ is the greater of r and r', and $N_{n\ell}$ is the number of electrons in each orbital $n\ell$.

Spin-averaged static-exchange potentials are obtained from the Furness–McCarthy (1973) equivalent-local approximation to the exchange potential:

$$V_E(r) = \tfrac{1}{2}[E + V_D(r) - \{(E + V_D(r))^2 - 2\pi\rho(r)^2\}^{\frac{1}{2}}] \,, \tag{37}$$

where $\rho(r)$ is the electron density. This is a high-energy approximation valid for $E > 100$ eV.

6. Program Description

The routines that control the main operations of the program and the input and output are described. Details of the subroutines called by these routines are not given. Adequate documentation is provided by comments in the Fortran listing. The necessary computer files for the program and trial run can be obtained from the author at the e-mail address ian@esm.ph.flinders.edu.au.

6·1 Main Program

The important operations of the main program are as follows:

Read run input on file 'E2E.INPUT'.
Set up integration meshes: CALL MESH.
Calculate the partial waves $u_L(k,r)$ of (24) and the radial bound-state orbital $u_{n\ell}(r)$ of (25): CALL WAVEFN.
Calculate (e, 2e) amplitudes (22), exchange amplitudes and cross sections (1): CALL DWBA.

Table 1. Names of Fortran variables and trial values for file 'E2E.INPUT'

Names	Trial values
EIV, ESLOW, EFAST	415·8,20·0,380·0
IPW, IPOT, IDWI, IEX, ICOPS	0,0,1,1,1
NTC, THCI, THCINC	1,1,5
NTD, THDI, THDINC	8,0,6
LM1, LM2, LM3	40,20,35

The Fortran names of the input variables and their values for a trial run are given in Table 1. The meanings of the input variables are as follows.

Electron kinetic energies.

EIV: Incident energy E_0 in (eV),
ESLOW: Slow outgoing energy E_s in (eV),
EFAST: Fast outgoing energy E_f in (eV).

Option switches.

IPW: NE·0, plane-wave run (distorting potentials set to zero),
           EQ·0, distorted-wave run,
IPOT: NE·0, atom potential for fast electron,
           EQ·0, ion potential for fast electron,
IDWI: NE·0, DWIA and DWBA calculated,
           EQ·0, only DWBA calculated,
IEX: EQ·1, exchange term included in DWBA,
           EQ·0, exchange term omitted,
ICOPS: EQ·0, noncoplanar symmetric kinematics,
           EQ·1, coplanar asymmetric kinematics,
           EQ·2, coplanar symmetric kinematics.

Fast electron angle data (redundant for coplanar symmetric option).

NTC:	number of angles,
THCI:	initial angle (degrees),
THCINC:	angular increment.

If THCINC.LT·0, NTC numerically specified angles are read.

Variable angle data. The variable angle is

ϕ (noncoplanar symmetric kinematics),

θ_s (coplanar asymmetric kinematics),

$\theta = \theta_f = \theta_s$ (coplanar symmetric kinematics).

NTD:	number of angles,
THDI:	initial angle (degrees),
THDINC:	angular increment.

If THDINC.LT·0, NTD numerically specified angles are read.

Maximum numbers of partial waves for each electron.

LM1:	incident electron,
LM2:	slow electron,
LM3:	fast electron.

A rough guide to the number of partial waves for momentum k is $kR + 4$, where R is a measure of the relevant size of the bound-state orbital. $R = 8$ is a good initial guess. A choice is tested by a plane-wave run (IPW=1, IEX=0), where the partial-wave cross sections in the column headed XSECN DW are compared with the analytic cross sections, obtained by replacing t_3 by v_3 in (17), in the column headed XSECN PW. If the electron plane wave for the coordinate r_2 is not orthogonal to the bound-state orbital (within the tolerance of the computation), then the numerical integration (23) is not convergent for the DWBA, even though the integral $\langle \mathbf{k}' | v_3 | \mathbf{k} \rangle$ exists. The plane-wave check is therefore invalid for the DWBA if the corresponding energy is below about 100 eV. The DWIA tests the convergence of the truncated partial-wave expansion in this case.

6·2 SUBROUTINE MESH

Sets up the radial grid data for the Numerov solution of the partial-wave differential equation (29) and for the radial matrix element (23). The input for the grid calculations is on lines 2, 3 and 4 of the file 'WF.DAT'. The Fortran variables and trial values are given in Table 2.

Table 2. Names of Fortran variables and trial values for file 'WF.DAT'

Line	Names	Trial values
1.	IPHASE, IWF, IDW0, IDW, IDWINC, LDW0, LDWINC	0,0,0,0, 0,0,0
2.	NMAX, HA(1)	16,0·69D−6
3.	NA(K), K = 1, NMAX	25,25,18,18,18,18,18,18,18, 18,18,18,18,18,400,11000
4.	LIM, UMIN, UMAX	4000,1D−4,1D−4

The Numerov method for integrating a second-order differential equation requires equally-spaced radial points in a succession of segments. The interval for each successive segment must be twice that for the previous segment.

The differential-equation grid data are set up in COMMON/DEGRID/. In describing the storage of a dimensioned Fortran variable we give the dimension, which is set up in the file 'pare2e' in a PARAMETER statement.

R(NXD):   radial points,
ILAST: index of last radial point r_0 (first point for matching to the external solution),
IMCH: index of second matching point r_1.

The radial values R(K) are multiplied by the momentum k (FKAY) to obtain the values RHO(K) of the dimensionless integration variable ρ in SUBROUTINE WAVEFN.

The integrations for the radial matrix element are performed by means of Simpson's rule, which requires equally-spaced points. The spacing must be small enough to obtain a sufficiently good representation of the incident partial waves over a wavelength. A rough guide is that at least five points are needed in the interval $0 \le kr \le \pi$. The minimum number of points is thus $5kr_0/\pi$. The radial integration for $\lambda = 1$ (dipole case) in the DWBA has an integrand that decreases as r^{-4} at long range. Generally $r_0 = 250$ is sufficiently large.

In order to obtain a sufficiently good representation of the 1s bound-state orbitals for large atoms, it is necessary to cluster radial points near the origin. This is done by the transformation

$$y = r - 1/\alpha r. \tag{38}$$

The Simpson's-rule integration is done for the variable y. The Jacobian

$$\frac{\mathrm{d}r}{\mathrm{d}y} = \frac{\alpha r^2}{\alpha r^2 + 1} \tag{39}$$

is included in the integration weights. The starting point of the integration is $r = \alpha^{-1}$. The value of the transformation parameter $\alpha = 100$ is good for most applications. For larger atoms such as xenon, $\alpha = 1000$ is better. The radial integration is tested by calculating the normalisations of the orbitals.

The radial integration data are set up in COMMON/RG/:

LIM: index of last point,
RDW(NR)):   radial points,
WDW(NR):   integration weights,
ALPHA: transformation parameter.

Partial waves with high values of angular momentum are extremely small at low radial values because of the centrifugal barrier. Integration efficiency is increased by starting at the first point for which the partial wave reaches the value UMIN (input). The indices of the starting points are stored in COMMON/LOCUT/ by SUBROUTINE INTMAT. They are IST1(L), IST2(L), IST3(L) for incident, slow and fast distorted waves respectively. UMIN is input in SUBROUTINE MESH.

The bound-state orbital decays exponentially for large radial points. The efficiency of the r_2 integration in (23) is increased by cutting it off at the index LIMT, which is the index of the first point at which $u_{n\ell}(r)$ falls below UMAX

(input). LIMT is stored in COMMON/HICUT/ by SUBROUTINE ORBIT. UMAX is input in SUBROUTINE MESH.

The meanings of the input variables of Table 2 are as follows.

Option switches for diagnostic prints (no print if switch is zero).

IPHASE:	Number of phase shifts to be printed for each distorted wave,
IWF:	Number of radial points for print of bound-state orbital,
IDW0:	Initial radial index for print of three distorted waves,
IDW:	Final radial index for print of three distorted waves,
IDWINC:	Interval between successive indices for radial print,
LDW0:	Index of first partial wave to be printed,
LDW:	Index of last partial wave to be printed.

Input data for differential-equation grid.

NMAX:	Number of integration segments,
HA(1):	Interval in the first segment,
NA(K):	Number of points in the Kth segment, K=1, NMAX.

Input data for radial integration grid.

LIM:	Number of integration points for partial-wave tabulation,
UMIN:	Minimum partial-wave value that contributes to the integration,
UMAX:	Minimum bound-state value that contributes to the integration.

6·3 SUBROUTINE WAVEFN

This subroutine calculates the partial waves $u_L(k, r)$ of (24) and the radial bound-state orbital $u_{n\ell}(r)$ of (25). Its important operations are as follows.

Loop over NWF=1,2,3 for incident, slow and fast distorted waves respectively.

Read orbital input for the incident (fast) distorting potential on file 'ORB1.DAT' ('ORB2.DAT').

Print orbital normalisations to check the input, and radial normalisation integrals to check the radial-integration grid.

Set up the distorting potential in VS(NXD). This is the spin-averaged static-exchange potential $V_D - \frac{1}{2}V_E$ obtained according to (36) and (37).

Set up the dimensionless potential for solving the differential equation (29) in UCR(NXD).

Set up the Coulomb phase factors $\exp(i\sigma_L)$ for each L in EXISL(JM1+1):CALL SIGMA.

Set up the Coulomb functions (Barnett *et al.* 1974) for matching to the boundary condition for each L. Regular and irregular functions FM(JM1), GM(JM1) (FI(JM1), GI(JM1)) are calculated at $\rho_0(\rho_1)$, represented by the Fortran variable RHOMAX (RHOMCH): CALL RCWFN.

Integrate the differential equation for each L, perform the matching, tabulate the absolute partial waves $v_L(k, r)$ (34) on the radial-integration grid in U1(JM1,NR), U2(JM2,NR), U3(JM3,NR) (COMMON/DW/) and the phase factors $\exp(i(\phi_L + \sigma_L))$ (35) in FNM1(JM1), FNM2(JM2), FNM3(JM3) (COMMON/CNORM/) for NWF: 1,2,3 respectively, print distorted-wave data for checking (optional): CALL INTMAT.

Set up the radial bound-state orbital $u_{n\ell}(r)$ (25) in WFN(NR) (COMMON/ KWF/) : CALL ORBIT.

Atomic orbitals are expressed in the Slater representation

$$u_{n\ell}(r) = \sum_j c_j f_j(r) \,, \tag{40}$$

where the basis function $f_j(r)$ is a normalised Slater-type orbital

$$f_j(r) = [(2n_j)!]^{-1/2} (2\zeta_j)^{n_j+1/2} \, r^{n_j} \exp(-\zeta_j r) \,. \tag{41}$$

Table 3.   Names of Fortran variables and trial values for file 'OVLP.DAT'

Line	Names	Trial values
1.	JDEV	6
2.	TARGET (A16)	ARGON 3P
3.	ZN, AE	18,18
4.	NORM	1
5.	NORB, NTS, NTP, NTD	1,0,4,0
6.	NS(J), ZS(J), J=1,NTS	No input for NTS=0
7.	NP(J), ZP(J), J=1,NTP	2, 11·07020
		2, 6·10658
		3, 2·90339
		3, 1·62255
8.	ND(J), ZD(J), J=1,NTD	No input for NTD=0
9.	L, NE, ES	1,6,0·5792
10.	C(J), J = 1, NJ (NJ = NTP for L = 1)	−0·04943
		−0·25138
		0·56956
		0·54309
	Repeat lines 9 and 10 for each subsequent orbital up to NORB	
11.	End of file flag	−1

The same format for the orbital input is used for the input files 'ORB1.DAT', 'ORB2.DAT' and 'OVLP.DAT'. The input is illustrated in Table 3 for the one-orbital file 'OVLP.DAT'. The extension to the many-orbital files is obvious. Slater representations of Hartree–Fock orbitals for atoms up to xenon have been tabulated by Clementi and Roetti (1974).

The meanings of the input variables are as follows.

JDEV:	Dummy (originally output device number),
TARGET:	Name of atom, ion or orbital,
ZN:	Nuclear charge,
AE:	Number of electrons in the atom or ion,
NORM:	NE·0, Slater basis coefficients are unnormalised,
	EQ·0, Slater basis coefficients are normalised,
NORB:	Number of orbitals,
NTS:	Number of s-basis functions,
NTP:	Number of p-basis functions,
NTD:	Number of d-basis functions,
NS(J),ZS(J):	Values of the parameters n_j and ζ_j (39) in the Jth s-basis function,

NP(J),ZP(J):	Values of the parameters n_j and ζ_j (39) in the Jth p-basis function,
ND(J),ZD(J):	Values of the parameters n_j and ζ_j (39) in the Jth d-basis function,
L:	Orbital angular momentum quantum number,
NE:	Number of electrons in the orbital,
ES:	Separation energy of the orbital (positive, hartrees),
C(J),J=1,NJ:	Coefficients c_j (38) of the Jth basis function.

6·4 SUBROUTINE DWBA

This subroutine calculates and outputs the differential cross section (1). It calculates the amplitudes (22) for DWBA and DWIA and the exchange amplitude for DWBA, using the radial functions that have been set up by SUBROUTINE WAVEFN in the COMMON blocks /DW/, /CNORM/ and /KWF/. The important operations are as follows.

Orthogonalise the partial waves ℓ of the final-state distorted waves to $u_{n\ell}(r)$ in order to ensure the convergence of the DWBA radial integral (23) at low energy (not done in the plane-wave case IPW=1).

Tabulate the spherical harmonics required for the kinematic option selected by ICOPS.

Perform the angular momentum sums to calculate the cross sections (1) (DWBA) and (20) (DWIA if required by IDWI) from the amplitude (22) and the exchange amplitude. The correspondence of the Fortran loop indices with the quantum numbers and angles of (1), (20) and (22) is given Table 4. The amplitudes (22), tabulated for the bound-state projection index M and the angle indices MTH, NTH, are squared and summed incoherently for M. DWBA and DWIA are summed separately. Cross section operations are performed if IEX.NE·1.

Table 4. Correspondence of Fortran indices with the quantum numbers and angles of equations (1), (20) and (22)

Quantity	Fortran name	Index	Loop limit
ℓ	LA		LA (input)
m	M1 = −LA, LA	M = M1+LA+1	
L'	L3 = LC−1	LC = 1, LM3	LM3 (input)
L''	L2 = LD−1	LD = 1, LM2	LM2 (input)
M''	M2 = −L2, L2	−	L2 (previous loop)
M'	M3 = M1+M2	−	−
λ	LAM1 = LAM−1	LAM = LAB, LAT, 2	LAB, LAT (selection rules)
L	L1 = LB−1	LB = 1, LM1	LM1 (input)
θ_f	THC(MTH)	MTH	NTC (input)
ϕ, θ_s, θ	THD(NTH)	NTH	NTD (input)

Calculate the factors multiplying the sums of squared amplitudes to form the cross sections.

Calculate analytic plane-wave cross sections for checking that sufficient partial waves have been included (using the option IPW.NE.0).

Write cross section output.

```
DISTORTED WAVE CROSS SECTION FOR (e,2e)
****************************************

CONTINUUM WAVES
***************
        ENERGY(eV)   LMAX
DW1:    415.80        40
DW2:     20.00        20
DW3:    380.00        35

                        NORMALIZATION CHECK: ORBITAL  NORMALIZATION  RADIAL CHECK

INPUT FOR TARGET POTENTIAL: ARGON ATOM
**************************
                                    1    1.00000638D+00  9.94889964D-01
                                    2    1.00001052D+00  9.99561972D-01
                                    3    9.99992906D-01  1.00001367D+00
                                    4    9.99998653D-01  1.00000116D+00
                                    5    9.99995600D-01  9.99956740D-01
INPUT FOR ION POTENTIAL: ARGON 3P HOLE
***********************
                                    1    1.00000638D+00  9.94889964D-01
                                    2    1.00001052D+00  9.99561972D-01
                                    3    9.99992906D-01  1.00001367D+00
                                    4    9.99998653D-01  1.00000116D+00
                                    5    9.99995600D-01  9.99956740D-01
BOUND STATE: ARGON 3P
************

                                         9.99998653D-01  1.00000115D+00


ION POTENTIAL FOR FAST ELECTRON
DIFFERENTIAL EQUATION GRID: RMAX = 253.43
MATRIX ELEMENT GRID, 4000 POINTS: ALPHA =  100.0, RMAX = 253.41


COPLANAR ASYMMETRIC KINEMATICS (WITH EXCHANGE)
*******************************

            *** DIFFERENTIAL CROSS SECTION (DWIA) ***
                    ATOMIC UNITS

THC = 1.00DEG,  ESLOW = 20.00eV,  EFAST = 380.00eV
*****************************************************
     ANGLE     XSECN PW     XSECN DW    ANGLE     XSECN PW     XSECN DW
      0.0     0.1580E+03   0.2235E+02    6.0     0.1611E+03   0.2066E+02
     12.0     0.1639E+03   0.1766E+02   18.0     0.1665E+03   0.1384E+02
     24.0     0.1687E+03   0.9899E+01   30.0     0.1704E+03   0.6681E+01
     36.0     0.1714E+03   0.4953E+01   42.0     0.1718E+03   0.5097E+01

            *** DIFFERENTIAL CROSS SECTION (DWBA) ***
                    ATOMIC UNITS

THC = 1.00DEG,  ESLOW = 20.00eV,  EFAST = 380.00eV
*****************************************************
     ANGLE     XSECN PW     XSECN DW    ANGLE     XSECN PW     XSECN DW
      0.0     0.3755E+03   0.5311E+01    6.0     0.3818E+03   0.5665E+01
     12.0     0.3860E+03   0.5915E+01   18.0     0.3881E+03   0.6047E+01
     24.0     0.3880E+03   0.6054E+01   30.0     0.3858E+03   0.5933E+01
     36.0     0.3814E+03   0.5689E+01   42.0     0.3749E+03   0.5329E+01

TIME FOR CROSS SECTION CALCULATION:  479.SEC
```

Table 5.   Computer output for the trial run

If IEX.EQ.1 exchange the quantities for the final-state electrons that are necessary to calculate the DWBA exchange amplitude. Return to the beginning of the angular momentum looping and calculate the exchange amplitude and the cross sections after setting IEX.EQ.2. The exchange amplitude is not calculated for the coplanar symmetric option ICOPS.EQ.2 since it is equal to the direct amplitude.

Details of the looping for accumulating the amplitude (22) within the m loop are as follows.

The angular momentum loops are in two groups: outer loops for the indices of the spherical harmonics L', L'', M'', and inner loops for λ, L. Reduced amplitudes (independent of m, L', L'', M'') are accumulated in SN1 (DWBA) and SN2 (DWIA) by the inner loops. They are multiplied by the appropriate spherical harmonics in loops for the appropriate kinematic angles (selected by ICOPS) and the amplitude is accumulated by the outer loops in AMPDI(M, MTH, NTH) (direct DWBA) and AMPEX(M, MTH, NTH) (exchange DWBA and DWIA). Angular momentum selection rules are checked at the earliest opportunity to eliminate forbidden calculations.

The radial integrals (23) are tabulated for λ and L to ensure that the integration is never repeated for the same set of quantum numbers. The two-dimensional integration for the DWBA is reduced to two one-dimensional integrations by utilising the partial separability of the multipole component (28) of v_3. The low-r and high-r cutoffs, described in Section 6·3, ensure that only relevant points are included in the quadrature sums. For $\lambda = 0$ the radial integration is not convergent unless the relevant $u_\ell(k, r)$ is orthogonal to $u_{n\ell}(r)$. For plane waves this is essentially true for energies >100 eV. For $\lambda = 1$ the radial integration converges as r^{-4}. The upper radial grid index LIMU is then equal to LIM, the limit of the partial-wave tabulation. For the next four values of λ, LIMU is reduced in equal steps to the upper cutoff value LIMT, which value it retains for higher λ. The integrations involve real arithmetic, using the absolute partial waves $v_L(k, r)$ of (34). The integrals are subsequently multiplied by the phase factors $\exp(i(\phi_L + \sigma_L))$ of (24) and (35), described in Section 6·3.

7. Trial Run

The trial run calculates the DWBA and DWIA for the 3p orbital of argon at an incident energy of 415·8 eV in coplanar asymmetric kinematics, for $E_f = 380$ eV, $E_s = 20$ eV, $\theta_f = 1°$, and θ_s runs from 0° to 42° at intervals of 6°. The ion potential is used for the fast electron. Exchange amplitudes are included. The computer output is given in Table 5. It is described here under its headings.

Continuum waves. Energies of the three distorted waves and the corresponding partial-wave maxima LM1, LM2, LM3 are printed.

Normalisation check. The target potential input on 'ORB1.DAT' is checked by the analytic normalisation of the input orbitals. Each orbital is then renormalised to unity and the radial integration grid is checked by calculating the normalisation again by integration. The input data for 'ORB1.DAT' are obtained from Clementi and Roetti (1974). The format is given Table 3. The same operations are performed for the ion potential input on 'ORB2.DAT', which is identical to

'ORB1.DAT' except that $AE = 17$ and $NE = 5$ for the 3p orbital (#4). The bound-state orbital on 'OVLP.DAT' (Table 3) is treated in the same way.

The maximum radii for the differential equation and matrix element grids are printed with the number of points and the transformation parameter α for the latter.

Cross section tables. The angles appropriate to the kinematic option ICOPS are printed under 'ANGLE'. Plane-wave and distorted-wave cross sections are printed under 'XSECN PW' and 'XSECN DW'.

Acknowledgments

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