Distorted Waves with Exact Non-Local Exchange: a Canonical Function Approach

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Abstract

It is shown how the Canonical Function approach can be used to obtain accurate solutions for the distorted wave problem taking account of direct static and polarisation potentials and exact non-local exchange. Calculations are made for electrons in the field of atomic hydrogen and the phaseshifts are compared with those obtained using a modified form of the DWPO code of McDowell and collaborators: for small wavenumbers our approach avoids numerical instabilities otherwise present. Comparison is also made with phaseshifts calculated using local equivalent-exchange potentials and it is found that these are inaccurate at small wavenumbers. Extension of our method to the case of atoms having other than s-type outer shells is discussed.
I. INTRODUCTION

Distorted Wave Born calculations of Triple Differential Cross Sections (TDCS) for electron impact ionization of an atom or ion require the resolution of the integro-differential equations satisfied by the radial parts of the free electron wavefunctions. Very often a simplifying approximation is made through replacement of the exchange operator by a central equivalent exchange potential (Furness and McCarthy [9], Bransden and Noble [3]). But while this is probably satisfactory for electrons with energies of a few eV and more it may cause problems near to threshold. Furthermore, to interpret the new generation of experiments using polarized electrons the proper inclusion of exchange may well be important. There exists a means of exact solution of the equation for the radial wavefunction including static and static-exchange terms (the diagonal parts of the direct potential and the exchange operator) and a polarisation potential. This is the Distorted Wave Polarised Orbital (DWPO) method of McDowell et al [15] which was developed for Distorted Wave Born calculations of excitation of Hydrogen (McDowell et al [16]) and of Helium [18] and replaces the integro-differential equation by coupled differential equations. In both cases, only an s-state of the atom is considered and the central potentials are expressed in analytical form.

The phase shift and the wavefunction in the asymptotic region were determined by use of the analytic second order JWKB solution (Burgess [5]). If the energy of the free electron is $k^2$ Ry the integro-differential equation can be rewritten in terms of the variable $kr$ but the value of the radius out to which exchange and the short-range part of the static potential remain significant is determined by the extent of the electron cloud of the atom. For small $k$ the second order JWKB solution is valid only at radii very much larger than that of the onset of the asymptotic region where exchange and short-range potentials are negligible. So we have modified the published McDowell et al code by using the iterative numerical JWKB code developed by Klapisch, Robaux and collaborators (see [1]), which is valid throughout the asymptotic region. The solutions are started by means of series expansions at the origin and continued by Numerov integration: the form of series corresponding to the regular solution is imposed by taking a power $r^{l'+1}$ at the origin in the $l'$ partial wave. For small $k$ the choice of integration step and changeover point is delicate, since convergence of the series requires small $r$ whereas the Numerov integration becomes unstable (picking up some of the irregular solution) if it is started at too small a radius. In spite of modifications to the
original code we have found it hard to obtain a solution which is stable in the sense of the phaseshift being independent of a 20% change in steplength to better than one significant figure at $k = 0.01$ and two significant figures at $k = 0.1$. But a similar but simpler code using equivalent-exchange potentials in a single differential equation is numerically stable.

The aim of the present work is to develop an alternative numerical method, based on the Canonical Function approach (Kobeissi et al [10, 11, 12], which overcomes the problems of numerical stability. In this approach two independent sets of solutions are generated starting at some central point and integrating inwards to the origin and outwards to the asymptotic region. Both contain linear combinations of the regular and the irregular solutions, but by suitably combining the two the irregular solution is eliminated. Integration can be made out to a very large radius, allowing the phase-shift to be determined by matching to plane or Coulomb wave solutions. It is not necessary to obtain a series expansion of the solution to start the integration, which makes it unnecessary to have a series expansion of the potential. Our method is therefore convenient when potentials are generated numerically rather than analytically, although here we have worked with the analytical potentials of McDowell and collaborators for the sake of comparison. Even in the case of small atoms, this is an advantage if numerical polarization-correlation potentials obtained from the density functional theory are used, although the series expansion of these near to the origin can be generated by a polynomial fit. Furthermore we can very easily extend our work to the case of p-state and d-state atoms whereas defining series starting solutions in these cases is difficult to do even on a case-by-case basis. The added complexity, with a much larger number of coupled equations to solve, would in any case probably cause even worse numerical instability at low $k$.

It is worthwhile developing a version of the DWBA approximation including non-local exchange and applicable to heavy atom targets. This is because the very successful Converged Close Coupling (CCC) approach of Bray [4] becomes increasingly difficult to apply as target complexity increases. In section 2 we discuss our present implementation of the DWPO method for the non-local exchange problem, which we propose to use to generate the necessary wavefunctions. We adopt essentially the notation of Rouet et al [17]: a full description of the DWPO method is given in the appendix of the latter paper. In section 3 we describe the use of the the Canonical Function approach to solve the resulting coupled differential equations. It is interesting to note that the present treatment of exchange can
ultimately be combined with the Canonical Function approach to the solution of coupled equations without exchange \([7, 8, 12]\) so as to get a full solution of the Close Coupling equations including all potentials and non-local exchange terms (diagonal and off-diagonal).

In section 4 we compare the phase shifts obtained by our new code with those given by our modified form of the McDowell code and by solution of single differential equations with local equivalent-exchange potentials. We highlight both the inaccuracies of the McDowell code, even in its modified form, and the inadequacies of local exchange approximations.

II. THE INTEGRO-DIFFERENTIAL EQUATION

We consider the impact of a free electron of energy \(k^2\) Ry on a one-electron atomic system of nuclear charge \(Z\) in a 1s atomic state of energy \(E_{10}\) Ry with a radial wavefunction \(R_{10}(r) = 2Z^{3/2}r \exp(-Zr)\). For a free electron with angular momentum quantum numbers \(l', m'\), if we include only on-diagonal potentials and exchange operators and replace the neglected off-diagonal coupling potentials by a polarisation potential \(V_{\text{pol}}(r)\), its radial wavefunction \(F_{l'}(k, r)\) satisfies the integro-differential equation:

\[
\left[ \frac{\partial^2}{\partial r^2} - \frac{l'(l' + 1)}{r^2} + k^2 + V_{1s}(r) + V_{\text{pol}}(r) + W_{l'}(r) \right] F_{l'}(k, r) = 0 \tag{1}
\]

where

\[
V_{1s}(r) = \frac{2Z}{r} - \frac{2}{r} \int_0^r |R_{10}(r')|^2 dr' - \int_{r}^{\infty} \frac{2}{r} |R_{10}(r')|^2 dr'
\]

\[
W_{l'}(r) F_{l'}(k, r) = (-1)^{S+1} R_{10}(r) \left\{ \left[ E_{10} - k^2 \right] \delta_{l',0} \int_0^\infty R_{10}(r') F_{l'}(k, r') dr' \right.
\]

\[
\left. - \frac{2}{r} \int_0^r R_{10}(r') F_{l'}(k, r') dr' \left( \int_r^\infty \frac{2}{r'} |R_{10}(r')|^2 dr' \right) \right\}
\]

This integro-differential equation can be transformed to the following system of coupled differential equations, which is the starting point for McDowell et al \([15, 16]\):

\[
\frac{\partial^2}{\partial r^2} F_{l'}(k, r) - \left[ \frac{l'(l' + 1)}{r^2} - V_{1s}(r) \right] F_{l'}(k, r) + (-1)^{S+1} R_{10}(r) \left[ \frac{2}{r} \frac{1}{2l' + 1} \right] G_{l'}(k, r) = (-1)^{S+1} R_{10}(r) \delta_{l',0} A(k)
\]

\[
\frac{\partial^2}{\partial r^2} G_{l'}(k, r) - \frac{l'(l' + 1)}{r^2} G_{l'}(k, r) + \frac{2l' + 1}{r} R_{10}(r) F_{l'}(k, r) = 0 \tag{2}
\]
where

\[ A(k) = \left[ k^2 - E_{10} \right] \int_0^\infty R_{10}(r') F_{l'}(k, r') dr' \]  

(3)

\( \delta_{l',0} \) is the Kronecker delta and \( V_{1s}(r) = k^2 + V_{1s}(r) + V_{pol}(r) \). Our aim is to solve this system subject to the boundary conditions

\[ F_{l'}(k, r) \rightarrow 0 \quad r \rightarrow 0 \quad G_{l'}(k, r) \rightarrow 0 \]  

(4)

\[ F_{l'}(k, r) \rightarrow a_{l'}(k) \left\{ s_{l'}(kr) - \tan[\delta_{l'}(k)] c_{l'}(kr) \right\} \quad G_{l'}(k, r) \rightarrow 0 \]  

(5)

where \( a_{l'}(k) \) is a normalisation factor, \( \delta_{l'}(k) \) is the phase shift for specific \( \{k, l'\} \) and \( s_{l'}(\rho) \) and \( c_{l'}(\rho) \) are respectively:

- \( \rho \) multiplied spherical Bessel and Neumann functions when \( Z = 1 \) (so that \( V_{1s}(r) \) is a short range potential falling off faster than \( r^{-1} \) as \( r \) tends to infinity);

- regular and irregular Coulomb wavefunctions when \( Z > 1 \) (so that \( V_{1s}(r) \) is a long range potential behaving like \( (Z-1)r^{-1} \) when \( r \) tends to infinity).

In the more general case of an ion with a frozen core and an outer shell of electrons in \( \{n, l\} \) states of radial wavefunction \( R_{nl}(r) \), and a free electron in the state \( \{k, l'\} \) we have a larger set of coupled equations:

\[ \frac{\partial^2}{\partial r^2} F_{l'}(k, r) - \left[ \frac{l'(l' + 1)}{r^2} - V_{nl}(r) \right] F_{l'}(k, r) = 0 \]

\[ (-1)^S R_{nl}(r) \frac{2}{r} \sum_\lambda \lambda J_{l,l',\lambda} G_{l'}^\lambda(k, r) = (-1)^{S+1} R_{nl}(r) \delta_{l.l'} A_{nl,l'}(k) \]

\[ \frac{\partial^2}{\partial r^2} G_{l'}^\lambda(k, r) - \frac{\lambda(\lambda + 1)}{r^2} G_{l'}^\lambda(k, r) + \frac{2\lambda + 1}{r} R_{nl}(r) F_{l'}(k, r) = 0 \]

subject to the boundary conditions, for all possible \( \lambda \) values

\[ F_{l'}(k, r) \rightarrow 0 \quad r \rightarrow 0 \quad G_{l'}^\lambda(k, r) \rightarrow 0 \]

\[ F_{l'}(k, r) \rightarrow a_{l'}(k) \left\{ s_{l'}(kr) - \tan[\delta_{l'}(k)] c_{l'}(kr) \right\} \quad G_{l'}^\lambda(k, r) \rightarrow 0 \]

Here

\[ V_{nl}(r) = k^2 + V_{nl}(r) \]

\[ -2 \sum_\lambda \lambda J_{l,l',\lambda} \left\{ \int_0^r \frac{r'^\lambda}{r^{\lambda+1}} |R_{nl}(r')|^2 dr' + \int_r^\infty \frac{r'^\lambda}{r^{\lambda+1}} |R_{nl}(r')|^2 dr' \right\} + V_{pol}(r) \]
\[ A_{nl,l'}(k) = \left[ k^2 - E_{nl} \right] \int_0^\infty R_{nl}(r')F_{l'}(k,r')dr' \]

\( I_{l,l',\lambda} \) and \( J_{l,l',\lambda} \) are angular integrals which depend on the number of electrons in the ion outer shell and the angular momentum coupling scheme. \( V_{nl}(r) \) is a central potential for attraction of an electron by the core and \( E_{nl} \) is the total energy of the outer shell electrons. This is not applicable to hydrogenic ions as the degeneracy of the energy in \( l \) makes it essential to include channel coupling potentials. So we will not consider it further here except to note that \( J_{l,l',\lambda} \) imposes the triangular rule \( |l-l'| \leq \lambda \leq l+l' \) and \( l+l'+\lambda \) even. This gives an idea of the number of different \( G_{l}^{\lambda} \) present and so of the extent of the problem we ultimately wish to solve, in the case of more complex atoms.

III. THE CANONICAL FUNCTION TECHNIQUE FOR SOLVING THE DWPO EQUATIONS:

In order to facilitate the presentation it is convenient to use \( f_1 \) in place of \( F_{l'} \) and \( f_2 \) in place of \( G_{l'} \) so as to rewrite the coupled equation system (2) as a special case of the more general system:

\[ f_1''(r) + V_{11}(r)f_1(r) + V_{12}(r)f_2(r) = \delta_{l,0}A(k)W_1(r) \]
\[ f_2''(r) + V_{22}(r)f_2(r) + V_{21}(r)f_1(r) = \delta_{l,0}A(k)W_2(r) \]

with

\[ V_{11}(r) = \mathcal{V}_{1a}(r) - \frac{l'(l'+1)}{r^2} \]
\[ V_{12}(r) = (-1)^SR_{10}(r) \left[ \frac{2}{r^2} \frac{1}{2l' + 1} \right] \]
\[ V_{21}(r) = \frac{2l' + 1}{r} R_{10}(r) \]
\[ V_{22}(r) = -\frac{l'(l'+1)}{r^2} \]
\[ W_1(r) = (-1)^{S+1}R_{10}(r) \]
\[ W_2(r) = 0 \]

We will solve this system by the canonical functions method of Kobeissi and Fakhreddine [12]. We can construct the general solution of equations (6) as

\[ f_1(r) = f_1(r_0)\alpha_{11}(r) + f'_1(r_0)\beta_{11}(r) \]
\[ + f_2(r_0)\alpha_{12}(r) + f'_2(r_0)\beta_{12}(r) + \delta_{l,0}A(k)\sigma_1(r) \]
\[ f_2(r) = f_1(r_0)\alpha_{21}(r) + f'_1(r_0)\beta_{21}(r) \]
\[ + f_2(r_0)\alpha_{22}(r) + f'_2(r_0)\beta_{22}(r) + \delta_{l,0}A(k)\sigma_2(r) \]
where \( \{ \alpha_1(r), \alpha_2(r) \} \) and \( \{ \beta_1(r), \beta_2(r) \} \) are two different pairs of independent solutions of the homogeneous system

\[
\begin{align*}
    g''_1(r) + V_{11}(r)g_1(r) + V_{12}(r)g_2(r) &= 0 \\
    g''_2(r) + V_{22}(r)g_2(r) + V_{21}(r)g_1(r) &= 0
\end{align*}
\] (7)
satisfying the initial conditions at an arbitrary point \( r = r_0 \)

\[
\alpha_{ij}(r_0) = \beta'_{ij}(r_0) = \delta_{i,j} \quad \alpha'_{ij}(r_0) = \beta_{ij}(r_0) = 0
\] (8)

and \( \{ \sigma_1(r), \sigma_2(r) \} \) is a particular solution of the inhomogeneous system

\[
\begin{align*}
    h''_1(r) + V_{11}(r)h_1(r) + V_{12}(r)h_2(r) &= W_1(r) \\
    h''_2(r) + V_{22}(r)h_2(r) + V_{21}(r)h_1(r) &= W_2(r)
\end{align*}
\] (9)
satisfying the initial conditions at \( r = r_0 \)

\[
\sigma_i(r_0) = \sigma'_i(r_0) = 0
\] (10)

In matrix form:

\[
Y(r) = \alpha(r)Y(r_0) + \beta(r)Y'(r_0) + \delta_{\nu,0}A(k)\sigma(r)
\] (11)

with

\[
Y(r) = \begin{pmatrix} f_1(r) \\ f_2(r) \end{pmatrix} \quad \alpha(r) = \begin{bmatrix} \alpha_{11}(r) & \alpha_{12}(r) \\ \alpha_{21}(r) & \alpha_{22}(r) \end{bmatrix}
\]

\[
\sigma(r) = \begin{pmatrix} \sigma_1(r) \\ \sigma_2(r) \end{pmatrix} \quad \beta(r) = \begin{bmatrix} \beta_{11}(r) & \beta_{12}(r) \\ \beta_{21}(r) & \beta_{22}(r) \end{bmatrix}
\]

Using the boundary conditions (4) imposes \( \alpha(0)Y(r_0) + \beta(0)Y'(r_0) + \delta_{\nu,0}A(k)\sigma(0) = 0 \), which leads to \( \beta^{-1}(0)\alpha(0)Y(r_0) + Y'(r_0) + \delta_{\nu,0}A(k)\beta^{-1}(0)\sigma(0) = 0 \) where \( \beta^{-1}(r) \) is the inverse of the matrix \( \beta(r) \). Thus the constant matrices \( Y'(r_0) \) and \( Y(r_0) \) are related by:

\[
Y'(r_0) = Y(r_0)\Lambda + \delta_{\nu,0}A(k)\lambda
\]

\[
\Lambda = -\beta^{-1}(0)\alpha(0) \quad \lambda = -\beta^{-1}(0)\sigma(0)
\]
Substituting back into (11) we then get
\[ Y(r) = \varphi(r)Y(r_0) + \delta_{\nu,0}A(k)\gamma(r) \]
\[ \varphi(r) = \alpha(r) + \beta(r)\Lambda \quad \gamma(r) = \beta(r)\lambda + \sigma(r) \]

The solution constructed from \( \varphi(r) \) and \( \gamma(r) \) is a particular solution of the coupled equations (6) for which the functions \{\( f_1(r) \), \( f_2(r) \)\} are regular at the origin. It corresponds to initial values (where \( I \) is the unit matrix) at the arbitrarily chosen starting point \( r = r_0 \):

\[ \varphi(r_0) = I \quad \varphi'(r_0) = \Lambda \quad \gamma(r_0) = 0 \quad \gamma'(r_0) = \lambda \]

It remains to determine \( A(k) \). Substituting equations (6), for the case \( l' = 0 \), into expression (3) we get
\[ A(k) = \left[ k^2 - E_{10} \right] \frac{f_1(r_0)I_1 + f_2(r_0)I_2}{1 - [k^2 - E_{10}] J} \]

or, in a simpler form,
\[ A(k) = A_1 f_1(r_0) + A_2 f_2(r_0) \]

\( A_1 = \frac{[k^2 - E_{10}] I_1}{1 - [k^2 - E_{10}] J} \quad A_2 = \frac{[k^2 - E_{10}] I_2}{1 - [k^2 - E_{10}] J} \)

From the second of the boundry conditions (5) we have
\[ f_1(r_0)\varphi_{21}(r) + f_2(r_0)\varphi_{22}(r) + A(k)\gamma_2(r) \xrightarrow{r \to \infty} 0 \]

and comparing equations (12) and (13) we get
\[ \frac{f_2(r_0)}{f_1(r_0)} = D_\infty = \lim_{r \to \infty} D(r) \quad D(r) = -\frac{\varphi_{21}(r) + a_1\gamma_2(r)}{\varphi_{22}(r) + a_2\gamma_2(r)} \]

which implies, considering \( f_1(r_0) \) as arbitrary,
\[ f_1(r) = f_1(r_0) \left\{ [\varphi_{11}(r) + a_1\gamma_1(r)] + D_\infty [\varphi_{12}(r) + a_2\gamma_1(r)] \right\} \]
From the first of boundary conditions (5) we can then determine the phaseshift \( \delta_l \) by

\[
\tan \delta_l = \lim_{r \to \infty} Q(r) \quad Q(r) = -\frac{f_1'(r)s_\nu(kr) - f_1(r)k s_\nu'(kr)}{f_1'(r)c_\nu(kr) - f_1(r)k c_\nu'(kr)}
\]

We follow Kobeissi et al [11] in using the recursion relations for \( s_\nu(\rho) \) and \( c_\nu(\rho) \):

\[
Z = 1 : Q(r) = \frac{f_1'(r) - \left(\frac{l'+1}{r}\right) f_1(r) \right] s_\nu(kr) + kf_1(r) s_{\nu+1}(kr)}{f_1'(r) - \left(\frac{l'+1}{r}\right) f_1(r) \right] c_\nu(kr) + kf_1(r) c_{\nu+1}(kr)}
\]

\[
Z > 1 : Q(r) = \frac{f_1'(r) + \left(\frac{Z-1}{k(l'+1)} - \frac{l'+1}{r}\right) f_1(r) \right] s_\nu(kr) + \sqrt{k^2 + \frac{(Z-1)^2}{(l+1)^2}} f_1(r) s_{\nu+1}(kr)}{f_1'(r) + \left(\frac{Z-1}{k(l'+1)} - \frac{l'+1}{r}\right) f_1(r) \right] c_\nu(kr) + \sqrt{k^2 + \frac{(Z-1)^2}{(l+1)^2}} f_1(r) c_{\nu+1}(kr)}
\]

The function \( Q(r) \) can be defined for any radius \( r \). We calculate it at large \( r \) values and examine its behaviour. When it tends to a constant limit we consider that the asymptotic region has been reached and the phaseshift is determined to within a multiple of \( 2\pi \). We must also check that \( D(r) \) of equation (14) tends to a constant limit when \( r \) becomes large. This should happen for radii larger than the effective extent of the atomic charge cloud, at which exchange effects become negligible. The value of \( F(r_0) \) is finally chosen to get the proper normalisation of the continuum function; a \( \delta \) function in momentum requires \( a_\nu(k) = \sqrt{2/\pi} \) in condition (5).

To summarise, solution of the coupled equation problem (6), without specification of the boundary conditions, is reduced to the determination of a set of functions having well determined initial values at some arbitrary radius \( r_0 \): the canonical functions given by the matrices \( \alpha(r) \), \( \beta(r) \) and \( \sigma(r) \). We then take linear combinations of these chosen to get other canonical functions \( \varphi(r) \) and \( \gamma(r) \) which satisfy the boundary condition (4) at the origin. Finally, the asymptotic boundary conditions (5) enable us to determine the appropriate linear combination of \( \varphi(r) \) and \( \gamma(r) \) and to obtain the phase-shift and the wavefunction. Essentially, we need only to develop a single algorithm for the solution of a system of two coupled equations of the form (7) or (9) and then apply it to the different cases represented by the initial conditions (8) or (10).

The enormous advantage of the present Canonical Functions approach is that the integration of equations (7) and (9) can be started at any desired radius \( r_0 \), in particular at a point far from the origin. Almost all previous methods require a starting solution in the region near to the origin, where numerical integration of the coupled equations cannot be directly initiated because of the singular behaviour of the potentials which contain terms
proportional to $r^{-1}$ and $r^{-4}$ and the angular momentum terms which are proportional to $r^{-2}$. It is possible to follow McDowell et al. [15, 16] in obtaining a series expansion of the regular solution at the origin, which requires the potentials to be expressable in an analytical form and their series expansions about the origin to be known. The solutions are continued by numerical integration of the coupled equations using one or another of the well-known integrators, such as the method of Numerov (1933). But for small $k$ the outwards Numerov integration of the regular solution can get out of control if it picks up even a very small fraction of the irregular solution, because of ill-conditioning due to round-off errors. An alternative is to modify the potential by introducing a hard core: $V_{nl}(r)$ is set artificially to infinity for $r < r_s$, where $r_s$ is the starting point of the integration and retains its original form for $r > r_s$. As mentioned by Bayliss et al. (1982), this method gives results sensitive to the point in the classically forbidden region at which the integration is started. If the starting point is too small some solutions become unstable; if it is too large for the initial conditions employed the solutions are quite simply inaccurate. In the Canonical Functions approach, the solutions $\alpha(r)$, $\beta(r)$ and $\sigma(r)$ initially generated are in fact linear combinations of the regular and irregular solutions of the coupled equations and by taking the linear combinations $\varphi(r)$ and $\gamma(r)$ we eliminate the irregular solution between them.

IV. RESULTS AND DISCUSSION

We apply the present method to the case of the collision of a low-energy electron with atomic hydrogen, i.e. generating the wavefunctions needed for DWBA calculations of electron impact ionization of atomic hydrogen. In this case the static potential is given by:

$$V_{1s}(r) = -2\left(1 + \frac{1}{r}\right)\exp(-2r)$$

Like McDowell and collaborators, we use a Callaway-Temkin polarization potential (see Drachman and Temkin [6]) which takes the form

$$V_{\text{pol}}(r) = -\frac{9}{2r^4} \left[1 - e^{-2r} \left(1 + 2r + 2r^2 + \frac{4}{3}r^3 + \frac{2}{3}r^4 + \frac{4}{27}r^5\right)\right]$$

To integrate the coupled equation systems (7) and (9) preference is given in the present work to the „integral superposition” (I.S.) method which was shown by Kobeissi et al. [8, 10, 13] to be highly accurate in the case of both single and coupled differential equations. This requires
potentials to be expressed in analytical form. However, numerical potentials can generally be fitted by analytical functions, for instance using cubic splines. The integration can be safely taken out to very large radius, where $V_{1s}(r)$ assumes its asymptotic form and the phase shift is determined by equation (17). We refer to this method as Kobeissi-Fakhreddine-Tweed Exact Exchange (KFTEE).

Numerov integration of the coupled equation system (2) starting from series solutions at the origin will be referred to as McDowell-Morgan-Myerscough (McDMM) although the code used differs from that of McDowell et al. [15] by the use of the Klapish-Robaux JWKB code as soon as the non-local exchange term is negligible. For the sake of comparison, we have also made calculations in which exact exchange is replaced by the use of the local equivalent-exchange potentials of Furness and McCarthy [9] or of Bransden and Noble [3]. These are referred to respectively as Furness-McCarthy Local Exchange (FMcCLE) or Bransden-Noble Local Exchange (BNLE). These require the solution of a single differential equation, rather than an integro-differential equation or a pair of coupled equations. We use Numerov integration starting from a series solution at the origin and continuation by the Klapish-Robaux JWKB solution from any convenient radius after the first point of inflexion. The code used is similar to our version of the DWPO code and we deliberately choose to switch to the JWKB solution at the same radius as in the McDMM calculations. We use a regular radial mesh with steps of $h$ for $0 \leq r \leq 1.2$, $2h$ for $1.2 < r \leq 4.8$, $4h$ for $4.8 < r \leq 40.8$ a.u., the changeover to the JWKB solution being made at a radius $r > 4.8$ determined by checking the matching in the DWPO case. (For the purposes of collision calculations, where we determine the tails of certain integrals by a method based on the second order JWKB solution, we continue the radial mesh with a step of $8h$ out to $r = 184.8$ a.u.) Calculations were made for three values of $h$: 0.004, 0.006 and 0.008 a.u. Whereas the phaseshifts are steplength-independent in the case of the Local Exchange calculations, this is not so for the McDMM calculations at low momentum. Results are given in tables 1 to 4 where they are compared to those obtained with the present new KFTEE code.

For $l' = 0$ (table 1) the McDMM code exhibits severe steplength dependence for $k$ up to about 0.5 a.u. (3.4 eV energy) for both singlet and triplet spin states. We also found that the singlet calculations for $k$ up to about 0.3 a.u. were sensitive to the extent of the mesh ranges chosen for the different steplength multiples. From $k = 0.6$ a.u. on the results appear to be stable to four decimal places. However, the phase-shifts differ from those obtained
TABLE I: Phase-shifts (rad.) for \( \ell' = 0 \) calculated as a function of \( k \) (a.u) using the McDMM code with three different steplengths \( h \) (a.u.), compared to those obtained using the KFTEE code.

| \( k \) | \( h = .004 \) | \( h = .006 \) | \( h = .008 \) | KFTEE | \( h = .004 \) | \( h = .006 \) | \( h = .008 \) | KFTEE |
|-------|------------|------------|------------|--------|------------|------------|------------|--------|
| 0.1   | 1.138750   | 1.134672   | 1.171174   | 2.527441 | 2.944466   | 2.944887   | 2.944556   | 2.948757 |
| 0.2   | 1.996521   | 1.995936   | 1.996479   | 2.034071 | 2.735678   | 2.735645   | 2.735678   | 2.735060 |
| 0.3   | 1.649999   | 1.650124   | 1.665189   | 2.527570 | 2.527588   | 2.527605   | 2.527605   | 2.523228 |
| 0.4   | 1.372797   | 1.372837   | 1.384975   | 2.329332 | 2.329341   | 2.329332   | 2.329332   | 2.322439 |
| 0.5   | 1.157391   | 1.157409   | 1.168257   | 2.146210 | 2.146215   | 2.146210   | 2.146210   | 2.137332 |
| 0.6   | 0.991071   | 0.991079   | 0.991087   | 1.980225 | 1.980225   | 1.980225   | 1.980225   | 1.969819 |
| 0.7   | 0.865011   | 0.865016   | 0.865020   | 0.873758 | 1.831592   | 1.831594   | 1.831596   | 1.819917 |
| 0.8   | 0.772639   | 0.772644   | 0.779612   | 1.699554 | 1.699556   | 1.699556   | 1.699556   | 1.743484 |
| 0.9   | 0.708203   | 0.708203   | 0.713415   | 1.582765 | 1.582765   | 1.582765   | 1.582765   | 1.621901 |
| 1.0   | 0.666187   | 0.666189   | 0.666178   | 1.479626 | 1.479627   | 1.479627   | 1.479627   | 1.507213 |
| 1.1   | 0.641285   | 0.641284   | 0.641271   | 1.388498 | 1.388498   | 1.388498   | 1.388498   | 1.407830 |
| 1.2   | 0.628568   | 0.628567   | 0.628552   | 0.630856 | 1.307821   | 1.307820   | 1.307809   | 1.320019 |
| 1.3   | 0.623787   | 0.623786   | 0.623773   | 0.625395 | 1.236182   | 1.236181   | 1.236170   | 1.242529 |
| 1.4   | 0.623565   | 0.623563   | 0.623551   | 0.624628 | 1.172346   | 1.172343   | 1.172333   | 1.174116 |
| 1.5   | 0.625441   | 0.625439   | 0.625429   | 0.626161 | 1.115244   | 1.115242   | 1.115232   | 1.113588 |

From the KFTEE code: at \( k = 0.6 \) a.u. the difference is about 0.01 rad. ; by \( k = 1.5 \) a.u. it has fallen to \(-0.0008\) rad. for singlet and \(+0.0017\) rad. for triplet states, which in both cases comes to about 0.1% error. This is probably due to the different ways in which the phaseshifts are determined. In the KFTEE code we know both \( f_1(r) \) and \( f_1'(r) \) and may use equation (14) to get \( \tan\delta_{\ell'} \) from their values at a single mesh-point. In the McDMM code we only dispose of \( f_1(r) \) and so have to use its values at two mesh-points to get \( \tan\delta_{\ell'} \); this procedure is more subject to numerical error, even if care is taken to choose points separated by a half-period of the JWKB phase function.

For \( \ell' = 1 \) (table 2) the steplength dependence of the McDMM code is less important. This is also the case for \( \ell' \geq 2 \) so in tables 3 and 4 we give McDMM results for \( h = 0.006 \) a.u. only. We again find that the McDMM phaseshifts differ from those calculated by the
TABLE II: Phase-shifts (rad.) for \( l' = 1 \) calculated using the McDMM code with three different steplengths, compared to those obtained using the KFTEE code.

The present KFTEE method. But the differences are much smaller than in the case of \( l' = 0 \): generally, from \( k = 0.6 \) a.u. onwards, only the fourth decimal changes. Presumably, the inhomogeneous solution is more sensitive than the homogeneous one to the use of Numerov integration. Instabilities may also arise in the determination of \( A(k) \), which depends on calculating short-range integrals for the overlap of the target wavefunction with solutions of the homogeneous and of the inhomogeneous equations. These integrals are sensitive to the behaviour of the solutions at small radius, so we would not expect them to be affected by errors which accumulate as the solution is integrated outwards. Even if the solutions become unstable at long range, \( A(k) \) should not be badly affected. So the errors and instabilities in the McDMM code for small \( k \) (energies below \( \sim 5 \) eV) can be imputed to the use of Numerov integration in a coupled equation problem and will presumably get worse as the number of equations increases. Hence the usefulness of the present Canonical Functions method in the case of a target with outer electron orbitals of angular momentum \( l > 0 \), which requires the solution of a system of many more coupled equations than only the two needed for hydrogenic atoms.

In tables 3 (singlet case) and 4 (triplet case) we compare phaseshifts from the McDMM
| $l' = 2$ | $l' = 2$ | $l' = 3$ | $l' = 3$ | $l' = 4$ | $l' = 4$ | $l' = 5$ | $l' = 5$ |
|---|---|---|---|---|---|---|---|
| $k$ | McDMM | KFTEE | McDMM | KFTEE | McDMM | KFTEE | McDMM |
| 0.1 | 0.001287 | 0.001344 | 0.000334 | unstable | 0.000204 | unstable | 0.000110 |
| 0.2 | 0.005231 | 0.005269 | 0.001765 | 0.001795 | 0.000776 | 0.000816 | 0.000401 | 0.000439 |
| 0.3 | 0.011215 | 0.011234 | 0.004005 | 0.004028 | 0.001817 | 0.001837 | 0.000962 | 0.000988 |
| 0.4 | 0.018215 | 0.018227 | 0.007071 | 0.007085 | 0.00324 | 0.003264 | 0.001743 | 0.001758 |
| 0.5 | 0.025156 | 0.025163 | 0.010797 | 0.010806 | 0.005074 | 0.005084 | 0.002733 | 0.002745 |
| 0.6 | 0.031323 | 0.031322 | 0.014959 | 0.014962 | 0.007263 | 0.007263 | 0.003942 | 0.003949 |
| 0.7 | 0.036537 | 0.036534 | 0.019299 | 0.019301 | 0.009737 | 0.009741 | 0.005354 | 0.005360 |
| 0.8 | 0.041023 | 0.041016 | 0.023616 | 0.023610 | 0.012437 | 0.012436 | 0.006953 | 0.006958 |
| 0.9 | 0.045182 | 0.045174 | 0.027784 | 0.027781 | 0.015271 | 0.015269 | 0.008710 | 0.008711 |
| 1.0 | 0.049394 | 0.049382 | 0.031763 | 0.031756 | 0.018163 | 0.018158 | 0.010593 | 0.010591 |

TABLE III: Phase-shifts (rad.) for $S = 0$ and $l' \geq 2$, calculated using the McDMM code with a steplength of $h = 0.006$, compared to those obtained using the KFTEE code.

| $l' = 2$ | $l' = 2$ | $l' = 3$ | $l' = 3$ | $l' = 4$ | $l' = 4$ | $l' = 5$ | $l' = 5$ |
|---|---|---|---|---|---|---|---|
| $k$ | McDMM | KFTEE | McDMM | KFTEE | McDMM | KFTEE | McDMM |
| 0.1 | 0.001295 | 0.001358 | 0.000334 | unstable | 0.000204 | unstable | 0.000110 |
| 0.2 | 0.005456 | 0.005492 | 0.001768 | 0.001798 | 0.000776 | 0.000816 | 0.000401 | 0.000439 |
| 0.3 | 0.012687 | 0.012706 | 0.004035 | 0.004059 | 0.001818 | 0.001837 | 0.000962 | 0.000988 |
| 0.4 | 0.023298 | 0.023310 | 0.007249 | 0.007262 | 0.003254 | 0.003270 | 0.001743 | 0.001758 |
| 0.5 | 0.037315 | 0.037320 | 0.011437 | 0.011446 | 0.005110 | 0.005120 | 0.002735 | 0.002748 |
| 0.6 | 0.054197 | 0.054200 | 0.016625 | 0.016628 | 0.007384 | 0.007392 | 0.003953 | 0.003961 |
| 0.7 | 0.072899 | 0.072899 | 0.022758 | 0.022760 | 0.010084 | 0.010088 | 0.005389 | 0.005396 |
| 0.8 | 0.092140 | 0.092132 | 0.029699 | 0.029696 | 0.013194 | 0.013197 | 0.007049 | 0.007053 |
| 0.9 | 0.110743 | 0.110721 | 0.037226 | 0.037223 | 0.016684 | 0.016684 | 0.008925 | 0.008928 |
| 1.0 | 0.127837 | 0.127824 | 0.044079 | 0.045069 | 0.020494 | 0.020494 | 0.011006 | 0.011007 |

TABLE IV: Phase-shifts (rad.) for $S = 1$ and $l' \geq 2$, calculated using the McDMM code with a steplength of $h = 0.006$, compared to those obtained using the KFTEE code.
and KFTEE codes for partial waves $l' = 2, 3, 4, 5$. We see that at $k = 0.1$ the McDMM code is either unstable or else fails to get even the first significant figure correct. Agreement to two significant figures at all $l'$ is only obtained for $k > 0.5$. Agreement to three significant figures is obtained from $k \approx 0.7$ a.u. (7 eV energy) onwards. At this energy it is necessary to include about ten partial waves in collision calculations and slight changes in the value of the phaseshift can significantly affect the cross section values even though the radial integrals (which depend mainly on the short range behaviour of the wavefunctions) show hardly any differences.

Finally, in figures 1 to 4, we compare, for the lowest two partial waves, the phaseshifts obtained using the KFTEE code with those from the local equivalent-exchange potential models FMcCLE and BNLE. Important differences are found up to $k \approx 1.1$ a.u. (15 eV energy). In the case of singlet spin states, for $l' = 0$ (figure 1) the equivalent-exchange models give severe underestimates but for $l' = 1$ (figure 3) they are acceptable. In the case of triplet spin states, for $l' = 0$ (figure 2) results are quite good but for $l' = 1$ the BNLE model gives a severe overestimate. For higher partial waves equivalent-exchange models give fairly satisfactory results. Since Distorted Wave Born collision calculations near to threshold converge with only about five partial waves, we would hesitate then to use a local equivalent-exchange potential.

V. CONCLUSIONS AND PROSPECTS

We have shown that a distorted wave code, with exact treatment of exchange but using Numerov integration, breaks down through numerical instabilities at energies below about 5 eV. We have also shown that codes with local equivalent-exchange potentials give poor results for low partial waves at energies below 15 eV. We propose an alternative method treating exchange exactly but using the Canonical Function technique to integrate the coupled equations. This we believe to be numerically stable even at extremely small energies. The present work is the first step towards a general code applicable to target atoms or molecules in any angular momentum state and capable of using numerically generated potentials. An alternative code is under development in which solutions are obtained by Runge-Kutta integration on a regular grid out to a radius where exchange terms are negligible; phase-shifts are obtained by comparison with the Klapisch-Robaux iterative JWKB code \[\text{[citation]}\]. In this
FIG. 1: Singlet state phase-shifts for $l' = 0$ as a function of impulsion $k$. Full line: present KFTEE non-local exchange model; dashed line: BNLE equivalent-exchange potential model; dot-dash line: FMcCLE equivalent-exchange potential model.

FIG. 2: Triplet state phase-shifts for $l' = 0$. As figure 1.
FIG. 3: Singlet state phase-shifts for $l' = 1$. As figure 1.

FIG. 4: Triplet state phase-shifts for $l' = 1$. As figure 1.
code we have on the one hand \( f_1(r) \) and \( f'_1(r) \) and on the other a phase function, its derivative and a slowly-varying amplitude function for which we can safely generate the derivative numerically. So we can get \( \tan \delta \nu \) using a single mesh point, but without the need to carry numerical integration of the coupled equations out to a radius (very big for small \( k \)) where the asymptotic behaviour is given by \( s_\nu(kr) \) and \( c_\nu(kr) \). The new code will give us the opportunity to check the relative accuracy of phaseshift determinations using respectively \( f_1(r) \) and \( f'_1(r) \) at one mesh-point or \( f_1(r) \) at two. We also intend to test the effects at low energy of using Bethe-Reeh type multipole polarisation potentials \[6\] which we will generate numerically, for instance in the case of \( Na \) and the rare gases; this will enable us to extend the work of Rouet \textit{et al.} \[17\]. We are particularly interested in applications to \((e, 2e)\) and \((\gamma, 2e)\) processes involving polarised electrons.

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