

Close-coupling Formalism for Electron/Positron–Atom Systems and Underlying Scattering Theory*

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Abstract

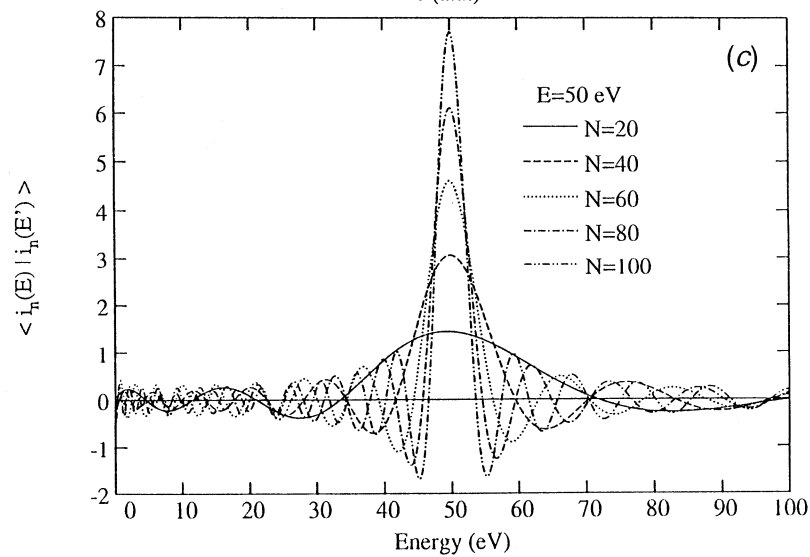
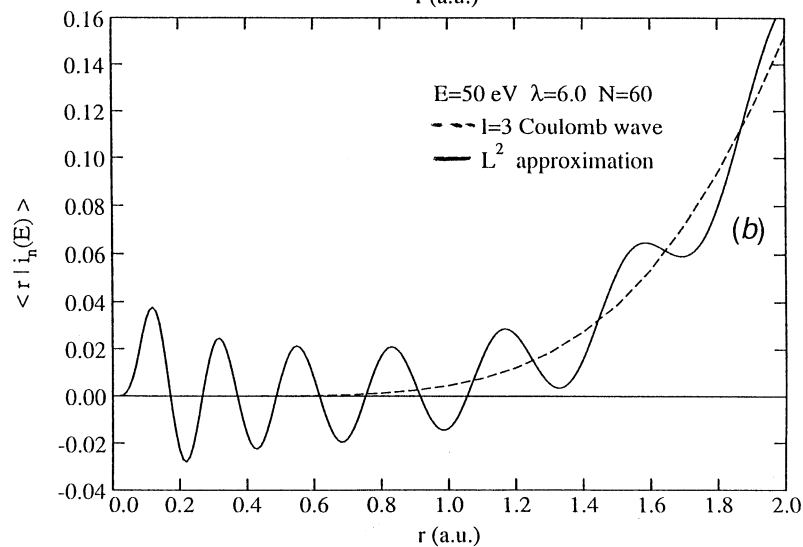
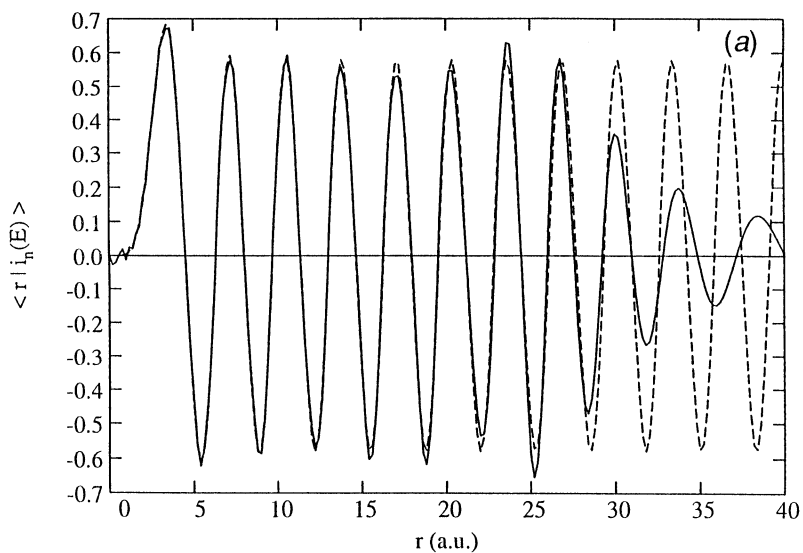
The close-coupling method for electron/positron–atom scattering promises to give a complete description of the scattering process provided the space of target states is properly spanned. This paper will discuss the structure of the equations, emphasising questions of stability associated with the expansions over sets of target states. For electron–atom scattering, the character of the solution is discussed and a simple example is given to illustrate the non-convergence of the half-shell T -matrix. This lack of convergence can be fixed by application of the symmetrisation boundary condition, leading to new forms of the equations. For positron–atom scattering, the standard equations yield convergent half-shell T -matrices for all but the largest calculations.

1. Introduction

The purpose of this paper is to review and discuss the close-coupling equations and to concentrate in particular on questions which have a bearing on the accuracy of their numerical solution. The close-coupling expansion seeks to represent the full scattering wave function in terms of a complete expansion over target states. This type of expansion seems physically reasonable since at large distances after the scattering, the boundary condition is that of a diverging spherical wave in the scattering-particle coordinate with the target atom left in some excited state. Even processes where the target is ionised by the collision can be taken into account through use of the continuum states of the target.

The key to the application of this method and the models it generates depends on the approximations we make to incorporate the ‘complete’ set of target states. Since the complete set always includes an infinite number of discrete excited states as well as non-normalisable continuum states, approximations will always have to be made. The simplest one is to omit all target states other than those for which we calculate excitation amplitudes. This is a rather drastic approximation usually, except at very low energies where excitation to neglected target states is virtual. Thus the close-coupling equations were solved in the low-energy regime in the early days of computer solutions. At the same time as these calculations

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were being undertaken, it was noted that for impact energies above the target ionisation threshold, the method was generally unsatisfactory since no account was taken of the excitation to the continuum states. The coupling to these states will remove flux from the channels whose scattering amplitudes we wish to obtain. Consequently close-coupling solutions with only a few low-lying states tended to overestimate the cross sections.

Progress towards improved close-coupling models for intermediate energies came initially by extending the close-coupling expansion through the addition of 'pseudostates' which are orthogonal to the included target states and therefore in some sense represent a linear combination of the states in the neglected portion of the target space. These states are of bound-state character and hence normalisable in the usual sense. By including these states (which are not true eigenstates of the target) the equations now had a mechanism in them to absorb flux from the transitions to the low-lying target states. An example of the way pseudostates approximate the continuum functions is shown in Fig. 1 for hydrogen targets where the overlap between a positive-energy pseudostate formed from the Laguerre basis

$$\xi_i = \left(\frac{\lambda i!}{(2\ell + 2 + i)!} \right)^{\frac{1}{2}} (\lambda r)^{\ell+1} \exp(-\lambda r/2) L_i^{2\ell+2}(\lambda r) \quad i = 0, 1, \dots$$

and the true continuum functions is shown for various numbers of expansion functions. The continuum functions are not square integrable and consequently this expansion converges rather slowly (see Stelbovics and Winata 1990) so we require large subsets of the full basis to obtain realistic models for continuum coupling. Generally the reduction of flux by using the pseudostates was successful in that the transition amplitudes gave improved agreement with experiment but at a cost; there were unphysical resonances introduced above the ionisation thresholds in some cases (Burke and Mitchell 1973). We now know that their effect is diminished whenever a large enough expansion set is used but this understanding has become clear only in the past few years when systematic calculations on a large scale could be attempted widely through the advent of the powerful work-stations [see for example Bray and Stelbovics (1995b) and references therein]. The trend is now inescapably towards close-coupling equations which couple large numbers of real target as well as pseudostates.

To solve the equations we favour recasting the coupled-channels equations from the Schrödinger to the Lippmann–Schwinger form. This is an alternative approach to solving the differential equations by use of Green's function techniques to yield an inhomogeneous integral equation which has the advantage that the boundary conditions are built into the inhomogeneous term.

Fig. 1. (*Left*) The L^2 approximations to an $l = 3$ hydrogen continuum wave at $E = 50$ eV. Fig. 1a shows a continuum target wave (dashed curve) and its L^2 expansion (solid curve) with $\lambda = 6.0$ truncated to $N = 60$ terms. Fig. 1b shows the details of the approximation for small radial distances. Fig. 1c shows the overlap between two truncated expansions as a function of N . For large N this gives a representation of a delta function in energy. In an actual calculation the energies E, E' are fixed by diagonalisation of the target Hamiltonian in the function set.

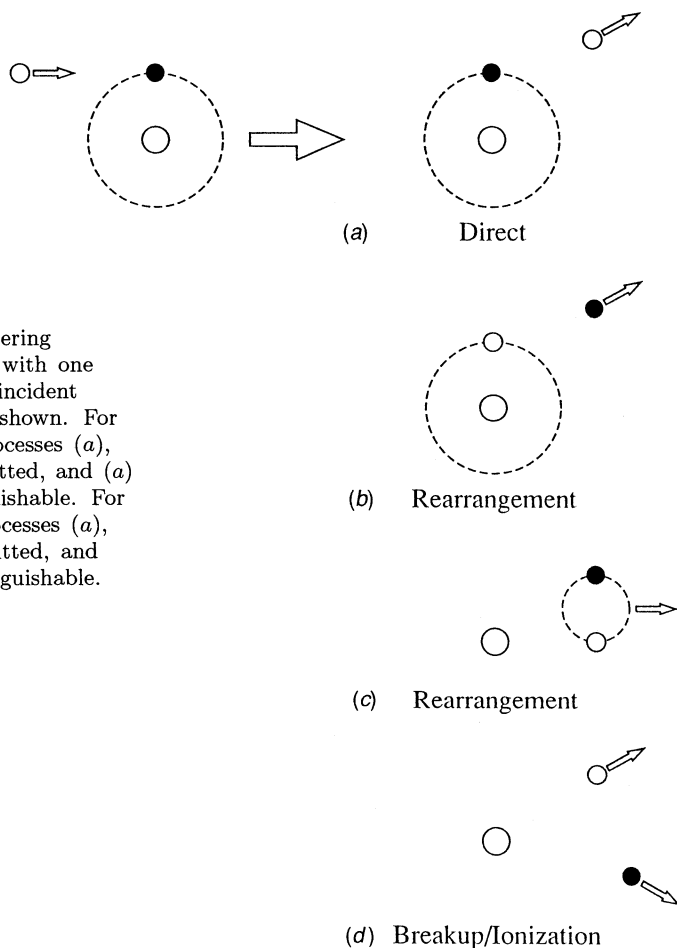


Fig. 2. Various scattering channels for a target with one valence electron and incident electron/positron are shown. For incident electrons, processes (a), (b) and (d) are permitted, and (a) and (b) are indistinguishable. For incident positrons processes (a), (c) and (d) are permitted, and (a) and (c) are distinguishable.

2. Electron-Atom Close-coupling Formalism

The close-coupling method is based on the expansion of the projectile plus target wave function in terms of the complete set of target states (see for example Burke and Seaton 1971). For the discussion we consider the simplest target, namely hydrogen, but indicate extensions to other targets later. The scattering channels are shown in Fig. 2 for electron and positron projectiles. We have labelled the incoming projectile by the white circle and the target valence electron by black. If we consider an electron projectile, the Pauli principle requires that the wave function be properly antisymmetrised under interchange of the black and white electrons. For the example of hydrogen this means the coordinate-space wave function obeys the symmetry

$$\Psi^S(\mathbf{r}_1, \mathbf{r}_2) = (-1)^S \Psi^S(\mathbf{r}_2, \mathbf{r}_1), \quad (1)$$

where S is the total spin quantum number for the system. Now if we denote target states by $|i_n\rangle$, then the wave function may be expanded in terms of the

complete set as

$$\langle \mathbf{r}_1, \mathbf{r}_2 | \Psi^S \rangle = \sum_n \langle \mathbf{r}_1 | i_n \rangle \langle \mathbf{r}_2 | F_n^S \rangle, \quad (2)$$

where

$$|F_n^S(2)\rangle = \langle i_n(1) | \Psi^S(1, 2) \rangle. \quad (3)$$

Here we indicate the space of the particle we are integrating over by the labels 1,2. The close-coupling equations are equations for the $|F^S\rangle$ which have a single coordinate label, but are also labelled by the target-state index i . The trade-off in reformulating the full scattering wave function in terms of $|F^S\rangle$ is that it is much easier to make physically reasonable approximations to the target space rather than attempting to solve equations in two coordinates. Expansion (2) is deceptively simple because the antisymmetrisation property (1) must still be imposed. The standard way this condition is enforced is to replace expansion (2) by an explicitly symmetrised one:

$$\Psi^S(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{2} \sum_n (i_n(\mathbf{r}_2) F_n^S(\mathbf{r}_1) + (-1)^S i_n(\mathbf{r}_1) F_n^S(\mathbf{r}_2)). \quad (4)$$

We now discuss the implications of the above choice of expansion (4).

(2a) Close-coupling Equations

The time independent Schrödinger equation for electron scattering from atomic hydrogen is

$$(E - H) |\Psi^S\rangle = 0, \quad (5)$$

where the Hamiltonian is

$$H = K_1 + v_1 + K_2 + v_2 + v_{12}. \quad (6)$$

Here $K_{1,2}$, $v_{1,2}$ refer to the kinetic-energy operators and potentials associated with electrons 1,2 and v_{12} is the electron-electron potential. To derive the close-coupling equations we note that the target states satisfy

$$(K_2 + v_2) |i_n\rangle = \epsilon_n |i_n\rangle. \quad (7)$$

Then inserting expansion (4) into the Schrödinger equation (6) and folding on the left with the target states one obtains the standard or 'old' form of close-coupling equations

$$\sum_n (K \delta_{mn} + V_{mn}^S) F_n^S = (E - \epsilon_m) F_m^S, \quad (8)$$

where

$$V_{mn}^S = \langle i_m | V^S | i_n \rangle, \quad V^S = v_1 + v_{12} + (-1)^S (H - E) P_r, \quad (9)$$

and where P_r is the space-exchange operator interchanging the coordinate labels for \mathbf{r}_1 and \mathbf{r}_2 and K is the kinetic energy. They may be written more compactly as

$$(E - \epsilon - K - V^S(E)) |F^S\rangle = 0, \quad (10)$$

where $|F^S\rangle$ is the column vector whose components are the F_m^S , ϵ is a diagonal matrix in the target indices m, n with elements the energies ϵ_m and V^S has components V_{mn}^S . Since our aim in solving these equations is to extract transition amplitudes, it is also convenient to write down the Lippmann–Schwinger (LS) forms of the equation for the F^S and the T -matrices. To this end we define the free channel Green function operator G_0 by

$$(G_0(E))_{mn} = \delta_{mn} (E - \epsilon_m - K)^{-1}. \quad (11)$$

The LS equation for the system is

$$|F_n^S\rangle = |n\mathbf{k}_n\rangle + G_0(E^{(+)}) V^S |F_n^S\rangle, \quad (12)$$

where $|n\mathbf{k}_n\rangle_m \equiv \delta_{mn} |i_n\mathbf{k}_n\rangle$ is the incident-channel asymptotic state function. We adopt the Green function $G_0(E^{(+)})$ which ensures outgoing spherical-wave boundary conditions. The LS equation for the T -matrix operator is derived by noting

$$|F_n^S\rangle = [1 + G_0(E^{(+)}) T^S(E^{(+)})] |n\mathbf{k}_n\rangle. \quad (13)$$

It is easy to check that the LS equation for T becomes

$$T^S(E^{(+)}) = V^S(E) + V^S(E) G_0(E^{(+)}) T^S(E^{(+)}) . \quad (14)$$

In order to solve the integral equation it is converted to a functional equation in momentum space. The momentum-space matrix elements of the T -operator are

$$\langle n\mathbf{p}_n | T^S(E^{(+)}) | m\mathbf{p}_m \rangle \equiv \langle \mathbf{p}_n | T_{nm}^S(E^{(+)}) | \mathbf{p}_m \rangle, \quad (15)$$

where the momenta $\mathbf{p}_n, \mathbf{p}_m$ are allowed to range over all possible values. The scattering amplitudes are derived from the on-shell amplitudes for which $\mathbf{p}_{m,n} = \mathbf{k}_{m,n}$ and $\epsilon_n + \frac{1}{2}k_n^2 = \epsilon_m + \frac{1}{2}k_m^2 = E$.

(2b) Questions of Uniqueness of Solutions

To model the electron scattering we now must decide how to treat the target states. The simplest method is to truncate the expansion so that only the first few excited states are included. For our examples we will confine ourselves to this class of approximations. The interested reader who would like to know how

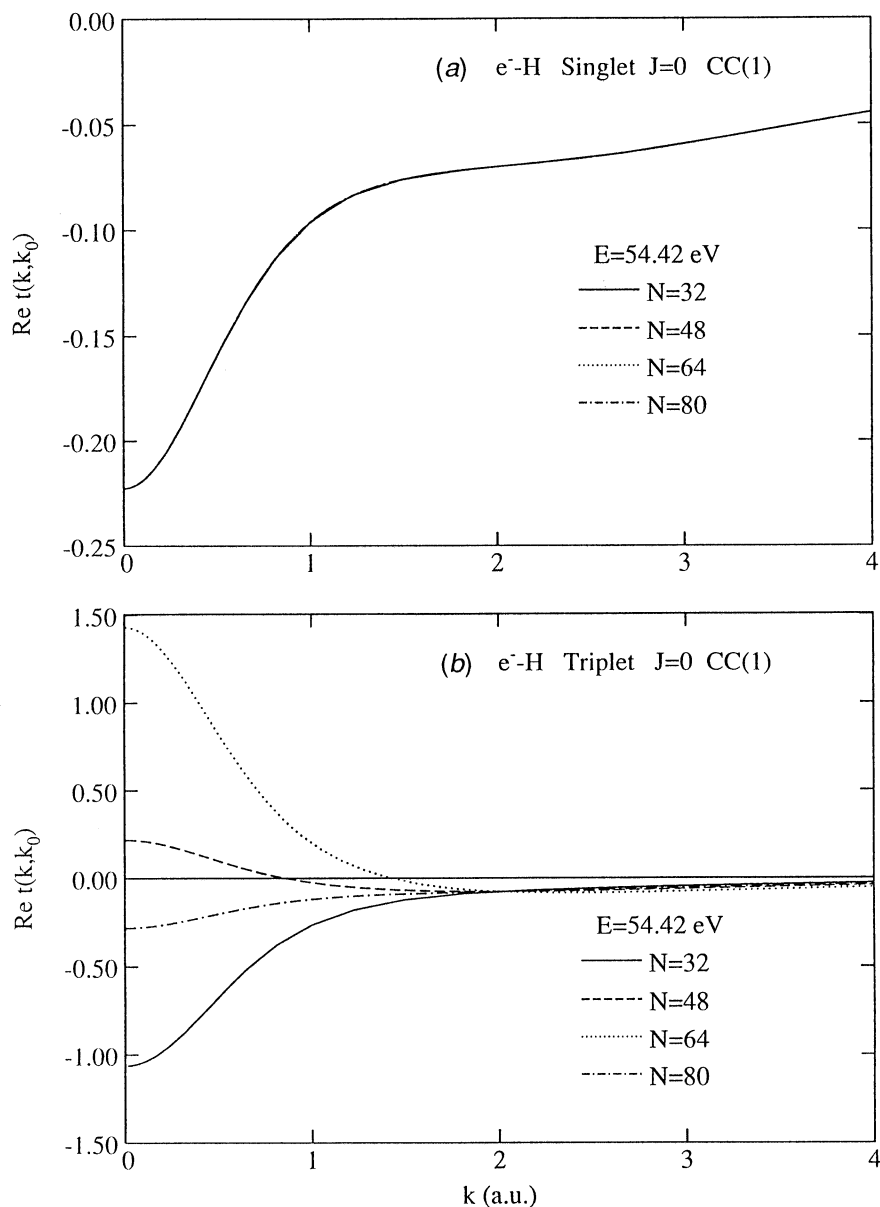


Fig. 3. Real part of the $J = 0$ partial-wave half-off-shell elastic scattering amplitude for electron scattering from the ground state of hydrogen in the CC(1) model is shown for (a) singlet and (b) triplet scattering as a function of the quadrature size N . Note the lack of convergence for the triplet channel. The kinetic energy of the incident electron is 54.42 eV.

the continuum and higher excited states can be accounted for is referred to Bray and Stelbovics (1995a).

The scattering equations (12) and (14) have interesting properties with regard to uniqueness of solutions. This has been studied by Stelbovics (1990) and an illustration is useful. Suppose we take the simplest possible subset of target states, that is, include only the ground state in the expansion. We refer to this

Table 1. Convergence with quadrature size N of the $J = 0$ partial-wave elastic scattering amplitude for an electron from the ground state of hydrogen is shown for models CC(1), CC(2), CC(3)

CC(N) indicates the first N target states are used in the close-coupling expansion. The incident electron kinetic energy is 54.42 eV. The meaning of the reciprocal condition number is discussed in the text

Quadrature size	Dimension of kernel matrix	Reciprocal condition no.	Number of eigs $ 1 - \lambda < 0.01$	T ls-ls Re	Im
$k = 2.0$ a.u. $E = 54.4232$ $E\nu$					
CC(1) singlet					
32	33	0.95e-02	0	-0.70430e-01	-0.42534e-01
48	49	0.46e-02	0	-0.70429e-01	-0.42533e-01
64	65	0.27e-02	0	-0.70430e-01	-0.42534e-01
80	81	0.18e-02	0	-0.70430e-01	-0.42534e-01
CC(2) singlet					
32	66	0.17352e-07	1	-0.65621e-01	-0.43337e-01
48	98	0.98881e-07	1	-0.65421e-01	-0.43173e-01
64	130	0.21437e-06	1	-0.65413e-01	-0.43155e-01
80	162	0.98319e-07	1	-0.65397e-01	-0.43134e-01
CC(3) singlet					
32	99	0.32e-04	1	-0.64311e-01	-0.42943e-01
48	147	0.66e-06	1	-0.64345e-01	-0.42968e-01
64	195	0.13e-06	1	-0.64348e-01	-0.42991e-01
80	243	0.14e-06	1	-0.64361e-01	-0.43008e-01
CC(1) singlet					
32	33	0.77e-06	1	-0.79285e-01	-0.86391e-01
48	49	0.17e-05	1	-0.79284e-01	-0.86400e-01
64	65	0.16e-06	1	-0.79284e-01	-0.86400e-01
80	81	0.13e-06	1	-0.79284e-01	-0.86400e-01
CC(2) singlet					
32	66	0.52e-08	3	-0.78232e-01	-0.86553e-01
48	98	0.19e-07	3	-0.78231e-01	-0.86503e-01
64	130	0.22e-07	3	-0.78229e-01	-0.86531e-01
80	162	0.16e-07	3	-0.78229e-01	-0.86535e-01
CC(3) singlet					
32	99	0.17e-05	4	-0.77467e-01	-0.86688e-01
48	147	0.33e-06	4	-0.77470e-01	-0.86685e-01
64	195	0.41e-07	4	-0.77480e-01	-0.86673e-01
80	243	0.41e-07	4	-0.77480e-01	-0.86674e-01

model as CC(1). Let us solve the T -matrix equation numerically by converting it to a partial-wave expansion and solving for each partial wave. Details of the numerical methods used are set out in McCarthy and Stelbovics (1983). We will consider the $J = 0$ wave only, as this contains the interesting phenomena. In Fig. 3 we show the real part of the half-off-shell T -matrix amplitude (the imaginary part behaves similarly) as a function of the channel quadrature size. The quadrature size refers to the number of Gaussian integration points used in the quadrature approximation to the momentum integrations occurring in the functional equation (14). For the singlet scattering ($S = 0$) it is seen that the half-off-shell T -matrix has converged to the thickness of the line by $N = 32$. On

the other hand for triplet ($S = 1$) scattering there is no convergence for the half-off-shell T -matrix except for a single momentum which happens to be the on-shell value. The on-shell amplitude has converged as is confirmed in Table 1.

The explanation for these behaviours is that the explicit symmetrisation of the three-body wave function introduced in equation (4) is sufficient to satisfy the Pauli condition (1) but is not strong enough to ensure that $|F^S\rangle$ is unique. For example if one looks at the triplet channel, if $|F^1\rangle$ is a solution then so is $|f^1\rangle = |F^1\rangle + a|i_1\rangle$ according to (4) where a is an arbitrary constant. This can also be checked by substituting directly into equation (10). From the LS equation point of view this non-uniqueness is dissatisfying because the whole purpose of the formalism is to convert the Schrödinger equation to an integral-equation form which incorporates the boundary conditions in the inhomogeneous term and has a unique solution. Clearly from Fig. 3 this is not so. The reason is easy to see. If we regard the LS equation (14) as a Fredholm equation of the second kind, its solution may be written as

$$T^S = (1 - V^S G_0)^{-1} V^S, \quad (16)$$

which requires the construction of the inverse to $(1 - V^S G_0)$ for scattering energies. A basic result of scattering theory (see for example Newton 1982) is that the inverse operator will exist provided there are no solutions to the homogeneous equation

$$T^S = V^S G_0 T^S \quad (17)$$

in the scattering region. The most direct way to establish if there are such solutions is to compute the spectrum of the operator $V^S G_0$:

$$V^S G_0 |\lambda_i^S\rangle = \lambda_i^S |\lambda_i^S\rangle, \quad i = 1, 2, \dots \quad (18)$$

The number of eigenvalues for which $\lambda_i^S = 1$ independent of the energy have a direct correspondence with the degree of non-uniqueness of the F^S . Altogether if the target expansion has N states, then the number of homogeneous solutions taken over singlet and triplet scattering is N^2 ; the number for each S is (Stelbovics 1990)

$$N^S = \frac{1}{2} N [N + (-1)^{S+1}]. \quad (19)$$

If we denote the basis for the N^S solutions to equation (10) by $\Phi^{Sj}, j = 1, \dots, N^S$ then it follows that $\{\Phi^{Sj}\} = \{G_0 |\lambda_i^S\rangle : \lambda_i^S = 1\}$. There may also be eigenvalues which are close to one over a small range of energies. These correspond to resonances in the three-body scattering process and we will not consider them further. Thus for model CC(1), we have $N^0 = 0$ and $N^1 = 1$, and the kernel of the singlet T -matrix admits no homogeneous solutions, whereas the triplet kernel possesses a single homogeneous solution. The lack of convergence of the half-shell triplet T -matrix is therefore due to the homogeneous solution. The effect of the homogeneous solution in equation (12) on the T -matrix LS equation (14) can

be readily deduced from equation (13). If $\langle \mathbf{p}_m | T_{mn}^S(E^{(+)}) | \mathbf{k}_n \rangle$ is a solution for the half-shell T -matrix then so are the half-shell T -matrices of the form

$$\langle \mathbf{p}_m | t_{mn}^S(E^{(+)}) | \mathbf{k}_n \rangle = \langle \mathbf{p}_m | T_{mn}^S(E^{(+)}) | \mathbf{k}_n \rangle + \frac{1}{2}(k_m^2 - p_m^2) \sum_{j=1}^{N^S} a_j^S \langle \mathbf{p}_m | \Phi^{Sj} \rangle_m. \quad (20)$$

The components m of Φ^{Sj} are linear combinations of the N target states and a_j^S are arbitrary constants. In particular, for the CC(1) example the sum reduces to a single term $\langle \mathbf{p} | i_1 \rangle$ which is just the momentum-space representation of the ground-state wave function. According to the above equation, the spurious solution vanishes on the energy shell. Hence we expect stability of this on-shell point as the quadrature meshes are varied. As we go off-shell to small \mathbf{p} the off-shell correction will vary essentially as the momentum-space wave function. For different quadrature schemes the arbitrary constants can vary widely as shown by Fig. 3.

In order to gauge the effect of the non-uniqueness of the LS equation on larger calculations, the on-shell T -matrix amplitude for elastic scattering from the ground state is shown in Table 1. The dimensionality of the final equation is the product of the number of coupled channels and the number of quadrature points in each channel (the quadrature size plus an extra quadrature for the on-shell point in each channel). The linear-equation solver used was the Lapack routine ZGESVX (Anderson *et al.* 1992). Model CC(2) comprises hydrogen 1s, 2s states and CC(3) 1s, 2s, 2p states. The reciprocal condition number is a measure of the degree of difficulty the routine encounters in solving the linear equations. As the number approaches the limit of the machine precision the solution may be subject to excessive roundoff. From the table it is seen that the inverse condition numbers decrease with increasing target expansion but are well above machine precision, indicating the discretised linear equations have been solved successfully. This decrease in inverse condition number is due to the increasing dimensionality (N^S) of the homogeneous solutions with increasing target space. The on-shell amplitudes converge satisfactorily despite a lack of convergence for the half-off-shell amplitudes (which are not shown). Note that the number of eigenvalues which are very close to unity, indicated in Table 1, are given by the formula (19) only for CC(1) and CC(2). The reason the formula does not catch all the eigenvalues for CC(3) is that when one includes the 2p orbital-angular-momentum states in the target space, not all the homogeneous solutions are contained in the $J = 0$ partial wave. Angular and parity selection rules ensure the remaining solutions are in the $J = 1$ partial wave.

Since momentum-space calculations of the close-coupling method have been used extensively since 1983, and the resolution of the uniqueness problem was only given in 1989, it may be helpful to comment on the accuracy of calculations by the Flinders group in that period. One of us (A.T.S.) had noticed that the solutions for the first few partial waves occasionally suffered from numerical instabilities but their source was not appreciated. By repeating calculations with a variety of meshes, on-shell amplitudes could be calculated for the affected partial waves to within a few percent accuracy. Since the differential cross sections are formed by summing over partial waves, the cross sections were affected to a lesser degree. Another reason it can be safely assumed that the work published

in that period is reliable is because a major part of it revolved around solving coupled channels equations with optical potentials added (the CCO method). The optical potentials, while being only an approximation, had the (desirable) side effect of eliminating the delicate balance of the coupled channel potentials which causes the non-uniqueness.

(2c) *Families of Equations with the Unique Solution*

Though we have shown that one can compute reliable amplitudes for smallish target sets using the integral equation for the T -matrix it is annoying that the half-shell amplitudes diverge. For larger target sets ($N > 15$) numerical instabilities begin to appear even for the on-shell amplitudes as the reciprocal condition numbers keep decreasing with the increasing number of homogeneous solutions. It is therefore important in large-scale models (such as Bray and Stelbovics 1992) to realise that one can formulate a set of integral equations which have no solutions to the homogeneous equation for scattering energies. The criterion to apply is the relation

$$\langle i_m | F_n^S \rangle = (-1)^S \langle i_n | F_m^S \rangle, \quad n, m = 1, \dots, N. \quad (21)$$

This identity is a result of applying the symmetry property (1) of the wave function to its close-coupling expansion (4). This relation is generally valid for finite target expansions, including those containing pseudostates. Its crucial importance in the scattering theory is that terms of the type $\langle i_m | F_n^S \rangle$ occur in the exchange part of the potentials V^S defined in equation (9). Therefore we are at liberty to modify the close-coupling equations with considerable generality. The result of applying the new symmetry condition liberally is to modify the form of the exchange potential to the extent that there are no homogeneous solutions in the new forms of LS equations. In practice this can be checked by computing the spectrum (18) and noting that no $\lambda_i^S = 1$ for the new form. The nature of the choices possible has been discussed at length (Stelbovics and Bransden 1989; Stelbovics 1990; Bray and Stelbovics 1992).

The techniques discussed here can be generalised to hydrogenic atoms (Bray and Stelbovics 1995*b*) in a straightforward manner. For general atoms, the antisymmetrisation condition must be applied to the full electron-plus-atom wave function including spin coordinates. Then it is no longer true that the radial coordinate wave functions have a definite symmetry but new forms can be developed in an analogous manner. Recently, Fursa and Bray (1995) have extended the method with success to helium. Other applications are being developed for inert gases with p-shells.

3. Positron-Atom Close-coupling Formalism

There are other complications which occur when the incident electron probe is replaced by one consisting of positrons. Positronium atoms may be formed in the process where the incoming positron strips the electron from the atom giving rise to a genuine rearrangement channel and a different set of coordinates is needed to describe the positronium atom as it moves away from the static core nucleus. For simplicity we limit the discussion to hydrogenic targets. For extensions to one-electron atoms with an inert core see Mitroy and Ratnavelu

(1994). The presence of elastic and rearrangement channels leads to a coupled set of close-coupling equations between hydrogen and positronium states. Mitroy (1993) has given a general formulation of the partial-wave matrix elements of the potentials in momentum space. Their computation is much more difficult and computationally time consuming than for electron-atom scattering. It is for this reason that the large scale of calculation we are familiar with for electron scattering is not yet evident for positron scattering.

(3a) Close-coupling Equations

Consider the case of a hydrogen target and expand the three-body scattering wave function in terms of a complete set of hydrogenic and positronium target states. In order to include the positronium-formation channel explicitly it is convenient to introduce the relative and centre-of-mass coordinates \mathbf{r}_3 and \mathbf{r}_4 for the positronium atom. Their relation to the original coordinates is

$$\mathbf{r}_3 = \mathbf{r}_1 - \mathbf{r}_2, \quad \mathbf{r}_4 = \frac{1}{2}(\mathbf{r}_1 + \mathbf{r}_2). \quad (22)$$

For incident positrons one must take into account the distinct direct and rearrangement channels; it is usual to adapt expansion (2) to include the rearrangement channels explicitly so that the asymptotic scattering boundary conditions can be directly imposed. This is achieved by writing

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = \sum_n i_n(\mathbf{r}_2) F_n(\mathbf{r}_1) + \sum_m j_m(\mathbf{r}_3) G_m(\mathbf{r}_4), \quad (23)$$

so that the close-coupling expansion for the positron-hydrogen system comprises a sum over two complete sets of target states. The eigenvalue equation for the hydrogen target is given by equation (7) and for the positronium states by

$$(K_3 + v_{12})|j_m\rangle = \epsilon'_m |j_m\rangle. \quad (24)$$

All quantities labelled by n, m will now refer to the hydrogen and positronium states respectively.

The coupled equations which result upon inserting the expansion into the Schrödinger equation are

$$\begin{aligned} (E - K_2 - \epsilon_n) F_n(\mathbf{r}_2) &= \sum_{n'} V_{nn'}(\mathbf{r}_2) F_{n'}(\mathbf{r}_2) + \sum_{m'} \int d\mathbf{r}_4 V_{nm'}(\mathbf{r}_3, \mathbf{r}_4) G_{m'}(\mathbf{r}_4), \\ (E - K_4 - \epsilon'_m) G_m(\mathbf{r}_4) &= \sum_{n'} \int d\mathbf{r}_2 V_{mn'}(\mathbf{r}_1, \mathbf{r}_2) F_{n'}(\mathbf{r}_2) + \sum_{m'} V_{mm'}(\mathbf{r}_4) G_{m'}(\mathbf{r}_4), \end{aligned} \quad (25)$$

where the potentials are given by

$$V_{nn'}(\mathbf{r}_2) = \langle i_n | v_2 + v_{12} | i_{n'} \rangle, \quad V_{mm'}(\mathbf{r}_4) = \langle j_m | v_1 + v_2 | j_{m'} \rangle, \quad (26)$$

$$V_{nm'}(\mathbf{r}_3, \mathbf{r}_4) = \langle i_n | H - E | j_{m'} \rangle, \quad V_{mn'}(\mathbf{r}_1, \mathbf{r}_2) = \langle j_m | H - E | i_{n'} \rangle = V_{n'm}^*(\mathbf{r}_3, \mathbf{r}_4), \quad (27)$$

and in a.u. $K_2 = \frac{1}{2}\nabla_2^2$ and $K_4 = \frac{1}{4}\nabla_4^2$.

We adopt an obvious matrix notation which is an extension of that used for electron scattering. A label η is defined which ranges over hydrogen states (n) and positron states (m) and $K_\eta = K_2$ if $\eta \in n$, and $K_\eta = K_4$ if $\eta \in m$. Now defining a scattering wave function by the column vector $|f\rangle = (F, G)^T$, we can write the LS equation for the coupled-channel equations (25) as

$$|f_{\eta_0}\rangle = |\eta_0, \mathbf{k}_{\eta_0}\rangle + G_0(E^{(+)})V(E)|f_{\eta_0}\rangle. \quad (28)$$

The inhomogeneous term is the asymptotic state for channel η and its component form in the channel space is $|\eta_0, \mathbf{k}_{\eta_0}\rangle_\eta = \delta_{\eta\eta_0}\Psi_{\eta_0}|\mathbf{k}_{\eta_0}\rangle$ where Ψ_{η_0} is either a hydrogen or positronium state. The physical scattering amplitudes are obtained from the subset of solutions for which the momentum in the initial and final channels is fully on-shell. We denote the general on-shell amplitude for the scattering from $\eta_0 \rightarrow \eta_f$ as $\langle \mathbf{k}_{\eta_f} | T(E^{(+)})_{\eta_f\eta_0} | \mathbf{k}_{\eta_0} \rangle$ where the on-shell momenta in a.u. for the hydrogen and positronium channels satisfy

$$\epsilon_n + \frac{1}{2}k_n^2 = \epsilon'_m + \frac{1}{4}k_m^2 = E. \quad (29)$$

(3b) Overcompleteness of Wave Function Expansions

Let us consider the possibility of non-unique solutions. Because there are two complete sets in the expansion (23) the choice of F and G cannot be unique. To see this, suppose we have managed to obtain a suitable set of F_n, G_m . Then we can replace this set with $F_n + \rho_n$, where the ρ_n are any square-integrable functions provided G_m is replaced with $G_m - \tau_m$, where

$$\tau_m(\mathbf{r}_4) = \int d\mathbf{r}_3 j_m^*(\mathbf{r}_3) \sum_n i_n(\mathbf{r}_1) \rho_n(\mathbf{r}_2), \quad (30)$$

since this leaves the wave function $\Psi(\mathbf{r}_1, \mathbf{r}_2)$ in equation (23) unaltered. From this argument it is clear that there is a very great degeneracy for the solutions to equations one constructs for the F, G . These solutions are artifacts of the close-coupling expansion and will be present at all energies. They convey no information about the physics of the system under investigation.

The pair of functions

$$|\zeta\rangle = (\rho_n, -\tau_m)^T \quad (31)$$

are a solution of the coupled equations (25) independent of energy and hence should cause non-uniqueness problems with the T -matrix formulation. But unlike the electron case there are no eigenvectors which are exact solutions in a finite target expansion over the hydrogen and positronium channels. To see this consider an expansion over the first N, M hydrogen and positronium states. The form of Ψ is basis dependent and we write

$$\Psi^{NM}(\mathbf{r}_1, \mathbf{r}_2) = \sum_n^N i_n(\mathbf{r}_1) F_n^N(\mathbf{r}_2) + \sum_m^M j_m(\mathbf{r}_3) G_m^M(\mathbf{r}_4). \quad (32)$$

Then if there exists a solution to the coupled-channel equations which is of a bound-state character it must have the form of equation (31) where the positron-channel component satisfies the conditions

$$\begin{aligned}\tau_m(\mathbf{r}_4) &= \int d\mathbf{r}_3 j_m^*(\mathbf{r}_3) \sum_n^N i_n(\mathbf{r}_1) \rho_n(\mathbf{r}_2), \quad m = 1, \dots, M, \\ 0 &= \int d\mathbf{r}_3 j_m^*(\mathbf{r}_3) \sum_n^N i_n(\mathbf{r}_1) \rho_n(\mathbf{r}_2), \quad m = M + 1, \dots, \infty.\end{aligned}\quad (33)$$

The orthogonality requirement is necessary in order to leave $\Psi^{NM}(\mathbf{r}_1, \mathbf{r}_2)$ invariant. Because the coordinate systems are different, as are the target states, there is no simplifying feature which reduces the expansions to a finite number of terms, so the orthogonality requirements (33) cannot be satisfied for all m . Thus for small target-state sets the solutions will be unique. Obviously as the expansion sets are increased and approach completeness, approximate solutions to (33) will emerge. Their character will be such that the spectrum of the T -matrix kernel will contain eigenvalues which are predominantly real and close to one whenever the N, M target spaces are extended to completeness.

(3d) *Manifestation of Non-uniqueness*

We have shown that while non-uniqueness is present even in the smallest symmetrised expansions for electrons, this should not be the case for positron scattering. The typical situation is best illustrated by looking at the spectra of the $J = 0$ kernel for the class of models denoted by $CC(M, N)$, where M, N denote the number of states of hydrogen and positronium included in the expansion [see Mitroy and Stelbovics (1994) for a comprehensive study of the $CC(3, 3)$ model]. In Table 2 we list the eigenvalues closest to unity for models that have received attention in recent calculations. The energy of 54.4 eV is chosen because there are no resonances in the vicinity for the $J = 0$ partial wave. If we consider the set of eigenvalues for which $|\lambda - 1| < 0.1$ it is seen that their number increases as one proceeds to larger target spaces and the eigenvalues begin clustering nearer to one. Since these models have a fairly restricted target space it is also interesting to see the effect a larger pseudostate expansion has on the eigenvalues. For this purpose we choose the model $CC(12, 8)$ (Mitroy *et al.* 1994). In this model, in addition to the 1s, 2s, 2p target states for hydrogen and positronium, nine pseudostates were added to the hydrogen and five to the positronium set. As suggested by the analysis of the previous subsection, the number of ‘near’ solutions has increased noticeably and some are very close. Table 3 shows the convergence of the elastic T -matrix amplitude for positrons incident on the ground state hydrogen atom with increasing quadrature number. In Fig. 4 the real part of the T -matrix elastic scattering amplitude from the hydrogen ground state has been plotted for several quadrature meshes for the $CC(12, 8)$ model. We see no evidence of convergence for the half-off-shell amplitude but the on-shell point is convergent.

Table 2. Eigenvalues of the T -matrix kernel with $|\lambda-1| < 0.1$ are shown for the $J = 0$ partial-wave for positron scattering from hydrogen for models CC(1, 1), CC(2, 2), CC(3, 3) and CC(12, 8) See text for description of the models. The incident positron kinetic energy is 54.42 eV except for CC(12, 8) when it is 3.4 eV

Quadrature size	Re	$ \lambda - 1 < 0.1$ 1s-1s Im	$ \lambda $
$k = 2.0$ a.u. $E = 54.4232$ eV			
CC(1, 1)			
64	0.97038264	-0.00043215	0.97038274
CC(2, 2)			
64	0.98894789	-0.00044302	0.98894799
	0.95843194	-0.00021126	0.95843196
	0.94554600	0.00175489	0.94554763
	0.93531813	0.07353459	0.93820431
CC(3, 3)			
64	1.02249672	0.00043149	1.02249681
	0.99546546	-0.00070767	0.99546571
	0.99238564	-0.00001098	0.99238564
	0.98237125	0.04257251	0.98329329
	0.96318957	-0.00012646	0.96318958
	0.92188729	0.03918330	0.92271963
	0.91765177	0.00184786	0.91765363
	0.90660362	-0.00008712	0.90660363
$k = 0.5$ a.u. $E = 3.4015$ eV			
CC(12, 8)			
36	1.05399113	-0.00089574	1.05399151
	1.04938626	0.00002459	1.04938626
	1.03456836	-0.03958499	1.03532539
	1.01393247	0.00000075	1.01393247
	1.01060415	0.00000000	1.01060415
	1.00439249	0.00000137	1.00439249
	0.99982208	0.00000000	0.99982208
	0.99911582	0.00000007	0.99911582
	0.99889724	0.00000001	0.99889724
	0.99854437	0.00000003	0.99854437
	0.99599563	0.00000011	0.99599563
	0.99402183	0.00000020	0.99402183
	0.99089457	0.00000001	0.99089457
	0.98533435	0.00000234	0.98533435
	0.98429355	0.00000090	0.98429355
	0.98294423	-0.00015416	0.98294424
	0.97392591	0.00000000	0.97392591
	0.97200059	0.00000002	0.97200059
	0.96887243	-0.01531666	0.96899349
	0.96222545	0.00000002	0.96222545
	0.95840453	0.00000000	0.95840453
	0.94576918	-0.00062887	0.94576939
	0.94555685	0.00000000	0.94555685
	0.93458276	0.00007428	0.93458276
	0.93239571	-0.00052213	0.93239585
	0.92579716	0.00000754	0.92579716
	0.91451950	0.00001766	0.91451950
	0.90119967	-0.00007490	0.90119967

Table 3. Convergence with quadrature size N of the $J = 0$ partial-wave elastic scattering amplitude for a positron from the ground state of hydrogen is shown for models CC(1,1), CC(2,2), CC(3,3) and CC(12,8)

See text for description of the models. The incident positron kinetic energy is 54.42 eV except for CC(12,8) when it is 3.4 eV

Quadrature size	Dimension of kernel matrix	Reciprocal condition no.	Number of eigs $ 1 - \lambda < 0.1$	T 1s-1s	
				Re	Im
$k = 2.0$ a.u. $E = 54.4232$ eV					
CC(1,1)					
32	66	0.47e-03	1	0.67972e-01	-0.39291e-01
48	98	0.33e-03	1	0.67973e-01	-0.39290e-01
64	130	0.24e-03	1	0.67973e-01	-0.39290e-01
80	162	0.18e-03	1	0.67973e-01	-0.39290e-01
CC(2,2)					
32	130	0.54e-04	4	0.65548e-01	-0.38160e-01
48	194	0.44e-04	4	0.65584e-01	-0.38326e-01
64	258	0.37e-04	4	0.65589e-01	-0.38324e-01
80	322	0.31e-04	4	0.65589e-01	-0.38324e-01
CC(3,3)					
32	194	0.10e-04	6	0.64888e-01	-0.36473e-01
48	290	0.70e-05	8	0.65111e-01	-0.38115e-01
64	386	0.13e-04	8	0.65130e-01	-0.38057e-01
80	482	0.11e-04	8	0.65130e-01	-0.38057e-01
$k = 0.5$ a.u. $E = 3.4015$ eV					
CC(12,8)					
32	641	0.66e-07	25	-0.38780e-01	-0.23711e-02
36	721	0.14e-06	28	-0.38903e-01	-0.23862e-02
40	801	0.22e-06	18	-0.39083e-01	-0.24084e-02
40	801	0.36e-06	18	-0.39036e-01	-0.24024e-02
40	801	0.50e-06	19	-0.38993e-01	-0.23969e-02

This is very similar behaviour to that discussed for the electron projectile. The reciprocal condition numbers are not too small and the discretised equations have been solved with negligible roundoff. It should be mentioned that this lack of stability is not in evidence for the CC(1,1), CC(2,2) and CC(3,3) models where the half-shell amplitudes are convergent with increasing quadrature size.

This CC(12,8) calculation suggests that the limit of usefulness of our present set of positron close-coupling equations is being reached. There is at present no easily implemented modification of the equations analogous to that outlined for incident electron beams. The condition (21) noted for electrons is not applicable because the total wave function has no special symmetry with respect to positron and electron coordinates.

4. Conclusion

We have demonstrated some properties of the close-coupling equations for electron and positron projectiles. For electron scattering we emphasised that solving the standard old form of coupled equations leads to half-shell amplitudes which do not converge with quadrature mesh. We showed by example that the numerical solutions for the on-shell amplitudes were accurate and did not suffer

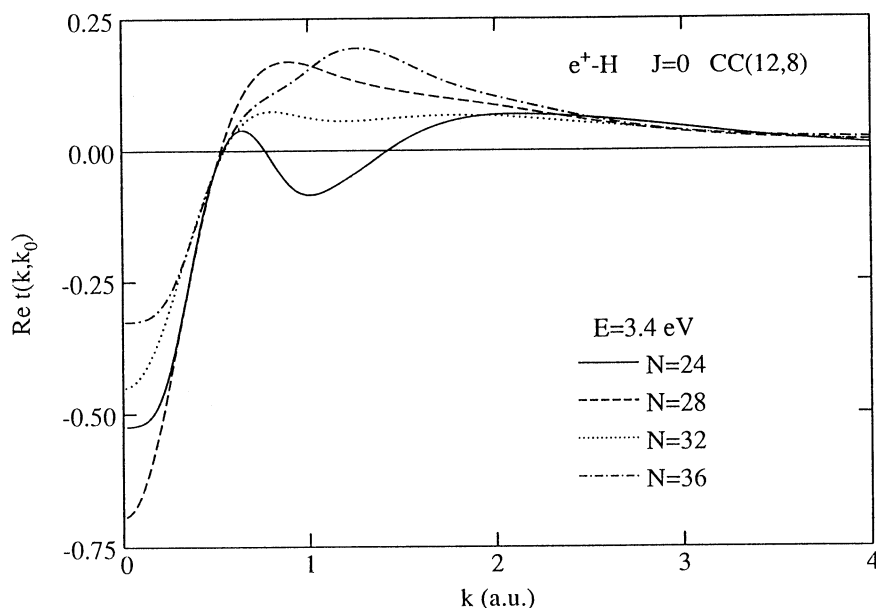


Fig. 4. Real part of the $J = 0$ partial-wave half-off-shell elastic scattering amplitude for positron scattering from the ground state of hydrogen in the CC(12,8) model is shown as a function of the quadrature size N . The kinetic energy of the incident positron is 3.4 eV.

from round-off for small target sets. It was also noted that this lack of uniqueness was a consequence of not applying all the information contained in the symmetry property of the full wave function. When this is put in properly, the effect is to create a family of equivalent close-coupling equations with effective potentials which differ only in their exchange term.

It has not been our purpose to study models using large pseudostate Laguerre bases (the so-called CCC method) which are required for realistic calculations. There it does prove advantageous to use forms of CC equations which have unique solutions for the half-shell amplitudes. These issues have been discussed at length in the literature (see Bray and Stelbovics 1995*a,b* and references therein).

The positron equations were also investigated from the point of stability and it was demonstrated that there will be an accumulation of T -matrix kernel eigenvalues at unity if complete target sets are used, leading potentially to problems analogous to those with electron projectiles. Our numerical results suggest this may be happening for the CC(12,8) model. Using it (the largest model within our computer limitations) we noted the accumulation of eigenvalues but the on-shell amplitudes were stable. However, there is a lack of convergence for the off-shell amplitudes which cannot be simply ascribed to numerical-analysis problems. It is concluded that the increasingly singular nature of the discretised equations will eventually lead to instability even for the on-shell amplitudes using the present equations. It remains to be seen how far the current target spaces can be increased before this becomes a serious problem.

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