

Pseudo-state Close Coupling in Electron–Atom Collisions*

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Abstract

In the last decade the role and nature of pseudo states applied to scattering problems has become better understood. The J -matrix technique has provided a direct physical interpretation for the pseudo states. Recent work in constructing and applying pseudo-state expansions based on analytic techniques is reviewed and convergence questions relating to the use of such expansions in the close-coupling equations are addressed.

1. Introduction

The close-coupling equations for electron–atom scattering constitute a formally complete description of the scattering process. They are derived by taking an expansion of the electron+atom wavefunction over the complete set of target states. Because there are an infinite number of discrete and continuum target states, approximations have to be made in order to render the equations numerically soluble. There are two main methods that have proved to be popular. The first is an optical-potential formulation. There one retains the channels of interest while projecting the remaining target states into a q -space. Then, carrying out a Feshbach projection one is left with equations which couple the channels of interest at the expense of introducing very complicated optical potentials. This approach has been employed extensively by I. E. McCarthy and coworkers with considerable success. The art in the method is to guess simple but accurate approximations to the three-body wavefunction embedded in the optical potentials. The reader is referred to McCarthy and Stelbovics (1983) and Bray *et al.* (1989) for further details.

The second approach which is the subject of this review is the pseudo-state method of treating the target continuum. There one chooses a basis of L^2 functions in which to diagonalise the target Hamiltonian. The functions are chosen so that the p -space channel wavefunctions are accurately determined. The remaining states represent an averaging over the true eigenfunctions, including the continuum. The assumption implicit in this method is that if a large enough set is chosen the answers converge to the ones obtained by solving the equations with the complete set of exact target states. In this paper, we examine the evidence for this assumption. We concentrate on the

* Dedicated to Professor Ian McCarthy on the occasion of his sixtieth birthday.

electron-hydrogen system for which the most extensive class of investigations of the pseudo-state method has been carried out. A review covering other systems has been given by Callaway (1980).

It was realised in the early 1970s that close-coupling calculations give inaccurate cross sections above the ionisation threshold if only discrete excited states are coupled. Typically cross sections were overestimated if no allowance for loss of flux to ionisation channels was made, particularly at intermediate energies. Burke and Webb (1970) demonstrated that inclusion of one or two pseudo states reduced the scattering cross sections in electron-hydrogen scattering and brought them into closer agreement with experiment. When it was realised that coupling to the continuum was an important effect at intermediate energies, systematic studies were undertaken to look at the convergence rates of the close-coupling amplitudes with an increasing number of states. One of the earliest studies of the convergence of pseudo-state expansions was carried out by Burke and Mitchell (1973). They looked at the $j=0$ partial wave of the close-coupling equations and added only s-wave target states. They noticed the pseudo states that were introduced gave unphysical pseudo resonances in the vicinity of the pseudo thresholds, for the singlet scattering amplitude. As the basis of pseudo states was increased, more pseudo resonances appeared. At energies away from the vicinity of a resonance the amplitudes appeared to converge. In the triplet channel pseudo resonances were not observed. This model has since been the subject of further investigation. The pseudo-resonance structure in calculations which include additional angular momentum target states appears similar, so the feeling is that if one understands the mechanism of their generation in this model one probably understands it in the general case.

A significant advance was made by Poet (1978). He noted that the model problem gave rise to a separable form of Schrödinger equation for the coordinate space wavefunction so the solutions of the differential equation could be written down analytically. The solutions do not have the required symmetry of the physical wavefunctions. But on imposing appropriate boundary conditions to a linear combination of the solutions he obtained a set of equations for the three-body wavefunction which could be solved to a high degree of accuracy. The model amplitudes he presented have since become the benchmark of later studies. Further investigations of the pseudo-resonance structure were carried out by Oza and Callaway (1983). They tested several pseudo-state bases including up to seven target states in their expansions. All the singlet amplitudes for elastic and inelastic scattering displayed pseudo-resonance structure. The bases chosen have at most two positive-energy pseudo states, one near the threshold and the other above 1.5 Ry. The resonance behaviour typically gave rise to a broad feature with width of about 0.5 Ry. This was in contrast with the previous study of Burke and Mitchell whose basis yielded narrower structure. Typical results for the above mentioned studies are shown in Fig. 1. Oza and Callaway then introduced an averaging technique which involved fitting the T -matrices to a low degree polynomial as a function of energy over a range of several Rydbergs from the ionisation threshold by means of a least squares fit. The averaged results gave almost perfect agreement with the exact results of Poet. The method is quite empirical although Burke *et al.*

(1981) tested the validity of such a procedure for averaging over the resonance structure in an R -matrix calculation. Whether this averaging can be given theoretical justification for the close-coupling approach remains to be seen. Subsequently Oza (1984) carried out a nine-state calculation which included five positive energy pseudo states. He found that the pseudo-resonance structure had reduced in width and the magnitude of the resonances had diminished, and concluded that his calculation demonstrated the convergence of the pseudo-state expansion. It should be noted that the biggest difference in the larger basis expansion compared to the previous calculation of Oza and Callaway is the inclusion of five positive-energy target states over the two used earlier.

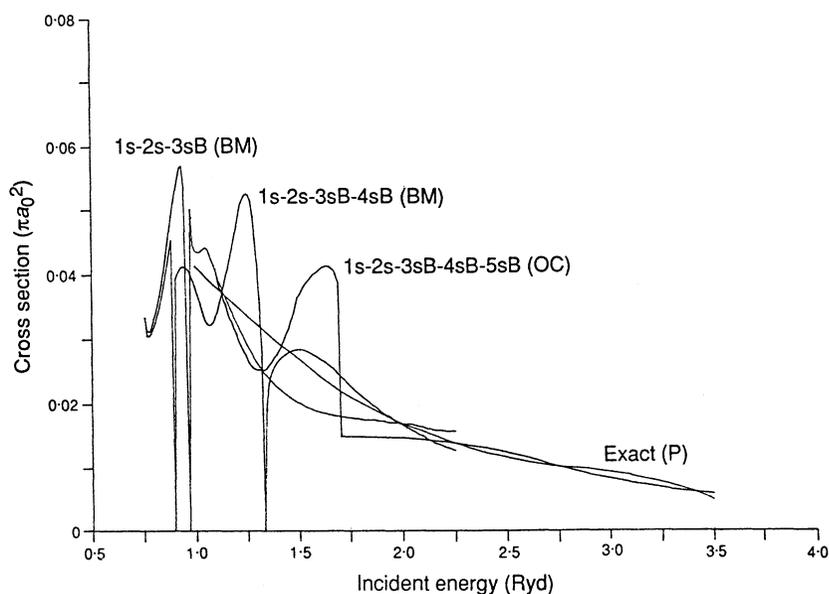


Fig. 1. Singlet $1s$ - $2s$ cross sections are shown for the Poet (1978) model. The exact solution is labelled (P). Two pseudo-state calculations (three and four states) of Burke and Mitchell (1973) are shown and labelled (BM). A five-state calculation of Oza and Callaway (1983) is also shown (OC). The pseudo states in the various bases are denoted by the suffix B.

Although the pseudo states were readily appreciated as taking into account the effects of the continuum, as illustrated by the above discussion, no attempt was made to study the relationship of pseudo states with true continuum functions by the close-coupling theorists. Interestingly Poet's calculations relied on overlaps between exact continuum Coulomb waves, although his final equations were quite different to the close-coupling equations. In the following sections we show more formally the sense in which the pseudo states converge to exact continuum functions for positive energies and how the completeness relation for the target is approximated in the sense of a finite Gaussian quadrature over the pseudo states. That such a connection existed was becoming evident through the work of Reinhardt and coworkers. They were investigating L^2 expansions of Green's functions and developing an equivalent quadrature approximation. Their work lead naturally to the

development of Fourier series expansions for continuum functions in an L^2 basis. In early work (Heller *et al.* 1973) examples of L^2 expansions for the kinetic energy operator eigenfunctions were considered. Their ideas were developed in a series of papers leading to the method known as the J -matrix method. Their most important contribution of relevance to us was the derivation by Yamani and Reinhardt (1975) of a Fourier expansion of the continuum Coulomb functions using a Laguerre-function basis. They were able to show that the Fourier coefficients primarily comprised Pollazeck polynomials which are a non-classical set of orthogonal polynomials. A study of their formal properties related to the Coulomb potential has been given by Bank and Ismail (1985). Heller and Yamani (1974) then also applied their basis to carry out some model J -matrix calculations using the s -target states and arrived at similar conclusions to Burke and Mitchell.

The close-coupling equations are summarised in Section 2. Analytic forms for the L^2 expansions of the target states are discussed in Section 3, as is their relationship to Gaussian quadrature. The pseudo-state close-coupling equations are shown to be an approximation to the exact set within the quadrature. Certain convergence questions of the implied L^2 expansions are studied in Section 4. Outstanding questions for further investigation and summary are given in Section 5.

2. Close-coupling Equations

The close-coupling equations are derived by making an expansion of the $N+1$ electron wavefunction in a complete set of target-atom wavefunctions. The simplest example of such a system is one with a hydrogen target. It is with this system in mind that we write our equations.

The e-H wavefunction may be expanded as

$$\psi^\pm(1,2) = \sum_i \phi_i(1) f_i^\pm(2), \quad (1)$$

where

$$\psi^\pm(1,2) = \pm(2,1) \quad (2)$$

is the symmetry requirement on the coordinate-space wavefunction. Here the + (−) superscripts denote singlet (triplet) scattering. The summation implied in (1) is a summation over the discrete excited states and an integration over the continuum. We can use (2) to make our initial expansion explicitly have the required symmetry:

$$\psi^\pm(1,2) = \frac{1}{2} \sum_i \{ \phi_i(1) f_i^\pm(2) \pm \phi_i(2) f_i^\pm(1) \}. \quad (3)$$

However, while this form of the expansion has been almost universally used as the starting point for a derivation of the equations, it should be noted that the f_i one obtains from (3) need not be the same as those in (1). To illustrate this point we note for example that in the triplet channel, if we make the substitution

$$\bar{f}_i \rightarrow \bar{f}_i + \alpha \phi_i, \quad (4)$$

the three-body wavefunction defined by (3) is unchanged. The reason this non-uniqueness is present is that we started with the two equations (1) and (2) and have formed (3) from them. There is therefore a second condition that can be obtained from the system (1)+(2):

$$\langle \phi_i | f_j^\pm \rangle = \pm \langle \phi_j | f_i^\pm \rangle. \quad (5)$$

The system (3)+(5) is equivalent to that of (1)+(2). If we return to our example (4), imposing condition (5) one finds that $\alpha = 0$.

(a) Standard Form

Applying the expansion (3) to the full three-body Hamiltonian one obtains the usual close-coupling equations (atomic units are assumed):

$$(-H_0 + E - \epsilon_j) f_j^\pm = \sum_k V_{jk}^\pm f_k^\pm. \quad (6)$$

It is convenient to partition the channel potentials into the form

$$V_{jk}^\pm = U_{jk}^\pm + W_{jk}^\pm \quad (7)$$

with

$$U_{jk}^\pm = \int d\mathbf{r}_1 \int d\mathbf{r}_2 | \mathbf{r}_1 \rangle \phi_j(\mathbf{r}_2) \left\{ \left(-\frac{1}{r_1} + \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \right) \phi_k(\mathbf{r}_2) \langle \mathbf{r}_1 | \right. \\ \left. \pm \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \phi_k(\mathbf{r}_1) \langle \mathbf{r}_2 | \right\}, \quad (8)$$

$$W_{jk}^\pm = \pm | \phi_k \rangle (\epsilon_j + \epsilon_k - E) \langle \phi_j |. \quad (9)$$

Until recently, the application of the symmetry (5) to the set (6)–(9) was accomplished by means of Lagrange multipliers. If the non-uniqueness is not removed numerical instabilities appear, as discussed by Norcross (1969).

(b) New Forms

The introduction of the extra orthogonalisation constraints through Lagrangian multipliers seemed to be a necessary part of the formalism of electron-atom scattering theory. Recently Stelbovics and Bransden (1989) showed that it was possible to invoke the condition (5) in a more natural way. The result is a modified form of the original equations which require no additional effort to solve. They are derived very simply by considering the portion W_{jk} of the channel potentials and utilising their separable form to write

$$W_{jk}^\pm | f_k^\pm \rangle = \pm | \phi_k \rangle (\epsilon_j + \epsilon_k - E) \langle \phi_j | f_k^\pm \rangle \\ = | \phi_k \rangle (\epsilon_j + \epsilon_k - E) \langle \phi_k | f_j^\pm \rangle \quad (10)$$

upon using (5). With this change a new form for the close-coupling equations is derived by replacing the channel potentials V by

$$V_{\text{SB}}^{\pm} = U^{\pm} + W_{\text{SB}}^{\pm}, \quad (11)$$

with

$$[W_{\text{SB}}^{\pm}]_{ij} = \delta_{ij} \sum_k |\phi_k\rangle \gamma_k^{\pm} (\epsilon_j + \epsilon_k - E) \langle \phi_k|, \quad (12)$$

with

$$\gamma_k^+ = 1, \quad \gamma_k^- = 1 - \delta_{jk}. \quad (13)$$

The form of γ_k^- follows from the observation $\langle \phi_i^- | f_i^- \rangle = 0$ as a consequence of (5). The proof that the new form of the close-coupling equations are free from uniqueness problems is difficult and we will not give it here. It is discussed by Stelbovics (1990). There it is also shown that there are an infinite number of different formulations of the close-coupling equations possessing the same (unique) solution.

(c) Allowance for Pseudo States

The forms discussed thus far all rely on an expansion over the complete set of target states. A direct solution of the equations in this form has not been attempted yet. It is probable that attempts will be made in this direction in the near future with the rapid advance in speed of our computers. In practice one replaces the target states by a set of pseudo states which are generated in the following manner. One takes a set of L^2 functions which can in principle be extended to completeness. There are prescriptions which ensure that linear dependence is avoided for large sets. For example, Klahn and Bingel (1977) discuss completeness criteria for several types of function sets. Similar theorems are given by Higgins (1977). Provided we have a suitable set, we diagonalise the target Hamiltonian h in the space spanned by the functions $\phi_i, i = 1, \dots, N$. The resulting vectors which are linear combinations of the basis functions are our pseudo states ϕ_i^N and the corresponding pseudo energies ϵ_i^N are given by

$$\langle \phi_i^N | h | \phi_j^N \rangle = \delta_{ij} \epsilon_i^N. \quad (14)$$

When hydrogen is the target one commonly chooses Slater functions for the basis. The physical channels we are modelling can then employ exact 1s, 2s and 2p wavefunctions. There is however a modification one must make in the close-coupling equations when pseudo states are included. This is because the exchange term in the form (9) is valid only for exact target states. The form appropriate to pseudo states is derived by considering the general matrix element

$$W_{jk}^{\pm} = \pm \langle \phi_j^N(1) | \{h(1) + h(2) - E\} | \phi_k^N(2) \rangle, \quad (15)$$

where 1,2 refer to the coordinate the states are operating on. Only a limited simplification is possible for pseudo states:

$$W_{jk}^{\pm} = \pm | \phi_k^N(2) \rangle \langle \phi_j^N(1) | h(1) \pm h(2) | \phi_k^N(2) \rangle \\ \times \langle \phi_k^N(2) | \pm | \phi_k^N(2) \rangle (-E) \langle \phi_j^N(1) | . \quad (16)$$

The pseudo-state expansion also suffers from the problem of spurious solutions as can be seen by repeating the arguments leading from (1)–(5). Thus, extra orthogonality constraints must be imposed via Lagrange multipliers or by deriving a new form of equation along the line of (12). It is straightforward to show that one acceptable form is

$$[W_{\text{PS}}^{\pm}]_{ij} = | \phi_j^N \rangle \langle \phi_i^N | h \pm h | \phi_j^N \rangle \langle \phi_i^N | \\ \pm \delta_{ij} \sum_{k=1}^N | \phi_k^N \rangle \gamma_k^{\pm} (-E) \langle \phi_k^N | . \quad (17)$$

This form is again but one of a variety of choices. It is manifestly symmetric and can therefore be easily incorporated into existing computer-program codes. A more extensive study of the general forms available for pseudo states will be given elsewhere.

3. Pseudo-state Bases

In order to study rates of convergence of pseudo-state expansions formally, one desires a basis set whose functions have a simple form so that the channel potentials can be evaluated analytically, or where this is not possible, computed rapidly and accurately. Hydrogen is the only target atom for which we know the continuum functions analytically and are thus able to test L^2 methods and pseudo-state expansions completely. An important Fourier expansion which provides us with the essential tools to study the pseudo-state method will now be given.

(a) Yamani–Reinhardt Expansion

Yamani and Reinhardt (1975) found a useful Fourier expansion for the continuum Coulomb waves upon choosing the basis

$$\phi_n^l(r) = (\lambda r)^{l+1} \exp(-\frac{1}{2}\lambda r) L_n^{2l+1}(\lambda r). \quad (18)$$

The functions are not orthogonal. Their inner product is

$$\langle \phi_n^l | \phi_m^l \rangle = \frac{\Gamma(m+2l+2)}{\Gamma(m+1)} \lambda^{-1} \{ -(n+1)\delta_{n+1,m} \\ + (2n+2l+2)\delta_{n,m} - (n+2l+1)\delta_{n,m+1} \}. \quad (19)$$

They constitute a basis (see for example Higgins 1977) which has the additional property that, together with the functions

$$\bar{\phi}_n^l(r) = r^{-1} \phi_n^l(r), \quad (20)$$

a biorthogonal system is formed, i.e.

$$\langle \bar{\phi}_n^l | \phi_m^l \rangle = \delta_{nm}. \quad (21)$$

The biorthogonal nature of the basis enables one to construct Fourier expansions in much the same way as for an orthonormal basis, as discussed in Higgins. We now turn to the Fourier expansions for the target states. The states for positive energy are regular Coulomb functions. For partial-wave number l and normalised to a delta function in energy, they are

$$U_l(k, r) = \left(\frac{2}{\pi k} \right)^{\frac{1}{2}} \exp(\frac{1}{2}\pi y) \frac{|\Gamma(l+1-iy)|}{\Gamma(2l+2)} \frac{1}{2}(2kr)^{l+1} \\ \times \exp(-ikr) {}_1F_1(l+1+iy, 2l+2, 2ikr), \quad (22)$$

while the bound states are

$$U_{nl}(r) = \frac{1}{n^{l+2}\Gamma(2l+2)} \left(\frac{\Gamma(n+l+1)}{\Gamma(n-l)} \right)^{\frac{1}{2}} (2r)^{l+1} \\ \times \exp(-r/n) {}_1F_1(l+1-n, 2l+2, 2r/n), \quad (23)$$

where

$$y = 1/k, \quad k = (2E)^{\frac{1}{2}}. \quad (24)$$

Using the biorthonormality of our basis set one can show that the Fourier expansion of the target wavefunctions is expressible in the form

$$U_l(k, r) = \sum_{n=0}^{\infty} B_n^l(E) P_n^{l+1}(x) \phi_n^l(r). \quad (25)$$

For the continuum functions, the coefficients denoted by B are

$$B_n^l(E) = 2^{n+\alpha-1} \frac{\Gamma(n+\alpha+a)}{\Gamma(\alpha+a)\Gamma(n+2\alpha)} \left(\frac{2}{\pi k} \right)^{\frac{1}{2}} |\Gamma(\alpha-iy)| \\ \times (1-x^2)^{\alpha/2} \exp\{(\theta - \frac{1}{2}\pi)y\}, \quad (26)$$

while for the bound states $E = E_i = -\frac{1}{2}(i+\alpha), i = 0, 1, \dots,$

$$B_n^l(E_i) = 2^n \frac{\Gamma(n+\alpha+a)}{\Gamma(\alpha+a)\Gamma(n+2\alpha)} \frac{(-a)^\alpha}{(i+\alpha)^{\alpha+1}} \left(\frac{\Gamma(i+2\alpha)}{\Gamma(i+1)} \right)^{\frac{1}{2}} \left(\frac{i+\alpha+a}{i+\alpha-a} \right)^i. \quad (27)$$

Here we have set $\alpha = l + 1$ and $a = -2/\lambda$, while

$$E \equiv \frac{1}{2}k^2 = \frac{\lambda^2}{8} \left(\frac{1+x}{1-x} \right), \quad (28)$$

$$x = \cos\theta, \quad 0 \leq \theta \leq \pi. \quad (29)$$

The $P_n^{l+1}(x)$ are orthogonal polynomials and are a generalisation of Pollaczek polynomials. We omit the l -superscript label in the sequel for simplicity. In the monic form their recurrence relation is

$$\begin{aligned} P_{-1}(x) &= 0, & P_0(x) &= 1, \\ P_n(x) &= (x - d_n)P_{n-1}(x) - \lambda_n P_{n-2}(x), & n &= 1, 2, \dots, \end{aligned} \quad (30)$$

with

$$\begin{aligned} \lambda_1 &= 2^{1-2\alpha} \pi \frac{\Gamma(2\alpha)}{\alpha + a}, \\ \lambda_{n+1} &= \frac{n(n+2\alpha-1)}{4(n+\alpha+a)(n+\alpha-1+a)}, & n &= 1, 2, \dots, \\ d_{n+1} &= \frac{a}{n+\alpha+a}. \end{aligned} \quad (31)$$

Their orthogonality relation is

$$(P_n, P_m) = \int_{-\infty}^{+\infty} d\mu(x) P_n(x) P_m(x) = \lambda_1 \lambda_2 \dots \lambda_{n+1} \delta_{nm}. \quad (32)$$

Note that the polynomials are positive definite if and only if

$$l + 1 > 2/\lambda. \quad (33)$$

Positive-definiteness is a property that is almost always assumed when constructing Gaussian quadrature approximations to the integral (32) with measure $\mu(x)$. It is only under this assumption that estimates of the convergence rates of the quadrature approximations are readily determined. An application of the L^2 method to a related model scattering problem where the polynomials are not positive definite has been given by Stelbovics and Slim (1987). There the properties of the Gaussian quadrature and weights are discussed. The polynomials and their relation to scattering problems have been further studied by Slim (1988).

The measure for the attractive Coulomb Pollaczek polynomials is

$$d\mu(x) = \left(\rho(x) + \sum_{i=0}^{\infty} R_i \delta(x - x_i) \right) dx, \quad (34)$$

where

$$\begin{aligned} \rho(x) &= (1-x^2)^{\alpha-\frac{1}{2}} |\Gamma(\alpha-iy)|^2 \exp\{(2\theta-\pi)\gamma\}, & x \in [-1, 1], \\ &= 0 & \text{otherwise,} \end{aligned} \tag{35}$$

$$R_i = \pi \frac{\Gamma(i+2\alpha)}{\Gamma(i+1)} 2^{2-\alpha} (-a)^{2\alpha+1} (i+\alpha)^{-2\alpha} (i+\alpha+a)^{2i-1} (i+\alpha-a)^{-2i-1}, \tag{36}$$

with

$$x_i = \frac{a^2 + (i+\alpha)^2}{a^2 - (i+\alpha)^2} \notin [-1, 1]. \tag{37}$$

(b) Finite-basis Constructions

The L^2 basis discussed provides a complete description of the target states if the expansion extends to infinity. Suppose we attempt to construct a set of pseudo states by limiting ourselves to the first N functions of the basis (18). Thus, we diagonalise the target Hamiltonian h in this truncated space and obtain N pseudo states:

$$\phi_i^N = \sum_{m=0}^{N-1} C_{Nim} \Phi_m. \tag{38}$$

The pseudo states have the normalisation

$$\langle \phi_i^N | \phi_j^N \rangle = \delta_{ij}. \tag{39}$$

The corresponding pseudo-state energies are obtained from (14). The Yamani-Reinhardt expansion enables us to determine the coefficients (apart from an overall normalisation factor) in terms of the Pollaczec polynomials. The reason for this remarkable fact is that the equations which the coefficients C_{Nim} satisfy are just the recurrences (30). (The matrix the coefficient vector acts on is tridiagonal, that is a Jacobi matrix, hence leading to the generic term J -matrix method.) The pseudo-state energies are determined by imposing the boundary condition

$$P_N(x) = 0. \tag{40}$$

Since the polynomial P_N is of degree N in x it follows through the mapping (28) that the N roots of this equation are

$$x_{Ni} = x(\epsilon_i^N). \tag{41}$$

The expansion coefficients are

$$C_{Nim} = A_{Ni} B_m(\epsilon_i^N) P(\epsilon_i^N), \tag{42}$$

where for positive energies it may be shown (Yamani and Reinhardt 1975) that

$$A_{Ni}^2 = \frac{\lambda}{\pi(1-x_{Ni})} \frac{\lambda_1 \lambda_2 \dots \lambda_N}{P_N(x_{Ni}) P_{N-1}(x_{Ni})} \left(\frac{2}{\pi k_{Ni}} \right)^{\frac{1}{2}} |\Gamma(\alpha - iy_{Ni})| \times (1 - x_{Ni}^2)^{\alpha - \frac{1}{2}} \exp\{(\theta_{Ni} - \frac{1}{2}\pi)y_{Ni}\}. \quad (43)$$

If we now compare the Fourier series of (25) at $x = x_{Ni}$ (where $\epsilon_i^N > 0$), truncated to the first N terms, with that of the pseudostates (38) subject to the normalisation (39) we see that the two expansions are equivalent within an overall factor A_{Ni} . Examples of the pseudo states and their convergence rates are given by Stelbovics and Winata (1990). A characteristic of the expansions is that the first few oscillations are reproduced tolerably well but the pseudo states eventually decay to zero on account of the exponential damping. The pointwise convergence of the series is shown to be of conditional type only. The relation of pseudo states to continuum functions has been discussed extensively in the context of the J -matrix method. The renormalisation constant (43) can be determined to arbitrary accuracy. For general basis sets no such obvious connection exists, but attempts have been made to give approximate descriptions. The best known of these is the Heller derivative rule. It has been studied by Broad (1978) who was able to give a justification for it. We adopt the view that the basis (18) is suitable for most numerical calculations and will therefore not consider the utility of these approximate procedures. A review of the subject is given by Macias *et al.* (1988).

(c) An Orthonormal Basis

The Yamani–Reinhardt expansion is special in the sense that it employs the only basis for which the Coulomb Hamiltonian pseudo states can be found analytically. If we drop the restriction that the pseudo states satisfy (14), other expansions can be derived which are orthonormal and converge to true continuum functions as the basis is expanded to completeness. In the limit of large N therefore, this type of basis will also satisfy (14) approximately. Consider the orthonormal basis functions

$$\Phi_n^*(r) = \left(\frac{\lambda \Gamma(N+1)}{\Gamma(N+2\alpha+1)} \right)^{\frac{1}{2}} (\lambda r)^\alpha \exp(-\frac{1}{2}\lambda r) L_n^{2\alpha}(\lambda r), \quad n = 0, 1, \dots \quad (44)$$

The asterisk is used to indicate that these functions are different from the previous basis. We adopt the convention that all the notation developed so far for the expansion coefficients will be retained, except that all corresponding quantities for this new basis will be identified by the asterisk. The expansion coefficients are found to be

$$B_n^*(E_i) = 2^{n+\alpha+\frac{3}{2}} \left(\frac{\Gamma(n+2\alpha+1)}{\Gamma(n+1)} \right)^{\frac{1}{2}} \frac{\Gamma(n+\alpha+a+1)}{\Gamma(\alpha+a)\Gamma(n+2\alpha+1)} (-a)^{\alpha+\frac{1}{2}} \left(\frac{\Gamma(2\alpha+i)}{\Gamma(\alpha+i)} \right)^{\frac{1}{2}} \times (i+\alpha)^{\alpha+1} (i+\alpha-a)^{-2\alpha-i-1} (i+\alpha+a)^{i-1} \quad (45)$$

for the bound states, and

$$\begin{aligned}
 B_n^*(E) &= 2^{n+\alpha} \frac{\Gamma(n+\alpha+a+1)}{\Gamma(\alpha+a)\Gamma(n+1)} \left(\frac{\Gamma(2\alpha)}{\lambda\Gamma(n+2\alpha+1)} \right)^{\frac{1}{2}} \left(\frac{2}{\pi k} \right)^{\frac{1}{2}} |\Gamma(\alpha-iy)| \\
 &= \times (1-x^2)^{\alpha-\frac{1}{2}} (1-x) \exp\{(\theta-\frac{1}{2}\pi)\gamma\} \tag{46}
 \end{aligned}$$

for the continuum states. The P_n^* are orthogonal polynomials. They satisfy the recurrence (30) with

$$\begin{aligned}
 \lambda_1^* &= 2^{-2\alpha} \pi \frac{\Gamma(2\alpha+1)}{(\alpha+a)^2}, \\
 \lambda_{n+1}^* &= \frac{n(n+2\alpha)}{4(n+\alpha+a)^2}, \quad n = 1, 2, \dots, \\
 d_{n+1}^* &= \frac{(n+1)2a+(2a-1)(\alpha+a)}{2(n+\alpha+a)(n+\alpha+a+1)}, \quad n = 0, 1 \dots
 \end{aligned} \tag{47}$$

It can be shown that the P_n^* are a form of kernel polynomial of the Pollaczeks. In contrast to the Pollaczeks they are positive definite for all values of the λ and l . This follows from (47) and (32). Their distribution is of the form (34) with

$$\begin{aligned}
 \rho^*(x) &= (1-x^2)^{\alpha-\frac{1}{2}} (1-x) |\Gamma(\alpha-iy)|^2 \exp\{(2\theta-\pi)\gamma\}, \quad x \in [-1, 1], \\
 &= 0 \quad \text{otherwise,} \\
 R_i^* &= \pi \frac{\Gamma(i+2\alpha)}{\Gamma(i+1)} 2^{2\alpha+3} (-a)^{2\alpha+1} (i+\alpha)^{2\alpha+2} \\
 &\quad \times (i+\alpha+a)^{2i-2} (i+\alpha-a)^{-4\alpha-2i-2}. \tag{48}
 \end{aligned}$$

We now demonstrate the manner in which expansions over pseudo-state bases can be regarded as equivalent to a Gaussian quadrature. This can be done with the basis of Yamani and Reinhardt, but its non-orthogonality and non-positiveness in all cases make the connection more complicated to show than is really necessary. Thus, we take the orthonormal basis (44) instead. The completeness relation for the target states can be expressed in terms of the Fourier expansions as

$$\begin{aligned}
 \sum_{i=0}^{\infty} |\phi_i\rangle \langle \phi_i| + \int_0^{\infty} dE |U_I(q)\rangle \langle U_I(q)| &= \int_{-\infty}^{\infty} d\mu^*(E) \sum_{n,m=0}^{\infty} |\Phi_n^*\rangle \frac{P_n^*(x)}{(\lambda_1^* \lambda_2^* \dots \lambda_{n+1}^*)^{\frac{1}{2}}} \\
 &\quad \times \frac{P_m^*(x)}{(\lambda_1^* \lambda_2^* \dots \lambda_{m+1}^*)^{\frac{1}{2}}} \langle \Phi_m^*| \\
 &= \sum_{n=0}^{\infty} |\Phi_n^*\rangle \langle \Phi_n^*|. \tag{49}
 \end{aligned}$$

Now let us construct a set of pseudo states by truncating the basis expansion to N functions. As before this can be achieved by the boundary condition (40) on the P_N^* . The pseudo-state energies are of course different from those of the previous basis. Then the completeness relation for the states can be expressed as

$$\begin{aligned} \sum_{i=0}^{N-1} |\phi_i^{*N}\rangle \langle \phi_i^{*N}| &= \sum_{i,n,m=0}^{N-1} |\Phi_n^*\rangle \frac{P_n^*(x_{Ni})}{(\lambda_1^* \lambda_2^* \dots \lambda_{n+1}^*)^{\frac{1}{2}}} W_{Ni} \frac{P_m^*(x_{Ni})}{(\lambda_1^* \lambda_2^* \dots \lambda_{m+1}^*)^{\frac{1}{2}}} \langle \Phi_m^*| \\ &= \sum_{n=0}^{N-1} |\Phi_n^*\rangle \langle \Phi_n^*|. \end{aligned} \quad (50)$$

The W_{Ni} are Gaussian weights,

$$W_{Ni} = \frac{\lambda_1^* \lambda_2^* \dots \lambda_N^*}{P_N^*(x_{Ni}^*) P_{N-1}^*(x_{Ni}^*)}, \quad (51)$$

whose sum is λ_1^* . In deriving (50) we used the property of Gaussian integration that polynomials in x of degree less than $2N-1$ are integrated exactly by the quadrature. The derivation requires the use of the Schwarz Christoffel relation (see for example Chihara 1978). If we compare the approximate completeness relation with the exact one we note that, apart from the replacement of the distribution $d\mu(x)$ by the quadrature, there is one further difference; the Fourier expansions of the target states have been truncated to the first N terms.

The orthogonal basis function expansions differ in an essential way from those of the first basis. There we had the additional property that the pseudo states were orthogonal with respect to the target Hamiltonian (14). Thus, one should not use these states in the usual pseudo-state close-coupling equations without qualification. For large basis sets, where the expansions are good approximations to the target states and the orthogonality is approximately satisfied, reliable results might be obtainable. The basis has not been widely used in close-coupling calculations. Bray *et al.* (1991) have applied it in a model problem and emphasised the advantage of using the orthonormal basis for numerical calculations. This expansion has appeared in other guises in related fields. The Stieltjes-Tchebycheff imaging-method example presented by Hermann and Langhoff (1983) is a special case of the Fourier series given as pointed out by Stelbovics (1989). Similarly the Sturmian-function expansions as defined by Rotenberg (1970) have Fourier coefficients which he calls Drang functions and presents as power series expansions. These expansions can be identified with the Pollaczec polynomials discussed here.

4. Convergence of Channel Potentials

The purpose of having an analytically expressible form of the pseudo states is that it enables one to study the convergence of the channel potentials to those obtained by folding between exact target states. In general we may consider three classes of these potentials connecting (1) bound-bound channels, (2) bound-free channels and (3) free-free channels.

The potentials (7) have two parts, U the dominant portion which includes the direct nucleus potential and the direct and exchange electron–electron terms, and W the separable terms which have an explicit energy dependence. Class (1) presents little difficulty. The channels of interest normally comprise wavefunctions with few nodes, and so if a basis set is chosen with appropriate range in the exponential term, a Laguerre-type basis will represent the true eigenstate adequately. The potentials coupling p -space channels are accurately reproduced even for small basis sets. The second class of channel potentials has been studied recently (Stelbovics and Winata 1990) using the Yamani–Reinhardt basis. There it was shown that the direct part of U from the hydrogen-1s state, coupled to a continuum state with angular momentum l , has a Fourier expansion whose n th term for large n behaves like

$$\begin{aligned}
 a_n^l(q, K) = & A^{-(n+l+1)} \frac{1}{\lambda q K} (2l+1) \exp\{(2\theta - \pi)\gamma\} \\
 & \times \cos[(n+l+1)\theta + \gamma \ln(2n \sin\theta) - \frac{1}{2}\pi(l+1) - \arg\Gamma(l+1 - iy)] \\
 & \times \{2(\cos\omega - A^{-1})\cos[(n+l+1)\omega - \frac{1}{2}\pi(l+1)] \\
 & + (1-A)\cos[(n+l)\omega - \frac{1}{2}\pi(l+1)] + O(n^{-1})\}, \quad (52)
 \end{aligned}$$

where

$$\tan\omega = \frac{K}{1 + K^2 - (\frac{1}{2}\lambda)^2}, \quad 0 \leq \omega \leq \pi, \quad (53)$$

$$A = \left(\frac{(1 + \frac{1}{2}\lambda)^2 + K^2}{(1 - \frac{1}{2}\lambda)^2 + K^2} \right)^{\frac{1}{2}}. \quad (54)$$

The series is essentially of geometric form. In the above equations K is the momentum transfer from initial to final states and q is the ejected electron wave vector. The convergence of the series may be relatively slow for some energies because the geometric term approaches 1 at high energies. This has the inevitable consequence that some continuum channels which we couple to will be represented more poorly than others in any finite basis. One could try omitting the pseudo states with large energies but this cannot be justified from the point of view of completeness of the approximate target space; one is then throwing away important information about the continuum. The separable exchange term W in momentum space is proportional to the momentum representation of the channel wavefunctions. In the case of the continuum channels this means that the finite-basis expansion must in the limit approach the partial-wave regular Coulomb function, which is a distribution in the momentum representation. For example, for the $l=0$ partial wave the momentum-space form is just the distribution resulting from a Fourier sine

transform of the $l=0$ regular Coulomb function (22):

$$\begin{aligned}
 U_0(k, p) &= \left(\frac{2}{\pi}\right)^{\frac{1}{2}} \int_0^{\infty} dr \sin(pr) U_0(k, r) \\
 &= \frac{4}{\pi} \sqrt{k \exp(\frac{1}{2}\pi\gamma)} |\Gamma(1 - i\gamma)| \\
 &\quad \times \lim_{\eta \rightarrow 0^+} \text{Im}[k^2 - (p + i\eta)^2]^{-1} \left(\frac{p + i\eta + k}{p + i\eta - k}\right)^{-iy}. \quad (55)
 \end{aligned}$$

If the potential is set to zero, (55) reduces to a delta function in momentum multiplied by a factor of $p^{1/2}$. It would appear therefore that the pseudo-state effective potential structure becomes increasingly complicated as the magnitude of the calculations increases, since the positive-energy momentum-space pseudo states approach the structure implied by (55). Subtraction methods to treat kernels containing such distributions have been studied by Van Haeringen and Kok (1980). It is thus a little surprising to find that there has been no indication of difficulties arising from the solution of the equations with larger sets of pseudo states. Indeed, if we return to Oza's (1984) comparison with the Poet (1978) model, the conclusion he reaches is that the pseudo-state solutions are converging to Poet's results. Moreover, all the reported calculations confirm that the triplet-channel amplitudes for elastic and inelastic scattering are free from the resonance structure which plagues the singlet channel. Since both channels have similar exchange terms, the singular nature of the matrix elements has not propagated through to the T -matrix solutions of the pseudo-state calculations.

The free-free potentials comprise direct and electron-electron exchange terms made up from Coulomb potentials folded between initial and final continuum states. There are also the energy dependent exchange terms, made up of products of continuum functions, whose momentum space form we have looked at above. The direct potentials may be evaluated in closed form as a sum over Appell functions (Jetzke and Broad 1985). To give some indication of the form of the resultant potential in momentum space, we consider the simplest possible case comprising plane-wave incident and final state continuum wavefunctions. Such an approximation removes the Gamow and Coulomb phase factors, but their omission does not invalidate our main conclusion. A typical free-free direct potential element then is of the form

$$\begin{aligned}
 V(q, K, q') &\propto \int_0^{\infty} \frac{\sin(qr) \sin(Kr) \sin(q'r)}{r} dr = 0 \quad \text{for } K < q - q' \text{ or } K > q + q' \\
 &= \frac{\pi}{8} \quad \text{if } K = q - q' \text{ or } K = q + q' \\
 &= \frac{\pi}{4} \quad \text{when } q - q' < K < q + q', \quad (56)
 \end{aligned}$$

where q, q' represent the momentum of the continuum initial and final target states and K is as before the momentum transfer. It has been assumed that

$q > q' > 0$ in writing (56). Thus, the potentials are bounded (in fact in a numerical application one further performs a partial wave integration over the scattering angle contained in K resulting in a continuous function of the momenta) and hence pose no numerical problems.

Similarly the electron–electron exchange term in this model involves only an interchange of the electron momenta and needs no further comment. No study of convergence rates for pseudo-state expansions of the free–free matrix elements has been undertaken to date. However, it is likely that the resultant series will have poor convergence properties. Certainly, the geometric rates found for the bound–free potentials (52) will not apply because they relied on the bound-state wavefunction cutting off the r -space integrals for large r .

Most pseudo-state applications to date have concentrated on determining scattering amplitudes coupling the lowest energy channels of the target. In these processes free–bound and free–free transitions are included as higher order processes. Thus even bad approximations to these potentials do not have a pronounced effect on the amplitudes. In new applications, such as the modelling of ionisation processes within this close-coupling framework, the bound–free potentials contribute at first-order level and their convergence properties will be important in assessing the accuracy of a calculation.

5. Outlook and Conclusions

In this review we have emphasised techniques for studying atomic scattering problems in the close-coupling formalism. Of particular importance is a proper understanding of the role the target continuum states play. In order to study the continuum effects by analytic methods we have concentrated on electron–hydrogen scattering where one has the advantage of knowing the target states exactly. We have seen precisely how the pseudo-state approximation to the target continuum can be formulated in a mathematical form; the completeness relation in the finite-basis approximation is equivalent to that over the full space in the sense of a generalised Gaussian quadrature in which the quadrature approximates the sum over all discrete, and integral over all continuum states; each pseudo state was seen to be, apart from an overall normalisation constant, equivalent to a Fourier expansion of the exact continuum wavefunction truncated to the finite basis.

We also looked at the channel potentials coupling to all combinations of levels. We demonstrated how one can approach the general problem of determining the rate of convergence for the various types of potentials. This is a task that has yet to be completed because the class of free–free potentials has not been studied. In principle, their analysis should be amenable to the methods presented in this review.

The convergence of the basis expansions to the exact target wavefunctions leads as a consequence to channel potentials which in the large-basis limit are just those obtained by using exact continuum functions. One therefore is prompted to ask whether it is not possible to solve the electron–hydrogen problem using exact target functions. The usual answer given is that this will be a time consuming problem because the analytic expressions are cumbersome. With the rapid progress in speed of computers, this objection is probably no longer valid. One would like some explicit demonstration, at least on the scale

of the Poet model, that the pseudo-state close-coupling equation amplitudes do converge to those obtained from the close-coupling equations employing exact target states.

We indicated that this would be a difficult problem, at least in the momentum-space formulation, because the exchange terms in the effective potentials contained distributions which in the zero-charge limit reduced to δ functions. Appropriate subtraction methods would need to be developed for the kernels of the T -matrix equations to handle them. The very complex structure of some of the channel potentials and the demonstrated convergence of the pseudo-state calculations raises further interesting questions. The pseudo-state calculations in the Poet model demonstrate excellent convergence in triplet scattering, but do not do so well for singlet scattering where pseudo-resonance structure is always present, although the largest study undertaken (Oza 1984) points to probable convergence. Clearly then, the fact that some parts of the potentials are 'converging' to distributions has not affected the calculations to date, since such terms occur in both singlet and triplet scattering. One is therefore led to enquire whether instabilities may yet arise in pseudo-state calculations with more extended bases. One may find that the meshes used routinely to discretise the T -matrix equations will fail when the singular parts of the potentials are more correctly described in the limit of large expansions.

A further point we wish to address is that of the choice of basis expansions. We have adopted the Laguerre basis of Yamani and Reinhardt as our preferred choice. Can one do better by using Slater functions? We suggest that the answer is no, at least for large calculations. The Laguerre basis is 'nearly' orthogonal and problems of linear dependence that can affect large Slater function bases do not arise. A preliminary study of the convergence of the Laguerre basis, with an optimised Slater set within the confines of a second Born approximation, by Stelbovics and Winata (1990) suggests that there is little difference for large bases. It would be interesting to see more comprehensive investigations in this direction.

Our concluding remark is to respond to the rhetorical question: 'Why be concerned with getting answers to such great precision for hydrogen? Surely pseudo-state methods appear to work and in any case for all other atoms this type of analytic approach is not feasible?' We adopt the position that one is attempting to understand atomic scattering completely and the conditions of validity of certain scattering formalisms. Only when we can claim to understand the scattering theory for this system fully can we approach its implementation to more complicated systems with confidence.

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References

- Bank, E., and Ismail, M. (1985). *Constr. Approx.* **1**, 103.
- Bray, I., Konovalov, D. A., and McCarthy, I. E. (1991). *Phys. Rev. A* **43** (in press).
- Bray, I., McCarthy, I. E., Mitroy, J., and Ratnavelu, K. (1989). *Phys. Rev. A* **39**, 4998.
- Broad, J. T. (1978). *Phys. Rev. A* **18**, 1012.

- Burke, P. G., Berrington, K. A., and Sukumar, C. V. (1981). *J. Phys. B* **14**, 289.
- Burke, P. G., and Mitchell, J. F. (1973). *J. Phys. B* **6**, 320.
- Burke, P. G., and Webb, T. G. (1970). *J. Phys. B* **3**, L131.
- Callaway, J. (1980). *Adv. Phys.* **29**, 771.
- Chihara, T. S. (1978). 'An Introduction to Orthogonal Polynomials', Vol. 13 of 'Mathematics and its Applications' (Gordon and Breach: New York).
- Heller, E. J., Reinhardt, W. P., and Yamani, H. A. (1973). *J. Comp. Phys.* **13**, 536.
- Heller, E. J., and Yamani, H. A. (1974). *Phys. Rev. A* **9**, 1209.
- Hermann, M. R., and Langhoff, P. W. (1983). *Phys. Rev. A* **28**, 1957.
- Higgins, J. R. (1977). 'Completeness and Basis Properties of Special Functions', Cambridge Tracts in Mathematics No. 72 (Cambridge Univ. Press).
- Jetzke, S., and Broad, J. T. (1985). *J. Phys. B* **19**, L199.
- Klahn, B., and Bingel, W. A. (1977). *Theoret. Chim. Acta* **44**, 9–26, 27.
- McCarthy, I. E., and Stelbovics, A. T. (1983). *Phys. Rev. A* **28**, 2693.
- Macias, A., Martin, F., Riera, A., and Yanz, M. (1988). *Int. J. Quant. Chem.* **XXXIII**, 279.
- Norcross, D. W. (1969). *J. Phys. B* **2**, 1300.
- Oza, D. H. (1984). *Phys. Rev. A* **30**, 1101.
- Oza, D. H., and Callaway, J. (1983). *Phys. Rev. A* **27**, 2840.
- Poet, R. (1978). *J. Phys. B* **11**, 13081.
- Rotenberg, M. (1970). In 'Advances in Atomic and Molecular Physics', Vol. 6 (Eds D. R. Bates and I. Esterman), p. 233 (Academic: New York).
- Slim, H. A. (1988). *J. Math. Anal. Appl.* **136**, 1.
- Stelbovics, A. T. (1989). *J. Phys. B* **22**, L159.
- Stelbovics, A. T. (1990). *Phys. Rev. A* **41**, 2536.
- Stelbovics, A. T., and Bransden, B. H. (1989). *J. Phys. B* **22**, L451.
- Stelbovics, A. T., and Slim, H. A. (1987). *Phys. Rev. A* **33**, 3993.
- Stelbovics, A. T., and Winata, T. (1990). *Aust. J. Phys.* **43**, 485.
- Van Haeringen, H., and Kok, L. O. (1980). Report THD-A-St 80 08, Dept. of Math., Delft University of Technology.
- Yamani, H. A., and Reinhardt, W. P. (1975). *Phys. Rev. A* **11**, 1144.

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