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Coupled-States Method for Scattering Calculations

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The eigenfunction-expansion method for calculating scattering of electrons and positrons from atoms has the very desirable property of providing phase-shift bounds, but is slowly convergent in some cases. Phase-shift bounds and improved convergence are combined in recently developed hybrid methods, but these are complicated to apply. An alternative method based on expansion in target states, some of which are chosen for best convergence rather than restricted to eigenstates, is proposed. The coupled equations are similar to those of the eigenfunction-expansion method and provide phase-shift bounds. The method was tested by calculation of S-wave positron-hydrogen scattering at energies of $k^2 = 0, 0.04, 0.16$, and 0.36. Target states used in the expansions ($1s2p'$ and $1s2p'3d'$) were of the same functional form as eigenstates, except that orbital exponents were not fixed at $\frac{1}{2}$ and $\frac{1}{3}$. Calculated phase shifts as a function of orbital exponent value have a broad maximum for exponent values larger than those of eigenfunctions, and phase shifts are considerably larger than those calculated with eigenfunction expansions.

INTRODUCTION AND DISCUSSION

In calculating approximate solutions of the nonrelativistic Schrödinger equation for atomic systems, it is desirable to have methods which are convenient to apply, converge rapidly, and lead to improved estimates of the relevant physical parameter as the approximation is increased in scope. A discussion is given of these properties as they apply to various methods of treating the scattering of positrons and electrons by atoms, as well as to bound-state calculations. A coupled-states scattering method, which is a modification of the familiar eigenfunction-expansion method, is proposed, and its effectiveness tested by application to S-wave scattering of positrons from hydrogen atoms.

Development of appropriate methods for treating scattering problems[1] has been more difficult than for bound states. Trial functions automatically provide an upper bound to the energy of the lowest discrete state of the same symmetry as the trial function[2]; hence variational estimates of energy necessarily improve as a trial function is made more flexible. Upper energy bounds are also provided for higher states by Rayleigh-Ritz calculations, involving variation of expansion coefficients, and sometimes by methods involving continuous variation of functions.[3] Of intuitive appeal are expansions formed from products of eigenfunctions of a one-electron Hamiltonian. It has long been realized, however, that such expansions converge very slowly.[4] This can be explained by noting that there are non-negligible contributions from continuum one-electron eigenstates. Alternatively, one can merely observe that the excited one-electron eigenfunctions become spatially quite diffuse, whereas extra flexibility of the trial function is needed in the vicinity of the nucleus. Thus, in spite of the elegance of eigenfunction expansions, it has proven desirable in bound-state problems to simply choose expansion states for best convergence.[4]

Similarly, it has been appealing to treat the scattering of positrons and electrons by atoms by the use of a trial function, expressed as a sum of products of target eigenstates with initially undetermined functions of coordinates of the scattered particle.[5] The equations are separated by multiplying by each of the target states in turn, and integrating over target coordinates. The resulting set of differential or integrodifferential equations are then solved numerically. This eigenfunction-expansion method, often called the close-coupling method, is relatively straightforward in application. It has been extensively employed and has led to quite important results, including prediction of scattering resonances,[6] but the convergence properties have turned out to be rather poor in some cases.[5]

By analogy with bound-state problems, one might expect improvement in convergence, if the expansion states were chosen to be spatially compact rather than restricting them from the outset to target eigenstates. This possibility has been mentioned by various authors,[5,7] but has not been extensively investigated. The so-called Sturmian functions have the desirable properties of being complete, though entirely discrete,[7] and of being spatially compact. With an expansion in these functions, the lowest of which is the hydrogen ground-state function, the resulting equations can be separated by multiplying with each target state in turn as well as by an orthogonalizing function. A calculation of positron-hydrogen scattering with this approach,[7] however, produced puzzling results.

It has been especially difficult to demonstrate the conditions under which methods for treating scattering problems will provide bounds on phase shifts. The Kohn and Hulthen[1] analogs of the Rayleigh-Ritz method do not guarantee phase-shift bounds at positive nonzero energies, even for one-dimensional scattering from a fixed potential. The effects of the lack of a bound were clearly demonstrated in C. Schwartz's extensive Kohn-type calculations of scattering of electrons and positrons from hydrogen,[8] though his final results are very good. Percival[9] considered this problem from the point of view of an extended Rayleigh-Ritz method in which the wave-function components which correspond to energetically accessible target states are treated by solution of differential equations resulting from continuous variation of functions (rather than variation of expansion coefficients). His results were suggestive but incomplete, and the proof was given relatively recently, in various forms, by Hahn, O'Malley, and Spruch[10,11] and by McKinley and Macek.[12] These proofs constitute a very important advance in scattering theory. The introduction of the Feshbach projection operators into atomic physics by the NYU group has indeed had profound effects on a number of developments in atomic and molecular theory (which we will not attempt to review here), including the treatment of resonances, and has, in addition, served as the basis of the phase-shift-bound proof by Hahn, O'Malley, and Spruch.[10,11] The latter authors[13] have pointed out that their proof does not apply to the Sturmian-function approach[7] (which was carried out prior to derivation of the phase-shift-bound proofs). It will be seen below, however, that these proofs, or minor modifications thereof, do apply to the method proposed herein, as well as to the eigenfunction-expansion method for which they were explicitly given.

The phase-shift bound is a very desirable feature which one would like to incorporate in a computational method, but at the same time one wants reasonably good convergence. In order to achieve these goals, various workers have introduced methods in which the open channels are treated by continuous variation of functions, while closed-channel components are treated by variation of coefficients; for convenience we will refer to these as hybrid methods, and will not distinguish between the different forms which such calculations take in the various approaches, since the results should be equivalent. Such a method was first developed by Hahn, O'Malley, and Spruch,[13] and is referred to by them as a variational-bound method. It has been very successfully used for scattering from hydrogen,[14-16] but seems quite complex because of the necessity of dealing with the Green's function of the static solution. It was noted by Hahn and Spruch,[14] and also by Hahn,[17] that one might be able to avoid evaluation of the Green's function. Gailitis[18] and also Burke and Taylor[19] have used hybrid methods which amount to bypassing the evaluation of the Green's function; even these calculations, however, seem rather involved.

METHOD

The proposed method is motivated by the hope of combining the relative simplicity of the eigenfunction-expansion method, improved convergence, and phase-shift bounds. We first consider scattering of low-energy positrons from hydrogen atoms (similar equations apply to scattering from more complex atoms). Incident energies are assumed to be below the lowest inelastic threshold. The trial function is written as an expansion in products of target states $u_i(\vec{r}_1)$ and scattering functions $F_i(\vec{r}_2)$:

$$\psi(\vec{r}_1, \vec{r}_2) = \sum_i u_i(\vec{r}_1) F_i(\vec{r}_2) . \tag{1}$$

Here the $u_i(\vec{r}_1)$ are not restricted exclusively to (energy) eigenstates of the target; only the energetically accessible eigenstates (open channels) need be included. Otherwise the derivation of differential equations is similar to that for eigenfunction expansions.[5] The exact wave function is annihilated by

$$E-H = \nabla_1^2 + \nabla_2^2 + \frac{2}{r_1} - \frac{2}{r_2} + \frac{2}{r_{12}} - 1 + k^2 . \tag{2}$$

The coupled equations are obtained by requiring that

$$\int u_j^*(\vec{r}_1)(E-H)\psi(\vec{r}_1, \vec{r}_2)d\vec{r}_1 = 0 \tag{3}$$

for each value of j. This leads to

$$\sum_i [N_{ji}(\nabla_2^2 + k^2 - 1) - E_{ji} - V_{ji}(\vec{r}_2)] F_i(\vec{r}_2) = 0 , \tag{4}$$

where

$$N_{ji} = \int u_j^*(\vec{r}_1) u_i(\vec{r}_1) d\vec{r}_1 , \tag{5}$$

$$-E_{ji} = \int u_j^*(\vec{r}_1) \left(\nabla_1^2 + \frac{2}{r_1}\right) u_i(\vec{r}_1) d\vec{r}_1 , \tag{6}$$

$$V_{ji}(\vec{r}_2) = \int u_j^*(\vec{r}_1) \left(\frac{2}{r_2} - \frac{2}{r_{12}}\right) u_i(\vec{r}_1) d\vec{r}_1 . \tag{7}$$

In order that the equations separate, it is necessary that the target states be chosen to be mutually orthogonal:

$$N_{ji} = \delta_{ji} . \tag{8}$$

Although it is not essential, a desirable simplification occurs if the finite set of target states are chosen so as to be diagonal with respect to the target Hamiltonian:

$$E_{ji}=E_j\delta_{ji}\,. \tag{9}$$

The latter property comes about automatically in the eigenfunction-expansion method, but in the present method it will require some relatively simple preliminary calculations unless it is automatically provided by symmetry. The resulting set of coupled differential equations,

$$(\nabla_2{}^2+k^2-1-E_j)F_j(\vec{r}_2)=\textstyle\sum_i V_{ji}(\vec{r}_2)F_i(\vec{r}_2)\,, \tag{10}$$

are of the same form as for eigenfunction expansions and of course become identical with the latter if all the $u_i(\vec{r}_1)$ are chosen as eigenstates. The method of solution is the same, the only differences being in the values of the E_j and the detailed form of the potentials $V_{ji}(\vec{r}_2)$. In practice, a partial-wave separation is first made and each partial wave is then treated as a separate problem. The choice of $u_0(\vec{r}_1)$ as the target ground-state function has the result that the asymptotic behavior of $F_0(\vec{r}_2)$ approximates that of the exact wave function, and hence that the calculated phase shift approximates the exact phase shift and would presumably approach it as the expansion is extended to completion.

Each target state is to be chosen as a product of a radial function, an angular function corresponding to a definite angular momentum, and a spin function. In treating scattering from hydrogen it is sometimes convenient to explicitly employ the angle between position vectors of the two light particles in a manner equivalent to coupling of angular functions of target-and scattered-particle coordinates. It is the additional flexibility (as compared to eigenfunction expansions) in the choice of radial functions of target states which we wish to exploit. In particular, the hope is that convergence can be improved by choosing spatially compact target functions.

The scattering of electrons can be similarly treated; for simplicity the discussion is again restricted to scattering from hydrogen at energies below the lowest inelastic threshold. The expansion is explicitly antisymmetrized with the spin factored out;

$$\psi(\vec{r}_1,\vec{r}_2)=\textstyle\sum_i[u_i(\vec{r}_1)F_i(\vec{r}_2)\pm F_i(\vec{r}_1)u_i(\vec{r}_2)]\,. \tag{11}$$

It is again assumed that the expansion states $u_i(\vec{r}_1)$ are diagonal with respect to target Hamiltonian. The resulting integrodifferential equations are

$$\begin{aligned}(\nabla_2{}^2+k^2-1-E_j)F_j(\vec{r}_2)=\textstyle\sum_i[-&V_{ji}(\vec{r}_2)F_i(\vec{r}_2)\\ &\mp\int K_{ji}(\vec{r}_1,\vec{r}_2)F_i(\vec{r}_1)d\vec{r}_1]\,,\end{aligned} \tag{12}$$

where
$$\begin{aligned}K_{ji}(\vec{r}_1,\vec{r}_2)&=\left(-1+k^2-\frac{2}{r_{12}}\right)u_j{}^*(\vec{r}_1)u_i(\vec{r}_2)\\ &+u_j{}^*(\vec{r}_1)v_i(\vec{r}_2)+v_j{}^*(\vec{r}_1)u_i(\vec{r}_2)\end{aligned} \tag{13}$$

and
$$v_k(\vec{r})=\left(\nabla^2+\frac{2}{r}\right)u_k(\vec{r})\,. \tag{14}$$

The equations are slightly more complicated than for the eigenfunction-expansion method, because of the necessity of introducing the functions $v_k(\vec{r})$.

Expansions in eigenfunctions would, of course, require inclusion of continuum states in order to attain completeness. The practical difficulty of actually including continuum states would apply to treatments of both scattering and bound states. For the latter, one at least knows how, in principle, to do the calculation. For problems involving a scattered particle which is identical with target particles, there may be continuum-exchange contributions to the scattering,[20] unless the scattering functions are suitably constrained. This difficulty does not apply to a method, such as the present one, in which the expansion could, at least in principle, be carried to completion with a set of purely discrete target states.

The present method can be most simply described as a modification of the eigenfunction-expansion method, made with attention to the requirement for phase-shift bounds. There is also an interesting connection with the hybrid method,[13,18,19] which superficially seems quite different. Consider a modification of the present method for S-wave scattering of low-energy positrons or electrons from hydrogen, in which the closed-channel radial function $F_0(\vec{r}_2)$ is permitted full flexibility and hence treated by a differential equation, while each of the remaining radial functions $F_i(\vec{r}_2)$ is approximated by a finite expansion

$$F_i(\vec{r}_2)=\textstyle\sum_j C_{ij}w_{ij}(\vec{r}_2)\,,\ i>0\,. \tag{15}$$

The functions $w_{ij}(\vec{r}_2)$ are fixed, but the expansion coefficients C_{ij} are subject to variation. This can be described as an example of the hybrid method in which each closed-channel expansion term has been restricted to the form of a product of a target function and a scattering function (this form was effectively adopted in Refs. 14–16 and 18, though it is not essential to the hybrid method and was not adopted in Ref. 19). The very good convergence which has been obtained with such forms of the hybrid method[14–16,18] is probably at least partially attributable to the inclusion, in the expansion, of target states which are spatially compact. In the example considered, the finite expansions of $F_i(\vec{r}_2)$ imply that the hybrid method would not give quite as good results as obtained by solution of the corresponding set of coupled differential equations. At energies not too close to zero, each $F_i(\vec{r}_2)$ could probably be represented adequately by only a few judiciously chosen $w_{ij}(\vec{r}_2)$. Presumably it would be difficult to choose a convenient set of $w_{ij}(\vec{r}_2)$ which would adequately represent the behavior of the $F_i(\vec{r}_2)$ at large r_2 for very low energies, and the hybrid method as such does not seem to have been used for zero-energy calculations (at zero energy, the hybrid method is very similar to the Kohn method). The difficulty of representing the long-range behavior of the zero-energy wave function with expansions in functions which are readily handled was explicitly noted by Schwartz in his Kohn-type calculations.[8] The present method, in common with the eigenfunction-expansion method, presents no special difficulties at zero energy; the solutions are started in the outer region with a different form of asymptotic expansion[21] which, however, is no more difficult to handle than the expansion used at positive energies.

The use of closed-channel functions of product form is a limitation of the present method; really good convergence may require use of several product functions for each relative partial wave, on account of "in-out" correlation. For extensive calculations it might prove useful to consider an alternative scheme combining features of the present method and current hybrid methods. The trial wave function would contain components treated by variation of coefficients as well as components (not limited to open channels) treated by continuous variation of functions, with the latter containing some noneigenfunction target states. We have not explored this alternative in detail, however. A somewhat similar extension of the hybrid method has been discussed in Appendix A of Ref. 13 which, however, does not seem to introduce the idea (which is the essential feature of the present approach) of using noneigenfunction target states in the continuous-variation part of the wave function.

PHASE-SHIFT BOUNDS

That the present method produces lower bounds on phase shifts, which increase as the target basis is extended, may be obvious to those familiar with the proofs given by Hahn, O'Malley, and Spruch[10,11] and by McKinley and Macek.[12] We note that the prediagonalization of target states is merely for computational convenience. The diagonalizing transformation leads to an equivalent set of equations which will therefore lead to the same phase shift as would be obtained from the untransformed equations, provided the boundary conditions are imposed consistently. Inclusion of the exact wave functions of the energetically accessible target states has the effect that the vanishing and nonvanishing boundary conditions at infinity do not get mixed together; hence the calculated phase shift is unaffected by the prediagonalization.

The proofs by Hahn *et al.*[10,11] are based on Feshbach projection operators, and are somewhat formal in the sense that some of the operators which appear in the theory cannot be explicitly constructed. Our method is equivalent to modifying some of the projection operators by inclusion of target functions which are not eigenfunctions. This preserves the property of P and Q being Hermitian, nonoverlapping projection operators, but does not preserve the property of P and Q commuting with the target Hamiltonian. Hahn *et al.*'s first type of proof[10] showed that lower bounds on phase shifts must result from solutions of coupled equations obtained with P and Q, for any energy below the lowest eigenvalue of QHQ; this result is unaffected by the present modification, though arguments establishing lower bounds on the lowest eigenvalue of QHQ must be suitably modified. Their second type of proof[11] shows that eigenfunction-expansion calculations must give lower bounds to phase shifts at all energies below the inelastic threshold; the proof assumes that P and Q commute with the target Hamiltonian, and hence it is not immediately applicable to the present type of expansion, though it can probably be made so by a minor modification. This paper[11] also discusses the question of defining an absolute phase shift.

McKinley and Macek's proof[12] applies to coupled-states equations of familiar form and does not introduce abstract operators; it is applicable to all energies below the appropriate inelastic threshold. Their proof is given for eigenfunction expansions, but a straightforward extension applies to the present method, and since the modified proof is brief we give it here. We consider only the simplest case of S-wave scattering with a single open channel. It is assumed we have first solved the system of equations resulting from expansion in N target states which have been previously diagonalized with respect to the target Hamiltonian. We wish to show that the solution of the system of $N+1$ equations, resulting from including one additional target state, must necessarily result in an increased estimate of phase shift. We introduce the parameter λ and write the radial equations which result after making the partial-wave decomposition:

$$[-T(q)+E-E_j]G_j(q,\lambda) = \sum_{i=0}^{N} V_{j,i}(q)G_i(q,\lambda) + \lambda[E_{j,N+1}+V_{j,N+1}(q)]\; G_{N+1}(q,\lambda),$$

and for $j=0, 1, \ldots N$, (16)

$$[-T(q)+E-E_{N+1,N+1}]G_{N+1}(q,\lambda) = \lambda\sum_{i=0}^{N}[E_{N+1,i}+V_{N+1,i}(q)]G_i(q,\lambda) + \lambda^2 V_{N+1,N+1}(q)G_{N+1}(q,\lambda). \tag{17}$$

The passage from $\lambda=0$ to $\lambda=1$ corresponds to passage from the original N-term expansion to the $(N+1)$-term expansion. There is no loss of generality in assuming all functions to be real. We first consider separately the equation corresponding to each value of j from 0 through $N+1$. The equation for $G_j(q,\lambda)$ is multiplied on the left by $G_j(q,\lambda+\Delta\lambda)$. We then take the corresponding equation for $G_j(q,\lambda+\Delta\lambda)$ and multiply on the left by $G_j(q,\lambda)$, subtract the previous product, and integrate over q. The left-hand side of the resulting equations will vanish for all closed-channel equations, but for the open-channel $j=0$ equation we obtain $-k\Delta\tan\eta(\lambda)$. We sum separately the left-hand and right-hand side of the resulting equations over all j. After dividing by $\Delta\lambda$ and taking the limit as $\Delta\lambda$ approaches zero, we obtain

$$\begin{aligned}-k\frac{d}{d\lambda}\tan\eta(\lambda)={}&\sum_{i=0}^{N}\int G_i(q,\lambda)[E_{i,N+1}+V_{i,N+1}(q)]\\&\times G_{N+1}(q,\lambda)dq+\sum_{i=0}^{N}\int G_{N+1}(q,\lambda)[E_{N+1,i}\\&+V_{N+1,i}(q)]G_i(q,\lambda)dq+2\lambda\int G_{N+1}(q,\lambda)\\&\times V_{N+1,N+1}(q)G_{N+1}(q,\lambda)dq.\end{aligned}\qquad(18)$$

If the scattered particle is distinguishable from all target particles, the $V_{j,i}(q)$ are ordinary potentials and are unaffected by interchanging j and i. For scattering of a particle which is identical with target particles, the $V_{j,i}(q)$ are integral operators with the property that the above integrals involving $V_{i,N+1}(q)$ are equal to the integrals involving $V_{N+1,i}(q)$. The present case differs from that discussed by McKinley and Macek only in the appearance of the additional quantities $E_{i,N+1}$ and $E_{N+1,i}$. But, of course, we also have that

$$E_{i,j}=E_{j,i}.\qquad(19)$$

We next consider Eq. (17) for the $(N+1)$st scattering function. We multiply to the left by $G_{N+1}(q,\lambda)$ and integrate over q. The sum of integrals appearing on the right-hand side, by virtue of the symmetry of $V_{j,i}(q)$ and $E_{j,i}$, is just $\frac{1}{2}\lambda$ times the sum of integrals appearing in Eq. (18). Thus we have that

$$\begin{aligned}-k(d/d\lambda)\tan\eta(\lambda)={}&(2/\lambda)\int G_{N+1}(q,\lambda)[-T(q)+E\\&-E_{N+1,N+1}]G_{N+1}(q,\lambda)dq.\end{aligned}\qquad(20)$$

The kinetic-energy operator $T(q)$ is positive-definite. The numerical quantity $(E-E_{N+1,N+1})$ must be negative for all energies up to the first inelastic threshold, since the target function $u_{N+1}(\vec{r})$ was required to be orthogonal to the ground-state function $u_0(\vec{r})$. It follows that

$$-k(d/d\lambda)\tan\eta(\lambda)\leqslant 0.\qquad(21)$$

Actually this equation holds only for values of λ for which the derivative exists. We adopt the convention that $\eta(\lambda)$ varies continuously as $\tan\eta(\lambda)$ passes through infinity.[11] With this understanding, it follows that

$$\eta_{N+1}\equiv\eta(\lambda=1)\geqslant\eta(\lambda=0)\equiv\eta_N.\qquad(22)$$

The purely manipulational part of the proof is concluded by simply putting

$$\eta_{\text{exact}}=\lim_{N\to\infty}\eta_N.\qquad(23)$$

This leads to the desired final result

$$\eta_{\text{exact}}\geqslant\eta_{N+1}\geqslant\eta_N.\qquad(24)$$

We next attempt to at least partially justify Eq. (23). The asymptotically nonvanishing part of the overall scattering wave function is associated with the target ground-state eigenfunction, which has been included in the expansion states. The remaining portion of the wave function is a complicated short-range function which we wish to represent by the remaining terms in the expansion. For this purpose it is only necessary that the expansion states $u_i(\vec{r})$ form a complete set of functions. The set of target eigenstates, including the continuum eigenstates, constitutes one such complete set. But we may also, in various ways, form a complete set of target functions which are purely discrete and include the target ground state. Thus, the present restriction to a purely discrete set of target states presents no difficulty in this respect. On the other hand, we have not mathematically demonstrated that η_N approaches a limit, though this seems eminently plausible. Provided the limit exists, we further need to identify it with the exact phase shift. We will merely assume this identification, while noting that there may even be difficulties in giving a logically satisfying definition of the exact phase shift (a measurement only establishes the phase-shift modulo π). We do not claim that the present proof is mathematically rigorous; there could be further complicating features such as nonexistence or nonuniqueness of solutions, bound states embedded in the continuum, etc. Hahn *et al*.[10,11] have given an excellent discussion of some of these possible complications and of the important differences between scattering from a static potential and scattering from a compound system. With these qualifications in mind, we consider the above to constitute a "proof" that the present method provides lower bounds to phase shifts. As a special case, the proof applies to a truncated expansion in discrete eigenstates, i.e., to the usual close-coupling scheme.

We wish to note that the present choice of purely discrete target functions obviates the "continuum-exchange" difficulty which arises in connection with the eigenfunction-expansion method. With the latter method, extension of the expansion to completeness would require introduction of continuum target eigenstates. This can lead to difficulties for scattering of a particle which is identical with target particles, e.g., $e^-+\mathrm{H}$ scattering. If some of the scattering functions $F_i(\vec{r})$ associated with continuum target states are not orthogonal to $u_0(\vec{r})$, there are additional contributions to η, which is no longer entirely given by the asymptotic behavior of $F_0(\vec{r})$. This problem has been discussed at some length by Levin.[20] In this respect McKinley and Macek's[12] phase-shift-bound proof was perhaps not complete. The complicating feature of "continuum-exchange" contributions does not arise (or perhaps one should say it is automatically accounted for) in the proofs by Hahn *et al*.[10,11] based on projection operators. Aside from the phase-shift-bound property, there remains the problem in practice of computing the contributions which correspond, in an eigenfunction expansion, to the continuum target states. Within the framework of the projection-operator approach, this problem was solved by Hahn *et al.*[13] by treating a portion of the wave function by varying the coefficients of expansion in a fixed set of functions, i.e., by adopting a hybrid approach. The present approach attempts to account for these contributions in a manner which involves exclusively the numerical solution of integrodifferential equations, an approach which in practice involves calculations very similar to those involved in the conventional eigenfunction-expansion method.

We have, of course, assumed that the $u_0(\vec{r})$ used in deriving the equations is the exact ground-state wave function of the target, and hence that

$$E_{0,i}=E_{i,0}=0. \qquad (25)$$

Without this assumption, the above proof does not go through, and we have not been able to demonstrate phase-shift bounds for a method which does not employ the exact target function. Hahn *et al.*[10] have noted that a very important extension would be to eliminate the requirement that the ground-state wave function be known exactly. Since the exact functions are not actually known for atoms with more than one electron, it is apparently not possible at present to guarantee phase-shift bounds for scattering from multi-electron atoms (by contrast, it may be possible in some cases to establish bounds on QHQ eigenvalues without making use of the explicit form of target functions[22]). We wish to note the following, however. Without knowing the exact target ground-state function, we might indefinitely continue a process of extending the target basis by one state, diagonalizing with respect to the target Hamiltonian, and solving resulting coupled equations. In the limit of a complete expansion, the lowest-energy target state would approach the true ground-state wave function, and presumably the calculated phase shift would approach the true value.

CALCULATIONS

As a test of the method, we have performed low-order calculations of the S-wave phase shift for positron-hydrogen scattering. This problem has by now been thoroughly treated, so that there are available not only very good approximations to the exact phase shifts,[8,14] but also the best values that can be obtained by expansions containing a specified number of angular momentum states of the target[14]. The phase shift converges only slowly as the number of angular momentum states (relative partial waves) is increased. Thus one cannot hope to obtain a really good over-all result with a low-order expansion. Of particular interest here is the extent to which one may approximate to the various relative-partial-wave limits with expansions of very low order; the eigenfunction-expansion method is poor in this regard. The inclusion of all $l=0$ target states results in a phase shift only slightly better than the static approximation (retaining only the 1s state); for this reason it is convenient to employ an expansion containing the ground state and a few higher angular momentum states of the target. It is also convenient to choose radial functions of the same analytic form as eigenfunctions, but with initially arbitrary orbital exponents which can be adjusted for best results; thus we chose p- and d-type target functions with (un-normalized) radial functions of the form $r\exp(-\delta r)$ and $r^2\exp(-\eta r)$. This choice enables us to make a simple check of the (IBM 1620) computer program by reproducing eigenfunction-expansion results after setting orbital exponents to their nominal values. In this way we reproduced to three significant figures the phase shifts obtained by Hahn *et al.*[14] for scattering at an energy of 0.16 Ry using (a) 1s, (b) 1s2p, (c) 1s3d, (d) 1s2p3d. For brevity, we refer to our expansions as 1s2p' and 1s2p'3d', the prime indicating an orbital exponent different from the hydrogenic value.

The differential equations were solved by a numerical method given by Hartree.[23] Solutions were started in the inner region by a Taylor series and in the outer region by an asymptotic expansion. The inner and outer solutions were then joined at a pair of intermediate radii, as described by Burke and Schey.[21] The matching was carried out at two or more pairs of radii in each calculation, as a consistency check. It turned out that satisfactory results could be obtained with radial increments of 0.1 in the inner region and 0.4 in the outer region. The asymptotic solution was usually started at $r=15$.

As a means of facilitating comparison of results at various energies, the phase shifts have been reduced to a normalized form in which 0 represents the static-approximation value and 1.0 represents the essentially exact value.[8,14] The normalized value is a measure of the extent to which the calculations account for the effects of correlation on the phase shift, analogous to the correlation energy in a bound-state calculation.

Figure 1 shows dependence of the calculated scattering length on the values of orbital exponents. With a 1s2p' expansion, there is a broad maximum at an orbital exponent of about 0.875. The upper curve shows dependence on the orbital exponent of 3d' for a 1s2p'3d' expansion in which the 2p' exponent has been fixed at 0.875. Here also there is a broad maximum. In view of the relative insensitivity to value of an orbital exponent, the exponent values used for other energies were somewhat arbitrarily selected.

Results at various energies are compared in Fig. 2 with results of other methods. The present two-term expansion gives considerably better results than a six-term eigenfunction expansion.[24] The two-term results are only slightly poorer than those obtained by Ruffine,[25] who used a two-term expansion in which the radial dependence of the p orbital was optimized in a self-consistent manner. Approximately optimal values of the 2p' orbital exponent in the present 1s2p' expansion can be deduced from Ruffine's[25] tabulated values of orbital energies.

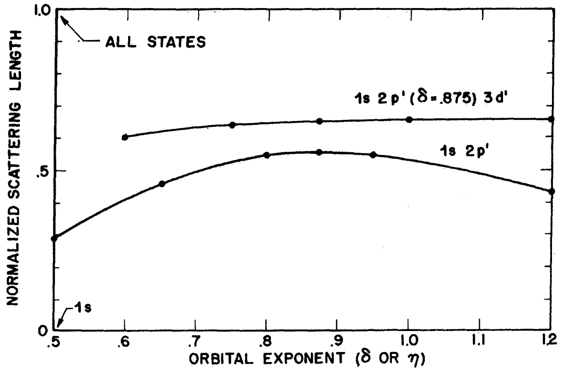

FIG. 1. Calculated values of e^+-H scattering length as a function of the values of orbital exponents of the target states used in the expansions. Normalized values of scattering length are presented on a linear scale in which 0 corresponds to static-approximation value and 1.0 corresponds to the (essentially) exact value (Refs. 8 and 14). The upper curve shows dependence on exponent of the *d* orbital, with the *p*-orbital exponent fixed at 0.875. Note that the maxima are broad; hence satisfactory results only require that the radial functions be reasonably compact.

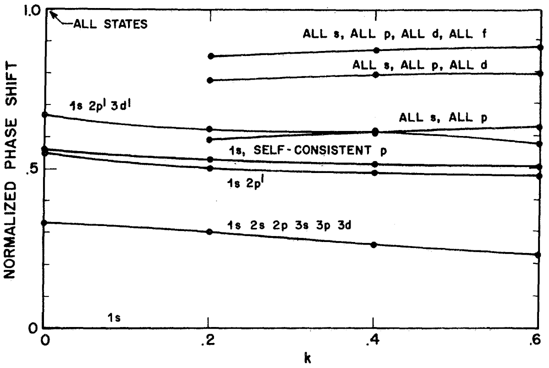

FIG. 2. Normalized values of *S*-wave phase shifts for e^+-H scattering at various values of *k* (points are connected by curves only for convenience in reading). Present results are labeled $1s2p'$ and $1s2p'3d'$. Results of Ruffine's self-consistent calculations (Ref. 25) are labeled 1*s*, self-consistent *p*. The three upper curves correspond to limiting values attainable by retaining in the expansion only the first two, three, or four relative partial waves (Ref. 14). The lowest curve gives results of a six-term eigenfunction expansion (Ref. 24).

The principal conclusion, as illustrated in Fig. 2, is that two- or three-term expansions of the present type provide phase shifts that are considerably larger (better) than those obtained from even longer expansions of the eigenfunction type. The $2p'$ function accounts for perhaps 80% of the correlation which can be introduced by including all *p* orbitals. Further inclusion of the $3d'$ function, however, only increases the normalized phase shift by perhaps half as much as it can be increased by including all *d* orbitals. The three-term expansion accounts for some 60% (depending slightly on energy) of the overall correlation effect. This may also be compared with the value of some 90% which was obtained by Hahn and Spruch[14] by use of a variational-bound (hybrid) method which employed 53 expansion terms and dealt with the six lowest relative partial waves.

Similar expansions can be used for scattering from helium, though in that case the phase-shift bound is no longer rigorous, because of the necessity of approximating to the target ground-state function. By assuming the fractional extent of convergence to be the same as for positron-hydrogen scattering, we obtain phase-shift estimates which are in reasonable agreement with various other calculations.[26–28] Until recently there had apparently not been a quasibound type calculation of positron-helium scattering. Recently Drachman[28] has calculated scattering of positrons from both hydrogen and helium by solving coupled differential equations based on use of the elliptical-coordinate adiabatic function. He accounted for some 90% of the difference between static-approximation and exact value of positron-hydrogen phase shifts, as compared to the value of about 60% obtained with the present method. The present method can of course employ larger numbers of expansion terms; the limited calculations reported here were primarily intended to test effectiveness of the method.

The present choice of closed-channel target functions was made with short-range correlation effects primarily in mind. Since the initial report of the present work,[29] our attention was called to a recent paper by Damburg and Karule[30] which suggests "a modification of the close-coupling approximation for *e*-H scattering allowing for the long-range interactions." They note that the $2p$ term of an eigenfunction expansion accounts for only 65.8% of the full dipole polarizability of the hydrogen atom $(\frac{9}{2})$,[31] and suggest replacing the $2p$ radial function by an adiabatic function of (un-normalized) form $(r+\frac{1}{2}r^2)e^{-r}$, which accounts for the full polarizability. Although they comment that their proposed modification itself accounts insufficiently for the short-range interactions, the adiabatic function is, in fact, rather compact and similar in form to the present $2p'$ function. Damburg and Karule do not seem to have carried out any calculations, but a zero-energy calculation of this form for positron-hydrogen scattering was earlier carried out by Ruffine[25]; the result accounts for almost as much of the over-all correlation effect as does either the present $1s2p'$ expansion or the Ruffine self-consistent calculation. Both the latter results have the property of accounting for most of the dipole polarizability in zero-energy calculations (about 4.4), but for smaller amounts at higher energies (about 3.6 at $k^2 = 0.36$). A comparison of the results of these various calculations does not permit assessment of relative importance of short-range and long-range effects. The relative importance of these effects will be considered from a different viewpoint in the following paragraph.

In expansions which effectively involve target states of definite angular momentum, the potentials $V_{j,i}(r)$ between states of zero angular momentum vanish exponentially for large r. The asymptotic falloff of other potentials (including diagonal potentials[31]) is slow, involving negative powers of r. As a result, some of the closed-channel scattering functions $F_i(r)$ also fall off essentially as negative powers of r (contrary to the assumption often seen in the literature that all closed-channel functions vanish exponentially[5,24]). The leading terms in the asymptotic expansion of the open-channel function $F_0(r)$ behave like those of a single-channel problem with an asymptotic potential $V(r)\approx \alpha r^{-4}$, where α is the dipole polarizability which is accounted for by the expansion. An estimate of the short-range contribution to a scattering length or phase shift can be obtained from the slope and value of the open-channel function $F_0(r)$ at some reasonably large cutoff value of $r=r_c$, under the assumption that the potentials vanish beyond r_c. At zero energy the long-range contribution is roughly proportional to α. Thus a suitably modified p-orbital radial function might improve the long-range contribution by as much as a factor of $1/0.658\approx 1.5$. At zero energy, the long-range contribution is substantial (it is comparable to the short-range contribution when estimated with $r_c=8$, using either a $1s2p$ or a $1s2p'$ expansion). The overall contribution of the $2p'$ expansion term turns out to be roughly 1.9 times as large as that from a $2p$ expansion term, however, and hence even at zero energy the improvement cannot be ascribed predominantly to long-range effects. Furthermore, the long-range contribution is quantitatively important only at very low energies. On the whole, it seems that the improvement which results from going from a $2p$ function to either the $2p'$ or the adiabatic function is largely a result of short-range effects. It is gratifying that use of spatially compact target functions improves both the short-range and long-range contributions.

We have not yet performed any calculations of electron-hydrogen scattering, but feel that an expansion of the form $1s2s'2p'$ is promising for this application. The (un-normalized) $2s'$ radial function could be taken as $[3-(\beta+1)r]e^{-\beta r}$. The first two angular momentum states of the target are known to provide some 93% of the correlation effect for ${}^1S$ (even more for ${}^3S$) scattering at $k^2=0.16$;[18] this compares very favorably with the value of 63% for positron-hydrogen scattering at the same energy.[14] It would be particularly interesting to investigate the effect of the spatial compactness of the $2s'$ and $2p'$ functions on the predicted positions of the lowest resonances.

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