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Many-Electron Pseudopotential Formalism for Atomic and Molecular Excited-State Calculations*

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The pseudopotential approach of Phillips and Kleinman is extended beyond the one-electron approximation for the purpose of obtaining correlated low-energy continuum and excited bound states of atomic and molecular systems with a minimum of computational effort. Pseudopotential equations are derived by a variational method. These and other nonvariational pseudopotential methods are shown to be quite useful in conjunction with either adiabatic or close-coupling methods. Calculations are performed on the following two-electron systems: e-H ^1S-wave elastic scattering, e-He$^+$ ^1S and ^3S elastic scattering, and ^1S and ^3S Rydberg states of He. In general, good results are obtained. The calculated Rydberg-state quantum defects usually agree with the experimental values to three decimal places, and the calculated e-H ^1S zero-energy scattering length of 5.90 ± 0.08, which is a strict upper bound to the true value, compares favorably with the value 5.965 ± 0.003 obtained by Schwartz in a very much more involved calculation. The possible extension of these methods to larger atomic systems and to molecules is discussed. A differential equation method for obtaining bound-state wave functions and energies based on asymptotic properties of Coulomb functions is outlined in the Appendix.

I. INTRODUCTION

Calculations of Rydberg and electronic continuum wave functions can be useful in describing many dynamic atomic and molecular processes such as photo-ionization, autoionization, photodetachment, elastic and inelastic electron scattering, etc. However, wave functions calculated by the Hartree-Fock method are frequently not good enough for this purpose. Accurate correlated wave functions are often needed.

The object of this paper is to develop *a priori* methods, based on the pseudopotential approach, by which one can calculate accurate correlated (bound or continuum) excited-state wave functions, but which involve only a small increase in computational effort over the Hartree-Fock method.

The "pseudopotential" approach developed by Phillips and Kleinman[1] for application to solid-state problems has recently been applied by several workers to the calculation of atomic and molecular wave functions.[2–11] The pseudopotential method, in its simplest form, arises from the one-electron approximation as a consequence of the Pauli principle that requires valence orbitals to be orthogonal to the occupied core orbitals. Szasz[11] and Weeks and Rice[9] have generalized the approach to a wide class of problems that involve orthogonality constraints. For example, equations for correlated pair functions can be simplified by replacing the "strong orthogonality" constraint with a pseudopotential.[9,11]

While many go beyond the one-electron approximation, all of the previous pseudopotential calculations cited here[2–11] are based on conditions of orthogonality to one-electron functions. In this paper we propose a straightforward extension of the basic Phillips-Kleinman approach that is based on many-electron orthogonality conditions. We show that, just as in the one-electron case, the many-electron pseudopotential formalism can provide useful physical insight into atomic and molecular excited-state calculations. This insight can guide one in utilizing information contained in accurately calculated bound functions to describe correlation and polarization effects in excited states of the same system.

Sample calculations of e-H and e-He^+ scattering states and He Rydberg states are performed by several related methods, with excellent results. These methods can be applied to much larger atomic systems and to molecules without the huge increase in complexity that occurs with some other methods, and yet can be expected to give accurate results for such systems. One of these pseudopotential methods, which is shown to satisfy a strict variational principle, shares those advantages common to variational methods: The calculated zero-energy scattering length is an upper bound to the true one, and the method can be subsequently improved in a systematic way to approach exact results.

The plan of the paper is as follows: The pseudopotential formalism is defined in Sec. II, and qualitative results of previous calculations within the one-electron scheme are considered in Sec. III. In Sec. IV the approach is extended to many-electron systems. The pseudopotential equations are derived by a variational principle in Sec. V. In the following section various alternative methods are used to obtain excited eigenstates of the atomic two-electron systems H^- and He. Section VII contains a discussion of the effects of the approximate nature of the bound functions used to construct the pseudopotential; it also includes a comparison of the present methods with the related one used by Kestner *et al.* to calculate electron-helium scattering states. We conclude by discussing the limitations of many-electron pseudopotential methods and the great potential of these methods in molecular excited-state calculations.

In this paper all positive-energy wave functions are obtained by numerical solution of radial differential equations. For bound-state calculations one is faced with an eigenvalue problem, so the differential equation method cannot be used directly. In order to obtain the Rydberg states in part D of Sec. VI, we use a very efficient method of solving the differential equation – eigenvalue problem based on the asymptotic properties of Coulomb functions as discussed by Seaton.[12] This procedure is outlined in the Appendix.

II. THE PSEUDOPOTENTIAL FORMALISM

Let

$$(T+V)\Psi=E\Psi \qquad (2.1)$$

be the equation for which we wish to find excited-state solutions. Equation (2.1) could be the complete many-electron equation for an atomic or molecular system or it could be a one-electron approximation to such a system. In either case, in this section and the following one, we will take (2.1) to be the exact problem; eigenfunctions will be considered approximate only to the extent that they do not satisfy (2.1) exactly. Assume that we know a few solutions of (2.1) exactly; i.e., we know the eigenfunctions Ψ_j, $j=1,\ldots,c$, satisfying

$$(T+V)\Psi_j=E_j\Psi_j,\quad j=1,\ldots,c\ . \qquad (2.2)$$

Hereafter in this paper we will assume that the Ψ_j are the lowest few bound solutions of (2.1), although for the present discussion they could be any eigenstates of $(T+V)$.

Following Phillips and Kleinman,[1] we can write

$$(T+V+V_R)\tilde{\Psi}=E\tilde{\Psi}\ , \qquad (2.3)$$

where $$V_R\tilde{\Psi}=\sum_{j=1}^{c}\beta_j(E-E_j)\Psi_j\ , \qquad (2.4)$$

and $$\tilde{\Psi}=\Psi+\sum_{j=1}^{c}\beta_j\Psi_j\ , \qquad (2.5)$$

where we have simply added and subtracted the term

$$\sum_{j=1}^{c}\beta_j\Psi_j$$

to Eq. (2.1), using the relation (2.2). For the present the β_j, i.e., the overlap $\langle\tilde{\Psi},\Psi_j\rangle$, may be considered completely arbitrary. Using the terminology of Weeks and Rice,[9] we call V_R, defined by (2.4), the "pseudopotential" and $(V+V_R)$ the "effective potential."[13] Equations (2.3)–(2.5) define what is meant by "pseudopotential formalism" in this paper: Instead of solving Eq. (2.1) for the wave function Ψ and eigenvalue E, one solves the modified equation (2.3) for a pseudo wave function $\tilde{\Psi}$ belonging to the same eigenvalue E. The pseudofunction $\tilde{\Psi}$, defined by (2.5), differs from Ψ in that $\tilde{\Psi}$ is not necessarily orthogonal to the states Ψ_i. The desired function Ψ is obtained simply by orthogonalizing $\tilde{\Psi}$ to all the Ψ_j.

ONE-ELECTRON PSEUDOPOTENTIALS

Several workers have recently applied the pseudopotential method within the one-electron approximation[6–8,10] where the function Ψ is the wave function of a valence electron (possibly excited) and the Ψ_j are occupied core orbitals of the same spin and symmetry as Ψ. The usual procedure employed is as follows:

1. The effective potential $(V+V_R)$ is approximated by a "model potential" V_m. Since the pseudopotential V_R is not unique due to the arbitrariness of the β_j, the choice of model potential involves, either explicitly or implicitly, a unique choice for the β_j.
2. The equation

$$(T+V_m)\tilde{\Psi}_m=E_m\tilde{\Psi}_m \qquad (3.1)$$

is solved, and the approximation to Ψ is obtained by orthogonalizing $\tilde{\Psi}_m$ to the core states Ψ_j.

It is usually not necessary to calculate V_R explicitly, so the pseudopotential method is more complicated than a direct solution chiefly in that it requires orthogonalization to core states. The use of the pseudopotential method in calculations can be justified if, when the effective potential is approximated by a relatively simple model potential, the resulting approximation to Ψ is better than that which would be obtained by solving (2.1) directly with a somewhat more complicated approximation to the real potential V. Szasz and McGinn have shown that the effective potential $V+V_R$ can be quite oscillatory,[4] and so it would seem unlikely that $V+V_R$ would be well represented by a simple model. Nevertheless, the results of the calculations cited[6–8,10] show that for several atomic and molecular systems the one-electron pseudopotential approach is very useful. We feel that the fundamental reasons why this method works so well are not completely understood. But we can note certain features which are common to all of these successful pseudopotential calculations. The coefficients β_j are chosen, either by the methods of Cohen and Heine[14] or otherwise, to remove the oscillations of Ψ inside the core, thereby generating a smooth pseudo wave function $\tilde{\Psi}$. The resulting decrease in kinetic energy of $\tilde{\Psi}$ must be accompanied by an increase of potential energy if $\tilde{\Psi}$ is to belong to the same eigenvalue E as Ψ. Therefore V_R is a strongly repulsive potential.[14,9] The "pseudo-electron" can be expected to spend only a relatively small fraction of its time in the region of space where V_R is most repulsive. Therefore, a model potential which deviates considerably from the true effective potential in this region but is reasonably accurate elsewhere produces an accurate approximation to $\tilde{\Psi}$ because the pseudo-electron ventures relatively infrequently into the region where the model is poorest. This effect is clear in the calculations of Abarenkov and Antonova[8] who show plots of approximate pseudo wave functions for a valence electron in the field of the Na^+ ion and a free electron in the field of Cl^-. It is even more striking in the results of Schneider *et al.*[10] on electron-helium and electron-oxygen atom scattering states. In all of these cases the pseudofunctions are quite smooth, but more importantly, for small r values the amplitudes of the pseudofunctions are very much smaller than the amplitudes of the corresponding real wave functions in this region.

IV. MANY-ELECTRON PSEUDOPOTENTIALS

Two of the most common general methods of treating low-energy electron-atom and electron-ion scattering are the adiabatic approximation and the close-coupling methods.[15] We will begin this section with a short review of some aspects of these methods.

The basic assumption of the adiabatic method as applied to electron-atom scattering is that the free electron moves much more slowly than the core electrons. A particularly good discussion of the adiabatic hypothesis is given by Sloan.[16] Summarizing the situation very briefly, while accurate for large r, the adiabatic approximation grossly overestimates the effective potential in the region of small r. However, the inaccuracy to which the adiabatic potential is usually calculated and the insertion of somewhat arbitrary cutoffs combine to cancel much of the error and frequently fortuitously good results are obtained by this method.

The close-coupling approximation is very powerful in describing certain resonance and inelastic processes, but the expansion is very slowly convergent. Burke and Schey,[17] from their close-coupling treatment of electron-hydrogen atom scattering, attribute this slow convergence mainly to the inadequacy of the method to include the short-range correlation effects. Most of the long-range α/r^4 polarization is provided by the inclusion of the lowest few p eigenstates of hydrogen.[18]

Both the close-coupling method and the adiabatic method are similar in that they describe long-range effects relatively well, but they are less accurate at small values of r. Recalling the discussion of the previous section, we might expect the pseudopotential formalism to be useful in conjunction with both of these methods if pseudo wave functions can be found which have small amplitudes in the region of small r. There is the further hope that the adiabatic assumption will be much more realistic when applied within the pseudopotential framework, because the pseudoelectron can be expected to move slowly everywhere due to the cancellation of kinetic and potential energy. But both the close-coupling and the adiabatic methods go beyond the one-electron approximation in an attempt to include correlation/polarization effects. It is therefore appropriate to abandon the one-electron approximation at this stage and use complete many-electron operators and wave functions in the pseudopotential equations (2.3)–(2.5).

We now assume that the Ψ_j in (2.5) are accurate correlated bound states of the complete N-electron system (not just the core), having the same overall symmetry and spin as the excited function we wish to calculate. The Ψ_j are assumed known. Since in practice they will probably be variationally obtained wave functions and will therefore be somewhat approximate, we will replace Eq. (2.4) with

$$V_R\tilde{\Psi}=\sum_{j=1}^{C}\beta_j(E-H)\Psi_j \quad . \tag{4.1}$$

But it is assumed that the Ψ_j reflect the true eigenstates to at least the accuracy which we hope to achieve in the excited-state solutions.

We may now proceed in a manner analogous to the procedure used in one-electron pseudopotential calculations. We pick a model potential (adiabatic or, implicitly, with the close-coupling approximation) to approximate the effective potential $V+V_R$. We must also remove the arbitrariness of the β_j. Methods for doing this will be discussed below. We then solve Eq. (2.3) to obtain the pseudo wave function $\tilde{\Psi}$, and, finally, obtain Ψ by orthogonalizing $\tilde{\Psi}$ to the lower bound states Ψ_j. For scattering problems for which we need only the asymptotic form of Ψ the final orthogonalization step is not necessary since $\tilde{\Psi}$ differs from Ψ only in regions where the Ψ_j are nonzero; i.e., the phase shift of $\tilde{\Psi}$ is the same modulo π as that for Ψ.

To illustrate the procedure more clearly, let us consider the two-electron problem of e-He$^+$ ion, S-wave elastic scattering. Let h be the Hamiltonian and ϕ_i be the ith wave function of the isolated He$^+$ core:

$$h_1\phi_i(1)=\epsilon_i\phi_i(1) \quad . \tag{4.2}$$

The equation we wish to solve is

$$(H-E)[\varphi(1,2)\pm\varphi(2,1)]$$
$$\equiv(h_1+h_2+1/r_{12}-E)[\varphi(1,2)\pm\varphi(2,1)]=0 \quad , \tag{4.3}$$

where + refers to singlet, and − to triplet. In this illustration we will use only one state, the lowest ^1S or ^3S state of the helium atom, to form the pseudopotential. Transforming to the pseudopotential scheme, using (2.3) and (4.1), we have

$$(h_1+h_2+1/r_{12}-E)[\tilde{\varphi}(1,2)\pm\tilde{\varphi}(2,1)]$$
$$+\beta(E-H)\Psi_0^{\pm}(1,2)=0 \quad , \tag{4.4}$$

where $\Psi_0^{\pm}(1,2)$ is an accurate approximation to the lowest singlet (+) or triplet (−) state of He.[19] We may expand the pseudofunction $\tilde{\varphi}(1,2)$ in terms of He$^+$ eigenstates:

$$\tilde{\varphi}(1,2)=\sum_i \alpha\phi_i(1)\tilde{\chi}(2) \, , \tag{4.5}$$

where α is the antisymmetrization operator. If we are considering only those energies E which are lower than the threshold for inelastic collisions, then only the elastic channel is open and the scattering process can be completely determined from the asymptotic part of $\tilde{\chi}_0$.[20] Using the Feshbach projection technique[21] [we multiply (4.4) from the left by $\phi_0(1)$ and integrate over $d\vec{r}_1$] we obtain the following equation for $\tilde{\chi}\equiv\tilde{\chi}_0$:

$$\left(h_2-\frac{k^2}{2}+\int\phi_0{}^*(1)\frac{1}{r_{12}}\phi_0(1)d\vec{r}_1\right)\tilde{\chi}(2)$$
$$\pm\left[\int\phi_0{}^*(1)\left(\epsilon_0-\frac{k^2}{2}+\frac{1}{r_{12}}\right)\tilde{\chi}(1)d\vec{r}_1\right]\phi_0(2)$$
$$+\beta(E-E_0{}^{\pm})\xi^{\pm}(2)$$
$$+\sum_{i\neq0}\left[\tilde{\chi}_i(2)\int\phi_0{}^*(1)\frac{1}{r_{12}}\phi_i(1)d\vec{r}_1\right.$$
$$\left.\pm\phi_i(2)\int\phi_0{}^*(1)\left(\epsilon_i-\frac{k^2}{2}+\frac{1}{r_{12}}\right)\tilde{\chi}_i(1)d\vec{r}_1\right]=0 \, , \tag{4.6}$$

where $k^2/2\equiv E-\epsilon_0$, (4.7)

$$\text{and}\quad \xi^{\pm}(2)\equiv\frac{\int\phi_0{}^*(1)(E-H)\Psi_0{}^{\pm}(1,2)d\vec{r}_1}{E-E_0{}^{\pm}}$$
$$\simeq\int\phi_0{}^*(1)\Psi_0{}^{\pm}(1,2)d\vec{r}_1 \quad . \tag{4.8}$$

$E_0{}^{\pm}$ is the expectation value $\langle\Psi_0{}^{\pm}H\Psi_0{}^{\pm}\rangle$.

We could remove the pseudopotential term in Eq. (4.6) by setting $\beta=0$. If we were to do this, (4.6) would become the usual Feshbach equation for the open channel. The potential in such an equation is often referred to as the "optical potential" or "effective potential" of the open channel, and in nuclear physics it is sometimes even called a "pseudopotential." Hereafter in this paper we will refer to this type of potential as the optical potential. The terms pseudopotential and effective potential will be used only as they were defined in Sec. II. Thus in this case

$$V_{\mathrm{opt}}\tilde{\chi}(2) = -(2/r)\tilde{\chi}(2)$$

$$+\sum_{i=0}^{\infty}\left[\tilde{\chi}_i(2)\int\phi_0{}^*(1)\frac{1}{r_{12}}\phi_i(1)d\vec{\mathrm{r}}_1\right.$$

$$\left.\pm\phi_i(2)\int\phi_0{}^*(1)\left(\epsilon_i-\frac{k^2}{2}+\frac{1}{r_{12}}\right)\tilde{\chi}_i(1)d\vec{\mathrm{r}}_1\right], \quad (4.9)$$

$$V_R\tilde{\chi}(2) = \beta(E-E_0{}^{\pm})\xi^{\pm}(2) \ , \quad (4.10)$$

and $V_{\mathrm{eff}} = V_{\mathrm{opt}} + V_R$. (4.11)

Equation (4.6) is exact for any value of β (even if $\Psi_0{}^{\pm}$ is approximate). Let us now use the one-state approximation to find an approximate solution to (4.6). The one-state approximation is obtained by assuming that all of the $\tilde{\chi}_i$, $i \neq 0$, are zero so that the last term of (4.6) vanishes, giving

$$\left(h_2-\frac{k^2}{2}+\int\phi_0{}^*(1)\frac{1}{r_{12}}\phi_0(1)d\vec{\mathrm{r}}_1\right)\tilde{\chi}(2)$$

$$\pm\left[\int\phi_0{}^*(1)\left(\epsilon_0-\frac{k^2}{2}+\frac{1}{r_{12}}\right)\tilde{\chi}(1)d\vec{\mathrm{r}}_1\right]\phi_0(2)$$

$$+\beta(E-E_0{}^{\pm})\xi^{\pm}(2) = 0 \ . \quad (4.12)$$

If we set $\beta = 0$, we have the ordinary one-state approximation. This is considered to be the exact starting equation to which one-electron pseudopotential methods are applied to find approximate solutions. But our earlier discussions suggest that zero is not the optimal choice for β. We would prefer to choose a value for β which would result in the pseudofunction $\tilde{\chi}$ being very small for small values of r. One way we might do this is to use methods similar to those suggested by Cohen and Heine[14] for the one-electron case. This has not been done in this paper. Instead, we have used two different methods of removing the arbitrariness of β. The first, which for convenience will be referred to as the "smallest pseudofunction" (s-p) criteria, is to find that solution of (4.6) for which $\tilde{\chi}(r)/r^l$ is identically zero at $r = 0$. As we shall show in Sec. VI, with a noniterative method similar to that proposed by Marriott and Percival,[22] and also by Omidvar,[23] this solution can be obtained from a linear combination of the solutions of two uncoupled differential equations. Since the solution to the ordinary one-state equation with $\beta = 0$ is also most conveniently found in this way, once $\xi^{\pm}$ has been calculated, the amount of effort required to solve the s-p equations is almost identical to that required to solve the one-state equations. In a series of calculations at different energies, $\xi^{\pm}$, or more precisely

$$\langle\phi_0(1)\Psi_0{}^{\pm}(1,2)\rangle \text{ and } \langle\phi_0(1)H\Psi_0{}^{\pm}(1,2)\rangle \ ,$$

need be calculated only once.

The second method of choosing β can be obtained from the following considerations. The one-state approximation in the pseudopotential scheme is equivalent to approximating the real wave function by

$$\Psi_{\mathrm{approx}} = \phi_0(1)\tilde{\chi}(2) \pm \phi_0(2)\tilde{\chi}(1)$$

$$+\beta\Psi_0{}^{\pm}(1,2) \ , \quad (4.13)$$

where $\tilde{\chi}$ is a solution of (4.12). We then have

$$\langle\Psi_{\mathrm{approx}}, \Psi_0\rangle$$

$$= 2\langle\phi_0(1)\tilde{\chi}(2)\Psi_0{}^{\pm}(1,2)\rangle + \beta$$

$$\approx 2\langle\tilde{\chi}(2)\xi^{\pm}(2)\rangle + \beta \ . \quad (4.14)$$

Therefore the choice of β which will result in Ψ_{approx} being (very nearly) orthogonal to $\Psi_0{}^{\pm}$ is

$$\beta = -2\langle\tilde{\chi}(2)\xi^{\pm}(2)\rangle \ . \quad (4.15)$$

The choice of this expression for β, which will be referred to as the "pseudopotential-variational" (p-v) method, will be derived from a variational principle in Sec. V. This choice of β results in a new nonlocal term in (4.12) in addition to the nonlocal exchange term. The solution of (4.12) in the p-v method involves the solution of three uncoupled differential equations, compared to two such equations in the one-state and s-p approximations.

Referring back to the exact equation (4.6) for e-He$^+$ elastic scattering, it is apparent that both the s-p and p-v methods can be easily extended to many-state close-coupling approximations. This will be done for the p-v case in Sec. V.

The adiabatic approximation consists of approximating the final summation in Eq. (4.6) by a polarization potential which for large r approaches α/r^4. In this case the p-v criterion for choosing β is no longer appropriate because we no longer have an explicit expression for the approximate total wave function analogous to (4.13). But the s-p criterion, which results in the smallest $\tilde{\chi}$ for very small r, is very appropriate. This method of choosing β does not arise from a variational principle, but by introducing an *ad hoc* polarization potential into (4.6) we have lost the variational principle anyway. We will call the method of choosing β by the s-p criterion while introducing a polarization ansatz into (4.6) the "pseudopotential-polarization" (p-p) method.

V. VARIATIONAL PRINCIPLE

The close-coupling approximation to the pseudo wave function $\tilde{\Psi}$ can be written

$$\tilde{\Psi}_{cc}(1,\ldots,N)=\sum_{i=1}^{S}\mathcal{A}\phi_i(1,\ldots,N-1)\tilde{\chi}_i(N)\ . \tag{5.1}$$

Rearranging Eq. (2.5) we then have for the approximation Ψ_t to the real wave function Ψ

$$\Psi_t(1,\ldots,N)=\sum_{i=1}^{S}\mathcal{A}\phi_i(1,\ldots,N-1)\tilde{\chi}_i(N)-\sum_{j=1}^{c}\beta_j\Psi_j(1,\ldots,N)\ . \tag{5.2}$$

It is instructive to use a wave function of this form as a trial function, to form the integral

$$I_t=\int\Psi_t^*(E-H)\Psi_t d\tau\ , \tag{5.3}$$

and to determine the β_j and the $\tilde{\chi}_i$ from the condition that I_t be stationary to arbitrary variations of Ψ_t.[24] To do this for the general many-electron case is straightforward but quite involved. Instead we will consider the special case discussed in the previous section, e-He$^+$ scattering with only one state appearing in the second summation in Eq. (5.2).

We choose a trial function of the form

$$\Psi_t(1,2)=\sum_{i=0}^{S-1}[\phi_i(1)\tilde{\chi}_i(2)\pm\phi_i(2)\tilde{\chi}_i(1)]+\beta\Psi_0^{\pm}(1,2)\ , \tag{5.4}$$

where β and the $\tilde{\chi}_i$ are undetermined. Substituting into (5.3), we have

$$I_t=2\sum_{i=0}^{S-1}\int\tilde{\chi}_i^*(2)\left[(E-\epsilon_i-h_2)\tilde{\chi}_i(2)-\sum_{j=0}^{S-1}\tilde{\chi}_j(2)\int\phi_i^*(1)\frac{1}{r_{12}}\phi_j(1)d\vec{r}_1\right.$$

$$\left.\pm\sum_{j=0}^{S-1}\phi_j(2)\int\phi_i^*(1)\left(E-\epsilon_i-h_2-\frac{1}{r_{12}}\right)\tilde{\chi}_j(1)d\vec{r}_1+2\beta\int\phi_i^*(1)(E-H)\Psi_0^{\pm}(1,2)d\vec{r}_1\right]d\vec{r}_2+\beta^2(E-E_0^{\pm})\ , \tag{5.5}$$

where we have used Eqs. (4.2), (4.3), and the relation $\Psi_0^{\pm}(1,2)=\pm\Psi_0^{\pm}(2,1)$. Setting $\partial I_t/\partial\beta=0$, as in the Kohn procedure, we obtain

$$4\sum_{i=0}^{S-1}\int\tilde{\chi}_i^*(2)\left[\int\phi_i^*(1)(E-H)\Psi_0^{\pm}(1,2)d\vec{r}_1\right]d\vec{r}_2+2\beta(E-E_0^{\pm})=0\ , \tag{5.6}$$

so the "best" choice of β is

$$\beta=-2\sum_{i=0}^{S-1}\langle\tilde{\chi}_i\xi_i^{\pm}\rangle \tag{5.7}$$

where $\xi_i^{\pm}(2)\equiv\int\phi_i^*(1)(E-H)\Psi_0^{\pm}(1,2)d\vec{r}_1/(E-E_0^{\pm})$. (5.8)

Substituting this choice of β back into (5.5), we have

$$I_t=2\sum_{i=0}^{S-1}\int\tilde{\chi}_i^*(2)\left\{(E-\epsilon_i-h_2)\tilde{\chi}_i(2)-\sum_{j=0}^{S-1}\tilde{\chi}_j(2)\int\phi_i^*(1)\frac{1}{r_{12}}\phi_j(1)d\vec{r}_1\right.$$

$$\left.\pm\sum_{j=0}^{S-1}\phi_j(2)\int\phi_i^*(1)\left(E-\epsilon_i-h_2-\frac{1}{r_{12}}\right)\tilde{\chi}_j(1)d\vec{r}_1+\beta(E-E_0^{\pm})\xi_i^{\pm}\right\}d\vec{r}_2\ . \tag{5.9}$$

This results in a set of S coupled Euler-Lagrange equations for the $\tilde{\chi}_i$:

$$(E-\epsilon_i-h_2)\tilde{\chi}_i(2)-\sum_{j=0}^{S-1}\tilde{\chi}_j(2)\int\phi_i^*(1)\frac{1}{r_{12}}\phi_j(1)d\vec{r}_1$$

$$\pm \sum_{j=0}^{S-1} \phi_j(2) \int \phi_i^*(1)\left(E - \epsilon_i - h_2 - \frac{1}{r_{12}}\right)\tilde{\chi}_j(1)d\vec{r}_1 + \beta(E - E_0^{\pm})\xi_i^{\pm} = 0 \quad . \tag{5.10}$$

Equations (5.7) and (5.10) define the p-v method in the close-coupling scheme. In the special case of the one-state approximation ($S = 1$), we obtain the same results as Eqs. (4.12) and (4.15) of the previous section.

In this section we never needed to mention the word "pseudopotential." We merely applied a Kohn variational approach to a trial function of the form (5.2) to obtain Eqs. (5.7) and (5.10). The pseudopotential formalism was important in our developing the insight which led to the choice (5.2) for the trial function. But there are other arguments which suggest that a trial function of this form might be very useful. In particular, the valence electron can be said to possess an instantaneous kinetic energy (K. E.) given by $T = E - V_{\text{opt}}$, where V_{opt} is the optical potential discussed in the previous section. V_{opt} becomes quite attractive at small r values, so that the instantaneous K. E. of the electron is approximately $-V_{\text{opt}}$ in this region. This is true for any low-energy eigenstates, and it leads to the conclusion that at small r values electrons behave quite similarly regardless of which low-energy eigenstate they happen to be in. This suggests that including in a trial function accurate eigenstates belonging to different energies might be useful in obtaining a good description of short-range correlation effects. We can further conclude that the closer the energies of these eigenstates are to the energy of the state that is being calculated, the better we can expect the description of the correlation to be.[25]

It is necessary to work within the pseudopotential formalism when the approximations used are not obtainable from a variational principle, as for example, when an adiabatic approximation is used. When the close-coupling approximation is used, the conceptual shift to the pseudopotential formalism is not necessary. Nevertheless, because of the simple physical pictures it suggests, even in this case the pseudopotential scheme can be quite useful in the role of a guide. We feel that this will be especially true when these methods are applied to molecular systems. This will be discussed more fully in Sec. VIII.

VI. CALCULATIONS OF EXCITED STATES OF H$^-$ AND He

A. Numerical Procedure

All of the results reported in this paper were for $l = 0$ states and were obtained by numerical solution of the radial equation

$$\begin{aligned}&[-\tfrac{1}{2}d^2/dr^2 - Z/r - \epsilon \\ &\quad + \int_0^\infty \phi_0(r')(1/r_>)\phi_0(r')r'^2 dr']\tilde{u}(r) \\ &\quad \pm r\phi_0(r)\int_0^\infty \phi_0(r')(\epsilon_0 - \epsilon + 1/r_>)\tilde{u}(r')r'dr' \\ &\quad + V_{\text{pol}}\tilde{u}(r) + \beta(E - E_0^{\pm})r\xi^{\pm}(r) = 0 \quad ,\end{aligned} \tag{6.1}$$

where $\epsilon = E - \epsilon_0$ and we use the fact that ϕ_0 and $\tilde{u}$ have $l = m = 0$ for the cases we treat. The approximation to $\tilde{\chi}(r)$ of Eq. (4.6) is given by $\tilde{u}(r)/r$. The results differ in the particular $\Psi_0^{\pm}(1, 2)$ used to construct the pseudopotential, the method of choosing β and the polarization potential V_{pol}.

Setting $\beta = 0$ in Eq. (6.1), we have the usual one-state approximation with or without the inclusion of a polarization ansatz, depending on whether or not V_{pol} is included. The solution in this case is obtained from

$$\tilde{u}_{1-S}(r) = x(r) + C_1 y(r) \quad , \tag{6.2}$$

where x is any nontrivial solution of the equation

$$(G - \epsilon)x(r) = 0 \quad , \tag{6.3}$$

and y is the solution of

$$(G - \epsilon)y(r) \pm r\phi_0(r) = 0 \quad , \tag{6.4}$$

which satisfies the boundary condition $(dy/dr)_{r=0} = 0$. The operator G is defined by

$$\begin{aligned}Gu(r) \equiv &[-\tfrac{1}{2}d^2/dr^2 - z/r \\ &+ \int_0^\infty \phi(r')(1/r_>)\phi(r')r'^2 dr']u(r) \\ &\pm r\phi_0(r)\int_0^r \phi_0(r')\left(\frac{1}{r} - \frac{1}{r'}\right)r'u(r')dr' \\ &+ V_{\text{pol}}u(r) \quad .\end{aligned} \tag{6.5}$$

Let us define an operator M such that

$$Mu \equiv \int_0^\infty \phi_0(r')(\epsilon_0 - \epsilon + 1/r')r'u(r')dr' \quad . \tag{6.6}$$

Then C_1 is given by[22]

$$C_1 = Mx/(1 - My) \quad . \tag{6.7}$$

The p-p (s-p) solution is

$$\tilde{u}_{\text{p-p}}(r) = C_2 y(r) + w(r) \quad , \tag{6.8}$$

where y is obtained from (6.4), and w is the solution of

$$(G - \epsilon)w(r) - 2r(E - E_0^{\pm})\xi^{\pm}(r) = 0 \quad , \tag{6.9}$$

satisfying the boundary condition $(dw/dr)_{r=0} = 0$. C_2 is given by

$$C_2 = Mw/(1 - My) \quad . \tag{6.10}$$

The p-v solution is

$$\tilde{u}_{\text{p-v}}(r) = x(r) + C_3 y(r) + \beta w(r)/2 \quad , \tag{6.11}$$

where

$$\beta = \frac{-2\{\langle x\xi^{\pm}\rangle + \langle y\xi^{\pm}\rangle Mx/(1-My)\}}{\{1+\langle w\xi^{\pm}\rangle + \langle y\xi^{\pm}\rangle Mw/(1-My)\}} \ , \qquad (6.12)$$

and $C_3 = M(x+\beta w/2)/(1-My)$. (6.13)

The differential equations (6.3), (6.4), and (6.9) were solved numerically by Milne's predictor-corrector method[26] with an interval between radial points of 0.05 to 0.025 a.u. For the He ^1S calculations, the equations were integrated to a distance $r_{\max} = 16$ a.u. For the H^- and He ^3S calculations $r_{\max} = 24$ a.u. Integrals were obtained by Simpson's rule. Phase shifts were obtained in this way with a probable numerical error of less than about ± 0.003 rad for e-H and about ± 0.0005 rad for e-He$^+$. Bound-state quantum defects were obtained to within ± 0.001. All calculations were carried out on the IBM 7094 computer of the University of Chicago Computation Center. A typical continuum-function calculation by the one-state, s-p or p-p methods required about 0.25 min, and by the p-v method, about 0.35 min. A typical Rydberg-state calculation required about 0.45 min per iteration.

TABLE I. Comparison of phase shifts (radians) for singlet S-wave electron-hydrogen atom scattering calculated by different methods. (Zero-energy scattering lengths are given in parentheses.)

k (a_0^{-1})	One state (Ref. 15, Chap. XVII)	Two state[31] (1S-2S)	Three state[17] (1S-2S-2P)	Present calculation s-p	Present calculation p-v	Temkin[30]	Schwartz[29]
0	(8.09)	(8.05)	(6.74)	(5.43) ± 0.08	(5.90) ± 0.08	(5.6)	(5.965) ± 0.003
0.1	2.396	2.404	2.491	2.604	2.552	2.59	2.553
0.2	1.871	1.878	1.974	2.107	2.042	2.11	2.067
0.4	1.239	1.257	• • •	1.461	1.371	1.45	1.415
0.6	0.869	0.89	0.93	1.057	0.953	• • •	1.041
0.8	0.651	0.70	0.77	0.802	0.698	0.87	0.886
0.85	0.615	• • •	>3.00	0.762	0.658	• • •	• • •

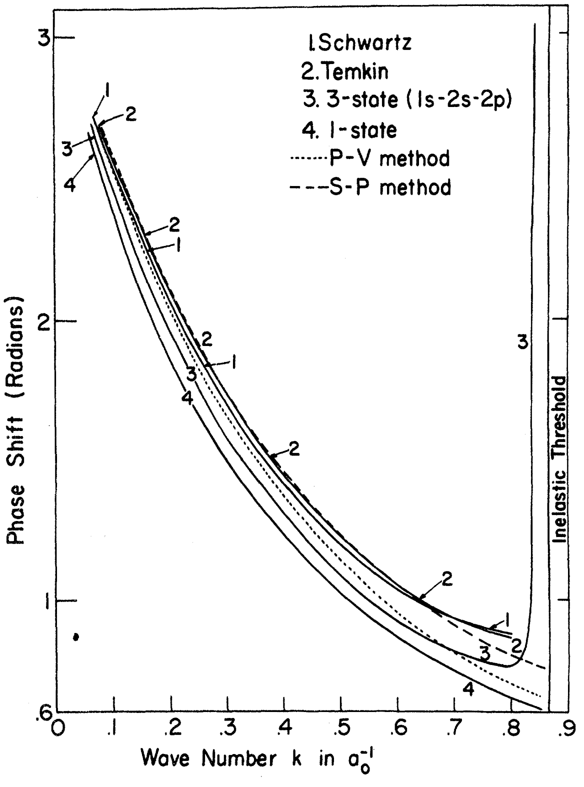

FIG. 1. Electron-hydrogen singlet S-wave phase shifts.

B. Singlet S-Wave Elastic e-H Scattering

A six-term multiconfiguration self-consistent-field (SCF) H$^-$ ground-state function,[27] with an energy expectation value $E_0 = 0.527\,00$ a. u. (Pekeris's value: − 0.527 75),[28] was used to form the pseudopotential. Table I and Fig. 1 show the resulting phase shifts by the one-state, s-p and p-v approximations with no polarization potential added. These are compared with calculations performed by other workers. The elaborate variational calculation by Schwartz using 50 Hylleraas-type functions,[29] and the results of Temkin's "nonadiabatic approach"[30] are the most accurate available calculations of this system at very low energies. The two-state (1S-2S) and three-state (1S-2S-2P) close-coupling calculations of Smith, McEachran, and Fraser,[31] and Burke and Schey,[18] respectively, are also included.

Results of the p-v method agree extremely well with Schwartz's calculations at very low k. The p-v zero-energy scattering length of 5.90 ± 0.08, which is a true upper bound to the exact value since it satisfies a Kohn variational principle,[32] compares quite favorably with Schwartz's value of 5.965 ± 0.003.[29] At higher k values ($\gtrsim 0.6a_0^{-1}$) the p-v results begin to deviate considerably from Schwartz's results. Table II, in which Schwartz's results are assumed to be exact, illustrates this

TABLE II. Percent of correlation in electron-hydrogen ^1S scattering calculations by various methods.

k (a_0^{-1})	One state (Ref. 15, Chap. XVII)	Two state[31]	Three state[17]	Present calculation p-v	Schwartz[29]
0.1	0	5	61	99	100
0.2	0	4	53	87	100
0.4	0	10	• • •	75	100
0.6	0	12	35	49	100
0.8	0	20	51	20	100

effect dramatically. Recalling the discussion at the end of Sec. V, this trend is not surprising. The H^- bound state which was used to construct the pseudopotential is bound by only − 0.027 a.u. and so it is very close in energy to the $k=0$ continuum function. We therefore expect the two-electron pseudopotential methods to work very well for this system. For higher k, the energy difference between bound and continuum functions begins to become significant, and as expected the pseudopotential does not describe the correlation effects as well. From Fig. 2 we can reach the same conclusions using the pseudopotential arguments of Sec. III. Figure 2 shows plots of $\tilde{u}(r) = r\tilde{\chi}(r)$ calculated by the one-state, s-p and p-v approximations. The $k=0.1$ pseudofunctions remain quite small compared with the one-state function out to a distance of 4 or 5 a.u. At this distance polarization is no longer very important, so we expect most of it to be accounted for by the pseudopotential. The $k=0.8$ pseudofunctions begin to become large at much smaller r, and will therefore less adequately take into account the long-range polarization. In most variational calculations of scattering states the very low energy ($k \lesssim 0.2a_0^{-1}$) states are more difficult to obtain accurately than those for somewhat higher k. This suggests the possibility of combining the pseudopotential approach with other basis functions in an attempt to obtain accurate results over a wider energy range.

It is interesting to note the behavior of the phase shift for k between $0.8a_0^{-1}$ and the inelastic threshold at $k=0.866a_0^{-1}$. The two- and three-state calculations show the presence of a resonance due to a long-lived 1S-2S H^- species. Resonances in this region have been experimentally verified.[33] Since the correlation in the H^- ground state used to form the pseudopotential introduces some 1S-2S character, we might have hoped that the pseudopotential calculations would also predict a resonance in this region. This is not the case. No trace of a resonance appears in the pseudopotential calculations.

Looking at the results of the s-p method, the zero-energy scattering length of 5.43 ± 0.08, while not a bound to the true value, is quite good when compared with the one-state value of 8.09. It is, in fact, remarkably good when it is remembered that the s-p method requires almost the identical amount of computational effort as the one-state approximation.[34,35] Phase shifts calculated by the s-p method are consistently larger than those calculated by the p-v method. Thus at higher k the s-p results are closer to the results of Schwartz than are the p-v results.

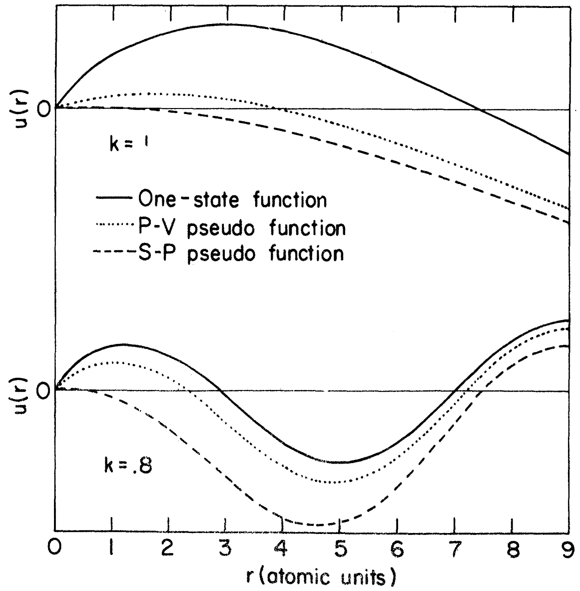

FIG. 2. Electron-hydrogen singlet S-wave wave functions $u(r) = r\chi(r)$. All functions have the same asymptotic normalization.

The simplest polarization ansatz is the Buckingham potential

$$V_{\text{pol}} = -\alpha/(r^2+d^2)^2 \quad , \qquad (6.14)$$

where the polarizability $\alpha = 9/2z^4$ for H-like systems, and d is a cut-off parameter which has the purpose of keeping the potential from becoming too large for small r values. The wave functions calculated using this potential are quite sensitive to the value of this parameter d, and there are no simple adequate criteria for choosing d.[16] From the pseudopotential discussion of Sec. III, we would expect that the pseudopotential formalism would reduce the sensitivity to the parameter d. In fact, if the pseudofunction can be kept small out to an r value for which the potential is accurately represented by its asymptotic value α/r^4, then the value chosen for d should hardly matter at all, so long as it is sufficiently small. Table III shows results of calculations in the one-state-plus-polarization and the p-p approximations with V_{pol} given by (6.14) using several values of d. The pseudopotential formalism does its job very well. When d is varied from 2.5 to 1.0 a.u., the $k=0.2$ phase shifts change by 0.706 rad when no pseudopotential is used, but by only 0.015 rad when the pseudopotential is included. The p-p results also agree quite well with Schwartz's results, but in this case the s-p results (no polarization added) are equally good except at high energies, and so e-H scattering does not serve as a good test of the p-p method.

TABLE III. Variation of electron-hydrogen atom singlet S-wave phase shifts for $k=0.2$ a.u. As a function of the parameter d in the polarization potential $-\alpha/(r^2+d^2)^2$ with $\alpha=\frac{9}{2}$.

d (a.u.)	∞ (no polarization)	2.5	2.0	1.5	1.0	Schwartz[29]
Without pseudopotential	1.869	1.966	2.028	2.162	2.672	2.067
With pseudopotential	2.107	2.113	2.110	2.106	2.098	

C. Singlet S-Wave Elastic e-He$^+$ Scattering

In this case the pseudopotential was constructed from a 10-term multiconfiguration SCF function[27] ($E_0=-2.902\,89$ a.u., Pekeris's $E_0=-2.903\,72$).[28] Table IV shows phase shifts calculated by the one-state, p-v and p-p methods. These are compared with phase shifts extrapolated from experimental quantum defects.[36] The latter are assumed to be essentially exact at very low energies.

The p-v method is not nearly as successful at very low energies in this case as it was in the e-H calculations, accounting for only ~50% of the correlation/polarization. But at higher energies the e-He$^+$ results do not appear to get significantly worse as they did in the e-H case. This behavior could have been anticipated since the energy of the bound He function used to construct the pseudopotential is considerably different from that of the continuum functions. Figure 3 shows plots of $\tilde{u}(r)$ calculated by the one-state, s-p and p-v methods. The pseudo wave functions become large at a much smaller value of r than the corresponding functions in the e-H case. Nevertheless, the s-p function is sufficiently small at very small r so that we can expect the p-p method to work well. Table V shows that the p-p functions are much less sensitive to the value of the cut-off parameter d than the one-state-plus-polarization wave functions, just as in the case of e-H. Table IV shows that the p-p phase shifts agree very well with those extrapolated from quantum defects.[36,37] We emphasize that the p-p method, with such a simple polarization ansatz, involves roughly the same computational effort as the one-state approximation. We conclude from these results that the p-p method might be very powerful, especially when applied to large systems for which close-coupling and accurate adiabatic methods become very tedious. Much less accurate polarization potentials are probably sufficient when used within the pseudopotential formalism.

TABLE IV. Phase shifts for singlet S-wave e-He$^+$ scattering.

	Present calculation			
k (a_0^{-1})	One state	p-v	p-p	QD[36]
0.1	0.384	0.409	0.437	0.436
0.2	0.381	0.407	0.434	0.433
0.3	0.376	0.402	0.430	0.427
0.4	0.370	0.395	0.423	0.420

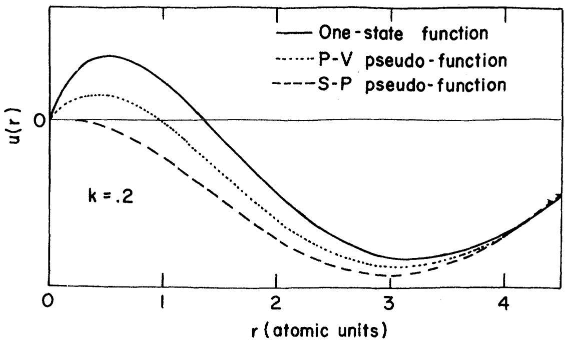

FIG. 3. Electron-He$^+$ ion singlet S-wave functions $u(r)=r\chi(r)$.

TABLE V. Variation of e-He$^+$ ion ^1S-wave phase shifts for $k=0.3$ as a function of the parameter d in the polarization potential $-\alpha/(r^2+d^2)^2$ with $\alpha=\frac{9}{32}$.

d (a.u.)	No polarization	2.0	1.5	1.1	0.9	0.7	QD[36]
Without pseudopotential	0.376	0.384	0.390	0.407	0.428	0.479	0.427
With pseudopotential	0.423	0.428	0.430	0.430	0.428	0.424	

D. Triplet S-Wave Elastic e-He$^+$ Scattering

A 19-term configuration interaction ^3S state of He[38] ($E_0=2.175\,21$ a.u., Pekeris's $E_0=-2.175\,23$)[28] was used to construct the pseudopotential. Phase shifts calculated by the one-state, p-v and quantum defect (QD) extrapolation[36] are tabulated in Table VI. At low k, the p-v and QD results agree exactly. At higher k the quantum-defect extrapolation becomes less accurate, and one might be tempted to attribute small deviations between the p-v and QD to this. However, it is known in this case that at higher energies the QD phase shifts err because they are too small,[36] although at $k=0.4$ they are probably still quite accurate. Thus the p-v results are even more in error at energies around $k=0.4$, and we see the same effect, although to a lesser extent, that occurred in e-H ^1S scattering: The p-v method becomes poorer as k increases.

The s-p and p-p methods are not directly applicable to ^3S e-He$^+$ scattering. This is due to the fact that $\tilde{\chi}(r)=\tilde{u}(r)/r$ may contain any arbitrary amount of the He$^+$ ground state $\phi_0(r)$, even when the pseudopotential formalism is used, and $\xi^-(r)$ is a "2S-like" function rather than 1S-like as is $\xi^+(r)$. The total wave function is written

$$\Psi(1,2)\cong\phi_0(1)\tilde{\chi}(2)-\phi_0(2)\tilde{\chi}(1)+\beta\Psi_0^-(1,2)\ , \qquad (6.15)$$

so any amount of ϕ_0 appearing in $\tilde{\chi}(2)$ will be subtracted out by the second term on the right-hand side (rhs) of (6.15). The s-p criteria of choosing β, i.e., requiring that $\tilde{\chi}(0)=0$, is therefore no longer unique in this case. Because of the great success of the p-v method for this system, no attempt was made to find simple satisfactory ways to remove this arbitrariness in the s-p method.

E. Rydberg States of He

Thus far we have talked almost exclusively in terms of the calculation of scattering states. But almost everything discussed applies equally to bound states. In particular, the equations (6.1) to (6.13) are valid for bound states as well as for continuum states. The major difference is due to the fact that for bound-state calculations we are faced with solving an eigenvalue problem; one does not in general know the eigenenergies before performing the calculation.

The usual procedure for determining the energies and wave functions of bound states by a differential equation approach is the following: (1) make an initial guess of the energy eigenvalue; (2) starting from $r=0$, integrate the differential equation with this value of E until the wave function begins to increase exponentially in the asymptotic region; (3) adjust the energy to reduce the amount of divergent behavior in the asymptotic region; and (4) iterate until an energy is found for which the wave function remains nearly zero in the asymptotic region.

For Rydberg states with principal quantum numbers greater than about 4 or 5, direct application of this method becomes intractable because the Rydberg orbitals become so diffuse that the integration would have to be carried out very accurately to extremely large distances. In this paper we use a modification of this method which takes advantage of the asymptotic properties of Coulomb functions. The procedure we use, which is discussed in detail in the Appendix, is the following: (1) guess a value for the energy; (2) integrate the differential equation for this energy to a distance r_0 at which the potential has become essentially a pure Coulomb potential. (For these calculations r_0 was taken to be 16 to 24 a.u.); and (3) by matching the solution and its derivative at r_0 to a linear combination of regular and irregular Coulomb functions of the same energy, we can calculate the quantum defect $\mu(E)$ for this value of E. If $\mu(E)$ is a slowly varying function of E, and if E is fairly close to an eigenvalue E_n, then $\mu(E)$ should be an excellent approxima-

TABLE VI. Phase shifts for triplet S-wave e-He$^+$ ion scattering.

k (a.u.)	Present calculation One state	 p-v	QD[36]
0.1	0.919	0.931	0.931
0.2	0.916	0.926	0.927
0.3	0.910	0.919	0.921
0.4	0.902	0.910	0.912

tion to $\mu(E_n)$. We can therefore obtain a better approximation to E_n from

$$E_n \simeq [n - \mu(E)]^{-2} \; . \qquad (6.16)$$

In these calculations $\mu(E)$ was found to vary slowly enough so that even for fairly crude initial guesses, the energy was found sufficiently accurately by only one solution of the equation; $\mu(E)$ and $\mu(E_n)$ agreed to at least 4 decimal places. So if one is interested only in the energy, the equations need only be solved once, just as in the case of positive-energy states. If the Rydberg wave function is desired, not just its energy, then the equations must be solved a second time using the correct energy.

Quantum defects were calculated for the ^1S states of He by the one-state, p-v and p-p methods. The correlated He ground-state function[27] reported in Part C of this section was used for these calculations. In Table VII these results are compared with the "best single configuration" calculations of Davidson[39] and with experiment. The results are very similar to those for singlet S-wave e-He$^+$ scattering reported in Part C of this section. Quantum defects calculated by the p-p method agree almost exactly with experiment, while those calculated by the p-v method contain only about 40–50% of the correlation.

The ^3S bound function[38] used in Part D of this section was used to construct the pseudopotential in the ^3S He Rydberg-state calculations. In Table VIII, ^3S quantum defects calculated by the one-state and p-v methods are compared with the results of Davidson[39] and with experiment. The p-v results are in essentially exact agreement with experiment, but in this case the correlation effects are small enough so that even the one-state approximation gives good results. The one-electron pseudopotential calculations of Hazi and Rice,[7] which should be almost equivalent to the one-state results, are also included in Table VIII.

VII. USE OF APPROXIMATE BOUND STATES IN CONSTRUCTING PSEUDOPOTENTIALS

In the calculations of the previous section, fairly accurate correlated bound-state functions were used to construct the pseudopotentials. Even so, these functions were not assumed to be exact eigenfunctions, since we replaced Eq. (2.4) by Eq. (4.1), and obtained $\xi(r)$ from Eq. (5.8). Some calculations were performed in which we assumed that these same $\Psi_0(1,2)$ functions were exact eigenfunctions of the two-electron Hamiltonian; i.e., we obtained $\xi(r)$ from the equation

$$\xi(r) = \int \phi_0{}^*(1)\Psi_0(1,2)d\vec{r}_1 \; , \qquad (7.1)$$

which would be exact if H $\Psi_0 = E_0\Psi_0$. In the e-He$^+$ ^1S calculations, making this assumption resulted in only a slight change in the phase shifts. However, in the e-H ^1S and the e-He$^+$ ^3S calculations, for which the bound functions Ψ_0 are much more diffuse than the helium ground state, using (7.1) instead of (5.8) gave erratic results. We conclude that (5.8) should be used unless the bound functions are extremely accurate.

The question remains: How effective is the pseudopotential method when the pseudopotential

TABLE VII. Comparison of calculated and experimental quantum defects for ^1S states of He.

		Present calculation			
n	Davidson[39]	One state	p-v	p-p	Experiment[a]
3	0.124	0.126	0.133	0.142	0.143
4	0.122	0.124	0.132	0.141	0.141
5	•••	0.124	0.132	0.140	0.141
10	•••	0.123	0.131	0.140	•••

[a] C. E. Moore, Atomic Energy Levels, National Bureau of Standards Circular No. 467 (U. S. Government Printing Office, Washington, D.C., 1949), Vol 1, p. 4.

TABLE VIII. Comparison of calculated and experimental quantum defects for ^3S states of He.

			Present calculation		
n	Davidson[39]	Hazi and Rice[7]	One state	p-v	Experiment[a]
3	0.298	0.298	0.297	0.301	0.302
4	0.298	0.296	0.295	0.299	0.299
5	•••	0.294	0.294	0.298	0.298
10	•••	•••	0.293	0.297	•••

[a] C. E. Moore, Atomic Energy Levels, National Bureau of Standards Circular No. 467 (U. S. Government Printing Office, Washington, D.C., 1949), Vol. 1, p. 4.

is constructed from bound functions which are not as accurate as those used in the previous section? In an attempt to partially answer this question, we calculated e-He$^+$ ^1S and ^3S phase shifts by the p-v method, using Hartree-Fock (H-F) bound wave functions[40] to construct the pseudopotential by Eq. (5.8). The results shown in Table IX confirm our expectation that H-F functions add almost no correlation at all. For e-He$^+$ ^1S, a p-p calculation was also performed using a H-F function. The results (Table IX) are very poor. This is somewhat puzzling considering the arguments of the next paragraph, but at least it can serve as a warning. In summary, it is important that the wave functions used to construct the many-electron pseudopotential be fairly accurate and contain a fair amount of correlation.

The calculations of Kestner *et al.*[2] on e-He scattering are very similar to our p-p method. They use the three-electron analog of Eq. (6.1) with quite accurate adiabatic polarization potentials. But instead of using bound He$^-$ three-electron wave functions to form the pseudopotential, as the p-p method would require, they simply let ξ in Eq. (6.1) be the He H-F one-electron core orbital. (Of course, a bound He$^-$ function does not exist, so the p-p method is not applicable to their system.) They obtain very good results in this way. However, the role played by the pseudopotential in their calculations seems to be contradictory to that which it plays in the present calculations. We use very accurate wave functions to construct a pseudopotential in order to lessen the effect of making a less accurate approximation, e.g., the adiabatic approximation, in solving the equation. In their work they use an adiabatic approximation which goes beyond the one-electron approximation, but the pseudopotential which modifies it is obtained within the one-electron approximation, so that at first glance it might seem that they would do better without the pseudopotential. They would not. The pseudopotential they use does not by itself introduce any correlation, as ours does, and it does introduce some error since it is obtained in the one-electron approximation. But because of the compactness of this orbital and the rather devious way in which it manifests itself in the calculation, this error can be argued to be relatively small. On the other hand, the error introduced by using an adiabatic approximation in the region of small r is quite large. Thus the role of the pseudopotential in the Kestner *et al.* calculation is really the same as in our p-p method: The pseudopotential makes it difficult for the pseudoelectron to venture close to the nucleus where the adiabatic potential is poor, and it slows the pseudoelectron down so that the adiabatic hypothesis is somewhat more valid in this region.

VIII. DISCUSSION

No triplet S-wave electron-hydrogen atom scattering calculations were reported in this paper. This is because no bound triplet states of H$^-$ exist, so the many-electron pseudopotential approach is inapplicable to this system. This points out a basic requirement of the many-electron pseudopotential method: The N-electron system must possess at least one bound state of the same total spin and symmetry as each of the excited states to be calculated. This is a very severe limitation on the applicability of the method to electron-neutral scattering (photodetachment) problems, as typified by the e-H system. On the other hand, for Rydberg state or electron-positive ion scattering (photo-ionization) calculations this is no limitation at all.

The second requirement of the many-electron pseudopotential method is that there exist reasonably accurate calculations of the correlated wave functions for these N-electron bound states. This might also be a serious limitation in some cases, although increasingly more bound-state calculations are becoming available.

Our calculations show that the many-electron pseudopotential method, even used in its simplest form with the one-state approximation, can in many instances give extremely accurate results with a minimum of effort. There are, however, two situations in which the pseudopotential in this simplest form cannot by itself account for most of the correlation effects. The first such situation is the one in which the bound state used to construct the pseudopotential has an energy very much lower than the excited states that one is calculating; e.g., the He ^1S calculations of this paper. It was shown for this case that a tremendous improvement results from the addition of a simple polarization ansatz, and that the in-

TABLE IX. The use of H-F versus correlated bound functions to construct pseudopotential. Phase shifts (in radians) for the He atom (S-wave, $k=0.2$).

	One state	p-v (H-F)	p-v (Corr.)	p-p (H-F)	p-p (Corr.)	QD
^1S	0.381	0.382	0.407	0.377	0.434	0.433
^3S	0.916	0.916	0.926	···	···	0.927

accuracies associated with using an adiabatic potential in the region of small r are almost completely eliminated. Another method of treating this situation which is perhaps superior to the addition of a polarization ansatz is the use of more than one bound function to construct the pseudopotential. For example, in the He ^1S problem, the first excited ^1S state of He has an energy even closer to the continuum than the lowest He ^3S state, and so it is reasonable to expect from the ^3S results that using both the ground and first excited ^1S states of He to construct the pseudopotential would give extremely good results. This method has the advantages that it obeys a strict Kohn variational principle and that it can be systematically improved by addition of more terms to the trial function, in particular, close-coupling terms. A further reason for possibly avoiding adiabatic methods is that, while they may provide very good phase shifts and energies, because they involve only the elastic channel they cannot provide the entire wave function to the same accuracy that the close-coupling pseudopotential methods can.

The second type of problem for which the pseudopotential with the one-state approximation is insufficient is the study of resonance effects or inelastic processes. For such cases, the pseudopotential and close-coupling methods should complement each other well. The close-coupling states can account fairly well for long-range polarization, and are the natural way to describe resonances and inelastic channels. The pseudopotential can supply the short-range correlation effects very well and therefore greatly reduce the slow convergence problem of the close-coupling method.[17,18]

Burke and Taylor[41] have performed very successful calculations on e-H and e-He$^+$ elastic and inelastic scattering using a trial function constructed of the 1S, 2S, and 2P close-coupling states and up to 16 "correlation terms." It is quite possible that by replacing the correlation terms by a pseudopotential, one might obtain comparable results while greatly reducing the labor involved.

Many dynamic molecular processes appear to require for their description the calculation of highly excited Rydberg states and of the corresponding low-energy electronic continuum states at a large number of fixed internuclear distances.[42] The angular dependence of these functions can usually be assumed to a very high degree of accuracy to be pure spherical harmonics in the asymptotically large r region.[43] But for small values of r the potential can become very nonspherical, causing the wave functions to be nonspherical as well. Temkin and Vasavada[44] have recently obtained a fairly good description of e-H$_2^+$ continuum states using their "method of polarized single-center orbitals," which restricts the angular dependence of the continuum function to be a single spherical harmonic at all r values. Since this is a poor approximation only for small r, the discussions of Secs. III and IV argue that the pseudopotential method, combined with Temkin and Vasavada's single-center approach (with or without an adiabatic potential) might be very effective in molecular calculations. A function of the form

$$\mathcal{A}[\phi_0(r_1,\ldots,r_{N-1})Y_{lm}(\theta_N,\varphi_N)X(r_N)]$$

$$+\sum_j\beta_j\Psi_j(r_1,\ldots,r_N) \ ,$$

where the $\Psi_j(r_1,\ldots,r_N)$ are accurate bound-state functions, might describe the nonspherical nature of the continuum or Rydberg states quite well, and still be easily calculated by solution of a "simple" radial equation.

In conclusion, it has been remarked that considering the fact that most interesting atomic and molecular processes involve excited states, there is at present a disproportionate amount of effort being applied to the calculation of lowest-energy bound wave functions. In this paper we have shown that there is a large amount of information about excited states that is contained in these lower bound functions, and that with the aid of the pseudopotential formalism, this information can be readily used in excited-state calculations.

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APPENDIX

In this Appendix we present a differential equation method for obtaining normalized wave functions and eigenenergies of bound states based on asymptotic properties of Coulomb functions. We make use of many of the results presented by Seaton,[12] and follow his notation closely.

Assume that there is a distance r_0 from the origin beyond which the potential is essentially purely Coulombic. Then we can write the differential equation in the form

$$\left(\frac{d^2}{dr^2}-\frac{l(l+1)}{r^2}-V(r)+\epsilon\right)P(\epsilon,l;r)=0 \ , \qquad \text{(A1)}$$

where V and $\epsilon=-1/\nu^2$ are in Rydberg units. $V(r)$

$= -2/r$ for $r > r_0$ and $V(r) = -2Z/r$ for r small. Consider the following solution $\mathfrak{F}(\nu, l; r)$ of (A1) which is regular at $r = 0$ but not necessarily regular at $r = \infty$:

$$\begin{aligned}\mathfrak{F}(\nu, l; r) = {} & [\pi\nu^l/\beta(\epsilon)\Gamma(l+1-\nu)] \\ & \times\{1+\beta(\epsilon)[A(\nu, l)\cot(\pi\nu)+G(\nu, l)]\} \\ & \times y_1(\nu, l; r)+y_5(\nu, l; r) \ , \end{aligned} \tag{A2}$$

where

$$A(\nu, l) = \Gamma(\nu+l+1)/\nu^{2l+1}\Gamma(\nu-l) \ , \tag{A3}$$

$$G(\nu, l) = \frac{1}{2\pi}\frac{\partial}{\partial l}A(\nu, l) \ , \tag{A4}$$

and

$$\beta(\epsilon) = [A(\nu, l)\cot(\pi\mu(\epsilon)) - G(\nu, l)]^{-1}, \ \epsilon < 0 \ . \tag{A5}$$

Equation (A5) defines the "quantun defect" $\mu(\epsilon)$ which is a continuous function of ϵ and which for eigenvalues satisfies

$$\mu(\epsilon_n) = n - \nu_n \ . \tag{A6}$$

For $\nu \neq n$, y_1 and y_5 are two linearly independent solutions of the pure Coulomb equation. y_1 is regular at $r = 0$ but increases exponentially for large r. y_5 approaches zero as $r \to \infty$ and can be written

$$\begin{aligned} y_5(\nu, l; r) = {} & -[\pi\nu^l/\Gamma(l+1-\nu)] \\ & \times[A(\nu, l)\cot(\pi\nu)y_1(\nu, l; r)+y_3(\nu, l; r)] . \end{aligned} \tag{A7}$$

The functions y_1 and y_3 can be conveniently obtained by expansions in powers of ϵ.[12,45] The expansion formulas given by Kuhn[45] were used in the calculations of this paper.

In order to obtain a solution of (A1) for a negative energy, one can solve (A1) numerically with an initial guess of the eigenenergy and at some points $r_1, r_2 > r_0$ match the resulting solution to the pure Coulomb functions y_1 and y_5 to find $\beta(\epsilon)$ in Eq. (A2). Then from (A5) one can obtain $\mu(\epsilon)$. If $\mu(\epsilon) \simeq \mu(\epsilon_n)$ then a much improved approximation to ϵ_n can be obtained by substituting $\mu(\epsilon)$ for $\mu(\epsilon_n)$ in Eq. (A6). This procedure can be repeated until the energy does not change.

Seaton[12] shows that for $r > r_0$ the normalized bound wave functions are given by

$$P_{ne}(r) = k(\nu_n, l)y_5(\nu_n, l; r), \quad r > r_0 \ , \tag{A8}$$

where

$$\begin{aligned} k(\nu, l) = {} & [\xi(\nu_n)\nu_n{}^2\Gamma(\nu_n+l+1) \\ & \times\Gamma(\nu_n-l)]^{-1/2} \ , \end{aligned} \tag{A9}$$

and

$$\xi(\nu_n) = 1+\partial\mu/\partial\nu \ , \tag{A10}$$

so the resulting solutions of Eq. (A1) can be easily normalized such that

$$\int P_{nl}{}^2(r)dr = 1 \ , \tag{A11}$$

without it being necessary to perform the integral (A11).

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