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Complex-coordinate method. Structure of the wave function

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The functional forms of the wave functions for the bound states of hydrogenic systems and for free particles as described by the complex-coordinate method are presented. Writing the wave function for an electron resonance as the sum of a "boundlike" or "Q-space" part and a "scatteringlike" or "P-space" part, we suggest functional forms or bases for these two parts based on the solutions of the hydrogenic and free-particle systems. We present an argument suggesting that when the rotation angle in the complex-coordinate method is greater than $|\arg(k_r)|$ for the electron resonance, this method is identical to calculations based on a Siegert resonance. This assumed structure of the wave function should yield a rate of convergence similar to other methods. The advantages of this method are that the basis functions are all square integrable, a single calculation yields both the position and width, only a solution of a straightforward eigenvalue problem is required, arbitrarily accurate target states are easily incorporated, and polarization terms can be explicitly included. Variational calculations for the position and width of the lowest ^2S resonance in the negative helium ion are reported using trial wave functions containing 39, 43, 55, 59, and 67 configurations. These wave functions contain 8, 8, 20, 24, and 32 "P-space" configurations, respectively. Values of 19.387 eV and 12.1 meV are obtained for the position and width, respectively, of the resonance. One also finds that inclusion of free-particle-like basis functions improves the representation of the scattering states.

I. INTRODUCTION

A number of techniques such as Feshbach, close coupling, stabilization, etc., exist for the computation of electronic resonance parameters. However, the application of these methods to systems of more than two electrons generally leads to conceptual or computational difficulties. For example, in the Feshbach formalism the form of the projectors for systems of more than two electrons has not been constructed, and in the close-coupling method the construction of the coupled differential equations is very complicated.

On the other hand, a relatively new technique,[1-3] the complex-coordinate method, has recently found application to a number of atomic processes. For example, it has been applied to scattering theory,[4] photoionization,[5] the Stark effect,[6] and electron resonances.[7-12] As previously used, this technique is not without its difficulties. Extremely large wave functions have been required to compute resonant parameters for systems with just two particles. Application to three-particle systems has either failed or yielded at best crude estimates of atomic resonance parameters again with very large wave functions. To overcome these problems, we previously suggested a partitioning of the resonant wave function[13] into a "boundlike" or "Q-space-like" part and a "scatteringlike" or "P-space" part and suggested certain functional forms for these parts based on the exact complex-coordinate solutions of certain simple systems. In this paper we present the details of that work along with a discussion of the scattering states.

Section II contains a discussion of the Balslev-Combes theorem on which the complex-coordinate method is based and of previous applications of the method to the computation of the position and width of electron resonances. In Sec. III we use the complex-coordinate method to compute the bound state energies and eigenfunctions of hydrogenic systems, while in Sec. IV the wave function of a free particle as described by the complex-coordinate method is obtained. We also discuss the form of the wave function for a noninteracting free particle and a system of bound particles in this section. Section V contains the bases and wave functions used for the variational calculations of the resonant parameters of the lowest ^2S resonance in He$^-$ with the results being presented in Sec. VI. The eigenvalues corresponding to the scattering states are discussed in Sec. VII. Finally, Sec. VIII contains concluding remarks. Except where otherwise noted, atomic units are used throughout.

II. BALSLEV-COMBES THEOREM AND PREVIOUS APPLICATIONS TO RESONANCES

Consider an N-electron Hamiltonian $\mathcal{H}$ for an atomic system, i.e.,

$$\mathcal{H}=-\frac{1}{2}\sum_j \nabla_{r_j}^2-\sum_j \frac{Z}{r}+\sum_{j<k}{}' r_{jk}^{-1}\equiv T+V \tag{1}$$

and a transformation[14] in which

$$r_j\rightarrow \rho_j e^{i\alpha}. \tag{2}$$

This defines the complex non-Hermitian Hamiltonian $\mathcal{H}_\alpha$,

$$\begin{aligned}\mathcal{H}_\alpha &\equiv -\tfrac{1}{2}e^{-2i\alpha}\sum_j \nabla_{\rho_j}^2+e^{-i\alpha}\left(\sum_{j<k}\rho_{jk}^{-1}-\sum_j\frac{Z}{\rho_j}\right)\\ &\equiv e^{-2i\alpha}T+e^{-i\alpha}V,\end{aligned} \tag{3}$$

where the last step is dependent on the fact that the potential only consists of sums of Coulomb potentials. According to the Balslev-Combes theorem,[2,3] the spectrum of $\mathcal{H}_\alpha$ can be divided into three groups. One group consists of the energies of the bound states of $\mathcal{H}$ which for $\mathcal{H}_\alpha$ remain real and independent of α. The second group consists of the energies of the scattering states of $\mathcal{H}$ which for $\mathcal{H}_\alpha$ have the form $E_T+Ee^{-2i\alpha}$, where E is the energy above the threshold energy E_T. That is, they lie on rays which begin at thresholds on the real axis and make an angle of -2α with the real axis. The elements of the third group arise whenever one of the rays crosses a pole of the resolvent, i.e., when

$$\alpha>\tfrac{1}{2}\left|\arg(E_R)\right|, \tag{4}$$

where E_R is a complex pole of the resolvent. Since the eigenfunctions of this third group are square integrable, this is a very attractive method for determining poles of the resolvent. That is, in principle one need only compute the eigenvalues of $\mathcal{H}_\alpha$ as a function of α and look for complex eigenvalues which are independent of α for α greater than some minimum value.

To illustrate these points, we consider the ^1S spectrum of H$^-$. In Fig. 1(a) we give the spectrum of $\mathcal{H}$ and note the first five thresholds, while in Fig. 1(b) we give the spectrum of $\mathcal{H}$ and note the first five thresholds, while in Fig. 1(b) we illustrate the spectrum of $\mathcal{H}_\alpha$ which shows the first four thresholds and the ionization threshold along with their associated cuts. The energy of the bound state of H$^-$ is at the same point in the complex energy plane in both 1(a) and 1(b), i.e., it is independent of α. In 1(b) we have also indicated one of the resonances which has been uncovered.

In the work of Balslev and Combes[2] the above results were shows to be valid for

$$0\leqslant\alpha<\tfrac{1}{4}\pi. \tag{5}$$

Simon[3] has shown that for certain classes of potentials the above result can be proved for

$$0\leqslant\alpha<\tfrac{1}{2}\pi. \tag{6}$$

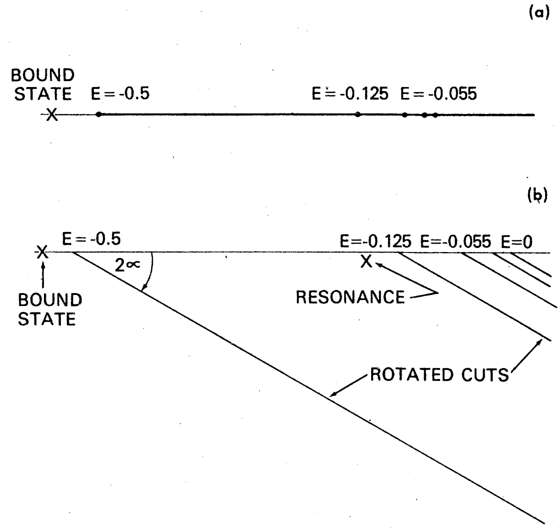

FIG. 1 (a) ^1S spectrum of H$^-$ as given by $\mathcal{H}$ with the bound state and first five thresholds indicated. (b) ^1S spectrum of H$^-$ as given by $\mathcal{H}_\alpha$ with the bound state, first four thresholds and the ionization threshold indicated.

Previous applications of this method to atomic and model systems have used a variational principle[7,8] of the form

$$E=\int d\tau\,\psi^*\mathcal{H}_\alpha\psi\bigg/\int d\tau\,\psi^*\psi. \tag{7}$$

Here ψ^* implies complex conjugation of the angular part but no complex conjugation of the radial part. One feature of all the basis functions employed in all of these calculations[7-12] is that they are real functions in the ρ-radial coordinate. As an example, consider the calculation of the ^1S resonance in H$^-$ by Doolen *et al.*[8] and Doolen.[9] They employed a trial Hyleraas type wave function of the form

$$\begin{aligned}\Psi=&\exp[-\tfrac{1}{2}a(\rho_1+\rho_2)]\\ &\times\sum_{l+m+n<N}C_{lmn}\rho_{12}^n(\rho_1^l\rho_2^m+\rho_1^m\rho_2^l).\end{aligned} \tag{8}$$

In Figs. 2 and 3 we have plotted the real and imaginary parts of the energy as a function of the rotation angle α for the 95 configuration wave function for values of a equal to 0.7, 0.8, and 0.9. These figures have been obtained from Fig. 1 of Ref. 9. The straight lines in the figures are the values of the complex energy of the resonance obtained by Ho *et al.*[15] The curves corresponding to the complex-coordinate calculations should overlap the lines from this precision calculation when (4) is satisfied. As these figures show, the complex energies are at best only a slowly varying function of α over a small angular range of α.

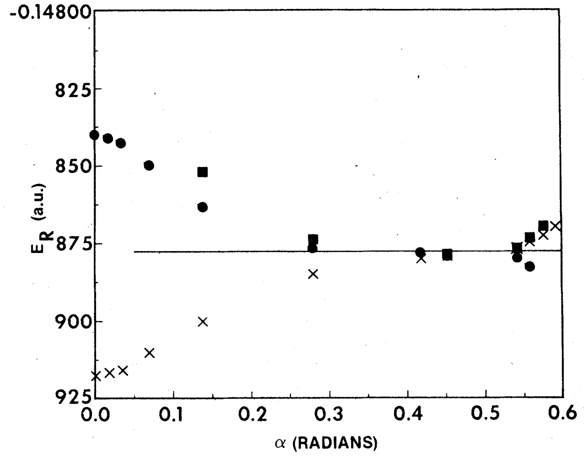

FIG. 2 Real part of complex resonant energy for the lowest ^1S resonance of H^- from the calculation of Doolen *et al.* (Refs. 8 and 9) as a function of α; ● $a=0.8$, ■ $a=0.9$, × $a=0.7$.

An attempt by Bain *et al.*[7] to use this method to compute the resonant parameters of the lowest ^2S resonance in He^- failed to yield a converged value for the complex energy. Similar application of this technique to the computation of resonant parameters in positronium hydride[10,11] have yielded only crude estimates and required large wave functions. Thus, the basis functions used in these calculations are clearly not an optimum choice.

One observation to be noted is that in all models or theories which yield total phase shifts, resonant phase shifts, or resonant widths (close coupling, stabilization, Feshbach, etc.), one uses a total wave function which contains continuum functions or one relates the resonant phase shift or width to a function of a matrix element between a boundlike or Q-space function and a scatteringlike or P-space function. We thus assume we can write the eigenfunctions of $\mathcal{H}_\alpha$ in the form

$$\Psi^\alpha = \Psi_Q^\alpha + \Psi_P^\alpha , \tag{9}$$

where Ψ_Q^α corresponds to a "Q-space" function and Ψ_P^α corresponds to a "P-space" function. In Sec. III, we present a discussion which suggests an appropriate form of Ψ_Q^α and, similarly, in Sec. IV we suggest a form of Ψ_P^α.

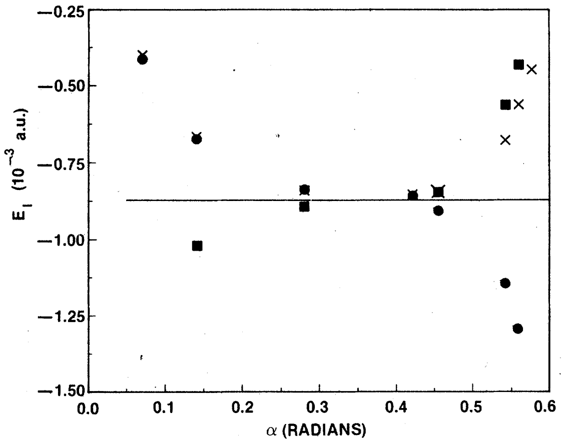

FIG. 3 Imaginary part of complex energy for the lowest ^1S resonance of H^- from the calculation of Doolen *et al.* (Refs. 8 and 9) as a function of α; ● $a=0.8$, ■ $a=0.9$, × $a=0.7$.

III. APPLICATION OF THE COMPLEX-COORDINATE METHOD TO HYDROGENIC ATOMS

We recall that according to the Balslev-Combes theorem the bound-state energies of $\mathcal{H}_\alpha$ are independent of α for all values of α while the resonant energies are independent of α when relation (4) is satisfied. We might expect to gain insight into the functional form of the wave function of a state whose energy is independent of the rotation angle by studying the bound states. The only atomic systems which can be solved analytically are hydrogenic systems.

For a hydrogenic atom the "Schrödinger equation" for $\mathcal{H}_\alpha$ takes the form

$$\left[\left(\frac{-e^{-2i\alpha}}{2\rho^2}\right)\left(\frac{\partial}{\partial\rho}\rho^2\frac{\partial}{\partial\rho}-L^2\right)-\frac{Ze^{-i\alpha}}{\rho}-E\right]\Psi(\vec{\rho})=0. \tag{10}$$

Let

$$\Psi(\vec{\rho})=\rho^l e^{-\delta\rho}u(\rho)Y_l^m(\theta,\varphi), \tag{11}$$

where

$$\delta=(-2E)^{1/2}e^{i\alpha}. \tag{12}$$

Substituting (11) and (12) into (10), one obtains

$$u''(\rho)-2[\delta-(l+1)/\rho]u'(\rho) + [Ze^{i\alpha}-2\delta(l+1)]u(\rho)/\rho=0. \tag{13}$$

Let

$$u(\rho)=\sum_{j=0}^{\infty}a_j\rho^j. \tag{14}$$

Equation (13) yields for the ratio of successive coefficients

$$\frac{a_{j+1}}{a_j}=-2e^{i\alpha}\frac{Z-(-2E)^{1/2}(j+l+1)}{(j+1)(j+2l+2)}. \tag{15}$$

Requiring the series to terminate at n so that the wavefunctions are square integrable, one obtains

$$E=-Z^2/[2(n+l+1)^2], \tag{16}$$

i.e., the normal hydrogenic energies.

Our main interest, however, is in the form of the eigenfunctions. From (11) one observes that the exponential contains the factor $\rho e^{i\alpha}$. Also, rewriting Eq. (15) using (16), one obtains

$$a_{j+1}/a_j = 2\delta(j-n)/[(j+1)(j+2l+2)]. \tag{17}$$

δ is the only complex factor and according to Eq. (12) it contains $e^{i\alpha}$. Thus, each term in the series contains an additional factor of $e^{i\alpha}$ as well as ρ and thus $u(\rho)$ is in fact a power series in $\rho e^{i\alpha}$. Thus, the eigenfunctions are the normal hydrogenic eigenfunctions with r replaced by $\rho e^{i\alpha}$. This is, in fact, what one would expect for analytically continuing the Schrödinger equation.

Based on these results, one might expect that the "bound-like" or "Q-space" part should be constructed from bound-type orbitals which are functions of $\rho e^{i\alpha}$ and not ρ as in previous applications of the complex-coordinate method. For example, one could use Slater-type orbitals (STO's) of the form

$$\mathcal{S}_{nlm} = N(\rho e^{i\alpha})^{n-1}\exp(-\gamma\rho e^{i\alpha})Y_l^m(\theta,\varphi), \tag{18}$$

where N is the normalization constant and γ is a real nonlinear parameter. Considering one-electron integrals with these orbitals with regard to operators of the form $O(\rho e^{i\alpha})$, we find

$$\begin{aligned} I_1^\alpha &= \int_0^{2\pi}\int_0^{\pi}\int_0^{\infty} \mathcal{S}^\alpha_{nlm}(\vec{\rho}e^{i\alpha})O(\vec{\rho}e^{i\alpha}) \\ &\quad \times \mathcal{S}^\alpha_{n'l'm'}(\vec{\rho}e^{i\alpha})\rho^2\,d\rho\sin\theta\,d\theta\,d\varphi \\ &= e^{-3i\alpha}\int_0^{2\pi}\int_0^{\pi}\int_0^{\infty} \mathcal{S}_{nlm}(\vec{r})O(\vec{r})\mathcal{S}_{n'l'm'}(\vec{r}) \\ &\quad \times r^2\,dr\sin\theta\,d\theta\,d\varphi, \end{aligned} \tag{19}$$

where the last integral is just a normal atomic integral. This result follows since

$$\lim_{\rho\to\infty}\mathcal{S}_{nlm}(\vec{\rho}e^{i\alpha}) \to 0 \tag{20}$$

for

$$0 \leqslant \alpha < \tfrac{1}{2}\pi. \tag{21}$$

From the above it is also clear that a similar result holds for the two-electron integrals I_2^α with the phase factor in front being replaced by $e^{-6i\alpha}$. Finally, from these results we find that, if M^α is a matrix element between two N-electron configurations in $\vec{\rho}e^{i\alpha}$ space and M is the corresponding matrix element in $\vec{r}$ space, these two matrix elements are related by

$$M^\alpha = e^{-3Ni\alpha}M. \tag{22}$$

Also,

$$I_1^{\alpha'} = \exp[-3i(\alpha'-\alpha)]I_1^\alpha, \tag{23a}$$

$$I_2^{\alpha'} = \exp[-6i(\alpha'-\alpha)]I_2^\alpha, \tag{23b}$$

and

$$M^{\alpha'} = \exp[-3Ni(\alpha'-\alpha)]M^\alpha. \tag{23c}$$

Thus, integrals and matrix elements for these functions need only be computed once instead of having to be recomputed for each value of α. Finally, it is obvious that all energies obtained from a variational wave function with just this type of configuration would necessarily be real since each matrix element is multiplied by the same phase which would factor out of the secular equation leaving only the normal unrotated Hermitian representation of the Hamiltonian.

IV. APPLICATION OF THE COMPLEX-COORDINATE METHOD TO THE FREE PARTICLE

In the various models or theories the scattering-like or P-space part is generally taken to be of the form of an antisymmetrized product of a target state function and a continuum orbital. As stated previously,[13] three points must be noted about this part of the wave function. First, the target wave function represents a bound state and should therefore be constructed from boundlike functions of $\rho e^{i\alpha}$. For example, for electron scattering from hydrogen at energies below the first excited state, a target function of the form

$$\mathcal{S}_T = C\exp(-\rho e^{i\alpha}) \tag{24}$$

should be used where C is a constant. Second, the "continuum orbital" must be square integrable. Third, the "continuum orbital" cannot be a real function of only $\rho e^{i\alpha}$ or the energies would all be real, which follows from Sec. III.

Now consider the solution of the "Schrödinger equation" (3) for a resonant state with energy

$$E_r = \tfrac{1}{2}k^2 = \tfrac{1}{2}|k|^2 e^{-2i\beta}. \tag{25}$$

If the potential is sufficiently short range, the resonant wave function should asymptotically satisfy the equation

$$[e^{-2i\alpha}T - \tfrac{1}{2}|k|^2 e^{-2i\beta}]\mathcal{S} = 0, \tag{26}$$

and thus behave asymptotically as

$$\begin{aligned} \mathcal{S} \sim e^{ikr} &= \exp(i|k|e^{-i\beta}\rho e^{i\alpha}) \\ &= \exp(i|k|\rho e^{i(\alpha-\beta)}), \end{aligned} \tag{27}$$

which is square integrable for

$$\alpha > \beta. \tag{28}$$

It may be noted that Eqs. (25) and (27) define the analytic continuation of a Siegert resonance. In addition, if we write

$$E_r = |E_r|\exp[-i|\arg(E_r)|] = |E_r|e^{-2i\beta}, \tag{29}$$

we see from combining (28) and (29) that the condition for the wave function to be square integrable can also be written

$$\alpha > \tfrac{1}{2}\left|\arg(E_r)\right|. \tag{30}$$

Recall that this is the condition for the corresponding pole of the resolvent to become an element in the spectrum of $\mathcal{H}_\alpha$. These results suggest that when (30) is satisfied that the complex-coordinate method is equivalent to computing a resonance using a Siegert boundary condition.

Although one can suggest the asymptotic form of the "continuum function," the interior of this function is the part which makes the major contribution to the calculation and the form of this part is *not* known. We thus require a suitable basis in which to represent this function, but do *not* wish to require a prior knowledge of k or the need for an iterative procedure to determine k and E_r self-consistently.[16] One could use a basis containing elements of the form (27), but this would yield a number of complex energies independent of α and no way of determining which correspond to resonances.

To this end consider the "Schrödinger equation" for a free particle with energy

$$E = |E|\,e^{-2i\alpha}. \tag{31}$$

That is,

$$\begin{aligned} 0 &= [\mathcal{H}_\alpha^0 - |E|\,e^{-2i\alpha}]\,\Psi(\vec{\rho}) \\ &= \left[\frac{-e^{-2i\alpha}}{2\rho}\left(\frac{\partial}{\partial\rho}\,\rho^2\,\frac{\partial}{\partial\rho} - L^2\right) - |E|\,e^{-2i\alpha}\right]\Psi(\vec{\rho}). \end{aligned} \tag{32}$$

Letting

$$\Psi(\vec{\rho}) = u_l(\rho)\,Y_l^m(\theta,\varphi), \tag{33}$$

and substituting into (32), one obtains

$$\left(\frac{d^2}{d\rho^2} + \frac{2}{\rho}\frac{d}{d\rho} + 2|E| - \frac{l(l+1)}{\rho^2}\right)u_l(\rho) = 0. \tag{34}$$

The solutions of (34) are just the familiar spherical Bessel, $j_l(|k|\rho)$, and spherical Neuman, $n_l(|k|\rho)$, functions[17] where

$$|E| = \tfrac{1}{2}|k|^2. \tag{35}$$

Although j_l and n_l appear to be functions of ρ and not $\rho e^{i\alpha}$ this is because in fact we have

$$E = |E|\,e^{-2i\alpha} = \tfrac{1}{2}|k|^2 e^{-2i\alpha} \equiv \tfrac{1}{2}k^2, \tag{36}$$

and thus

$$\begin{aligned} u_l(\rho) &= f_l(|k|\rho) \\ &= f_l(|k|\,e^{-i\alpha}\rho e^{i\alpha}), \\ &= f_l(kr) \end{aligned} \tag{37}$$

where f_l is either j_l or n_l.

Now if we consider the complex Hamiltonian for a system of bound particles plus a noninteracting free particle, we have

$$(\mathcal{H}_\alpha^0 - E_T)\Psi_0^\alpha = (\mathcal{H}_\alpha^b - E_b + \mathcal{H}_\alpha^f - |E_f|\,e^{-2i\alpha})\Psi_0^\alpha = 0, \tag{38}$$

where $\mathcal{H}_\alpha^b$ and E_b are the Hamiltonian and energy for the bound system and $\mathcal{H}_\alpha^f$ and $|E_f|\,e^{-2i\alpha}$ are the Hamiltonian and energy for the free particle. The exact solution of (38) may be written

$$\Psi_0^\alpha = \Psi_\alpha^b(\vec{\rho}_1 e^{i\alpha}, \ldots, \vec{\rho}_n e^{i\alpha})\,\Psi_\alpha^f(\vec{\rho}_0), \tag{39}$$

where Ψ_α^b is the bound state eigenfunction of $\mathcal{H}_\alpha^b$ and Ψ_α^f is the free-particle function. Ψ_0^α corresponds to the asymptotic form of the solutions for the scattering states lying on the rays which are rotated from the real axis by -2α.

These functions could serve as a relatively simple basis for representing the "P-space" function so long as the "continuum orbital" is multiplied by a cutoff factor such as $e^{-\nu\rho}$ to make it square integrable. In the present calculation, we have used the basis functions

$$\mathcal{S}_\nu^\pm = e^{\pm ip\rho}e^{-\nu\rho}(1 - e^{-\rho})/\rho \tag{40}$$

to represent the S-wave "continuum orbital." The factor $1 - e^{-\rho}$ ensures that the function behaves properly as $\rho \to 0$. In each calculation, a set of functions with a range of ν-values is used. In addition, calculations are performed with different values of ρ to test the sensitivity of the calculation to this parameter.

Another way of visualizing these functions is the following:

$$\mathcal{S}_\nu^\pm = \exp[i(\pm p + i\nu)\,e^{-i\alpha}r] \equiv e^{ik'r}. \tag{41}$$

That is, these form a set of functions like those in Eqs. (27) with different complex k' values. One should note here, however, that both functions, $e^{ip\rho}$ and $e^{-ip\rho}$ are required for the scattering states on the rays, while only functions of the form e^{ikr} represent resonant states. The basis elements in (41) are simply a convenient basis in which to try to represent the resonant function and avoid an iterative procedure to determine k_r and E_r self-consistently.

V. CONSTRUCTION OF A VARIATIONAL WAVE FUNCTION FOR THE LOWEST RESONANCE IN He$^-$

We have applied the complex-coordinate method using a wave function constructed according to Secs. III and IV to a three-electron system—He$^-$. In particular, we considered the lowest ^2S resonance. The "Q-space" part of the wave function contains 27 of the 28 configurations used in a pre-

TABLE I. Configurations for Q-Space part of wave function.[a]

$1s'2s2s$	$3s2s2s'$	$2s2p'2p'$	$3d2p2p'$
$1s''2s3s$	$3s2s'2s'$	$2s2p2p'$	$3d2p'2p'$
$3s1s''2s$	$1s''2p2p$	$2p'2s2p$	$3d2p'3p$
$1s''2s4s$	$1s''2p3p$	$3s2p'2p'$	$1s''2s5s$
$4s1s''2s$	$3p1s''2p$	$1s''3d3d$	$5s1s''2s$
$1s''3s3s$	$1s''2p4p$	$1s''3d4d$	$1s''3s4s$
$2s2s'2s'$	$4p1s''2p$	$4d1s''3d$	$4s1s''3s$
$2s2s'3s$	$1s''3p3p$	$2p'2p3d$	

[a] Three *different* orbitals can be spin coupled to give two linearly independent doublet spin functions. In this Table the last two orbitals in each set are coupled to give zero spin.

vious quasi-Feshbach calculation[18] of this resonance plus 4 additional configurations. In Table I, we have listed the configurations used, where the last four configurations are the ones we added. We did not include the configuration $2p'3p'3d$ from the previous calculation. STO's of the form (18) are used in these configurations.

The "P-space" part consists of a number of configurations of the form $\mathcal{S}_\nu^{\pm}1s1s'$ as suggested in Sec. IV where $\mathcal{S}_\nu^{\pm}$ is defined in Eq. (40). Calculations are reported with 8, 20, 24, and 32 configurations of this type. In addition four configurations of the form $2s1s1s'$, $3s1s1s'$, $4s1s1s'$, and $5s1s1s'$ are included where the ns orbitals are all of the form (18).

It should be noted that we are, in fact, interested in eigenvalues and eigenfunctions of $\mathcal{H}_\alpha$ corresponding to resonances and not the scattering states. The scattering states of $\mathcal{H}_\alpha^0$, multiplied by an appropriate cutoff factor, merely serve as a convenient basis for representing the "P-space" part. By using a number of configurations with different values for ν, we can hopefully represent the "P-space" part.

Although in the asymptotic limit p is related to E_T by

$$E_T = E_b + \tfrac{1}{2}p^2 e^{-2i\alpha}, \tag{42}$$

this is not necessarily the optimum value of p at small values of the radial coordinate. In fact, inclusion of "continuum orbitals" with a number of values for p would probably result in a better basis. One would hope that the method would not be too sensitive to p, and to check this we have performed calculations with values for p of 0.0, 1.19, and 1.5, where the value of 1.19 is approximately the asymptotic value for the resonance.

TABLE II. Nonlinear Slater-orbital parameters.

Orbital	γ	Orbital	γ
$1s$	2.1832	$5s$	0.5017
$1s'$	1.1886	$2p$	0.4921
$1s''$	1.9911	$2p'$	2.1238
$2s$	0.5094	$3p$	0.5761
$2s'$	2.0583	$4p$	0.4779
$3s$	0.4287	$3d$	1.2165
$4s$	1.1957	$4d$	0.9759

TABLE III. Values of ν for various calculations.

Number of continuum configurations	ν sets
8	1.0, 0.5, 0.1, 0.05
20	(8 set), 2.5, 2.0, 1.5, 0.075, 0.025, 0.01
24	(20 set), 0.75, 0.25
32	(24 set), 0.0075, 0.005, 0.0025, 0.001

In Table II we give the values for all of the nonlinear Slater parameters. Finally, Table III contains the values of ν used in the calculations with 8, 20, 24, and 32 "continuum" configurations.

VI. $1s(2s)^2\ {}^2S$ RESONANCE IN He$^-$

The complex Hamiltonian for this three electron-problem is

$$\mathcal{H}_\alpha = \frac{e^{-2i\alpha}}{2}\sum_{j=1}^{3}\nabla^2_{\rho_j} + e^{-i\alpha}\Bigl(\sum_{j>k}\rho_{jk}^{-1} - \sum_j 2\rho_j^{-1}\Bigr). \tag{43}$$

As previously stated, computations using the variational principle (7) and the Hamiltonian (43) were performed with variational wave functions with 39, 43, 55, 59, and 67 configurations. The latter four wave functions contained all of the configurations in Table I. The five wave functions contained 8, 8, 20, 24, and 32 configurations with "continuum orbitals," respectively. One point which should be considered is that as α increases, the STO's become more diffuse since

$$\begin{aligned}\exp(-\gamma\rho e^{i\alpha}) &= \exp[-\gamma\rho(\cos\alpha + i\sin\alpha)]\\ &= \exp(-\gamma\rho\cos\alpha)\exp(i\gamma\rho\sin\alpha).\end{aligned} \tag{44}$$

After α is sufficiently large for a given "P-space" part, the resonant eigenvalue becomes erratic. Thus, one needs to ensure that the "continuum orbital" basis which is independent of α is sufficiently large to describe the system for the larger values of α.

Figures 4 and 5 summarize the results of the calculations of the resonant energies performed with $p=1.19$. At the angles 0.02, 0.08, 0.2, and 0.8, the real part of the energies for the three lar-

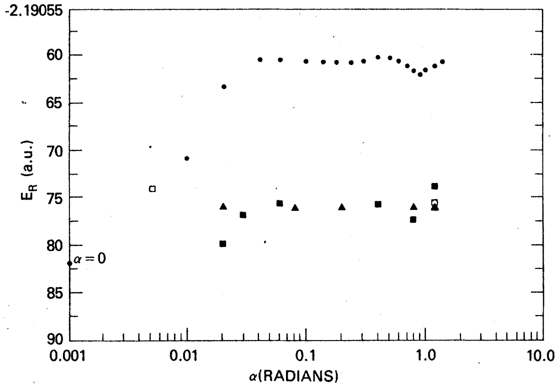

FIG. 4 Real part of the energy for the lowest ^2S resonance of He$^-$ for the five wave functions used; ● 39 configurations, ■ 43 configurations, ▲ 55 configurations, ○ 59 configurations, □ 67 configurations. Note that at $\alpha = 0.02$, 0.08, 0.2 and 0.8 the results for the 59 and 67 configuration wave function are not indicated since they lie on the 55 configuration wave function result.

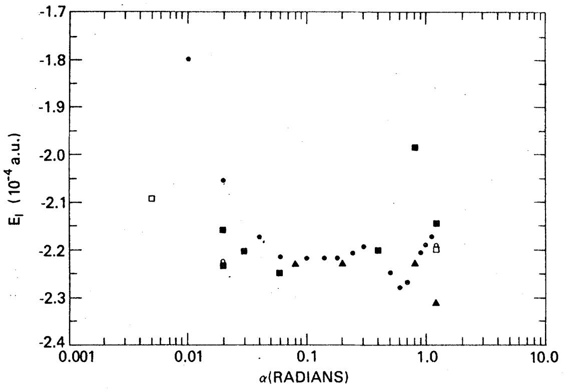

FIG. 5 Imaginary part of the energy for the lowest ^2S resonance of He$^-$ for the five wave functions used. The symbols are the same as in Fig. 4. At $\alpha = 0.08$, 0.2, and 0.8 the three largest wave functions yielded identical results. Also note that the lower solid square at $\alpha = 0.02$ is actually a composite of ▲ and □.

gest wave functions are identical and independent of α to four significant figures. Using the values of -2.190758 a.u. given by the 67-configuration wave function for the real part of the energy, a value of -79.0016 eV for the He ground-state energy, and a conversion factor of 27.211652 eV/a.u., one obtains a value of 19.387 eV for the position of the resonance. The three largest wave functions yielded identical values for the imaginary part of the energy to four significant figures for α values of 0.08, 0.2, and 0.8 and to three significant figures at 0.02. For the 67-configuration wave function the value of the imaginary part at α-values of 0.02, 0.08, 0.2, and 0.8 is -2.228×10^{-4} a.u. This gives a width of 12.13 meV.

Table IV compares the results of this calculation with other calculations and experiments. The experimental values fall basically into two groups—one around 9 meV from differential scattering data and one around 12 meV from transmission experiments. Golden *et al.*[27] state that their values result from an instrumentation improvement and replace previous results of Golden and Zecca.[23] In addition, the unpublished value of 12 meV for the width obtained by Andrick and Enrhardt supersedes their

TABLE IV. Comparison of experiment and theory for the lowest ^2S resonance of He$^-$.

Reference	Method	Energy (eV)	Width (meV)
Andrick and Ehrhardt (Ref. 19)	Transmission	19.3	17.5 ± 2.5
Andrick and Ehrhardt (Ref. 20)	Transmission	19.3	12
Ehrhardt *et al.* (Ref. 21)	Transmission	19.3	12
Gibson and Dolder (Ref. 22)	Differential scattering		8
Golden and Zecca (Ref. 23)	Transmission	19.30 ± 0.01	8 ± 2
Sanche and Schultz (Ref. 24)	Transmission	19.34 ± 0.02	
Mazeau *et al.* (Ref. 25)	Differential scattering	19.35 ± 0.02	
Cvejanovic *et al.* (Ref. 26)	Differential scattering	19.367 ± 0.009	9 ± 1
Golden *et al.* (Ref. 27)	Transmission	19.35 ± 0.02	13
Kwok and Mandl (Ref. 28)	Variational	19.45 ± 0.15	19 ± 11
Burke *et al.* (Ref. 29)	Close coupling	19.33	39
Eliezer and Pan (Ref. 30)	Stabilization	19.3	
Weiss and Krauss (Ref. 31)	Stabilization	19.368	
Temkin *et al.* (Ref. 18)	Quasiprojector operators	19.386	14
Sinfailam and Nesbet (Ref. 32)	Variational	19.4	15
Ormonde and Golden (Ref. 33)	Close coupling	19.38	11.5
Bain *et al.* (Ref. 7)	Complex coordinate	19.398	12
This work	Complex coordinate	19.387	12.1

TABLE V. Complex energies for several values of p. Numbers in parentheses denote powers of 10, e.g., $6.839(-5) = 6.839 \times 10^{-5}$.

p	0.0		1.19		1.50	
α	$-E_R$	$-E_I$	$-E_R$	$-E_I$	$-E_R$	$-E_I$
0.005	2.190 59	6.839(−5)	2.190 74	2.093(−4)	2.190 99	5.049(−5)
0.02	2.190 63	3.062(−5)	2.190 76	2.228(−4)	2.190 92	1.592(−4)
0.08	2.190 61	7.132(−5)	2.190 76	2.228(−4)	2.190 77	2.157(−4)
0.2	2.190 68	2.060(−4)	2.190 76	2.228(−4)	2.190 76	2.228(−4)
0.4	2.190 75	2.254(−4)	2.190 76	2.228(−4)	2.190 76	2.228(−4)
0.8	2.190 75	2.260(−4)	2.190 76	2.228(−4)	2.190 76	2.228(−4)
1.0	2.190 75	2.275(−4)	2.190 76	2.227(−4)	2.190 76	2.228(−4)

previously published value of 17.5 ± 2.5 meV. On the other hand, the theoretical values for the width range from 11.5 to 15 meV if the two earlier calculations are ignored. In fact Ormonde and Golden[33] suggest that the close-coupling calculation of Burke *et al.*[29] is not converged. In addition, if one includes the nonorthogonality of the quasi-Feshbach projectors used by Temkin *et al.*[18] in the derivation of an expression for the width, one obtains several terms[34] in addition to the "golden rule" expression for the width. If the largest of these additional terms is added to the "golden rule" term this width via the quasiprojector technique[34] is 13 meV employing the same wave functions used by Temkin *et al.* Thus, at present, the more recent theoretical values and transmission experiments appear to be in fairly good agreement.

In order to test the sensitivity of the calculation to the value of p used in $\mathcal{S}_\nu^\pm$, we have also computed the resonance parameters using values of 0.0 and 1.5 for p in place of 1.19. The results of these calculations are given in Table V for the 67-configuration wave function. Note, however, that when $p = 0.0$,

$$\mathcal{S}_\nu^+ = \mathcal{S}_\nu^- \tag{45}$$

so that for this value of p, the variational wave function only contains 51 configurations. We see that the two large wave functions yield identical results over a considerable range of α while the smaller wave function yields a value for the imaginary part of the energy which is slightly higher. Even in this case the value of the widths differ by less than 1.5%. Thus, the value of the complex energy appears to be quite insensitive to the particular value of p used in the "continuum orbital" basis. This also indicates that the complex energy is not an overly sensitive function of the asymptotic form of the wave function and thus avoids an iterative procedure to determine p and E in some self-consistent manner. In fact, unlike in any previous application of this method to two-particle systems, the complex energy for this three-electron system is independent of α over about two orders of magnitude of the angle α.

VII. SCATTERING STATE OF $\mathcal{H}_\alpha$ FOR He$^-$

As discussed in Sec. II, the spectrum of $\mathcal{H}_\alpha$ contains energies corresponding to scattering states. These energies are of the form

$$\begin{aligned} E &= E_T + E_s e^{-2i\alpha} \\ &= [E_T + E_s \cos(2\alpha)] - iE_s \sin(2\alpha), \end{aligned} \tag{46}$$

where E_T is the threshold energy which corresponds to an energy of the bound particles and E_s is the energy of the extra particle relative to the threshold value. These energies lie on rays below the real axis which begin at each threshold and make an angle of 2α with the real axis.

Since this is a variational calculation, the energies only approximate the energies of these states. In Figs. 6 and 7, we have plotted the comples energies for all eigenvalues with -3.0 a.u. $< \mathrm{Re}(E) < -1.5$ a.u. for α equal to 0.02 and 0.2, respectively, and $p = 1.19$. A large number of the eigenvalues correspond to scattering states associated with the lowest ^1S threshold of He. In fact, in each figure about a half dozen energies in the vicinity of the dip have been omitted for the sake of clarity.

Although the scattering states associated with the ^1S threshold do not lie exactly on the ray from this threshold, they lie in the general area on a smooth curve with a dip. To understand the source of the dip, consider Eq. (46) with $|k| = 1.19$:

$$\begin{aligned} E &= [E_T + \tfrac{1}{2}|k|^2 \cos(2\alpha)] - i\tfrac{1}{2}|k|^2 \sin(2\alpha) \\ &= [E_T + 0.7081 \cos(2\alpha)] - i0.7081 \sin(2\alpha). \end{aligned} \tag{47}$$

For $\alpha = 0.02$, the real part of the energy of the scattering states with $k = 1.19$ is $E_T + 0.7075$ a.u. and the imaginary part is -0.0283 a.u. On the other hand, when α is 0.2, the corresponding

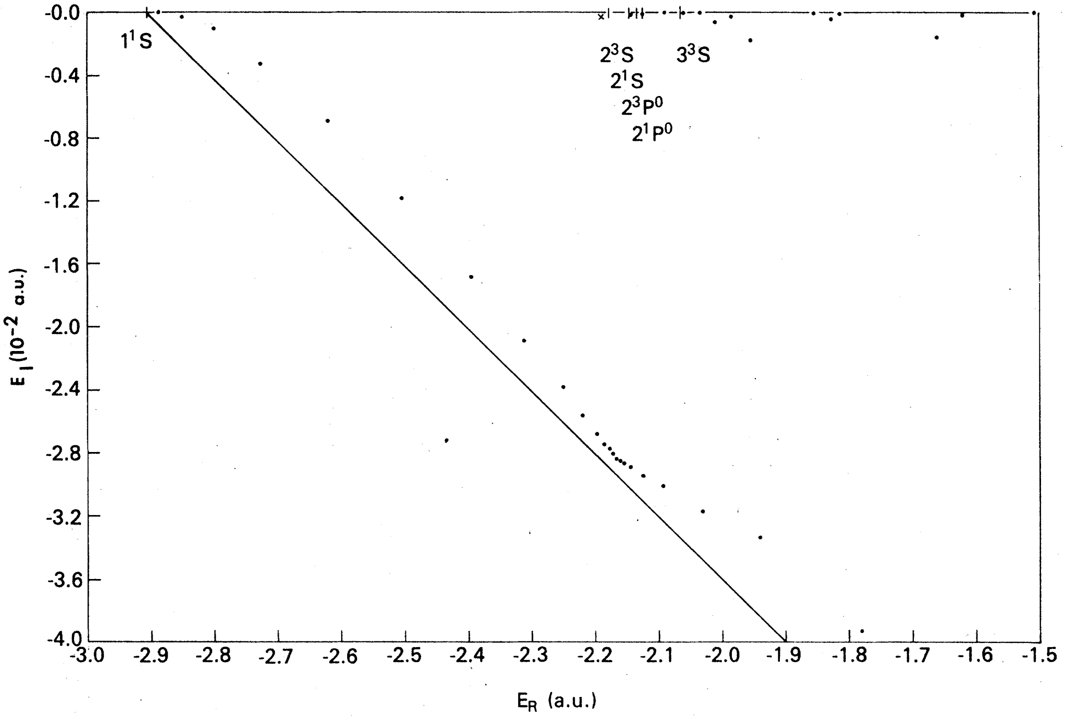

FIG. 6. Eigenvalues of $\mathcal{H}_\alpha$ for $\alpha = 0.02$ for which $+3.0 < |E| < +1.5$ a.u.

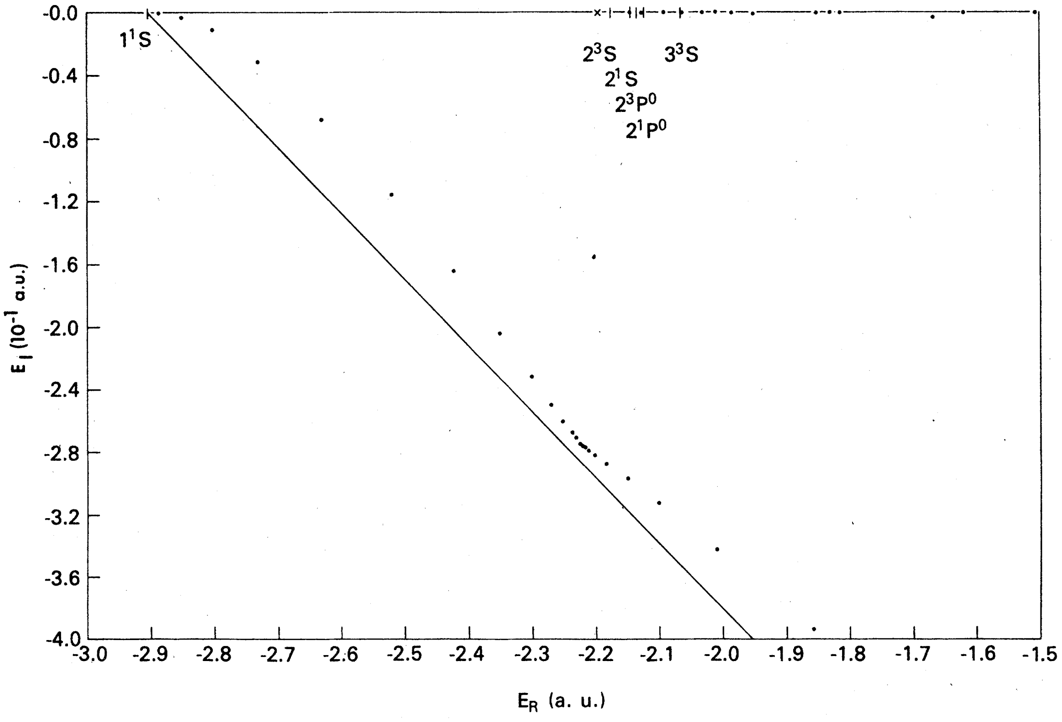

FIG. 7. Eigenvalues of $\mathcal{H}_\alpha$ for $\alpha = 0.2$ for which $+3.0$ a.u. $< |E| < +1.5$. Note the scale difference between Figs. 6 and 7.

quantities are $E_T + 0.6522$ a.u. and -0.2757 a.u. These values agree well with the location of the dips in the curves in the two figures. A similar plot for the $k = 1.5$ calculations yields a similar result with a dip occurring in the complex energy region where

$$E = [E_T + 1.125\cos(2\alpha)] - i1.125\sin(2\alpha). \tag{48}$$

Thus, as one might expect from the nature of the "continuum orbitals," the scattering states for energies in the region given by the above expressions are better represented than those at other energies.

VIII. CONCLUSION

We have obtained the analytic continuation of the wave functions corresponding to the continuation of the Hamiltonian operator. Using these results and an analogy to other techniques for computing resonances, we suggested a partitioning of the wave function into a "boundlike" or "Q-space" part and a "scatteringlike" or "P-space" part as well as a functional form for each. Although we do not have maximum or minimum bounds on the complex energy, we can construct a variational principle. We have used these results to compute the complex energy corresponding to the lowest ^2S resonance in He$^-$ using several variational wave functions. The resulting complex energies obtained are independent of the rotation angle α over about two orders of magnitude of α and agree well with other calculations.

The variational principle basically yields a variational determination of the "continuum orbital" in terms of a basis which consists of free-particle orbitals multiplied by cutoff factors. Although this may not necessarily be an optimum basis, it can be used successfully if one realizes that, while the boundlike functions of $\rho e^{i\alpha}$ expand with increasing α, these functions do not. Thus one must have long-range and short-range functions in the "continuum orbital" basis. In a future publication we will consider other bases.

The inclusion of the "free-particle-like" functions in the basis also improves the representation of the actual scattering states. The energies of these states should lie on rays beginning at the thresholds and making an angle of -2α with respect to the real axis as discussed in Sec. II. We find that the energies of scattering states which satisfy Eq. (46) lie closest to this line.

In conclusion, we have presented an argument suggesting a relationship between the complex-coordinate method and the Siegert boundary condition. In addition, we have presented a discussion and numerical calculations which suggest the basic structure of the resonant wave function. With this technique of constructing the wave function, one can incorporate physical insight into the choice of configurations as one does in other methods and can apply the complex-coordinate method to many-electron systems with an expected rate of convergence similar to other techniques. Its advantages are that a single calculation yields the position and width of the resonance, only square-integrable functions are used, only a solution of a straightforward eigenvalue problem is required unlike some methods, arbitrarily accurate target states are easily incorporated, and polarization terms can easily be explicitly included.

Finally, employing these techniques for constructing the wave functions when applying the complex-coordinate method to other atomic processes, one should be able to improve the rate of convergence and precision of the parameters being calculated. In particular, if "continuum orbitals" with a range of values for p are included in "P-space" configurations in a variational calculation, the scattering states should be better represented. For example, in applying this method to photoionization one could probably get better convergence if one included "continuumlike" orbitals in the energy region corresponding to the ejected particle energy.

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[1] C. Lovelace, in *Strong Interaction and High Energy Physics*, edited by R. C. Moorehouse, (Oliver and Royal, London, 1964); B. Simon, Ann. Math. 97, 242 (1973); C. Van Winter, Math. Anal. App. 49, 88 (1975).

[2] E. Balslev and J. M. Combes, Commun. Math. Phys. 22, 280 (1971).

[3] B. Simon, Commun. Math. Phys. 27, 1 (1972).

[4] J. Nuttall and H. L. Cohen, Phys. Rev. 188, 1542 (1969); F. A. McDonald and J. Nuttall, Phys. Rev. Lett. 23, 361 (1969); F. A. McDonald and J. Nuttall, Phys. Rev. A 4,

1821 (1971); T. N. Rescigno and W. P. Reinhardt, *ibid.* 8, 158 (1974); R. T. Baumel, M. C. Crocker, and J. Nutall. *ibid.* 12, 522 (1975).

[5] T. N. Rescigno and V. McKoy, Phys. Rev. A 12, 522 (1975); T. N. Rescigno, C. W. McCurdy, Jr., and V. McKoy, J. Chem. Phys. 64, 477 (1976); S. I. Chu and W. P. Reinhardt, Phys. Rev. Lett. 39, 1195 (1977).

[6] W. P. Reinhardt, Int. J. Quant. Chem. S10, 359 (1976).

[7] R. A. Bain, J. N. Bardsley, B. R. Junker, and C. V. Sukumar, J. Phys. B 7, 2189 (1974).

[8] G. D. Doolen. J. Nuttall, and R. W. Stagat, Phys. Rev. A 10, 1612 (1974).

[9] G. D. Doolen, J. Phys. B 8, 525 (1975).

[10] R. J. Drachman and S. K. Houston, Phys. Rev. A 12, 885 (1975).

[11] Y. K. Ho, Phys. Rev. A 5, 1675 (1978).

[12] M. Hidalgo, J. Nuttall, and R. Stagat, *Atomic Physics*, edited by S. J. Smith and C. K. Walters, (Plenum, New York, 1973), Vol. 3, p. 257; S. B. Raju and G. Doolen, Phys. Rev. A 9, 1965 (1974); G. D. Doolen, *ibid.* 12, 1121 (1975); A. P. Hickman, A. D. Isaacson, and W. H. Miller, Chem. Phys. Lett. 37, 63 (1976); Y. K. Ho, J. Phys. B Lett. 10, L373 (1977).

[13] B. R. Junker and C. L. Huang, *Abstracts of the Tenth International Conference on The Physics of Electronic and Atomic Collisions, Paris, 1977*, edited by M. Barat and J. Reinhardt (Commisariat à l'Energie Atomique, Paris, 1977), p.614.

[14] There is only one radial coordinate for the *j*th particle, but for clarity we will use ρ_j in the sense defined in Eq. (2).

[15] Y. K. Ho, A. K. Bhatia, and A. Temkin, Phys. Rev. A 15, 1423 (1977).

[16] J. N. Bardsley and B. R. Junker, J. Phys. B 5, L178 (1972).

[17] See for example, L. I. Schiff, *Quantum Mechanics* 2nd ed. (McGraw-Hill, New York, 1955), p. 77.

[18] A. Temkin, A. K. Bhatia, and J. N. Bardsley, Phys. Rev. A 5, 1663 (1972).

[19] D. Andrick and H. Ehrhardt, Z. Phys. 192, 99 (1966).

[20] See footnote 13 of Ref. 21.

[21] H. Ehrhardt, L. Laughans, and F. Linder, Z. Phys. 214, 179 (1968).

[22] J. R. Gibson and K. T. Dolder, J. Phys. B 2, 741 (1969).

[23] D. E. Golden and A. Zecca, Phys. Rev. A 1, 241 (1970); D. E. Golden and A. Zecca, Rev. Sci. Instrum. 42, 210 (1971).

[24] L. Sanche and G. J. Schulz, Phys. Rev. A 5, 1672 (1972).

[25] J. F. Mazeau, F. Gresteau, G. Joyez, J. Reinhardt, and R. I. Hall, J. Phys. B 5, 1890 (1972).

[26] S. Cvejanovic, J. Comer, and F. H. Read, J. Phys. B 7, 468 (1974.

[27] D. E. Golden, F. D. Schowengerdt, and J. Macek, J. Phys. B 7, 478 (1974).

[28] K. L. Kwok and F. Mandl, Proc. Phys. Soc. (Lond.) 86, 501 (1965).

[29] P. G. Burke, J. W. Cooper, and S. Ormonde, Phys. Rev. Lett. 17, 345 (1966); P. G. Burke, J. W. Cooper, and S. Ormonde Phys. Rev. 183, 245 (1969).

[30] I. Elizer and Y. K. Pan, Theor. Chim. Acta 16, 63 (1970).

[31] A. Weiss and M. Krauss, J. Chem. Phys. 52, 4363 (1970).

[32] A. L. Sinfailam and R. K. Nesbet, Phys. Rev. A 6. 2118 (1972).

[33] S. Ormonde and D. E. Golden, Phys. Rev. Lett. 31, 1161 (1973).

[34] B. R. Junker (unpublished).