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## Two-electron wave functions in hyperspherical coordinates

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In order to investigate the potential precision of quantitative calculations using hyperspherical coordinates, we have reexamined this method in detail. By developing an analytic solution of the angular equation in the form of a series expansion in the variable  $x = \tan(\alpha/2)$ , we are able to isolate the numerical errors in the solution from those caused by the truncation of the angular momentum expansion and by the exclusion of radial coupling terms, which we then examine separately. This new method enables us to extend the calculation of the potential curves and channel functions to the large- $R$  region and to obtain asymptotic expansions for the potential curves and radial couplings. From these we determine general expressions for the boundary conditions of the radial equation. Finally, we present the first nonadiabatic result for the ground-state energy of helium.

### I. INTRODUCTION

Hyperspherical coordinates have been frequently used in atomic physics to obtain wave functions in two-electron systems, such as He and  $H^-$ , or more generally in divalent atoms.<sup>1</sup> The method is particularly intended for the construction of wave functions in the continuum with one unbound electron. In this context it was used, in a pioneer work by Macek, to calculate the positions of resonances of helium corresponding to autoionizing states ending on  $n=2$ .<sup>2</sup> This calculation was done in the so-called adiabatic approximation in which the radial equations are decoupled by neglecting off-diagonal coupling coefficients. His results are in qualitative agreement with experiment.<sup>3-6</sup> The classification of states, computation of potential curves, and analysis of correlations for various channels were subsequently given by Lin.<sup>7-10</sup> Further calculations were carried out for the scattering phase shift of  $H^-$ , still within the adiabatic approximation, with satisfactory results only very near threshold.<sup>11</sup> An application of the method to Be and  $K^-$  was performed by Greene,<sup>12</sup> taking into account nonadiabatic couplings and using a Hartree-Fock potential for the atomic core. An examination of the large- $R$  behavior through the introduction of "diabatic states" was performed by Christensen-Dalsgaard.<sup>13</sup> A critical discussion of the method and some suggestions for improvement have been given by Macek in a recent publication.<sup>14</sup> However, it is apparent from this work that the question of whether the hyperspherical method is really suitable for a more quantitatively accurate construction of wave functions is still undecided. Therefore, a careful analysis of this method aimed at evaluating its accuracy and appraising its potential for precision computation of wave functions is warranted. The results of this analysis are presented in this paper.

Section II reproduces material which already exists in the literature;<sup>1,2</sup> we include it here in order to make this

paper more self-contained and to establish notation. The Schrödinger equation is written in hyperspherical coordinates consisting of the angular variables of the electrons  $\Omega_1(\theta_1, \phi_1)$ ,  $\Omega_2(\theta_2, \phi_2)$  and two variables,  $\alpha$  and  $R$ , related to the radial coordinates by

$$r_1 = R \sin \alpha, \quad r_2 = R \cos \alpha.$$

The wave function for a state of total angular momentum  $L$  with azimuthal component  $M$  and principal quantum number  $K$  is expressed in the form

$$\Psi^{KLM}(\mathbf{r}_1, \mathbf{r}_2) = \sum_{\mu, l_1, l_2} (R^{5/2} \sin \alpha \cos \alpha)^{-1} F_{\mu}^{KL}(R) \times u_{\mu l_1 l_2}^L(R, \alpha) Y_{l_1 l_2}^{LM}, \quad (1)$$

where  $Y_{l_1 l_2}^{LM}$  represents a state in which the two electrons have angular momentum  $l_1$  and  $l_2$ , respectively;  $u_{\mu l_1 l_2}^L(R, \alpha)$  are the components with indices  $l_1, l_2$  of a channel function labeled by a discrete quantum number  $\mu$  (or a set of quantum numbers). They are solutions of coupled Schrödinger equations in the variable  $\alpha$ , with  $R$  as a parameter. The eigenvalues  $U_{\mu}^L(R)$  become potential functions for the multicomponent radial wave functions  $F^{KL}(R) = \{F_{\mu}^{KL}(R)\}$ , where  $\mu$  is a component index and  $K$  stands for a set of quantum numbers, including the energy. The sum in  $l_1, l_2$  in Eq. (1) is restricted to a finite number of terms by imposing on them a cutoff  $l_1, l_2 \leq l_{\max}$ . A cutoff in the  $\mu$  index has to be made as well.

In Sec. III the analytic structure of the functions  $u_{\mu l_1 l_2}^L$  in the variable  $x = \tan(\alpha/2)$  is investigated, and an analytic solution is obtained in the form of a power-series expansion. The expansion coefficients, which depend on the parameter  $R$ , are determined by means of recursion relations. The  $R$  dependence of the angular functions and

the potential curves is discussed, with particular attention to the behavior of the potential curves as they avoid crossing, and to the asymptotic forms for large  $R$ . A classification of these wave functions based on the  $R=0$  and  $R=\infty$  solutions is briefly reviewed.

In Sec. IV we describe a computer code designed to solve numerically the recursion relations and to determine the potential functions. An analysis of the error propagation in the expansion coefficients, particularly relevant for large  $R$ , serves to control the precision of the calculated potential curves and channel functions. The code also normalizes the channel functions and computes the radial coefficients  $P_{\mu\nu}(R)$  and  $Q_{\mu\nu}(R)$ . Results are presented for the singlet  $S=0$  states of helium with  $L=0$  and principal quantum numbers  $n=1, 2$ , and  $3$ .

In Sec. V we analyze the truncation of the expansion (1) both by a cutoff  $l_{\max}$  on the angular momentum states and by the exclusion of channel functions  $u_{\mu}^L(R, \alpha)$  with principal quantum numbers  $n \geq l_{\max} + 1$ . For  $L=0$ ,  $S=0$ , we compare potential curves calculated using values of  $l_{\max}$  from 0 to 3. In the absence of electron-electron interaction the system of equations for  $u_{\mu}^{L, l_1, l_2}$  decouples as  $l_1, l_2$  become good quantum numbers. In this case we can compare exact Coulomb solutions with their expansion in terms of the orthogonal functions  $u_{\mu}^L(R, \alpha)$ . This was done for the ground-state wave function ( $L=0, l_1=l_2=0$ ) using  $\mu$  values corresponding to the four lowest curves  $U_{\mu}^0(R)$ .

In Sec. VI we consider the radial equation. In subsection A the boundary conditions are formulated for bound states and for states in the continuum. In the adiabatic approximation the wave function is regular at  $R=0$ . However, for the system of coupled equations one recovers the long-established logarithmic singularities.<sup>17-19</sup> At large  $R$ ,  $P_{\mu\nu}(R)$  behaves as  $p_{\mu\nu}^{(1)}/R$ .<sup>14</sup> We have derived an expression for  $p_{\mu\nu}^{(1)}$  which shows that it vanishes when the states  $u_{\mu}$  and  $u_{\nu}$  become degenerate at  $R=\infty$ , i.e., they have principal quantum numbers  $n_{\mu}=n_{\nu}$  at  $R=\infty$ . The boundary conditions at  $R=0$  and at large  $R$  require an expansion of the potentials and radial coefficients in powers of  $R$  and  $1/R$ , respectively. The first coefficients in these expansions are determined by means of perturbation theory.<sup>2</sup> Numerical calculation of higher-order coefficients for large  $R$  requires rather precise determination of the potentials and wave functions. In subsection B we present results for  $L=0$  of the expansion coefficients for the potential curves with principal quantum numbers  $n=1, 2, 3$  and for the  $P_{\mu\nu}$ 's between the ground state and excited states with  $n=2$  and  $3$ .

We have performed the calculation of the ground-state wave function of helium using one- and two-channel functions and four states of angular momentum ( $l_1=l_2=0, 1, 2, 3$ ). The energy eigenvalue found in the latter, nonadiabatic, case is  $E=-2.899$ . Finally in the last section we present a summary of the results of our analysis.

## II. SCHRÖDINGER EQUATION IN HYPERSPHERICAL COORDINATES

### A. Potential curves and channel functions

The nonrelativistic Schrödinger equation in hyperspherical coordinates  $R, \alpha, \Omega_1, \Omega_2$  for two electrons in a central potential  $Z(r)$  is<sup>1,2</sup>

$$\left[ - \left( \frac{\partial^2}{\partial R^2} + \frac{1}{4R^2} \right) - \frac{1}{R^2} \frac{\partial^2}{\partial \alpha^2} + \frac{1}{R^2} \left( \frac{\mathbf{L}_1^2}{\sin^2 \alpha} + \frac{\mathbf{L}_2^2}{\cos^2 \alpha} \right) - \frac{2}{R} \left( \frac{Z(R \sin \alpha)}{\sin \alpha} + \frac{Z(R \cos \alpha)}{\cos \alpha} \right) \right] + \frac{2}{R} [1 - \sin(2\alpha) \cos \theta_{12}]^{1/2} - 2E \left( \psi R^{5/2} \sin \alpha \cos \alpha \right) = 0 \quad (2)$$

and we are using atomic units throughout. We introduce the wave functions  $\phi = R^{5/2} \sin \alpha \cos \alpha \psi$  which are defined in a Hilbert space with coordinates  $R, \alpha, \Omega_1(\theta_1, \phi_1), \Omega_2(\theta_2, \phi_2)$ , and measure of integration  $dR d\alpha d\Omega_1 d\Omega_2$ . As the total angular momentum  $\mathbf{L} = \mathbf{L}_1 + \mathbf{L}_2$  commutes with the Hamiltonian, one chooses a basis  $\Phi^{KLM}$  in the space of eigenstates of the total angular momentum operator  $L^2$  with eigenvalue  $L(L+1)$  and of its azimuthal component with eigenvalue  $M$ .  $K$  is the set of principal quantum numbers, including the energy. These eigenstates can be expanded in terms of generalized spherical harmonics  $\mathbf{Y}^{LM}_{l_1, l_2}(\Omega_1, \Omega_2)$  defined by

$$\mathbf{Y}^{L, M}_{l_1, l_2}(\Omega_1, \Omega_2) = \sum_{m_1, m_2} \langle l_1, m_1, l_2, m_2 | L, M \rangle \times Y_{l_1}^{m_1}(\Omega_1) Y_{l_2}^{m_2}(\Omega_2), \quad (3)$$

where  $l_1$  and  $l_2$  are the orbital angular momenta of the individual electrons. Thus we shall write

$$\Phi^{KLM}_{l_1, l_2} = \sum_{l_1, l_2} \omega^{KL}_{l_1, l_2}(R, \alpha) \mathbf{Y}^{L, M}_{l_1, l_2}(\Omega_1, \Omega_2) \quad (4)$$

and the functions  $\omega^{KL}_{l_1, l_2}(R, \alpha)$  are solutions of the infinite system of coupled equations

$$\left[ - \left( \frac{\partial^2}{\partial R^2} + \frac{1}{4R^2} \right) - \frac{1}{R^2} \frac{\partial^2}{\partial \alpha^2} + \frac{1}{R^2} \left( \frac{l_1(l_1+1)}{\sin^2 \alpha} + \frac{l_2(l_2+1)}{\cos^2 \alpha} \right) - \frac{2}{R} \left( \frac{Z(R \sin \alpha)}{\sin \alpha} + \frac{Z(R \cos \alpha)}{\cos \alpha} \right) - 2E \right] \times \omega^{KL}_{l_1 l_2}(R, \alpha) + \frac{2}{R} \sum_{l'_1, l'_2} C^L_{l_1 l_2 l'_1 l'_2}(\alpha) \omega^{KL}_{l'_1 l'_2}(R, \alpha) = 0 \quad (5)$$

with the symmetry implied by the Pauli principle:

$$\omega^{KL}_{l_1 l_2}(R, \pi/2 - \alpha) = (-1)^{L+S+l_1+l_2} \omega^{KL}_{l_2 l_1}(R, \alpha). \quad (6)$$

Here  $S=0,1$  is the total spin of the electron pair. The coefficients  $C^L_{l_1 l_2 l'_1 l'_2}(\alpha)$  are invariant under the transformation  $\alpha \rightarrow \pi/2 - \alpha$ . For  $\alpha$  in the interval  $(0, \pi/4)$  they are given by

$$C^L_{l_1 l_2 l'_1 l'_2}(\alpha) = \frac{1}{\cos \alpha} \sum_j (\tan \alpha)^j C^{Lj}_{l_1 l_2 l'_1 l'_2}, \quad (7)$$

where the coefficients  $C^{Lj}_{l_1 l_2 l'_1 l'_2}$  are defined in Ref. 1.

In the absence of the electron-electron interaction, the equations for  $\omega^{KL}_{l_1 l_2}$  decouple as  $l_1$  and  $l_2$  become good quantum numbers. The equations for the noninteracting system are completely separable in the variables  $R$  and  $\alpha$ . The solutions are of the form

$$\left[ \frac{\partial^2}{\partial \alpha^2} - \frac{l_1(l_1+1)}{\sin^2 \alpha} - \frac{l_2(l_2+1)}{\cos^2 \alpha} + 2R \left( \frac{Z(R \sin \alpha)}{\sin \alpha} + \frac{Z(R \cos \alpha)}{\cos \alpha} \right) \right] u^L_{\mu l_1 l_2} + 2R^2 U^L_{\mu}(R) - 2R \sum_{l'_1, l'_2} C^L_{l_1 l_2 l'_1 l'_2}(\alpha) u^L_{\mu l'_1 l'_2} = 0. \quad (11)$$

The  $U^L_{\mu}(R)$ 's are potential curves determined by the imposition of regular boundary conditions at  $\alpha=0, \pi/2$  and the symmetry due to the Pauli principle. It is often convenient to use the functions  $W^L_{\mu}(R) = 2R^2 U^L_{\mu}(R)$ . The functions  $u^L_{\mu l_1 l_2}(R, \alpha)$  shall be regarded as the components of a multicomponent wave function  $u^L_{\mu}(R, \alpha)$  belonging to an orthogonal set in the space of the coordinate  $\alpha$ . We shall normalize them by

$$\int_0^{\pi/2} \sum_{l_1, l_2} u^L_{\mu l_1 l_2}(R, \alpha) u^L_{\nu l_1 l_2}(R, \alpha) d\alpha = \delta_{\mu\nu}. \quad (12)$$

Five-dimensional channel functions  $\phi^L_{\mu}(R, \alpha, \Omega_1, \Omega_2)$  are then constructed according to

$$\phi^L_{\mu}(R, \alpha, \Omega_1, \Omega_2) = \sum_{l_1, l_2} u^L_{\mu l_1 l_2} Y^{LM}_{l_1 l_2}(\Omega_1, \Omega_2). \quad (13)$$

Since we are considering states of well-defined  $L$ , to simplify the notation we will henceforth drop the superscript  $L$ .

In order to handle the system of Eqs. (11) one has to reduce it to a finite one by restricting the values of  $\{l_1, l_2\}$  in the expansion (4) by imposing a condition such as  $l_1, l_2 \leq l_{\max}$ .

$$\omega^{KL}_{l_1 l_2}(R, \alpha) = \sum_j R^{1/2} J_m(R\sqrt{2E}) (\sin \alpha)^{l_1+1} (\cos \alpha)^{l_2+1} \times P_j^{(l_1+1/2, l_2+1/2)}(\cos(2\alpha)) \quad (8)$$

where  $J_m$  is a Bessel function with index

$$m = 2j + l_1 + l_2 + 2 \quad (9)$$

and  $P_j^{(l_1+1/2, l_2+1/2)}$  is a Jacobi polynomial<sup>15</sup> with integer index  $j$ .

When the interactions are turned on, the Eqs. (5) no longer separate. There is some freedom of choice of a basis for the expansion of  $\omega^{KL}_{l_1 l_2}(R, \alpha)$  regarded as a function of the angular variable  $\alpha$ . We shall follow here a standard procedure<sup>1,2</sup> of separating  $\omega$  in the form

$$\omega^{KL}_{l_1 l_2}(R, \alpha) = \sum_{\mu} F^{\mu KL}(R) u^L_{\mu l_1 l_2}(R, \alpha), \quad (10)$$

where  $u^L_{\mu l_1 l_2}(R, \alpha)$  are solutions, specified by a set of discrete quantum numbers  $\mu$ , of the system of equations

## B. The radial equations

The radial equations for the expansion coefficients  $F_{\mu}(R)$  are obtained by taking projections of Eq. (5) on the basis of functions  $u_{\mu}(R, \alpha)$ . The result is

$$\left[ \left( \frac{\partial^2}{\partial R^2} + \frac{1}{4R^2} \right) - 2U_{\mu}(R) + 2E \right] F_{\mu}(R) + \sum_{\nu} \left[ 2P_{\mu\nu}(R) \frac{\partial}{\partial R} + Q_{\mu\nu}(R) \right] F_{\nu}(R) = 0, \quad (14)$$

where the nonadiabatic couplings are given by

$$Q_{\mu\nu}(R) = \left\langle u_{\mu} \left| \frac{\partial^2}{\partial R^2} u_{\nu} \right. \right\rangle, \quad (15)$$

$$P_{\mu\nu}(R) = \left\langle u_{\mu} \left| \frac{\partial}{\partial R} u_{\nu} \right. \right\rangle. \quad (16)$$

Here the brackets denote integration over the variable  $\alpha$  and summation over the pair of indices  $l_1, l_2$ .

An expression for the  $P_{\mu\nu}$ 's which does not involve derivatives of the wave functions and for the  $Q_{\mu\nu}$ 's with first-order derivatives only can be obtained by taking the

derivative with respect to  $R$  of the equation for  $u_\mu(R, \alpha)$  and integrating in  $\alpha$  with  $u_\nu(R, \alpha)$ . This also gives an expression for the slope of the potential curve. One finds

$$(i) \text{ for } \mu = \nu, \quad \dot{W}_\mu = 2 \langle u_\mu | V | u_\nu \rangle, \quad (17)$$

$$(ii) \text{ for } \mu \neq \nu, \quad P_{\mu\nu} = -2 \langle u_\mu | V | u_\nu \rangle / (W_\mu - W_\nu). \quad (18)$$

A dot designates differentiation with respect to  $R$  and the angle brackets have the same meaning as in (15) and (16).  $V$  is the following matrix:

$$V_{l'_1 l'_2 l_1 l_2}(\alpha) = -Z \left[ \frac{1}{\sin \alpha} + \frac{1}{\cos \alpha} \right] \delta_{l'_1 l_1} \delta_{l'_2 l_2} + C^L_{l'_1 l'_2 l_1 l_2}(\alpha). \quad (19)$$

The  $Q$ 's are then calculated by

$$Q_{\mu\nu} = \dot{P}_{\mu\nu} - \langle \dot{u}_\mu | \dot{u}_\nu \rangle = \dot{P}_{\mu\nu} - \sum_\lambda P_{\mu\lambda} P_{\nu\lambda}. \quad (20)$$

Therefore in (14) the operator

$$\left[ 2P_{\mu\nu} \frac{d}{dR} + Q_{\mu\nu} \right]$$

can be written as

$$\left[ P_{\mu\nu} \frac{d}{dR} + \frac{d}{dR} P_{\mu\nu} - \langle \dot{u}_\mu | \dot{u}_\nu \rangle \right], \quad (21)$$

which is manifestly Hermitian. At  $R=0$ ,  $\dot{W}_\mu$  and the  $P_{\mu\nu}$ 's can be calculated by first-order perturbation theory.

$$\left[ \frac{1}{4}(1+x^2) \frac{d}{dx} (1+x^2) \frac{d}{dx} - (1+x^2)^2 \left[ \frac{l_1(l_1+1)}{4x^2} + \frac{l_2(l_2+1)}{(1-x^2)^2} \right] + 2ZR(1+x^2) \left[ \frac{1}{2x} + \frac{1}{1-x^2} \right] + W(R) \right] u_{l_1 l_2} - 2R \frac{1+x^2}{1-x^2} \sum_{J, l'_1, l'_2} \left[ \frac{2x}{1-x^2} \right]^J C^{LJ}_{l_1 l_2 l'_1 l'_2} u_{l'_1 l'_2} = 0 \quad (22)$$

for  $x$  in the interval  $(0, x_0)$  where  $x_0 = \tan(\pi/8) = \sqrt{2} - 1$ . For  $x_0 \leq x \leq 1$  one has to replace in the electron-electron interaction  $\alpha$  by  $(\pi/2 - \alpha)$  which transforms  $x$  to  $y = (1-x)/(1+x)$ . Because of the symmetry of the Hamiltonian it is sufficient to solve this system of equations in the interval  $(0, x_0)$  and use the conditions

$$u_{\mu l_1 l_2}(R, x) = (-1)^{L+S+l_1+l_2} u_{\mu l_2 l_1}(R, y) \quad (23)$$

set by the Pauli principle to determine the wave functions throughout the interval  $0 \leq x \leq 1$ . Finally we impose the continuity of the wave function and its first derivative at  $x = x_0$ :

### III. THE ANGULAR WAVE FUNCTIONS

#### A. Analytic solutions of the angular equations

We shall now consider the system (11) of  $N_e$  coupled equations, where  $N_e$  is found in terms of  $L$ ,  $l_{\max}$ , and the parity  $P = (-1)^{l_1+l_2}$  of the state, to be

$$N_e = S(l_{\max} + \epsilon) - S(l_{\max} - 2L - \epsilon),$$

where

$$\epsilon = [1 + (-1)^L P] / 2$$

and

$$S(n) = \begin{cases} 0, & n < 0 \\ n(n+2)/4, & n = \text{even integer} \\ (n+1)^2/4, & n = \text{odd integer} \end{cases}$$

The coefficients in these equations are singular at the boundaries  $\alpha = (0, \pi/2)$  of the physical region. The physical solutions are required to be regular at these points.

A number of methods have been employed in the solution of this system of equations. As pointed out by Lin,<sup>16</sup> early methods suffer limitations in the form of numerical instabilities, lack of convergence at large  $R$ , and inaccuracies when a large number of channels is introduced. These problems hindered the calculation of the nonadiabatic coupling terms as well as the investigation of the convergence of the angular momentum expansion. We have developed here an analytic approach which is not beset by these difficulties for the specific case of a Coulomb central potential  $Z(r) = Z/r$ . For this purpose it is convenient to introduce a new variable  $x = \tan(\alpha/2)$ , so that the coefficients of the differential Eqs. (11) become rational functions of  $x$ . The equations then read

$$u_{\mu l_1 l_2}(R, x_0) = (-1)^{L+S+l_1+l_2} u_{\mu l_2 l_1}(R, x_0), \quad (24)$$

$$\left. \frac{d}{dx} u_{\mu l_1 l_2}(R, x) \right|_{x=x_0} = -(-1)^{L+S+l_1+l_2} \left. \frac{d}{dy} u_{\mu l_2 l_1}(R, y) \right|_{y=x_0}. \quad (25)$$

These boundary conditions determine the eigenvalue  $W_\mu(R)$ .

Let us now study the analytic structure of this system of differential equations. In the absence of the electron-electron interaction there are regular singularities at  $x = 0, \infty, \pm 1$ , and  $\pm i$ . The electron-electron interaction is not

represented by the same analytic function in the two intervals  $(0, x_0)$  and  $(x_0, 1)$ . Although the system of Eqs. (22) with or without electron-electron interaction has the same analytic structure, except for the nature of the singularities at  $x = \mp 1$ , the analytic continuation of its solution from the interval  $(0, x_0)$  to  $(x_0, 1)$  coincides with the function obtained by using (23) only in the absence of the electron-electron interaction. Since this interaction is continuous at  $x = x_0$  but its first derivative is not, the conditions (24) and (25) ensure the continuity of the wave functions and their derivatives up to second order only.

The singularities at  $x = 0$  and at  $x = 1$  are at the boundaries of the physical region. Their indicial equations are

$$s_i(s_i - 1) = l_i(l_i + 1), \quad (i = 1, 2)$$

with solutions  $s_i = l_i + 1$  and  $s_i = -l_i$ . The physical wave functions correspond to solutions whose indices have values  $(l_1 + 1)$  at  $x = 0$  and  $(l_2 + 1)$  at  $x = 1$ . These regular solutions can be represented in the interval  $(0, x_0)$  by a power-series expansion in  $x$  with a radius of convergence  $x = 1$ , since the nearest singularity to the origin lies on the unit circle. The fact that all the singularities other than at  $x = 0$  and  $x = \infty$  lie on the unit circle indicates that the choice of the variable  $x$  is the best for a power-series representation of the wave functions in the interval  $(0, x_0)$ . The indicial equation for the singular points  $x = \mp i$  is  $s^2 = 2R^2U(R) = W(R)$ .

At  $R = 0$  the eigenvalues are  $W(R) = m^2$  where  $m$  is an integer given by (9). In the regular solution (8)  $P_j^{(l_1+1/2, l_2+1/2)}(\cos 2\alpha)$  is a polynomial of degree  $j$  in  $\cos 2\alpha$ , hence the index of this solution is  $-m$ . The indices  $s = \mp \sqrt{2U(R)}$  will be imaginary when  $U(R)$  becomes negative. It is not difficult to see that two real independent solutions behave as  $\exp[\mp \alpha R \sqrt{-2U(R)}]$  and the solution which is regular at  $x = 0$  will be of the form

$$u_{\mu_1 l_2}(R, x) = u_{\mu_1 l_2}^-(R, x) \exp[-\alpha R \sqrt{-2U(R)}] + u_{\mu_1 l_2}^+(R, x) \exp[+\alpha R \sqrt{-2U(R)}]. \quad (26)$$

$$g_{\mu_1 l_2}(R, x_0) = (-1)^{L+S+l_1+l_2} g_{\mu_1 l_2}(R, x_0), \quad (30)$$

$$\left[ \frac{d}{dx} g_{\mu_1 l_2}(R, x) \right]_{x=x_0} - \frac{2}{1+x_0^2} [2jx_0 + E(R)] g_{\mu_1 l_2}(R, x_0) = -(-1)^{L+S+l_1+l_2} \left[ \frac{d}{dx} g_{\mu_2 l_1}(R, x) \right]_{x=x_0} - \frac{2}{1+x_0^2} [2jx_0 + E(R)] g_{\mu_2 l_1}(R, x_0). \quad (31)$$

From (30) and (31) one obtains a set of homogeneous equations for the coefficients  $A_{\mu_1 l_2}(R, 0)$  which are eigenvalue equations for the potential functions  $W(R)$ .

#### B. $R$ dependence of the angular functions

At  $R = 0$  the solution of the angular equation with quantum numbers  $j, l_1, l_2$  is given by Eq. (8), with eigenvalue  $W_\mu(0) = m^2$  and  $m$  given by (9). For a given value

The imposition of the boundary condition at  $x = x_0$  suppresses the increasing exponential term by a factor  $\approx \exp[-(\pi/2)R\sqrt{-2U}]$ . Actually in the absence of the electron-electron interaction  $u^-$  and  $u^+$  are related by

$$u_{\mu_1 l_2}^+(R, x) = (-1)^{L+S+l_1+l_2} u_{\mu_2 l_1}^-(R, y) \times \exp\left[-\frac{\pi}{2} R \sqrt{-2U(R)}\right]. \quad (27)$$

For large  $R$ ,  $2U(R)$  approaches an eigenvalue  $-Z^2/n^2$  of the Coulomb Hamiltonian for a single electron, and the behavior of the wave function is dominated by the decreasing exponential in the range  $(\pi/4 - \alpha)R \gg 1$ . This analysis suggests a representation for the wave function with quantum number  $m$ , in the interval  $(0, x_0)$ , of the form

$$u_{\mu_1 l_2}(R, \alpha) = (2x)^{l_1+1} (1-x^2)^{l_2+1} (1+x^2)^{-m} \times \exp[-\alpha E(R)] g_{\mu_1 l_2}(R, x), \quad (28)$$

where  $g_{\mu_1 l_2}(R, x)$  has a power-series expansion:

$$g_{\mu_1 l_2}(R, x) = \sum_{k=0}^{\infty} A_{\mu_1 l_2}(R, k) x^k \quad (29)$$

and  $E(R)$  behaves as  $R\sqrt{-2U(\infty)}$  for large  $R$  and vanishes at  $R = 0$ . For practical reasons we have chosen  $E(R) = R\sqrt{-2U(\infty)}$ . The first factor in (28) will ensure the proper behavior of the wave function at  $x = 0$ ; the second was introduced for convenience and could have been left out; the third will improve the convergence for small  $R$ ; while the exponential will improve the convergence for large  $R$ . Upon inserting the expression (28) in the Eq. (22), one obtains a system of differential equations for the functions  $g_{\mu_1 l_2}(R, x)$ . Substitution of these functions by their power expansion (29) generates recursion formulas for the coefficients  $A_{\mu_1 l_2}(R, k)$ . The boundary conditions for  $g_{\mu_1 l_2}(R, x)$  are

of  $m$  one obtains a degenerate set of solutions.

As one moves away from  $R = 0$ , the degeneracy is removed by the interactions. Each energy eigenstate will have a limit for  $R \rightarrow 0$  which is a linear combination of Jacobi polynomial solutions that can be obtained by first-order perturbation theory. These eigenstates can be classified by a set  $\mu = (j_1, j_2, j)$  of positive numbers according to the following rule. If the electron-electron interaction is adiabatically switched off, the wave function reduces to a

pair of components with indices  $l_1, l_2$  and  $l_2, l_1$ . The set  $(j_1, j_2)$  is given by the pair  $(l_1, l_2)$  subjected to the condition  $j_1 \leq j_2$ , and  $j$  is defined in terms of the eigenvalue at  $R=0$  by (9). The range of values of these numbers for states of total orbital angular momentum  $L$ , total spin  $S$ , and parity  $P = (-1)^{j_1+j_2}$ , corresponding to potential curves which start at the same value  $W(0) = m^2$  at  $R=0$ , is given by

- (i)  $0 \leq j_2 - j_1 \leq L \leq j_2 + j_1 \leq m - 2$ ;
- (ii)  $j \leq (m - L - 2)/2$ ;
- (iii) if  $j_1 = j_2$ , then  $(-1)^j = (-1)^{L+S}$ .

$$V_{l_1 l_2 l'_1 l'_2}^L(R, \alpha) = \left[ \frac{l_1(l_1+1)}{2\rho^2} - \frac{Z}{\rho} - \frac{Z-1}{R} + \left[ \frac{1}{6}l_1(l_1+1) + \frac{1}{2}l_2(l_2+1) - \frac{Z}{6}\rho \right] \frac{1}{R^2} \right] \times \delta_{l_1 l'_1} \delta_{l_2 l'_2} + \frac{\rho}{R^2} C_{l_1 l_2 l'_1 l'_2}^{L1} + O(R^{-3}). \quad (32)$$

Accordingly the wave function has an asymptotic expansion of the form

$$u_\mu(R, \alpha) = \Lambda(R) \sum_{k=0} \{ u_\mu^{(k)}(R\alpha) + (-1)^{L+S+l_1+l_2} \times [u_\mu^{(k)}(R(\pi/2-\alpha))]^T \} / R^k, \quad (33)$$

where  $(u_{\mu l_1 l_2}^{(k)})^T = u_{\mu l_2 l_1}^{(k)}$  and  $\Lambda(R)$  is a normalization factor which for  $R \rightarrow \infty$  behaves as  $(R/2)^{1/2}$ . To order  $1/R$  the equations for  $u_{\mu l_1 l_2}$  separate; the eigenfunctions are bound-state Coulomb functions with eigenvalue  $W_\mu = -(Z^2/n_\mu^2) + 2(Z-1)/R$ . In this approximation there will in general be a set of degenerate eigenstates  $u_\mu^{(0)}(\rho)$  with the same eigenvalue  $n_\mu$ . We shall say that the indices  $\mu$  and  $\nu$  of the channel functions  $u_\mu$  and  $u_\nu$  belong to the same equivalence class,  $\mu \sim \nu$ , if  $n_\mu = n_\nu$ . This degeneracy is removed in the next order,  $1/R^2$ . The components of the zeroth-order wave function  $u_\mu^{(0)}(\rho)$  are expressed in terms of bound-state Coulomb wave functions  $\psi_{nl}(\rho)$  by

$$u_{\mu l_1 l_2}^{(0)}(\rho) = a_{\mu l_1 l_2} \psi_{n l_1}(\rho); \quad (n = n_\mu), \quad (34)$$

where the  $\psi$ 's are normalized by

$$\int \psi_{n l_1}(\rho) \psi_{n l_1}(\rho) d\rho = \delta_{n l_1} \quad (35)$$

and  $a_{\mu l_1 l_2} = 0$  if  $l_1 > n - 1$ . For  $l_1 \leq n - 1$ , the  $a$ 's are the orthonormalized solutions of the eigenvalue equations:

$$\sum_{l'_1, l'_2} V_{n; l_1 l_2 l'_1 l'_2}^{(2)} a_{\mu l'_1 l'_2} = U_\mu^{(2)} a_{\mu l_1 l_2}, \quad (36)$$

where  $V_{n; l_1 l_2 l'_1 l'_2}^{(2)}$  is the matrix element of the coefficient of the  $1/R^2$  term in the effective potential between states  $\psi_{n l_1}$  and  $\psi_{n l_2}$ .

The channel states can likewise be classified in terms of

In the absence of the electron-electron interaction the Eqs. (22) decouple. The eigenvalues  $W_\mu(R)$  for two different eigenfunctions, with the same quantum numbers  $L, S, P$  do, in some instances, cross at some value  $R_0$  of  $R$ . However when the electron-electron interaction is turned on and a sufficiently large value of  $l_{\max}$  is chosen, the potential curves always avoid crossing.

At large  $R$ , the equation for the channel functions  $u_\mu^L(R, \alpha)$  may be written, following Macek,<sup>2</sup> in terms of the variable  $\rho = R\alpha$ , for  $\alpha \leq \pi/4$ ; the effective potential expanded in inverse powers of  $R$  is then given by

a set  $\mu = \{n_1, n_2, n\}$ , where  $n$  is the principal quantum number and  $n_1, n_2$  are given by the angular momenta  $l_1, l_2$  of the leading component of the asymptotic wave function as  $R \rightarrow \infty$ , with the electron-electron interaction turned off.

For states of given  $L$ , the range of these numbers is

- (i)  $|n_2 - n_1| \leq L \leq n_2 + n_1$ ,
- (ii)  $n_1 \leq n - 1$ .

Because of avoided crossings the correspondence be-

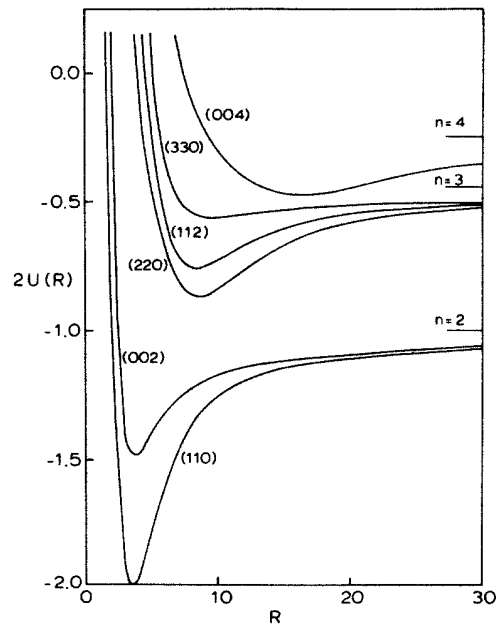


FIG. 1. Excited-state potential curves. The curves are labeled according to the convention  $(j_1, j_2, j)$ , where  $j$  is defined by Eq. (9). Note the avoided crossing of the (330) and (004) curves at  $R \approx 15$  brought about by the electron-electron interaction.

tween the labels  $(j_1, j_2, j)$  and  $\{n_1, n_2, n\}$  is not the same with and without electron-electron interaction. An example of an avoided crossing is shown in Fig. 1 between the curves (3,3,0) and (0,0,4). In the absence of electron-electron interaction they start off at  $m=8$  and  $m=10$ , cross at some value of  $R$  and end up at  $n=4$  and  $n=3$ , respectively, with corresponding labels  $\{3,3,4\}$  and  $\{0,0,3\}$ . Actually the situation is somewhat more complicated because the curve (0,0,4) also crosses the curves (1,1,2) and (2,2,0) which both end at  $n=3$ . With the electron-electron interaction included, all the crossings are avoided. Then the three curves ending at  $n=3$ , namely  $\{0,0,3\}$ ,  $\{1,1,3\}$ , and  $\{2,2,3\}$  will be respectively identified with (2,2,0), (1,1,2), and (3,3,0). Other examples are given in Ref. 1.

#### IV. COMPUTATIONAL ANALYSIS

##### A. Numerical methods

We have written a computer code to calculate the angular wave functions  $u_{\mu l_1 l_2}^L(R, \alpha)$  and the potential curves  $U_{\mu}^L(R)$ , for  $L=0$  and  $L=1$ . The first task is to solve the recursion formulas at equally spaced values of  $R$ . The number of terms  $N(R)$  kept in the power expansion is adjusted to give a selected precision  $\epsilon$  in  $W_{\mu}^L(R)$ . At each value of  $R$  the recursion relations are initially solved for two trial values of  $W_{\mu}^L(R)$  as a starting point for an iterative linear interpolation of  $W_{\mu}^L(R)$  designed to minimize the determinant of the linear system of boundary conditions at  $x=x_0$ . As  $R$  is successively increased, values for  $W_{\mu}^L(R)$  are provided by Newton's method of forward differences. The procedure converges rapidly; usually only very few iterations are required to achieve the desired precision. Next the channel functions are normalized according to Eq. (12) using a fifth-order Gaussian integration method with Legendre polynomials as basis. This method is highly efficient, and the errors of integration are smaller than those due to other approximations. The components of the channel functions and their first derivatives are then calculated at  $x=x_0$  to check how well the boundary conditions are satisfied at a given value of  $R$ .

At small  $R$ , the precision in the wave functions can be increased by increasing the value of  $N(R)$ . At large  $R$ , the propagation of errors in the expansion coefficients prevents one from an arbitrary choice of  $N(R)$ . Beyond a certain value of  $R$ , best results are obtained for decreasing values of  $N(R)$ .

Let us consider a state whose eigenvalue, in the limit  $R \rightarrow \infty$  is  $2U(\infty) = -Z^2/n^2$ , and introduce an effective parameter  $\rho = 2ZR/n$  which approximately scales the behavior of the expansion coefficients  $A(R, k)$ . When  $k$  reaches a value such that

$$[(2\rho)^k/k!] \exp(-\pi\rho/4) \cong 1, \quad (k \cong \rho/2),$$

the coefficients change with  $k$  approximately as  $A(R, k)/A(R, k-1) \cong 2\rho/k$ , reflecting the presence of the exponentially increasing term in the wave function. On the other hand, for large  $R$ , the error  $\Delta A_{l_1 l_2}(R, k)$  in

$A_{l_1 l_2}(R, k)$  due to an error  $\epsilon$  in the potential  $W(R)$ , propagates according to a similar law

$$\Delta A_{l_1 l_2}(R, k) / \Delta A_{l_1 l_2}(R, k-1) \cong 2\rho / (k + l_1 + 1),$$

but this behavior starts at  $k=2$ . When  $x_0^k \Delta A_{l_1 l_2}(R, k) \cong A_{l_1 l_2}(R, 0)$  the wave function at  $x=x_0$  is overcome by the error in the  $k$ th order and following terms. At this point the expansion must be terminated. The value of  $N(R)$  required to give a precision  $\epsilon$  in  $W(R)$  can be accurately estimated and was verified in the course of the calculation. In double precision, i.e.,  $|\epsilon/W(R)| \cong 10^{-16}$ , the maximum value of  $N(R)$  is  $N_{\max} \cong 63$  for  $\rho \cong 26$ . For larger values of  $\rho$ ,  $N(R)$  will decrease. Consequently a determination of the potentials at large  $R$  with the required precision can be achieved with only relatively few terms, e.g., 20–23 terms for double precision at  $\rho=50$ .

##### B. Potential curves and radial couplings

Potential curves for the singlet states of helium with  $L=0$ , ending on  $n=1, 2$ , and 3, calculated with  $l_{\max}=3$  are shown in Figs. 1–3.

The radial couplings  $P_{\mu\nu}(R)$  and  $Q_{\mu\nu}(R)$  can be calculated either by means of Eqs. (15) and (16) or Eqs. (18) and (20). The first and second derivatives of the wave functions can be calculated using data at points  $R$  and  $R \pm \delta R$ , with an intrinsic error of order  $(\delta R)^2$ . If  $\epsilon(R, \alpha)$  is the random numerical error in the wave function, the first and second derivatives will have random numerical errors

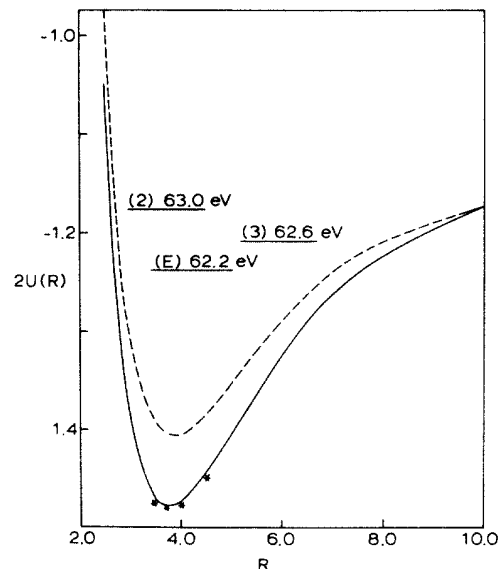


FIG. 2. Channel dependence of (002) potential curve. The dashed line is the calculation using two channels ( $l=0, 1$ ), and the smooth line is the calculation with three channels ( $l=0, 1, 2$ ). The stars indicate the alteration in the potential minimum due to the addition of the fourth channel ( $l=3$ ). This is much less than the difference between the three-channel energy calculation (3) (Ref. 2) and the experimental result (E) (Ref. 5).



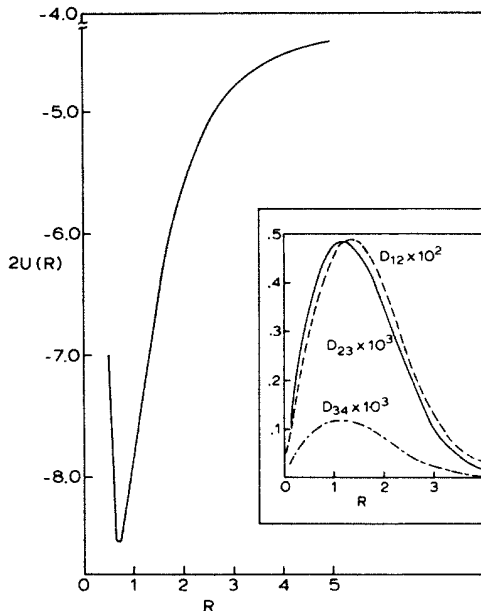


FIG. 3. Ground-state potential curve. Four channels were used in the calculation of the curve shown here. In the inset is depicted the percentage difference in the effective physical potential,  $[W(R) - m^2]$ , as one successively includes further channels, i.e.,  $D_{ij} = [W_i(R) - W_j(R)] / [W_j(R) - m^2]$ , where the subscript refers to the number of channels used in the calculation.

of the order  $\varepsilon/\delta R$  and  $\varepsilon/(\delta R)^2$ , respectively. Choosing the value of  $\delta R$  so as to minimize the total error in the first derivative ( $\delta R \cong |\varepsilon|^{1/3}$ ), one obtains a precision in the determination of the first and second derivatives of order  $|\varepsilon|^{2/3}$  and  $|\varepsilon|^{1/3}$ , respectively. The advantage of using Eqs. (18) and (20) is that the long-range radial cou-

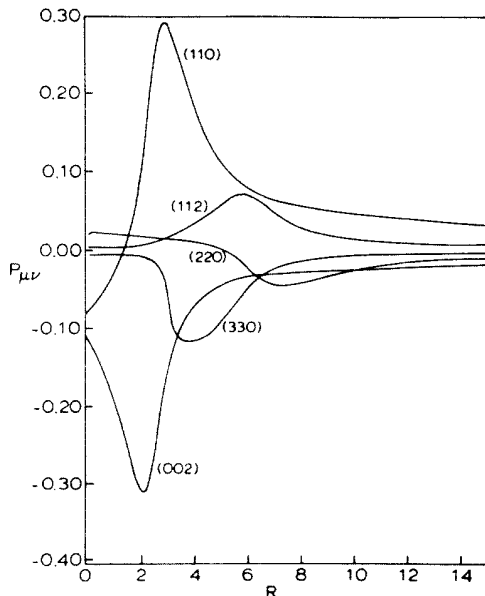


FIG. 4. Nonadiabatic mixing coefficients. Here are shown the values of the  $P_{\mu\nu}$  for the ground-state curve mixed with each of the five curves ending on  $n=2$  and  $n=3$ . As expected, the mixing with the  $n=2$  curves is largest, but that with the  $n=3$  curves is not negligible.

plings  $P_{\mu\nu}$  are calculated as precisely as are the channel functions, and the  $Q_{\mu\nu}$  couplings have the accuracy of the first derivative. Numerical results using these formulas for channel functions with  $l_{\max}=3$ , are shown in Fig. 4 for the  $P_{\mu\nu}$  couplings between the ground state and all the excited states ending on  $n=2$  and  $n=3$ .

## V. ROTATIONAL AND RADIAL EXCITATIONS

### A. Rotational excitations

The contribution of rotational excitations to a given state is restricted by the truncation of the angular momentum channels included in the expansion (4). As a rule, one expects higher angular momenta to have little effect on the low-lying states and resonances, but to become paramount for the correct description of highly excited states and resonances, which would require a large value of  $l_{\max}$  to even appear in a first approximation. Hence for highly excited rotational states the choice of hyperspherical coordinates may become impractical.

In order to investigate quantitatively the effect of the cut on the angular momentum channels we have done a calculation of the potential curves for singlet states with total angular momentum  $L=0$ , taking values of  $l_{\max}$  from 0 to 3. In this case  $l_1=l_2=l$  so that we have channel functions with 1 to 4 components. In Fig. 3 is shown the ground-state potential curve calculated for four coupled channels. In the inset is shown the percentage change in the effective potential ( $2U - m^2/R^2$ ) as a function of  $R$ , when  $l_{\max}$  is successively increased by one unit. The relative difference  $D_{12}$  between the curves calculated with one and two channels is as much as 5% for  $R \cong 1$ , but the difference  $D_{34}$  between the curves calculated with three and four channels decreases to  $10^{-4}$ . This means that the exclusion of angular momentum channels with  $l \geq 4$  should give an error in the energy of the ground state and low-lying excited states of order  $1/10000$ . For the curves shown in Fig. 1, corresponding to excited states, these differences become increasingly larger. An illustration is given in Fig. 2 which shows the potential curves for the state (0,0,2) calculated with two, three, and four channels. For reference, the experimental value<sup>5</sup> for the position of the first autoionizing state is indicated, as well as the theoretical value obtained by Macek<sup>2</sup> using the adiabatic approximation. The resonance positions obtained with the inclusion of two and three channels seem to indicate that the discrepancy with the theoretical value cannot be solely attributed to the neglect of larger angular momentum channels. Beyond the last curve shown in Fig. 1 reliable calculations must include channels with higher values of  $l$ .

### B. Radial excitations

The coupling in the angular equations of rotational states with different values of angular momenta  $l_1, l_2$  for the electrons is exclusively due to the electron-electron interaction. By contrast, the coupling in the radial equation of radially excited states is due to the nonseparability of the Hamiltonian in hyperspherical coordinates, even in

the absence of the electron-electron interaction.

The effect of truncating the wave-function expansion in terms of eigenfunctions  $u_\mu(R, \alpha)$  of the angular equations can be investigated by considering the two-electron system under only the Coulomb interaction with the nucleus. One can then compare the expansion with the exact solution. In this case the angular momenta  $l_1$  and  $l_2$  of the electrons are good quantum numbers and, together with the principal quantum number  $n$ , label the eigenstates  $u_\mu(R, \alpha)$ ,  $\mu = \{l_1, l_2, n\}$ , of the angular equation. Let us consider the ground-state wave function  $\Psi_1 = \Psi_{\{l_1=l_2=0, n=0\}}(R, \alpha)$  and expand it in terms of  $u_{\{0,0,n\}}(R, \alpha)$ . We have

$$\begin{aligned} \Psi_1(R, \alpha) &= \frac{Z^3}{2} \exp[-ZR(\sin\alpha + \cos\alpha)] \\ &= \frac{1}{R^{5/2} \sin\alpha \cos\alpha} \sum_n F^n(R) u_n(R, \alpha), \end{aligned} \quad (37)$$

where  $u_n(R, \alpha)$  stands for  $u_{\{0,0,n\}}(R, \alpha)$ . Let us denote by  $\phi_N(R, \alpha)$  a normalized approximation of  $\Psi_1(R, \alpha)$  by the first  $N$  terms in the expansion and let  $\bar{E}_N = \langle \phi_N | H | \phi_N \rangle$ . Then we have for the percentage error in the ground-state energy  $E_1$ :

$$(E_1 - \bar{E}_N)/E_1 = 1 - \sum_{n=1}^N |\langle \phi_N | \Psi_n \rangle|^2 (E_n/E_1). \quad (38)$$

Since

$$|\langle \phi_N | \Psi_2 \rangle|^2 < 1 - |\langle \phi_N | \Psi_1 \rangle|^2 = (1 - \lambda^2),$$

then,

$$(1 - \lambda^2) \geq (E_1 - \bar{E}_N)/E_1 \geq (1 - \lambda^2)(1 - E_2/E_1) = \frac{3}{4}(1 - \lambda^2). \quad (39)$$

Now one can immediately find that  $\lambda = \langle \phi_N | \Psi_1 \rangle$  is maximized by the following choice of  $F^n(R)$ :

$$F^n(R) = \frac{1}{\lambda} \int u_n(R, \alpha) \Psi_1(R, \alpha) R^{5/2} \sin\alpha \cos\alpha \, d\alpha \quad (40)$$

which gives

$$\lambda^2 = \sum_{n=1}^N \int R^5 dR \left[ \int u_n(R, \alpha) \Psi_1(R, \alpha) \sin\alpha \cos\alpha \, d\alpha \right]^2. \quad (41)$$

This parameter  $\lambda$  is related to the norm of the difference of the wave functions  $\Psi_1$  and  $\phi_N$  by the following:

$$\|\Psi_1 - \phi_N\|^2 = 2(1 - \lambda),$$

The values of  $(1 - \lambda^2)$  for  $N = 1$  to 4 are given in Table I. The energy eigenvalue for  $N = 1$ , corresponding to the adiabatic approximation, is already correct to a precision of order  $1/1000$ . The inclusion of eigenfunctions with  $n \leq 4$  improves the precision to  $2 \times 10^{-8}$ . These results attest to the quasiseparability in hyperspherical coordinates of the Coulomb Hamiltonian for two electrons, at least for the ground state. Of course the convergence of the expansion (10) may not be as good when the electron-electron interaction is included. One expects the errors resulting from the truncation of such an expansion to be

TABLE I. Value of  $(1 - \lambda^2)$  for the ground-state curve.  $N$  is the maximum number of potential curves employed in the expansion of the analytic wave function. The coefficient in parentheses is the power of ten which multiplies the number.

$N$	$1 - \lambda^2$
1	1.47(-3)
2	5.86(-6)
3	2.26(-7)
4	2.10(-8)

comparable to those arising from the cut in angular momentum channels.

## VI. THE RADIAL FUNCTIONS

### A. Boundary conditions

Since the number of solutions of the angular system is infinite (they form a complete set in the interval  $0 \leq \alpha \leq \pi/2$  with appropriate behavior at the boundaries), the system of radial equations (14) is also infinite. However, because of the truncation of the spherical harmonic expansion, only a limited number  $N_f$  of solutions corresponding to a set of low-lying eigenvalues can be meaningfully included in the expansion (1). The resulting system of  $N_f$  second-order equations will have in general  $2N_f$  independent solutions. The physical solutions are required to be continuous and have continuous derivatives at  $R = 0$  and at  $R = \infty$ . We shall now set up the boundary conditions for Eq. (14) compatible with this behavior.

(i)  $R = 0$ . At  $R = 0$  the coefficients  $P_{\mu\nu}$  and  $Q_{\mu\nu}$  are regular, while  $2U_\mu$  has a double pole with residue  $m_\mu^2$ . The point  $R = 0$  is therefore a regular singularity of the system of differential equations with corresponding set of indices  $\{s = \mp m_\mu + \frac{1}{2}\}$ . The continuous solutions have the form

$$F_\nu(R) = \sum_{\hat{\mu}} R^{m_{\hat{\mu}} + 1/2} f_{\nu\hat{\mu}}(R) b_{\hat{\mu}}, \quad (42)$$

where the second index with a caret labels a particular solution, and the first is a component index. The function  $f_{\nu\hat{\mu}}(R)$  will have only logarithmic singularities which occur as a result of the differences  $(m_\nu - m_{\hat{\mu}})$  being positive (even) integers. The reduced equations for the functions  $f$  are

$$\begin{aligned} \left[ \delta_{\mu\nu} \frac{d^2}{dR^2} + \left( (2m_{\hat{\mu}} + 1) \delta_{\mu\nu} \frac{1}{R} + 2P_{\mu\nu} \right) \frac{d}{dR} + Q_{\mu\nu} \right. \\ \left. + (2m_{\hat{\mu}} + 1) \frac{P_{\mu\nu}}{R} + \left( 2E - 2U_\nu + \frac{m_{\hat{\mu}}^2}{R^2} \right) \delta_{\mu\nu} \right] f_{\nu\hat{\mu}} = 0 \end{aligned} \quad (43)$$

with boundary conditions at  $R = 0$  given by

$$\begin{aligned}
\text{(i) } f_{\nu\hat{\mu}}^{(0)} &= \delta_{\nu\hat{\mu}} \\
\text{(ii) } \nu = \hat{\mu}: f_{\nu\hat{\mu}}^{(1)} &= \dot{W}_{\hat{\mu}} / (2m_{\hat{\mu}} + 1) \\
\text{(iii) } \nu \neq \hat{\mu}: f_{\nu\hat{\mu}}^{(1)} &= -\frac{(2m_{\hat{\mu}} + 1)P_{\nu\hat{\mu}}}{(m_{\hat{\mu}} + 1)^2 - m_{\nu}^2}. \quad (44)
\end{aligned}$$

The second derivative at  $R=0$  is obtained from the differential equation. One finds

$$f_{\nu\hat{\mu}}^{(2)} = -\frac{B_{\nu\hat{\mu}}}{(m_{\hat{\mu}} + 2)^2 - m_{\nu}^2}, \quad (45)$$

where

$$\begin{aligned}
B_{\nu\hat{\mu}} &= \sum_{\lambda} \{ [(2m_{\hat{\mu}} + 3)P_{\nu\lambda} - \dot{W}_{\nu}\delta_{\nu\lambda}] f_{\lambda\hat{\mu}}^{(1)} \} \\
&+ (2m_{\hat{\mu}} + 1)\dot{P}_{\nu\hat{\mu}} + Q_{\nu\hat{\mu}} + (2E - \dot{W}_{\nu}/2)\delta_{\nu\hat{\mu}}, \quad (46)
\end{aligned}$$

All the functions and derivatives in these expressions are taken at  $R=0$ . Higher-order coefficients can be obtained in the same way. If there is a channel  $u_{\nu}$  with  $m_{\nu} = m_{\hat{\mu}+2}$ , the second derivative of  $f_{\nu\hat{\mu}}$  becomes infinite. The function develops a logarithmic singularity of the form  $f_{\nu\hat{\mu}}^{(2,1)} R^2 \ln R$ . The coefficient  $f_{\nu\hat{\mu}}^{(2,1)}$  is found to be

$$f_{\nu\hat{\mu}}^{(2,1)} = -\frac{B_{\nu\hat{\mu}}}{2(m_{\hat{\mu}} + 2)} \quad (47)$$

and one can take  $f_{\nu\hat{\mu}}^{(2)} = 0$ . Because of this logarithmic singularity, in a numeric integration of the equations the propagation from the origin to the next point has to be done analytically. The general form of the functions  $f_{\nu\hat{\mu}}(R)$  is then

$$\begin{aligned}
f_{\nu\hat{\mu}}(R) &= \sum_{n=0}^{\infty} \frac{1}{n!} f_{\nu\hat{\mu}}^{(n)} R^n \\
&+ \sum_{n=2}^{\infty} \sum_{m=1}^{\infty} f_{\nu\hat{\mu}}^{(n,m)} R^n (\ln R)^m. \quad (48)
\end{aligned}$$

The existence of a logarithmic singularity in the variable  $R$  was first established by Bartlett<sup>17</sup> based on work by Pierce.<sup>18</sup> An expansion of the form (48) was proposed by Fock<sup>19</sup> and used in variational calculations of the He ground-state wave function.<sup>20,21</sup>

(ii)  $R \rightarrow \infty$ . At large  $R$  one uses the asymptotic expansions:

$$2U_{\mu}(R) = -\frac{Z^2}{n_{\mu}^2} - \frac{2(Z-1)}{R} + \frac{2U_{\mu}^{(2)}}{R^2} + \frac{2U_{\mu}^{(3)}}{R^3} + \dots, \quad (49)$$

$$P_{\mu\nu}(R) = \frac{P_{\mu\nu}^{(1)}}{R} + \frac{P_{\mu\nu}^{(2)}}{R^2} + \frac{P_{\mu\nu}^{(3)}}{R^3} + \dots, \quad (50)$$

$$Q_{\mu\nu}(R) = \frac{q_{\mu\nu}^{(2)}}{R^2} + \frac{q_{\mu\nu}^{(3)}}{R^3}. \quad (51)$$

Because the first correction to the zeroth-order asymptotic wave function is of order  $1/R^2$ , it follows that  $p_{\mu\nu}^{(2)} = 0$  and  $q_{\mu\nu}^{(3)} = 0$ .

We shall now derive an expression for the coefficient  $p_{\mu\nu}^{(1)}$  in (50) which shows that it vanishes whenever  $\mu \sim \nu$ . We start with the asymptotic expression<sup>14</sup>

$$p_{\mu\nu}^{(1)} = \int u_{\mu}^{(0)}(\rho) \rho \frac{d}{d\rho} u_{\nu}^{(0)}(\rho) d\rho \quad (52)$$

and consider the Schrödinger equation for the nonvanishing components of  $u_{\mu}^{(0)}(\rho)$ :

$$\left[ \frac{d^2}{d\rho^2} - \frac{l_1(l_1+1)}{\rho^2} + \frac{2Z}{\rho} - \frac{Z^2}{n_{\mu}^2} \right] u_{\mu l_1 l_2}^{(0)}(\rho) = 0. \quad (53)$$

Multiply this equation by  $u_{\nu l_1 l_2}^{(0)}(\rho)$ , interchange  $\nu$  with  $\mu$  and integrate the difference of the two equations from 0 to  $\rho$ . One obtains

$$\begin{aligned}
u_{\nu l_1 l_2}^{(0)} \frac{d}{d\rho} u_{\mu l_1 l_2}^{(0)} - u_{\mu l_1 l_2}^{(0)} \frac{d}{d\rho} u_{\nu l_1 l_2}^{(0)} \\
= Z^2 \left[ \frac{1}{n_{\mu}^2} - \frac{1}{n_{\nu}^2} \right] \int_0^{\rho} u_{\mu l_1 l_2}^{(0)} u_{\nu l_1 l_2}^{(0)} d\rho. \quad (54)
\end{aligned}$$

Multiplying by  $\rho$ , integrating in the interval  $(0, \infty)$ , and summing over the indices  $l_1, l_2$ , one finds

$$2p_{\mu\nu}^{(1)} = Z^2 \left[ \frac{1}{n_{\mu}^2} - \frac{1}{n_{\nu}^2} \right] \int_0^{\infty} \phi_{\mu\nu}(\rho) \rho d\rho, \quad (55)$$

where

$$\phi_{\mu\nu}(\rho) = \sum_{l_1, l_2} \int_0^{\rho} u_{\mu l_1 l_2}^{(0)}(\rho') u_{\nu l_1 l_2}^{(0)}(\rho') d\rho' \quad (56)$$

and  $\phi_{\mu\nu}(\infty) = \delta_{\mu\nu}$ . The difference  $[\phi_{\mu\nu}(\rho) - \delta_{\mu\nu}]$  approaches zero as a decreasing exponential in  $\rho$ .

Integrating by parts one finally obtains

$$p_{\mu\nu}^{(1)} = \frac{Z^2}{4} \left[ \frac{1}{n_{\nu}^2} - \frac{1}{n_{\mu}^2} \right] \int_0^{\infty} \sum_{l_1, l_2} u_{\mu l_1 l_2}^{(0)} u_{\nu l_1 l_2}^{(0)} \rho^2 d\rho. \quad (57)$$

If  $n_{\mu} = n_{\nu}$ ,  $p_{\mu\nu}^{(1)} = 0$ . Since  $p_{\mu\nu}^{(2)} = 0$ , the leading term in the  $P_{\mu\nu}$  will be in this case of order  $1/R^3$ .

A complete set of solutions for the radial equations may be defined in terms of boundary conditions at large  $R$ . In order to establish these conditions let us write

$$F_{\nu\hat{\mu}}^{\pm}(R) = R^{s_{\hat{\mu}}^{\pm}} \exp(\pm K_{\hat{\mu}} R) f_{\nu\hat{\mu}}^{\pm}(R), \quad (58)$$

where  $f_{\nu\hat{\mu}}^{\pm}(R)$  has an asymptotic expansion in inverse powers of  $R$

$$f_{\nu\hat{\mu}}^{\pm}(R) \cong \sum_i \frac{f_{\nu\hat{\mu}}^{\pm(i)}}{R^i}, \quad (59)$$

$$K_{\hat{\mu}} = \left[ -2E - \frac{Z^2}{n_{\hat{\mu}}^2} \right]^{1/2}, \quad (60)$$

$$s_{\hat{\mu}}^{\pm} = \mp \frac{Z-1}{K_{\hat{\mu}}}. \quad (61)$$

The boundary conditions for the solutions  $f_{\hat{\mu}}(R)$  with components  $f_{\nu\hat{\mu}}$  are the following.

(i)  $n_{\nu} = n_{\hat{\mu}}$ . For components  $f_{\nu\hat{\mu}}$  such that  $\nu \sim \hat{\mu}$ :

$$\begin{aligned} f_{\nu\hat{\mu}}^{(0)} &= \delta_{\nu\hat{\mu}}, \\ f_{\nu\hat{\mu}}^{(1)} &= \frac{1}{2K_{\hat{\mu}}} [2U_{\hat{\mu}}^{(2)} - (s_{\hat{\mu}} - \frac{1}{2})^2 \delta_{\nu\hat{\mu}} - q_{\nu\hat{\mu}}^{(2)}] \\ &\quad + \sum_{\lambda} P_{\nu\lambda}^{(1)} f_{\lambda\hat{\mu}}^{(1)}. \end{aligned} \quad (62)$$

(ii)  $n_{\nu} \neq n_{\hat{\mu}}$ . For components  $f_{\nu\hat{\mu}}$  with  $\nu$  not  $\sim \hat{\mu}$ , one gets

$$\begin{aligned} f_{\nu\hat{\mu}}^{(0)} &= 0, \\ f_{\nu\hat{\mu}}^{(1)} &= -\frac{2K_{\hat{\mu}}}{K_{\nu}^2 - K_{\hat{\mu}}^2} P_{\nu\hat{\mu}}^{(1)}. \end{aligned} \quad (63)$$

We have suppressed in these expressions the superscript  $\pm$  in the  $f$ 's and  $s$ . In Eq. (62) the sum is for  $\lambda$  not equivalent to  $\nu$  and  $f_{\lambda\hat{\mu}}^{(1)}$  is to be replaced by the expression (63).

For physical solutions we have to distinguish two cases.

$$F^{E\hat{\kappa}}_{\nu} = R^{s_{\hat{\kappa}}+} \exp(+ik_{\hat{\kappa}}R) f^{+}_{\nu\hat{\kappa}}(R) + \sum_{\hat{\mu}(\text{open})} R^{s_{\hat{\mu}}-} \exp(-ik_{\hat{\mu}}R) f^{-}_{\nu\hat{\mu}}(R) c_{\hat{\mu}\hat{\kappa}} + \sum_{\hat{\mu}(\text{closed})} R^{s_{\hat{\mu}}-} \exp(-K_{\hat{\mu}}R) f^{-}_{\nu\hat{\mu}}(R) c_{\hat{\mu}\hat{\kappa}}, \quad (66)$$

where the index  $\hat{\kappa}$  specifies the outgoing state. The first sum extends over all the open channels (imaginary  $K_{\hat{\mu}}$ ) and the second sum over the closed channels (real  $K_{\hat{\mu}}$ ). Again matching the function  $F_{\nu}(R)$  given by (42) with  $F^{E\hat{\kappa}}_{\nu}$  as given by (66) will produce a system of inhomogeneous equations for the determination of the coefficients  $b_{\hat{\mu}}$  and  $c_{\hat{\mu}}$ . The wave functions for the different open channels at a given energy are labeled by the index  $\hat{\kappa}$ . In order to obtain asymptotic wave functions for the ion and the outgoing electron with angular momenta  $l_1$  and  $l_2$ , respectively, one has to take linear combinations of the above solutions,  $\sum_{\hat{\kappa}} F_{\nu\hat{\kappa}} a_{\hat{\kappa}l_1l_2}$  with  $a_{\hat{\kappa}l_1l_2}$  defined by Eq. (36).

In electron scattering on an atom the asymptotic initial state is the product of the wave function for the atom and a plane wave for the incoming electron. The final state is asymptotically a superposition of the incoming plane wave plus outgoing spherical waves. The plane wave may be decomposed in partial waves of angular momentum carrying incoming and outgoing waves. The partial waves will be specified by the amplitude of the incoming spherical wave, hence they will be given by  $F^{E\hat{\kappa}}(R)^*$ . In general the scattering is off the ground state of the atom, which is nondegenerate. However one may also consider scattering from excited states, in which case one should take the appropriate linear combination of the independent solutions

### 1. Bound states

In this case  $K$  is a real number, and the solution has to behave as a *decreasing* exponential. Therefore it will be a linear combination of the form

$$F_{\nu}(R) = \sum_{\hat{\mu}} R^{s_{\hat{\mu}}-} \exp(-K_{\hat{\mu}}R) f^{-}_{\nu\hat{\mu}}(R) c_{\hat{\mu}}. \quad (64)$$

By solving the radial equations we obtain a set of homogeneous equations for the coefficients  $b_{\hat{\mu}}$  in Eq. (42) and  $c_{\hat{\mu}}$  which also determine the discrete energy eigenvalues.

### 2. Scattering states

For states in the continuum,  $K$  is purely imaginary,  $K_{\hat{\mu}} = ik_{\hat{\mu}}$ , where

$$k_{\hat{\mu}} = \left[ 2E + \frac{Z^2}{n_{\hat{\mu}}^2} \right]^{1/2}. \quad (65)$$

Solutions  $F^+$  correspond to outgoing spherical waves, and  $F^-$  to incoming spherical waves. In photoionization a solution with outgoing spherical waves specifies an open channel that can be produced at a given energy  $E$ . All the other solutions must have incoming waves or decreasing exponentials. Therefore the wave functions will be of the form

that corresponds to the asymptotic initial state.

For any pair of solutions with the same energy  $E$  and vanishing at  $R=0$ , the following identity holds:

$$\begin{aligned} \sum_{\mu,\nu} [F^{E\hat{\kappa}'}_{\mu}(R)]^* \dot{F}^{E\hat{\kappa}}_{\nu}(R) - [\dot{F}^{E\hat{\kappa}'}_{\mu}(R)]^* F^{E\hat{\kappa}}_{\nu}(R) \delta_{\mu\nu} \\ + 2[F^{E\hat{\kappa}'}_{\mu}(R)]^* P_{\mu\nu}(R) F^{E\hat{\kappa}}_{\nu}(R) = 0 \end{aligned} \quad (67)$$

which expresses the conservation of the electric current across a spherical surface of radius  $R$ . It follows from this identity that, in scattering states, one has

$$\sum_{\hat{\mu}(\text{open})} c_{\hat{\mu}\hat{\kappa}}^* k_{\hat{\mu}} c_{\hat{\mu}\hat{\kappa}} = \delta_{\hat{\kappa}'\hat{\kappa}} k_{\hat{\kappa}}, \quad (68)$$

where the sum extends over all the open channels. The scattering states are then normalized by

$$\int_0^{\infty} \sum_{\nu} [F^{E'\hat{\kappa}'}_{\nu}(R)]^* F^{E\hat{\kappa}}_{\nu}(R) dR = 2\pi k_{\hat{\kappa}} \delta_{\hat{\kappa}\hat{\kappa}'} \delta(E - E'). \quad (69)$$

### B. Numerical solutions: Ground state of He

The radial equations have to be solved numerically by any standard method which propagates the function from one point to the next. In order to enforce correct

boundary conditions, the best procedure is to start from both ends, i.e., at  $R=0$  and at a suitably chosen large value of  $R$ , propagate the function to some intermediate value,  $R_{\text{match}}$ , where the two functions and their first derivatives are matched together. The boundary conditions at  $R=0$  depend on  $W_\mu(0)$ ,  $\dot{W}_\mu(0)$ , and  $P_{\mu\nu}(0)$ , all of which can be calculated in closed form, except for  $P_{\mu\nu}(0)$  between two states with degenerate eigenvalues  $W_\mu = W_\nu$ . In this case one can either calculate it numerically by means of Eq. (16) or by the expression

$$P_{\mu\nu}(0) = -2 \sum_\lambda P_{\mu\lambda} \frac{W_\mu - W_\lambda}{\dot{W}_\mu - \dot{W}_\nu} P_{\lambda\nu} \quad (70)$$

derived from (18) using L'Hôpital's rule. However, because of the logarithmic singularity, in order to propagate the wave function away from  $R=0$  using the expansion (48) one also needs the  $Q_{\mu\nu}$ 's and higher-order derivatives of the potential function  $W_\mu(R)$  and of the radial couplings at  $R=0$ . These have to be determined numerically. (See Table III.)

At large  $R$ , according to Eqs. (58) and (59), the boundary conditions require the values of the coefficients in the asymptotic expansions (49)–(51) up to terms in  $1/R^2$ . The coefficients  $W_\mu^{(2)}$ ,  $p_{\mu\nu}^{(1)}$ , and  $q_{\mu\nu}^{(2)}$  can be computed perturbatively in closed form. If the boundary conditions are not imposed at a sufficiently large value of  $R$ , in order to improve their precision, particularly in the case of scattered states, one may want to extend the expansion (59) by the inclusion of additional terms in higher inverse powers of  $R$ . In this case one needs further terms in the expansions (49)–(51). However we should bear in mind that in view of the asymptotic nature of these  $1/R$  expansions, they should not be used for too low values of  $R$ . A reliable evaluation of these higher-order terms will require an accurate determination of the potential curves and channel functions. Using double precision, one should be able to determine up to four of these additional

TABLE II. Asymptotic expansion coefficients. The number in parentheses is the power of ten which multiplies the quoted number.

Curve	$W(R)$		
	$A^{(0)}$	$A^{(1)}$	$A^{(2)}$
(000)	-0.50000	-0.75000	-0.375
(110)	-3.8541	-8.03	-43
(002)	2.8541	-4.00	30
(220)	-11.2345	-21.3	-65(1)
(112)	0.9202	-52.2	21(1)
(330)	8.8142	-0.77	53

$P_{\mu\nu}(000) - (j_1 j_2 j)$	
$(j_1 j_2 j)$	$p^{(1)}$
(110)	0.4753
(002)	-0.2937
(220)	-0.1753
(112)	-0.1485
(330)	-0.0810

TABLE III. Derivatives of the potential curves and radial coupling coefficients at  $R=0$ .

Curve	$W^{(1)}$	$W^{(2)}$	$W^{(3)}$
(000)	-11.1804	-0.290	-0.378
(110)	-9.3989	-0.279	-0.372
	$p_{\mu\nu}^{(0)}$	$p_{\mu\nu}^{(1)}$	$p_{\mu\nu}^{(2)}$
(000)-(110)	0.08003	0.043	0.008
	$q_{\mu\nu}^{(0)}$		
Curve-Curve	(000)	(110)	
(000)	-0.0207	0.0472	
(110)	-0.0388	-0.0138	
	$q_{\mu\nu}^{(1)}$		
Curve-Curve	(000)	(110)	
(000)	-0.006	+0.012	
(110)	-0.004	+0.006	

coefficients for the potentials and one or two for the  $P_{\mu\nu}$ 's and  $Q_{\mu\nu}$ 's. In Table II a set of these asymptotic expansion coefficients is reported.

We have solved the radial equations for the ground state of helium with one- and two-channel functions (0,0,0) and (1,1,0) and four angular momentum channels ( $l_1=l_2=0$  to 3). A fourth-order Runge-Kutta method was used to solve the differential equations, taking a grid of points separated by intervals  $\Delta R=0.04$ . This spacing is sufficient to keep the errors smaller than those resulting from the truncation in the expansions (4) and (10). The wave function was initially calculated analytically at  $R=0.04$ , which was the starting point for the propagation from below. From the other end we started at  $R=18$ . The matching point was chosen at  $R_{\text{match}}=2.6$ .

As expected, for the bound-state solution the energy eigenvalue is much more sensitive to the boundary conditions at  $R=0$  than at large  $R$ . In the one-channel calculation (adiabatic approximation) we obtained for the energy the value  $E=-2.895$ , in agreement with the result of Miller and Starace.<sup>22</sup>

The two-channel calculation gives an improved value of  $E=-2.899$ . For comparison, Pekeris's result<sup>23</sup> of variational calculation is  $E=-2.9037$ . The inclusion of all the channel functions corresponding to potential curves with principal quantum numbers  $n=2,3$  at  $R=\infty$ , should significantly improve our result.

## VII. CONCLUDING REMARKS AND SUMMARY OF RESULTS

In this paper we have developed a new procedure for computing wave functions for He and  $H^-$  using hyperspherical coordinates. The angular equation for the channel functions is solved analytically using a power-series expansion in the variable  $x=\tan(\alpha/2)$ . The expansion coefficients, given by recursion formulas, are calculated

numerically for fixed values of  $R$ . The propagation of errors can be rigorously controlled, in particular, for large values of  $R$ . Beyond a certain value, which depends on the desired precision, a decreasing number of terms in the expansion should be kept in order to achieve a selected precision for the potential functions  $W(R)$ . As a result one can avoid instabilities at large  $R$  that beset other approaches.

We have done an analysis of the effects of truncating the expansion of the wave function both in terms of the angular momentum states and the channel functions. It shows that the convergence of the expansion in the angular momentum channels is somewhat slow. However keeping only three terms in this expansion already reaches a precision comparable to the accuracy of the adiabatic approximation (only one-channel function). Therefore a consistent improvement of the method would require the inclusion of more angular momentum states as well as channel functions. We have established exact boundary conditions for the coupled radial equations. One finds that, as long as one retains the coupling of channel functions in the radial equations, the radial wave functions will have logarithmic singularities at  $R=0$ . The radial equations were solved for the ground state of helium using two-channel functions and four angular momentum states. Our result represents an improvement over a previous calculation using the adiabatic approximation.

We note that the hyperspherical method was primarily intended for the computation of wave functions for excited states and in the continuum. The results of our analysis and of the preliminary calculation of the helium ground-state energy suggest that it is possible to achieve a degree of precision such that one should be able to make reliable determinations of observables in scattering processes which are particularly sensitive to the details of the wave functions. Our computer codes were written for eigenstates of total angular momentum  $L=0$  and  $L=1$ . They are readily available for the computation of parameters in the density matrix of excited states of  $\text{He}^+$  in photoionization processes. A calculation of the alignment of the first excited state of  $\text{He}^+$  by photoionization is in progress.

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