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Analytical channel functions for two-electron atoms in hyperspherical coordinates

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By expressing the two-electron wave functions in hyperspherical coordinates (R,Ω) in an adiabatic approximation $F_\mu(R)\Phi_\mu(R;\Omega)$, I describe a simple procedure for obtaining the channel functions $\Phi_\mu(R;\Omega)$ analytically. These analytical functions, $\Phi_\mu(R;\Omega)$ in the finite-R region, are obtained by generalizing the known hydrogenic solutions in the asymptotic $(R\rightarrow\infty)$ limit for each channel μ and are required to satisfy proper boundary conditions in the hyperangles Ω rigorously. It is shown that these analytical functions compare well with the channel functions obtained previously from numerical calculations and, in a straightforward manner, describe the + and − channels of doubly excited states. The implication of this result as a method of generalizing hyperspherical coordinates to many-electron problems is discussed.

I. INTRODUCTION

In recent years hyperspherical coordinates have been used in studying various properties of two-electron atoms.[1-8] In particular, many interesting features of low-lying doubly excited states of H$^-$ and He have been predicted and the results have since been confirmed by recent experiments.[9-10] However, except for the preliminary applications to three-electron systems,[11] this method has been limited to two-electron systems because of conceptual and practical difficulties. The independent-particle model (or the shell model) which has been so successful in atomic and nuclear physics, does not emerge simply from the treatment in hyperspherical coordinates. In addition, the numerical difficulties encountered in treating problems in hyperspherical coordinates prevents this method from becoming a competitive technique of dealing with many-electron atoms. On the other hand, when electron correlations are important, the independent electron approximation is not useful; previous works indicated that such systems might be conveniently treated in hyperspherical coordinates.

In this article I describe the attempt in linking the two treatments by generalizing the solutions from the independent electron model to solutions in hyperspherical coordinates. In terms of the usual spherical coordinates (r_1, θ_1, ϕ_1) and (r_2, θ_2, ϕ_2) of the two electrons, the hyperspherical coordinates are obtained by replacing r_1 and r_2 by a hyperradius $R=(r_1^2+r_2^2)^{1/2}$ and a hyperangle $\alpha=\arctan(r_1/r_2)$. In this coordinate system, R measures the "size" of the atom and $\Omega\equiv\{\alpha,\hat{r}_1,\hat{r}_2\}$, where $\hat{r}_i=(\theta_i,\phi_i)$, denotes the orientation of the electrons in the space. For low-lying states, earlier works indicated that the two-electron wave functions are well represented by an adiabatic approximation

$$\Psi_\mu^n(R;\Omega)=R^{-5/2}F_\mu^n(R)\Phi_\mu(R;\Omega)\,, \tag{1}$$

where μ specifies the channel and n defines the different excited or continuum states in that channel.

All the important properties of electron correlation are contained in the channel functions $\Phi_\mu(R;\Omega)$. Values of $R\sim 0$ mean that the two electrons are packed more tightly than in ordinary states and accordingly possess very high kinetic energy, and values of $R\rightarrow\infty$ mean that the two-electron system is fragmented into two parts where the two electrons are separated by a distance R from each other. Each channel function $\Phi_\mu(R;\Omega)$ describes the gradual evolution of the tightly packed state at $R\sim 0$ to the fragmented state at large R in an "adiabatic" procedure. The asymptotic forms of the channel functions in the fragmented state are known, they correspond to the hydrogenic wave functions; the channel function in the limit $R\rightarrow 0$ are also known analytically[1,2,12] despite that they are less familiar. By examining the two limiting solutions in the two limits I propose in this article simple analytical functions which are to serve as the approximate channel functions for the region of R in between. The validity of these proposed analytical functions are checked against earlier numerical calculations. In Sec. II, I outline the mathematical equations satisfied by $\Phi_\mu(R;\Omega)$. Since an exact analytical solution of $\Phi_\mu(R;\Omega)$ at finite R is not available, the proposed approximate analytical solution is required to satisfy certain conditions. In Sec. III, the desired simple analytical functions are "deduced" through examples. Admittedly, these deduced analytical functions are not unique, but I show that they reproduce the numerical results very well. Further discussions about these functions and the applications to structure and collision calculations are presented in Sec. IV.

II. CHANNEL EQUATIONS IN HYPERSPHERICAL COORDINATES

In the adiabatic approximation (1), the channel function $\overline{\Phi}_\mu(R;\Omega)$ satisfies the partial differential equation

$$\left(\frac{-\Lambda^2}{R^2}+\frac{2C}{R}\right)\overline{\Phi}_\mu(R;\Omega)=\overline{U}_\mu(R)\overline{\Phi}_\mu(R;\Omega)\,, \qquad (2)$$

where Λ^2 is the squared grand angular momentum operator and $-C/R$ is the total Coulomb interaction potential

$$\frac{-C}{R}=\frac{1}{R}\left(-\frac{Z}{\sin\alpha}-\frac{Z}{\cos\alpha}+\frac{1}{(1-\sin 2\alpha\cos\theta_{12})^{1/2}}\right). \qquad (3)$$

In (3), Z is the nuclear charge and θ_{12} is the angle subtended to the nucleus by the two electrons. Atomic units are used in (2) and (3) and throughout the rest of this article.

By introducing the substitution

$$\overline{\Phi}_\mu(R;\Omega)=\frac{\Phi_\mu(R;\Omega)}{\sin\alpha\cos\alpha}\,, \qquad (4)$$

and expressing Λ^2 explicitly, Eq. (2) reduces to

$$\left(\frac{1}{R^2}\frac{d^2}{d\alpha^2}-\frac{\vec{l}_1^{\,2}}{R^2\sin^2\alpha}-\frac{\vec{l}_2^{\,2}}{R^2\cos^2\alpha}+\frac{2C}{R}\right)\Phi_\mu(R;\Omega)$$

$$=U_\mu(R)\Phi_\mu(R;\Omega)\,, \qquad (5)$$

where $U_\mu=\overline{U}_\mu-4$. For low-lying doubly excited states, it is convenient to expand $\Phi_\mu(R;\Omega)$ as

$$\Phi_\mu(R;\Omega)=A\sum_{[l_1l_2]}f^{(\mu)}_{l_1l_2}(R;\alpha)\mathcal{Y}_{l_1l_2LM}(\hat{r}_1,\hat{r}_2)\,, \qquad (6)$$

where A is the suitable symmetrization or antisymmetrization operator (the spin function is not explicitly considered in this article) and $\mathcal{Y}_{l_1l_2LM}(\hat{r}_1,\hat{r}_2)$ is the coupled orbital angular momentum function of the two electrons. Because of the symmetrization, the summation over the pair $[l_1l_2]$ is not different from the summation over the pair $[l_2l_1]$.

Substitution of a truncated expansion (6) into (5) results in a set of coupled differential equations for $f^{(\mu)}_{l_1l_2}(R;\alpha)$ which are solved to obtain the eigenvalues $U_\mu(R)$. Three different methods have been employed in solving these equations: (1) Numerical integration of the coupled equations,[1,7] (2) diagonalization using eigenfunctions of the Λ^2 operator,[2,6] and (3) the finite difference method.[3,4] All three methods have some limitations. The numerical integration method often suffers from instability and the finite difference method is inefficient when the expansion (6) has to include many pairs of $[l_1l_2]$. The diagonalization method is inaccurate at large R because a large basis set is needed. Because of these limitations, only low-lying doubly excited states have been investigated and the convergence in the $[l_1l_2]$ truncation is not carefully examined.

The solutions of (5) in the limits of $R=0$ and $R\to\infty$ are well known. In the absence of electron-electron interaction, the expansion (6) can be truncated to a single pair of $[l_1l_2]$. This condition is approximately satisfied in the two limits $R=0$ and $R\to\infty$. As $R\to 0$, the kinetic energy term $-\Lambda^2/R^2$ is much larger than the potential energy term $2C/R$, thus $[l_1l_2]$ pair is a set of good quantum numbers. As shown in Ref. 2, the channel function $\Phi_\mu(R=0;\Omega)$ in this limit is given by

$$u_{l_1l_2m}=A[f_{l_1l_2m}(\alpha)\mathcal{Y}_{l_1l_2LM}(\hat{r}_1,\hat{r}_2)]\,, \qquad (7)$$

where

$$f_{l_1l_2m}(\alpha)=N_{l_1l_2m}(\sin\alpha)^{l_1+1}(\cos\alpha)^{l_2+1}$$
$$\times F(-m,l_1+l_2+2m+2\,|\,l_1+\tfrac{3}{2}\,|\cos^2\alpha)\,. \qquad (8)$$

The function $F(-m,l_1+l_2+2m+2\,|\,l_1+\frac{3}{2}\,|\cos^2\alpha)$ is proportional to a Jacobi polynomial of degree of m in $\cos^2\alpha$ and $N_{l_1l_2m}$ is a normalization constant. In the other limit that one electron remains in the core and the other stays far out, corresponding to $R\to\infty$ and $\alpha\to 0$, the electron-electron interaction can be neglected and $\Phi_\mu(R;\Omega)$ is

$$\Phi_\mu(R;\Omega)\xrightarrow[R\to\infty;\ \alpha\to 0]{}r_1R_{nl_1}(r_1)\mathcal{Y}_{l_1l_2LM}(\hat{r}_1,\hat{r}_2)\,. \qquad (9)$$

This corresponds to the fact that electron 1 is in its nl_1 hydrogenic orbital and electron 2 has angular momentum l_2.

In the two limits considered, only a single pair of $[l_1l_2]$ is needed. For the purpose of seeking approximate analytical expression for the channel functions, it is advantageous initially to consider $\Phi_\mu(R;\Omega)$ in a single $[l_1l_2]$ pair subspace. This will allow us to study the variation of the α-dependent part of the channel function with R only, as the dependence of $\Phi_\mu(R;\Omega)$ on $\hat{r}_1$ and $\hat{r}_2$ is given by $\mathcal{Y}_{l_1l_2LM}(\hat{r}_1,\hat{r}_2)$ at all values of R. The solution (7) is valid throughout the whole range of α, $0\leq\alpha\leq\pi/2$, at $R=0$, but (9) is valid only for $\alpha\to 0$ as $R\to\infty$. Before the analytical expression in the intermediate region of R can be sought, we have to generalize (9) to the whole range of α first.

III. ANALYTICAL CHANNEL FUNCTIONS IN AN $[l_1l_2]$ SUBSPACE

Within the $[l_1l_2]$ subspace, the channel function (6) is expressed as

$$\phi^{(\mu)}_{l_1l_2}(R;\Omega)=A[g^{(\mu)}_{l_1l_2}(R;\alpha)\mathcal{Y}_{l_1l_2LM}(\hat{r}_1,\hat{r}_2)]\,. \qquad (10)$$

For $\phi^{(\mu)}_{l_1 l_2}(R;\Omega)$ to satisfy all the boundary conditions rigorously, we note that $g^{(\mu)}_{l_1 l_2}(R;\alpha)$ has to vanish at $\alpha=0$ and $\pi/2$. If $l_1=l_2=l$, the symmetry condition also imposes $g^{(\mu)}_{ll}(R;\alpha)$ to be symmetric or antisymmetric with respect to the reflection at $\alpha=\pi/4$. These boundary conditions will be enforced throughout all the range of R since the relaxation of these conditions corresponds to solving Eq. (5) with incorrect boundary conditions.

To generalize (9) to the whole range of α and to satisfy boundary conditions rigorously, we first note that (9) does not satisfy the boundary condition $g^{(\mu)}_{l_1 l_2}(R;\alpha=\pi/2)=0$. To find the proper generalization we proceed by examples:

A. Lowest nondegenerate channels for H⁻

Consider first the lowest $\mu=1$ channel for ${}^1S^e$ in the $[l_1 l_2]=[00]$ subspace. In the large R limit,

$$g^{(1)}_{00}(R;\alpha)\xrightarrow[R\to\infty;\ \alpha\to 0]{} r_1 e^{-r_1}=R\sin\alpha\, e^{-R\sin\alpha} \tag{11}$$

to within a normalization constant. Currently (11) does not satisfy two boundary conditions: It does not vanish at $\alpha=\pi/2$, nor is it symmetric with respect to $\alpha=\pi/4$. The usual symmetrization procedure where (11) is replaced by $[R\sin\alpha\, e^{-R\sin\alpha}+R\cos\alpha\, e^{-R\cos\alpha})$ is not useful since it does not vanish at $\alpha=0$ and $\alpha=\pi/2$. A possible guidance to the desirable form is to notice that (11) is valid only for $\alpha\to 0$ and thus multiplication of $\cos\alpha$ to (11) will not change the asymptotic form (11) in the region $\alpha\to 0$. It is clear that a generalized function

$$g^{(1)}_{00}(R;\alpha)=N(R)\sin 2\alpha\, e^{-R\sin\alpha\cos\alpha}\quad (\text{for } {}^1S^e) \tag{12}$$

does satisfy all the boundary conditions and reduces to (11) as $\alpha\to 0$ and $R\to\infty$. Furthermore, (12) also reduces to the function $f_{000}(\alpha)$ [cf. (8)] at $R=0$. With the normalization constant $N(R)$ determined by

$$\int_0^{\pi/2}[g^{(1)}_{00}(R;\alpha)]^2 d\alpha=1$$

for each R, we expect (12) to represent the α-dependent part of the channel function $\phi^{(1)}_{00}(R;\Omega)$ adequately. Before comparing with numerical results, consider the corresponding $\mu=1$ curve for ${}^3S^e$ in the [00] subspace. The function $g^{(1)}_{00}$ in this case reduces to (11) in the limits $R\to\infty$ and $\alpha\to 0$ but the generalized form is required to be antisymmetric with respect to $\alpha=\pi/4$ and reduces to $\sin 2\alpha\cos 2\alpha$ at $R=0$. An obvious generalization is

$$g^{(1)}_{00}(R;\alpha)=N(R)\sin 2\alpha\cos 2\alpha\, e^{-R\sin\alpha\cos\alpha}\quad (\text{for } {}^3S^e)\,. \tag{13}$$

To show these are indeed very good generalizations, in Fig. 1 I compare the potential curves for H⁻ obtained from these analytical functions (in dashed lines) with the "exact" numerical solutions (in solid lines). The good agreement shows the quality of the simple analytical expressions (12) and (13) throughout the whole range of R.

Next consider the lowest $\mu=1$ channels in the [01] subspaces for ${}^1P^o$ and ${}^3P^o$, the generalized analytical functions take the form

$$\phi^{(1)}_{01}(R;\Omega)=\frac{N(R)}{\sqrt{2}}[\sin\alpha\cos^2\alpha\, e^{-R\sin\alpha}\mathcal{Y}_{0110}(\hat{r}_1,\hat{r}_2) \pm\cos\alpha\sin^2\alpha\, e^{-R\cos\alpha}\mathcal{Y}_{1010}(\hat{r}_1,\hat{r}_2)]\,, \tag{14}$$

where the +(−) sign is for ${}^1P^o$ (${}^3P^o$) channel. The analytical functions (14) reduces to u_{010} at $R=0$ and to the hydrogenic 1s orbital in the limits $R\to\infty$ and $\alpha\to 0$. It is straighforward to generalize (14) to other 1$s\epsilon l$ channels. One simply replaces $\sin\alpha\cos^2\alpha$ in (14) by $\sin\alpha\,(\cos\alpha)^{l+1}$ and the second term is obtained by symmetrization. In Fig. 1 the $\mu=1$ potential curves for $1s\epsilon p\,{}^1P^o$ and $1s\epsilon d\,{}^1D^e$ of H⁻ obtained from the analytical calculations are shown; they do not show any noticeable difference from the numerical calculations represented by the solid lines.

It is interesting to note that among the potential curves shown in Fig. 1, only the ${}^1S^e$ curve has the attractive well to support a bound state, corres-

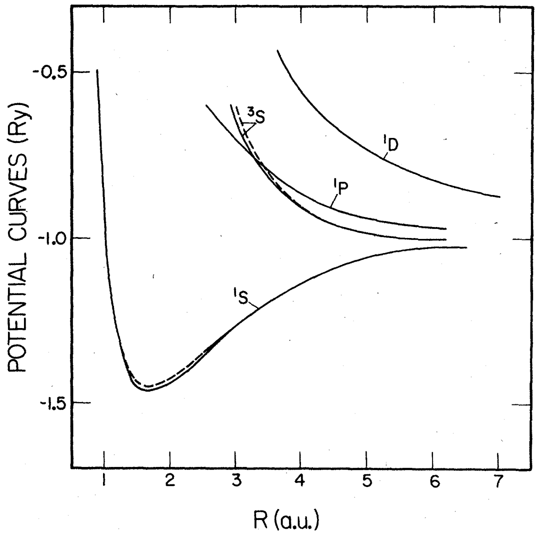

FIG. 1. Lowest potential curve of H⁻ for each symmetry shown. Those from the accurate numerical calculations are shown in solid lines. Those from the simple analytical functions are shown in dashed lines. For ${}^1P$ and ${}^1D$, there is no difference in the two results within the scale shown.

ponding to the ground state of H$^-$. The energy level calculated from Fig. 1 is -1.02617 Ry (Ref. 13) which is to be compared with the best value -1.055502 Ry according to Pekeris.[14,15] The difference is due mostly to the neglect of angular correlation which can be easily taken into account in this approach, as will be discussed in Sec. IV. The failure of Hartree-Fock calculations in predicting a bound state for H$^-$ is thus primarily due to the failure of properly representing radial correlations.

B. Doubly excited channels

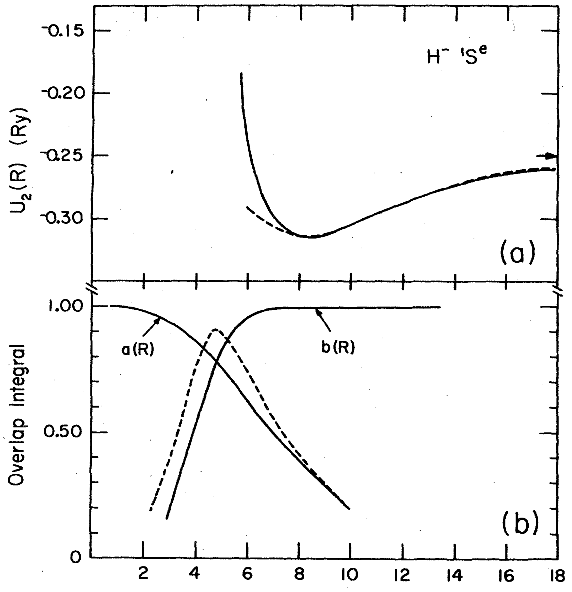

FIG. 2. (a) Potential curve for the doubly excited $2s\epsilon s\ ^1S^e$ of H$^-$. Solid line is the exact result from numerical calculation, the dotted lines are calculated from the analytical function g_{2s}, Eq. (16). (b) Mixing coefficients $a(R)$ and $b(R)$, see Eq. (17).

Consider the first doubly excited channel $\mu=2$ for ^1S in the [00] subspace, i.e., the channel in which $2s\epsilon s\ ^1S^e$ states belong. This channel dissociates to the hydrogenic $2s$ state and is represented by

$$\begin{aligned} r_1 R_{2s}(r_1) &= r_1(1-\tfrac{1}{2}r_1)e^{-1/2r_1} \\ &= R\sin\alpha\,(1-\tfrac{1}{2}R\sin\alpha)e^{-1/2R\sin\alpha} \end{aligned} \tag{15}$$

in the limit $R\to\infty$ and $\alpha\to 0$. This is generalized to

$$g_{2s}(R;\alpha)=N(R)\sin 2\alpha\,(1-\tfrac{1}{2}R\sin\alpha\cos\alpha)e^{-1/2R\sin\alpha\cos\alpha} \tag{16}$$

at finite values of R. The generalized function (16) vanishes at $\alpha=0$ and $\alpha=\pi/2$. It is symmetric with respect to the reflection at $\alpha=\pi/4$. However, g_{2s} does *not* reduce to the solution f_{002} at $R=0$. Notice that $f_{002}\sim\sin 2\alpha\ (1-\frac{4}{3}\sin^2 2\alpha)$ where the polynomial inside the parentheses is second degree in $\sin 2\alpha$, whereas the corresponding polynomial in (16) is first degree in $\sin 2\alpha$. At large R, the node in α is given by the equation $\sin 2\alpha=4/R$. This node disappears for $R<4$ and thus the nodal structure for $g_{2s}(R;\alpha)$ is not preserved at smaller R. To obtain a smooth variation, it is apparent that a more complicated polynomial in $\sin 2\alpha$ is needed if a single function of the form (16) is pursued. On the other hand, it is more convenient to express

$$g_{00}^{(2)}(R;\alpha)=a(R)f_{002}(\alpha)+b(R)g_{2s}(R;\alpha)\,, \tag{17}$$

where $a(R)$ and $b(R)$ are obtained by minimizing the energy $U(R)$ at each R.

The function g_{2s}, although it does not reduce to f_{002} at $R=0$, actually represents the outer region of R very well. In Fig. 2(a), I show the $\mu=2$ potential curve calculated from g_{2s} *alone* (in dashed lines). It agrees quite well with the result from the numerical calculations at larger R. The deviation occurs near the minimum of the potential well. In Fig. 2(b), I show the coefficients $a(R)$ and $b(R)$ of (17). Both coefficients are large only in a limited range of R. In this region the overlap integral $\langle f_{002}|g_{2s}\rangle$ [shown in dashed lines in Fig. 2(b)] is also large.

The generalization of (16) to $2s\epsilon s\ ^3S^e$ states is straightforward. All we have to do is to multiply $\cos 2\alpha$ to (16). In the case of $2p\epsilon p\ ^1S^e$, the generalization proceeds as

$$r_1R_{2p}(r_1)\xrightarrow[R\to\infty;\,\alpha\to 0]{} r_1^2e^{-1/2r_1}\to R^2\sin^2\alpha\cos^2\alpha\ e^{-1/2R\sin\alpha\cos\alpha}\,. \tag{18}$$

Since there is no node in α, the generalized function (18) reduces to f_{110} at $R=0$. Notice that $\cos^2\alpha$ has been multiplied to the asymptotic form such that the proper limit f_{110} is obtained at $R=0$.

C. The + and − channels

If there are two degenerate hydrogenic nl_1 and nl_2 states in the dissociation limit, then the so-called "+" and "−" channels arise.[2,16] Consider, for example, the $\mu=2$ and 3 channels for $^{1,3}P^o$ state of H$^-$ in the [01] subspace. These two channels dissociate to the $n=2$ limit of the hydrogen atom. They originate from the two degenerate hydrogenic $2s$ and $2p$ states in the asymptotic limit. The weak dipole interaction between the two electrons allows the exchange of the two orbital angular momenta l_1 and l_2. If this dipole interaction is included, new channels (simply called + and − channels) are obtained whose eigenfunctions are linear combinations of hydrogenic $2s$ and $2p$ functions. By generalizing the $2s$ and $2p$ functions separately to smaller R, we obtain the generalized $2s$ for ${}^{1,3}P^o$ states

$$\Phi_{2s}(R;\Omega)=A[\sin\alpha\cos^2\alpha\,(1-\tfrac{1}{2}R\sin\alpha)\times e^{-(R/2)\sin\alpha}\mathcal{Y}_{0110}(\hat{r}_1,\hat{r}_2)] \tag{19}$$

and the corresponding $2p$:

$$\Phi_{2p}(r;\Omega)=A[\sin^2\alpha\cos\alpha\sin\alpha\, e^{-(R/2)\sin\alpha}\mathcal{Y}_{1010}(\hat{r}_1,\hat{r}_2)] \tag{20a}$$

$$=A[\cos^2\alpha\sin\alpha\cos\alpha\, e^{-(R/2)\cos\alpha}\mathcal{Y}_{0110}(\hat{r}_1,\hat{r}_2)]\,, \tag{20b}$$

where A is the suitable symmetrization operator. The + and − channels at large R are now represented by

$$\Phi_{\pm}^{(0)}(R;\Omega)=a_{2s}^{\pm}(R)\Phi_{2s}+a_{2p}^{\pm}(R)\Phi_{2p}\,. \tag{21}$$

In Fig. 3(a), I show the potential curves (in dashed lines) for the + and − channels in ${}^3P^o$ calculated from $\Phi_{\pm}^{(0)}$ and compare them with the numerical calculations (shown in solid lines). The agreement in the large-R region is quite satisfactory which indicates that a *single* $\Phi_0^+(\Phi_0^-)$ is adequate in representing the outer region for the +(−) channel within the specified $[l_1l_2]$ subspace. In Fig. 3(b), I show the variation of a_{2s}^+ and a_{2p}^+ with R. Notice that the absolute values of a_{2s}^+ and a_{2p}^+ (and similarly a_{2s}^- and a_{2p}^-) remain very close to each other in the region $R>6$. Their ratio approaches the values given by the close-coupling approximation $a_{2p}^+/a_{2s}^+=-\frac{4}{3}$ and $a_{2p}^-/a_{2s}^-=\frac{3}{4}$, only in the large-$R$ region.

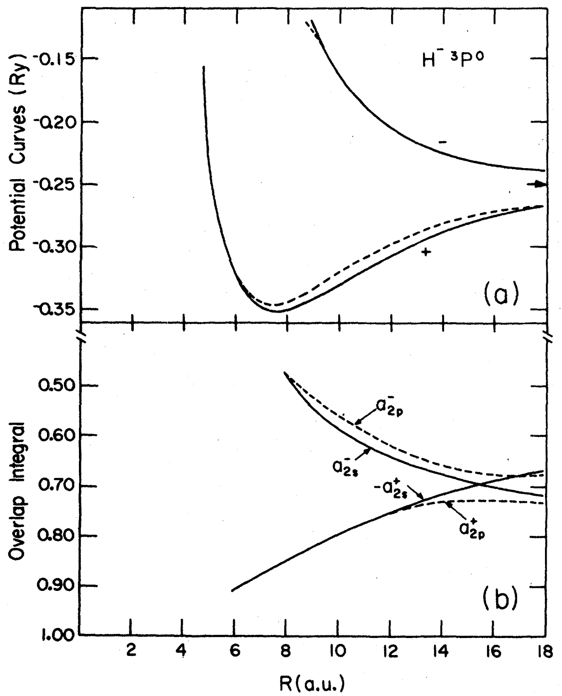

FIG. 3. (a) the + and − potential curves of $2sp\ {}^3P^o$ for H⁻. Solid lines are from the exact numerical calculation, the dotted lines are from the calculations using zeroth-order + and − analytical functions, Eq. (21). (b) Mixing coefficients $a_{2s}^{\pm}$ and $a_{2p}^{\pm}$, see Eq. (21).

D. General form of the analytical channel functions

The preceding examples allow us to find the general form of the channel function in each $[l_1l_2]$ subspace. If $l_1=l_2=l$, the function $g_{nl}(R;\alpha)$, which converges to the hydrogenic nl state, is obtained by replacing every r_1 in the r-weighted radial hydrogenic wave function $r_1R_{nl}(r_1)$ by $R\sin\alpha\cos\alpha$ if $L+S=$ even; an additional factor $\cos2\alpha$ is multiplied if $L+S=$ odd. If $l_1<l_2$, the generalized analytical function is as follows:

(1) Express $r_1R_{nl_1}=r_1r_1^{l_1}P_{nl_1}(r_1)e^{-r_1/n}$ (22)
where $P_{nl_1}(r_1)$ is the Laguerre polynomial.

(2) Replace r_1 above by $R\sin\alpha$ and multiply $(\cos\alpha)^{l_2+1}$ to obtain the symmetrized generalized analytical function

$$\Phi_{nl_1}=A[(\sin\alpha)^{l_1+1}(\cos\alpha)^{l_2+1}P_{nl_1}(R\sin\alpha)\times e^{-R\sin\alpha/n}\mathcal{Y}_{l_1l_2LM}(\hat{r}_1,\hat{r}_2)]\,. \tag{23}$$

The multiplication of $(\cos\alpha)^{l_2+1}$ to the asymptotic form (22) is *essential*, since the kinetic energy term of Eq. (5) requires such a symmetric treatment, as can be seen from the solution of (5) at $R=0$ [cf. Eq. (8)]. The term containing $\vec{l}_2^{\,2}$ in Eq. (5) is often not considered in the single-particle approximation because in this approximation only the region $\alpha\to0$ is properly treated.

The generalized channel function given in (23) allows us to obtain a local potential which depends upon L and S even within a one-channel approximation. These potentials differ from the usual local-potential models of atoms. They are similar to the so-called $V^{N-1}(LS)$ potentials[17-19] in the many-body perturbation theory except that these later potentials are nonlocal.

If there are two hydrogenic limits for a given n within the $[l_1l_2]$ pair, then the generalized functions are the zeroth-order + and − channel functions. One first obtains a generalized

$$\Phi_{nl_2} = A[(\sin\alpha)^{l_2+1}(\cos\alpha)^{l_1+1} P_{nl_2}(R\sin\alpha) \times e^{-R\sin\alpha/n}\mathcal{Y}_{l_2 l_1 LM}(\hat{r}_1,\hat{r}_2)]\,, \tag{24}$$

the zeroth-order + and − functions are then obtained by diagonalizing (5) in the two basis functions (23) and (24). There are no analogous potentials in the many-body perturbation theory for the + and − potentials.

IV. DISCUSSIONS

In this article I propose simple analytical functions in hyperspherical coordinates which can be used in atomic structure and scattering calculations. These functions can be used in a diagonalization procedure to obtain adiabatic channel functions $\Phi_\mu(R;\Omega)$. Since only *one* such a function is needed for each dissociated $[l_1 l_2]$ channel in the outer region, the number of basis functions in the outer-R region is very limited. To implement the deficiency of these simple functions in the small-R region, the low-lying eigenfunctions $u_{l_1 l_2 m}$ of Λ^2 operator can be used. Therefore, in the diagonalization procedure for calculating adiabatic potential curves several functions described here and several $u_{l_1 l_2 m}$ functions are used as basis functions. For example, to obtain all the potential curves which converge to the hydrogenic limits $n \leq 3$ in a single calculation, only about 15 basis states are needed to get good convergence.

The analytical functions described here can also be used as "target" states in a close-coupling or an R-matrix calculation for electron-atom scattering problems. Notice these target states are unlike the target states used in the traditional close-coupling calculation where the distortion of the target by the impinging electron is not allowed. Using the target states described here the scattering problem reduces to coupled differential equations instead of the coupled interodifferential equations.

The procedure discussed here can also be generalized to two-valence electron atoms if the core is approximated by a certain model potential. The solutions in the limit $R \to \infty$ and $\alpha \to 0$ are expressed as linear combinations of Slater functions. The generalization procedure in Sec. III D can be applied directly.

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[1] J. H. Macek, J. Phys. B 1, 831 (1968).
[2] C. D. Lin, Phys. Rev. A 10, 1986 (1974).
[3] C. D. Lin, Phys. Rev. Lett. 35, 1150 (1975).
[4] C. D. Lin, Phys. Rev. A 14, 30 (1976).
[5] H. Klar, Phys. Rev. A 15, 1452 (1977).
[6] H. Klar and M. Klar, J. Phys. B 13, 1057 (1980).
[7] C. H. Greene, J. Phys. B 13, L39 (1980).
[8] V. Fano, Phys. Today 29, No. 9, 32 (1976).
[9] H. C. Bryant, B. D. Dieterle, J. Donahue, H. Sharifian, H. Tootoonchi, D. M. Wolfe, P. A. M. Gram, and M. A. Yates-Williams, Phys. Rev. Lett. 38, 228 (1977).
[10] M. E. Hamm, R. W. Hamm, J. Donahue, P. A. M. Gram, D. A. Clark, H. C. Bryant, C. A. Frost, and W. W. Smith, Phys. Rev. Lett. 43, 1715 (1979).
[11] C. W. Clark and C. H. Greene, Phys. Rev. A 21, 1786 (1980).
[12] P. M. Morse and H. Feshbach, *Methods of Theoretical Physics* (McGraw-Hill, New York, 1953), p. 1755.
[13] C. D. Lin, Phys. Rev. A 12, 493 (1975).
[14] C. L. Pekeris, Phys. Rev. 126, 1470 (1962).
[15] H. Hotop and W. C. Lineberger, J. Phys. Chem. Ref. Data 4, 539 (1975).
[16] J. W. Cooper, U. Fano, and F. Prats, Phys. Rev. Lett. 10, 518 (1963).
[17] M. Ya Amusia and N. A. Cherepkov, Case Stud. At. Phys. 5, 47 (1975).
[18] T. N. Chang, Phys. Rev. A 15, 2392 (1977).
[19] H. P. Kelly and R. L. Simons, Phys. Rev. Lett. 30, 529 (1973).