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Hyperspherical hierarchy of three-electron radial excitations

Toru Morishita,* Oleg I. Tolstikhin,† Shinichi Watanabe, and Michio Matsuzawa
Department of Applied Physics and Chemistry, University of Electro-Communications, 1-5-1 Chofu-ga-oka, Chofu-shi, Tokyo 182, Japan

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We investigate hierarchical representation of three-electron radial excitations, relying on the replacement of a sequence of ordered individual electron radial coordinates by a hierarchical sequence of hyperspherical radial variables. In the spirit of the hyperspherical method we argue that the latter variables allow adiabatic quasiseparability of the three-electron wave function. We examine this by approximately evaluating hyperspherical adiabatic potential curves and channel functions for the Li(s^3) configuration. The hierarchical representation permits one to display manifold aspects of the triply excited states with a pair of radial quantum numbers. [S1050-2947(97)02011-8]

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I. INTRODUCTION

Despite the success of the hyperspherical method for the three-body Coulomb problem [1–7], its extension to systems with a larger number of particles is still in its infancy. Even the problem of three-electron atoms under the assumption of an infinitely heavy nucleus has not been solved to a satisfactory level yet. The nontriviality in such a generalization of the method rests on its unique perspective toward many-body effects. Indeed, while various more conventional approaches in the field of atomic calculations use the individual electron coordinates as a basic set of independent variables, allowing the many-body effects to enter only through the choice of basis functions and the way of constructing their proper linear combinations, the hyperspherical method incorporates part of the interelectron correlations from the outset by adopting a coordinate system consisting of collective variables. While use of the individual electron coordinates effectively reduces calculation of the Hamiltonian matrix elements to one-dimensional integrations, the hyperspherical method usually requires evaluating integrals of a higher dimensionality, which becomes a technical bottleneck of the problem. The three-electron atom problem is where this technical difference manifests itself whereas the difference is marginal for two-electron atoms. Imposing permutation symmetry on the total wave function is another problem, for the commonly considered hyperspherical angular variables are not invariant under the permutations of the identical particles again with the exception of two-electron atoms. It is thus undeniable that at the present stage of its development the hyperspherical method faces a few technical problems that make its extension to genuinely many-electron atoms prohibitively difficult. In fact such attempts have been restricted so far to only a few qualitative discussions (see, e.g., [8]). Yet, there are features in the hyperspherical method so strongly attractive that continued efforts are being made to elevate this method to a level of practical applicability. For instance, the hyperspherical method correctly singles out the hyperradius, a variable that plays a special role for systems with Coulomb interactions. The hyperspherical coordinates are usually close to the normal mode coordinates of the system to such an extent that the hyperspherical quantum numbers approximately represent excitation of internal collective degrees of freedom. At last, but not the least, the hyperspherical potential curves provide, simply by sight, valuable information about the system's energetics.

A brief history and the current situation in applications of the hyperspherical method to three-electron atoms are as follows. A first attempt was made by Clark and Greene in 1980 [9] who used the hyperspherical harmonics as a basis set for expanding the adiabatic channel functions. They noted some general features concerning the grouping of hyperspherical channels into those separately supporting doubly and triply excited states as well as sharply avoided crossings among different groups of curves that suggested a dramatic difference in normal mode patterns between the different groups. The convergence, however, was so poor on account of the use of the hyperspherical harmonics that even the asymptotic thresholds did not come out correctly. This convergence problem was resolved by Watanabe *et al.* [10] by the use of Slater-type orbitals transcribed for the hyperspherical coordinates. The resonance positions of He$^-$ were evaluated for states of $^4S^o$, $^4P^o$ [10], and $^2P^o$ [11] symmetries, achieving a reasonable precision even within the adiabatic approximation. A similar basis was later used by Greene and Clark for analysis of $^2P^o$ states of Li [12]. Later, a more flexible approach for solving the adiabatic eigenvalue problem by employing direct numerical schemes such as the B-spline method was pursued by Yang *et al.* [13]. The hyperspherical adiabatic channel functions so-obtained have been analyzed by way of their graphical display in the case of the Li(s^3) configuration [13]. In the wake of the recent experimental reports on the hollow lithium atom [14,15] (hollow or vacant with respect to the two $1s$ orbitals but the $2s$ orbital remaining occupied), Yang *et al.* [16] extended their study to Li($^2P^o$) states. Besides these hyperspherical calculations, the recent experiments prompted a number of theoretical studies by different methods. The configuration interaction results

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*Present address: Department of Physics, Kansas State University, Manhattan, Kansas 66506-2601.

†Present address: Institute for Molecular Science, Myodaiji, Okazaki 444, Japan. Permanent address: P. N. Lebedev Physical Institute, Russian Academy of Sciences, Leninsky Prospect 53, 117924, Moscow, Russia.

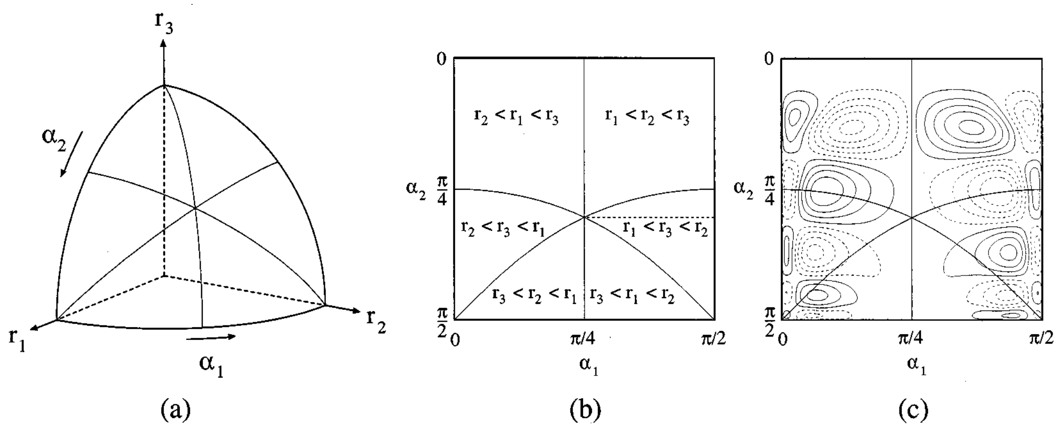


FIG. 1. (a) Three-dimensional image of D. r_1, r_2, and r_3 are individual electron radii, α_1 and α_2 are angular variables, which are similar to standard spherical polar angles but over a restricted domain of one octant of a sphere, used for the present parametrization of D. (b) Division of the α_1-α_2 plane into six domains according to the relative magnitudes of the radial variables. An interchange of any pair of the three electrons is equivalent to interchanging a pair of neighboring domains. Our attention focuses on the upper right domain where $r_1 < r_2 < r_3$, referred to as $D_{1/6}$. (c) A contour plot for a typical adiabatic channel function (for doublet symmetry) demonstrating quasiseparability in the two upper domains.

by Chung and Gou [17] as well as the multiconfigurational Dirac-Fock calculations of Koike and co-workers [15] seem to identify the measured resonance positions reasonably well. From a numerical view point, the recent R-matrix work [18] seems largely capable of providing spectroscopically valuable information. However, regarding some details of the experimental features and their explanations there still remains room for interpretation and thus for further studies by alternative methods. In particular, a normal mode analysis by the hyperspherical method is expected to cast some light on the observed triply excited spectra, as it did so successfully for doubly excited ones. It is in this spirit that the present article begins, but its aim will be restricted to bringing attention to some fundamental construction arising within the context of the hyperspherical method whose recognition might help one to understand manifold aspects of three-electron correlations.

Specifically, we study adiabatic quasiseparability of three-electron wave functions with respect to a certain hierarchy of hyperspherical radial variables. Our original motivation stems from a simple observation of the graphical material presented in [13]. Let us make the point explicit with the aid of Fig. 1. Here, as in [13], we restrict ourselves to the s^3 configuration. Using the parametrization of [9], the configuration space of the hyperspherical adiabatic eigenvalue problem can be conveniently represented by one-eighth of a sphere in three-dimensional space [see also Fig. 1(a)], which we shall call D. We observe that the nodal structure of the adiabatic channel functions displayed in [13] indicates *adiabatic* quasiseparability with respect to α_1 regarded as a "fast" and α_2 as a "slow" variable for the present parametrization of D in each of the two domains adjacent to the upper corner in Fig. 1(a) [see Fig. 1(c)]. There are totally six such domains; each constitutes one sixth of D. All six domains are, of course, physically equivalent. However, the present parametrization of D introduces an essential difference between them in the sense that the quasiseparability emerges as due only to the two upper domains. Note that these upper domains are not where the authors of [13] focused their primary attention. As a preliminary attempt for qualitative support of the quasiseparability, we introduce here an approximate treatment based on restricting the configuration space of the problem from the entire D to the upper right domain $r_1 < r_2 < r_3$, which we shall denote as $D_{1/6}$. Such treatment is achievable by assuming suitable approximate boundary conditions on the boundaries of $D_{1/6}$. We examine the quality of this approximation against a rigorous diagonalization of the adiabatic Hamiltonian. A brief account of this work was presented earlier [19]. It is possible to represent the configuration space using an alternative parametrization such as that suggested in Ref. [20]. We continue to concentrate on the hyperspherical parametrization in this paper.

II. FORMULATION OF THE PROBLEM

The hyperspherical method roughly consists of three stages in its actual implementation. The first one is the construction of adiabatic channel functions with which this paper is concerned, hence this point will be amply described in this section. The second stage is the adiabatic expansion of the total wave function using the adiabatic channel functions as a basis set. A most strongly recommended method of solution for the second stage is currently the combination of the slow/smooth variable discretization (SVD) method [4] and the R-matrix propagation technique [21]. The third stage is to extract the S matrix or its equivalent from the propagated solution [5,6]. Both the second and the third stages are independent of the first one, and are thus applicable to a broader range of problems. Such being the case, here we will focus on the first stage only.

A. Hierarchical approximation: General idea

In order to convey the gist of our theme, we begin our discussion with the definition of a sequence of hyperradii. Let us consider a somewhat general context to render the meaning of "hierarchy" explicit. Let Ψ be a total wave function of an N-electron atom, and let $\mathbf{r}_i=(r_i,\theta_i,\phi_i)$ be the position vectors of the individual electrons. Let us disregard for the moment the spin variables, assuming that Ψ has only one spatial component. Due to the permutation symmetry of Ψ, it is sufficient to consider the sector where $r_1\leqslant r_2\leqslant\cdots\leqslant r_N$. We replace the individual radii r_i by a sequence of hyperradial variables $R_1=r_1, R_2=\sqrt{R_1^2+r_2^2},\ldots,R_N=\sqrt{R_{N-1}^2+r_N^2}$. All the individual angles (θ_i,ϕ_i) will be collectively denoted as ω. Note the importance of the ordering $r_1\leqslant r_2\leqslant\cdots\leqslant r_N$ and the corresponding definition of the hyperradii. The key idea of the hyperspherical method lies in the assumption of approximate *adiabatic* separability of the motion in R_N from those in all the other variables. There are two consequences following from this assumption: (1) The total wave function can be approximated by $\Psi=F^{(N)}(R_N)\Phi^{(N)}(R_1,\ldots,R_{N-1},\omega;R_N)$, where the radial factor $F^{(N)}(R_N)$ represents the major dependence of Ψ on R_N, while the adiabatic channel function $\Phi^{(N)}$ depends on R_N only parametrically. (2) The channel function $\Phi^{(N)}$ evolves *smoothly* with respect to R_N, preserving its nodal structure, except for localized regions where the adiabatic potential energies to be discussed later encounter quasidegeneracies, namely, avoided crossings as well as where R_N is so small that the ordering $r_1\leqslant r_2\leqslant\cdots\leqslant r_N$ is insignificant. Thus the approximation for $\Phi^{(N)}$ that is valid asymptotically as $R_N\to\infty$ should qualitatively hold for all the values of R_N. Note that within the sector $r_1\leqslant r_2\leqslant\cdots\leqslant r_N$, the limit $R_N\to\infty$ actually means $r_N\to\infty$. In this limit, $F^{(N)}(R_N)$ coincides with the radial wave function of the outermost electron. Meanwhile the parent atom is characterized by its own hyperradius R_{N-1}, and using the argument of adiabatic separability again leads to the further decomposition

$$\Phi^{(N)}=F^{(N-1)}(R_{N-1};R_N)\times\Phi^{(N-1)}(R_1,\ldots,R_{N-2},\omega;R_{N-1},R_N).$$

A recursive use of this argument provides a picture of hierarchy of the adiabatic separation with respect to the hyperradial variables R_i such that the total wave function in the sector $r_1\leqslant r_2\leqslant\cdots\leqslant r_N$ can be approximated by

$$\Psi=F_{n_N}^{(N)}(R_N)F_{n_{N-1}}^{(N-1)}(R_{N-1};R_N)\cdots\times F_{n_1}^{(1)}(R_1;R_2,\ldots,R_N)\mathcal{Y}_a^{LM}(\omega). \tag{1}$$

Here the factor $\mathcal{Y}_a^{LM}(\omega)$ represents the total dependence of Ψ on ω, where LM and a stand for the total and all the intermediate angular momentum quantum numbers, respectively. Let us call this formula the ''hierarchical representation.'' Each radial factor $F_{n_i}^{(i)}$ in Eq. (1), labeled by its number of zeros n_i with respect to R_i, depends parametrically on all the ''senior'' hyperradii $R_{j>i}$. The functions $F_{n_i}^{(i)}$ should also bear dependence on all the ''junior'' indices $n_{j<i}$ which, however, we do not show explicitly for simplicity. This parametric dependence, however, does not affect n_i, thus within the hierarchical representation, Eq. (1), the set of indices n_i together with a and LM define a complete set of quantum numbers specifying a given state.

Formula (1) applies within the sector $r_1\leqslant r_2\leqslant\cdots\leqslant r_N$. Using the permutation symmetry of the total wave function, one should be able to extend this formula to the whole configuration space. This implies that the function (1) must satisfy certain conditions on the boundaries between different sectors where two of the individual radii r_i coincide. For example, a totally antisymmetric wave function should vanish on each boundary of the sector $r_1\leqslant r_2\leqslant\cdots\leqslant r_N$. In principle, such boundary conditions can be formulated also for a general case when the total wave function Ψ, including its dependence on the spin variables, has more than one spatial components. In reality, the boundary surface of the sector cannot be made separable with respect to the hierarchical variables R_i. As mentioned in the Introduction, this is a common problem for the hyperspherical method. Though we do not know a consistent and, at the same time, practically applicable solution to this boundary condition problem, some *ad hoc* procedure for three-electron atoms will be described in Sec. II C below. In spite of this lack of rigor, we hope formula (1) is transparent enough to convey our basic idea.

B. Rigorous numerical treatment

From here on, let us return to the problem of a three-electron atom. In investigating the plausibility of the hierarchy of radial correlations, we restrict ourselves to considering the s^3 configuration in much the same way as the authors of [9] and [13]. Following [9], we employ the most straightforward parametrization of D by means of the two angles α_1 and α_2 as illustrated in Fig. 1(a):

$$r_1=R\sin\alpha_2\cos\alpha_1,\quad r_2=R\sin\alpha_2\sin\alpha_1,\quad r_3=R\cos\alpha_2. \tag{2}$$

Here $R=\sqrt{r_1^2+r_2^2+r_3^2}$ is the global hyperradius as commonly defined, which coincides with R_3 using the hierarchical notation of the previous section. The Schrödinger equation for the rescaled wave function $\psi=Rr_1r_2r_3\Psi$ then reads

$$\left(-\frac{1}{2}\frac{\partial^2}{\partial R^2}+\frac{H_{\mathrm{ad}}(\alpha_1,\alpha_2;R)}{R^2}-E\right)\psi=0, \tag{3}$$

where the adiabatic Hamiltonian $H_{\mathrm{ad}}(\alpha_1,\alpha_2;R)$ is an operator in α_1 and α_2 that depends parametrically on R, namely,

$$H_{\mathrm{ad}}(\alpha_1,\alpha_2;R)=-\frac{1}{2}\left(\frac{1}{\sin\alpha_2}\frac{\partial}{\partial\alpha_2}\sin\alpha_2\frac{\partial}{\partial\alpha_2}+\frac{1}{\sin^2\alpha_2}\frac{\partial^2}{\partial\alpha_1^2}\right)+RC(\alpha_1,\alpha_2) \tag{4}$$

and $C(\alpha_1,\alpha_2)$ is the effective charge representing the Coulomb potential energy averaged over the s^3 configuration:

$$C(\alpha_1,\alpha_2)=R\left(-\frac{Z}{r_1}-\frac{Z}{r_2}-\frac{Z}{r_3}+\frac{1}{(r_{12})_>}+\frac{1}{(r_{23})_>}+\frac{1}{(r_{31})_>}\right). \tag{5}$$

Here $(r_{ij})_>$ means the greater of r_i and r_j, and Z is the Coulomb charge of the nucleus.

Following the prescriptions of the hyperspherical method [22] we assume the total wave function of the system for a state with total spin S to be in the form

$$\psi^S=\sum_\nu F_\nu(R)\left(\sum_{S_{12}} \Phi_\nu^{S,S_{12}}(\alpha_1,\alpha_2;R)\chi_{S_{12}}^S\right). \tag{6}$$

In this formula $F_\nu(R)$ is the radial function, which does not concern us in this article, $\Phi_\nu^{S,S_{12}}$ is the adiabatic channel function on which we will focus in the following, and $\chi_{S_{12}}^S$ is the spin function defined, as usual, as

$$\chi_{S_{12}}^S=[[\chi(1)\chi(2)]^{S_{12}}\chi(3)]^S, \tag{7}$$

where S_{12} is the total spin of the electrons having indices 1 and 2.

The adiabatic channel function $\Phi_\nu^{S,S_{12}}$ and its associated potential energy $U_\nu^{S,S_{12}}(R)$ are defined as solutions of the hyperspherical adiabatic eigenvalue problem

$$[H_{\rm ad}(\alpha_1,\alpha_2;R)-U_\nu(R)]\Phi_\nu(\alpha_1,\alpha_2;R)=0. \tag{8}$$

All the basis functions $\Phi_\nu^{S,S_{12}}$ of Eq. (6) are among solutions to this equation. However, not all the solutions of Eq. (8) satisfy the Pauli principle because the sum over S_{12} must result in a totally antisymmetric wave function. Indeed, for the quartet symmetry $S=\frac{3}{2}$, the sum over S_{12} in Eq. (6) contains only one spatial component $\Phi_\nu^{3/2,1}$ corresponding to a triplet parent, whose wave function is antisymmetric with respect to a permutation of any two electrons. For the doublet symmetry $S=\frac{1}{2}$, there are two spatial components $\Phi_\nu^{1/2,0}$ and $\Phi_\nu^{1/2,1}$ which multiply the singlet and triplet parent spin functions, respectively. These functions form a basis for a two-dimensional representation of the permutation group S_3 and they have degenerate eigenvalues $U_\nu^{1/2,0}(R)=U_\nu^{1/2,1}(R)$ for all the values of R. Besides, Eq. (8) has also totally symmetric solutions, which, however, do not satisfy the Pauli principle and must be omitted.

We solve the two-dimensional eigenvalue problem (8) numerically using a variational procedure with the direct product of two sets of discrete variable representation (DVR) [23] basis functions, constructed from appropriately shifted and renormalized Jacobi polynomials in α_1 and α_2. This technique is a two-dimensional generalization of the numerical method [24], which has been used for calculating the adiabatic channel functions in our previous studies on the three-body Coulomb problem [3,4] and two-electron atoms [5,6]. The method is characterized by features common to other DVR schemes, namely, fast convergence with respect to the increase of the number of quadrature points, high accuracy, stability, and relative ease of implementation. By selecting a particular set of Jacobi polynomials this method is easily extendable to an arbitrary (l_1,l_2,l_3) angular configuration.

This numerical procedure yields a variational approximation to *all* low-lying solutions of Eq. (8), disregarding their symmetry properties. To sort out appropriate solutions as well as to eliminate totally symmetric ones we apply the projection operator

$$P=E+(123)+(132)-(12)-(23)-(13). \tag{9}$$

Namely, for each numerically obtained solution Φ_ν of Eq. (8) we calculate the matrix element $\langle\Phi_\nu\chi_{S_{12}}^S|P|\Phi_\nu\chi_{S_{12}}^S\rangle$. The matrix elements of each component of P with respect to the spin functions are very well known. The action of the projection operator on the spatial part Φ_ν is carried out numerically by acting the permutation operators directly on the configuration space defined by the α_1 and α_2 variables [25]. In this manner, we sort out a quartet and two proper components of the doublet eigenfunctions, which provide accurate numerical information to be used further for comparison with the hierarchical approximation.

C. Hierarchical approximation for three-electron atoms

Hyperradii R_i can be expressed by

$$R_1=R\sin\alpha_2\cos\alpha_1, \tag{10}$$

$$R_2=R\sin\alpha_2, \tag{11}$$

$$R_3=R. \tag{12}$$

According to the discussion of Sec. II A, we focus on the sector $r_1<r_2<r_3$. First of all we should fix the value of R_3, which is regarded as ''slowest'' variable. Because R_3 coincides with R, this step is in agreement with the usual strategy of the hyperspherical method. The adiabatic separability of R leads to the standard adiabatic expansion (6) and this variable is not our concern here. The section of the sector $r_1<r_2<r_3$ with the hypersphere $R=$const coincides with what we have defined as the $D_{1/6}$ domain. From here on, we will focus on this domain only. Next, we fix the value of R_2. According to Eq. (11), this amounts to fixing the α_2 variable. After that, there remains only one variable R_1, which is regarded as ''fastest'' and which is now in one-to-one correspondence with α_1; see Eq. (10). Thus, we consider Eq. (8) in the domain $D_{1/6}$ assuming adiabatic separability between α_1 and α_2. To this end we rewrite the adiabatic Hamiltonian (4) as follows:

$$H_{\rm ad}(\alpha_1,\alpha_2;R)=-\frac{1}{2}\frac{1}{\sin\alpha_2}\frac{\partial}{\partial\alpha_2}\sin\alpha_2\frac{\partial}{\partial\alpha_2}+\frac{h_{\rm ad}(\alpha_1;\alpha_2,R)}{\sin^2\alpha_2}, \tag{13}$$

where we introduce the ''junior'' adiabatic Hamiltonian

$$h_{\rm ad}(\alpha_1;\alpha_2,R)=-\frac{1}{2}\frac{\partial^2}{\partial\alpha_1^2}+R\sin^2\alpha_2 C(\alpha_1,\alpha_2), \tag{14}$$

which is an operator in α_1 and depends on α_2 and R only parametrically. Now we define the ''junior'' adiabatic eigenvalue problem

$$[h_{\rm ad}(\alpha_1;\alpha_2,R)-u_{n_1}(\alpha_2,R)]g_{n_1}(\alpha_1;\alpha_2,R)=0, \tag{15}$$

where n_1 represents the number of nodes of the solution $g_{n_1}(\alpha_1;\alpha_2,R)$ as a function of α_1. Hierarchical approximation to Eq. (8) amounts to substituting in Eq. (13) the operator $h_{\rm ad}(\alpha_1;\alpha_2,R)$ by its eigenvalue $u_{n_1}(\alpha_2,R)$ obtained from solution of Eq. (15). By doing so, Eq. (8) reduces to

$$\left[-\frac{1}{2}\frac{1}{\sin\alpha_2}\frac{\partial}{\partial\alpha_2}\sin\alpha_2\frac{\partial}{\partial\alpha_2}+\frac{u_{n_1}(\alpha_2,R)}{\sin^2\alpha_2}\right.$$
$$\left.-\tilde{U}_{n_1n_2}(R)\right]f_{n_1n_2}(\alpha_2;R)=0, \tag{16}$$

where n_2 represents the number of nodes of $f_{n_1n_2}(\alpha_2)$ as a function of α_2. In this approximation, the index ν labeling different solutions of Eq. (8) is specified by the pair of integers (n_1,n_2), while the hyperspherical adiabatic potentials U_ν and channel functions Φ_ν are defined by

$$U_\nu(R)\simeq\tilde{U}_{n_1n_2}(R), \tag{17}$$

$$\Phi_\nu(\alpha_1,\alpha_2;R)\simeq f_{n_1n_2}(\alpha_2;R)g_{n_1}(\alpha_1;\alpha_2,R). \tag{18}$$

Let us first list the exact boundary conditions:

(1) The regularity condition at $r_1=r_2=0$ (i.e., $\alpha_2=0$),

$$\Phi_\nu^{S,S_{12}}|_{\alpha_2=0}=0, \tag{19}$$

and at $r_1=0$ (i.e., $\alpha_1=\pi/2$),

$$\Phi_\nu^{S,S_{12}}|_{\alpha_1=\pi/2}=0. \tag{20}$$

This applies to all combinations of S and S_{12}.

(2) The permutation symmetry under the (12) operator

$$(12)\Phi_\nu^{3/2,1}=-\Phi_\nu^{3/2,1}\rightarrow\Phi_\nu^{3/2,1}|_{\alpha_1=\pi/4}=0, \tag{21}$$

$$(12)\Phi_\nu^{1/2,1}=-\Phi_\nu^{1/2,1}\rightarrow\Phi_\nu^{1/2,1}|_{\alpha_1=\pi/4}=0, \tag{22}$$

$$(12)\Phi_\nu^{1/2,0}=+\Phi_\nu^{1/2,0}\rightarrow\frac{\partial\Phi_\nu^{1/2,0}}{\partial\alpha_1}\Big|_{\alpha_1=\pi/4}=0. \tag{23}$$

(3) The permutation symmetry under the (13) operator

$$(13)\Phi_\nu^{3/2,1}=-\Phi_\nu^{3/2,1}\rightarrow\Phi_\nu^{3/2,1}|_b=0, \tag{24}$$

$$(13)\Phi_\nu^{1/2,1}=\frac{1}{2}\Phi_\nu^{1/2,1}+\frac{\sqrt{3}}{2}\Phi_\nu^{1/2,0}\rightarrow\frac{1}{2}\Phi_\nu^{1/2,1}\Big|_b$$
$$=-\frac{\sqrt{3}}{2}\Phi_\nu^{1/2,0}\Big|_b, \tag{25}$$

$$(13)\Phi_\nu^{1/2,0}=\frac{\sqrt{3}}{2}\Phi_\nu^{1/2,1}-\frac{1}{2}\Phi_\nu^{1/2,0}\rightarrow\frac{\sqrt{3}}{2}\frac{\partial\Phi_\nu^{1/2,1}}{\partial n}\Big|_b$$
$$=\frac{1}{2}\frac{\partial\Phi_\nu^{1/2,0}}{\partial n}\Big|_b. \tag{26}$$

where the symbol $\partial/\partial n$ represents the normal derivative with respect to the boundary b, a line that is defined by $r_2=r_3$ or by an implicit equation $\sin\alpha_2\sin\alpha_1=\cos\alpha_2$.

In view of the fact that the domain $D_{1/6}$ is nearly rectangular, our first approximation is to replace $D_{1/6}$ by the rectangle whose vertices are located at $(\alpha_1,\alpha_2)=(\pi/4,0),(\pi/2,0),(\pi/2,\tan^{-1}\sqrt{2}),(\pi/4,\tan^{-1}\sqrt{2})$. The boundary b should then be replaced by $\tilde{b}$, the straight line that joins $(\pi/4,\tan^{-1}\sqrt{2})$ and $(\pi/2,\tan^{-1}\sqrt{2})$.

One obvious approximate boundary condition is

$$\Phi^{3/2,1}|_{\tilde{b}}=0 \tag{27}$$

for quartet. Also it is evident that nonphysical solutions that pertain to totally symmetric wave functions would have vanishing normal derivatives at $\tilde{b}$ and $\alpha_1=\pi/4$ in the present approximation. It stands to reason that we consider a region extended by reflecting $D_{1/6}$ with respect to the approximate boundary line $\tilde{b}$ as well as $\alpha_1=\pi/4$ so that the solutions would automatically satisfy the reflection symmetry with respect to $\alpha_1=\pi/4$ and $\tilde{b}$. Both the totally symmetric and totally antisymmetric solutions have approximate parity demanded by reflection. But there follow naturally two other types of solutions, one of which is symmetric with respect to $\alpha_1=\pi/4$ but antisymmetric with respect to $\tilde{b}$. Likewise, the other one is antisymmetric with respect to $\alpha_1=\pi/4$ but symmetric with respect to $\tilde{b}$. It is natural to associate them with doublet states, presuming a unique association is possible for all the four types of solutions, namely,

$$\Phi^{1/2,0}|_{\tilde{b}}=0 \quad (\text{for singlet parent}), \tag{28}$$

$$\frac{\partial\Phi^{1/2,1}}{\partial n}\Big|_{\tilde{b}}=0 \quad (\text{for triplet parent}). \tag{29}$$

The former is symmetric with respect to $\alpha_1=\pi/4$, and the latter antisymmetric. In the next section, this assumption of unique association will be exploited without further notice.

III. AN ILLUSTRATIVE EXAMPLE AND DISCUSSIONS

Let us illustrate the idea of ‘‘hierarchy’’ on the example of Li. First, we would like to point out that the three-electron hyperspherical adiabatic Hamiltonian consists of the two-electron hyperspherical Hamiltonian and the residue, the major role of the latter being to represent the outermost electron. With the introduction of a new variable $\rho=\sqrt{r_1^2+r_2^2}=R\sin\alpha_2\leqslant\sqrt{\frac{2}{3}}R$, it follows that as $R\rightarrow\infty$, then $r_3\rightarrow\infty$ in such a way that

$$h_{\rm ad}(\alpha_1;\alpha_2,R)=H_{\rm ad}^{(2)}(\alpha_1;\rho)-\frac{Z-2}{R}\left[1-\left(\frac{\rho}{R}\right)^2\right]^{-1/2}\rho^2, \tag{30}$$

where $H_{\rm ad}^{(2)}(\alpha_1;\rho)$ is the Hamiltonian of a two-electron subsystem,

$$H_{\rm ad}^{(2)}(\alpha_1;\rho)=-\frac{1}{2}\frac{\partial^2}{\partial\alpha_1^2}+\rho\left(-\frac{Z}{\sin\alpha_1}-\frac{Z}{\cos\alpha_1}\right.$$
$$\left.+\frac{1}{\max(\cos\alpha_1,\sin\alpha_1)}\right). \tag{31}$$

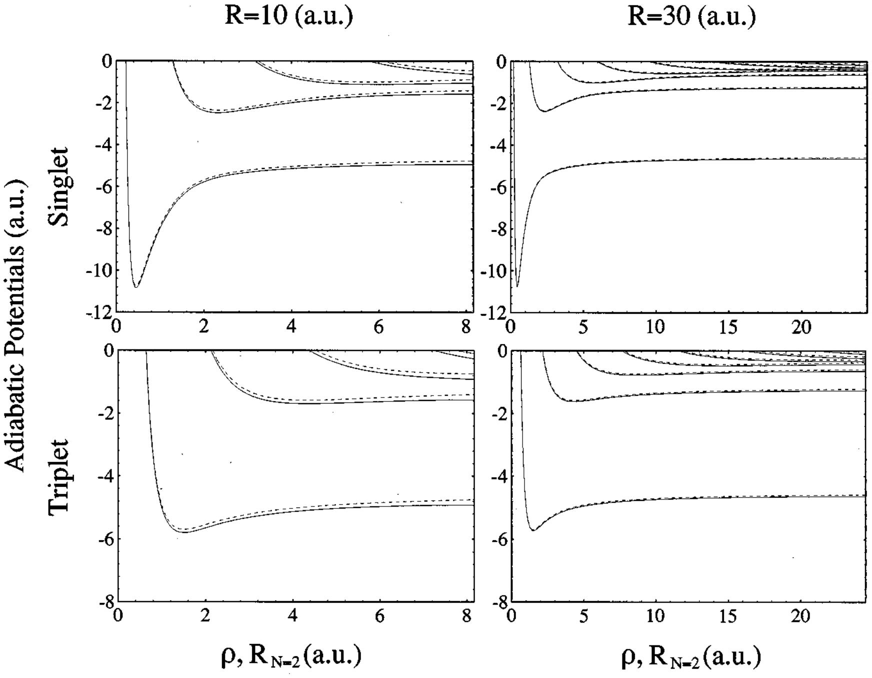


FIG. 2. Adiabatic potential energies of $h_{\rm ad}(\alpha_1;\alpha_2,R)$ (solid curves) are compared to those of the two-electron adiabatic Hamiltonian (dashed curves). They coincide for large values of R.

Except for the screened Coulomb potential and a small fictitious quadrupolelike correction term, $h_{\rm ad}$ coincides with the two-electron Hamiltonian $H_{\rm ad}^{(2)}$. The asymptotic target states are thus represented by the two-electron hyperspherical Hamiltonian. However, when R is finite, the two-electron Hamiltonian becomes confined in a bounded region of space. The adiabatic eigenvalue problem of the two-electron subsystem is thus defined under the restriction of $\rho \leq \sqrt{\frac{2}{3}}R$, and yields approximate adiabatic potential energies of the two-electron subsystem. This point is illustrated in Fig. 2, which shows eigenvalues of $h_{\rm ad}(\alpha_1;\alpha_2,R)$ as a function of ρ together with the adiabatic potential curves calculated using our two-electron adiabatic code [2] as a function of $R_{N=2} = \sqrt{r_1^2+r_2^2}$. As R becomes large, adiabatic eigenstates of the subsystem approach those of the s^2 configuration of Li$^+$ and the variation of α_2 becomes equivalent to that of ρ, thus the target state energies emerge. When R is of moderate size, the residual difference, namely, the last term in Eq. (30), tends to be appreciable.

As regards the character of three-electron adiabatic potential curves, we show lower ones for both doublet and quartet symmetries in Fig. 3 in atomic units against the hyperradius R. These curves are obtained by the rigorous numerical procedure. The general appearance of the adiabatic potential curves do not differ markedly from those of two-electron atoms such as He in that for each curve there is the typical small-R region where the dominance of the kinetic energy leads to the repulsive mock-centrifugal potential. In the intermediate region, the potential curve reaches the minimum with a basin where resonances can be formed due to the screened Coulomb attraction of the nucleus. A trivial but noticeable difference between quartet and doublet symmetries is the absence of singlet parent states in the quartet symmetry leading to the absence of a curve that would converge to the $1s^2$ ^1S state of Li$^+$ asymptotically. Now there are curves that converge to the singly excited states of Li$^+$ that support doubly excited resonances of Li of type $1snsn's$. In principle, there are infinitely many potential curves so that the method can represent the two-electron continuum states of type $1s\epsilon s\epsilon's$. Then there are also infinitely many curves that converge to the $2sns$ states of Li$^+$ $^{1,3}S$ that can support triply excited states of type $2snsn's$ as well as represent the two-electron continuum states of type $2s\epsilon s\epsilon's$. The argument may be repeated. The method can represent, in principle, triply excited states of type $nsn'sn''s$ and even the three-electron continuum states within the single framework. For convenience, let us use the term singly excited curves to indicate those that converge to the $1s^2$

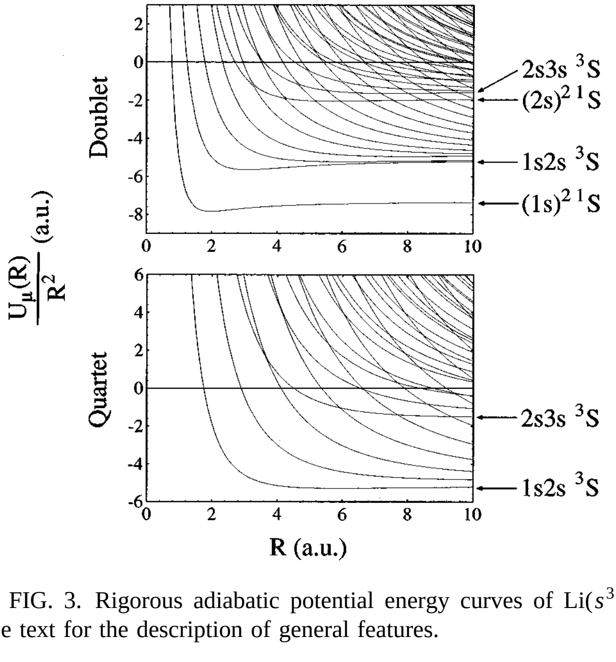


FIG. 3. Rigorous adiabatic potential energy curves of Li(s^3). See text for the description of general features.

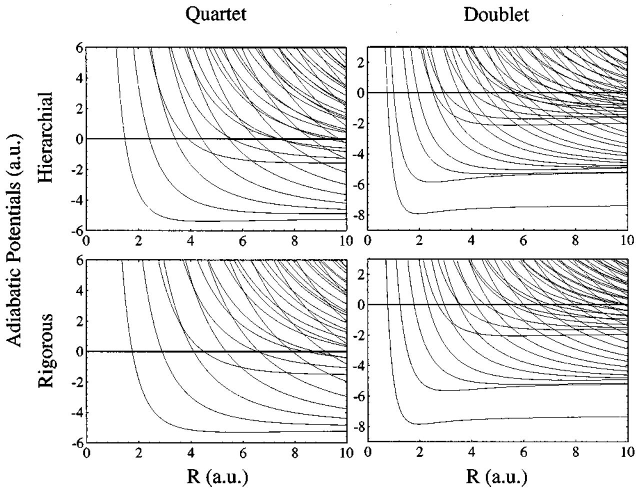


FIG. 4. Comparison of hierarchical and rigorous potential energy curves for Li(s^3). Note close resemblance of the general features noted in reference to Fig. 3 above.

state asymptotically, the term doubly excited curves for those that converge to the $1sns$ ($n \geqslant 2$) states, the term the lowest group of triply excited curves for those that converge to $2sns$ ($n \geqslant 2$), and so forth.

Returning to Fig. 3, we observe that at least the doubly excited curves and the lowest group of triply excited curves have very sharply avoided crossings. These suggest, of course, that those states possessing different inner core orbitals tend to be mutually orthogonal, and that dominant couplings are expected to prevail firstly among channels belonging to the same group of adiabatic states through the so-called T-branch avoided crossings [27] or the two-electron ridge states [29]. Indeed, the recently observed symmetric double ionization yield caused by the decay of the lowest triply excited state into double continuum [26] is thought to be a support to the weak coupling between different groups.

Let us compare the rigorous numerical potential curves, side by side, with the approximate hierarchical ones in Fig. 4. It can be seen that the general features of potential curves noted in the previous paragraph are not altered by the hierarchical approximation. For instance, it holds that the asymptotic target state energies are the same for both because the approximation pertains merely to the boundary condition so that the Hamiltonian remains unmodified and because the channel functions tend to concentrate in the region of configuration space away from the boundary b as $R \rightarrow \infty$. The behavior of each potential curve in the small and intermediate regions are similar. Importantly, curves belonging to different groups now cross, the pair (n_1, n_2) being good quantum numbers in this approximation. The feature of these crossings, despite the approximation, resembles closely that of sharply avoided crossings in the rigorous numerical treatment. Stated differently, the region near the boundary b does not play a dominant role in nonadiabatic transitions between different groups of curves although as stated earlier the breaking of wave fronts in this region is potentially important for channels of the same group. The approximate potential curves do differ from the rigorous ones in detail. The location of crossings (avoided or exact), for instance, could be appreciably different. It is certainly questionable if the approximation applies to accurate evaluations of resonance positions and widths, which require accurate potential energy curves as well as nonadiabatic couplings. However, qualitative information could be unassailably gained from an approximate Hamiltonian matrix that is capable of yielding relative level positions of the resonances. What is of importance here is that the approximate boundary condition pins down the character of each adiabatic state in terms of its numbers of nodes with respect to α_1 and α_2.

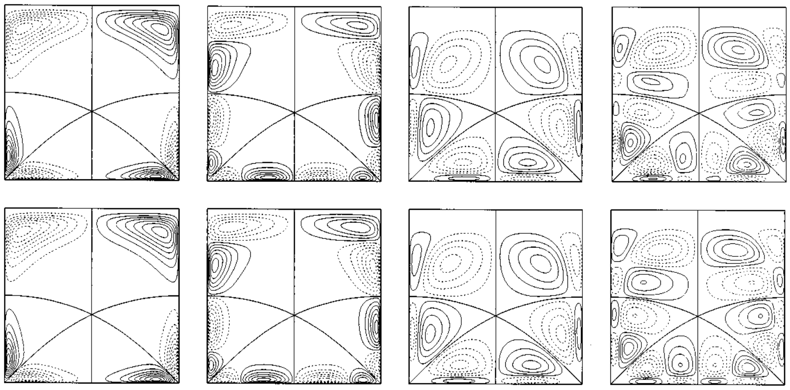
Let us now move on to check the qualitative features of some low-lying channel functions. We label the channel functions by a pair of integers (n_1, n_2), which represent the above-mentioned numbers of nodes. We show in Fig. 5 a series of contour plots pertaining to the low-lying quartet channel functions evaluated near $R = 10$. In each frame, the upper panel shows the density of an approximate channel function and the lower one the corresponding rigorous result. For the (0,0) channel, $R = 10$ is already asymptotic as the density recedes from the boundary. For the others, this is not necessarily the case. Nevertheless, the general feature of each channel function is represented properly except for details. The region near the boundary b is certainly a source of errors for the present approximation, which is the reason the approximate potential curves tend to fail at moderate values of R. To see this, let us present in Table I the projection of each approximate channel function onto the corresponding rigorous one, namely, $|\langle \Phi_{\text{hierarchical}} | \Phi_{\text{rigor}} \rangle|$, as a function of R for some representative radial distances. One general tendency is that the further the distance R is, the closer it is to unity. And another feature is that at a given value of R the higher the channel lies in energy, the poorer the projection. Nonetheless, in what is shown the difference does not exceed one-half so that the hierarchical approximation with the modified boundary condition is not grossly in error.

The discrepancy at moderate radial distances where the channel function has a moderate amplitude near the boundary b is actually in agreement with the fact that the three-electron correlations are strong enough to modify our independent-particle picture based on the pair of quantum numbers (n_1, n_2). Indeed, molecule-type normal modes are envisaged to emerge as discussed in Ref. [28]. Such normal modes are expected to center in the region where $r_1 = r_2 = r_3$, namely, the tip where all the six regions meet (see Fig. 1). One of the remaining tasks is to understand the connection between the present hierarchical picture and the molecular normal mode analysis of Watanabe and Lin [28] in anticipation, however, of realistic level calculations by the hyperspherical method.

IV. CONCLUSIONS

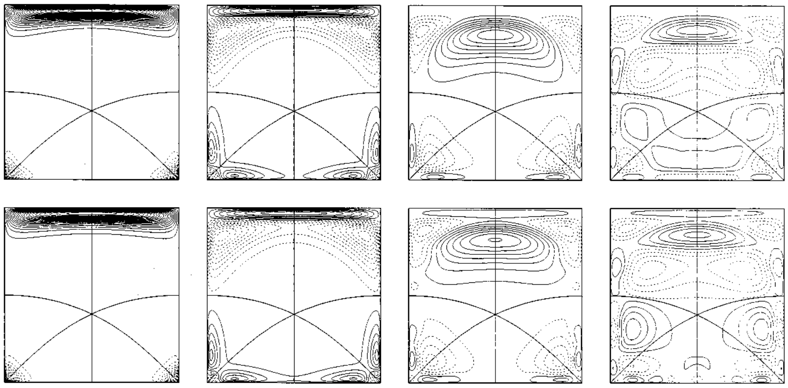
Through this work, we have pointed out the relevance of focusing on a particular domain of the three-electron configuration space on the hypersphere where we observed the occurrence of quasiseparability of the adiabatic hyperspherical Hamiltonian. The quasi-separability prevails, however, in the asymptotic region such that the amplitude of the channel function is rather small near the border of a neighboring one-sixth of the configuration space. An approximate boundary condition that takes advantage of this circumstance leads to a set of adiabatic potential curves and channel functions whose features are shown to agree with those calculated by a

Quartet



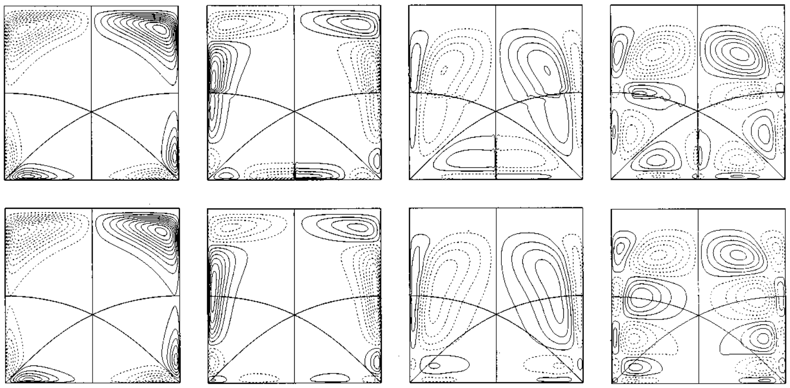
(0,0) (0,1) (1,0) (1,1)

Doublet (Singlet Parent)



(0,0) (0,1) (1,0) (1,1)

Doublet (Triplet Parent)



(0,0) (0,1) (1,0) (1,1)

FIG. 5. Comparison of hierarchical and rigorous adiabatic channel functions. Contour plots of probability density are shown for representative channels identified by (n_1,n_2) at $R \simeq 10$ a.u. A slight shift of R is effected to stay away from avoided crossings. Here again the general features show reasonable resemblance though details near the boundaries indicate breakdown of the approximation. For each panel, the upper row pertains to the hierarchical approximation and the lower one to the rigorous treatment.

rigorous numerical method. We have noted, however, that the region where the three-electron correlations play a central role is where the three electrons come close, that is in the neighborhood of the point $r_1 = r_2 = r_3$. The employed approximate boundary condition is expected to fail there. This poses a question as to the practicality of applying the present somewhat naive approximate boundary condition to such a circumstance. Nonetheless, the perspective gained from the present work as well as the choice of a particular domain on the hypersphere for identifying a hierarchical set of hyperradii, and hence eventually a hierarchical set of quantum numbers may become of value when the hyperspherical method

TABLE I. The projection $|\langle \Phi_{\mathrm{hierarchy}} | \Phi_{\mathrm{rigor}} \rangle|$ as a function of the hyperradius R. The pair of integers (n_1,n_2) pertain to the numbers of nodes of $\Phi_{\mathrm{hierarchy}}$ with respect to α_1 and α_2, respectively.

		R (a.u.)			
	(n_1,n_2)	0.1	1	5	10
	(0,0)	0.9779	0.9809	0.9948	0.9996
Quartet symmetry:	(0,1)	0.7589	0.7741	0.9239	0.9931
	(1,0)	0.8736	0.9071	0.9819	0.9949
	(1,1)	0.4683	0.5239	0.7520	0.8948

		R (a.u.)				
	(n_1,n_2)	0.1	1	5	9.6	10
	(0,0)	0.9524	0.9693	0.9989		0.9988
Doublet symmetry:	(0,1)	0.8092	0.8089	0.8838		0.9973
Singlet parent	(1,0)	0.6799	0.7770	0.9723	0.9870	
	(1,1)	0.4169	0.5032	0.7585		0.8489

		R (a.u.)				
	(n_1,n_2)	0.1	1	5	9.6	10
	(0,0)	0.8000	0.8255	0.9096		0.9992
Doublet symmetry:	(0,1)	0.6649	0.6740	0.7921		0.8967
Triplet parent	(1,0)	0.6911	0.7331	0.8389		0.8937
	(1,1)	0.5343	0.5662	0.6660	0.7576	

is extended to take account of more than three electrons in excited states.

Finally, let us supplement the argumentation for quasiseparability as mentioned toward the end of the Introduction. From the SVD viewpoint developed in Ref. [4], slow dependence on R is not always required for the hierarchical representation to be valid. It is rather a *smooth* dependence on R that would allow the system to evolve without strong mixing. Indeed, the smooth dependence of the wave function on the relative distance between particles or between aggregates of particles appear to hold quite generally in Coulomb problems.

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