

## Hyperspherical approach to three-electron atomic systems

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The hyperspherical coordinates approach to three-electron atomic systems is further refined by taking into account the symmetry of the electrons analytically. Spins are treated explicitly for both doublet and quartet cases to reduce the three-electron Schrödinger equation to a set of coupled two-dimensional partial differential equations in a compact, symmetric form ready for numerical calculations. It is shown that the resulting equations can be accurately solved using  $B$  splines. By adopting the adiabatic approximation, the hyperspherical potential curves for singly, doubly, and triply excited states for the  ${}^2P^o$  symmetry of Li are obtained. [S1050-2947(96)03506-8]

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### I. INTRODUCTION

The systematic investigation of the nature of electron correlation in atomic systems started about three decades ago with the observation of doubly excited states in helium atoms [1]. Since then, it has become one of the major themes in atomic physics [2]. Triply excited states of atoms are expected to reveal even richer and stronger correlations and the study of these systems has gained increasing attention in the past few years. With the developments in laser and synchrotron radiation spectroscopy, more systematic studies of triply excited states are beginning to emerge [3]. While some individual triply excited states have been observed, a classification scheme for these states is yet to be formed [4]. Such a scheme will emerge only after the nature of electron correlation in three-electron systems is understood.

The understanding of electron correlation requires implementation of new theoretical methods different from the independent-electron model. Among others [5], the hyperspherical coordinate approach [6] has been shown to be successful in the analysis of electron correlations for different doubly excited states and in the classification of these states [7]. The recent implementation of the hyperspherical close coupling method illustrates that this approach is capable of performing accurate calculations over a broad energy region for any physical parameters for two-electron systems, such as photoionization cross sections and resonance positions and widths [8].

The early attempts at employing the hyperspherical approach to three-electron atomic systems using basis expansion were made by two groups [9,10] and the results were reviewed in Ref. [11]. These authors illustrated qualitatively that the adiabatic hyperspherical potential curves could be sorted into three groups, supporting singly, doubly, and triply excited states, respectively. However, their numerical results were not accurate enough for a quantitative investigation. To achieve high accuracy, a method different from basis set expansion has to be developed. This was achieved recently in a formulation by Bao and Lin [12] (this reference is shortened as BL hereafter) where the solution of the adiabatic hyper-

spherical potential curves is reduced to the solution of a set of partial differential equations in two hyperangles. In this formulation the solutions have proper exchange symmetry built in and the states have well-defined total spin and total orbital angular momentum quantum numbers, as well as parity. In an earlier paper, the practical methods of solving these partial differential equations in terms of a set of  $B$  splines were illustrated [13] within a special angular momentum configuration  $s^3$  and it was shown that accurate hyperspherical potential curves were obtained even at a large hyperradius.

Following this initial success, the method was generalized to treat real atomic systems. Calculations that included all the important angular momentum components for the  ${}^2P^o$  symmetry were carried out to study three-electron systems such as Li and  $H^{2-}$  [14]. The calculated adiabatic potential curves were used to interpret the recent observation of triply excited states of Li [3] and to illustrate that there are no resonances in  $H^{2-}$  as claimed in the earlier experiments [15] and theory [16], but in agreement with recent experiment [17] and theory [18]. In the process of developing these calculations, the formulation of BL was refined and the resulting equations are more amenable to numerical calculations. This paper presents the analytical developments leading to this improvement.

In Sec. II, we derive a set of partial differential equations slightly different from those of BL. These equations are equivalent to the original set in the BL paper. However, they are more compact and explicitly symmetric; therefore they are easier for numerical calculation. The role of spins is treated analytically in Sec. III. The quartet states and doublet states are separately analyzed. With the symmetry analyzed in Sec. IV, we obtain the hyperangle dependence for the couplings between different equations. These developments make it possible to reduce greatly the burden of numerical calculations. In Sec. V, the numerical implementation of the hyperspherical approach is briefly discussed and the channel potential curves for the prototype three-electron atomic system, Li, are analyzed. A summary is given in Sec. VI. The derivation employs numerous results from symmetry group

analysis. To simplify the presentation of the method most of the analytical details are presented in the Appendixes.

## II. SYMMETRIC FORM OF DIFFERENTIAL EQUATIONS FOR HYPERSPHERICAL CHANNEL FUNCTIONS

### A. Hyperspherical approach

The hyperspherical coordinates for a three-electron atomic system are obtained by replacing the radial distances  $r_1$ ,  $r_2$ , and  $r_3$ , of the three electrons by a hyperradius  $R$  and two hyperangles  $\alpha_1$  and  $\alpha_2$ , defined by

$$\begin{aligned} r_1 &= R \sin \alpha_1 \cos \alpha_2, \\ r_2 &= R \sin \alpha_1 \sin \alpha_2, \\ r_3 &= R \cos \alpha_1, \end{aligned} \quad (1)$$

where  $0 \leq R \leq \infty$  and  $0 \leq \alpha_1, \alpha_2 \leq \pi/2$ . In this coordinate system, the nine spatial degrees of freedom of the three electrons in the laboratory frame are represented by a hyperradius  $R$  representing the size of the atomic system, and eight angles. Besides the two angles  $\alpha_1$  and  $\alpha_2$ , the other six angles are the spherical angles  $\hat{r}_i$  of each electron. However, the spatial and spin parts of the wave functions cannot be separated in general (unless for quartet states) and thus the construction of the properly symmetrized wave functions is much more complicated than for two-electron systems.

The total wave function  $\Psi$  is more conveniently rewritten as

$$\Psi = \psi / (R^4 \sin^2 \alpha_1 \cos \alpha_1 \sin \alpha_2 \cos \alpha_2) \quad (2)$$

where the prefactor is given by the Jacobian determinant. The volume element for  $\alpha_1$  and  $\alpha_2$  dimensions is  $d(\cos \alpha_1) d\alpha_2$ . The Schrödinger equation satisfied by  $\psi$  is

$$\left( -\frac{1}{2} \frac{\partial^2}{\partial R^2} + T_s + V \right) \psi = E \psi \quad (3)$$

where  $T_s$  and  $V$  are given by

$$T_s = -\frac{1}{2R^2} \left( \frac{\partial^2}{\partial \alpha_1^2} + \frac{\cos \alpha_1}{\sin \alpha_1} \frac{\partial}{\partial \alpha_1} + \frac{1}{\sin^2 \alpha_1} \frac{\partial^2}{\partial \alpha_2^2} \right) \quad (4)$$

and

$$V = \frac{1}{2R^2} \left( \frac{\vec{l}_1^2}{\sin^2 \alpha_1 \cos^2 \alpha_2} + \frac{\vec{l}_2^2}{\sin^2 \alpha_1 \sin^2 \alpha_2} + \frac{\vec{l}_3^2}{\cos^2 \alpha_1} \right) + V_c, \quad (5)$$

respectively. In Eq. (5),  $\vec{l}_i$  is the orbital angular momentum of electron  $i$  and  $V_c$  is the Coulomb potential,

$$V_c = -Z \left( \frac{1}{r_1} + \frac{1}{r_2} + \frac{1}{r_3} \right) + \frac{1}{r_{12}} + \frac{1}{r_{23}} + \frac{1}{r_{31}}, \quad (6)$$

where  $Z$  is the charge of the nucleus and  $r_{ij}$  is the separation between the two electrons. In this paper, atomic units are used unless explicitly stated otherwise.

We expand the wave function  $\psi$  in terms of adiabatical channel functions  $\Phi_\mu$ ,

$$\psi = \sum_{\mu} F_{\mu}(R) \Phi_{\mu}(R; \Omega) \quad (7)$$

where  $\Omega$  is the set of all angles ( $\alpha_1$ ,  $\alpha_2$ , and the spherical angles  $\hat{r}_i$ ) and spins.  $\Phi_{\mu}(R; \Omega)$  is the eigenfunction of Eq. (3) at constant hyperradius, i.e.,

$$(T_s + V) \Phi_{\mu}(R; \Omega) = U_{\mu}(R) \Phi_{\mu}(R; \Omega) \quad (8)$$

with  $\mu$  being a channel index.

### B. Reduction of the hyperspherical channel equation

Since the prefactor in Eq. (2) and  $F_{\mu}(R)$  are totally symmetric under the permutation of any pair of electrons, the channel functions  $\Phi_{\mu}(R; \Omega)$  should be totally antisymmetric. Following BL and Appendix A, this is guaranteed by the expansion

$$\begin{aligned} \Phi = & \sum_{\Gamma} (P_1 X_{\Gamma}^{(a)})(Q_2 \mathcal{Y}_{\Gamma}) + \sum_{\Gamma} (P_2 X_{\Gamma}^{(b)})(Q_1 \mathcal{Y}_{\Gamma}) \\ & + \frac{1}{\sqrt{2}} \sum_{\Gamma} [(P_3 X_{\Gamma}^{(c)})(Q_5 \mathcal{Y}_{\Gamma}) + (P_4 X_{\Gamma}^{(c)})(Q_6 \mathcal{Y}_{\Gamma})] \quad (9) \end{aligned}$$

where  $P_i$  are the elements of the algebra of the  $S_3$  group acting on the radial distances among the three electrons and  $Q_i$  are the similar elements but acting on the spherical angles and spins. Each function  $\mathcal{Y}_{\Gamma}$  is the product of coupled spherical harmonics and spin functions given explicitly by

$$\mathcal{Y}_{\Gamma} = |l_1 l_2 (l_0) l_3; L \rangle \left| \frac{1}{2} \frac{1}{2} (s_0) \frac{1}{2}; S \right\rangle \equiv |\gamma \rangle |s_0 \rangle, \quad (10)$$

with given total angular momentum  $L$  and total spin  $S$ . In Eq. (9), the summation is over those  $\Gamma = (l_1, l_2, l_3, l_0, s_0) \equiv (\gamma, s_0)$  with a well-defined parity given by  $\pi = (-)^{l_1 + l_2 + l_3}$ . The quantum numbers  $L$ ,  $S$ , their azimuthal components, and the parity  $\pi$ , are exact conserved quantities. Note that the  $Q_i \mathcal{Y}_{\Gamma}$  are the projections of  $\mathcal{Y}_{\Gamma}$  onto a subspace satisfying a specified permutation symmetry. In general, the dimension of this subspace is smaller than the dimension of the whole space spanned by the functions  $\mathcal{Y}_{\Gamma}$ . Therefore not all the projected functions  $Q_i \mathcal{Y}_{\Gamma}$  are independent. It is necessary to select the linearly independent ones in the sum of Eq. (9).

The last sum of Eq. (9) needs special attention. Here one function  $\mathcal{Y}_{\Gamma}$  is to be projected onto two different subspaces,  $Q_5$  and  $Q_6$ . This requires that the independent projections of both  $Q_5 \mathcal{Y}_{\Gamma}$  and  $Q_6 \mathcal{Y}_{\Gamma}$  be generated by the same set of  $\mathcal{Y}_{\Gamma}$ ; thus they can be mapped one on one from one subspace to another. Similarly,  $X_{\Gamma}^{(c)}$  is to be projected onto  $P_3$  and  $P_4$  subspaces; therefore the projections of  $P_3$  and  $P_4$  should also be related. As analyzed in Lemmas A2 and A3, these requirements are satisfied. Because  $X_{\Gamma}^{(c)}$  appears in both terms of this sum, a normalization factor of  $1/\sqrt{2}$  [which is missing in the original expansion of BL's Eq. (33)] is needed such that all  $X_{\Gamma}^{(i)}$  are treated on the same footing.

Equation (9) indicates that the independent equations for  $X_{\Gamma}^{(i)}$  can be obtained by using  $P_1 Q_2 \mathcal{Y}_{\Gamma}$ ,  $P_2 Q_1 \mathcal{Y}_{\Gamma}$ , and

$(1/\sqrt{2})[P_3Q_5\mathcal{Y}_\Gamma + P_4Q_6\mathcal{Y}_\Gamma]$  to project out Eq. (8). Notice that not all the elements of the coupling matrix,

$$V_{\Gamma'\Gamma}^{i'i} = \langle Q_{i'}\mathcal{Y}_{\Gamma'} | V | Q_i\mathcal{Y}_\Gamma \rangle, \quad (11)$$

are independent when acted on by  $P_j$ . Appendix B gives the relations among these matrix elements. After these equalities are substituted the final differential equations can be simplified into matrix form:

$$\begin{aligned} & \begin{pmatrix} P_1(T_s D^{(2)} + V^{22})P_1 & P_1 V^{21}P_2 & \sqrt{2}P_1 V^{25}P_3 \\ P_2 V^{12}P_1 & P_2(T_s D^{(1)} + V^{11})P_2 & \sqrt{2}P_2 V^{15}P_3 \\ \sqrt{2}P_3 V^{52}P_1 & \sqrt{2}P_3 V^{51}P_2 & P_3(T_s D^{(5)} + V^{55})P_3 + P_3 V^{56}P_4 \end{pmatrix} \begin{pmatrix} X^{(a)} \\ X^{(b)} \\ X^{(c)} \end{pmatrix} \\ & = U \begin{pmatrix} D^{(2)}P_1 & & \\ & D^{(1)}P_2 & \\ & & D^{(5)}P_3 \end{pmatrix} \begin{pmatrix} X^{(a)} \\ X^{(b)} \\ X^{(c)} \end{pmatrix} \end{aligned} \quad (12)$$

where  $X^{(i)} = (X_\Gamma^{(i)})$  are vectors and  $V^{i'i} = (V_{\Gamma'\Gamma}^{i'i})$  and  $D^{(i)} = (D_{\Gamma'\Gamma}^{(i)})$  are matrices themselves. The overlap matrix  $D_{\Gamma'\Gamma}^{(i)}$  is given by

$$D_{\Gamma'\Gamma}^{(i)} = \langle Q_i\mathcal{Y}_{\Gamma'} | Q_i\mathcal{Y}_\Gamma \rangle. \quad (13)$$

By comparing to the original differential equations (34) of BL obtained by the projections of  $Q_2\mathcal{Y}_\Gamma$ ,  $Q_1\mathcal{Y}_\Gamma$ , and  $Q_5\mathcal{Y}_\Gamma$ , Eq. (12) shows explicitly what basis should be used to calculate the elements of  $V$ . For example,  $P_1 V^{25} P_3$  indicates that the elements of  $V$  in this block should be evaluated through the inner products with left functions from  $\{P_1\} \otimes \{Q_2\}$  subspace and right functions from  $\{P_3\} \otimes \{Q_5\}$  subspace. The superfluous terms in the original equations of BL are eliminated due to Lemma B1 and the equations here are more compact. Unlike the original differential equations of BL, the partial differential equations in the matrix form Eq. (12) are explicitly symmetric. This is clear by rewriting the last equation of Lemma B1 as  $(P_3 V_{\Gamma'\Gamma}^{56} P_4)^\dagger = P_3 V_{\Gamma'\Gamma}^{56} P_4$ . Since the major numerical task is to calculate the matrix in the left hand side of Eq. (12), the symmetric formulation reduces greatly the amount of calculation and ensures the use of a real diagonalization algorithm.

### III. CONSTRUCTION OF BASIS FUNCTIONS $\mathcal{Y}_\Gamma$

To reduce the matrix equation (12) further, we need to treat the angular parts involving spherical harmonics and spin functions explicitly. For the doublet case ( $S=1/2$ ), there are two spin functions constructed by coupling the first two spins into either a triplet ( $\chi_1 = |\frac{1}{2}\frac{1}{2}(1)\frac{1}{2}; \frac{1}{2}\rangle$ ) or a singlet ( $\chi_0 = |\frac{1}{2}\frac{1}{2}(0)\frac{1}{2}; \frac{1}{2}\rangle$ ) state, while a quartet case ( $S=3/2$ ) has only one spin function ( $\chi = |\frac{1}{2}\frac{1}{2}(1)\frac{1}{2}; \frac{3}{2}\rangle$ ). The properties of these spin functions under the permutations are treated explicitly in Appendix C.

For  $S=3/2$ ,  $\chi$  can be factorized:

$$Q_i\mathcal{Y}_\Gamma = Q_i(|\gamma\rangle\chi) = \chi Q_i|\gamma\rangle. \quad (14)$$

Here we have decomposed  $Q_i$  into the sum of the products of two factors [Eq. (A5)], one acting on  $\chi$  and another on  $|\gamma\rangle$ . According to Eq. (C1a), only one term involving the totally spin symmetric operator does not vanish, which thus leads to the right hand side of the above equation. Therefore, for the quartet case,  $\chi$  is dropped from the differential equations and  $V_{\Gamma'\Gamma}^{i'i}$  are simply replaced by  $\mathcal{Y}_{\gamma'\gamma}^{i'i} \equiv \langle Q_{i'}\gamma' | V | Q_i\gamma \rangle$ . The structure of the equations remains the same. In this case, the properties of the system are independent of the spin polarization.

For  $S=1/2$ , spin functions are essentially involved. We analyze first  $\{Q_2\mathcal{Y}_\Gamma\}$  which is the union of  $\{Q_2(|\gamma\rangle\chi_1)\}$  and  $\{Q_2(|\gamma\rangle\chi_0)\}$ , i.e.,

$$\{Q_2\mathcal{Y}_\Gamma\} = \{Q_2(|\gamma\rangle\chi_1)\} \cup \{Q_2(|\gamma\rangle\chi_0)\}, \quad (15)$$

where  $\{f_n\}$  denotes the space spanned by the functions  $f_n$ . Each function  $Q_2(|\gamma\rangle\chi_1)$  can be obtained by expanding  $Q_2$  into the products of  $Q'_i$  and  $Q''_j$  acting on  $|\gamma\rangle$  and  $\chi_1$ , respectively [Eq. (A5b)]. As shown by Eq. (C1b), only two terms, containing  $Q''_3\chi_1$  and  $Q''_4\chi_1$ , are nonzero. Thus,

$$Q_2(|\gamma\rangle\chi_1) = \frac{1}{2}(\chi_0 Q_6|\gamma\rangle + \chi_1 Q_5|\gamma\rangle), \quad (16)$$

where we have dropped the superscript of  $Q'_i$  on the right hand side without confusion. Similarly we have  $Q_2(|\gamma\rangle\chi_0) = \frac{1}{2}(\chi_0 Q_3|\gamma\rangle - \chi_1 Q_4|\gamma\rangle)$ . Following Lemma A6,  $Q_3|\gamma\rangle$  and  $-Q_4|\gamma\rangle$  can in turn be expanded in terms of  $Q_6|\gamma\rangle$  and  $Q_5|\gamma\rangle$  with the same expansion coefficients. Therefore,

$$\begin{aligned} Q_2(|\gamma\rangle\chi_0) &= \frac{1}{2} \sum_{\gamma'} c_{\gamma\gamma'} (\chi_0 Q_6|\gamma'\rangle + \chi_1 Q_5|\gamma'\rangle) \\ &= \sum_{\gamma'} c_{\gamma\gamma'} Q_2(|\gamma'\rangle\chi_1). \end{aligned} \quad (17)$$

This shows that  $Q_2(|\gamma\rangle\chi_0)$  is linearly dependent on  $Q_2(|\gamma\rangle\chi_1)$ . Hence  $\{Q_2(|\gamma\rangle\chi_1)\} \cup \{Q_2(|\gamma\rangle\chi_0)\} = \{Q_2(|\gamma\rangle\chi_1)\}$  and

$$\{Q_2\mathcal{Y}_\Gamma\} = \left\{ \frac{1}{\sqrt{2}}(\chi_0 Q_6|\gamma\rangle + \chi_1 Q_5|\gamma\rangle) \right\} \equiv \{\mathcal{Y}_\gamma^{(a)}\}, \quad (18a)$$

where we have normalized the function to 1. Notice that we cannot decompose  $\{Q_2\mathcal{Y}_\Gamma\}$  further into two orthogonal subspaces,  $\{\chi_0 Q_6|\gamma\rangle\}$  and  $\{\chi_1 Q_5|\gamma\rangle\}$ , since these two subspaces are not invariant under the operation of  $Q_2$  individually, as indicated by Eq. (C2a).

In a parallel fashion, we can derive

$$\{Q_1\mathcal{Y}_\Gamma\} = \left\{ \frac{1}{\sqrt{2}}(\chi_0 Q_5|\gamma\rangle - \chi_1 Q_6|\gamma\rangle) \right\} \equiv \{\mathcal{Y}_\gamma^{(b)}\}. \quad (18b)$$

The analysis of the subspace  $\{Q_5\mathcal{Y}_\Gamma\}$  is slightly more complicated. Expanding  $Q_5$  into the products of two factors and using Eq. (C1b), we have

$$\begin{aligned} Q_5(|\gamma\rangle\chi_1) &= \chi_1 Q_2|\gamma\rangle - \frac{1}{2}(\chi_0 Q_6|\gamma\rangle - \chi_1 Q_5|\gamma\rangle), \\ Q_5(|\gamma\rangle\chi_0) &= \chi_0 Q_1|\gamma\rangle + \frac{1}{2}(\chi_0 Q_3|\gamma\rangle + \chi_1 Q_4|\gamma\rangle) \\ &= \chi_0 Q_1|\gamma\rangle + \frac{1}{2} \sum_{\gamma'} c_{\gamma\gamma'} \\ &\quad \times (\chi_0 Q_6|\gamma'\rangle - \chi_1 Q_5|\gamma'\rangle) \end{aligned} \quad (19)$$

where in the last line above we have used Lemma A6. The above equation indicates that  $\{Q_5\mathcal{Y}_\Gamma\} = \{Q_5(|\gamma\rangle\chi_1)\}$

$\cup \{Q_5(|\gamma\rangle\chi_0)\}$  is spanned by  $\chi_0 Q_1|\gamma\rangle$ ,  $\chi_1 Q_2|\gamma\rangle$ , and  $\chi_0 Q_6|\gamma\rangle - \chi_1 Q_5|\gamma\rangle$ . Following the results in Eq. (C2c), these three orthogonal functions are invariant under  $Q_5$  individually; therefore,

$$\begin{aligned} \{Q_5\mathcal{Y}_\Gamma\} &= \{\chi_0 Q_1|\gamma\rangle\} + \{\chi_1 Q_2|\gamma\rangle\} \\ &\quad + \left\{ \frac{1}{\sqrt{2}}(\chi_0 Q_6|\gamma\rangle - \chi_1 Q_5|\gamma\rangle) \right\} \\ &\equiv \{\mathcal{Y}_\gamma^{(c1)}\} + \{\mathcal{Y}_\gamma^{(c2)}\} + \{\mathcal{Y}_\gamma^{(c3)}\}, \end{aligned} \quad (18c)$$

i.e., the subspace  $\{Q_5\mathcal{Y}_\Gamma\}$  is now split into three orthogonal ones, each itself being invariant under  $Q_5$ . Since  $Q_6 = Q_6 Q_5$ , subspace  $\{Q_6\mathcal{Y}_\Gamma\}$  can be obtained by operating  $Q_6$  on the above equation. Equation (C2d) gives the evaluation of the operation. The result is

$$\begin{aligned} \{Q_6\mathcal{Y}_\Gamma\} &= \{-\chi_1 Q_1|\gamma\rangle\} + \{\chi_0 Q_2|\gamma\rangle\} \\ &\quad + \left\{ \frac{1}{\sqrt{2}}(\chi_0 Q_5|\gamma\rangle + \chi_1 Q_6|\gamma\rangle) \right\} \\ &= \{Q_6\mathcal{Y}_\gamma^{(c1)}\} + \{Q_6\mathcal{Y}_\gamma^{(c2)}\} + \{Q_6\mathcal{Y}_\gamma^{(c3)}\}. \end{aligned} \quad (18d)$$

From the results of Eqs. (18a)–(18d), the main task for constructing the basis functions then is to find all the independent  $Q_1|\gamma\rangle$ ,  $Q_2|\gamma\rangle$ , and  $Q_5|\gamma\rangle$  ( $Q_6|\gamma\rangle$  are obtained by  $Q_6 Q_5|\gamma\rangle$ ).

From the definition of coupled spherical harmonics, we have

$$s_2 |l_1 l_2(l_0) l_3; L\rangle = (-1)^{l_1 + l_2 - l_0} |l_2 l_1(l_0) l_3; L\rangle \quad (20)$$

where  $s_2 = (12)$  is the second element of the  $\mathcal{S}_3$  group. The symmetric and antisymmetric subspaces under the permutation of electrons 1 and 2 (denoted as  $\{f^+\}$  and  $\{f^-\}$ , respectively, in Appendix A) can now be analytically constructed as  $|\gamma^\pm\rangle \propto \frac{1}{2}(1 \pm s_2) |l_1 l_2(l_0) l_3; L\rangle$ , which leads to

$$|\gamma^\pm\rangle = \begin{cases} \frac{1}{\sqrt{2}} [ |l_1 l_2(l_0) l_3; L\rangle \pm (-1)^{l_1 + l_2 - l_0} |l_2 l_1(l_0) l_3; L\rangle ] & \text{for } l_2 > l_1, \\ |l_1 l_1(l_0) l_3; L\rangle, & l_0 = \text{even for } +, l_0 = \text{odd for } -. \end{cases} \quad (21)$$

As analyzed by Eq. (A9a),  $\{Q_1\} + \{Q_3\} = \{|\gamma^+\rangle\}$ . Thus the diagonalization of  $Q_1$  in subspace  $\{|\gamma^+\rangle\}$  decomposes this space into  $\{Q_{11}\}$  and  $\{Q_{31}\}$  as follows: the former consists of those eigenfunctions with eigenvalues 1 and the latter consists of those eigenfunctions with eigenvalues 0 (see Lemma

A1). Similarly, from Eq. (A9b),  $\{Q_2\} + \{Q_5\} = \{|\gamma^-\rangle\}$  and the diagonalization of  $Q_2$  decomposes this space into  $\{Q_{21}\}$  and  $\{Q_{51}\}$ .

Substitution of Eq. (18) into Eq. (9) results in the channel functions for  $S = 1/2$ ,

$$\begin{aligned} \Phi = & \sum_{\gamma} (P_1 X_{\gamma}^{(a)}) \mathcal{Y}_{\gamma}^{(a)} + \sum_{\gamma} (P_2 X_{\gamma}^{(b)}) \mathcal{Y}_{\gamma}^{(b)} \\ & + \frac{1}{\sqrt{2}} \sum_{c_i=c_1, c_2, c_3} \sum_{\gamma} [(P_3 X_{\gamma}^{(c_i)}) \mathcal{Y}_{\gamma}^{(c_i)} + (P_4 X_{\gamma}^{(c_i)}) \\ & \times (Q_6 \mathcal{Y}_{\gamma}^{(c_i)})] \end{aligned} \quad (22)$$

where the sum of  $c_i$  is over the three orthogonal subspaces  $\{\mathcal{Y}_{\gamma}^{(c_i)}\}$  of  $\{Q_5 \mathcal{Y}_{\Gamma}\}$ . The corresponding differential equations become

$$\begin{pmatrix} H_{11} & H_{12} & H_{13} & H_{14} & H_{15} \\ H_{21} & H_{22} & H_{23} & H_{24} & H_{25} \\ H_{31} & H_{32} & H_{33} & H_{34} & H_{35} \\ H_{41} & H_{42} & H_{43} & H_{44} & H_{45} \\ H_{51} & H_{52} & H_{53} & H_{54} & H_{55} \end{pmatrix} \begin{pmatrix} X^{(a)} \\ X^{(b)} \\ X^{(c_1)} \\ X^{(c_2)} \\ X^{(c_3)} \end{pmatrix} = U \begin{pmatrix} \mathcal{D}^{(5)} P_1 & & & & \\ & \mathcal{D}^{(5)} P_2 & & & \\ & & \mathcal{D}^{(1)} P_3 & & \\ & & & \mathcal{D}^{(2)} P_3 & \\ & & & & \mathcal{D}^{(5)} P_3 \end{pmatrix} \times \begin{pmatrix} X^{(a)} \\ X^{(b)} \\ X^{(c_1)} \\ X^{(c_2)} \\ X^{(c_3)} \end{pmatrix} \quad (23a)$$

where the overlap matrix is defined by  $\mathcal{D}^{(i)} = (\mathcal{D}_{\gamma' \gamma}^{(i)}) = (\langle Q_i \gamma' | Q_i \gamma \rangle)$ .

The matrix elements in each block  $H_{ij}$  are given by the inner products of the basis functions,  $P_1 \mathcal{Y}_{\gamma}^{(a)}$ ,  $P_2 \mathcal{Y}_{\gamma}^{(b)}$ , and  $(1/\sqrt{2})[P_3 \mathcal{Y}_{\gamma}^{(c_i)} + P_4 (Q_6 \mathcal{Y}_{\gamma}^{(c_i)})]$ , with respect to the operator  $T_s + V$ . For example,  $(H_{11})_{\gamma' \gamma} = P_1 \langle \mathcal{Y}_{\gamma'}^{(a)} | T_s + V | \mathcal{Y}_{\gamma}^{(a)} \rangle P_1$ . Substituting Eq. (18a) into this equation,  $(H_{11})_{\gamma' \gamma} = P_1 (\langle Q_6 \gamma' | T_s + V | Q_6 \gamma \rangle + \langle Q_5 \gamma' | T_s + V | Q_5 \gamma \rangle) P_1 / 2$  where we have used the fact that  $T_s + V$  is independent of spins. Notice that  $T_s$  is independent of spherical angles and  $\mathcal{D}_{\gamma' \gamma}^{(6)} = \mathcal{D}_{\gamma' \gamma}^{(5)}$  (Lemma A7); we have  $(H_{11})_{\gamma' \gamma} = P_1 [T_s \mathcal{D}_{\gamma' \gamma}^{(5)} + (\mathcal{V}_{\gamma' \gamma}^{66} + \mathcal{V}_{\gamma' \gamma}^{55}) / 2] P_1$ . Following this procedure the explicit expressions of  $H_{ij}$  are

$$\begin{aligned} H_{11} &= P_1 \left( T_s \mathcal{D}^{(5)} + \frac{\mathcal{V}^{66} + \mathcal{V}^{55}}{2} \right) P_1, \\ H_{12} &= P_1 \frac{\mathcal{V}^{65} - \mathcal{V}^{56}}{2} P_2, \quad H_{13} = P_1 \mathcal{V}^{61} P_3, \\ H_{14} &= P_1 \mathcal{V}^{52} P_3, \quad H_{15} = P_1 \sqrt{2} \frac{\mathcal{V}^{66} - \mathcal{V}^{55}}{2} P_3, \end{aligned}$$

$$H_{22} = P_2 \left( T_s \mathcal{D}^{(5)} + \frac{\mathcal{V}^{66} + \mathcal{V}^{55}}{2} \right) P_2, \quad (23b)$$

$$H_{23} = P_2 \mathcal{V}^{51} P_3, \quad H_{24} = -P_2 \mathcal{V}^{62} P_3,$$

$$H_{25} = P_2 \sqrt{2} \frac{\mathcal{V}^{56} + \mathcal{V}^{65}}{2} P_3,$$

$$H_{33} = P_3 (T_s \mathcal{D}^{(1)} + \mathcal{V}^{11}) P_3, \quad H_{34} = P_3 \mathcal{V}^{12} P_4,$$

$$H_{35} = P_3 \sqrt{2} \mathcal{V}^{16} P_3,$$

$$H_{44} = P_3 (T_s \mathcal{D}^{(2)} + \mathcal{V}^{22}) P_3, \quad H_{45} = -P_3 \sqrt{2} \mathcal{V}^{25} P_3,$$

$$H_{55} = P_3 \left( T_s \mathcal{D}^{(5)} + \frac{\mathcal{V}^{66} + \mathcal{V}^{55}}{2} \right) P_3 + P_3 \frac{\mathcal{V}^{65} - \mathcal{V}^{56}}{2} P_4,$$

$$H_{ji} = H_{ij}^{\dagger},$$

where  $\mathcal{V}^{i'i} = (\mathcal{V}_{\gamma' \gamma}^{i'i})$  and results in Lemma B2 were used to eliminate the superfluous terms. Notice that  $H_{ij}$  are still operators rather than numbers and further inner products in the dimensions of  $\alpha_1$  and  $\alpha_2$  are yet to be performed.  $H_{ij}^{\dagger}$  is the conjugate operator of  $H_{ij}$ . By choosing the representation as usual such that the coordinates are diagonalized (i.e., are numbers),  $\mathcal{V}_{\gamma' \gamma}^{i'i}$  become the ordinary functions of the two hyperangles.

#### IV. HYPERANGLE DEPENDENCE OF THE COUPLING ELEMENTS

In order to carry out numerical calculation, it is convenient to obtain the simplest form of the explicit dependence of  $\mathcal{V}_{\gamma' \gamma}^{i'i}$  on the two hyperangles. This in turn needs the analysis of the symmetries of  $\mathcal{V}_{\gamma' \gamma}^{i'i}$ . The closure relation Eq. (A7) ensures that any arbitrary function of  $\alpha_1$  and  $\alpha_2$  can be expanded as  $f = P_1 f + P_2 f + P_3 f + P_5 f$ , i.e., the Hilbert space of the functions of the two hyperangles can be decomposed into four subspaces each with a definite permutation symmetry. The functions with  $P_1 f = f$  (and therefore  $P_i f = 0$ ,  $i=2,3,5$ ) form the subspace of totally symmetric functions under the permutations of any pairs of  $r_i$ . The functions in the subspace of  $P_2 f = f$  are totally antisymmetric under the exchange of  $r_i$ . The symmetries of the functions in the other two subspaces, formed by the functions of  $P_3 f = f$  and  $P_5 f = f$ , respectively, are mixed.

We first rewrite  $V$  in terms of functions with certain symmetries. Define the auxiliary functions

$$Y_{ij}^{(l)} = \frac{4\pi}{2l+1} \sum_{m=-l}^l Y_{lm}^*(\hat{r}_i) Y_{lm}(\hat{r}_j) \quad (24)$$

where  $Y_{lm}$  are the spherical harmonics, and two other sets of functions

$$t_1 = \frac{1}{\sin^2 \alpha_1 \cos^2 \alpha_2},$$

$$t_2 = \frac{1}{\sin^2 \alpha_1 \sin^2 \alpha_2}, \quad (25)$$

$$t_3 = \frac{1}{\cos^2 \alpha_1},$$

and

$$\begin{aligned} g_{13}^{(l)} &= \frac{(\sin \alpha_1 \cos \alpha_2, \cos \alpha_1)_{<}^l}{(\sin \alpha_1 \cos \alpha_2, \cos \alpha_1)_{>}^{l+1}}, \\ g_{23}^{(l)} &= \frac{(\sin \alpha_1 \sin \alpha_2, \cos \alpha_1)_{<}^l}{(\sin \alpha_1 \sin \alpha_2, \cos \alpha_1)_{>}^{l+1}}, \\ g_{12}^{(l)} &= \frac{(\sin \alpha_1 \cos \alpha_2, \sin \alpha_1 \sin \alpha_2)_{<}^l}{(\sin \alpha_1 \cos \alpha_2, \sin \alpha_1 \sin \alpha_2)_{>}^{l+1}}, \end{aligned} \quad (26)$$

where  $< (>)$  represents the smaller (larger) of the two terms in the parentheses.  $V$  is then given by

$$\begin{aligned} V &= \frac{1}{2R^2} \left[ 2Rw + \tilde{l}_1^2 t_1 + \tilde{l}_2^2 t_2 + \tilde{l}_3^2 t_3 + 2R \sum_{l>0} (Y_{13}^{(l)} g_{13}^{(l)} \right. \\ &\quad \left. + Y_{23}^{(l)} g_{23}^{(l)} + Y_{12}^{(l)} g_{12}^{(l)}) \right] \end{aligned} \quad (27a)$$

where

$$\begin{aligned} w &= \frac{1}{(\sin \alpha_1 \cos \alpha_2, \cos \alpha_1)_{>}} + \frac{1}{(\sin \alpha_1 \sin \alpha_2, \cos \alpha_1)_{>}} \\ &\quad + \frac{1}{(\sin \alpha_1 \cos \alpha_2, \sin \alpha_1 \sin \alpha_2)_{>}} - Z \left( \frac{1}{\sin \alpha_1 \cos \alpha_2} \right. \\ &\quad \left. + \frac{1}{\sin \alpha_1 \sin \alpha_2} + \frac{1}{\cos \alpha_1} \right) \end{aligned} \quad (27b)$$

and we have used  $Y_{ij}^{(0)} = 1$ . Notice that  $w$  is independent of spherical angles  $\hat{r}_i$  and is totally symmetric for the three electrons, i.e.,  $P_1 w = w$ .

From three independent functions  $t_i$ , another set of three independent functions can be constructed,

$$\begin{aligned} h_1 &= t_1 + t_2 + t_3, \\ h_3 &= t_1 + t_2 - 2t_3, \\ h_5 &= t_1 - t_2. \end{aligned} \quad (28)$$

Similarly, three new independent functions are constructed as

$$\begin{aligned} g_1^{(l)} &= g_{13}^{(l)} + g_{23}^{(l)} + g_{12}^{(l)}, \\ g_3^{(l)} &= g_{13}^{(l)} + g_{23}^{(l)} - 2g_{12}^{(l)}, \\ g_5^{(l)} &= g_{13}^{(l)} - g_{23}^{(l)}. \end{aligned} \quad (29)$$

These functions are constructed to exhibit certain symmetries,

$$P_j h_i = \delta_{ji} h_i, \quad P_j g_i^{(l)} = \delta_{ji} g_i^{(l)}, \quad j=1,2,3,5, \quad i=1,3,5. \quad (30)$$

Notice that no invariant functions of  $P_2$  can be formed by  $t_i$  or by  $g_{ij}^{(l)}$ .

We can now express  $V$  in terms of  $h_i$  and  $g_i^{(l)}$

$$\begin{aligned} V &= \frac{1}{2R^2} \left[ 2Rw + \frac{\tilde{l}_1^2 + \tilde{l}_2^2 + \tilde{l}_3^2}{3} h_1 + \frac{\tilde{l}_1^2 + \tilde{l}_2^2 - 2\tilde{l}_3^2}{6} h_3 \right. \\ &\quad + \frac{\tilde{l}_1^2 - \tilde{l}_2^2}{2} h_5 + 2R \sum_{l>0} \left( \frac{Y_{13}^{(l)} + Y_{23}^{(l)} + Y_{12}^{(l)}}{3} g_1^{(l)} \right. \\ &\quad \left. + \frac{Y_{13}^{(l)} + Y_{23}^{(l)} - 2Y_{12}^{(l)}}{6} g_3^{(l)} + \frac{Y_{13}^{(l)} - Y_{23}^{(l)}}{2} g_5^{(l)} \right) \left. \right] \end{aligned} \quad (31)$$

in which each term shows the explicit symmetry.

Appendix D displays that  $\mathcal{V}_{\gamma'\gamma}^{i'i}$  (or their simple linear combinations) possess certain permutation symmetries and, therefore, can be divided into four groups. The first group is in the  $P_1 f = f$  subspace. From Eqs. (30) and (31), we conclude that the coefficients of  $h_3$ ,  $h_5$ ,  $g_3^{(l)}$ , and  $g_5^{(l)}$  should be zero. Therefore, for this group,

$$(\tilde{l}_3^2)_{\gamma'\gamma}^{i'i} = (\tilde{l}_2^2)_{\gamma'\gamma}^{i'i} = (\tilde{l}_1^2)_{\gamma'\gamma}^{i'i},$$

$$(Y_{12}^{(l)})_{\gamma'\gamma}^{i'i} = (Y_{23}^{(l)})_{\gamma'\gamma}^{i'i} = (Y_{13}^{(l)})_{\gamma'\gamma}^{i'i} \quad (32)$$

where  $(\tilde{l}_j^2)_{\gamma'\gamma}^{i'i}$  and  $(Y_{jk}^{(l)})_{\gamma'\gamma}^{i'i}$  are the elements of  $\tilde{l}_j^2$  and  $Y_{jk}^{(l)}$  between  $|Q_i \gamma'\rangle$  and  $|Q_i \gamma\rangle$ , respectively. Hence we have

$$\begin{aligned} \mathcal{V}_{\gamma'\gamma}^{ii} &= \frac{1}{2R^2} \left[ 2R \mathcal{D}_{\gamma'\gamma}^i w + (\tilde{l}_1^2)_{\gamma'\gamma}^{ii} h_1 \right. \\ &\quad \left. + 2R \sum_{l>0} (Y_{13}^{(l)})_{\gamma'\gamma}^{ii} g_1^{(l)} \right], \quad (ii) = (11), (22), \end{aligned} \quad (33a)$$

$$\begin{aligned} \frac{\mathcal{V}_{\gamma'\gamma}^{55} + \mathcal{V}_{\gamma'\gamma}^{66}}{2} &= \frac{1}{2R^2} \left[ 2R \mathcal{D}_{\gamma'\gamma}^5 w + \frac{(\tilde{l}_1^2)_{\gamma'\gamma}^{55} + (\tilde{l}_1^2)_{\gamma'\gamma}^{66}}{2} h_1 \right. \\ &\quad \left. + 2R \sum_{l>0} \frac{(Y_{13}^{(l)})_{\gamma'\gamma}^{55} + (Y_{13}^{(l)})_{\gamma'\gamma}^{66}}{2} g_1^{(l)} \right], \end{aligned} \quad (33b)$$

where we have used  $\mathcal{D}_{\gamma'\gamma}^5 = \mathcal{D}_{\gamma'\gamma}^6$  (Lemma A7). This group enters in the diagonal blocks  $H_{ii}$  ( $i=1,2,3,4,5$ ) of Eq. (23b).

The second group is in the subspace of  $P_3 f = f$ . In this group, Eqs. (30) and (31) indicate that the coefficients of  $h_1$ ,  $h_5$ ,  $g_1^{(l)}$ , and  $g_5^{(l)}$  should be zero, i.e.,

$$(\tilde{l}_2^2)_{\gamma'\gamma}^{i'i} = (\tilde{l}_1^2)_{\gamma'\gamma}^{i'i}, \quad (\tilde{l}_3^2)_{\gamma'\gamma}^{i'i} = -2(\tilde{l}_1^2)_{\gamma'\gamma}^{i'i},$$

$$(Y_{23}^{(l)})_{\gamma'\gamma}^{i'i} = (Y_{13}^{(l)})_{\gamma'\gamma}^{i'i}, \quad (Y_{12}^{(l)})_{\gamma'\gamma}^{i'i} = -2(Y_{13}^{(l)})_{\gamma'\gamma}^{i'i}, \quad (34)$$

which leads to

$$\mathcal{V}_{\gamma'\gamma}^{j'i} = \frac{1}{2R^2} \left[ (\tilde{l}_1^2)_{\gamma'\gamma}^{i'i} h_3 + 2R \sum_{l>0} (Y_{13}^{(l)})_{\gamma'\gamma}^{i'i} g_3^{(l)} \right],$$

$$(i'i) = (25), (52), (16), (61), \quad (35a)$$

$$\frac{\mathcal{V}_{\gamma'\gamma}^{66} - \mathcal{V}_{\gamma'\gamma}^{55}}{2} = \frac{1}{2R^2} \left[ \frac{(\tilde{l}_1^2)_{\gamma'\gamma}^{66} - (\tilde{l}_1^2)_{\gamma'\gamma}^{55}}{2} h_3 \right. \\ \left. + 2R \sum_{l>0} \frac{(Y_{13}^{(l)})_{\gamma'\gamma}^{66} - (Y_{13}^{(l)})_{\gamma'\gamma}^{55}}{2} g_3^{(l)} \right]. \quad (35b)$$

The third group is in the  $P_5 f = f$  subspace and the coefficients of  $h_1$ ,  $h_3$ ,  $g_1^{(l)}$ , and  $g_3^{(l)}$  should be zero, i.e.,

$$(\tilde{l}_2^2)_{\gamma'\gamma}^{i'i} = -(\tilde{l}_1^2)_{\gamma'\gamma}^{i'i}, \quad (\tilde{l}_3^2)_{\gamma'\gamma}^{i'i} = 0, \\ (Y_{23}^{(l)})_{\gamma'\gamma}^{i'i} = -(Y_{13}^{(l)})_{\gamma'\gamma}^{i'i}, \quad (Y_{12}^{(l)})_{\gamma'\gamma}^{i'i} = 0. \quad (36)$$

Thus

$$\mathcal{V}_{\gamma'\gamma}^{j'i} = \frac{1}{2R^2} \left[ (\tilde{l}_1^2)_{\gamma'\gamma}^{i'i} h_5 + 2R \sum_l (Y_{13}^{(l)})_{\gamma'\gamma}^{i'i} g_5^{(l)} \right],$$

$$(i'i) = (15), (51), (26), (62), (65), (56). \quad (37)$$

The last group is in the subspace of  $P_2 f = f$  and all the coefficients of  $h_i$  and  $g_i^{(l)}$  ought to be zero. Therefore we have

$$(\tilde{l}_2^2)_{\gamma'\gamma}^{i'i} = (\tilde{l}_3^2)_{\gamma'\gamma}^{i'i} = (\tilde{l}_1^2)_{\gamma'\gamma}^{i'i} = 0, \\ (Y_{12}^{(l)})_{\gamma'\gamma}^{i'i} = (Y_{23}^{(l)})_{\gamma'\gamma}^{i'i} = (Y_{13}^{(l)})_{\gamma'\gamma}^{i'i} = 0, \quad (38)$$

and

$$\mathcal{V}_{\gamma'\gamma}^{12} = \mathcal{V}_{\gamma'\gamma}^{21} = 0, \quad (39a)$$

$$\mathcal{V}_{\gamma'\gamma}^{65} - \mathcal{V}_{\gamma'\gamma}^{56} = 0. \quad (39b)$$

This is the result of the fact that from  $t_i$  and  $g_{ij}^{(l)}$  no invariant functions of  $P_2$  can be constructed.

With these results, all the angular momentum algebra is expressed in terms of elementary analytical expressions and the dependence on the two hyperangles  $\alpha_1$  and  $\alpha_2$  is obtained, and the resulting equations Eq. (23a) can be solved numerically.

## V. NUMERICAL IMPLEMENTATION AND CHANNEL POTENTIAL CURVES

A straight adiabatic expansion as indicated in Eq. (7) would require the solution of Eq. (23a) for all the important  $\gamma$ 's. The order of the resulting coupled second-order partial differential equations in  $\alpha_1$  and  $\alpha_2$  will be quite large and the resulting potential curves will have numerous avoided crossings. In the present application, we will adopt a two-step numerical implementation which is based on the decomposition of  $V$  into two terms,

$$V = \left( \sum_{\{\gamma'\}=\{\gamma\}} + \sum_{\{\gamma'\} \neq \{\gamma\}} \right) |\gamma'\rangle \langle \gamma'| V |\gamma\rangle \langle \gamma| \equiv V_0 + V_1, \quad (40)$$

where  $|\gamma\rangle = |l_1 l_2 (l_0) l_3; L\rangle$  and  $\{\gamma'\} = (\neq) \{\gamma\}$  indicates that  $(l'_1, l'_2, l'_3)$  and  $(l_1, l_2, l_3)$  are (not) in the same angular momentum configuration. In future applications it is anticipated that instead of the pure adiabatic expansion Eq. (7), the wave function will be expanded as

$$\psi = \sum_{\mu, \beta} F_{\mu, \beta}(R) \Phi_{\mu, \beta}(R; \Omega) \quad (41)$$

where  $\beta = (l_1, l_2, l_3)$  and  $\Phi_{\mu, \beta}(R; \Omega)$  satisfies Eq. (8) in the subspace of fixed angular momentum configuration  $\beta$ . This is the procedure adopted in the hyperspherical close coupling method.

At present we are interested in obtaining adiabatic potential curves in two steps. We use angular momentum configuration to imply basis functions or states that have a well-defined  $(l_1, l_2, l_3)$ , irrespective of the order in which each  $l_i$  appears since they are properly symmetrized. Thus in step 1,  $T_s + V_0$  can be diagonalized independently within each configuration to produce intermediate channel potential curves  $U_{\mu}^0(R)$  and intermediate channel functions  $\Phi_{\mu}^0(R; \Omega)$ . The numerical details of such a diagonalization are given in Ref. [13]. In the second stage of the diagonalization procedure, a selected set of  $\Phi_{\mu}^0(R; \Omega)$  are then chosen from the different individual configurations as basis functions to solve the whole eigenproblem of Eq. (8). The resulting final channel potential curves and wave functions are expected to be close to the actual adiabatic potential curves if all the important intermediate channel functions are used as basis functions in the second diagonalization.

This two-step approach offers advantages both in numerical calculations and in physical interpretation of the spectra of a three-electron system. The complicated final potential curves can be understood by a set of simpler intermediate potential curves of individual angular momentum configurations, and only ‘‘important’’ intermediate channels are needed in the calculation of the final channel potential curves and wave functions; thus the amount of calculation can be greatly reduced. We have used this method to obtain accurate channel potentials for the atomic systems Li,  $H^{2-}$ , and  $He^-$  with the  ${}^2P^o$  symmetry. The recent observation of triply excited states of Li [3] is analyzed by the calculated potential curves. Furthermore, the adiabatic potential curves for the  $H^{2-}$  system are used to ‘‘prove’’ that there are no resonances of any kind. These results are reported elsewhere [14]. In the remainder of this paper we show potential curves from the first-step diagonalization and then the final adiabatic curves for the Li atoms to illustrate the procedure and the interpretation that the first-step calculation can offer.

Figure 1(a) displays the intermediate potential curves of the angular momentum configuration (001), i.e.,  $s^2p$ , for the  ${}^2P^o$  states of the lithium atom ( $Z=3$ ), with those that converge to the doubly excited states in the large  $R$  limit expanded in Fig. 1(b). From the traditional independent-particle configuration interaction viewpoint, the potential curves include all configurations of the type  $n_1 s n_2 s n_3 p$

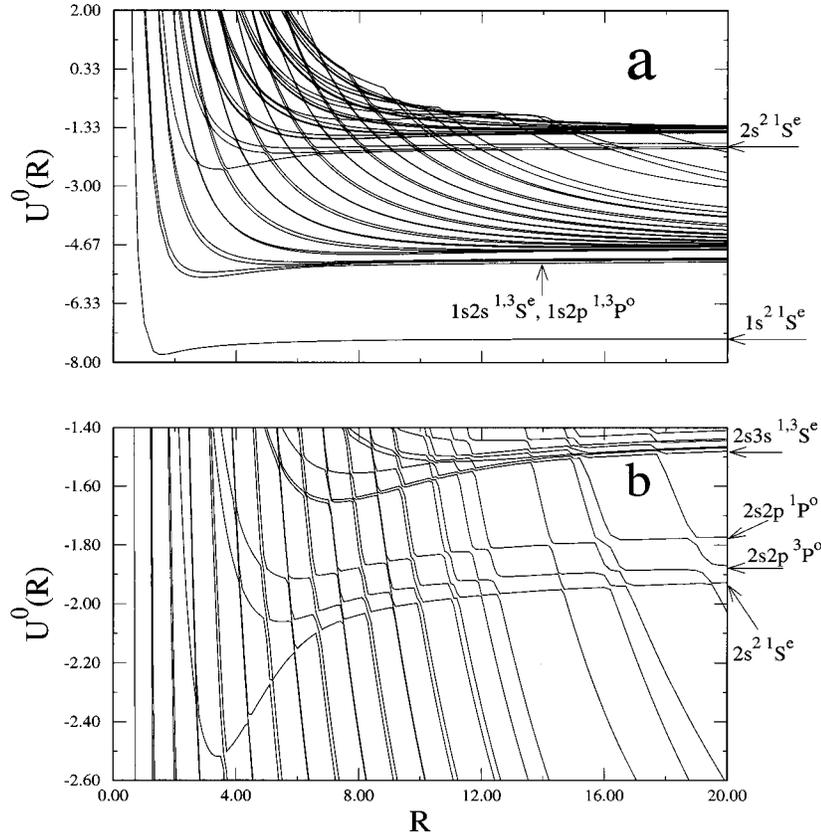


FIG. 1. The intermediate potential curves within the (001) configuration of the lithium atom as functions of  $R$ . The members of (1,1), (1,2), and (2,2) shells are labeled. The energy region where the channels support triply excited states is enlarged in (b). Atomic units are used here.

( $n_1, n_2 \geq 1, n_3 \geq 2$ ) which can couple to  ${}^2P^o$  states. In the limit of  $R \rightarrow \infty$ , one electron is far away from the “core,” hence the potential curves  $U_\mu(R)$  must tend to one of the eigenenergies of the residual two-electron  $\text{Li}^+$  system. This asymptotic behavior can serve as the criterion for checking the numerical convergence and the accuracy. Good agreement was found between the asymptotic potential curves within this angular momentum configuration and the previous calculations of the eigenenergies of  $\text{Li}^+$  [19].

As discussed in Ref. [13] for the configuration  $s^3$ , the most striking feature of Fig. 1 is that potential curves can be easily identified into three groups. Each group is recognized by its asymptotic state corresponding to the state of the  $\text{Li}^+$  ion. The first group consists only of the lowest potential curve which goes to the  $1s^2 1S^e$  limit of  $\text{Li}^+$ . This potential curve supports singly excited states of Li of the type  $1s^2 np$  states. The second group of potential curves approach the  $1sns({}^{1,3}S^e)$  or  $1snp({}^{1,3}P^o)$  singly excited states of  $\text{Li}^+$ ; they support doubly excited states of Li. The third group of potential curves approach doubly excited states of  $\text{Li}^+$  asymptotically and they support triply excited states of Li. Note the numerous crossings between the second and the third group of potential curves.

Within a fixed  $(l_1, l_2, l_3)$ , each potential curve can be labeled by the two-electron states in the asymptotic limit. Thus each channel can be labeled as  $Nl'nl^{2S+1}L^\pi$  ( $N \leq n$ ). However, this labeling has little physical significance at smaller values of  $R$ . On the other hand, the group of curves (four curves, for example, in the second group) within each  $(N, n)$  stays relatively close for all values of  $R$ . As shown in Ref. [13] for the  $s^3$  configuration, the  $(N, n)$  quantum numbers can serve as bookkeeping for the nodal structure in the

$\alpha_1$  and  $\alpha_2$  coordinates, in addition to the nodal lines set up by the symmetry imposed by the quantum numbers  $2S+1L^\pi$ .

An important question to answer is whether  $(N, n)$  are still approximately conserved after the coupling between angular momentum configurations  $V_1$  has been included. We used the lowest 50 intermediate channels from the configurations (001), (012), (111), and (113), respectively, to form the basis for the diagonalization of  $T_s + V$ . Other, ignored, configurations do not contribute channels to the (2,2) shell which we are interested in. The final channel potential curves are plotted in Fig. 2. Apparently, the shell structure is still recognizable. The number of final channels in a given shell  $(N, n)$  is the sum of the numbers of the intermediate channels in the same shell. For example, the (2,2) shell has nine channels, three from the configuration (001), three from (111), two from (012) and one from (113). They are strongly mixed by the coupling between angular momentum configurations  $V_1$ . However, the channels from different shells are seldom mixed by  $V_1$ .

In Fig. 2(b) we display also the values of (2,2) potential curves obtained at  $R = 18$  by using only the nine intermediate channels in the (2,2) shell in the second-step diagonalization. The results are almost identical with the results of the full calculation, in which many other shells are included. This indicates that  $(N, n)$  can still be used as “good” quantum numbers to label the final channel potential curves and wave functions. On the other hand, from the study of doubly excited states, this labeling in terms of  $(N, n)$  will fail for higher values of  $N$  and  $n$  as the energy separation between different “shells” becomes smaller. Anyway, the main point is that the two-step diagonalization procedure allows us to

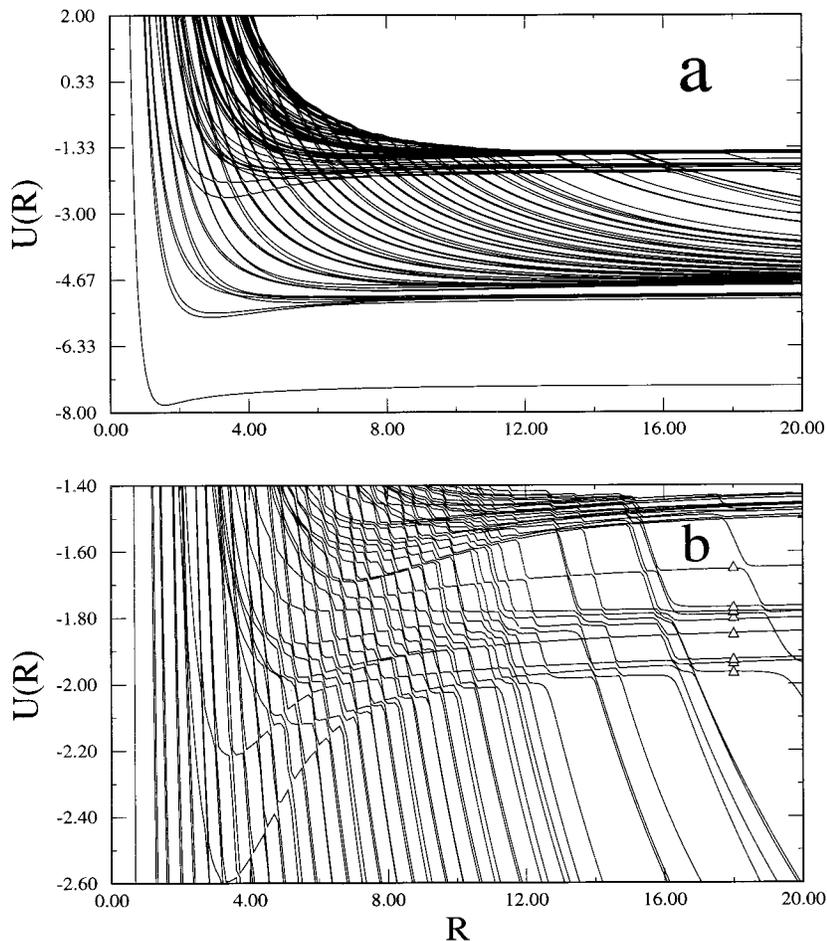


FIG. 2. The final potential curves for the  $2P^o$  state of the lithium atom as functions of  $R$ . The energy region where the channels support triply excited states is enlarged in (b). The triangles are calculated involving only nine channels from the (2,2) shell at  $R=18$ . Atomic units are used here.

obtain accurate adiabatic potential curves for the semiquantitative analysis of all the spectra of a three-electron system. The power of such a method for analyzing the spectra of triply excited states of Li was illustrated in Ref. [14].

## VI. SUMMARY

We have further developed the analytical formulation in the hyperspherical approach to three-electron systems. The partial differential equations for solving the hyperspherical channels are reduced to a compact, symmetric form. Spins are treated analytically and the hyperangle dependence of the couplings between different equations are obtained. The numerical solutions of these equations for the Li atom were obtained to illustrate the employment of this approach. Calculations for all possible different symmetries are under way and interesting features of three-electron correlation are expected to emerge soon.

## ACKNOWLEDGMENTS

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## APPENDIX A: $S_3$ ALGEBRA

In this appendix, we present and derive some properties of  $S_3$  algebra which are needed in the analysis of our hyperspherical approach.

The  $S_3$  group has six permutations as its elements,

$$s_1 = 1, \quad s_2 = (12), \quad s_3 = (13), \quad s_4 = (23), \quad s_5 = (123), \\ s_6 = (132), \quad (\text{A1})$$

with the multiplications given in Table I. The algebra elements are defined by

TABLE I. Multiplication table for the  $S_3$  group elements  $s_i s_j$ .

$i$	$j$					
	1	2	3	4	5	6
1	$s_1$	$s_2$	$s_3$	$s_4$	$s_5$	$s_6$
2	$s_2$	$s_1$	$s_6$	$s_5$	$s_4$	$s_3$
3	$s_3$	$s_5$	$s_1$	$s_6$	$s_2$	$s_4$
4	$s_4$	$s_6$	$s_5$	$s_1$	$s_3$	$s_2$
5	$s_5$	$s_3$	$s_4$	$s_2$	$s_6$	$s_1$
6	$s_6$	$s_4$	$s_2$	$s_3$	$s_1$	$s_5$

TABLE II. Multiplication table for the product  $S_i S_j$  of the elements of the  $S_3$  algebra. The blank indicates that the product vanishes.

$i$	$j$					
	1	2	3	4	5	6
1	$S_1$					
2		$S_2$				
3			$S_3$			$S_6$
4			$S_4$			$-S_5$
5				$S_4$	$S_5$	
6				$-S_3$	$S_6$	

$$S_k = \sum_{i=1}^6 c_i^k s_i, \quad k=1, \dots, 6, \quad (\text{A2})$$

where  $c_i^k$  are given in BL. With this definition, the products of  $S_i S_j$  are shown in Table II.

The corresponding conjugate operators are defined by  $\langle S_k f_1 | f_2 \rangle = \langle f_1 | S_k^\dagger f_2 \rangle$  which leads to

$$S_k^\dagger = \sum_{i=1}^6 c_i^k s_i^{-1}, \quad (\text{A3})$$

where  $f_1$  and  $f_2$  are arbitrary functions and  $s_i^{-1}$  is the inverse of  $s_i$ . Using Table I to get  $s_i^{-1}$ , we have

$$\begin{aligned} S_k^\dagger &= S_k \quad (k=1,2,3,5), \\ S_4^\dagger &= -S_6, \\ S_6^\dagger &= -S_4. \end{aligned} \quad (\text{A4})$$

To evaluate  $S_k f_1 f_2$ , it is convenient to decompose  $S_k$  into the sum of the products of two  $S_3$  algebras, ( $P_i$ ) and ( $Q_j$ ), acting on  $f_1$  and  $f_2$ , respectively. The decomposition can be obtained explicitly (see BL):

$$S_1 = P_1 Q_1 + P_2 Q_2 + \frac{1}{2}(P_3 Q_3 + P_4 Q_4 + P_5 Q_5 + P_6 Q_6), \quad (\text{A5a})$$

$$S_2 = P_1 Q_2 + P_2 Q_1 + \frac{1}{2}(P_3 Q_5 + P_4 Q_6 + P_5 Q_3 + P_6 Q_4), \quad (\text{A5b})$$

$$\begin{aligned} S_3 &= P_1 Q_3 + P_2 Q_5 + P_3(Q_1 + Q_3/2) - P_4 Q_4/2 \\ &\quad + P_5(Q_2 + Q_5/2) - P_6 Q_6/2, \end{aligned} \quad (\text{A5c})$$

$$\begin{aligned} S_4 &= P_1 Q_4 + P_2 Q_6 - P_3 Q_4/2 + P_4(Q_1 - Q_3/2) - P_5 Q_6/2 \\ &\quad + P_6(Q_2 - Q_5/2), \end{aligned} \quad (\text{A5d})$$

$$\begin{aligned} S_5 &= P_1 Q_5 + P_2 Q_3 + P_3(Q_2 + Q_5/2) - P_4 Q_6/2 \\ &\quad + P_5(Q_1 + Q_3/2) - P_6 Q_4/2, \end{aligned} \quad (\text{A5e})$$

$$S_6 = P_1 Q_6 + P_2 Q_4 - P_3 Q_6/2 + P_4(Q_2 - Q_5/2) - P_5 Q_4/2$$

$$+ P_6(Q_1 - Q_3/2). \quad (\text{A5f})$$

Table II and Eq. (A2) indicate

$$S_i S_j = \delta_{ij} S_i \quad (i, j = 1, 2, 3, 5) \quad (\text{A6})$$

and

$$S_1 + S_2 + S_3 + S_5 = 1, \quad (\text{A7})$$

respectively. Therefore  $S_1, S_2, S_3$ , and  $S_5$  form a complete set of projection operators and project functions onto four orthogonal subspaces satisfying specified permutation symmetries. Hence we have the following lemma.

*Lemma A1.* The eigenvalues of  $S_1, S_2, S_3$ , and  $S_5$  are either 0 or 1.

We call an eigenfunction of  $P_i$  ( $i=1,2,3,5$ ) with eigenvalue equal to 1 (i.e.,  $P_i f = f$ ) ‘‘invariant’’ of  $P_i$ .

Let  $\{f_n\}$  be a Hilbert space spanned by functions  $f_n$ . Suppose the space is ‘‘closed,’’ i.e., all  $S_k f_n$  ( $k=1, \dots, 6$ ) are within this space. The space can be decomposed into two,  $\{f_n^+\} = \{\frac{1}{2}(1+s_2)f_n\} + \{\frac{1}{2}(1-s_2)f_n\} \equiv \{f^+\} + \{f^-\}$ , where the  $\{f^+\}$  subspace is symmetric while  $\{f^-\}$  is antisymmetric under the exchange of the electrons 1 and 2. From Table I we get

$$S_1 s_2 = s_2 S_1 = S_1, \quad S_3 s_2 = s_2 S_3 = S_3, \quad (\text{A8a})$$

$$S_2 s_2 = s_2 S_2 = -S_2, \quad S_5 s_2 = s_2 S_5 = -S_5, \quad (\text{A8b})$$

$$S_4 s_2 = S_4, \quad s_2 S_4 = -S_4, \quad S_6 s_2 = -S_6, \quad s_2 S_6 = S_6. \quad (\text{A8c})$$

Therefore, if we denote  $\{S_k\}$  as the subspace spanned by  $S_k f_n$  and  $d\{k\}$  as its dimension, then

$$S_{1,3}\{f^+\} \subset \{f^+\}, \quad S_{1,3}\{f^-\} = 0, \quad \{f^+\} = \{S_1\} + \{S_3\}, \quad (\text{A9a})$$

$$S_{2,5}\{f^-\} \subset \{f^-\}, \quad S_{2,5}\{f^+\} = 0, \quad \{f^-\} = \{S_2\} + \{S_5\}, \quad (\text{A9b})$$

$$S_4\{f^+\} \subset \{f^-\}, \quad S_4\{f^-\} = 0, \quad S_6\{f^-\} \subset \{f^+\}, \quad S_6\{f^+\} = 0, \quad (\text{A9c})$$

i.e.,  $S_1$  and  $S_3$  ( $S_2$  and  $S_5$ ) project a function in  $\{f^+\}$  ( $\{f^-\}$ ) onto another function in the same subspace and  $\{f^+\}$  ( $\{f^-\}$ ) is divided into two orthogonal subspaces spanned by the projections of  $S_1$  and  $S_3$  ( $S_2$  and  $S_5$ ), while  $S_4$  ( $S_6$ ) maps a function in  $\{f^+\}$  ( $\{f^-\}$ ) onto another function in  $\{f^-\}$  ( $\{f^+\}$ ). In this paper, we do not distinguish ‘‘mapping’’ and ‘‘projection’’ and all  $S_i f_n$  are called the projection of  $f_n$  by  $S_i$ .

*Lemma A2.* If a set of functions  $f_n^+$  generate independent projections of  $S_3 f_n^+$ , they generate independent projections of  $S_4 f_n^+$  also.

*Proof.* Suppose  $f_n^+$  generate independent  $S_3 f_n^+$ , but not all  $S_4 f_n^+$  are independent. Hence we can find a set of nonzero constants  $c_n$  such that  $\sum_n c_n S_4 f_n^+ = 0$ . But from Table II we have  $S_6 S_4 = -S_3$ . Thus  $S_6$  times the previous equation leads to  $\sum_n c_n S_3 f_n^+ = 0$ , which conflicts with the initial assumption that all  $S_3 f_n^+$  are independent. Therefore, all  $S_4 f_n^+$  are also independent.

*Lemma A3.* If a set of functions  $f_n^-$  generate independent projections of  $S_5 f_n^-$ , they generate independent projections of  $S_6 f_n^-$  also.

The proof is similar with the use of  $S_4 S_6 = -S_5$ . The immediate conclusion of Lemmas A2 and A3 is the following.

*Lemma A4.*  $d\{3\} = d\{4\}$  and  $d\{5\} = d\{6\}$ .

Furthermore, we have Lemma A5.

*Lemma A5.*  $\{S_4\} = \{S_5\}$  and  $\{S_6\} = \{S_3\}$ .

*Proof.* Since  $\{S_2\} \perp \{S_4\}$  (due to  $S_2^\dagger S_4 = S_4^\dagger S_2 = 0$ ) and  $\{S_1\} \perp \{S_6\}$  (due to  $S_1^\dagger S_6 = S_6^\dagger S_1 = 0$ ), Eq. (A9c) leads to  $\{S_4\} \supseteq \{S_5\}$  and  $\{S_6\} \supseteq \{S_3\}$ , which indicate  $d\{4\} \leq d\{5\}$  and  $d\{6\} \leq d\{3\}$ . On the other hand, Lemma A4 should be satisfied. Therefore  $d\{4\} = d\{5\} = d\{6\} = d\{3\}$  and Lemma A5 is concluded. With the help of this lemma and  $S_4 S_1 = 0$  and  $S_6 S_2 = 0$ , we get

$$S_4 \{S_3\} = \{S_5\}, \quad S_4 \{S_{1,2,5}\} = 0, \quad (\text{A10a})$$

$$S_6 \{S_5\} = \{S_3\}, \quad S_6 \{S_{1,2,3}\} = 0. \quad (\text{A10b})$$

Hence  $S_3 f_m^+$  and  $S_4 f_m^+$  can be expanded by  $S_6 f_n^-$  and  $S_5 f_n^-$ , respectively. These two expansions are related as follows.

*Lemma A6.* If  $S_3 f_m^+ = \sum_n c_{mn} S_6 f_n^-$ , then  $S_4 f_m^+ = -\sum_n c_{mn} S_5 f_n^-$ .

*Proof.* The second equation can be obtained by the multiplication of  $S_4$  with the first one.

The projections  $S_4 f_n^+$  and  $S_3 f_m^+$  (similarly,  $S_6 f_n^-$  and  $S_5 f_m^-$ ) are further related by the following lemma.

*Lemma A7.*  $\langle S_4 f_n^+ | S_4 f_m^+ \rangle = \langle S_3 f_n^+ | S_3 f_m^+ \rangle$  and  $\langle S_6 f_n^- | S_6 f_m^- \rangle = \langle S_5 f_n^- | S_5 f_m^- \rangle$ .

The proof is straightforward by noticing that  $S_6^\dagger = -S_4$ ,  $-S_4 S_6 = S_5 = S_5 S_5 = S_5^\dagger S_5$ , and  $-S_6 S_4 = S_3 = S_3 S_3 = S_3^\dagger S_3$ .

Notice that the lemmas and equations in this appendix are the general properties of  $S_3$  algebra and hence are valid not only for  $S_i$ , but also for  $P_i$  and  $Q_i$  as well. The necessary and sufficient condition for  $\Phi$  to be totally antisymmetric is given by

$$S_2 \Phi = \Phi \quad (\text{A11})$$

which leads to Eq. (9) (see BL for details).

## APPENDIX B: RELATIONS BETWEEN THE ELEMENTS OF THE COUPLING MATRIX

Among the elements of the coupling matrix  $V_{\Gamma'\Gamma}^{j'i}$ , not all of them are independent when acted on by  $P_j$ . The lemmas in this appendix display some of the relations between them.

*Lemma B1.*

$$P_1 V_{\Gamma'\Gamma}^{25} P_3 = P_1 V_{\Gamma'\Gamma}^{26} P_4, \quad P_2 V_{\Gamma'\Gamma}^{15} P_3 = P_2 V_{\Gamma'\Gamma}^{16} P_4,$$

$$P_4^\dagger V_{\Gamma'\Gamma}^{62} P_1 = P_3 V_{\Gamma'\Gamma}^{52} P_1, \quad P_4^\dagger V_{\Gamma'\Gamma}^{61} P_2 = P_3 V_{\Gamma'\Gamma}^{51} P_2,$$

$$P_4^\dagger V_{\Gamma'\Gamma}^{66} P_4 = P_3 V_{\Gamma'\Gamma}^{55} P_3, \quad P_4^\dagger V_{\Gamma'\Gamma}^{65} P_3 = P_3 V_{\Gamma'\Gamma}^{56} P_4.$$

We prove the first one as an example. Equation (A5a) allows us to decompose  $P_1$  as a sum of six products of two factors,

$P_i'$  and  $P_j''$ , with  $P_i'$  acting on  $V_{\Gamma'\Gamma}^{25}$  and  $P_j''$  on  $P_3$ , respectively. Only two terms containing  $P_3''$  and  $P_4''$  are not zero due to the multiplication rules of  $P_3$  (see Table II), thus  $P_1 V_{\Gamma'\Gamma}^{25} P_3 = [(P_3' V_{\Gamma'\Gamma}^{25}) P_3 + (P_4' V_{\Gamma'\Gamma}^{25}) P_4]/2$  where we have dropped the superscripts of  $P_i'$  and used the results of the multiplications  $P_i P_3$ . Notice that [Eq. (B.4) of BL]

$$(P_j' V_{\Gamma'\Gamma}^{i'i}) = Q_j \langle Q_i' \mathcal{Y}_{\Gamma'} | V | Q_i \mathcal{Y}_{\Gamma'} \rangle. \quad (\text{B1})$$

where  $Q_j$  acts on both  $Q_i' \mathcal{Y}_{\Gamma'}$  and  $Q_i \mathcal{Y}_{\Gamma'}$ . Hence

$$P_1 V_{\Gamma'\Gamma}^{25} P_3 = [(Q_3 \langle Q_2 \mathcal{Y}_{\Gamma'} | V | Q_5 \mathcal{Y}_{\Gamma'} \rangle) P_3 + (Q_4 \langle Q_2 \mathcal{Y}_{\Gamma'} | V | Q_5 \mathcal{Y}_{\Gamma'} \rangle) P_4]/2.$$

Decomposing again  $Q_3$  and  $Q_4$  into the sum of the products of two factors acting on  $Q_2 \mathcal{Y}_{\Gamma'}$  and  $Q_5 \mathcal{Y}_{\Gamma'}$ , respectively, and using Table II to select nonvanishing terms, we obtain

$$P_1 V_{\Gamma'\Gamma}^{25} P_3 = \frac{1}{2} (V_{\Gamma'\Gamma}^{25} P_3 + V_{\Gamma'\Gamma}^{26} P_4). \quad (\text{B2})$$

By parallel reasoning,

$$P_1 V_{\Gamma'\Gamma}^{26} P_4 = \frac{1}{2} (V_{\Gamma'\Gamma}^{25} P_3 + V_{\Gamma'\Gamma}^{26} P_4). \quad (\text{B3})$$

The comparison of Eqs. (B2) and (B3) leads to the first equation of the lemma. In fact, for this particular case, using  $P_1$  to multiply Eq. (B2) from the left gives the result directly while the method demonstrated above is more general. Similarly, we can prove the following lemma.

*Lemma B2.*

$$P_3 V_{\Gamma'\Gamma}^{16} P_3 = P_3 V_{\Gamma'\Gamma}^{15} P_4, \quad P_3 V_{\Gamma'\Gamma}^{61} P_3 = P_3 V_{\Gamma'\Gamma}^{51} P_4,$$

$$P_3 V_{\Gamma'\Gamma}^{25} P_3 = -P_3 V_{\Gamma'\Gamma}^{26} P_4, \quad P_3 V_{\Gamma'\Gamma}^{52} P_3 = -P_3 V_{\Gamma'\Gamma}^{62} P_4,$$

$$P_1 V_{\Gamma'\Gamma}^{66} P_3 = -P_1 V_{\Gamma'\Gamma}^{55} P_3, \quad P_3 V_{\Gamma'\Gamma}^{66} P_1 = -P_3 V_{\Gamma'\Gamma}^{55} P_1,$$

$$P_1 V_{\Gamma'\Gamma}^{66} P_1 = P_1 V_{\Gamma'\Gamma}^{55} P_1, \quad P_2 V_{\Gamma'\Gamma}^{66} P_2 = P_2 V_{\Gamma'\Gamma}^{55} P_2.$$

Notice that the above proofs are independent of any specific features of  $\mathcal{Y}_{\Gamma}$ . Therefore they are the general properties of the coupling matrix. For example, they are also valid for  $\mathcal{Y}_{\gamma'\gamma}^{j'i}$ .

## APPENDIX C: EXPLICIT TREATMENT OF SPINS

The projections of spin functions are given by

$$Q_k \chi = \delta_{k1} \chi, \quad (\text{C1a})$$

$$Q_{1,2,5,6} \chi_1 = 0, \quad Q_3 \chi_1 = \chi_1, \quad Q_{1,2,3,4} \chi_0 = 0, \quad Q_5 \chi_0 = \chi_0,$$

$$Q_4 \chi_1 = \chi_0, \quad Q_6 \chi_0 = -\chi_1. \quad (\text{C1b})$$

These equations are the results of the evaluations of the operations of  $Q_k$  on the spin functions and the analytic formula of the evaluations in terms of  $6j$  symbols are given in Eqs. (22)–(25) of BL. From Eq. (C1) we see that  $\chi$  is totally symmetric while  $\chi_1$  ( $\chi_0$ ) is (anti)symmetric about the ex-

change of the electrons 1 and 2 but is not so when the exchanges involve the electron 3.

The following equations are useful in the analysis of the invariant subspaces of  $Q_i$  operators in the Hilbert space of  $\{|\gamma\rangle\}$ :

$$Q_2\chi_0Q_6 = Q_2\chi_1Q_5 = (\chi_0Q_6 + \chi_1Q_5)/2, \quad (C2a)$$

$$Q_1\chi_0Q_5 = -Q_1\chi_1Q_6 = (\chi_0Q_5 - \chi_1Q_6)/2, \quad (C2b)$$

$$Q_5\chi_0Q_1 = \chi_0Q_1, \quad Q_5\chi_1Q_2 = \chi_1Q_2,$$

$$Q_5\chi_0Q_6 = -Q_5\chi_1Q_5 = (\chi_0Q_6 - \chi_1Q_5)/2, \quad (C2c)$$

$$Q_6\chi_0Q_1 = -\chi_1Q_1, \quad Q_6\chi_1Q_2 = \chi_0Q_2,$$

$$Q_6\chi_0Q_6 = -Q_6\chi_1Q_5 = (\chi_0Q_5 + \chi_1Q_6)/2. \quad (C2d)$$

These equations are derived by decomposing  $Q_i$  into the sum of the products of two factors acting on  $\chi_i$  and  $Q_j$ , respectively [Eq. (A5)], and Eq. (C1b) is used to eliminate the vanishing terms. From Eq. (C2a), we know that although  $\chi_0Q_6|\gamma\rangle$  and  $\chi_1Q_5|\gamma\rangle$  are not invariant of  $Q_2$  individually,  $\chi_0Q_6|\gamma\rangle + \chi_1Q_5|\gamma\rangle$  is indeed invariant of  $Q_2$ . Similarly,  $\chi_0Q_5|\gamma\rangle - \chi_1Q_6|\gamma\rangle$  is invariant of  $Q_1$  and  $\chi_0Q_1|\gamma\rangle$ ,  $\chi_1Q_2|\gamma\rangle$ , and  $\chi_0Q_6|\gamma\rangle - \chi_1Q_5|\gamma\rangle$  are invariant of  $Q_5$ . Using Eq. (C2d), we can map the invariant subspace of  $Q_5$  into the subspace of  $\{Q_6\mathcal{V}_\Gamma\}$ .

#### APPENDIX D: SYMMETRIES OF THE ELEMENTS OF THE COUPLING MATRIX

In this appendix, we analyze the permutation symmetries of  $\mathcal{V}_{\gamma'\gamma}^{j'i}$ . With these properties, their dependence on the hyperangles can be derived. Since the analysis is independent

of the specific features of  $|\gamma\rangle$ , the results are also valid for other choices of basis. For example, they are also valid for  $\mathcal{V}_{\Gamma'\Gamma}^{j'i}$ .

Since  $P_1 + P_2 + P_3 + P_5 = 1$  [Eq. (A7)], we expect to find four groups. The first group is formed by  $\mathcal{V}_{\gamma'\gamma}^{11}$ ,  $\mathcal{V}_{\gamma'\gamma}^{22}$ , and  $\mathcal{V}_{\gamma'\gamma}^{55} + \mathcal{V}_{\gamma'\gamma}^{66}$  which are totally symmetric under the permutation of radial distances of electrons, i.e., we have the following lemma.

*Lemma D1.*  $P_1\mathcal{V}_{\gamma'\gamma}^{11} = \mathcal{V}_{\gamma'\gamma}^{11}$ ,  $P_1\mathcal{V}_{\gamma'\gamma}^{22} = \mathcal{V}_{\gamma'\gamma}^{22}$ , and  $P_1(\mathcal{V}_{\gamma'\gamma}^{55} + \mathcal{V}_{\gamma'\gamma}^{66}) = \mathcal{V}_{\gamma'\gamma}^{55} + \mathcal{V}_{\gamma'\gamma}^{66}$ .

*Proof:* Equation (B1) leads to  $P_1\mathcal{V}_{\gamma'\gamma}^{j'i} = Q_1\langle Q_i\gamma' | V | Q_i\gamma \rangle$ .  $Q_1$  is in turn decomposed into the sum of products of two factors acting on  $Q_i\gamma'$  and  $Q_i\gamma$  respectively [Eq. (A5a)]. Lemma D1 is then derived by the multiplications of Table II.

The second group and the third group are invariant of  $P_3$  and  $P_5$ , respectively. Their symmetries are mixed.

*Lemma D2.*  $P_3\mathcal{V}_{\gamma'\gamma}^{25} = \mathcal{V}_{\gamma'\gamma}^{25}$ ,  $P_3\mathcal{V}_{\gamma'\gamma}^{52} = \mathcal{V}_{\gamma'\gamma}^{52}$ ,  $P_3\mathcal{V}_{\gamma'\gamma}^{16} = \mathcal{V}_{\gamma'\gamma}^{16}$ ,  $P_3\mathcal{V}_{\gamma'\gamma}^{61} = \mathcal{V}_{\gamma'\gamma}^{61}$ , and  $P_3(\mathcal{V}_{\gamma'\gamma}^{66} - \mathcal{V}_{\gamma'\gamma}^{55}) = \mathcal{V}_{\gamma'\gamma}^{66} - \mathcal{V}_{\gamma'\gamma}^{55}$ .

*Lemma D3.*  $P_5\mathcal{V}_{\gamma'\gamma}^{15} = \mathcal{V}_{\gamma'\gamma}^{15}$ ,  $P_5\mathcal{V}_{\gamma'\gamma}^{51} = \mathcal{V}_{\gamma'\gamma}^{51}$ ,  $P_5\mathcal{V}_{\gamma'\gamma}^{26} = \mathcal{V}_{\gamma'\gamma}^{26}$ ,  $P_5\mathcal{V}_{\gamma'\gamma}^{62} = \mathcal{V}_{\gamma'\gamma}^{62}$ ,  $P_5\mathcal{V}_{\gamma'\gamma}^{56} = \mathcal{V}_{\gamma'\gamma}^{56}$ , and  $P_5\mathcal{V}_{\gamma'\gamma}^{65} = \mathcal{V}_{\gamma'\gamma}^{65}$ .

The members of the last group,  $\mathcal{V}_{\gamma'\gamma}^{12}$ ,  $\mathcal{V}_{\gamma'\gamma}^{21}$ , and  $\mathcal{V}_{\gamma'\gamma}^{65} - \mathcal{V}_{\gamma'\gamma}^{56}$ , are totally antisymmetric under the permutations of radial distances of electrons, i.e., we have the following.

*Lemma D4.*  $P_2\mathcal{V}_{\gamma'\gamma}^{12} = \mathcal{V}_{\gamma'\gamma}^{12}$ ,  $P_2\mathcal{V}_{\gamma'\gamma}^{21} = \mathcal{V}_{\gamma'\gamma}^{21}$ , and  $P_2(\mathcal{V}_{\gamma'\gamma}^{65} - \mathcal{V}_{\gamma'\gamma}^{56}) = \mathcal{V}_{\gamma'\gamma}^{65} - \mathcal{V}_{\gamma'\gamma}^{56}$ .

Other  $\mathcal{V}_{\gamma'\gamma}^{j'i}$  which are not listed in the above lemmas (e.g.,  $\mathcal{V}_{\gamma'\gamma}^{14}$ ) have no use in the formulation.

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- [1] R. P. Madden and K. Codling, Phys. Rev. Lett. **10**, 516 (1963).  
 [2] See C. D. Lin, in *Review of Fundamental Processes and Applications of Atoms and Ions*, edited by C. D. Lin (World Scientific, Singapore, 1993), p. 357, and the literature cited therein.  
 [3] Y. Azuma *et al.*, Phys. Rev. Lett. **74**, 3768 (1995); L. Journel *et al.*, Phys. Rev. Lett. **76**, 30 (1996); L. M. Kiernan *et al.*, Phys. Rev. Lett. **72**, 2359 (1994); J. Phys. B **28**, L161 (1995).  
 [4] S. Watanabe and C. D. Lin, Phys. Rev. A **36**, 511 (1987).  
 [5] D. R. Herrick and O. Sinanoglu, Phys. Rev. A **11**, 97 (1975); J. M. Feagin and J. S. Briggs, Phys. Rev. Lett. **57**, 984 (1986); R. Stephen Berry, Contemp. Phys. **30**, 1 (1989).  
 [6] J. H. Macek, J. Phys. B **2**, 831 (1968).  
 [7] C. D. Lin, Phys. Rev. A **29**, 1019 (1984).  
 [8] J. Z. Tang, S. Watanabe, and M. Matsuzawa, Phys. Rev. A **46**, 2437 (1992); B. Zhou, C. D. Lin, J. Z. Tang, S. Watanabe, and M. Matsuzawa, J. Phys. B **26**, 2555 (1993); B. Zhou and C. D. Lin, *ibid.* **26**, 2575 (1993); A. Menzel, S. P. Frigo, S. B. Whitfield, C. D. Caldwell, M. O. Krause, J. Z. Tang, and I. Shimamura, Phys. Rev. Lett. **75**, 1479 (1995).  
 [9] C. W. Clark and C. H. Greene, Phys. Rev. A **21**, 1786 (1980); C. H. Greene and C. W. Clark, *ibid.* **30**, 2161 (1984).  
 [10] S. Watanabe, M. Le Dourneuf, and L. Pelamourgues, J. Phys. (Paris) Colloq. **43**, C2-223 (1982).  
 [11] U. Fano and A. R. P. Rau, *Atomic Collisions and Spectra* (Academic Press, Orlando, 1986).  
 [12] C. G. Bao and C. D. Lin, Few-Body Syst. **16**, 47 (1994).  
 [13] X. Yang, J. Xi, C. G. Bao, and C. D. Lin, Phys. Rev. A **52**, 2029 (1995).  
 [14] X. Yang, C. G. Bao, and C. D. Lin (unpublished).  
 [15] D. S. Walton *et al.*, J. Phys. B **3**, L148 (1970); **4**, 1343 (1971); B. Peart and K. T. Dolder *ibid.* **6**, 1497 (1973).  
 [16] H. S. Taylor and L. D. Thomas, Phys. Rev. Lett. **28**, 1091 (1972).  
 [17] L. H. Andersen *et al.*, Phys. Rev. Lett. **74**, 892 (1995).  
 [18] F. Robicheaux *et al.*, Phys. Rev. A **49**, 1866 (1994).  
 [19] P. Faucher, Vo Ky Lan, J. C. Chang, and F. Bely-Dubau, in *Proceedings of the 19th International Conference on the Physics of Electronic and Atomic Collisions: Scientific Program and Abstracts of Contributed Papers*, Whistler, British Columbia, Canada, 1995 (University of Western Ontario, London, 1995), p. 318; L. Lipsky, R. Anania, and M. J. Conneely, At. Data Nucl. Data Tables **20**, 127 (1977).