N-electron wave functions described with hyperspherical coordinates

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We describe the N-electron atomic wave functions within the hyperspherical-coordinate framework. The wave functions, being solutions of the Schrödinger equation, are made to adapt the permutation symmetry of the symmetric group S_N. The effects of permutations on the wave functions are deduced, and the matrix elements of the atomic potential are presented.

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I. INTRODUCTION

One of the primary important problems in the field of atomic and molecular quantum mechanics is to solve accurately the Schrödinger equation of a many-body system. The same problem is also encountered and has been pursued systematically by many theorists in the field of solid-state physics and chemistry. In the course of this development, many methods aimed at solving this problem have been proposed, most of which admit only solutions in the sense of an average.

The hyperspherical-coordinate (HC) method, on the other hand, can admit accurate and analytical solutions of the Schrödinger equation of a many-body system. Indeed, the application of the HC method to He, H^-, and some few-particle systems has resulted in very accurate ground-state eigenvalues of these systems [1–3]. The method also yields encouraging results when applied to the calculation of the ground-state energies of a lithium atom (Li) and a hydrogen molecular ion (H_2^+) [4,5].

It is well known that the wave functions of a many-electron system should be antisymmetric to the interchange of any two electrons because of the fermionic property of the electron. Many excellent texts have dealt with this problem in great detail [6]. Cavagnero, for instance, has antisymmetrized wave functions by using Racah coefficients of fractional parentage [7]. In this paper we present the antisymmetric wave functions in terms of the hyperspherical coordinates. We first antisymmetrize wave functions by directly permuting electrons and then investigate the effects of the permutation of electrons on these wave functions. The effects of permutation on a three-electron system have been surveyed before [8] and in this paper we extend it to an N-electron system. Finally, we use the antisymmetric wave functions to simplify the calculation of matrix elements of the atomic potential.

II. ANTISYMMETRIZATION OF WAVE FUNCTIONS

For an N-electron atom, after the usual procedures of separation of the center of mass coordinates (practically on the nucleus), there are still $3N$ coordinates left for N electrons. Following Knirk [9], we use the hyperspherical-coordinate system in which the Cartesian coordinates are first transformed into spherical coordinates and then the radii of electrons are cast into hyperspherical coordinates. We have

$$\begin{aligned}
&z_i = r_i \cos\theta_i \ , \\
&x_i = r_i \sin\theta_i \cos\phi_i \ , \quad i = 1,2,\ldots,N \\
&y_i = r_i \sin\theta_i \sin\phi_i \ , \\
&r_N = R\cos\eta_N \ , \\
&r_{N-1} = R\sin\eta_N \cos\eta_{N-1} \ , \\
&\vdots \\
&r_i = R\sin\eta_N \sin\eta_{N-1} \cdots \sin\eta_{i+1} \cos\eta_i \ , \\
&\vdots \\
&r_2 = R\sin\eta_N \sin\eta_{N-1} \cdots \sin\eta_3 \cos\eta_2 \ , \\
&r_1 = R\sin\eta_N \sin\eta_{N-1} \cdots \sin\eta_3 \sin\eta_2 \ ,
\end{aligned} \tag{1}$$

where

$$0 \le \eta_i \le \frac{\pi}{2} \ . \tag{2}$$

The Schrödinger equation (in a.u.) reads

$$\left\{ -\frac{1}{2}\left[\frac{\partial^2}{\partial R^2} + \frac{3N-1}{R}\frac{\partial}{\partial R} - \frac{\hat{\Lambda}^2(N)}{R^2} \right] + V \right\} \Psi = E\Psi \ , \tag{3}$$

where V is the potential of the N-electron atom. In three-dimensional Cartesian coordinate system this potential operator resumes the form

$$V=-\sum_{i=1}^{N}\frac{Z_N}{r_i}+\sum_{i<j}^{N}\frac{1}{r_{ij}} . \tag{4}$$

After transforming into a hyperspherical-coordinate system, the potential operator may be written as

$$V=\frac{Z_N(\Omega)}{R} . \tag{4'}$$

In Eq. (3), $\hat{\Lambda}^2(N)$ is the generalized angular momentum scalar operator of N electrons and it resumes the form

$$\hat{\Lambda}^2(N)=-\frac{\partial^2}{\partial\eta_N^2}-\frac{(3N-4)\cos^2\eta_N-2\sin^2\eta_N}{\sin\eta_N\cos\eta_N}\frac{\partial}{\partial\eta_N}+\frac{\hat{l}_N^2}{\cos^2\eta_N}+\frac{\hat{\Lambda}^2(N-1)}{\sin^2\eta_N} . \tag{5}$$

Since quantum numbers L and M_L of the total angular momentum scalar operator and its third component are good quantum numbers, the eigenfunctions of Eq. (3) may be chosen to be the simultaneous eigenfunctions of these operators and can be specified with L and M_L, namely,

$$\Psi_{L,M_L}(R,\Omega)=\sum_{\lambda_N\mu_N}F_{\lambda_N\mu_N}(R)\mathcal{Y}_{\lambda_N\mu_N LM_L}(\Omega) , \tag{6}$$

where $\mathcal{Y}_{\lambda_N\mu_N LM_L}(\Omega)$ are eigenfunctions of the operator $\hat{\Lambda}^2(N)$,

$$\hat{\Lambda}^2(N)\mathcal{Y}_{\lambda_N\mu_N LM_L}(\Omega)=\lambda_N(\lambda_N+3N-2)\mathcal{Y}_{\lambda_N\mu_N LM_L}(\Omega) \tag{7}$$

and are represented by

$$\mathcal{Y}_{\lambda_N\mu_N LM_L}(\Omega)=[\cdots[[Y_{l_1}(\hat{1})Y_{l_2}(\hat{2})]^{L_2}Y_{l_3}(\hat{3})]^{L_3}\cdots\times Y_{l_N}(\hat{N})]^{L}_{M_L}\times\prod_{j=2}^{N}y_j^{l_j/2}(1-y_j)^{\lambda_{j-1}/2}\times\omega_N(-n_j,n_j+\rho_j;\gamma_j|y_j) . \tag{8}$$

In writing Eqs. (7) and (8) we have used the following notation: $Y_{l_i}(\hat{i})$ is the spherical harmonics and $\hat{i}=\theta_i,\phi_i$; $y_j=\cos^2\eta_j$; $\omega_N(-n_j,n_j+\rho_j;\gamma_j|y_j)$ is the normalized Jacobi polynomial of degree n_j;

$$\begin{aligned}&\mu_N=(l_1,l_2,\ldots,l_N;\lambda_2,\lambda_3,\ldots,\lambda_{N-1};L_2,L_3,\ldots,L_{N-1}) ;\\ &\rho_j=l_j+\lambda_{j-1}+\tfrac{3}{2}j-1 ;\\ &\lambda_j=2n_j+\lambda_{j-1}+l_j ;\\ &\gamma_j=l_j+\tfrac{3}{2} ;\\ &n_j,l_j=0,1,2,\ldots ;\\ &j=2,3,\ldots,N .\end{aligned} \tag{9}$$

The Hamiltonian on the left-hand side of Eq. (3) is symmetric with respect to electron permutation and is commutable with permutation operators. The Hamiltonian and permutation operators therefore, have, common eigenfunctions. Let $\Psi_{L,M_L}(R,\Omega)$ be an eigenfunction of Eq. (3) with eigenvalue E and let $Y^{[f](r)}$ be a Young operator belonging to the irreducible representation $[f]$ and row (r) of the symmetric group S_N. Then

$$\Psi^{[f](r)}_{L,M_L}(R,\Omega)=Y^{[f](r)}\Psi_{L,M_L}(R,\Omega) \tag{10}$$

is also the eigenfunction of Eq. (3) with eigenvalue E. We then construct the spin wave function $\Theta^{[\tilde{f}](\bar{r})}_{S,M_S}(\sigma)$ with spin quantum numbers S and M_S belonging to the irreducible representation $[\tilde{f}]$ and row $(\bar{r})$ conjugating to $[f]$ and (r). Thus we have the following antisymmetric wave function of N-electron atom:

$$\Psi([f]SLM_SM_L|R,\Omega,\sigma)=\frac{1}{\sqrt{h_f}}\sum_{(r)}(-1)^{p_r}\Psi^{[f](r)}_{L,M_L}(R,\Omega)\Theta^{[\tilde{f}](\bar{r})}_{S,M_S}(\sigma) , \tag{11}$$

where h_f is the dimension of the irreducible representation $[f]$.

III. EFFECTS OF PERMUTATION ON THE WAVE FUNCTION

In this section we will investigate the effects of permutations on the wave functions given in Eq. (11). First, we observe that $F_{\lambda_N\mu_N}(R)$ is symmetric with respect to permutations; hence the effects of permutations on $\Psi_{L,M_L}(R,\Omega)$ are just on the hyperspherical harmonics, namely,

$$\Psi^{[f](r)}_{L,M_L}(R,\Omega)=\sum_{\lambda_N\mu_N}F_{\lambda_N\mu_N}(R)\mathcal{Y}^{[f](r)}_{\lambda_N\mu_N LM_L}(\Omega) . \tag{12}$$

Next we note that every permutation can be expressed as the product of two cycles of consecutive integers such as $(j,j+1)$. Thus we need only to search for the effects of transposition $(j,j+1)$ on the hyperspherical harmonics $\mathcal{Y}_{\lambda_N\mu_N LM_L}(\Omega)$.

The effects of transposition $(j,j+1)$ on the spherical harmonics of the wave function can be obtained by the Racah coupling and recoupling method. By transposition (1,2) we get

$$(1,2)[\cdots[[Y_{l_1}(\hat{1})Y_{l_2}(\hat{2})]^{L_2}Y_{l_3}(\hat{3})]^{L_3}\cdots Y_{l_N}(\hat{N})]^L_{M_L}$$
$$=[\cdots[[Y_{l_1}(\hat{2})Y_{l_2}(\hat{1})]^{L_2}Y_{l_3}(\hat{3})]^{L_3}\cdots Y_{l_N}(\hat{N})]^L_{M_L}$$
$$=(-1)^{l_1+l_2-L_2}[\cdots[[Y_{l_2}(\hat{1})Y_{l_1}(\hat{2})]^{L_2}Y_{l_3}(\hat{3})]^{L_3}\cdots Y_{l_N}(\hat{N})]^L_{M_L}\ . \tag{13}$$

By transposition $(j,j+1)$ we get

$$(j,j+1)[\cdots[[[\ ]^{L_{j-1}}Y_{l_j}(\hat{j})]^{L_j}Y_{l_{j+1}}(\hat{j}+1)]^{L_{j+1}}\cdots Y_{l_N}(\hat{N})]^L_{M_L}$$
$$=[\cdots[[[\ ]^{L_{j-1}}Y_{l_j}(\hat{j}+1)]^{L_j}Y_{l_{j+1}}(\hat{j})]^{L_{j+1}}\cdots Y_{l_N}(\hat{N})]^L_{M_L}$$
$$=\sum_{L_j'}C_{L_j'}[\cdots[[[\ ]^{L_{j-1}}Y_{l_{j+1}}(\hat{j})^{L_j'}]Y_{l_j}(\hat{j}+1)]^{L_{j+1}}\cdots Y_{l_N}(\hat{N})]^L_{M_L}\ . \tag{14}$$

The expansion coefficients $C_{L_j'}$ are derived in Appendix A and have the expression

$$C_{L_j'}=(-1)^{L_{j-1}+L_j'-L_j-L_{j+1}}U(l_jL_{j-1}L_{j+1}l_{j+1};L_jL_j')\ , \tag{15}$$

where $U(l_jL_{j-1}L_{j+1}l_{j+1};\ L_jL_j')$ is the Racah coupling coefficient. We have followed Baymann [10] in deriving the Racah coefficient $U(a,b,c,d;e,f)$ and fixing the phase factors by using the relation $U(a,b,c,0;e,f)=\delta_{ec}\delta_{bf}\varepsilon_{abe}$, where $\varepsilon_{abe}=1$, if abe satisfies a triangle relation; otherwise $\varepsilon_{abe}=0$.

The effects of permutation on the hyperspherical harmonics, are similar to that on spherical harmonics, but more complex. With the definition of Eqs. (2) and (9), we have

$$y_j=\frac{r_j^2}{\sum_{i\,(=1)}^{j}r_i^2}\ , \tag{16a}$$

$$y_{j+1}=\frac{r_{j+1}^2}{\sum_{i\,(1)}^{j+1}r_i^2}\ . \tag{16b}$$

By transposition $(j,j+1)$, y_{j+1} is transformed to

$$y_{j+1}\to\frac{r_j^2}{\sum_{i\,(1)}^{j+1}r_i^2}=y_j(1-y_{j+1}) \tag{17a}$$

and y_j is transformed to

$$y_j\to\frac{r_{j+1}^2}{\sum_{i\,(1)}^{j-1}r_i^2+r_{j+1}^2}=\frac{y_{j+1}}{[1-y_j(1-y_{j+1})]}\ . \tag{17b}$$

These relations show that the transposition $(j,j+1)$ affects the hyperspherical harmonics of y_j and y_{j+1} only; hence we will concentrate on them. Now consider the function

$$K(y_j,y_{j+1})=y_{j+1}^{l_{j+1}/2}(1-y_{j+1})^{\lambda_j/2}\omega_N(-n_{j+1},n_{j+1}+\rho_{j+1};\gamma_{j+1}|\gamma_{j+1})y_j^{l_j/2}(1-y_j)^{\lambda_{j-1}/2}\omega_N(-n_j,n_j+\rho_j;\gamma_j|y_j)$$
$$=N^{-1/2}(n_{j+1},\rho_{j+1},l_{j+1})N^{-1/2}(n_j,\rho_j,l_j)y_{j+1}^{l_{j+1}/2}(1-y_{j+1})^{\lambda_2/2}$$
$$\times\omega(-n_{j+1},n_{j+1}+\rho_{j+1};\gamma_{j+1}|y_{j+1})y_j^{l_j/2}(1-y_j)^{\lambda_{j-1}/2}\omega(-n_j,n_j+\rho_j;\gamma_j|y_j)\ . \tag{18}$$

Making use of Eqs. (17a) and (17b) we have

$$(j,j+1)K(y_j,y_{j+1})=N^{-1/2}(n_{j+1},\rho_{j+1},l_{j+1})N^{-1/2}(n_j,\rho_jl_j)[y_j(1-y_{j+1})]^{l_{j+1}/2}[1-y_j(1-y_{j+1})]^{\lambda_j/2}$$
$$\times\omega(-n_{j+1},n_{j+1}+\rho_{j+1};\gamma_{j+1}|y_j(1-y_{j+1}))$$
$$\times\left[\frac{y_{j+1}}{1-y_j(1-y_{j+1})}\right]^{l_j/2}\left[1-\frac{y_{j+1}}{1-y_j(1-y_{j+1})}\right]^{\lambda_{j-1}/2}$$
$$\times\omega\left[-n_j,n_j+\rho_j;\gamma_j\left|\frac{y_{j+1}}{1-y_j(1-y_{j+1})}\right.\right]$$
$$=N^{-1/2}(n_{j+1},\rho_{j+1},l_{j+1})N^{-1/2}(n_j,\rho_j,l_j)y_{j+1}^{l_j/2}(1-y_{j+1})^{(\lambda_{j-1}+l_{j+1})/2}$$
$$\times y_j^{l_{j+1}/2}(1-y_j)^{\lambda_{j-1}/2}[1-y_j(1-y_{j+1})]^{n_j}$$
$$\times\omega(-n_{j+1},n_{j+1}+\rho_{j+1};\gamma_{j+1}|y_j(1-y_{j+1}))\omega\left[-n_j,n_j+\rho_j;\gamma_j\left|\frac{y_{j+1}}{1-y_j(1-y_{j+1})}\right.\right]\ . \tag{19}$$

First, we note that there is no singular point in expression (19) because the highest power in $\omega(-n_j,n_j+\rho_j;\gamma_j|y_{j+1}/[1-y_j(1-y_{j+1})])$ is n_j; therefore the denominator is canceled by the factor $[1-y_j(1-y_{j+1})]^{n_j}$ present in the expression. Second, we notice that the Jacobi polynomials form a complete orthonormal set and expression (19) can be expanded in terms of these polynomials with the parameters ρ and γ not uniquely determined, but free at our disposal. We fix these parameters by the following considerations.

Comparing Eqs. (18) and (19) we find the following correspondence relations:

$$y_{j+1}^{l_{j+1}/2}\text{(in Eq. (18)]}\rightarrow y_{j+1}^{l_j/2}\text{ [in Eq. (19)]},$$
$$y_j^{l_j/2}\text{ [in Eq. (18)]}\rightarrow y_j^{l_{j+1}/2}\text{ [in Eq. (19)]}.$$

With the definition for γ in Eq. (18) we also have

$$\gamma_{j+1}\rightarrow\gamma_j \text{ for } y_{j+1},$$
$$\gamma_j\rightarrow\gamma_{j+1} \text{ for } y_j.$$

From Eqs. (8) and (9) we note that λ_j is present in both $\omega(-n_{j+1},n_{j+1}+\rho_{j+1};\gamma_{j+1}|y_{j+1})$ and $\omega(-n_j,n_j+\rho_j;\gamma_j|y_j)$. Thus we may choose λ_{j+1}, which is present in $\omega(-n_{j+2},n_{j+2}+\rho_{j+2};\gamma_{j+2}|y_{j+2})$, to be also present in the expansion $\omega(-n'_{j+1},n'_{j+1}+\rho'_{j+1};\gamma_{j+1}|y_{j+1})$. In the same way, λ_{j-1}, which is present in $\omega(-n_{j-1},n_{j-1}+\rho_{j-1};\gamma_{j-1}|y_{j-1})$, is also chosen to be present in the expression of the Jacobi polynomial $\omega(-n'_j,n'_j+\rho'_j;\gamma_{j+1}|y_j)$.

Later we will show that $n'_{j+1}+n'_j=n_{j+1}+n_j$ [see Eq. (23)]. There is, therefore, only one dummy index in the expansion, which we will choose to be n'_j because $\lambda'_j=2n'_j+\lambda_{j-1}+l_{j+1}$ is present in both $\omega(-n'_{j+1},n'_{j+1}+\rho'_{j+1};\gamma_j|y_{j+1})$ and $\omega(-n'_j,n'_j+\rho'_j;\gamma_{j+1}|y_j)$.

By these examinations, Eq. (9) can be written as

$$(j,j+1)K(y_j,y_{j+1})=\sum_{n'_j}C_{n'_j}N^{-1/2}(n'_{j+1},\rho'_{j+1},l_j)N^{-1/2}(n'_j,\rho'_j,l_{j+1})y_{j+1}^{l_j/2}(1-y_{j+1})^{\lambda'_j/2}y_j^{l_{j+1}/2}(1-y_j)^{\lambda_{j-1}/2}$$
$$\times\omega(-n'_{j+1},n'_{j+1}+\rho'_{j+1};\gamma_j|y_{j+1})\omega(-n'_n,n'_j+\rho'_j;\gamma_{j+1}|y_j), \tag{20}$$

where

$$\begin{aligned}\rho'_{j+1}&=l_j+\lambda'_j+\tfrac{3}{2}(j+1)-1,\\ \rho'_j&=l_{j+1}+\lambda_{j-1}+\tfrac{3}{2}j-1,\\ \lambda'_j&=2n'_j+l_{j+1}+\lambda_{j-1}.\end{aligned} \tag{21}$$

Since λ_{j+1} is unchanged by operation $(j,j+1)$, we have

$$\begin{aligned}\lambda_{j+1}&=2n_{j+1}+l_{j+1}+\lambda_j\\ &=2n_{j+1}+2n_j+l_{j+1}+l_j+\lambda_{j-1}\\ &=2n'_{j+1}+l_j+\lambda'_j\\ &=2n'_{j+1}+2n'_j+l_{j+1}+l_j+\lambda_{j-1}.\end{aligned} \tag{22}$$

Therefore, the sum $n_{j+1}+n_j$ is also unchanged by operation $(j,j+1)$, that is

$$n_{j+1}+n_j=n'_{j+1}+n'_j. \tag{23}$$

The expansion coefficients $C_{n'_j}$ are derived in Appendix B. It is shown there that the interchange of electrons j and $j+1$ is equivalent to interchanging orbitals l_j and l_{j+1}, as in spherical parts.

The transposition (1,2) needs to be considered separately. With (1,2) we have $y_2\rightarrow 1-y_2$. Only $K(y_2)$ is affected by this operation

$$\begin{aligned}(1,2)K(y_2)&=(1,2)N^{-1/2}(n_2,\rho_2,l_2)y_2^{l_2/2}\\ &\times(1-y_2)^{l_1/2}\omega(-n_2,n_2+\rho_2;\gamma_2|y_2)\\ &=N^{-1/2}(n_2,\rho_2,l_2)(1-y_2)^{l_2/2}y_2^{l_1/2}\\ &\times\omega(-n_2,n_2+\rho_2;\gamma_2|1-y_2)).\end{aligned}$$

Since

$$\rho_2=l_2+l_1+2,\quad \gamma_2=l_2+\tfrac{3}{2},$$

we find

$$\rho_2-\gamma_2+1=l_1+\tfrac{3}{2}=\gamma_1.$$

With the help of Eq. (B3) of Appendix B, we get

$$\begin{aligned}(1,2)K(y_2)&=(-1)^{n_2}\left[\frac{N(n_2,\rho_2,l_1)}{N(n_2,\rho_2,l)}\right]^{1/2}\frac{(\gamma_1)_{n_2}}{(\gamma_2)_{n_2}}\\ &\times y_2^{l_1/2}(1-y_2)^{l_2/2}\\ &\times\omega(-n_2,n_2+\rho_2;\gamma_1|y_2).\end{aligned} \tag{24}$$

Again, the interchange of elections 1 and 2, is equivalent to interchanging orbitals l_1 and l_2.

IV. MATRIX ELEMENTS

Substituting Eq. (11) into Eq. (3), we get

$$\frac{1}{\sqrt{h_f}}\sum_{(r)}(-1)^{p_r}\sum_{\lambda_N\mu_N} y^{[f](r)}_{\lambda_N\mu_N LM_L}(\Omega)\Theta^{[\tilde{f}](\tilde{r})}_{SM_S}(\sigma)$$
$$\times\left\{-\frac{1}{2}\left[\frac{d^2}{dR^2}+\frac{3N-1}{R}\frac{d}{dR}-\frac{\lambda_N(\lambda_N+3N-2)}{R^2}\right]-E\right\}F_{\lambda_N\mu_N}(R)$$
$$-\frac{1}{\sqrt{h_f}}\sum_{(r)}(-1)^{p_r}\sum_{\lambda_N\mu_N}\left[\frac{Z_N(\Omega)}{R}y^{[f](r)}_{\lambda_N\mu_N LM_L}(\Omega)\Theta^{[\tilde{f}](\tilde{r})}_{SM_S}(\sigma)\right]F_{\lambda_N\mu_N}(R)=0\ . \quad (25)$$

Since

$$\frac{1}{\sqrt{h_f}}\sum_{(r)}(-1)^{p_r}y^{[f](r)}_{\lambda_N\mu_N LM_L}(\Omega)\Theta^{[\tilde{f}](\tilde{r})}_{SM_S}(\sigma)$$

with all possible λ_N,μ_N form a complete set, the second term on the left-hand side of Eq. (25) can be rewritten as

$$-\frac{1}{\sqrt{h_f}}\sum_{(r)}(-1)^{p_r}\sum_{\lambda_N\mu_N}\sum_{\lambda'_N\mu'_N}\sum_{(r')}\sum_{(r'')}\frac{1}{h_f}(-1)^{p_{r'}+p_{r''}}\langle[f](r')\lambda'_N\mu'_N SLM_S M_L|Z_N(\Omega)|[f](r)\lambda_N\mu_N SLM_S M_L\rangle$$
$$\times y^{[f](r'')}_{\lambda'_N\mu'_N LM_L}(\Omega)\Theta^{[\tilde{f}](\tilde{r}'')}_{SM_S}(\sigma)\frac{1}{R}F_{\lambda_N\mu_N}(R)\ .$$

By interchanging the dummy indices $\lambda_N,\mu_N,r\leftrightarrow\lambda'_N,\mu'_N,r''$ Eq. (25) is reduced to

$$\left\{-\frac{1}{2}\left[\frac{d^2}{dR^2}+\frac{3N-1}{R}\frac{d}{dR}-\frac{\lambda_N(\lambda_N+3N-2)}{R^2}\right]-E\right\}F_{\lambda_N\mu_N}(R)$$
$$-\frac{1}{R}\sum_{\lambda'_N\mu'_N}\frac{1}{h_f}\sum_{(r')}\sum_{(r'')}(-1)^{p_{r'}+p_{r''}}Z^{[f](r')(r'')}_{\lambda_N\mu_N,\lambda'_N\mu'_N}F_{\lambda'_N\mu'_N}(R)=0\ , \quad (26)$$

where

$$Z^{[f](r')(r'')}_{\lambda_N\mu_N\lambda'_N\mu'_N}=\langle[f](r')\lambda_N\mu_N SLM_S M_L|Z_N(\Omega)|[f](r'')\lambda'_N\mu'_N SLM_S M_L\rangle \quad (27)$$

and

$$\langle\Omega,\sigma|[f](r')\lambda_N\mu_N SLM_S M_L\rangle=y^{[f](r')}_{\lambda_N\mu_N LM_L}(\Omega)\Theta_{SM_S^{[\tilde{f}](\tilde{r}')}}(\sigma)\ . \quad (27')$$

Since the wave function is antisymmetric and the potential V is symmetric with respect to the interchange of any two electrons, $Z^{[f](r')(r'')}_{\lambda_N\mu_N\lambda'_N\mu'_N}$ can be reduced to

$$Z^{[f](r')(r'')}_{\lambda_N\mu_N\lambda'_N\mu'_N}=\left\langle[f](r')\lambda_N\mu_N SLM_S M_L\left|NZ_N\frac{R}{r_N}-\frac{N(N-1)}{2}\frac{R}{r_{12}}\right|[f](r'')\lambda'_N\mu'_N SLM_S M_L\right\rangle\ . \quad (28)$$

In standard representation, the basis functions belonging to different rows of the same representation are orthogonal,

$$\langle\Theta^{[f](r)}_{SM_S}|\Theta^{[f](r'')}_{SM_S}\rangle=\delta(r,r'')\ . \quad (29)$$

Equation (28) can be further reduced to

$$Z^{[f](r')(r'')}_{\lambda_N\mu_N\lambda'_N\mu'_N}=Z^{[f](r')}_{\lambda_N\mu_N\lambda'_N\mu'_N}\delta(r',r'')\ , \quad (30)$$

which says that only diagonal elements of the degenerated representation $[f]$ exist. With these results, Eq. (26) can be rewritten as

$$\left\{-\frac{1}{2}\left[\frac{d^2}{dR^2}+\frac{3N-1}{R}\frac{d}{dR}-\frac{\lambda_N(\lambda_N+3N-2)}{R^2}\right]-E\right\}F_{\lambda_N\mu_N}(R)$$
$$-\frac{1}{R}\sum_{\lambda'_N\mu'_N}\bar{Z}^{[f]}_{\lambda_N\mu_N\lambda'_N\mu'_N}F_{\lambda'_N\mu'_N}(R)=0\ , \quad (31)$$

where

$$\bar{Z}_{\lambda_N\mu_N\lambda'_N\mu'_N}=\frac{1}{h_f}\sum_{(r)}Z^{[f](r)}_{\lambda_N\mu_N\lambda'_N\mu_N}, \quad (32)$$

is the average of the potential matrix elements of repre-

sentation $[f]$. Equation (31) is the coupled differential equation for hyperradial functions. In matrix notation it becomes

$$\left\{-\frac{1}{2}\left[\frac{d^2}{dR^2}+\frac{3N-1}{R}\frac{d}{dR}-\frac{\Lambda}{R^2}\right]-E\right\}F(R) - \frac{\overline{Z}^{[f]}}{R}F(R)=0 , \quad (33)$$

where Λ is a diagonal matrix and $\overline{Z}^{[f]}$ is a square matrix. Equation (33) is similar to that for hydrogenlike ions with the matrix $\overline{Z}^{[f]}$ playing the role of number of nuclear charges, except for hydrogenlike ions; $\overline{Z}^{[f]}$ is diagonal matrix.

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APPENDIX A

By the Racah coupling and recoupling method, Eq. (14) may be written as

$$\begin{aligned}
&(j,j+1)[\cdots[[[\,]^{L_{j-1}}Y_{l_j}(\hat{j})]^{L_j}Y_{l_{j+1}}(\hat{j}+1)]^{L_{j+1}}\cdots Y_{l_N}(\hat{N})]^{L}_{M_L}\\
&\quad=[\cdots[[[\,]^{L_{j-1}}Y_{l_j}(\hat{j}+1)]^{L_j}Y_{l_{j+1}}(\hat{j})]^{L_{j+1}}\cdots Y_{l_N}(\hat{N})]^{L}_{M_L}\\
&\quad=(-1)^{L_{j+1}+l_j-L_j}[\cdots[[Y_{l_j}(\hat{j}+1)[\,]^{L_{j-1}}]^{L_j}Y_{l_{j+1}}(\hat{j})]^{L_{j+1}}\cdots Y_{l_N}(\hat{N})]^{L}_{M_L}\\
&\quad=(-1)^{L_{j-1}+l_j-L_j}\sum_{L_j'}U(l_jL_{j-1}L_{j+1}l_{j+1};L_jL_j')[\cdots[Y_{l_j}(\hat{j}+1)[[\,]^{L_{j-1}}Y_{l_{j+1}}]^{L_j'}]^{L_{j+1}}\cdots Y_{l_N}(\hat{N})]^{L}_{M_L}\\
&\quad=\sum_{L_j'}(-1)^{L_{j-1}+L_j'-L_j-L_{j+1}}U(l_jL_{j-1}L_{j+1}l_{j+1};L_jL_j')\\
&\qquad\times[\cdots[[[\,]^{L_{j-1}}Y_{l_{j+1}}(\hat{j})]^{L_j'}Y_{l_j}(\hat{j}+1)]^{L_{j+1}}\cdots Y_{l_N}(\hat{N})]^{L}_{M_L}\\
&\quad=\sum_{L_j'}C_{L_j'}[\cdots[[[\,]^{L_{j-1}}Y_{l_{j+1}}(\hat{j})]^{L_j'}Y_{l_j}(\hat{j}+1)]^{L_{j+1}}\cdots Y_{l_N}(\hat{N})]^{L}_{M_L} .
\end{aligned} \quad (A1)$$

The recoupling constants $C_{L_j'}$ are

$$C_{L_j'}=(-1)^{L_{j-1}+L_j'-L_j-L_{j+1}}U(l_jL_{j-1}L_{j+1}l_{j+1};L_jL_j') . \quad (A2)$$

APPENDIX B

Equations (19) and (20) are required to be identical for any value of y_{j+1}. By equating Eqs. (19) and (20), eliminating the common factor $y_{j+1}^{l_j/2}$, and setting y_{j+1} equal to zero, we get

$$\begin{aligned}
&N^{-1/2}(n_{j+1},\rho_{j+1}l_{j+1})N^{-1/2}(n_j,\rho_j,l_j)y_j^{l_{j+1}/2}(1-y_j)^{n_j+\lambda_{j-1}/2}\omega(-n_{j+1},n_{j+1}+\rho_{j+1};\gamma_{j+1}|y_j)\\
&\qquad=\sum_{n_j'}C_{n_j'}N^{-1/2}(n_{j+1}',\rho_{j+1}',l_j)N^{-1/2}(n_j',\rho_j',l_{j+1})y_j^{l_{j+1}/2}(1-y_j)^{\lambda_{j-1}/2}\omega(-n_j',n_j'+\rho_j';\gamma_{j+1}|y_j) .
\end{aligned} \quad (B1)$$

Multiply both sides by

$$y_j^{l_{j+1}/2}(1-y_j)^{\lambda_{j-1}/2}\omega(-\bar{n}_j,\bar{n}_j+\rho_j';\gamma_{j+1}|y_j)\tfrac{1}{2}y_j^{1/2}(1-y_j)^{(3j-5)/2}dy_j$$

and integrate. The factor $\frac{1}{2}y_j^{1/2}(1-y_1)^{(3j-5)/2}dy_j$ is the differential surface element of jth electron. Taking advantage of the orthogonality of Jacobi polynomials, we get

$$\begin{aligned}
C_{\bar{n}_j}=&\left\{\frac{N(\bar{n}_{j+1},\bar{\rho}_{j+1}',l_j)N(\bar{n}_j,\rho_j',l_{j+1})}{N(n_{j+1},\rho_{j+1},l_{j+1})N(n_j,\rho_j,l_j)}\right\}^{1/2}N^{-1}(\bar{n}_j,\rho_j',l_{j+1})\\
&\times\tfrac{1}{2}\int_0^1 dy_1 y_1^{\gamma_{j+1}-1}(1-y_j)^{(n_j+\rho_j'-\gamma_{j+1})}\omega(-\bar{n}_j,\bar{n}_j+\rho_j';\gamma_{j+1}|y_j)\omega(-n_{j+1},n_{j+1}+\rho_{j+1};\gamma_{j+1}|y_j) .
\end{aligned} \quad (B2)$$

Making use of the relation [11]

$$\omega(-\bar{n}_j,\bar{n}_j+\rho'_j;\gamma_{j+1}|y_j)=\frac{(-1)^{\bar{n}_j}(\rho'_j-\gamma_{j+1}+1)_{\bar{n}_j}}{(\gamma_{j+1})_{\bar{n}_j}}\omega(-\bar{n}_j,\bar{n}_j+\rho'_j;\rho'_j-\gamma_{j+1}+1|(1-y_j)) \ . \tag{B3}$$

Substituting Eq. (B3) into Eq. (B2), the integral becomes

$$\begin{aligned}
&\frac{(-1)^{\bar{n}_j}(\rho'_j-\gamma_{j+1}+1)_{\bar{n}_j}}{(\gamma_{j+1})_{\bar{n}_j}}\int_0^1 dy_j y_j^{\gamma_{j+1}-1}(1-y_j)^{(n_j+\rho'_j-\gamma_{j+1})} \\
&\times\omega(-\bar{n}_j,\bar{n}_j+\rho'_j;\rho'_j-\gamma_{j+1}+1|1-y_j)\omega(-n_{j+1},n_{j+1}+\rho_{j+1};\gamma_{j+1}|y_j) \\
&=\frac{(-1)^{\bar{n}_j}(\rho'_j-\gamma_{j+1}+1)_{\bar{n}_j}}{(\gamma_{j+1})_{\bar{n}_j}}\sum_{k=0}^{\bar{n}_j}\frac{\overline{(-n_j)}_k(\bar{n}_j+\rho'_j)_k}{k!(\rho'_j-\gamma_{j+1}+1)_k}(\gamma_{j+1})_{n_{j+1}}^{-1} \\
&\times\int_0^\infty dy_j(1-y_j)^{n_j+k+\rho'_j-\rho_{j+1}}\frac{d^{n_{j+1}}}{dy_j^{n_{j+1}}}[y_j^{(n_{j+1}+\gamma_{j+1}-1)}(1-y_j)^{(n_{j+1}+\rho_{j+1}-\gamma_{j+1})}] \ .
\end{aligned}$$

By repeated partial integration we get

$$\begin{aligned}
C_{\bar{n}_j}=&\left\{\frac{N(\bar{n}_{j+1},\bar{\rho}'_{j+1},l_j)N(\bar{n}_j,\rho'_j,l_{j+1})}{N(n_{j+1},\rho_{j+1},l_{j+1})N(n_j,\rho'_j,l_j)}\right\}^{1/2}[N(\bar{n}_j,\rho'_j,l_{j+1})]^{-1} \\
&\times\frac{(-1)^{n_{j+1}+n_j-\bar{n}_j}(\rho'_j-\gamma_{j+1}+1)_{\bar{n}_j}(n_j+\lambda_{j-1}-\lambda_j-\frac{3}{2})!(n_{j+1}+\gamma_{j+1}-1)!}{2(\gamma_{j+1})_{\bar{n}_j}(\gamma_{j+1})_{n_{j+1}}(n_{j+1}+n_j+\lambda_{j-1}-\lambda_j-\frac{3}{2})!} \\
&\times\frac{[n_j+\lambda_{j-1}+\frac{3}{2}(j-1)-1]!}{(n_j+n_{j+1}+l_{j+1}+\lambda_{j-1}+\frac{3}{2}j-1)!}{}_4F_3(A,B,C,D;E,F,G|1) \ ,
\end{aligned} \tag{B4}$$

where ${}^4F_3(A,B,C,D;E,F,G|1)$ is a generalized hypergeometric function with argument $y=1$ and

$$\begin{aligned}
&A=-\bar{n}_j \ , \quad B=\bar{n}_j+\gamma_{j+1}+\lambda_{j-1}+\tfrac{3}{2}(j-1)-1 \ , \quad C=n_j+\lambda j-1-\lambda_j-\tfrac{1}{2} \ , \quad D_{n_j}+\lambda_{j-1}+\tfrac{3}{2}(j-1) \ , \\
&E=\lambda_{j-1}+\tfrac{3}{2}(j-1) \ , \quad F=n_j-n_{j+1}+\lambda_{j-1}-\lambda_j-\tfrac{1}{2} \ , \quad G=n_j+n_{j+1}+l_{j+1}+\lambda_{j+1}+\tfrac{3}{2}j \ .
\end{aligned} \tag{B5}$$

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