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Applications of the unitary-group approach to variational calculations in many-electron atoms

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We present methods for utilizing the unitary-group approach to many-electron systems as a basis for performing variational calculations using Hylleraas coordinates. We discuss the construction of wave functions and evaluation of operator matrix elements for both spin-independent and spin-dependent interaction types.

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I. INTRODUCTION

Until recently, high-precision variational calculations for many-electron atoms have been quite difficult to perform [1–5]. In the cases of helium and lithiumlike ions, Drake and co-workers [6–8] have produced accurate results using trial wave functions, expressed in terms of Hylleraas coordinates, and the technique of multiple basis sets, defined by multiple sets of exponential parameters associated with a single spin function. Their approach constitutes a hybrid of pure Hylleraas and other techniques, such as superposition of correlated configuration methods [7].

The motivation behind the approach of Drake and coworkers is to avoid severe numeric problems associated with the linear dependence that arises in methods utilizing single sets of exponential parameters for each spin function [9]. What is appealing about this approach is that the number of sets of exponential parameters is relatively small, convergence of calculations is improved over previous methods, and a consistent physical interpretation based on core and valence orbitals is obtained.

Our purpose in this work is to present a generalization of the above techniques to many-electron ions in the context of the unitary group approach [10–14] (UGA). In this regard the UGA affords a consistent scheme whereby a substantial portion of the computational effort is made efficient.

In Sec. II, we present the basic theory involving definition of states in the UGA scheme and calculation of matrix elements. We study a many-electron Hamiltonian that includes both spin-independent and spin-dependent interaction terms. In the remaining Secs. III and IV, we deal with these successively.

II. BASIC THEORY

We assume from the outset that many-electron trial wave functions are represented by Weyl-Young tableaux (WYT's), which incorporate orbital functions dependent on the electronic and interelectronic coordinates. Thus, $\mathbf{r}_{0i}$ and $\mathbf{s}_{0i}$ describe the position and spin vectors, respectively, for the ith electron, while $\mathbf{r}_{ij}=\mathbf{r}_{0i}-\mathbf{r}_{0j}$ describes the radial vector between the ith and jth electrons. In general, the orbital part of the electronic wave function is expressed as a linear combination of products of functions of radial coordinates, r_{0i} and r_{ij}, and spherical harmonics, $Y^{[j]}_{l_i m_i}=Y_{l_i m_i}(\theta_j,\phi_j)$, with l and m the angular-momentum eigenvalues.

Many-electron basis states are constructed in the unitary group approach (UGA) by correlating the spin and orbital single-electron wave functions according to the product group of space and spin, $\mathrm{U}(2n)\downarrow\mathrm{U}(n)\times\mathrm{SU}(2)$, where n is the number of orbitals ($n=2l+1$ for pure configurations), and also the unitary group chain $\mathrm{U}(n)\supset\mathrm{U}(n-1)\supset\cdots\supset\mathrm{U}(1)$. The latter point assures that a coupling chain ordering (genealogy) is consistently observed and uniquely labeled; namely, that states of $\mathrm{U}(n')$ involve only those single-electron wave functions whose $m\geq l+1-n'$, when $n'<n$, and they are symmetry adapted to states of intermediate total spin. We note that the construction of states results in a product of conjugate tableaux; we shall suppress the spin tableau henceforth.

Thus, $T_{N,S,\{l,m\}}$ refers to a two-column WYT with $(N+2S)/2$ boxes in the first column and $(N-2S)/2$ boxes in the second column. The labels in the boxes correspond to l and m, and are strictly nondecreasing across the rows and increasing down the columns.

Consideration of the orbital tableau shows that each box carries a set of labels including single-electron wave-function angular-momentum labels l and m; the enumeration index $i=1,\ldots,N$, which states the order in which the box was added to the tableau following the group chain hierarchy; the intermediate spin (the number of unmatched boxes in the first column, divided by 2); and, as required, the $\mathbf{S}_0$ eigenvalue M_s or other spatial symmetry labels. Not all of these labels need be stated explicitly.

The enumeration labels are particularly important in the current context. A tableau $T_{N,S}$ is simply a shorthand notation for a Young operator, corresponding to an irreproducible representation $[N/2-S,2S,n-N/2-S]$ of the symmetric group S_N applied to a set of enumeration labels. The orbital Young operator $Y_R(T)$ acts on the labels in the tableau boxes by performing antisymmetrization (denoted by [ ]) on all enumeration indices in the same column, and symmetrization [denoted by ( )] on all indices in the same row.

Trial wave functions are constructed as linear combinations of orbital functions, represented in part by the orbital WYT multiplied by the conjugate spin tableau. Hence

$$\Psi_{N,S,\{l,m\},\{v,\{\mu_v\},\{a_v\}\}}=\sum_{q=0}^{v}\sum_{\mu_q}C_{q,\mu_q}T_{N,S,(l,m)}(\Phi_{q,\mu_q,\alpha_q}) , \tag{1}$$

where

$$\Phi_{q,\mu_q,\alpha_q}=\prod_{i=0}^{N-1}\prod_{j=i+1}^{N}r_{ij}^{n_{qij}}\exp(-\alpha_{qij}r_{ij}) . \tag{2}$$

The tableau $T(\Phi)$ is defined as

$$T_{N,S,\{l,m\}}(\Phi_{q,\{\mu_q\},\{\alpha_q\}})=Y_R(T)\left\{\prod_{k=1}^{N}Y_{l_k m_k}(\theta_k,\phi_k)\Phi_{q,\{\mu_q\},\{\alpha_q\}}\right\} . \tag{3}$$

It should be noted that Y_R acts only on the coordinates, and not on other indexed quantities. The coefficients C_{q,μ_q} are to be determined through iteration as part of the variational optimization of the energy when diagonalizing the Hamiltonian. Finally, the index v refers to the number of sets of exponential parameters $\{\alpha_q\}$, while $\{\mu_q\}$ refers to the tuple of $N(N-1)/2$ non-negative integer powers n_{qij}.

For example, we consider the case of three p electrons with total spin $S=\frac{1}{2}$. Assigning tableau labels 1, 2, and 3 to the respective m_l values 1, 0, and -1, the WYT $\begin{smallmatrix}1 & 1\\ 2 & \end{smallmatrix}$ is written explicitly, in accordance with (3), in terms of the orbital Young operator Y_R, assuming a single set of parameters, as

$$\begin{smallmatrix}1_1 & 1_2\\ 2_3 & \end{smallmatrix}_{(m,n,\alpha)}=Y_R((12),[13])\{r_1^{m_1}r_2^{m_2}r_3^{m_3}r_{12}^{n_{12}}r_{13}^{n_{13}}r_{23}^{n_{23}}e^{-(\alpha_1r_1+\alpha_2r_2+\alpha_3r_3+\alpha_{12}r_{12}+\alpha_{13}r_{13}+\alpha_{23}r_{23})}Y_{10}^{[3]}Y_{11}^{[2]}Y_{11}^{[1]}\} . \tag{4}$$

The primary labels on the left-side tableau are the m_l related labels, the subscripts are the enumeration indices, and (m,n,α) refer to the entire sets of powers and exponent indices appearing on the right side.

In this case, the Young operator $Y_R(1,2),[1,3])$ performs symmetrization of indices 1 and 2 and antisymmetrization of indices 1 and 3. Using the permutation operators e_{ij}, which juxtapose enumeration indices i and j on the coordinates only, the Young operator in (4) can be expressed as the product of projectors,

$$Y((1,2),[1,3])=C(1-e_{13})(1+e_{12}) , \tag{5}$$

where C is a normalization factor. These projectors are applied in the same order in which boxes are coupled to the intermediate tableau states.

The orbital part is expanded using the Young operator acting on a product of orbital components stated in normal-order form. The form chosen is that suggested by the tableau itself; thus the spherical harmonics are arranged so that the m values are nonincreasing from right to left. The symmetric (antisymmetric) permutations corresponding to the positions of labels in the same row (column) are applied to the normal form. Expanding (4), we obtain

$$\begin{aligned}\begin{smallmatrix}1 & 1\\ 2 & \end{smallmatrix}_{\{m,n,\alpha\}}=C\Phi_{\{m\},\{n\},\{\alpha\}}\{&[1+\rho_{21}^{\mu_{12}}\lambda_{321}^{\kappa_{312}}e^{(A_{12}\delta_{12}+B_{312}\Delta_{312})}]Y_{10}^{[3]}Y_{11}^{[2]}Y_{11}^{[1]}\\ &-\rho_{31}^{\mu_{13}}\lambda_{231}^{\kappa_{213}}e^{(A_{13}\delta_{13}+B_{213}\Delta_{213})}[1+\rho_{23}^{\mu_{12}}\lambda_{123}^{\kappa_{312}}e^{(A_{12}\delta_{32}+B_{312}\Delta_{132})}]Y_{11}^{[3]}Y_{11}^{[2]}Y_{10}^{[1]}\} ,\end{aligned} \tag{6}$$

where we have defined

$$\rho_{ij}=r_i/r_j , \quad \lambda_{ijk}=r_{ij}/r_{ik} , \tag{7a}$$

$$\delta_{ij}=r_i-r_j , \quad \Delta_{ijk}=r_{ij}-r_{ik} , \tag{7b}$$

$$\mu_{ij}=m_i-m_j , \quad \kappa_{ijk}=n_{ij}-n_{ik} , \tag{7c}$$

$$A_{ij}=\alpha_i-\alpha_j , \quad B_{ijk}=\alpha_{ij}-\alpha_{ik} . \tag{7d}$$

From (6) we can deduce the effect of different relative length scales and also different values of exponents. It has been customary [15–18], heretofore, to set $\alpha_{ij}\equiv 0$ for $i>0$, hence $B_{ijk}=0$ in all cases. In a single-basis-set approach, one finds that $A_{12}=0$. Finally, if we consider r_1 and r_2 to be nearly equal (core orbitals) while r_3 to be much larger (valence orbital), then it follows that the second product of spherical harmonics predominates over the first in determining the wave function; physically, this can be interpreted that the valence p electron couples to a triplet p^2P state. For each such set of relative distances r_i, a different set of α_{ij} is assumed, with a different physical interpretation for each. It is precisely this type of analysis that is used to justify the multiple-basis-set approach of Drake and co-workers [6–8]. Thus, the labeling of the WYT simultaneously accounts for the correlation of the spins, the genealogy of the orbital functions, and the permutation symmetry with respect to interchange of particle indices.

Next comes the evaluation of operator matrix elements. There are two issues involved: first, the effect of an operator on the order of spin coupling, and second, the evaluation of the orbital integrals.

The representation of operators in terms of the U(n) generators, E_{ij} and their products, has been dealt with by various authors [10–14]. Those results, however, pertain only to the evaluation of the matrix elements of the generators, and they do not address the issue of orbital integrals. We note that the generators play two roles. The first is they act in the spin space to decouple and recouple an electron in the spin chain; the second is they act as permutations e_{ij} in the orbital space.

We note that it is often assumed that the orbital integrals that arise reduce to one- or two-electron integrals; the integrations over remaining orbitals are obviated by orthonormality considerations. While this is so when the tableau basis is adapted to particular symmetries (for example, *LS* adaptation), it is not always the case. For an N-electron system, there arise N-electron integrals in general. As seen from (3), matrix elements that arise in the tableau basis require the evaluation of a number of integrals, the actual number being defined by the number of permutations implied by the tableau labeling. What is sought, therefore, are efficient methods for evaluating these integrals.

Recently, Fromm and Hill [19] developed a method that uses radial and angular generating functions to bypass the need to perform repeated explicit integrations over all spatial variables. Although their results are restricted to three-electron cases (and, in limiting cases, two-electron integrals and two-center two-electron molecular integrals), current work by the present authors [20] suggests that their approach can be extended to four-electron integrals, and perhaps beyond.

The method of Fromm and Hill starts with the use of variational trial wave functions of the form

$$\psi'=\psi_0+\sum_{i<j=2}^{N}|\mathbf{r}_i-\mathbf{r}_j|\psi_{ij}\ , \tag{8}$$

where ψ_0 and ψ_{ij} are finite sums of products of single-particle functions. For atoms the appropriate choice is Slater-type orbitals, which simplify problems associated with the electron-nucleus cusp behavior [21].

Fromm and Hill obtain the analytic form for the integral of the generating function,

$$I(\{\alpha_{ij}\})=\int\left[\prod_{i<j=1}^{N}r_{ij}^{-1}\right]\times\exp\left[-\sum_{i<j=1}^{N}\alpha_{ij}r_{ij}\right]\prod_{i=1}^{N}(d^3\mathbf{r}_{0i})\ , \tag{9}$$

where the α_{ij} are the (physically relevant) parameters to be determined. Using $I(\{\alpha_{ij}\})$, one may express integrals of the form

$$J(\{n_{ij},\alpha_{ij}\})=\int\left[\prod_{i<j=1}^{N}r_{ij}^{n_{ij}-1}\right]\times\exp\left[-\sum_{i<j=1}^{N}\alpha_{ij}r_{ij}\right]\prod_{i=1}^{N}(d^3\mathbf{r}_{0i})=\prod_{i<j=1}^{N}\left[-\frac{\partial}{\partial\alpha_{ij}}\right]^{n_{ij}}I(\{\alpha\})\ , \tag{10}$$

where, at the last step, differentiation is used to obtain the more complicated integral representing, say, an operator matrix element.

One important feature of the Fromm-Hill approach is that integration is to be replaced by differentiation over certain variables that are determined by the physics of the problem.

The analytic form of the Fromm-Hill three-electron generating integral is defined as

$$I(\{\alpha\})=\frac{16\pi^3}{\sigma}\left[\sum_{j=1}^{3}u(\beta_0^{(0)}\beta_0^{(j)})+\sum_{j=0}^{3}\sum_{k=0}^{3}v\left[\frac{\gamma_k^{(j)}}{\sigma}\right]\right]\ , \tag{11}$$

where the functions u and v are defined as

$$u(z)=\mathrm{Li}_2(z)-\mathrm{Li}_2\left[\frac{1}{z}\right]\ , \tag{12a}$$

$$v(z)=\tfrac{1}{2}\mathrm{Li}_2\left[\frac{1-z}{2}\right]-\tfrac{1}{2}\mathrm{Li}_2\left[\frac{1+z}{2}\right]-\tfrac{1}{4}\ln^2\left[\frac{1-z}{2}\right]+\tfrac{1}{4}\ln^2\left[\frac{1+z}{2}\right]\ , \tag{12b}$$

and where $\mathrm{Li}_2(z)$ is the dilogarithm function [26,27] defined as

$$\mathrm{Li}_2(z)=-\int_0^z\frac{\ln(1-\zeta)}{\zeta}d\zeta\ . \tag{13}$$

The $\beta_k^{(j)}$ are defined as

$$\beta_k^{(j)}=\frac{\sigma-\gamma_k^{(j)}}{\sigma+\gamma_k^{(j)}}=\frac{1-\dfrac{\gamma_k^{(j)}}{\sigma}}{1+\dfrac{\gamma_k^{(j)}}{\sigma}}\ . \tag{14}$$

The quantities σ^2 and $\gamma_k^{(j)}$ are homogeneous sixth- and third-degree polynomials, respectively, in the α's. We refer the reader to Sec. II A of Ref. [19] for complete definitions. For purposes of comparison, in the case of two-electron systems, the integrals reduce to

$$I(\alpha_{01},\alpha_{02},\alpha_{12})=\frac{16\pi^2}{(\alpha_{01}+\alpha_{02})(\alpha_{01}+\alpha_{12})(\alpha_{02}+\alpha_{12})}\ . \tag{15}$$

Differentiation of expressions (11) or (15) can be performed efficiently by computer. A caveat is in order, however. Owing to the structure of (11), individual terms may possess singularities; hence it is necessary to have an understanding of the behavior of the generating functions in order to avoid problems arising from this. Notwithstanding, since numerical differentiation is more accurate than integration, it is expected that results obtained for integrals, such as (10), using this approach will be easier to obtain and more numerically reliable than with other approaches.

The increase in algebraic complexity in going from two- to three-electron generating integrals suggests that higher-order cases may be intractable with respect to analytic solution. Preliminary studies [20] indicate that solution of the four-electron integrals involve elliptic and hyperelliptic functions [25] as well as the generalized polylogarithm [26,27]. Although analytic solutions are considered highly desirable, however, they are not required for the sake of accurate computations. If the generating integrals can be computed numerically, then differentiation in the manner prescribed above can still be performed.

Following Fromm and Hill (cf. Sec. III G of Ref. [19]), the treatment of more general N-electron integrals that contain factors involving spherical harmonics, such as

$$r_{0j}^{l_j} Y_{l_j m_j}(\theta_{0j},\phi_{0j}) , \tag{16}$$

can be reduced to the form (9) by averaging over orientations of the coordinate system. Such cases arise in this treatment owing to the inclusion of spherical harmonics in the basic definition of states. By contrast, calculations of ground-state energies involving S states only [8] do not contain this difficulty.

Using the addition relations for spherical harmonics, we find

$$\begin{aligned} &Y_{l'm'}(\theta,\phi)Y_{lm}(\theta,\phi) \\ &\quad=\sum_{L,M}\left[\frac{(2l'+1)(2l+1)(2L+1)}{4\pi}\right]^{1/2} \\ &\qquad\times\begin{pmatrix} l' & l & L \\ m' & m & M\end{pmatrix}\begin{pmatrix} l' & l & L \\ 0 & 0 & 0\end{pmatrix} Y_{LM}(\theta,\phi) \end{aligned} \tag{17}$$

for each bra and ket Y_{lm} pair. Choosing, say, $\mathbf{r}_1$ as the z axis and applying the rotation operators $D^{(1)}(\alpha,\beta,\gamma)$, we can express the angular dependence of all $Y_{L,M}$'s in terms of relative direction θ_{ij},ϕ_{ij} alone. Recently, Kent, Schlesinger, and Drake [22–24] developed methods for dealing with many-electron operator matrix elements using L adaption. In this approach, they reduced the products of Y_{lm}'s to a finite sum of terms involving products of 6-j and 12-j symbols.

In order to illustrate the above approach in the remainder of the paper, we shall consider the Hamiltonian

$$H=H_{\mathrm{CF}}+H_{e\text{-}e}+H_{\mathrm{SO}}+H_{\mathrm{SS}} \tag{18}$$

In the following sections we discuss, first, spin-independent terms, and second, spin-dependent terms.

III. SPIN-INDEPENDENT INTERACTIONS

For the spin-independent terms in the Hamiltonian, the tableaux are eigenstates of total spin S. Including nuclear attraction and electronic repulsion terms, the Hamiltonian can be written symbolically as

$$\begin{aligned} H_{\mathrm{SI}}=\sum_{i=1}^{N}&\left\{-\frac{1}{2}\left[\frac{\partial^2}{\partial r_{0i}^2}+\frac{2}{r_{0i}}\frac{\partial}{\partial r_{0i}}+\frac{L_i^2}{r_{0i}^2}-\frac{2Z}{r_{0i}}\right]\right\} \\ &-\sum_{i=1}^{N-1}\sum_{j=2}^{N}\left\{\frac{\partial^2}{\partial r_{ij}^2}+\frac{2}{r_{ij}}\frac{\partial}{\partial r_{ij}}+\frac{(r_{0i}^2+r_{ij}^2-r_{0j}^2)}{r_{0i}r_{ij}}\frac{\partial^2}{\partial r_{0i}\partial r_{ij}}\right. \\ &\left.\qquad-2(\boldsymbol{\nabla}_i^Y\cdot\mathbf{r}_{0j})\frac{1}{r_{ij}}\frac{\partial}{\partial r_{ij}}+\frac{1}{r_{ij}}\right\} , \end{aligned} \tag{19}$$

where the angular-momentum operator, in the UGA scheme, is expressed as the product of two first-rank tensors and has the form [10,14]

$$L^2=-L_1^1L_{-1}^1-L_{-1}^1L_1^1+L_0^1L_0^1 , \tag{20}$$

with

$$L_\lambda^1=\sum_{i,j=1}^{n}\langle l_i\|L\|l_i\rangle V_\lambda^1(i,j) , \quad \lambda=-1,0,1 \tag{21}$$

where $\langle l\|L\|l\rangle=[l(l+1)(2l+1)/3]^{1/2}$. The unit irreducible tensor $V_\lambda^q(j,k)$ is expressed

$$V_\lambda^q(j,k)=\sqrt{2q+1}(-1)^{l_j'-m_j'}\begin{pmatrix} l_j' & q & l_k \\ -m_j' & \lambda & m_k\end{pmatrix}E_{jk} . \tag{22}$$

The L operators have the effect that, when they are applied to a given tableau state, they change the value of m_l. Since, in general, this produces a state with nonstandard ordering of orbital labels, this state is expressed as a linear combination of other tableaux, that is, different spin-coupling chains. The utility of the generators is that their matrix elements account for the reordering of the spin-coupling chain.

The vector operator $\mathbf{r}_i$ and gradient operator $\boldsymbol{\nabla}_i^Y$ act only on the spherical harmonics that arise in the expression of the ith electron's wave function when using the central-field approximation. These operators are expressible in the forms

$$\mathbf{r}_i=r_i\sum_{m,q}(-1)^{l_i-m_i}\left\{-l_i\sqrt{l_i+1}\begin{pmatrix} l_i & 1 & l_j' \\ -m_i & q & m_j'\end{pmatrix}\delta_{l_j',l_i+1}+(l_i+1)\sqrt{l_i}\begin{pmatrix} l_i & 1 & l_j' \\ -m_i & q & m_j'\end{pmatrix}\delta_{l_j',l_i-1}\right\}E_{ij}\mathbf{e}_{\mathbf{q}} \tag{23}$$

and

$$\boldsymbol{\nabla}_i=\frac{1}{r_i}\sum_{m,q}(-1)^{l_i-m_i}\left\{l_i\sqrt{l_i+1}\begin{pmatrix} l_i & 1 & l_j' \\ -m_i & q & m_j'\end{pmatrix}\delta_{l_j',l_i+1}+(l_i+1)\sqrt{l_i}\begin{pmatrix} l_i & 1 & l_j' \\ -m_i & q & m_j'\end{pmatrix}\delta_{l_j',l_i-1}\right\}E_{ij}\mathbf{e}_q , \tag{24}$$

respectively, where $\mathbf{e}_q$ ($q=1,0,-1$) are R(3) unit vectors.

Drake and Schlesinger [10] showed that two-body operators, such as the interelectron potential $g=1/r_{ij}$, can be expressed in the UGA scheme in terms of linear combinations of two U(n) generator products, namely,

$$\begin{aligned} \mathbf{g}=&\langle l_i'm_i'l_j'm_j'|g|l_km_kl_lm_l\rangle E_{ik}E_{jl} \\ &+\langle l_j'm_j'l_i'm_i'|g|l_km_kl_lm_l\rangle E_{il}E_{jk} , \end{aligned} \tag{25}$$

where, for example,

$$\langle ij|\mathbf{g}|kl\rangle=\int Y^{*}_{l_i'm_i'}Y^{*}_{l_j'm_j'}gY_{l_km_k}Y_{l_lm_l}\times\Phi_{q,\{\mu_q'\},\{\alpha_q'\}}\Phi_{q,\{\mu_q\},\{\alpha_q\}}\times\prod_{p\neq i,j,k,l}Y_{l_p'm_p'}Y_{l_pm_p}\prod_{p=1}^{N}d^3\mathbf{r}_p\ . \tag{26}$$

These operators act on two electrons, whose states are labeled i and j, which are transformed to states k and l. Since these respective states may occupy different spin-chain positions in the tableau states, the role of the generator-product matrix elements is to represent the overlap contributions from the spin recouplings in the respective parent tableaux.

Similarly, matrix elements of operators like the gradient, usually in combination (scalar or tensor product) with another operator [22] (e.g., $\nabla_i^Y\cdot\mathbf{r}_j$ or $\nabla_i^Y\cdot\nabla_j^Y$), as well as $r_{ij}{}^t$, can produce changes in the relative ordering of single-particle states in given tableaux. These cases can also be represented as operators in the UGA scheme, as for the g_{ij} operator above. Such operators act only on the radial parts of wave functions; however, they produce configuration mixing and require the use of mixed-configuration representations of tableaux [14], therefore.

All operator matrix elements separate into spin and orbital parts, the first handled by U(n) generator matrix elements and the second by means of the Fromm-Hill techniques. One important aspect of these calculations is that only one or two terms of the linear combination (3) induced by the Young operator survive, owing to orthogonality considerations.

IV. SPIN-DEPENDENT INTERACTIONS

Spin-dependent terms in the Hamiltonian break the S symmetry; nevertheless, the UGA is still a powerful scheme for evaluating matrix elements. For light atoms, perturbative calculations result in energy shifts due to spin-orbit and spin-spin interactions, while in heavier atoms, states can be defined which are linear combinations of spin-adapted tableaux.

In the case of spin-orbit type interactions, we write

$$\sum_{i,j=1}^{N}\xi_{ij}\mathbf{L}_i\cdot\mathbf{S}_j=(-1)^{S_N+S_N'-M_N'+S_{N-1}+1/2}\begin{Bmatrix}S_N & \frac{1}{2} & S_{N+1}\\ \frac{1}{2} & S_N' & 1\end{Bmatrix}^{-1}\times\sum_{i,j=1}^{N}\xi_{ij}\left[\frac{l_i(l_i+1)(2l_i+1)}{6}\right]^{1/2}\sum_{\lambda=-1}^{1}(-1)^{l_i'-m_i'+\lambda}\begin{bmatrix}l_i' & 1 & l_j\\ -m_i' & -\lambda & m_j\end{bmatrix}\begin{bmatrix}S_N' & 1 & S_N\\ -M_N' & \lambda & M_N\end{bmatrix}\times(E_{i,N+1}E_{N+1,j}+\tfrac{1}{2}E_{ij})\ , \tag{27}$$

where $\xi_{ij}=(\alpha^2)\xi_{0ij}/r_{ij}^3$. The spin-own-orbit interaction includes all terms for which $i=j$; remaining terms comprise the spin-other-orbit interactions.

Both spin-orbit operators involve matrix elements between states of either the same or different total spin, as well as possible configuration mixing. Matrix elements calculated using UGA require the embedding of bra and ket tableau states in a higher-order group U($n+1$) in order to utilize the generators $E_{i,N+1}$ and $E_{N+1,i}$, which are not defined in U(n). In the case of Weyl-Young-tableau representations of states, this is equivalent to adding one extra box labeled $n+1$ to the bra and ket tableaux [10,28], so that the total spin of the modified states is $S_{N+1}=(S_N'+S_N)/2$.

The spin-spin interactions are represented as the scalar product of two second-rank tensors, $R_2(r_i,r_j)$ and $S_2(s_i,s_j)$. The interaction is expressed as

$$H_{\mathrm{SS}}(i,j)=\frac{\alpha^2}{r_{ij}^3}[\mathbf{s}_i\cdot\mathbf{s}_j-3(\mathbf{s}_i\cdot\mathbf{r}_{ij})(\mathbf{s}_j\cdot\mathbf{r}_{ij})/r_{ij}^2]\ . \tag{28}$$

The first term is the zeroth-order component of the second-rank spin tensor, which in turn is proportional to the scalar product of rank-1 spin tensors; this term yields only matrix elements diagonal in total spin [U(n) irreducible representations]. These can be calculated easily in terms of diagonal (number) generators [2], E_{ii}.

The remaining term involves the other components of the tensor product. In the UGA scheme, Kent, Schlesinger, and Shavitt [29,30] determined that the sum of spin tensors, up to rank 2, can be expressed as a sum of terms involving products of four generators,

$$\sum_{K=0}^{2}(2K+1)\|\mathbf{S}_K(ij)\|_{n+2}=E_{i,n+1}E_{n+1,i}E_{j,n+2}E_{n+2,j}+\tfrac{1}{2}E_{ii}E_{n+1,n+1}E_{j,n+2}E_{n+2,j}+\tfrac{1}{2}E_{i,n+1}E_{n+1,i}E_{jj}E_{n+2,n+2}+\tfrac{1}{4}E_{ii}E_{jj}E_{n+1,n+1}E_{n+2,n+2}\ . \tag{29}$$

The reduced-matrix elements of $\mathbf{S}_2$ are expressed symbolically as

$$\langle T'\|S_2(i,j)\|T\rangle=(-1)^{S_{N+2}'+S_{N+1}+1/2}\sqrt{15[S_{N+1}][S_{N+1}'][S_{N+2}][S_{N+2}']}\times\begin{Bmatrix}S_{N+1} & \frac{1}{2} & S_{N+2}\\ \frac{1}{2} & S_{N+1} & 1\end{Bmatrix}\begin{Bmatrix}S_{N+1} & 1 & S_{N+1}\\ S_N' & 2 & S_N\\ \frac{1}{2} & 1 & \frac{1}{2}\end{Bmatrix}D^{(2)}_{N+2,1}D^{(4)}_{N+1,2}\prod_{t=j+1}^{N}B^{(4)}_{t,2}C^{(4)}_{j,2}\prod_{t=i+1}^{j-1}B^{(2)}_{t,1}C^{(2)}_{i,1}\ , \tag{30}$$

where $[S]=2S+1$. The $D^{(Q)}$, $B^{(Q)}$, and $C^{(Q)}$ quantities above represent various Racah (6-j) symbols ($Q=2$) and Fano (9-j) coefficients ($Q=4$), together with multiplying factors, which derive from intermediate two-electron and four-electron couplings; all factors are defined in Ref. [30].

The remaining part of the scalar product, $R_2(r_i,r_j)$, is expressed as

$$R_{2m}(r_i,r_j)=\left[\frac{8\pi}{5}\right]^{1/2}\frac{\alpha^2}{r_{ij}^3}Y_{2m}(\hat{\mathbf{r}}_{ij})\ , \tag{31}$$

which can be evaluated using

$$\langle l_i'm_i']Y_{2m}|l_jm_j\rangle=\sqrt{[l_j'][l_j]}(-1)^{l_i'-m_i'+l_j}\times\begin{bmatrix} l_i' & 2 & l_j \\ -m_i' & m & m_j \end{bmatrix}\begin{bmatrix} l_i' & 2 & l_j \\ 0 & 0 & 0 \end{bmatrix}\ . \tag{32}$$

As in the case of spin-orbit interaction, spin-spin operator matrix elements calculated using UGA also involve mixing states of differing total spin. Spins of the respective bra and ket irreducible representation may differ by 0, 1, or 2. In order to utilize the generators to express the spin tensors, however, one requires the embedding of each U(n) state in either U($n+1$) or U($n+2$), equivalent to adding one or two boxes to each bra and ket tableau. From the expression for matrix elements of $\mathbf{Y}_2$, it is also clear that the spin-spin interaction connects states in which $l_i'-l_j$ is zero or an even integer. Thus, H_{SS} is also, in general, a configuration-mixing interaction. As in the cases of spin-independent matrix elements, only one or two terms of the linear combination (3) induced by the Young operator survive, owing to orthogonality considerations.

V. CONCLUSION

We have presented an approach whereby techniques for utilizing Hylleraas coordinates and multiple basis sets in the construction of basis states and operators and the evaluation of matrix elements are formulated in the context of the unitary-group approach. Heretofore, unitary-group techniques have been found to be particularly useful in configuration-interaction calculations [31]. More recently, interest has developed in using the approach in nuclear magnetic resonance studies [32–34].

It is shown that utilizing these powerful techniques facilitates the extension of methods by Drake and coworkers [6–8] from cases of two or three electrons to the more challenging cases of many-electron systems. What is presently required is the explicit extension of the methods by Fromm and Hill in evaluating radial generating integrals to four-electron systems and beyond. We are presently attempting such an extension.

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