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Modified configuration-interaction method

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A detailed presentation of the modified configuration-interaction (CI) method [S. P. Goldman, Phys. Rev. Lett. **73**, 2541 (1994)] is given. The standard two-electron test case is used to introduce the concepts, as well as to show a sharp increase in the convergence of the calculations. Space-ordered radial coordinates and generalized angular functions involving the addition of large numbers of spherical harmonics are used. As a result, accuracies that exceed those of the usual CI method by several orders of magnitude are obtained with small basis sets. For example, in the case of helium, energies are obtained with relative errors of 2.6×10^{-9}, 1.4×10^{-8}, and 2.0×10^{-10} for the $1\,^1S$, $2\,^1S$, and $2\,^3S$ states with 420, 276, and 264 two-electron basis functions, respectively. A detailed discussion of the calculation of matrix elements and angular coefficients and of the extension to the many-electron case is presented.

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I. INTRODUCTION

The standard configuration-interaction (CI) method provides a straightforward technique to perform calculations on systems involving several interacting electrons in terms of products of one-electron functions. At the heart of the CI method is the expansion of the inter-electron potential in terms of single-electron spherical coordinates. Consider for example, the case of the helium Hamiltonian

$$H=-\tfrac{1}{2}\nabla^2_{\mathbf{r}_1}-\tfrac{1}{2}\nabla^2_{\mathbf{r}_2}-\frac{Z}{r_1}-\frac{Z}{r_2}+\frac{1}{r_{12}}\,. \quad (1)$$

For the purpose of CI calculations the electron-electron potential is expanded as

$$\frac{1}{r_{12}}=\sum_{\lambda=0}^{\infty}\frac{4\pi}{2\lambda+1}\frac{r_<^{\lambda}}{r_>^{\lambda+1}}\sum_{q=-l}^{l}Y^*_{\lambda q}(\hat{\mathbf{r}}_1)Y_{\lambda q}(\hat{\mathbf{r}}_2)\,. \quad (2)$$

It is this expansion that characterizes the CI method, as it allows one to approximate the wave function in terms of symmetrized or antisymmetrized products of one-electron (hydrogenic) basis functions. In the case of two electrons, the two-electron basis functions for a state with total angular momentum L will be of the form

$$\varphi_i^{\mathrm{CI}}=f_{1,i}(r_1)f_{2,i}(r_2)\;\Lambda^{LM}_{l_{1i}l_{2i}}(\hat{\mathbf{r}}_1,\hat{\mathbf{r}}_2)\pm(\mathbf{r}_1\rightleftharpoons\mathbf{r}_2), \quad (3)$$

where

$$\Lambda^{LM}_{l_{1i}l_{2i}}(\hat{\mathbf{r}}_1,\hat{\mathbf{r}}_2)=\sum_{m_1,m_2}\langle l_{1i}m_1l_{2i}m_2|LM\rangle \times Y_{l_{1i},m_1}(\hat{\mathbf{r}}_1)\;Y_{l_{2i},m_2}(\hat{\mathbf{r}}_2) \quad (4)$$

and the second term in Eq. (3) is obtained from the first term by interchanging $\mathbf{r}_1$ and $\mathbf{r}_2$.

The main difference between different approaches to perform CI calculations is the choice of one-electron radial functions. Calculations have been done using, for example, Slater-type functions [1,2], piecewise polynomials [3], and B splines [4]. A typical CI basis set using radial Slater-type functions is given by

$$\varphi_i^{\mathrm{Slater}}=e^{-\alpha_i r_1-\beta_i r_2}\,r_1^{a_i}r_2^{b_i}\;\Lambda^{LM}_{l_{1i}l_{2i}}(\hat{\mathbf{r}}_1,\hat{\mathbf{r}}_2)\pm(\mathbf{r}_1\rightleftharpoons\mathbf{r}_2), \quad (5)$$

where α_i and β_i are arbitrary nonlinear parameters.

The quality of the results in a CI calculation will depend then on the number of radial functions in the basis set as well as the number of different angular configurations included. In the limit in which the number of both is infinite, the result will be exact. The task at hand is to be able to obtain as accurate a calculation as possible with as few basis functions as possible. In the case of Slater basis sets (5), for example, one searches for convergence of the variational energy eigenvalue (or any other property being calculated) as the number of powers of r_1 and r_2 is increased and as the number of values of the one-electron angular-momentum quantum numbers l_{1i} and l_{2i} is increased. It is this angular mixing that will take care of the different angular terms in the expansion of r_{12} and will account for correlation effects. The role of the exponential parameters is to optimize the calculation for a specific set of radial powers and spherical harmonics. The CI convergence of the variational energy eigenvalues is, however, very poor as both the number of radial powers and the number of spherical harmonics are increased [1–5].

The radial convergence is slow independently of the type of radial functions used. In Table I we present results for radial convergence using Slater basis functions and natural orbitals (piecewise polynomials). The results for Slater functions are obtained as the number of powers of the radial coordinates in the basis set is increased. In the case of natural orbitals (NO's), the size of the basis set is kept fixed at 666 basis functions, with the number of NO's derived from this basis set being increased [3]. The results isolate the radial behavior for the helium ground-state case by restricting the trial functions to the case $l_1=l_2=0$. The convergence is very slow, and because of the advent of numerical dependency

1050-2947/95/52(5)/3718(12)/$06.00 52

TABLE I. Radial convergence of the ground-state *s* configuration for a nuclear charge $Z=2$ using Slater, natural orbital, and MCI radial functions. E is the variational eigenvalue in a.u., N is the number of two-electron radial basis functions used in each case, and N_o is the number of natural orbitals used, each built with N basis functions.

Slater		Natural orbital			MCI	
N	E	N_o	N	E	N	E
2	-2.848	1	666	-2.861531102		
6	-2.8780	2	666	-2.877925513		
12	-2.8789	3	666	-2.878844046	6	-2.8788
20	-2.87899	4	666	-2.878980274		
30	-2.879016	5	666	-2.879012045	7	-2.879014
42	-2.8790237	6	666	-2.879021844		
56	-2.8790264	7	666	-2.879025502		
		8	666	-2.87902707		
		12	666	-2.879028537	11	-2.87902861
		18	666	-2.879028735		
		24	666	-2.879028756		-2.879028752
					20	-2.87902876718
					30	-2.879028767314
					45	-2.8790287673190
					54	-2.879028767319173
					73	-2.8790287673192123
					86	-2.879028767319214160
					100	-2.879028767319214320
					125	-2.879028767319214388
					extrapolated	-2.87902876731921441

problems in the matrix diagonalizations, the basis set size cannot be increased and better values cannot be obtained. In the Slater case, if N_r denotes the number of two-electron radial functions, the energy convergence is $\delta E/E \approx N_r^{-3}$. In the case of natural orbitals, there is an improvement with $\delta E/E \approx N_r^{-5}$, although a (constant) very large number of basis functions is necessary (a comparison with the convergence of the *best* NO value for different *basis set sizes* would be more appropriate).

TABLE II. Angular convergence of the ground-state energy E of helium using Slater, natural orbital, and MCI radial functions. E is the variational eigenvalue in a.u. and $l_{\max}$ refers to the largest angular momentum used by the Slater and MCI methods and the largest generalized angular function used by the MCI method.

l_{max}	Slater	Natural orbital	MCI
1	-2.900516	-2.900516	-2.903320776
2	-2.902767	-2.902767	-2.903687982
3	-2.903321	-2.903321	-2.903718403
4	-2.903518	-2.903518	-2.903722701
5	-2.903606	-2.903600	-2.903723671
6	-2.903650	-2.903644	-2.903724070
8	-2.903689	-2.903682	-2.903724287
10		-2.903697	-2.903724340
11		-2.903701	-2.903724345
13			-2.903724362
16			-2.903724369

The angular convergence is also very slow with $\delta E/E \approx N_l^{-3}$, where N_l is the number of spherical harmonics used. This convergence is independent of the radial functions used. One of the main reasons for the need of a good radial representation is the ability to obtain, for each angular contribution, good accuracy with a small number of radial functions in order to allow one to include in the calculation a large selection of spherical harmonics. In Table II the angular convergence is given for both the Slater and natural-orbitals representations as a function of the number of spherical harmonics.

We have then in the CI method a procedure to calculate atomic (and molecular) states that can be implemented very easily. The reason is that the functions involved are simple products of orthonormal one-electron functions. Therefore the matrix elements of functions or operators that depend on a single radial coordinate result in one-dimensional integrations, while matrix elements of functions involving $r_<$ and $r_>$ are just two dimensional. Not only is the implementation simple, but it also yields a clear picture of the nature of the solutions in terms of superpositions of different *types* of one-electron functions. The price we pay is a poor convergence that does not allow one to achieve very accurate results. In the following sections we will describe ways of improving the radial and angular convergences of the CI method.

II. RADIAL VARIABLES

A. Angular and radial matrix elements

In the CI method, the radial matrix elements are easily calculated given that the wave function is a simple product of one-electron functions, written in terms of the radial coordinates r_1 and r_2. The poor radial convergence is due to the fact that these "smooth" radial functions of r_1 and r_2 cannot easily represent the cusp present in the two-electron (or many-electron) wave functions. This cusp is a consequence of the Coulomb interaction between the two electrons. It appears because the repulsion potential r_{12}^{-1} has discontinuous derivatives at $r_1 = r_2$ or in the expansion (2) at $r_< = r_>$. Notice that a similar cusp is present, for each electron, at the origin if a point nucleus is used. This hydrogenic cusp at the origin is masked by the use of radial coordinates, but would be apparent if Cartesian coordinates were used. This idiosyncrasy of the wave function at $r_< = r_>$ can be incorporated in a basis set if we allow the basis functions to depend explicitly on $r_<$ and $r_>$. The use of $r_<$ and $r_>$ in the context of CI calculations has been discussed previously by Schwartz in 1962 [1] and later on in several works on the CI method [2,6,7].

In this work, we start by extending the Slater functions to the basis set [8]:

$$\phi_i = e^{-\alpha_i r_1 - \beta_i r_2 - \sigma_i r_< - \tau_i r_>} r_1^{a_i} r_2^{b_i} r_<^{s_i} r_>^{t_i} \Lambda_{l_{1i} l_{2i}}^{LM}(\hat{\mathbf{r}}_1, \hat{\mathbf{r}}_2) \pm (\mathbf{r}_1 \rightleftharpoons \mathbf{r}_2) \tag{6}$$

that includes the variables

$$r_< = \min(r_1, r_2) \quad \text{and} \quad r_> = \max(r_1, r_2), \tag{7}$$

which have discontinuous derivatives at $r_1 = r_2$ and will be able to represent the radial cusp much more efficiently. These variables are symmetric functions of r_1 and r_2:

$$r_<(r_1, r_2) = r_<(r_2, r_1), r_>(r_1, r_2) = r_>(r_2, r_1). \tag{8}$$

Notice that (6) is not the most general Slater-type basis set involving $r_<$ and $r_>$. For example, considering that $r_< / r_> \leq 1$, the basis functions used in (6) can be extended to

$$\theta_i = \eta_i \, \Lambda_{l_{1i} l_{2i}}^{LM}(\hat{\mathbf{r}}_1, \hat{\mathbf{r}}_2) \pm (\mathbf{r}_1 \rightleftharpoons \mathbf{r}_2), \tag{9}$$

with the new radial functions

$$\eta_i = e^{-\alpha_i r_1 - \beta_i r_2 - \sigma_i r_< - \tau_i r_> - \omega_i r_< / r_>} r_1^{a_i} r_2^{b_i} r_<^{s_i} r_>^{t_i}. \tag{10}$$

The family of basis functions we need, however, is much smaller: there is no need in (9) for an explicit dependence on r_1 and r_2 at all (except for a simple dependence in the case of triplet states). The reason is that the Hamiltonian (1) can be rewritten without using $\mathbf{r}_1$ or $\mathbf{r}_2$ at all as

$$H = -\tfrac{1}{2}\nabla_{\mathbf{r}_<}^2 - \tfrac{1}{2}\nabla_{\mathbf{r}_>}^2 - \frac{Z}{r_<} - \frac{Z}{r_>} + \sum_{\lambda, m} \frac{4\pi}{2\lambda + 1} \frac{r_<^{\lambda}}{r_>^{\lambda+1}} Y_{\lambda m}^{*}(\hat{\mathbf{r}}_<) Y_{\lambda m}(\hat{\mathbf{r}}_>) , \tag{11}$$

where we used the fact that for a symmetric function $f(\mathbf{r}_1, \mathbf{r}_2) = f(\mathbf{r}_2, \mathbf{r}_1)$ is $f(\mathbf{r}_1, \mathbf{r}_2) = f(\mathbf{r}_<, \mathbf{r}_>)$. For symmetric radial functions we need then only the radially symmetric basis set

$$\tilde{\varphi}_i = \tilde{\xi}_i(r_<, r_>) \, \Lambda_{l_{1i} l_{2i}}^{LM}(\hat{\mathbf{r}}_<, \hat{\mathbf{r}}_>) , \tag{12}$$

with

$$\tilde{\xi}_i = e^{-\sigma_i r_< - \tau_i r_> - \omega_i r_< / r_>} r_<^{s_i} r_>^{t_i} . \tag{13}$$

The functions φ_i are the subset of the general set θ_i [Eq. (9)] with $a_i = b_i = \alpha_i = \beta_i = 0$. For the case of radial antisymmetric states we follow an idea by Schwarz [1]: we keep the exponential portion of the radial basis functions as is and introduce the antisymmetry in the polynomial portion of the variational representation. The most general such expansion is given by

$$\tilde{\xi}_i^{\text{antisym}} = (r_1 - r_2) \, \tilde{\xi}_i . \tag{14}$$

All the radial integrals necessary for the calculation of matrix elements can be written in terms of the general integral

$$Q_{ij}(c,d,p,q) = \int_0^\infty \int_0^\infty \eta_i \, \eta_j \, r_1^c \, r_2^d \, r_<^p \, r_>^q \, r_1^2 dr_1 r_2^2 dr_2 \tag{15}$$

that has the closed-form expression

$$Q_{ij}(c,d,p,q) = Q_{ij}^<(c,d,p,q) + Q_{ij}^>(c,d,p,q), \tag{16}$$

$$Q_{ij}^<(c,d,p,q) = R_{ij}^<(c,d,p,q) + \sum_{n=1}^{\infty} \frac{(-\omega_i - \omega_j)^n}{n!} R_{ij}^<(c,d,p+n,q-n), \tag{17}$$

$$Q_{ij}^>(c,d,p,q) = R_{ij}^>(c,d,p,q) + \sum_{n=1}^{\infty} \frac{(-\omega_i - \omega_j)^n}{n!} R_{ij}^>(c,d,p+n,q-n), \tag{18}$$

where

$$R_{ij}^<(c,d,p,q) = \frac{(T-1)!}{W^T} \frac{1}{B} F\left(1, T; B+1; \frac{\mu}{\mu+1}\right), \tag{19}$$

$$R_{ij}^>(c,d,p,q) = \frac{(T-1)!}{W^T} \frac{1}{A} F\left(1, T; A+1; \frac{\nu}{\nu+1}\right) , \tag{20}$$

with

$$
\begin{aligned}
T&=a+b+s+t+2\ ,\\
A&=a+s+1\ ,\\
B&=b+s+1\ ,\\
a&=a_i+a_j+c+2\ ,\\
b&=b_i+b_j+d+2\ ,\\
s&=s_i+s_j+p\ ,\\
t&=t_i+t_j+q\ ,\\
W&=\alpha_i+\alpha_j+\beta_i+\beta_j+\sigma_i+\sigma_j+\tau_i+\tau_j\,,\\
\mu&=\frac{\beta_i+\beta_j+\sigma_i+\sigma_j}{\alpha_i+\alpha_j+\tau_i+\tau_j}\,,\\
\nu&=\frac{\alpha_i+\alpha_j+\sigma_i+\sigma_j}{\beta_i+\beta_j+\tau_i+\tau_j}\ .
\end{aligned}
\tag{21}
$$

$R^<$ and $R^>$, which denote integrations for $r_2 \leqslant r_1$ and $r_1 \leqslant r_2$, respectively, are given in terms of the hypergeometric function F

$$
F(u,v;w;z)={}_2F_1(u,v;w;z)=\sum_{n=0}^{\infty}\frac{(u)_n(v)_n}{(w)_n}\frac{z^n}{n!} \tag{22}
$$

with

$$
(u)_n=\frac{\Gamma(u+n)}{\Gamma(u)}\ . \tag{23}
$$

The necessary angular integrals can all be written in terms of the general integral

$$
\begin{aligned}
\Xi_{ij}^{\lambda}=\frac{4\pi}{2\lambda+1}\sum_q \int\int \Lambda_{l_{1i}l_{2i}}^{*L_iM_i}(\hat{\mathbf{r}}_1,\hat{\mathbf{r}}_2)Y_{\lambda,q}(\hat{\mathbf{r}}_1)\\
\times Y_{\lambda,q}^{*}(\hat{\mathbf{r}}_2)\Lambda_{l_{1j}l_{2j}}^{L_jM_j}(\hat{\mathbf{r}}_1,\hat{\mathbf{r}}_2)\ d\Omega_1\ d\Omega_2\,,
\end{aligned}
\tag{24}
$$

which yields

$$
\begin{aligned}
\Xi_{ij}^{\lambda}=(-1)^{\lambda+L_i}\delta_{L_iL_j}\delta_{M_iM_j}[l_{1i},l_{2i},l_{1j},l_{2j}]^{1/2}\\
\times\begin{pmatrix} l_{1i} & \lambda & l_{1j}\\ 0 & 0 & 0\end{pmatrix}\begin{pmatrix} l_{2i} & \lambda & l_{2j}\\ 0 & 0 & 0\end{pmatrix}\begin{Bmatrix} l_{2i} & l_{1i} & L_i\\ l_{1j} & l_{2j} & \lambda\end{Bmatrix}
\end{aligned}
\tag{25}
$$

with

$$
[a,b,\ldots]=(2a+1)(2b+1)\cdots\ . \tag{26}
$$

The case $\lambda=0$ addresses the straight overlap of the orthonormal functions $\Lambda_{l_{1i}l_{2i}}^{L_iM_i}(\hat{\mathbf{r}}_1,\hat{\mathbf{r}}_2)$, correctly yielding

$$
\Xi_{ij}^{0}=\delta_{L_iL_j}\delta_{M_iM_j}\delta_{l_i^1l_j^1}\delta_{l_i^2l_j^2}\ . \tag{27}
$$

For the S states used as examples in this paper $L_i=L_j=0$ and (25) reduces to

$$
\begin{aligned}
\Xi_{ij}^{\lambda}(L_i=L_j=0)\\
=(-1)^{\lambda}[l_{1i},l_{1j}]^{1/2}\delta_{l_{1i}l_{2i}}\delta_{l_{1j}l_{2j}}\begin{pmatrix} l_{1i} & \lambda & l_{1j}\\ 0 & 0 & 0\end{pmatrix}^2\ .
\end{aligned}
\tag{28}
$$

In terms of these results, we can write the general overlap integrals as

$$
\begin{aligned}
\int\int \eta_i\Lambda_{l_{1i}l_{2i}}^{*LM}\ \eta_j\Lambda_{l_{1j}l_{2j}}^{LM}\ d^3\mathbf{r}_1\ d^3\mathbf{r}_2\\
=Q_{ij}(0,0,0,0)\ \delta_{l_{1i}l_{1j}}\delta_{l_{2i}l_{2j}}\ .
\end{aligned}
\tag{29}
$$

The Hamiltonian matrix elements can be written as

$$
\begin{aligned}
\int\int \eta_i\Lambda_{l_{1i}l_{2i}}^{*LM}\ H\ \eta_j\Lambda_{l_{1j}l_{2j}}^{LM}\quad d^3\mathbf{r}_1\ d^3\mathbf{r}_2\\
=(h_{ij}+\tilde{h}_{ij})\ \delta_{l_{1i}l_{1j}}\delta_{l_{2i}l_{2j}}+\sum_{\lambda=0}^{\infty} g_{ij}^{\lambda}\ \Xi_{ij}^{\lambda}\ .
\end{aligned}
\tag{30}
$$

h_{ij} and $\tilde{h}_{ij}$ denote the portion of the Hamiltonian matrix dealing with the interaction of the electrons with the nucleus, while the terms in g_{ij}^{λ} deal with the electron-electron interaction. h_{ij} involves the usual integrals of products of one-electron functions, while $\tilde{h}_{ij}$ takes care of terms involving derivatives of the form

$$
\begin{aligned}
\frac{\partial r_>}{\partial r_2}&=\zeta(r_2-r_1),\\
\frac{\partial r_<}{\partial r_2}&=1-\zeta(r_2-r_1)\ ,
\end{aligned}
\tag{31}
$$

and

$$
\frac{d\zeta(x)}{dx}=\delta(x)\ , \tag{32}
$$

where ζ is the Heaviside function

$$
\zeta(x)=\begin{cases}1 & \text{if}\quad x>0\\ 0 & \text{if}\quad x<0\ .\end{cases} \tag{33}
$$

We obtain

$$
\begin{aligned}
h_{ij}=&-\tfrac{1}{2}[(\alpha_j+\tau_j)^2+(\beta_j+\sigma_j)^2]Q_{ij}^{<}(0,0,0,0)-\tfrac{1}{2}[(\alpha_j+\sigma_j)^2+(\beta_j+\tau_j)^2]Q_{ij}^{>}(0,0,0,0)\\
&+(\alpha_j+\tau_j)(a_j+t_j+1)Q_{ij}^{<}(-1,0,0,0)+(\beta_j+\sigma_j)(b_j+s_j+1)Q_{ij}^{<}(0,-1,0,0)\\
&+(\alpha_j+\sigma_j)(a_j+s_j+1)Q_{ij}^{>}(-1,0,0,0)+(\beta_j+\tau_j)(b_j+t_j+1)Q_{ij}^{>}(0,-1,0,0)\\
&-\tfrac{1}{2}(a_j+t_j+1)(a_j+t_j)Q_{ij}^{<}(-2,0,0,0)-\tfrac{1}{2}(b_j+s_j+1)(b_j+s_j)Q_{ij}^{<}(0,-2,0,0)\\
&-\tfrac{1}{2}(a_j+s_j+1)(a_j+s_j)Q_{ij}^{>}(-2,0,0,0)-\tfrac{1}{2}(b_j+t_j+1)(b_j+t_j)Q_{ij}^{>}(0,-2,0,0)\\
&+\omega_j(\alpha_j+\tau_j)Q_{ij}^{<}(-2,1,0,0)-\omega_j(\beta_j+\sigma_j)Q_{ij}^{<}(-1,0,0,0)-\omega_j(\alpha_j+\sigma_j)Q_{ij}^{>}(0,-1,0,0)\\
&+\omega_j(\beta_j+\tau_j)Q_{ij}^{>}(1,-2,0,0)-\omega_j(a_j+t_j)Q_{ij}^{<}(-3,1,0,0)+\omega_j(b_j+s_j+1)Q_{ij}^{<}(-1,-1,0,0)\\
&+\omega_j(a_j+s_j)Q_{ij}^{>}(-1,-1,0,0)-\omega_j(b_j+t_j+1)Q_{ij}^{>}(1,-3,0,0)\\
&-\frac{\omega_j^2}{2}Q_{ij}^{<}(-4,2,0,0)-\frac{\omega_j^2}{2}Q_{ij}^{<}(-2,0,0,0)-\frac{\omega_j^2}{2}Q_{ij}^{>}(0,-2,0,0)-\frac{\omega_j^2}{2}Q_{ij}^{>}(2,-4,0,0)\\
&+\tfrac{1}{2}l_{1j}(l_{1j}+1)Q_{ij}(-2,0,0,0)+\tfrac{1}{2}l_{2j}(l_{2j}+1)Q_{ij}(0,-2,0,0)-Z\ Q_{ij}(-1,0,0,0)-Z\ Q_{ij}(0,-1,0,0),
\end{aligned}
\tag{34}
$$

$$
\tilde{h}_{ij}=e^{-(\omega_i+\omega_j)}\,\frac{(T+2)!}{W^{T+2}}\left(\frac{\tau_j-\sigma_j}{W}+\frac{s_j-t_j-2\omega_j}{T+2}\right),
\tag{35}
$$

with T and W defined in (21), and

$$
g_{ij}^{\lambda}=Q_{ij}(0,0,\lambda,-\lambda-1)\ .
\tag{36}
$$

All the calculations in this paper were done with the radial basis set (13) with $\omega=0$ as a value of $\omega\neq 0$ did not improve convergence enough to justify an extra non-linear parameter. This makes all the overlap integrals much simpler by replacing everywhere $a=b=\alpha=\beta=\omega=0$ and by using R_{ij} instead of Q_{ij}:

$$
\begin{aligned}
h_{ij}=&-\tfrac{1}{2}(\sigma_j^2+\tau_j^2)[R_{ij}^{<}(0,0,0,0)+R_{ij}^{>}(0,0,0,0)]+\sigma_j(s_j+1)[R_{ij}^{<}(0,-1,0,0)+R_{ij}^{>}(-1,0,0,0)]\\
&+\tau_j(t_j+1)[R_{ij}^{<}(-1,0,0,0)+R_{ij}^{>}(0,-1,0,0)]-\tfrac{1}{2}(s_j+1)s_j[R_{ij}^{<}(0,-2,0,0)+R_{ij}^{>}(-2,0,0,0)]\\
&-\tfrac{1}{2}(t_j+1)t_j[R_{ij}^{<}(-2,0,0,0)+R_{ij}^{>}(0,-2,0,0)]+\tfrac{1}{2}l_{1j}(l_{1j}+1)R_{ij}(-2,0,0,0)+\tfrac{1}{2}l_{2j}(l_{2j}+1)R_{ij}(0,-2,0,0)\\
&-Z\,[R_{ij}(-1,0,0,0)+R_{ij}(0,-1,0,0)]\ ,
\end{aligned}
\tag{37}
$$

$$
\tilde{h}_{ij}=\frac{(T+2)!}{W^{T+2}}\left(\frac{\tau_j-\sigma_j}{W}+\frac{s_j-t_j}{T+2}\right),
\tag{38}
$$

$$
g_{ij}^{\lambda}=R_{ij}(0,0,\lambda,-\lambda-1)\ .
\tag{39}
$$

B. Radial convergence

The radial convergence was studied by setting $l_1=l_2=0$ and $L=0$ using the ground state as the test case. The radial basis set used in these calculations is then

$$
f_i=e^{-\sigma_i r_< -\tau_i r_>}\ r_<^{s_i}\ r_>^{t_i}\ ,
\tag{40}
$$

with

$$
\begin{aligned}
&i=1,\ldots,N_{\text{exp}}\\
&s_i=s_i^{\min},\ s_i^{\min}+1,\ldots,s_i^{\max}\ ,\\
&t_i=t_i^{\min},\ t_i^{\min}+1,\ldots,t_i^{\max}\ .
\end{aligned}
\tag{41}
$$

Three sets of exponential parameters were used. σ_1 and τ_1 were fixed at the exact hydrogenic values; this improves the stability and convergence of the basis set by accounting for most of the hydrogenic contribution. Only the necessary number of powers for an exact hydrogenic result were included in this first exponential set, e.g., $t_1^{\max}$ is 1 for the ground state, 2 for the first excited state, and so on. The two other sets of exponential parameters were determined by a variational minimization of the energy. Each of these two sets of nonlinear parameters were multiplied by different sets of radial powers. Following is a summary of the basis set used: for the first set: $N_{\text{exp}}=3$;

$$\sigma_1 = Z/n_<\,, \quad \tau_1 = (Z-1)/n_>\,,$$

$$s_1^{\min} = 0, s_1^{\max} = n_< - 1\,,$$

$$t_1^{\min} = 0, t_1^{\max} = n_> - 1\,;$$

for the second set: σ_2 and τ_2 are determined by optimization,

$$s_2 = 0, 1, \ldots, n_2^s - 1, \text{ with } n_2^s \text{ an integer}$$

$$t_2 = 0, 1, \ldots, n_2^t - 1, \text{ with } n_2^t \text{ an integer} \qquad (42)$$

$$s_2 + t_2 \leq st_2^{\max}, \text{ with } st_2^{\max} \text{ an integer}\,;$$

for the third set: σ_3 and τ_3 are determined by optimization,

$$s_3 = 0, 1, \ldots, n_3^s - 1, \text{ with } n_3^s \text{ an integer}$$

$$t_3 = -s_3 + 1, -s_3 + 2, \ldots, \max\{-s_3 + n_3^t, 0\},$$

$$\text{with } n_3^t \text{ an integer}$$

$$s_3 + t_3 \leq st_2^{\max}, \text{ with } st_2^{\max} \text{ an integer}\ .$$

Notice that $r_>$ is allowed to have negative powers. It is the inclusion of these negative powers that substantially improves the radial convergence. As an example, the optimized parameters used for the best calculation involving 125 two-electron radial functions are $\sigma_2 = 0.828\,78$, $\tau_2 = 0.904\,99$, $n_2^s = 9$, $n_2^t = 9$, $st_2^{\max} = 10$, $\sigma_3 = 0.913\,89$, $\tau_3 = 1.192\,99$, $n_3^s = 11$, and $n_3^t = 5$.

The results obtained are presented in Table I, where they are compared with those obtained using Slater functions and natural orbitals constructed with piecewise polynomials. These results present the variational ground state obtained when only s states are included in the basis set. N denotes the number of two-electron radial basis functions and E the ground-state variational eigenvalue in a.u. The Slater and the modified-configuration-interaction (MCI) columns describe convergence as the number of two-electron basis functions is increased, while in the case of natural orbitals convergence is analyzed as the number N_o of natural orbitals is increased keeping the total number N of basis functions fixed [3]. In each case the best calculated value is presented. (In the case of natural orbitals one can construct 36 natural orbitals with the 666 two-electron basis functions, but the convergence seems to tail off at $N_o = 24$ [3].) Setting $\delta_{\rm rel}E = E/E_{\rm exact} - 1$, one obtains for the best results $\delta_{\rm rel}E_{\rm Slater} \approx 8.4 \times 10^{-7}$ with 56 two-electron basis functions, $\delta_{\rm rel}E_{\rm NO} \approx 3.9 \times 10^{-9}$ with 666 two-electron basis functions, and $\delta_{\rm rel}E_{\rm MCI} \approx 3.5 \times 10^{-18}$ with 125 two-electron basis functions. MCI provides a convergence that is 11 and 9 orders of magnitude better than Slater functions and NO's, respectively. A good MCI value was used as $E_{\rm exact}$ in the first two cases, while for the MCI values themselves the value used is an extrapolation of E, obtained iteratively from a linear regression of the cumulative errors of the calculated MCI values. It is interesting to observe the *rate* of convergence for each of the methods. For this purpose, a power law was fitted in each case to $\delta_{\rm rel}E$ using linear regression. The values obtained were $\delta_{\rm rel}E_{\rm Slater} \sim N^{-2.8}$, $\delta_{\rm rel}E_{\rm NO} \sim N_o^{-4.7}$, and $\delta_{\rm rel}E_{\rm MCI} \sim N^{-9.8}$. Notice that in the NO case, the convergence refers to the addition of natural orbitals keeping the basis set size fixed at 666 two-electron vectors. Also the convergence rates quoted here are for the *error in the energy* unlike the commonly quoted convergence of the energy increments as new vectors are added to the calculation, which yields rather the convergence of $\delta E/\delta N$ and therefore has a faster convergence rate by roughly one extra power of N. The different rates of convergence can be clearly seen in Fig. 1.

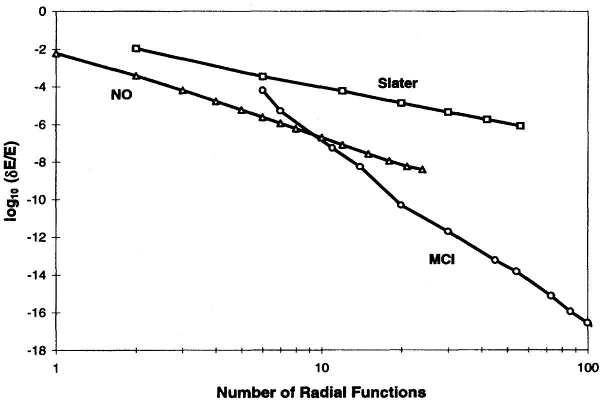

FIG. 1. Radial convergence of the ground-state s configuration for a nuclear charge $Z = 2$ using Slater, natural orbital, and MCI radial functions. $\delta E/E$ is the relative error of the variational eigenvalue. The abscissa gives the number of two-electron radial basis functions used in the Slater and MCI cases and the number of natural orbitals used in the NO case, each built with 666 basis functions.

III. ANGULAR FUNCTIONS

In the CI method, correlation effects are accounted for by the introduction of basis functions containing coupled spheri-

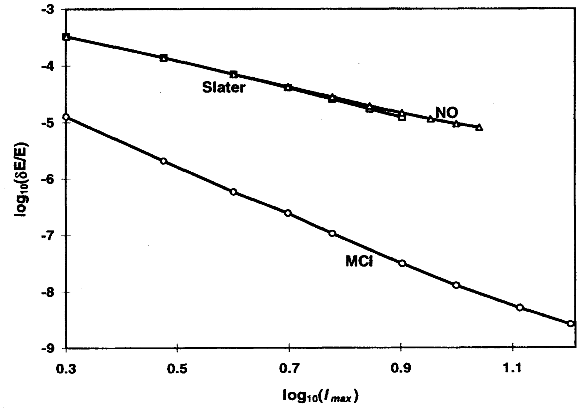

FIG. 2. Angular convergence of the ground-state energy of helium using Slater, natural orbital, and MCI radial functions. $\delta E/E_{\rm exact}$ is the relative error of the variational eigenvalue. $l_{\rm max}$ refers to the largest angular momentum used by the Slater and MCI methods and the largest generalized angular function used by the MCI method.

cal harmonics with the same total angular momentum but with different one-electron angular-momentum quantum numbers. Each basis function will then contain an angular part of the form (4) with correlation entering in the calculations by including different values of l_1 and l_2. These different angular functions will be mixed by the infinite angular sum in (2) upon the diagonalization of the Hamiltonian matrix. As a result, one obtains a wave function containing *linear* combinations of coupled spherical harmonics with different values of l_1 and l_2 (the Hamiltonian diagonalization minimizes these linear coefficients). The convergence of the variational energies as the number of different one-electron spherical harmonics is increased is, however, very slow, as can be seen form the results for Slater and NO functions in the first two sets of values in Table II and the two top curves in Fig. 2. In the Slater case, the calculations were performed using the radial functions of Sec. II, given that the basis sets become prohibitively large if functions of r_1 and r_2 are used, diminishing the number of possible angular configurations to include. The Slater and NO curves are almost identical, with the NO one being able to calculate values with a few more angular momenta, but the Slater curve with a slightly better accuracy for the larger values of l for which the NO calculation had to resort to smaller radial basis sets. The best NO value, which is the best value obtained with standard radial representations (i.e., in terms of r_1 and r_2), is obtained with a basis set of 640 two-electron vectors with which 118 natural orbitals were constructed and yields for the helium ground state a relative error of 8.0×10^{-6} [3]. In this section we shall present an approach to the angular representation that will yield a best result for the energy with a relative error of 2.6×10^{-9}. To increase the NO accuracy to 3.0×10^{-9} one would need of the order of 200 angular momenta and a basis set of about 10^6 vectors [3].

As mentioned in the preceding paragraph, the standard CI method mixes *linearly* different angular configurations through the diagonalization of the Hamiltonian matrix. In this paper we propose to improve the angular convergence of the CI calculations by introducing an *a priori* superposition of angular functions that will depend on a set of *nonlinear* variational parameters. In other words, rather than letting the diagonalization do the work of mixing angular configurations, we will start the calculation with a set of angular functions in which spherical harmonics were already mixed in large quantities. As we do not know the exact form of this mixing, we write these functions in terms of a few (nonlinear) parameters that will be varied and optimized by energy minimization. In other words, rather than using the coupled spherical harmonics

$$\Lambda^{LM}_{l_{1i}l_{2i}}(\hat{\mathbf{r}}_1,\hat{\mathbf{r}}_2)=\sum_{m_1,m_2}\langle l_{1i}m_1l_{2i}m_2|LM\rangle \times Y_{l_{1i},m_1}(\hat{\mathbf{r}}_1)\;Y_{l_{2i},m_2}(\hat{\mathbf{r}}_2)\;,$$

we introduce linear combinations of these [8]:

$$\Theta^{LM}_{\tilde{l}_1\tilde{l}_2}(\hat{\mathbf{r}}_1,\hat{\mathbf{r}}_2)=\sum_{i}^{N_\Theta} C^i_{\tilde{l}_1\tilde{l}_2}(\mathbf{u})\;\Lambda^{LM}_{l_{1i}l_{2i}}(\hat{\mathbf{r}}_1,\hat{\mathbf{r}}_2)\;, \qquad (43)$$

where $\mathbf{u}$ denotes a set of nonlinear (angular) parameters $u_1, u_2, \ldots, n_u$. The values of $\tilde{l}_1$ and $\tilde{l}_2$ refer to the angular momenta that provide the most important contribution to Θ in the limit of small correlation effects, with $\mathbf{u}=0$ in the case of no correlation:

$$\lim_{\mathbf{u}\to0}\Theta^{LM}_{\tilde{l}_1\tilde{l}_2}(\hat{\mathbf{r}}_1,\hat{\mathbf{r}}_2)=\Lambda^{LM}_{l_1l_2}(\hat{\mathbf{r}}_1,\hat{\mathbf{r}}_2)\;. \qquad (44)$$

The power of this approach is based on the fact that a small number n_u of angular parameters controls the linear combination of a very large number N_Θ of spherical harmonics with different angular momenta. In this way one can mix a very large number of angular configurations: e.g., 200–300 values of l_1 and l_2 were used in this work versus the 10 or so that is the most that can be used in the standard CI method. The set of nonlinear parameters $\mathbf{u}$ is optimized in the same way in which the radial exponential parameters are optimized: by a minimization of the variational energy eigenvalues. The basis sets (12) and (14), although efficient in the radial representation, still use the usual inefficient CI angular approach. Each basis function φ_i of the basis sets used here involves the linear combinations of large numbers of the basis functions $\tilde{\varphi}_i$ (12), all with the same radial part but different angular components. The functions used in this work for the helium-like S states are

$$\varphi_i=f_i(r_<,r_>)\;\Theta^{LM}_{\tilde{l}_{1i}\tilde{l}_{2i}}(\hat{\mathbf{r}}_1,\hat{\mathbf{r}}_2) \qquad (45)$$

and

$$\varphi_i^{\text{antisym}}=(r_1-r_2)\;\varphi_i\,, \qquad (46)$$

with f_i defined in Eqns. (40) and (41),

$$f_i=e^{-\sigma_i r_<-\tau_i r_>}\;r_<^{s_i}\;r_>^{t_i}\;,$$

with

$$i=1,\ldots,N_{\text{exp}}$$
$$s_i=s_i^{\min},\;s_i^{\min}+1,\ldots,s_i^{\max}$$
$$t_i=t_i^{\min},\;t_i^{\min}+1,\ldots,t_i^{\max}\,.$$

The remaining question is how to select the coefficients $C^i_{\tilde{l}_1\tilde{l}_2}(\mathbf{u})$, specifically their dependence on the parameters u_i. An "experimental" approach has been followed in this work, trying a few different possible functional forms for the angular expansion coefficients and comparing the efficiency with which the energy could be minimized. In all cases the $C^i_{\tilde{l}_1\tilde{l}_2}(\mathbf{u})$ were expressed in terms of the coefficients in the Taylor expansion of a function of $\mathbf{u}$ to guarantee that the norm of the angular functions will remain finite in the limit $N_\Theta\to\infty$.

In this paper we present correlated calculations for S states of helium. In this case the total angular momentum is $L=0$ and therefore $l_1=l_2$ for any l_i. The following coefficients and parameters were used for the radial (40) and angular (43) functions: for the first set: $N_{\text{exp}}=3$;

$$\sigma_1=Z/n_<\,,\quad \tau_1=(Z-1)/n_>,$$

$$s_1^{\min}=0, s_1^{\max}=n_<-1,\quad t_1^{\min}=0, t_1^{\max}=n_>-1,$$

$$\tilde{l}_1=0\quad,\quad N_{\Theta 1}=1;$$

for the second set: σ_2 and τ_2 are determined by optimization,

$$s_2=0,\,1,\,\ldots,n_2^s-1,\ \text{with}\ n_2^s\ \text{an integer}$$

$$t_2=0,\,1,\,\ldots,\max\{n_2^t-1-\tilde{l}_2,0\},\ \text{with}\ n_2^t\ \text{an integer} \tag{47}$$

$$\tilde{l}_2=0,\,1,\,\ldots,n_2^{\tilde{l}}-1,\ \text{with}\ n_2^{\tilde{l}}\ \text{an integer}$$

$$N_{\Theta 2}>1,$$

$$s_2+t_2\leqslant st_2^{\max},\quad t_2+\tilde{l}_2+1\leqslant st_2^{\max},$$

$$\text{with}\ st_2^{\max}\ \text{an integer;}$$

for the third set: σ_3 and τ_3 are determined by optimization,

$$s_3=0,\,1,\,\ldots,n_3^s-1,\ \text{with}\ n_3^s\ \text{an integer}$$

$$t_3=-s_3+1,\,-s_3+2,\,\ldots,\max\{-s_3+n_3^t,\,-\tilde{l}_3\},$$

$$\text{with}\ n_3^t\ \text{an integer}$$

$$\tilde{l}_3=0,\,1,\,\ldots,n_3^{\tilde{l}}-1,\ \text{with}\ n_3^{\tilde{l}}=n_2^{\tilde{l}}$$

$$N_{\Theta 3}=N_{\Theta 2},$$

$$s_3+t_3\leqslant st_2^{\max},\quad t_3+\tilde{l}_3+1\leqslant lt_3^{\max},$$

$$\text{with}\ lt_3^{\max}\ \text{an integer.}$$

The coefficients of the angular expansions were chosen as follows:

$$C_{\tilde{l}\tilde{l}}^{i}=\begin{cases}0 & \text{if}\ l_i<\tilde{l}\quad\text{or}\ l_i>\tilde{l}+N_\Theta-1\\ b(\tilde{l},l_i)/b(\tilde{l},\tilde{l}) & \text{otherwise, with}\ l_i=i-1,\ i=1,2,\ldots,N_\Theta\end{cases}\ , \tag{48}$$

where $b(\tilde{l},l_i)$ is given by the ith term in the Taylor expansion of $(1+x)^y$ around $x=0$, i.e.,

$$b(\tilde{l},l_i)=\begin{cases}1 & \text{if}\ i=1\\ b(\tilde{l},l_i)=y(y-1)\cdots(y-l_i+1)x^{l_i}/l_i! & \text{if}\ i>1\end{cases}\ , \tag{49}$$

and x and y are defined in terms of four nonlinear coefficients u_i with

$$x=u_1/(\tilde{l}+1)+u_2\tilde{l},\quad y=u_3+u_4\tilde{l}\ . \tag{50}$$

We present now the values used for these parameters for two calculations of the ground-state energy (the best in this paper and another using a smaller basis set), as well as for the best calculations in this paper for the $2\,^1S$ and $2\,^3S$ states. The best calculation for the ground-state variational energy in this paper yields $E=-2.903\,724\,369\,49$ a.u. (a relative accuracy of 2.6×10^{-9}, almost four orders of magnitude better than the best previous CI value) with a total of 420 two-electron basis vectors and the following parameter values: $n_2^s=7$, $n_2^t=7$, $n_3^s=8$, $n_3^t=5$, $st_2=10$, $lt_3=4$, $\sigma_2=2.088\,182\,40$, $\tau_2=0.994\,649\,76$, $\sigma_3=0.732\,059\,45$, $\tau_3=1.095\,069\,97$ $n^{\tilde{l}}=16$, $N_\Theta=227$, $u_1=0.038\,007\,06$, $u_2=0.055\,107\,87$, $u_3=0.554\,292\,47$, and $u_4=-1.829\,253\,92$. The MCI basis set that yields a variational ground-state energy slightly better than the best previous traditional CI value gives $E=-2.903\,687\,981\,776\,80$ a.u. (a relative accuracy of 1.3×10^{-5}) with a total of only 98 two-electron basis vectors (involving only three generalized angular functions) and the following parameter values: $n_2^s=6$, $n_2^t=5$, $n_3^s=8$, $n_3^t=1$, $st_2=8$, $lt_3=1$, $\sigma_2=1.603\,15$, $\tau_2=0.875\,64$, $\sigma_3=1.022\,94$, $\tau_3=0.727\,91$, $n^{\tilde{l}}=3$, $N_\Theta=85$, $u_1=0.009\,48$, $u_2=0.364\,59$, $u_3=0.710\,37$, and $u_4=-0.645\,12$. The best calculation for the $2\,^1S$ variational energy in this paper yields $E=-2.145\,974\,015\,97$ a.u. (a relative accuracy of 1.4×10^{-8}) with a total of 276 two-electron basis vectors and the following parameter values: $n_2^s=6$, $n_2^t=6$, $n_3^s=7$, $n_3^t=3$, $st_2=10$, $lt_3=4$, $\sigma_2=1.131\,753\,59$, $\tau_2=0.547\,525\,64$, $\sigma_3=0.684\,841\,15$, $\tau_3=0.744\,577\,67$, $n^{\tilde{l}}=12$, $N_\Theta=110$, $u_1=0.274\,333\,23$, $u_2=0.099\,219\,69$, $u_3=1.793\,456\,40$, $u_4=-1.598\,088\,47$. The best calculation for the $2\,^3S$ variational energy in this paper yields $E=-2.175\,229\,377\,806\,9$ a.u. (a relative accuracy of 2×10^{-10}) with a total of 264 two-electron basis vectors and the following parameter values: $n_2^s=6$, $n_2^t=6$, $n_3^s=7$, $n_3^t=3$, $st_2=10$, $lt_3=4$, $\sigma_2=0.795\,031\,46$, $\tau_2=0.526\,120\,74$, $\sigma_3=0.754\,946\,29$, $\tau_3=0.644\,119\,30$ $n^{\tilde{l}}=10$, $N_\Theta=110$, $u_1=-0.000\,215\,12$, $u_2=0.084\,142\,86$, $u_3=1.393\,304\,29$, and $u_4=-1.225\,916\,58$.

The convergence of the ground-state variational energy values obtained in this paper is described in Table II and in Fig. 2. An interpolation of the form $\delta_{\text{rel}}E\sim(L_{\max}+c)^{-p}$ yields different values of p for different values of c with very similar statistical correlation tests; however, for each choice of c the power p using the MCI method *approximately doubles* that obtained using either Slater or natural orbital basis sets. The best correlation is obtained for $c=0$ for which the CI method converges as $\delta_{\text{rel}}E\sim(L_{\max})^{-2.2}$ and the MCI method (present work) as $\delta_{\text{rel}}E\sim(L_{\max})^{-4.1}$. For $c=1$ we obtain for the CI method $\delta_{\text{rel}}E\sim(L_{\max})^{-2.8}$ and for the MCI method $\delta_{\text{rel}}E\sim(L_{\max})^{-5.1}$, both with high statistical correlation.

The accuracy of the MCI results was obtained by comparing with the accurate results for the S states of helium obtained using correlated basis sets [9], which yield the following upper bounds (numbers in italics did not converge): for the ground state $E=-2.903\,724\,377\,034\,119\,\mathit{479}$ a.u. with 1262 two-electron basis functions, for the $2\,{}^1S$ state $E=-2.145\,974\,046\,054\,412\,\mathit{8}$ a.u. with 995 two-electron basis functions, and for the $2\,{}^3S$ state $E=-2.175\,229\,378\,236\,791\,30\mathit{0}\,\mathit{8}$ a.u. with 954 two-electron basis functions. Notice that configuration interaction cannot compete *yet* with the accuracy of the correlated calculations for the low-lying states of two-electron systems with small nuclear charge, for which correlated basis sets yield roughly seven digits more accuracy. On the other hand, the configuration interaction has, unlike correlated basis sets, the advantage of providing a strightforward implementation for many-electron systems and molecules.

Finally, a comment on the numerical calculation of the angular integrals. The 3-j symbols necessary for the calculation of these integrals (28) involve now very large values of angular momentum quantum numbers (e.g., $N_\Theta=227$) for the best ground-state calculation. These 3-j symbols require then factorials of very large arguments ($\sim 6N_\Theta$). In order to avoid loss of numerical precision in the calculation of these integrals, the 3-j symbols were expressed in terms of binomial coefficients, which in turn were calculated using powers of primes (the use of logarithms of factorials results in a large loss of numerical precision). Setting $a=(l_1+l_2-l_3)/2$, $b=(l_1+l_3-l_2)/2$, $c=(l_2+l_3-l_1)/2$, and therefore $a+b+c=(l_1+l_2+l_3)/2$, we can write

$$\left|\begin{pmatrix} l_1 & l_2 & l_3 \\ 0 & 0 & 0 \end{pmatrix}\right| = \frac{(a+b+c)!}{a!\;b!\;c!}\left[\frac{(2a)!\;(2b)!\;(2c)!}{(2a+2b+2c+1)!}\right]^{1/2} \tag{51}$$

$$= \frac{1}{(2a+2b+2c+1)^{1/2}}\,\frac{\begin{pmatrix} a+b+c \\ a \end{pmatrix}}{\begin{pmatrix} 2(a+b+c) \\ 2a \end{pmatrix}^{1/2}} \times \frac{\begin{pmatrix} b+c \\ b \end{pmatrix}}{\begin{pmatrix} 2(b+c) \\ 2b \end{pmatrix}^{1/2}} . \tag{52}$$

The 3-j symbols can then be written as

$$\begin{pmatrix} l_1 & l_2 & l_3 \\ 0 & 0 & 0 \end{pmatrix} = \frac{(-1)^{a-b+c}}{(2a+2b+2c+1)^{1/2}}\,B(b+c,a)\;B(c,b), \tag{53}$$

where the functions $B(x,y)$ involve small numbers and are given by

$$B(x,y)=\frac{\begin{pmatrix} x+y \\ y \end{pmatrix}}{\begin{pmatrix} 2(x+y) \\ 2y \end{pmatrix}^{1/2}} . \tag{54}$$

IV. EXTENSION TO MORE ELECTRONS

In this section we discuss methods of extending the MCI method using basis sets of the form (45) to systems with more than two electrons. The extension of the angular functions (43) is trivial. In the case of more electrons, the coupling of as many spherical harmonics as electrons is needed as in the conventional CI method. The only difference is that the functions (43) mix different angular configurations with the same total angular momentum *a priori*.

The extension of the radial functions, however, modifies one of the main simplifications in conventional CI calculations. In the conventional CI method, the radial basis functions are built in terms of (orthogonal) one electron functions, i.e., functions of the form $f(r_i)$, where $0\leqslant r_i\leqslant\infty$ is the radial coordinate of the ith electron. In this way, overlaps involving correlation terms will result in only two-dimensional integrations of the form (15). Coupled radial integrals of higher dimensionality are not present in calculations involving a Hamiltonian that contains only two-electron interactions, such as the (lowest-order) nonrelativistic Hamiltonian for N_e electrons in the presence of a nucleus with charge Z

$$H=-\frac{1}{2}\sum_{i=1}^{N_e}\nabla^2_{\mathbf{r}_i}-\sum_{i=1}^{N_e}\frac{Z}{r_i}+\sum_{i=1}^{N_e}\sum_{j>i}^{N_e}\frac{1}{|r_i-r_j|} . \tag{55}$$

In the extension of this work to systems with several electrons, higher-dimensional integrals will be encountered. These integrals are not as complex as those appearing when correlated basis sets are used [9] and their values can actually be calculated analytically in terms of simple expressions in a straightforward way. In order to extend the method introduced in this paper to a system with N_e electrons, we introduce the *ordered* set of radial variables

$$x_i=r_{j(i)},$$

where $j(i)$ is a one to one (reordering) mapping such that

$$x_1\leqslant x_2\cdots\leqslant x_{N_e}.$$

Given the symmetry of the Hamiltonian under an exchange of any two electrons, it can be rewritten as

$$H=-\frac{1}{2}\sum_{i=1}^{N_e}\nabla^2_{\mathbf{x}_i}-\sum_{i=1}^{N_e}\frac{Z}{x_i}+\sum_{i=1}^{N_e}\sum_{j>i}^{N_e}\frac{1}{|x_i-x_j|} . \tag{56}$$

This suggests, as before, the extension of the radial symmetric basis set (40) to an N_e electron fully symmetric basis set composed of functions of the form

$$f_k=\prod_{i=1}^{N_e} e^{-\tau_{k,i}x_i}\, x_i^{t_{k,i}} \ . \tag{57}$$

The integrals involved in the calculations will be of the form

$$I_{N_e}=\int_0^\infty dr_1\int_0^\infty dr_2\cdots\int_0^\infty dr_{N_e}\, g(r_1,r_2,\ldots,r_{N_e}), \tag{58}$$

where g is symmetric in all the variables. This integral can be rewritten in terms of the variables x_i as

$$I_{N_e}=N_e!\int_0^\infty dx_{N_e}\int_0^{x_{N_e}} dx_{N_e-1}\cdots\int_0^{x_2} dx_1 \times g(x_1,x_2,\ldots,x_{N_e}). \tag{59}$$

With the radial basis set (57), this integral will consist of linear combinations of integrals of the form

$$\begin{aligned}K^{(n)}(u)&=K^{\sigma_n\sigma_{n-1}\cdots\sigma_2\sigma_1}_{s_ns_{n-1}\cdots s_2s_1}(u)\\ &=\frac{\sigma_1\sigma_2\cdots\sigma_n}{(s_1+s_2+\cdots+s_n)!}\int_0^u dx_n\, e^{-\sigma_nx_n}\,(\sigma_nx_n)^{s_n}\\ &\quad\times\int_0^{x_n}dx_{n-1}\, e^{-\sigma_{n-1}x_{n-1}}\,(\sigma_{n-1}x_{n-1})^{s_{n-1}}\cdots\int_0^{x_3}dx_2\, e^{-\sigma_2x_2}\,(\sigma_2x_2)^{s_2}\int_0^{x_2}dx_1\, e^{-\sigma_1x_1}\,(\sigma_1x_1)^{s_1},\end{aligned} \tag{60}$$

with $u\rightarrow\infty$.

General expressions for (60) can be derived in terms of the one-dimensional integral

$$K_s^\sigma(u)=\frac{\sigma}{s!}\int_0^u(\sigma x)^se^{-\sigma x}\,dx \ . \tag{61}$$

Upon successive integrations by parts, we obtain

$$K_s^\sigma(u)=1-e^{-\sigma u}\sum_{i=0}^{s}\frac{(\sigma u)^i}{i!} \ , \tag{62}$$

$$K_s^\sigma(u)=(\sigma u)^{s+1}e^{-\sigma u}\sum_{i=0}^{\infty}\frac{(\sigma u)^i}{(i+s+1)!} \ , \tag{63}$$

with

$$K_s^\sigma(\infty)=\frac{\sigma}{s!}\int_0^\infty(\sigma x)^se^{-\sigma x}\,dx=1. \tag{64}$$

The infinite sum form (63) is to be used for small values of the quantity σu for which (62) will involve large cancellations. There is, however, another important use of (63), which we will address shortly, namely, the case in which radial variables with negative powers are used in the case of several electrons.

For example, in the two-dimensional case we obtain

$$K^{\sigma_2\sigma_1}_{s_2s_1}(u)=\frac{\sigma_1\sigma_2}{(s_1+s_2)!}\int_0^u(\sigma_2x_2)^{s_2}e^{-\sigma_2x_2}\,dx_2 \times\int_0^{x_2}(\sigma_1x_1)^{s_1}e^{-\sigma_1x_1}\,dx_1 \tag{65}$$

$$=\sigma_2\frac{s_1!}{(s_1+s_2)!}\int_0^u(\sigma_2x_2)^{s_2}e^{-\sigma_2x_2}\,K^{\sigma_1}_{s_1}(x_2)\,dx_2$$

$$=g_0^{(2)}K^{\sigma_2}_{s_2}(u)-\sum_{i=0}^{s_1}g_i^{(2)}K^{\sigma_1+\sigma_2}_{s_2+i}(u) \ , \tag{66}$$

where

$$g_i^{(2)}=\frac{(s_2+i)!s_1!}{(s_1+s_2)!i!}\,\frac{\sigma_2^{s_2+1}\sigma_1^i}{(\sigma_2+\sigma_1)^{s_2+i+1}} \ , \tag{67}$$

$$g_0^{(2)}=\frac{s_2!s_1!}{(s_1+s_2)!} \ . \tag{68}$$

In the case in which $r_>$ has negative powers, i.e., $s_2<0$, we can use (63) to obtain

$$K^{\sigma_2\sigma_1}_{s_2s_1}(u)=\sum_{i=s_1+1}^{\infty}g_i^{(2)}K^{\sigma_1+\sigma_2}_{s_2+i}(u) \ . \tag{69}$$

In particular,

$$K^{\sigma_2\sigma_1}_{s_2s_1}(\infty)=\frac{\sigma_1\sigma_2}{(s_1+s_2)!}\int_0^\infty(\sigma_2x_2)^{s_2}e^{-\sigma_2x_2}\,dx_2 \times\int_0^{x_2}(\sigma_1x_1)^{s_1}e^{-\sigma_1x_1}\,dx_1 \tag{70}$$

$$=g_0^{(2)}-\sum_{i=0}^{s_1}g_i^{(2)}$$

$$=\sum_{i=s_1+1}^{\infty}g_i^{(2)} \ .$$

Equation (70) is equivalent to the usual expressions in terms of hypergeometric functions used in Sec. III.

The expressions obtained for the one- and two-dimensional integrations can be now used to calculate coupled integrals of higher dimensionality, which can be obtained iteratively in terms of $K_s^\sigma(u)$. For the most general case of the n-dimensional integral defined in (60), one obtains the general result

$$K^{(n)}(u)=\sum_{i_2=s_1+1}^{\infty}\ \sum_{i_3=s_2+i_1+1}^{\infty}\cdots\sum_{i_n=s_n+i_{n-1}+1}^{\infty} \times g^{(n)}_{i_2,i_3\cdots i_n}K^{\sigma_1+\sigma_2+\cdots+\sigma_n}_{s_n+i_n}\ , \tag{71}$$

where the constants $g^{(n)}$ are defined by

$$g^{s_1,s_2,\ldots,s_n}_{i_2,i_3,\ldots,i_n}(\sigma_1,\sigma_2,\ldots,\sigma_n)=\frac{s_1!(s_2+i_2)!\cdots(s_n+i_n)!}{i_2!\cdots i_n!(s_1+s_2+\cdots+s_n)!} \times\frac{\sigma_2^{s_2+1}\sigma_3^{s_3+1}\cdots\sigma_n^{s_n+1}(\sigma_1+\sigma_2)^{i_3}\cdots(\sigma_1+\sigma_2+\cdots+\sigma_{n-1})^{i_n}}{(\sigma_1+\sigma_2)^{s_2+i_2+1}(\sigma_1+\sigma_2+\sigma_3)^{s_3+i_3+1}\cdots(\sigma_1+\sigma_2+\cdots+\sigma_n)^{s_n+i_n+1}}\ , \tag{72}$$

$$g^{s_1,s_2,\ldots,s_n}_{0,0,\ldots,0,i_{j+1},i_{j+2},\ldots,i_n}(0,0,\ldots0,\sigma_j,\sigma_{j+1},\ldots,\sigma_n)=\lim_{\sigma_{j-1}\to0}\lim_{\sigma_{j-2}\to0}\cdots\lim_{\sigma_1\to0}g^{s_1,s_2,\ldots,s_n}_{i_2,i_3,\ldots,i_n}(\sigma_1,\sigma_2,\ldots,\sigma_n)\ , \tag{73}$$

with the shorthand notation

$$g^{(n)}_{i_2,i_3,\ldots,i_n}=g^{s_1,s_2,\ldots,s_n}_{i_2,i_3,\ldots,i_n}(\sigma_1,\sigma_2,\ldots,\sigma_n)\ , \tag{74}$$

$$g^{(n)}_{0,\ldots,0,i_{j+1},i_{j+2},\ldots,i_n}=g^{s_1,s_2,\ldots,s_n}_{0,\ldots,0,i_{j+1},i_{j+2},\ldots,i_n}(0,\ldots,0,\sigma_j,\sigma_{j+1},\ldots,\sigma_n) \tag{75}$$

in the case of a standard set of parameters. For example, in the case of three- and four-electron integrals, one obtains

$$K^{\sigma_3\sigma_2\sigma_1}_{s_3s_2s_1}(u)=\sum_{i=s_1+1}^{\infty}\ \sum_{j=s_2+i+1}^{\infty} g^{(3)}_{i,j}\ K^{\sigma_1+\sigma_2+\sigma_3}_{s_3+j}(u), \tag{76}$$

$$K^{\sigma_4\sigma_3\sigma_2\sigma_1}_{s_4s_3s_2s_1}(u)=\sum_{i=s_1+1}^{\infty}\ \sum_{j=s_2+i+1}^{\infty}\ \sum_{k=s_2+j+1}^{\infty} g^{(4)}_{i,j,k}\ K^{\sigma_1+\sigma_2+\sigma_3+\sigma_4}_{s_4+k}(u), \tag{77}$$

in particular,

$$K^{\sigma_3\sigma_2\sigma_1}_{s_3s_2s_1}(\infty)=\sum_{i=s_1+1}^{\infty}\ \sum_{j=s_2+i+1}^{\infty} g^{(3)}_{i,j}\ , \tag{78}$$

$$K^{\sigma_4\sigma_3\sigma_2\sigma_1}_{s_4s_3s_2s_1}(\infty)=\sum_{i=s_1+1}^{\infty}\ \sum_{j=s_2+i+1}^{\infty}\ \sum_{k=s_2+j+1}^{\infty} g^{(4)}_{i,j,k}\ , \tag{79}$$

The infinite summations can be replaced by finite sums in the cases in which the powers involved are such that do not lead to factorials of negative integers. This can be accomplished, for example, using the equivalent results (66) and (69) or the identity in (70). For example, in the case of three electrons, the necessary three-dimensional integrals result in several different closed-form expressions

$$K^{(3)}(u)=\frac{\sigma_1\sigma_2\sigma_3}{(s_1+s_2+s_3)!}\int_0^u(\sigma_3x_3)^{s_3}e^{-\sigma_3x_3}\,dx_3 \times\int_0^{x_3}(\sigma_2x_2)^{s_2}e^{-\sigma_2x_2}\,dx_2\int_0^{x_2}(\sigma_1x_1)^{s_1}e^{-\sigma_1x_1}\,dx_1 \tag{80}$$

$$=\frac{\sigma_3\ (s_1+s_2)!}{(s_1+s_2+s_3)!}\int_0^u(\sigma_3x_3)^{s_3}e^{-\sigma_3x_3}\ K^{\sigma_2\sigma_1}_{s_2s_1}(x_3)\,dx_3 \tag{81}$$

$$=g_0^{s_1,s_2+s_3}K^{\sigma_3\sigma_2}_{s_3s_2}(u)-\sum_{i=0}^{s_1} g_i^{s_1,s_2+s_3}(\sigma_1,\sigma_2) \times\left(\frac{\sigma_1+\sigma_2}{\sigma_2}\right)^{s_3}K^{\sigma_3,\sigma_1+\sigma_2}_{s_3,s_2+i}(u) \tag{82}$$

$$=\sum_{i=s_1+1}^{\infty} g_i^{s_1,s_2+s_3}(\sigma_1,\sigma_2)\left(\frac{\sigma_1+\sigma_2}{\sigma_2}\right)^{s_3} \times K^{\sigma_3,\sigma_1+\sigma_2}_{s_3,s_2+i}(u) \tag{83}$$

$$=\sum_{i=s_1+1}^{\infty}\ \sum_{j=s_2+i+1}^{\infty} g^{(3)}_{i,j}K^{\sigma_1+\sigma_2+\sigma_3}_{s_3+j}(u) \tag{84}$$

$$=\sum_{i=s_2+1}^{\infty} g^{(3)}_{0,i}K^{\sigma_2+\sigma_3}_{s_3+i}(u)-\sum_{i=0}^{s_1}\ \sum_{j=s_2+i+1}^{\infty} g^{(3)}_{i,j} \times K^{\sigma_1+\sigma_2+\sigma_3}_{s_3+j}(u) \tag{85}$$

$$=\left[g^{(3)}_{0,0}-\sum_{i=0}^{s_1} g^{s_3,s_1,s_2}_{0,i}(0,\sigma_1,\sigma_2)\right]K^{\sigma_3}_{s_3}(u) -\sum_{i=0}^{s_2} g^{(3)}_{0,i}K^{\sigma_2+\sigma_3}_{s_3+i}(u)+\sum_{i=0}^{s_1}\ \sum_{j=0}^{s_2+1} g^{(3)}_{i,j} \times K^{\sigma_1+\sigma_2+\sigma_3}_{s_3+j}(u), \tag{86}$$

which in the limit $u \to \infty$ for the three-electron case yield

$$K^{(3)}(\infty) = \sum_{i=s_1+1}^{\infty} \sum_{j=s_2+i+1}^{\infty} g_{i,j}^{(3)} \tag{87}$$

$$= \sum_{i=s_2+1}^{\infty} g_{0,i}^{(3)} - \sum_{i=0}^{s_1} \sum_{j=s_2+i+1}^{\infty} g_{i,j}^{(3)} \tag{88}$$

$$= g_{0,0}^{(3)} - \sum_{i=0}^{s_1} g_{0,i}^{s_3,s_1,s_2}(0,\sigma_1,\sigma_2)$$

$$- \sum_{i=0}^{s_2} g_{0,i}^{(3)} + \sum_{i=0}^{s_1} \sum_{j=0}^{s_2+1} g_{i,j}^{(3)} \ . \tag{89}$$

Different expressions for these integrals can be obtained by systematically applying recursion relations or transformation properties of the two-dimensional integrals, such as

$$K_{s_2 s_1}^{\sigma_2 \sigma_1}(u) = g_0^{(2)} K_{s_2}^{\sigma_2}(u) - \sum_{i=0}^{s_1} g_i^{(2)} K_{s_2+i}^{\sigma_1+\sigma_2}(u) \tag{90}$$

$$= \sum_{i=s_1+1}^{\infty} g_i^{(2)} K_{s_2+i}^{\sigma_1+\sigma_2}(u) \tag{91}$$

$$= g_0^{(2)} K_{s_1}^{\sigma_1}(u) K_{s_2}^{\sigma_2}(u) - g_0^{(2)} K_{s_1}^{\sigma_1}(u)$$

$$+ \sum_{i=0}^{s_2} g_i^{s_2,s_1}(\sigma_2,\sigma_1) K_{s_1+i}^{\sigma_1+\sigma_2}(u) \tag{92}$$

$$= g_0^{(2)} K_{s_1}^{\sigma_1}(u) K_{s_2}^{\sigma_2}(u)$$

$$- \sum_{i=s_2+1}^{\infty} g_i^{s_2,s_1}(\sigma_2,\sigma_1) K_{s_1+i}^{\sigma_1+\sigma_2}(u) . \tag{93}$$

By using these types of transformations, with others yet to be derived, one can improve the convergence patterns of the calculations for specific sets of parameters for which convergence would otherwise be slow.

The form chosen in (60) is not the only way to write the integral (59) in terms of ordered variables or ordered regions of the multidimensional space of the variables r_i. The ordering chosen in (60) is, however, necessary, given that the "larger" variables can have negative powers. Recall that the MCI method derives in large measure its power from the presence of these negative powers. With this ordering, all values remain finite during the intermediate stages of the calculations of the integrals given that as the integrations progress toward the leftmost integral, the negative powers of the larger radial variables are offset by the positive powers carried on from the "smaller" radial variables.

V. CONCLUSIONS

We have introduced a modification to the configuration-interaction method that departs from the standard approach in two ways: the use of ordered one-electron radial variables and of generalized angular functions that are linear combinations of large numbers of the coupled spherical harmonics used in the CI method.

The use of ordered radial variables improves the radial convergence of the basis sets by over ten orders of magnitude with a small number of functions. On the other hand, the extreme simplicity of the radial integrals in the standard CI method is lost. The present integrations are slightly more complex but simpler than those necessary for calculations involving correlated basis sets. In the case of Slater-type basis functions, all the integrals can be performed analytically both in the case of a point nucleus or in the case of a finite-nuclear-size potential.

The generalized angular functions introduced can be used with any set of radial functions. This technique mixes in advance a large number of coupled spherical harmonics with the correct total angular momentum. The degree or nature of the mixing is controlled by a set of (angular) nonlinear parameters. In this way one is able to introduce in the CI calculations a very large number of angular configurations, at least an order of magnitude greater than the largest number of angular configurations that one is able to mix in the standard CI method. In this way, the angular convergence is vastly improved as is the number of significant digits in the energy eigenvalues that one is able to obtain. For example, the *best* available standard CI calculation for the ground state of helium yields an accuracy of 2×10^{-5} a.u. That same accuracy was obtained by the present work using only three generalized angular functions in a basis set of only 98 two-electron basis functions, a calculation that is easily performed on a microcomputer. On the other hand, to match the accuracy of 7.5×10^{-9} a.u. obtained in this paper, the conventional CI method would need over a 10^6 two-electron functions [4]. Still, work to better understand and improve this angular representation must be pursued.

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