Configuration-interaction calculations with infinite angular expansions

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A simplification of the modified configuration-interaction (MCI) method [S. P. Goldman, Phys. Rev. A **52**, 3718 (1995)] is introduced. In its original form, the MCI method improves dramatically the convergence of standard CI calculations by a modification of the radial representation and an *a priori* mixing of a large number of angular configurations. In this work, the large but finite number of angular configurations mixed is replaced by an *infinite* number of configurations. Angular integrations are performed in closed form, resulting in simpler angular momentum calculations. Numerical accuracy and stability are substantially improved as one avoids handling very large values of angular momentum quantum numbers. As a result, calculations involving very high angular mixing can be done with a much shorter amount of CPU time. This angular method can be used in the framework of CI or MCI (i.e., using standard or *ordered* radial electron coordinates). [S1050-2947(97)08602-2]

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I. INTRODUCTION

The standard configuration-interaction (CI) method has been very widely used and is still very widely used in its unaltered form to perform calculations on systems of several electrons, although it is well known that the convergence patterns of CI are very slow [1,2]. At the heart of CIs success is a straightforward simplicity and ease of implementation that results from the expansion of the interelectron potential in terms of single-electron spherical coordinates. Consider, for example, the case of the helium Hamiltonian (atomic units will be used throughout this paper)

$$H=-\tfrac{1}{2}\nabla_{\mathbf{r}_1}^2-\tfrac{1}{2}\nabla_{\mathbf{r}_2}^2-\frac{Z}{r_1}-\frac{Z}{r_2}+\frac{1}{r_{12}}\,, \tag{1}$$

in which, for the purpose of CI calculations, the electron-electron potential is expanded as

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

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, for example, the two-electron basis functions for a state with total angular momentum L will be of the form

$$\psi_i^{\mathrm{CI}}=f_{1,i}(r_1)f_{2,i}(r_2)\Lambda_{l_{1i}l_{2i}}^{LM}(\hat{\mathbf{r}}_1,\hat{\mathbf{r}}_2)\pm\mathbf{r}_1\rightleftharpoons\mathbf{r}_2\,, \tag{3}$$

where

$$\Lambda_{l_{1i}l_{2i}}^{LM}(\hat{\mathbf{r}}_1,\hat{\mathbf{r}}_2)=\sum_{m_1,m_2}\langle l_{1i}m_1l_{2i}m_2|LM\rangle Y_{l_{1i},m_1}(\hat{\mathbf{r}}_1)Y_{l_{2i},m_2}(\hat{\mathbf{r}}_2)\ . \tag{4}$$

Recently, a modification to standard CI was introduced [3] that results in a vast improvement on the accuracies obtained using standard CI calculations. This new method, called the modified configuration-interaction (MCI) method, introduced two major changes to standard CI: (i) the use of ordered radial coordinates which improved the radial convergence of CI calculations by over nine orders of magnitude, and (ii) the mixing *a priori* of a large number of spherical configurations which results in a much faster rate of convergence. In this paper we shall not concern ourselves with the radial functions used, but we shall concentrate on a new type of generalized angular representations. These angular basis functions will provide a vast improvement in convergence over the usual (simple) functions $\Lambda_{l_{1i}l_{2i}}^{LM}(\hat{\mathbf{r}}_1,\hat{\mathbf{r}}_2)$ [Eq. (4)]. The angular functions introduced here can be used with *any* type of radial functions of the CI or MCI types. In other words, the angular modification introduced here will result in a vast improvement in convergence and therefore in accuracy when applied to standard CI calculations.

The modified angular functions introduced in this paper are both a generalization and a simplification of the original angular functions introduced by MCI. We start then with a short review of the MCI angular strategy.

In standard CI calculations, the basis set used is composed of basis functions containing each one set of coupled spherical harmonics [Eq. (3)], all 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 different basis functions including different values of l_1 and l_2. Correlation effects enter in the calculations as these different angular functions are mixed by the infinite angular sum in Eq. (2) upon the diagonalization of the Hamiltonian matrix. As a result, one obtains a wave function containing *linear* combinations of

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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. In MCI the angular convergence of the CI calculations is vastly improved by introducing an *a priori* superposition of angular functions that depends on a set of *nonlinear* variational parameters. In other words, rather than letting the diagonalization do the work of mixing angular configurations, one starts with a set of angular functions in which spherical harmonics are already mixed in large quantities. These functions are written in terms of a few (nonlinear) parameters that are varied and optimized through energy minimization. In other words, MCI introduces the linear combinations of coupled spherical harmonics,

$$\Theta^{LM}_{\tilde{l}_1\tilde{l}_2}(\hat{\mathbf{r}}_1,\hat{\mathbf{r}}_2)=\sum_{i=1}^{N_\Theta} C^i_{\tilde{l}_1\tilde{l}_2}(\mathbf{u})\Lambda^{LM}_{l_{1i}l_{2i}}(\hat{\mathbf{r}}_1,\hat{\mathbf{r}}_2)\ , \tag{5}$$

where $\mathbf{u}$ denotes a set of nonlinear (angular) parameters u_1, $u_2,\ldots,u_{n_u}$. 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 $\mathbf{u}=\mathbf{0}$ in the case of no correlation:

$$\lim_{\mathbf{u}\to\mathbf{0}} \Theta^{LM}_{\tilde{l}_1\tilde{l}_2}(\hat{\mathbf{r}}_1,\hat{\mathbf{r}}_2)=\Lambda^{LM}_{l_1l_2}(\hat{\mathbf{r}}_1,\hat{\mathbf{r}}_2)\ . \tag{6}$$

The power of this approach is based on the fact that a small number n_u of angular parameters control 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 [1] rather than the ten or so that is the most that can be used in standard CI. 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. This simple technique results in energy eigenvalues that are several orders of magnitude more accurate than those of standard CI with much smaller basis set sizes. There are however a couple of concerns as the number N_Θ of angular functions becomes very large. The angular portion of the calculations involves integrals of the type

$$\int\int \Lambda^{*LM}_{l_{1a}l_{2a}}(\hat{\mathbf{r}}_1,\hat{\mathbf{r}}_2)\omega_l\Lambda^{LM}_{l_{1b}l_{2b}}(\hat{\mathbf{r}}_1,\hat{\mathbf{r}}_2)d\Omega_1 d\Omega_2,$$

where $\Lambda^{LM}_{l_{1i}l_{2i}}(\hat{\mathbf{r}}_1,\hat{\mathbf{r}}_2)$ is defined in Eq. (4), and ω_l is given by

$$\omega_l=(-1)^l\frac{4\pi}{(2l+1)^{1/2}}\Lambda^{00}_{ll}=P_l(\cos\theta_{12})\ , \tag{7}$$

where $P_l(z)$ is a Legendre polynomial and $\theta_{12}=\hat{\mathbf{r}}_1\cdot\hat{\mathbf{r}}_2$. This integral is calculated using the orthonormality of the $\Lambda^{LM}_{l_{1i}l_{2i}}$ and the relation

$$\omega_l\ \Lambda^{L_aM_a}_{l_{1a}l_{2a}}=\sum_{k_1,k_2} b^{L_a}_{l_ak;l}\Lambda^{L_aM_a}_{k_1k_2}, \tag{8}$$

where, for arbitrary values of the angular momentum quantum numbers, b is

$$\begin{aligned} b^L_{l_al_b;l}&=b^L_{l_{1a}l_{2a}l_{1b}l_{2b};l}\\ &=(-1)^{l+L}\frac{[l_{1a},l_{2a},l_{1b},l_{2b}]^{1/2}}{2l+1}\\ &\quad\times T_{l_{1a}l_{1b};l}T_{l_{2a}l_{2b};l}\begin{Bmatrix} l_{1a} & l_{1b} & l\\ l_{2b} & l_{2a} & L\end{Bmatrix}, \end{aligned} \tag{9}$$

with

$$T_{k_1k_2;k}=T_{k_2k_1;k}=(-1)^k(2k+1)^{1/2}\begin{pmatrix} k_1 & k & k_2\\ 0 & 0 & 0\end{pmatrix}, \tag{10}$$

where we used the standard notation

$$[a,b,\ldots]=(2a+1)(2b+1)\cdots\ . \tag{11}$$

The quantity $T_{k_1k_2;k}$ is nonzero only for

$$k=|k_1-k_2|,\ \ |k_1-k_2|+2,\ldots,k_1+k_2 \tag{12}$$

and satisfies

$$\sum_k\ T^2_{k_1k_2;k}=1$$

and

$$T_{0k_1;k_2}=T_{k_1k_2;0}=\delta_{k_1k_2}\ .$$

With these results we obtain

$$\int\int \Lambda^{*LM}_{l_{1a}l_{2a}}(\hat{\mathbf{r}}_1,\hat{\mathbf{r}}_2)\omega_l\Lambda^{LM}_{l_{1b}l_{2b}}(\hat{\mathbf{r}}_1,\hat{\mathbf{r}}_2)d\Omega_1 d\Omega_2 \tag{13}$$

$$=b^L_{l_al_b;l}. \tag{14}$$

Notice that a sum over q_i involving the coefficients $T_{q_1q_2;q_3}$, where q_i is any of its indices, will always be taken with $\delta q_i=2$ between $|q_j-q_k|\leqslant q_i\leqslant q_j+q_k$, where q_j and q_k are the two other indices in $T_{q_1q_2;q_3}$. In the case $L=0$, for example, Eq. (9) becomes

$$b^0_{l_a,l_b;l}=(-1)^l[l_{1a},l_{1b}]^{1/2}\delta_{l_{1a}l_{2a}}\delta_{l_{1b}l_{2b}}\begin{pmatrix} l_{1a} & l & l_{1b}\\ 0 & 0 & 0\end{pmatrix}^2\ .$$

As a consequence, (i) the number of angular overlaps (14) to calculate increases quadratically with N_Θ, and (ii) the 3-j symbols involved in the calculation of these overlaps involve very large angular momentum quantum numbers, making it difficult to maintain numerical accuracy (e.g., one has to calculate quantities involving factorials that can easily exceed factorials of thousands). Notice that the overlaps (14) appear in standard CI as well as MCI, so that these are problems *inherent* to CI. Standard CI did not encounter these problems yet because it is *unable* to deal with more than a few angular momenta before exceeding machine limitations. In Sec. II

proceed to formulate a strategy that addresses these concerns, based on allowing $N_\Theta \to \infty$ in the expansion (5).

Before we proceed, we introduce another definition that will be useful for the rest of this paper. We introduce the general integral

$$b^L_{l_a l_b;k_1 k_2} = \int\int \Lambda^{*LM}_{l_{1a} l_{2a}}(\hat{\mathbf{r}}_1,\hat{\mathbf{r}}_2)\omega_{k_1}\omega_{k_2}\Lambda^{LM}_{l_{1b} l_{2b}} \times(\hat{\mathbf{r}}_1,\hat{\mathbf{r}}_2)d\Omega_1 d\Omega_2, \tag{15}$$

a calculation of which yields

$$b^L_{l_a l_b;k_1 k_2} = \sum_k T^2_{k_1 k_2;k} b^L_{l_a l_b;k} \tag{16}$$

and

$$b^L_{l_a l_b;k0} = b^L_{l_a,l_b;0k} = b^L_{l_a l_b;k}, \tag{17}$$

with $b^L_{l_a l_b;k}$ given in Eq. (9).

II. INFINITE EXPANSIONS

A. Angular functions

In this section we introduce angular basis functions that perform an *a priori* mixing of an infinite number of angular orbitals. We call these angular functions F_a, and give them the general form

$$F_a = \Lambda^{L_a M_a}_{l_{1a} l_{2a}} G_a(\omega_1)\ , \tag{18}$$

where $\Lambda^{L_a M_a}_{l_{1a} l_{2a}}$ is the usual single angular basis function of standard CI, defined in Eq. (4) and ω_1 is defined in Eq. (7).

The method is based on requiring the function $G_a(\omega_1)$ to satisfy the following requirements: (i) G_a can be expanded in the form

$$G_a(\omega_1) = \sum_{n=0}^{\infty} G_{a,n}\frac{\omega_1^n}{n!}, \tag{19}$$

(Taylor expansion), where we have used the notation

$$f_{,n} = \left.\frac{d^n f(x)}{dx^n}\right|_{x=0},$$

(ii) G_a can be expanded in the form

$$G_a(\omega_1) = \sum_{l=0}^{\infty} c^a_l \omega_l, \tag{20}$$

where c^a_l are constants, and (iii) G_a satisfies an associative condition that we denote with the shorthand notation

$$G_a(\omega_1)G_b(\omega_1) = G_{a+b}(\omega_1). \tag{21}$$

The function $G_a(\omega_1)$ introduces the *a priori* angular mixing. This can be seen explicitly using the expansion of Eq. (20) in the generalized angular function F_a:

$$F_a = \sum_{l=0}^{\infty} c^a_l \omega_l \Lambda^{L_a M_a}_{l_{1a} l_{2a}} = \sum_{l=0}^{\infty}\sum_{k_1,k_2} c^a_l b^{L_a}_{l_a k;l}\Lambda^{L_a M_a}_{k_1 k_2},$$

where the coefficients $b^{L_a}_{l_a k;l}$ are defined in Eq. (9). The power-series expansion will be used to find a closed-form expression for the operator L_i^2, while the associative condition will help to simplify the angular matrix elements.

In spherical coordinates, the Hamiltonians (1) and (2) can be written as

$$H = -\frac{1}{2r_1}\frac{\partial^2}{\partial r_1^2}r_1 - \frac{1}{2r_2}\frac{\partial^2}{\partial r_2^2}r_2 + \frac{1}{2}\frac{L_1^2}{r_1^2} + \frac{1}{2}\frac{L_2^2}{r_2^2} - \frac{Z}{r_1} - \frac{Z}{r_2} + \sum_{\lambda=0}^{\infty}\frac{r_<^\lambda}{r_>^{\lambda+1}}\omega_\lambda, \tag{22}$$

where ω_λ is defined in Eq. (7) and $\mathbf{L}_i$ is the angular momentum operator for the ith electron. In order for the method to be successful, we need to be able to calculate in closed form the angular matrix elements

$$\langle F_a|L_i^2|F_b\rangle = \int\int \Lambda^{*L_a M_a}_{l_{1a} l_{2a}} G^*_a(\omega_1) L_i^2 \Lambda^{L_b M_b}_{l_{1b} l_{2b}} \times G_b(\omega_1)d\Omega_1 d\Omega_2$$

and

$$\langle F_a|\omega_l|F_b\rangle = \int\int \Lambda^{*L_a M_a}_{l_{1a} l_{2a}} G^*_a(\omega_1)\omega_l \Lambda^{L_b M_b}_{l_{1b} l_{2b}} \times G_b(\omega_1)d\Omega_1 d\Omega_2.$$

In the following sections we shall find simple expressions for these matrix elements that avoid the sums over expansions of the type of Eq. (5).

B. Operators L_i^2 and ω_l

We start by finding a closed-form expression for $L_i^2 G(\omega_1)$, where $G(\omega_1)$ is any function that satisfies the conditions (19)–(21). We first note that

$$\begin{aligned} L_i^2(\omega_1^n) &= \mathbf{L}_i\cdot(\mathbf{L}_i\omega_1^n) = n\mathbf{L}_i\cdot[(\mathbf{L}_i\omega_1)\omega_1^{n-1}] \\ &= n(L_i^2\omega_1)\omega_1^{n-1} + n(n-1)(\mathbf{L}_i\omega_1)^2\omega_1^{n-2} \\ &= 2n\omega_1^{n-1} + n(n-1)(\mathbf{L}_i\ \omega_1)^2\omega_1^{n-2}. \end{aligned}$$

We can use this result in expansion (19):

$$\begin{aligned} L_i^2 G_a(\omega_1) &= \sum_{n=1}^{\infty}\frac{2\omega_1^n}{(n-1)!}G_{a,n} + \sum_{n=2}^{\infty}(\mathbf{L}_i\omega_1)^2\frac{\omega_1^{n-2}}{(n-2)!}G_{a,n} \\ &= 2\omega_1\sum_{n=0}^{\infty}\frac{\omega_1^n}{n!}G'_{a,n} + (\mathbf{L}_i\omega_1)^2\sum_{n=0}^{\infty}\frac{\omega_1^n}{n!}G''_{a,n} \\ &= 2\omega_1\frac{\partial G_a}{\partial\omega_1} + (\mathbf{L}_i\omega_1)^2\frac{\partial^2 G_a}{\partial\omega_1^2} \end{aligned}$$

to finally obtain

$$L_i^2 G_a(\omega_1) = 2\omega_1 \frac{\partial G_a}{\partial \omega_1} + \frac{2}{3}(\omega_2 - \omega_0)\frac{\partial^2 G_a}{\partial \omega_1^2}. \tag{23}$$

The result of the last equation is crucial for the success of the method presented in this paper, and presents a fundamental departure from methods based on expansion (5). For those methods, including standard CI, a concise result like the one in Eq. (23) is not possible, and an explicit sum over partial angular momenta is necessary. Such a sum is fully avoided when an infinite angular expansion is used.

Armed with the powerful result of Eq. (23), we can now address the problem of L_i^2 acting on the general angular functions F_a [Eq. (18)]:

$$\begin{aligned} L_i^2 F_a &= L_i^2[\Lambda^{L_a M_a}_{l_{1a} l_{2a}} G_a(\omega_1)] \\ &= l_{ia}(l_{ia}+1)\Lambda^{L_a M_a}_{l_{1a} l_{2a}} G_a(\omega_1) + \Lambda^{L_a M_a}_{l_{1a} l_{2a}}[L_i^2 G_a(\omega_1)] \\ &\quad + 2(\mathbf{L}_i \Lambda^{L_a M_a}_{l_{1a} l_{2a}}) \cdot (\mathbf{L}_i G_a(\omega_1)), \end{aligned}$$

which results in

$$\begin{aligned} L_i^2 F_a &= L_i^2[\Lambda^{L_a M_a}_{l_{1a} l_{2a}} G_a(\omega_1)] \\ &= l_{ia}(l_{ia}+1)\Lambda^{L_a M_a}_{l_{1a} l_{2a}}\left[G_a(\omega_1) - \omega_1 \frac{\partial G_a(\omega_1)}{\partial \omega_1}\right] \\ &\quad - \sum_{k_1,k_2} k_i(k_i+1) b^{L_a}_{l_a k;1} \Lambda^{L_a M_a}_{k_1 k_2} \frac{\partial G_a(\omega_1)}{\partial \omega_1} \\ &\quad + \tfrac{2}{3}(\omega_2 - \omega_0)\Lambda^{L_a M_a}_{l_{1a} l_{2a}} \frac{\partial^2 G_a(\omega_1)}{\partial \omega_1^2}, \end{aligned} \tag{24}$$

where $b^{L_a}_{l_a k;1}$ is defined in Eq. (9), and the sum is restricted to the values $k_1 = \pm l_{1a}$ and $k_2 = \pm l_{2a}$.

The formula of Eq. (24) constitutes one of the most important results of this work. Given that it involves only a few terms, it avoids the very high values of angular momentum quantum numbers present in the previous generation of MCI. This implies a greater numerical accuracy as well as avoiding the large number of terms in the otherwise explicit expansion of L_i^2 acting on each partial wave in expansion (5).

We use now the expressions introduced in Sec. II A, and the expansion of Eq. (20) to calculate the angular matrix elements of ω_l in the basis set F_a to obtain

$$\langle F_a | \omega_l | F_b \rangle = \sum_k c_k^{a+b} b^L_{l_a l_b; lk}, \tag{25}$$

where the sum is taken over all values of k that yield nonzero n-j symbols in $\omega^L_{l_a l_b; lk}$. These matrix elements are needed for the computation of the electron-electron potential

$$\sum_{l=0}^{\infty} \frac{r_<^l}{r_>^{l+1}} \omega_l. \tag{26}$$

The sum in Eq. (26) cannot be avoided by writing it in closed form, as was the case for the operator L_i^2. The reason is that the coefficients in the sum depend on the radial matrix elements. It has therefore to be calculated term by term until a desired convergence is achieved. This feature *characterizes* the configuration-interaction method. For these terms, the associative rule (21) is instrumental to simplify substantially the matrix elements.

III. ANGULAR BASIS SETS

A. Exponential basis functions

An example of an angular function that satisfies the three conditions of Eqs. (19)–(21) is given by the exponential function

$$g_a = e^{\gamma_a \omega_1}, \tag{27}$$

for which

$$\text{(i)} \qquad g_a = e^{\gamma_a \omega_1} = \sum_{n=0}^{\infty} \frac{\gamma_a^n}{n!} \omega_1^n, \tag{28}$$

$$\text{(ii)} \qquad g_a = e^{\gamma_a \omega_1} = \sum_{l=0}^{\infty} (2l+1) u_l(\gamma_a) \omega_l, \tag{29}$$

$$\text{(iii)} \qquad g_a\, g_b = e^{\gamma_a \omega_1} e^{\gamma_b \omega_1} = e^{(\gamma_a + \gamma_b)\omega_1}, \tag{30}$$

where $u_l(z)$ in Eq. (29) is a modified spherical Bessel function of the first kind [4]:

$$u_l(z) = \left(\frac{\pi}{2z}\right)^{1/2} I_{l+\frac{1}{2}} = (-i)^l j_l(iz). \tag{31}$$

The functions $u_l(z)$ can be written in terms of a series expansion

$$\begin{aligned} u_l(z) = \frac{z^l}{1\times 3\times 5\times \cdots \times (2l+1)}\Bigg[1 + \frac{\frac{1}{2}z^2}{1!(2l+3)} \\ + \frac{(\frac{1}{2}z^2)^2}{1!(2l+3)(2l+5)} + \cdots \Bigg], \end{aligned}$$

or in terms of hyperbolic functions

$$u_l(z) = v_l(z)\sinh z + v_{-l-1}(z)\cosh z,$$

$$v_0(z) = z^{-1}, \qquad v_1(z) = -z^{-2},$$

$$v_{l-1}(z) - v_{l+1}(z) = (2l+1) z^{-1} v_l(z),$$

and satisfy the useful recurrence relations [4]

$$u_l(z) = \frac{z}{2l+1}[u_{l-1}(z) - u_{l+1}(z)], \tag{32}$$

$$\frac{du_l(z)}{dz} = \frac{l}{2l+1} u_{l-1}(z) + \frac{l+1}{2l+1} u_{l+1}(z). \tag{33}$$

Although we shall concentrate on the functions g_a [Eq. (27)] for the purpose of illustrating the method, later in the paper we shall introduce other possible choices for the generalized angular functions $G_a(\omega_1)$.

We define then the angular basis functions

$$\varphi_l^a = \varphi^a_{l_{1a}l_{2a}} = \Lambda^{L_a M_a}_{l_{1a}l_{2a}} e^{\gamma_a \omega_1}. \tag{34}$$

We now apply the results of Sec. II to the functions φ_l^a of Eq. (34) to obtain

$$\begin{aligned} L_i^2 \varphi_l^a &= L_i^2 [\Lambda^{L_a M_a}_{l_{1a}l_{2a}} e^{\gamma_a \omega_1}] \\ &= l_{ia}(l_{ia}+1)(1-\gamma_a\omega_1)\varphi_l^a \\ &\quad - \gamma_a \sum_{k_1,k_2} k_i(k_i+1) b^{L_a}_{l_a k;1} \varphi_k^a \\ &\quad + \tfrac{2}{3}\gamma_a^2(\omega_2-\omega_0)\varphi_l^a. \end{aligned} \tag{35}$$

This expression satisfies the correct boundary condition

$$\lim_{\gamma_a \to 0} L_i^2 \varphi_l^a = l_{ia}(l_{ia}+1)\varphi_l^a .$$

We can now write, using the shorthand notation

$$\gamma = \gamma_a + \gamma_b , \tag{36}$$

the matrix elements of L_i^2 for the most general basis set φ_l^a:

$$\begin{aligned} \langle \varphi_l^a | L_i^2 | \varphi_l^b \rangle = \sum_q (2q+1) u_q(\gamma) \Big\{ & l_{ib}(l_{ib}+1) \\ & \times [b^L_{l_a l_b;q} - \gamma_b b^L_{l_a l_b;1q}] - \gamma_b \sum_{k_1,k_2} k_i(k_i+1) \\ & \times b^L_{l_b k;1} b^L_{l_a k;q} + \tfrac{2}{3}\gamma_b^2 [b^L_{l_a l_b;2q} - b^L_{l_a l_b;q}] \Big\}, \end{aligned} \tag{37}$$

where the sum over q is limited to the values for which the n-j symbols involved are nonzero [Eq. (12)], resulting in general in a small number of contributing terms. For example, for the bound states of heliumlike ions we obtain

$$\langle \varphi^a_{0l_{2a}} | L_1^2 | \varphi^b_{0l_{2b}} \rangle = \delta_{l_{2a}l_{2b}} \left\{ 2\frac{\gamma_a\gamma_b}{\gamma} u_1(\gamma) \right\} , \tag{38}$$

$$\begin{aligned} \langle \varphi^a_{0l_{2a}} | L_2^2 | \varphi^b_{0l_{2b}} \rangle = \delta_{l_{2a}l_{2b}} \Big\{ & -2\frac{\gamma_b^2}{\gamma} u_1(\gamma) + l_{2b}(l_{2b}+1) \\ & \times [u_0(\gamma) - \gamma_b u_1(\gamma)] + \gamma_b u_1(\gamma) \\ & \times \sum_{k=|l_{2b}-1|}^{l_{2b}+1} k(k+1) T^2_{l_{2b}1;k} \Big\}, \end{aligned} \tag{39}$$

$$\begin{aligned} \langle \varphi^a_{l_{1a}0} | L_1^2 | \varphi^b_{0l_{2b}} \rangle = \delta_{l_{1a}l_{2b}} \Big\{ & -\tfrac{2}{3}\gamma_b^2 u_{l_{2b}}(\gamma) \\ & + 2\gamma_b \sum_{k=|l_{2b}-1|}^{l_{2b}+1} T^2_{l_{2b}1;k} u_k(\gamma) \\ & + \tfrac{2}{3}\gamma_b^2 \sum_{k=|l_{2b}-2|}^{l_{2b}+2} T^2_{l_{2b}2;k} u_k(\gamma) \Big\}, \end{aligned} \tag{40}$$

$$\begin{aligned} \langle \varphi^a_{l_{1a}0} | L_2^2 | \varphi^b_{0l_{2b}} \rangle = \delta_{l_{1a}l_{2b}} \Big\{ & [l_{2b}(l_{2b}+1) - \tfrac{2}{3}\gamma_b^2] u_{l_{2b}}(\gamma) \\ & + \gamma_b \sum_{k=|l_{2b}-1|}^{l_{2b}+1} k(k+1) T^2_{l_{2b}1;k} u_k(\gamma) \\ & - \gamma_b l_{2b}(l_{2b}+1) \sum_{k=|l_{2b}-1|}^{l_{2b}+1} T^2_{l_{2b}1;k} u_k(\gamma) \\ & + \tfrac{2}{3}\gamma_b^2 \sum_{k=|l_{2b}-2|}^{l_{2b}+2} T^2_{l_{2b}2;k} u_k(\gamma) \Big\} , \end{aligned} \tag{41}$$

where $\delta k = 2$ in all the sums.

Again, there are only a few terms involved in the calculation of the matrix elements of L_i^2 and these involve small angular momentum quantum numbers. This replaces the large number N_Θ of terms in the first generation of MCI involving angular momenta of the order of N_Θ.

For the matrix elements of ω_l, needed to calculate the electron-electron interaction potential [Eq. (26)], we obtain

$$\langle \varphi_l^a | \omega_l | \varphi_l^b \rangle = \sum_k (2k+1) u_k(\gamma) b_{l_a l_b;kl} , \tag{42}$$

which for the bound states of helium, for example, yields

$$\langle \varphi^a_{0l_{2a}} | \omega_l | \varphi^b_{0l_{2b}} \rangle = \delta_{l_{2a}l_{2b}} u_l(\gamma) \tag{43}$$

and

$$\langle \varphi^a_{l_{1a}0} | \omega_l | \varphi^b_{0l_{2b}} \rangle = \delta_{l_{1a}l_{2b}} \sum_k T_{l_{2b}l;k} u_k(\gamma) , \tag{44}$$

with $\gamma = \gamma_a + \gamma_b$.

We now show examples of angular functions that optimize the variational energy of two of the bound states of helium. In the calculations, we follow the strategy of MCI in two respects: (i) we use basis functions that include the generalized radial structure of MCI, i.e., our basis functions are of the form

$$\phi_{ij} = e^{-\alpha_i r_1 - \beta_i r_2 - \sigma_i r_< - \tau_i r_>} r_1^{a_i} r_2^{b_i} r_<^{s_i} r_>^{t_i} \varphi_l^j \pm \mathbf{r}_1 \rightleftharpoons \mathbf{r}_2 ,$$

and (ii) the basis set is divided into two parts: the basis functions in which both $r_<$ and $r_>$ appear with positive powers ($s_i > 0$ and $t_i > 0$) (call these basis functions ϕ_{ij}^+), and those in which the powers of $r_>$ are negative ($t_i < 0$) (call these ϕ_{ij}^-). We then call the corresponding angular functions φ_l^{j+} and φ_l^{j-}, and adopt the MCI strategy to optimize them separately. Interestingly φ_l^{j+} and φ_l^{j-} are of a very different

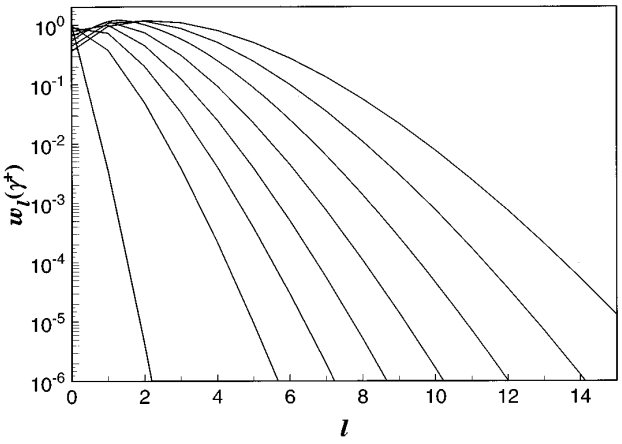

FIG. 1. Relative distribution of single-orbital angular functions for a basis set with eight exponential-type generalized angular functions, for the ϕ^+ basis set optimized for the $1\,^1S$ state of helium. l refers to the quantum number of ω_l, and w_l is the normalized coefficient in the expansion of $e^{\gamma\omega_1}$.

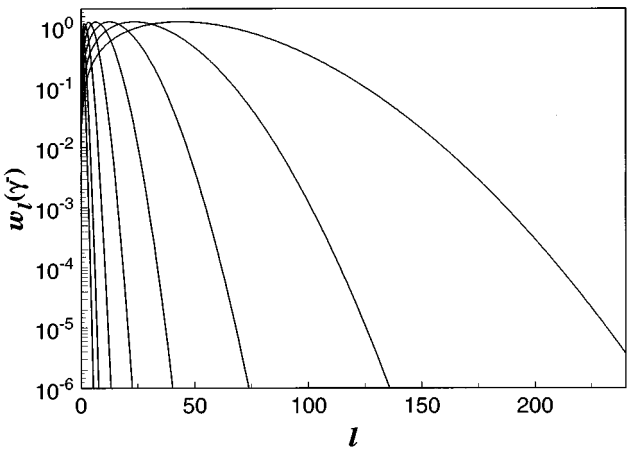

FIG. 2. Relative distribution of single-orbital angular functions for a basis set with eight exponential-type generalized angular functions, for the ϕ^- basis set optimized for the $1\,^1S$ state of helium. l refers to the quantum number of ω_l, and w_l is the normalized coefficient in the expansion of $e^{\gamma\omega_1}$.

nature. Consider, for example, a calculation using eight angular functions for the ϕ_{ij}^+ and the ϕ_{ij}^- basis functions, i.e., $j=1,2,\ldots,j_{\max}$, with $j_{\max}=8$. The optimization process can be accelerated by writing the complete set of angular nonlinear parameters γ_j in terms of only two variational parameters (we call them x and y) in the following way:

$$\gamma_j=\sinh[(j-1)x+y] \quad \text{with} \quad j=1,2,\ldots,j_{\max}. \tag{45}$$

In this way only two parameters need to be optimized. The functional form of Eq. (45) was not derived from a fundamental principle, but rather was found experimentally to approximate well the optimized angular nonlinear parameters of a large set of trial runs.

For the ground state of helium, for a double precision calculation with $j_{\max}=8$, yielding a precision of $\delta E/E\approx 10^{-8}$, we obtain the following optimized values: $x^+=0.385\,812$, $y^+=-3.493\,391\times10^{-3}$, $x^-=1.226\,034$, and $y^-=-0.318\,313$. In order to analyze these results, we define the *normalized* exponential angular function

$$\tilde{g}_a(\omega_1)=\frac{g_a(\omega_1)}{[u_0(\gamma_a)]^{1/2}} \tag{46}$$

satisfying

$$\int\int |\tilde{g}_a(\omega_1)|^2\, d\Omega_1 d\Omega_2=1\ .$$

Using Eq. (29), we can then write

$$\tilde{g}_a(\omega_1)=\sum_l w_l(\gamma_a)\ \omega_l, \tag{47}$$

where

$$w_l(\gamma_a)=\frac{1}{[u_0(2\gamma_a)]^{1/2}}\,(2l+1)\ u_l(\gamma_a) \tag{48}$$

will give us the relative distribution of different values of different values of l in $\tilde{g}_a$. This distribution is presented in Figs. 1 and 2 for the ϕ^+ and ϕ^- states, respectively. Each curve in these diagrams corresponds to one of the eight values of γ in Eq. (45) for the ground state of helium, with the values of γ increasing for the curves further to the right. The mixing of different angular orbitals is clearly seen. The larger the value of γ, the larger the value of l at which the angular distribution peaks and the larger the width of that distribution. Both peak and width scale roughly as $\gamma^{1/2}$. It is interesting to observe the fundamentally different angular nature of the angular distributions between the ϕ^+ and ϕ^- basis functions. The radial component of the ϕ^+ basis functions peaks further away from the nucleus than that of the ϕ^- functions, and therefore is affected less by the correlation effects. As a consequence we find that in the ϕ^+ the number of angular orbitals mixed is an order of magnitude smaller than that with the same weight in the ϕ^- basis functions. The same behavior is observed in Figs. 3 and 4, which are the corresponding ones for the $3\,^1P$ state of helium. In this case eight generalized orbitals were also used [i.e., $j_{\max}=8$ in Eq. (45)]. The following optimized values were used: $x^+=0.526\,817$, $y^+=2.554\,357\times10^{-5}$, $x^-=0.921\,248$, and $y^-=-0.060\,222$. Notice that the positive-power functions ϕ^+ use a similar small number of angular distributions in the $1\,^1S$ and $3\,^1P$ cases, while the negative ones mix a smaller number of orbitals in the $3\,^1P$ case than in the $1\,^1S$ case, a result of the smaller correlation effects. Notice also that, in both cases, the optimization favors the inclusion for the ϕ^+ states, of an angular function with $\gamma\approx 0$ which results in the original unperturbed (uncorrelated) two-electron angular state being part of the basis set.

B. Basis functions with exponentials and powers

The basis set of Sec. III A can be generalized to the set

$$\eta_l^a=\eta_{l_{1a}l_{2a}}^a=\Lambda_{l_{1a}l_{2a}}^{L_aM_a}\omega_1^{n_a}e^{\gamma_a\omega_1}.$$

This extension can be done easily using the property

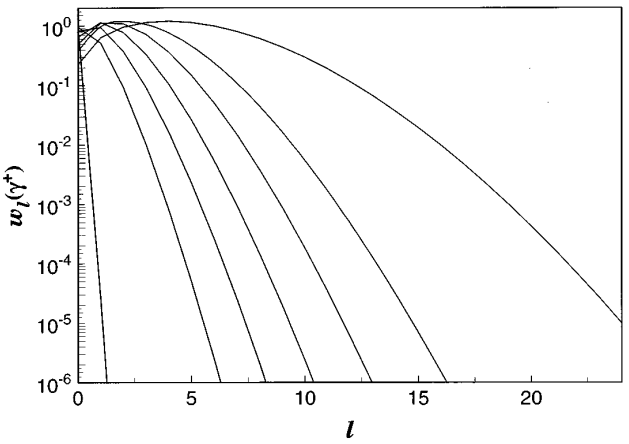

FIG. 3. Relative distribution of single-orbital angular functions for a basis set with eight exponential-type generalized angular functions, for the ϕ^+ basis set optimized for the $3\,^1P$ state of helium. l refers to the quantum number of ω_l, and w_l is the normalized coefficient in the expansion of $e^{\gamma\omega_1}$.

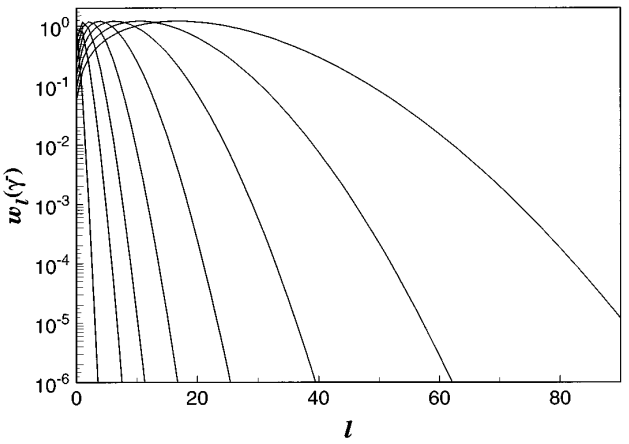

FIG. 4. Relative distribution of single-orbital angular functions for a basis set with eight exponential-type generalized angular functions, for the ϕ^- basis set optimized for the $3\,^1P$ state of helium. l refers to the quantum number of ω_l, and w_l is the normalized coefficient in the expansion of $e^{\gamma\omega_1}$.

$$\eta_l^a=\omega_1^{n_a}\varphi_l^a=\frac{\partial^{n_a}}{\partial\gamma_a^{n_a}}\varphi_l^a\,,$$

with φ_l^a the exponential basis functions defined in Eq. (34).

With this result we obtain simply

$$\langle\eta_l^a|L_i^2|\eta_l^b\rangle=\frac{\partial^{n_a+n_b}}{\partial\gamma^{n_a+n_b}}\langle\varphi_l^a|L_i^2|\varphi_l^b\rangle$$

and

$$\langle\eta_l^a|\omega_l|\eta_l^b\rangle=\frac{\partial^{n_a+n_b}}{\partial\gamma^{n_a+n_b}}\langle\varphi_l^a|\omega_l|\varphi_l^b\rangle\ .$$

These matrix elements can then be easily calculated using the results of Sec. III A and recurrence relations of the type of Eq. (33).

C. Exponentials of imaginary arguments

The basis set

$$\xi_l^a=\xi_{l_{1a}l_{2a}}^a=\Lambda_{l_{1a}l_{2a}}^{L_aM_a}e^{i\gamma_a\omega_1}$$

is very similar in structure to the previously introduced basis sets, with expansion (20) now given by

$$e^{i\gamma_a\omega_1}=\sum_{l=0}^{\infty}(2l+1)i^l j_l(\gamma_a)\omega_l\,,$$

where $j_l(\gamma)$ is a spherical Bessel function of the first kind [4]. These functions are automatically normalized. This basis set is relevant only within a multiexponential framework, as otherwise it reverts to traditional CI given that in the matrix elements the exponential factor cancels out through $(e^{i\gamma_a\omega_1})^*e^{i\gamma_a\omega_1}=1$. Within the multiexponential sets, there is one that makes the exponential factors orthogonal:

$$\frac{1}{16\pi^2}\int\int e^{-i(\gamma_a+n\pi)\omega_1}e^{i(\gamma_a+m\pi)\omega_1}d\Omega_1 d\Omega_2=\delta_{n,m},$$

where we used

$$\frac{1}{16\pi^2}\int\int e^{iz\omega_1}d\Omega_1 d\Omega_2=j_0(z)=\frac{\sin z}{z}.$$

All the formulas of Secs. III A and III B can be used by replacing u_l with $i^l j_l$. The matrix elements obtained will, in general, be complex. This could be avoided by using, instead of $e^{i\gamma_a\omega_1}$, the two basis sets $\cos(\gamma_a\omega_1)$ and $\sin(\gamma_a\omega_1)$.

D. Powers of rational functions

The basis set presented in this section presents a fundamental departure from those introduced earlier in the paper as it does not rely on an exponential function to satisfy the associative condition [Eq. (21)], but rather on powers of the square root of a second-order polynomial. The basis set has the form

$$\zeta_a=\Lambda_{l_{1a}l_{2a}}^{L_aM_a}\theta_a^{n_a}\,,\tag{49}$$

where

$$\theta_a=[1+\gamma_a^2-2\gamma_a\omega_1]^{1/2},\tag{50}$$

the power n_a of θ is a positive or negative integer, and γ_a is a variational parameter satisfying

$$|\gamma_a|<1\ .\tag{51}$$

The three conditions of Eqs. (19)–(21) are satisfied in the following way [5]:

$$\text{(i)}\quad\theta^n=\sum_{k=0}^{\infty}(1+\gamma^2)^{(n/2)-k}\frac{(-2\,\omega_1)^k}{k!\left(\frac{n}{2}+1\right)_{(-k)}}\,,\tag{52}$$

where

$$z_{(j)}=\frac{\Gamma(z+j)}{\Gamma(z)}\ ,$$

$$\text{(ii)}\quad \theta^n=\sum_{l=0}^{\infty} A_{nl}\omega_l, \tag{53}$$

with

$$A_{nl}=\frac{\left(-\frac{n}{2}\right)_{(l)}}{\left(\frac{1}{2}\right)_{(l)}}\gamma^l\ {}_2F_1\left(l-\frac{n}{2},-\frac{1+n}{2};l+\frac{3}{2};\gamma^2\right)\ ,$$

and

$$\text{(iii)}\qquad \theta^{n_a}\ \theta^{n_b}=\theta^{n_a+n_b}\ , \tag{54}$$

where ${}_2F_1$ is a hypergeometric function.

For the angular momentum operator we use Eq. (23) and

$$\frac{\partial\theta^n}{\partial\omega_1}=-n\gamma\theta^{n-2}$$

to initially obtain

$$L_1^2\theta^n=-2n\gamma\omega_1\theta^{n-2}+\tfrac{2}{3}(\omega_2-1)n(n-2)\gamma^2\theta^{n-4}\ .$$

Now using Eq. (53) and rewriting Eq. (50) as

$$\omega_1=-\frac{\theta^2}{2\gamma}+\frac{1+\gamma^2}{2\gamma}\ ,$$

after some algebra we obtain:

$$L_1^2\theta^n=\frac{n}{2}\left(\frac{n}{2}+1\right)\theta^n-2\left(\frac{n}{2}\right)^2(1+\gamma^2)\theta^{n-2}+\frac{n}{2}\left(\frac{n}{2}-1\right)(1-\gamma^2)\theta^{n-4}\ .$$

With these expressions in hand, all the necessary matrix elements can be simply calculated following the steps of the previous sections. Although this basis set does not have the flexibility of the ones in the previous sections, it has the advantage that it depends on a single overall nonlinear parameter to optimize.

IV. CONCLUSIONS

The angular convergence of calculations using the traditional CI method is very slow. This forces one to use very large arrays even for low accuracies, placing a strong limitation on the precision of the results. The MCI method, in its original form, is able to drastically increase the CI accuracy by mixing angular configurations in advance (i.e., before the diagonalization process). One can mix then a small or a large number of angular configurations, with the maximum number to mix decided by the sought accuracy and by the limitations on that accuracy imposed by the radial functions in the basis set. With that simple strategy, MCI is able to improve the accuracy of the CI results by several orders of magnitude with much smaller basis sets. In the cases in which correlation effects are very strong however, one needs to include a very large number of angular configurations. For example, for the ground state of helium to a relative accuracy of the order of 10^{-8} one needs of the order of 250–300 angular functions. Note that it is not a weakness of MCI, it is the number of angular configurations one would need in standard CI to obtain such an accuracy [2]. In this case, MCI is faced with the calculation of a very large number of matrix elements between the individual terms in expansion (5). These are the cases addressed by this paper, in which a vast simplification is introduced by the use of *infinite* admixtures of angular orbitals satisfying specific expansion and associative criteria. The accuracies obtained are similar to those using expansions (5) of MCI (as those were optimized for the accuracies obtained); however, the computations are much quicker (and tidier) given that the closed-form expressions derived involve a much smaller number of calculations, and the numerical accuracy is higher. For example, one is now able to perform calculations in double precision arithmetic that required before quadruple precision for the same level of accuracy. In a sense (and particularly if orthogonalized in advance), the angular functions F_a of Eq. (18) for which only L and M are good quantum numbers, replace the angular functions of CI based on the hydrogenic quantum numbers l_i.

The extension to systems composed of more than two electrons is straightforward. The angular momentum mixing follows the same rationale as traditional CI, only that an infinite number of orbitals are mixed in advance, or a finite number (as in MCI). To illustrate we shall consider the case of three electrons, in which the single-orbital angular functions can be written in terms of

$$\Lambda^{k_aLM}_{l_{1a}l_{2a}l_{3a}}(1,2;3)=\sum_{m_{ka},m_{3a}}\langle k_a m_{ka} l_{3a} m_{3a}|LM\rangle\Lambda^{k_a m_{ka}}_{l_{1a}l_{2a}}(\hat{\mathbf{r}}_1,\hat{\mathbf{r}}_2)\times Y_{l_{3a}m_{3a}}(\hat{\mathbf{r}}_3)\ .$$

The MCI extension will be given by

$$F_a(1,2;3)=\Lambda^{k_aLM}_{l_{1a}l_{2a}l_{3a}}(1,2;3)G_a(1,2,3),$$

where, in its more general form,

$$G_a(1,2,3)=G_a(1,2)G_a(2,3)G_a(3,1)\ ,$$

with $G_a(i,j)$ a function of the type of Eqs. (19)–(21).

Closed-form expressions for $L_i^2F_a$ can be found on the basis of the general expression (23) following the same steps as in the case of two-electron systems. The matrix elements of L_i^2 and ω_l can be calculated using the orthogonality relation

$$\int\int\int \Lambda^{*k_aLM}_{l_{1a}l_{2a}l_{3a}}(1,2;3)\Lambda^{k_bLM}_{l_{1b}l_{2b}l_{3b}}(1,2;3)d\Omega_1 d\Omega_2 d\Omega_3 = \delta_{k_ak_b}\delta_{l_{1a}l_{1b}}\delta_{l_{2a}l_{2b}}\delta_{l_{3a}l_{3b}}\ ,$$

the recoupling transformation [6]

$$\Lambda^{k_a LM}_{l_{1a}l_{2a}l_{3a}}(1,2;3)=\sum_{k_c}\Lambda^{k_c LM}_{l_{2a}l_{3a}l_{1a}}(2,3;1)(-1)^{l_{1a}+l_{2a}+l_{3a}+L}\times[k_a,k_c]^{1/2}\begin{Bmatrix} l_{1a} & l_{2a} & k_a \\ l_{3a} & L & k_c \end{Bmatrix},$$

and the relation of Eq. (8),

$$\omega_l\Lambda^{L_aM_a}_{l_{1a}l_{2a}}=\sum_{k_1,k_2} b^{L_a}_{l_a k;l}\Lambda^{L_aM_a}_{k_1k_2}.$$

In the cases of very weak correlation in which a small amount of angular mixing occurs, or in the cross-correlation cases involving, for example, $G(1,2)G(2,3)$, $G(i,j)$ might be set to the original MCI form or to just 1, reverting to the traditional CI single-orbital basis functions. The efficiency of the method in the case of more electrons will certainly be superior to that of standard CI, as one does not have to deal with the explicit choice of a small number of configurations to be added, as an infinite number (or a very large number in the original MCI strategy) is automatically introduced. On the other hand, the increased accuracy of MCI will bring further questions about the relevance of contributions that are negligible within the low accuracy of CI, like multiple excitations. How these will affect the efficiency of the method will be discussed in subsequent work on three- and four-electron systems.

ACKNOWLEDGMENT

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