Modified Configuration Interaction Method for Accurate Calculations with Small Basis Sets

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A very efficient modified configuration interaction method is introduced for accurate atomic and molecular calculations with basis sets that are substantially smaller than those used by conventional configuration interaction (CI). The energy of the ground state of *helium,* for example, is obtained with a relative error of 3×10^{-8} *with a total of only 393 basis functions* (no extrapolations). This is accomplished by means of (i) a radial representation that converges as N_r^{-9} where N_r is the number of two-electron radial functions and (ii) $N_{\bar{l}}$ generalized two-electron angular functions with which the energy converges as $N_{\bar{l}}^{-6}$. (The standard functions of conventional CI converge as $N_r^{-2.9}$ and N_l^{-3}.)

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The configuration interaction (CI) method provides a straightforward way to perform atomic physics calculations involving correlation effects between electrons. The actual wave function for the system under consideration is expanded in terms of a set of symmetrized (antisymmetrized) variational basis vectors each with a radial part that depends on the radial coordinates r_i and an angular part given by the coupling of spherical harmonics $Y_{l_i m_i}(\hat{\mathbf{r}}_i)$ to a total angular momentum L, where $\mathbf{r}_i$ are the coordinates of each electron. One starts the CI expansion with a set of basis functions in which the (single) angular part is the one giving the most important angular contribution; for example, for an atom with two electrons in an nS state, the initial configuration would couple two s electrons. To this set one then adds basis vectors with different one-electron angular momentum quantum numbers l_i. A typical CI basis set using Slater-type radial functions in the two-electron case is given by

$$\varphi_i^{\text{Slater}} = e^{-\alpha_i r_1 - \beta_i r_2} r_1^{a_i} r_2^{b_i} \Lambda_{l_{1i} l_{2i} LM}(\hat{\mathbf{r}}_1, \hat{\mathbf{r}}_2) \pm \mathbf{r}_1 \rightleftharpoons \mathbf{r}_2 , \tag{1}$$

where

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

and α_i and β_i are arbitrary nonlinear parameters.

One looks then for convergence as one increases (i) the number of powers of r_i and (ii) the number of spherical configurations $\Lambda_{l_1 l_2 LM}$. The convergence with l is poor [1–3], specially in the case of small nuclear charge Z as correlation effects scale as $1/Z$ (e.g., the energy of the ground state of helium converges as l^{-3}). The CI approach is, on the other hand, attractive because it is a simple method, simpler, for example, than the correlated basis set approach, mainly due to the fact that only two-dimensional radial integrals are involved in the calculations as against the three-dimensional integrations (over r_1, r_2, and r_{12}) necessary in the case of correlated calculations. Because of its inherent simplicity and the fact that it can fully describe correlation effects, the CI method is widely used for many-electron atomic and molecular systems; therefore, a substantial improvement in its speed of convergence will be of great significance.

In what follows we will use two-electron systems as a test case to introduce this new method. This allows for simplicity in the formation without loss of generality given that the extension to systems with more electrons is straightforward. In particular, we shall present numerical results for the case of the ground state of helium in the simple nonrelativistic, infinitely massive point nucleus case.

The relative simplicity of the CI calculations mentioned earlier stems from the fact that the (two-electron) Hamiltonian can be written as

$$H = -\frac{1}{2}\nabla^2_{\mathbf{r}_1} - \frac{1}{2}\nabla^2_{\mathbf{r}_2} - \frac{Z}{r_1} - \frac{Z}{r_2} + \sum_{l=0}^{\infty} \sum_{m=-l}^{l} \frac{r_<^l}{r_>^{l+1}} Y^*_{lm}(\hat{\mathbf{r}}_<) Y_{lm}(\hat{\mathbf{r}}_>) , \tag{3}$$

where $r_< = \min(r_1, r_2)$ and $r_> = \max(r_1, r_2)$. The angular integrals involved in the calculations are simple to perform using angular momentum algebra while the radial integrals consist, in the worst case, of two-dimensional integrations.

The fact that the convergence with l is very poor is well known; not so well know is the fact that, for a given configuration, the convergence as the powers of r_i are increased is also poor [1,4]. The convergence of basis set (1) as the number of powers is increased is presented in the upper curve of Fig. 1 for the case in which the basis set contains the single spherical harmonic configuration s^2. A least-squares fit of the residual error δE in the variational energy eigenvalue scaled by Z^2 as a function of N_r, the number of radial functions, yields $\delta E \approx 0.22 \times N_r^{-2.9}$. This is a slow rate of convergence with which it is very difficult to obtain results accurate to more than a few significant digits. For example, one would need about 50 radial functions to obtain a convergence of $\delta E/E \approx 10^{-6}$, 500 for $\delta E/E \approx 10^{-9}$, and 5000 for $\delta E/E \approx 10^{-12}$. The results are not better if finite-element techniques

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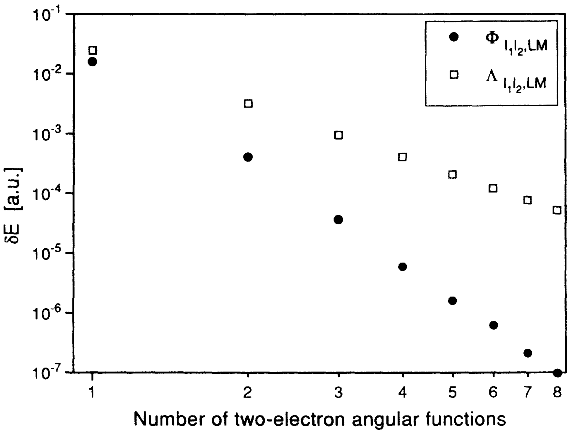

FIG. 1. Convergence of the variational eigenvalues of the two-electron Hamiltonian using a basis set with the single angular configuration s^2, as the number of two-electron radial basis functions is increased. δE is the residual error in the contribution to E/Z^2 in a.u. The empty squares denote the results using Slater basis sets (1). The filled circles denote the results using the new radial functions of Eqs. (5) and (6).

are used. For example, in the case of heliumlike neon ($Z = 10$) one needs of the order of 1600 B splines [2] to converge to $\delta E/E \approx 10^{-8}$. Calculations using natural orbitals are somewhat better: with a radial convergence of 10^{-9} a.u. using 24 s orbitals with 36 vectors each [1], although the error in the calculation is of order 10^{-7} a.u. The reason for the poor convergence of the radial functions is that it is very hard for a smooth function of r_1 and r_2 to represent the ratio $r_<^l/r_>^{l+1}$ appearing in the Hamiltonian, which has discontinuous derivatives with respect to r_i at $r_1 = r_2$ resulting in a cusp-type singularity of the wave function. This feature of the wave function having "cusps" at the points in which the potential is singular has been identified before [5], and attempts to address this by including r_{12} in the CI wave function have been pursued [3]. In this work we present a new approach to the radial representation that dramatically improves the convergence of the variational eigenvalues by directly addressing this problem while keeping the simplicity of the CI approach. The motivation for this new representation is found by rewriting the Hamiltonian (3) in the form

$$H = -\frac{1}{2}\nabla^2_{\mathbf{r}_<} - \frac{1}{2}\nabla^2_{\mathbf{r}_>} - \frac{Z}{r_<} - \frac{Z}{r_>} + \sum_{l,m} \frac{r_<^l}{r_>^{l+1}} Y^*_{lm}(\hat{\mathbf{r}}_<) Y_{lm}(\hat{\mathbf{r}}_>), \tag{4}$$

where we used the fact that for a function $f(\mathbf{r}_1, \mathbf{r}_2) = f(\mathbf{r}_2, \mathbf{r}_1)$ is $f(\mathbf{r}_1, \mathbf{r}_2) = f(\mathbf{r}_<, \mathbf{r}_>)$.

We introduce then instead of (1), the following basis set, which is an extension of a basis first suggested by Schwartz in 1962 [6–8]:

$$\varphi_i = e^{-\alpha_i r_1 - \beta_i r_2 - \sigma_i r_< - \tau_i r_>} r_1^{a_i} r_2^{b_i} r_<^{s_i} r_>^{t_i} \Lambda_{l_{1i} l_{2i} LM}(\hat{\mathbf{r}}_1, \hat{\mathbf{r}}_2) \pm \mathbf{r}_1 \rightleftharpoons \mathbf{r}_2 \,. \tag{5}$$

The basis set has built in the ability to easily deal with the electron-electron potential at $r_< = r_>$. Here we present results for the helium ground state, for which we use

$$\begin{aligned} &\alpha_i = \beta_i = a_i = b_i = 0, \\ &s_i = 0, 1, 2, \ldots, \\ &t_i = 0, 1, 2, \ldots \quad \text{if } s_i = 0, 1, \\ &t_i = -s_i + 1, -s_i + 2, \ldots \quad \text{if } s_i > 1 \,. \end{aligned} \tag{6}$$

The results obtained for the case in which the basis set contains the single spherical harmonic configuration s^2 are presented in the lower curve in Fig. 1. The convergence using basis set (5) is much faster: a convergence of $\delta E/E \approx 10^{-12}$ is obtained with only 34 two-electron radial basis vectors. A least-squares fit of δE yields $\delta E \approx 8.25 N_r^{-8.94}$; the power of N_r is a factor of 3 times larger than in the Slater case. The result obtained for the single s configuration is $E_s = -2.879\,028\,767\,315(4)$ a.u. while the previous accurate value by Carroll, Silverstone, and Metzger is $E_s = -2.879\,028\,758$ a.u.

We now turn our attention to the improvement of the convergence of the CI energy eigenvalues as the number of angular configurations in the basis set is increased. In usual CI calculations, correlation is introduced in the basis set by mixing different angular configurations of the form of Eq. (2). The contribution of each configuration is decided by the diagonalization of the Hamiltonian matrix, which is equivalent to a minimization of the energy as the *linear* coefficients are varied. The convergence of this type of basis set [Eq. (7)] with the number of spherical configurations is presented in the upper curve of Fig. 2,

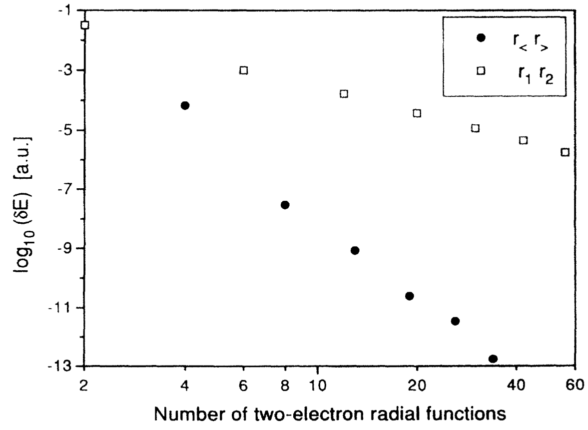

FIG. 2. Convergence of the variational eigenvalues of the ground state of helium as the number of two-electron angular functions is increased. δE is the residual error in the energy in a.u. The empty squares denote the results using spherical harmonics (5). The filled circles denote the results using the new angular functions of Eqs. (7)–(15).

in which δE is now the cumulative error in the energy eigenvalue as the number N_l of angular configurations is increased. Again the convergence is poor with a least-squares fit yielding $\delta E \approx 0.025 N_l^{-3.0}$. It must be stressed at this point that not all the points in this curve in Fig. 2 could have been plotted if radial functions of r_1 and r_2 were used, as a prohibitive number of vectors would have been needed for the necessary convergence with seven or eight angular configurations.

The angular convergence can, however, be improved substantially if we introduce for the angular functions the same convergence-accelerating technique used successfully for radial functions, namely, *nonlinear* (angular) variational parameters. We replace then the *radially* improved basis set (5) with the new set

$$f_i = e^{-\alpha_i r_1 - \beta_i r_2 - \sigma_i r_< - \tau_i r_>} r_1^{a_i} r_2^{b_i} r_<^{s_i} r_>^{t_i} \Phi^{LM}_{\tilde{l}_{1i}\tilde{l}_{2i}}(\hat{\mathbf{r}}_1, \hat{\mathbf{r}}_2) \pm \mathbf{r}_1 \rightleftharpoons \mathbf{r}_2 , \tag{7}$$

where the $\Phi^{LM}_{\tilde{l}_{1i}\tilde{l}_{2i}}$ are orthonormalized linear combinations of a set of optimized angular functions $\Theta^{LM}_{\tilde{l}_{1i}\tilde{l}_{2i}}$, i.e.,

$$\Phi^{LM}_{\tilde{l}_1\tilde{l}_2}(\hat{\mathbf{r}}_1, \hat{\mathbf{r}}_2) = \sum_{a,b}^{n_a,n_b} w^{ab}_{\tilde{l}_1\tilde{l}_2} \Theta_{abLM}(\hat{\mathbf{r}}_1, \hat{\mathbf{r}}_2) , \tag{8}$$

where $\tilde{l}_1, \tilde{l}_2, a, b = 0, 1, 2, \ldots$ and the coefficients $w^{ab}_{\tilde{l}_1\tilde{l}_2}$ are obtained by diagonalizing the overlap matrix of the angular functions $\Theta^{LM}_{\tilde{l}_{1i}\tilde{l}_{2i}}$ so that

$$\int\!\!\int \Phi^{LM}_{pq}(\hat{\mathbf{r}}_1, \hat{\mathbf{r}}_2) \Phi^{L'M'}_{p'q'}(\hat{\mathbf{r}}_1, \hat{\mathbf{r}}_2)\, d\Omega_1\, d\Omega_2 = \delta_{pp'}\delta_{qq'}\delta_{LL'}\delta_{MM'} . \tag{9}$$

The new optimized angular functions $\Theta^{LM}_{\tilde{l}_1\tilde{l}_2}(\hat{\mathbf{r}}_1, \hat{\mathbf{r}}_2)$ are defined by

$$\Theta^{LM}_{\tilde{l}_1\tilde{l}_2}(\hat{\mathbf{r}}_1, \hat{\mathbf{r}}_2) = \sum_{a,b}^{n_a,n_b} C^{ab}_{\tilde{l}_1\tilde{l}_2}(\sigma) \Lambda_{abLM}(\hat{\mathbf{r}}_1, \hat{\mathbf{r}}_2) , \tag{10}$$

where Λ_{abLM} is defined in (2) and σ denotes a set of nonlinear parameters σ_i with $i = 1, 2, \ldots, n_\sigma$. The values of $\tilde{l}_1$ and $\tilde{l}_2$ are defined by the relation for $\sigma = 0$:

$$\lim_{\sigma \to 0} \Theta^{LM}_{\tilde{l}_1\tilde{l}_2}(\hat{\mathbf{r}}_1, \hat{\mathbf{r}}_2) = \Lambda_{l_1 l_2 LM}(\hat{\mathbf{r}}_1, \hat{\mathbf{r}}_2) . \tag{11}$$

Notice that in (10) n_σ can be very small while n_a and n_b can be very large, so that only a few angular nonlinear parameters are needed to optimize a large number of component angular functions in $\Theta^{LM}_{\tilde{l}_1\tilde{l}_2}$.

In this Letter we present as an example the ground state of helium for which $L = 0$ and therefore $\tilde{l}_1 = \tilde{l}_2$ and $a = b$ in the summation in (10). The calculation was performed with the basis set

$$f_i = e^{-\sigma_i r_< - \tau_i r_>} r_<^{s_i} r_>^{t_i} \Phi^{LM}_{\tilde{l}_i\tilde{l}_i}(\hat{\mathbf{r}}_1, \hat{\mathbf{r}}_2) , \tag{12}$$

where s_i and t_i are defined in (6) with the additional constraint $s_i + t_i < \tilde{l}_i + 3$; $n_a = 85$; and the coefficients in (10) are chosen as

$$\begin{aligned} C^{aa}_{\tilde{l}l} &= 0 && \text{if } a < \tilde{l} \text{ or } a > \tilde{l} + n_a , \\ C^{aa}_{\tilde{l}\tilde{l}} &= b(\tilde{l}, a)/b(\tilde{l}, \tilde{l}) && \text{otherwise} , \end{aligned} \tag{13}$$

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

$$C^{aa}_{\tilde{l}l} = \begin{cases} 1 & \text{if } a = 0 , \\ \frac{1}{a!} y(y - 1) \cdots (y - a + 1) x^a & \text{if } a > 0 , \end{cases} \tag{14}$$

x and y are defined in terms of the nonlinear coefficients σ_i with

$$x = \sigma_1/(\tilde{l} + 1) + \sigma_2 \tilde{l} \quad \text{and} \quad y = \sigma_3 + \sigma_4 \tilde{l} . \tag{15}$$

The coefficients are written in terms of a Taylor expansion to guarantee that the norms of the Θ functions are finite in the limit of an infinite spherical harmonic expansion. Only four angular nonlinear parameters are used to control 85 spherical configurations for each value of $\tilde{l}$ (in fact, σ_1 is very nearly zero and can be omitted with a very small loss in precision). The results obtained using this basis set appear in the lower curve of Fig. 2. The residual error in the ground-state energy using basis set (12) converges as $\delta E \approx 0.026 N_{\tilde{l}}^{-6.0}$, where $N_{\tilde{l}}$ is the number of two-electron angular functions. The power of $N_{\tilde{l}}$ is twice as large as the one using combinations of spherical harmonics. This yields a relative error $\delta E/E \approx 7.2 \times 10^{-8}$ with only seven angular functions and a total of 309 basis vectors, and a relative error $\delta E/E \approx 3.3 \times 10^{-8}$ with only eight angular functions and a total of 393 basis vectors. (The previous accurate CI value for the He ground state by Carroll, Silverstone, and Metzger [1] has a relative error of order 8.4×10^{-6}.) One would need of the order of 60 spherical-harmonics-type functions [basis set (5)] for a similar convergence. Again, notice that using the usual Slater spherical harmonics functions, it is very hard to exceed more than a few angular configurations, a case in which one has already used an unpractically large number of vectors [3,9]. For the sake of argument, with 60 angular functions, this new basis set would attain a convergence $\delta E/E \approx 5.4 \times 10^{-13}$. All the calculations in this Letter were performed on an IBM R6000-375 workstation.

In conclusion, the proper use of $r_<$ and $r_>$ in the basis set reduces drastically the number of radial functions, while the new angular functions Φ accelerate substantially the rate of convergence of the variational energy eigenvalues. Between both, we have obtained a dramatic reduction in the number of basis functions needed in CI calculations. The application of this method to atoms with more electrons and to molecules is straightforward although far more powerful than previous CI implementations. It is in these complex systems where the large reduction in the number of basis vectors will be of greatest use. The angular functions can be trivially extended to systems with more electrons, while the radial functions can be written, for example, as products of one-electron functions of ordered radial variables. Notice that, as in the two-electron case, the Hamiltonian for systems with more electrons can also be rewritten in terms of these variables only.

Both the number of functions needed for a certain convergence and the convergence patterns themselves might be even further improved from those presented in this Letter. For this, a search of better choices of powers for the radial functions and of coefficients for the angular functions is needed.

In the future, it would be interesting to extend this method also to relativistic calculations in two-electron systems. CI has been already tried successfully although no calculations for $Z < 5$ have yielded accurate results because of the enormous arrays necessary [2]. The application of the new angular procedure will be straightforward resulting in an increase in convergence. The application of the new radial functions, however, will be more complicated because of the partial presence of correlation in the basis set, so that the continuum dissolution of the variational eigenvalues is a possibility. On the other hand, at any point in space these radial functions are simple products of one-electron functions so that a boundary condition might exist that will guarantee bounds.

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Note added.—Since the initial submission of this Letter, the convergence for the case in which the basis set contains the single spherical harmonic configuration s^2 has improved to $\delta E/E \approx 5 \times 10^{-18}$ with 125 two-electron radial basis vectors, while the full calculation for the ground state of helium yields $\delta E/E = 4.6 \times 10^{-9}$ with 305 two-electron basis functions.

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