

A procedure to obtain an accurate approximation to a full CI wavefunction

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Based on Jacobi elementary rotations, a simple, elegant procedure to obtain approximate CI wavefunctions is discussed. Essentially, a sequence of (2×2) matrices is built-up, and the eigenvector attached to the lowest eigenvalue is used to construct a stepwise set of coefficients, which become a very good approximation to the *exact* CI result. Full CI calculations could easily be reached in this way. An example formed by some atoms of the He isoelectronic sequence is provided in order to test the flexibility and accuracy of the procedure. A Fortran 90 code is available.

1. Introduction

The CI theoretical framework is a widespread quantum chemical procedure which has been treated by many authors. From early times [1] a stepwise procedure to solve the involved huge CI eigensystem has been described. A sample of the history of CI development can be found in ref. [2]. In some instances, see for example [3], the problem has been studied in order to simplify the computational burden. More recently, many authors have been involved with the study of better algorithms to obtain eigenvalues and eigenvectors of large symmetric matrices, see citations in ref. [4] for a recent view and a clever discussion.

For many years our laboratory has been working on the quantum mechanical applications of elementary Jacobi rotations. Various papers have been devoted to the direct optimization of the electronic energy [5] and more recently various alternatives [6] to the well-known Jacobi diagonalization algorithm [7] have been studied. Also, several times, the CI problem has been studied by us. In an early paper dealing with quantum similarity and MO taxonomy [8], a choice of appropriate virtual orbitals to obtain better CI convergence was proposed and illustrated with an example. More recently, within the application framework of the so-called nested summation symbols [9], the CI formulation was presented from a very general point of view. In the same theoretical context it was shown how a generalized Slater rule, dealing with matrix elements of many electronic operators, over determinantal functions, can be easily deduced [9]. Also these last studies were connected to parallel computational features.

The convergence of both sets of ideas: Jacobi rotations and nested summation symbols dealing with CI, have been the motivation of the present paper. Thus, in comparison to a quite general CI study, it has been clear to us that describing a reasonable way to obtain low cost, accurate enough, full CI wavefunctions may be of some help to computational quantum chemists. The present paper will be devoted to this task.

First, a simple but efficient and cost effective algorithm will be described in order to compute accurate enough CI wavefunctions up to any excitation level. A simple example, involving two-electron He-like atomic structures will be presented next, as a way to illustrate the practical use of the proposed algorithm.

2. A procedure and some algorithms

Let us suppose that a starting approximate ground state normalized wavefunction $|0, 0\rangle = |0\rangle$ and the associated electronic energy $E(0, 0)$ are known, such as

$$E(0, 0) = \langle 0, 0 | H | 0, 0 \rangle. \quad (1)$$

A new approximate wavefunction $|0, 1\rangle$ may be defined by just picking up some appropriate excited state basis function $|1\rangle$, and using

$$|0, 1\rangle = c|0, 0\rangle + s|1\rangle, \quad (2)$$

where $c^2 + s^2 = 1$, so the scalars $\{c, s\}$ behave as rotation cosine and sine, respectively.

The polyelectronic basis functions pair used so far describes a Hamiltonian (2×2) matrix representation scaled by the initial energy value $E(0, 0)$ in such a way that

$$\mathbf{h} = \begin{pmatrix} 1 & \beta \\ \beta & \alpha \end{pmatrix}, \quad (3)$$

where

$$\beta = \langle 0, 0 | H | 1 \rangle [E(0, 0)]^{-1} \quad (4)$$

and

$$\alpha = \langle 1 | H | 1 \rangle [E(0, 0)]^{-1}. \quad (5)$$

The eigenvalue of \mathbf{h} associated with the lowest energy corresponds to

$$\gamma = \frac{1}{2} [1 + \alpha + ((\alpha - 1)^2 + 4\beta^2)^{1/2}], \quad (6)$$

with the parameters $\{\alpha, \beta\}$ defined above in eqs. (4) and (5).

Once eq. (6) has been computed, the corrected new ground state energy may be written as

$$E(0, 1) = \gamma E(0, 0). \tag{7}$$

The values of the $\{c, s\}$ coefficients pair may be obtained by diagonalizing the (2×2) matrix \mathbf{h} , defined in eq. (3), by means of Algorithm A0.

a) Define $\tau = (\alpha - 1)(2\beta)^{-1}$ and $t = |\tau| + (1 + \tau^2)^{1/2}$.
 b) One has: $s = \text{sign}(\tau)(1 + t^2)^{-1/2}$ and $c = st$.

Algorithm A0. Obtaining the cosine and sine pair $\{c, s\}$ from the elements of the matrix (3).

Algorithm A0 constitutes the usual way in which the Jacobi diagonalization proceeds [17]. So far the fundamental formulae for the proposed computation of the approximate CI wavefunction coefficients are complete. Algorithm A1 illustrates how to proceed in the n th step.

Using the simple computational device as described in Algorithm A1, a set of coefficients $\{d_p^{(n)}\}$ can be obtained in terms of the successive $\{c, s\}$ pairs, such as

$$|0, n\rangle = d_n^{(n)}|n\rangle + \sum_{p=0}^{n-1} d_p^{(n)}|p\rangle, \tag{8}$$

where

0) Suppose known the approximate energy $E(0, n)$ and wavefunction $|0, n\rangle$.
 1) Choose the next step approximate excited state basis set function $|n + 1\rangle$.
 2) Compute the parameters $\beta = \langle 0, n|H|n + 1\rangle[E(0, n)]^{-1}$
 $\alpha = \langle n + 1|H|n + 1\rangle[E(0, n)]^{-1}$
 3) Compute γ using equation (6). In this way: $E(0, n + 1) = \gamma E(0, n)$.
 4) Compute $\{c^{(n+1)}, s^{(n+1)}\}$ using algorithm A0. Then, the new wavefunction is

$$|0, n + 1\rangle = c^{(n+1)}|0, n\rangle + s^{(n+1)}|n + 1\rangle.$$

5) If $n > n_{\max}$ then exit
 else $E(0, n) \leftarrow E(0, n + 1); |0, n\rangle \leftarrow |0, n + 1\rangle$
 cycle to 1).

Algorithm A1. Obtaining the successive approximations to the CI wavefunction.

$$d_p^{(n)} = s^{(p)} \prod_{k=p+1}^n c^{(k)} \quad (9)$$

and

$$d_n^{(n)} = s^{(n)}. \quad (10)$$

Algorithm A1 needs the n th row or column of the Hamiltonian matrix representation over the chosen basis set: $\{ \langle p | H | n \rangle; 0 \leq p \leq n \}$, which produces an $n + 1 = N$ dimensional vector. Due to the variational principle, the obtained energy at the n th step, $E(0, n)$, will always be greater than or equal to the exact value, E_0 , which can be obtained by diagonalizing an $(N \times N)$ matrix and taking the minimal valued one. The energy difference will be small and the approximate functions, $|0, a_n\rangle$, and the exact ones, $|0, f_n\rangle$, will differ in a small measurable amount:

$$\epsilon_n^{(2)} = \| |0, a_n\rangle - |0, f_n\rangle \|_2 N^{-1}, \quad (11)$$

N being the column or row space dimension. It seems to be a general fact that the function $|0, a_n\rangle$ has the same coefficient signs and appropriate magnitude as the exact CI calculation.

3. An example

The He isoelectronic family has been chosen due to the well-known values of the He energy, computed long time ago and collected by Parr [10]. In this sense, the whole program constructed for this task in Fortran 90 (TWOEL-96) [11] can be easily tested. In the two-electron case, the basis set functions have been chosen as ns STO, whose integrals are readily evaluated, see for example [12]. SCF calculations have also been carried out for every system, a two-electron SCF subroutine has been included into the code as a source of one-electron functions. Then, the basis set integrals are transformed and used to construct the elements of the Hamiltonian matrix, which can be easily evaluated using Algorithm A2.

After the elements of the Hamiltonian matrix H are available, then Algorithm A1 can be used over them, taking at each elementary step the excitation functions basis set: $\{ |[ij] \rangle \}$, sequentially. Paired excitation CI functions and energies, involving basically the wavefunction subset $\{ |[ij] \rangle \}$, have also been included in the present study for computational purposes and comparisons sake.

Full CI energy evaluation has been included within TWOEL-96 and performed using a parallelizable Jacobi algorithm developed in our laboratory [6], permitting the computation of the lowest eigenvalue and the attached eigenvector only.

As a first TWOEL-96 program test, a calculation with $n = 30$, involving 14 1s, 6 2s, 4 3s, 3 4s, 2 5s and 1 6s well-tempered STO functions, was performed, providing an SCF energy of -2.86167995 a.u. which agrees quite well with the accurate

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0) Known an initial basis set  $\{\varphi_i\}$  (which here is taken as the SCF orbitals),
1) Compute the integrals


$$\mathbf{h} = \{h_{ij}\} = \{\langle \varphi_i | h | \varphi_j \rangle\}$$



$$\mathbf{R} = \{R_{ijkl}\} = \{\langle \varphi_i \varphi_j | r^{-1} | \varphi_k \varphi_l \rangle = (ij|kl)\}$$


2) do  $i = 1, n$ ; do  $j = 1, i$ ;  $[ij] = j + (i^2 - i)/2$ 
   do  $k = 1, n$ ; do  $l = 1, k$ ;  $[kl] = l + (k^2 - k)/2$ 
     if  $[ij] \geq [kl]$  then
       
$$\langle [ij] | H | [kl] \rangle = 2^{-(\delta_{ij} + \delta_{kl})/2} \{ \delta_{jl} h_{ik} + \delta_{jk} h_{il} + \delta_{il} h_{jk} + \delta_{ik} \delta_{jl} + (ik|jl) + (jk|il) \}$$

     end if
   end do  $k, l$ 
end do  $i, j$ 

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Algorithm A2. Evaluation of the integrals involved into the computation of a two-electron CI wavefunction.

value reported by Bunge et al. [13]. The set of 465 generated configurations has provided a full CI energy of -2.87900628 a.u., which is in agreement with the value of -2.8790 a.u. reported by Parr [10] as the limit of the non-angular terms wavefunction. The proposed approximate calculation yielded an energy equal to -2.87888990 a.u., with an eigenvector quadratic mean error of 2.17×10^{-5} with respect to the exact full CI.

Table 1 provides the energies of an assorted set of two-electron atoms belonging to the He isoelectronic sequence. The one-electron basis set was taken as a sequence of well-tempered 1s AO STO functions described by Koga et al. [14]. The well-tempered sequence parameters have not been reoptimized, the number of functions was also kept and were taken as defined in the full electron atoms.

The approximate wavefunction $|0, a\rangle$ error reported in Table 1 was computed with respect to the full CI function $|0, f\rangle$ as the Euclidean norm:

$$e = \| |0, a\rangle - |0, f\rangle \|_2 N^{-1}, \quad (12)$$

where N is the number of configurations in the full CI. In this two-electron case, $N = (n^2 + n)/2$, n being the number of STO basis functions used.

As a consequence of the approximate nature of the present (2×2) procedure, the energies $E(0, a)$ become slightly more positive than the full CI ones. The energy deviations,

Table 1

Results obtained for several He-like atoms. Tabulated data are: Atom name; atomic number (Z); number of 1s STO basis functions (n); α and β ; well-tempered parameters; SCF energy; Virial coefficient; energy obtained considering the paired excitations; the full CI energy and the one obtained by the approximate method (Algorithm A1) discussed here. The last column corresponds to the *eigenvector* quadratic error of the approximate method with respect to the full CI result. All the energies are tabulated in atomic units.

Atom	Z	n	α	β	SCF	-Virial/2	Paired	Full CI	Algorithm A1	Error
He	2	4	0.853931	1.660897	-2.861679875	1.000000004	-2.874176229	-2.878841857	-2.878777788	0.604E-3
C	6	7	0.705082	1.669878	-32.36119128	1.000005037	-32.36720506	-32.37619653	-32.37618752	0.263E-4
Ne	10	7	1.187022	1.683000	-93.86110782	1.000006749	-93.86706813	-93.87577833	-93.87577539	0.84E-5
S	16	10	1.187022	1.683000	-246.1109501	1.000013287	-246.1162344	-246.1255179	-246.1255168	0.163E-5
Ti	22	11	0.420420	1.481960	-470.3610048	1.000002588	-470.3662173	-470.3747763	-470.3747757	0.731E-6
Br	35	11	0.980206	1.392420	-1203.235932	0.9999994747	-1203.241039	-1203.249445	-1203.249445	0.287E-6
Pd ^a	46	13	1.678062	1.339474	-2087.361022	0.9999999725	-2087.365229	-2087.375226	-2087.375226	0.126E-6
I	53	13	0.854821	1.409715	-2775.985982	1.000000452	-2775.990816	-2775.999807	-2775.999807	0.889E-7

^a Using a modified α value respect to ref. [14].

$$\epsilon = |E(0, a) - E(0, f)|, \quad (13)$$

are small ($10^{-7} < \epsilon < 10^{-3}$) and decrease as the atoms possess a higher atomic number and more STO functions are used.

4. Notes about some methodological features

Due to the step by step nature of the proposed approximate wavefunctions the algorithm can also be used as a means to choose the most relevant configurations of a given electronic system.

The obtained approximate eigenvector could be further refined using an exact algorithm such as the one proposed by Nesbet [15] or by Davidson [16]. The Jacobi based algorithm proposed by us [6] can also be used. TWOEL-96¹ includes this test as well as the Rayleigh quotient test [17a,c], which is fulfilled by both full CI vectors and the (2×2) approximate ones.

Full CI results produce an electronic energy value which is invariant upon the chosen mono-electronic basis set. Indeed, SCF or one-electron core Hamiltonian vectors yield the same energy but a different, rotated, wavefunction.

With respect to the (2×2) approximate calculation, SCF vectors produce more accurate energy and wavefunctions than one-electron core Hamiltonian vectors. When using SCF vectors, the coefficient associated with the first monoexcitation, if used as a first-step correction, becomes zero, according to the fulfillment of Brillouin's theorem.

Better results could be obtained by augmenting the dimension of the matrix h in eq. (3). This means attaching more than one excited configuration at each step and in this way destroying perhaps the elegant simplicity of the proposed algorithm.

5. Conclusions

The small errors encountered in the comparison of the proposed procedure and the full CI preclude that the proposed (2×2) Algorithm A1 constitutes an accurate and simple way to compute approximate wavefunctions up to full CI.

A simple and powerful, Jacobi related (2×2) procedure has been described.

¹ TWOEL-96 source can be downloaded from the following WWW address:
<http://stark.udg.es/~emili/twoel96.htm>

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