

## Approximate multiconfiguration variational calculations using partially localized orbitals

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**Abstract.** A new method is described in which important intra-atomic correlation terms are approximated in a multiconfiguration self-consistent-field (MCSCF) framework without generating large Hamiltonian or Fock matrices. Description in terms of partially localized orbitals (PLO) is preferred over the ordinarily delocalized molecular orbitals (MO). A new approach is also adopted for choosing the virtual excitations as well as for calculating the vector-coupling coefficients.

**Keywords.** Quantum chemistry; ab-initio theory; multiconfiguration self-consistent field; partially localized orbitals.

### 1. Introduction

Recently ab-initio calculations have been carried out by several authors (Goodgame and Goddard 1981; Walch *et al* 1983; Das and Jaffe 1984) to investigate the bonding forces in transition metal clusters. It was clear from the rather extensive complete active space (CAS)SCF calculations by Walch *et al* (1983) that it is necessary to include higher-order correlation effects (such as the intra-atomic correlation) to obtain an adequate picture of bonding in these systems. Das and Jaffe (1984) have demonstrated that the inclusion of these higher-order terms within the conventional MCSCF/CI framework [Wahl and Das 1977] is simplified considerably by going over to representation in terms of what has been called partially localized orbitals (PLO). These are 'Lowdin-orthonormalized' (1980) orbitals that are localized in the sense of Wannier orbitals (1962) at their individual centres. Using this representation important inter-atomic effects can be included very efficiently.

### 2. General considerations on the importance of nonvalence terms

In the course of our calculations on Cr<sub>2</sub> (Das and Jaffe 1984) we have observed that for accurate wavefunctions beyond the 'valence-only' level, we need to consider only two types of terms involving the virtual orbitals: (a) single excitations representing correlation due to readjustment of the orbitals in the charged environment and (b) the double excitations representing the intra-atomic correlation. It is possible to argue that this is generally true for most systems.

In an MCSCF framework, there is an important distinction between the virtual orbitals to be used for the above two types of excitations. Firstly single excitations of category (a) require one virtual for each valence orbital and hardly ever use a basis space larger

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Dedicated to Professor Sadhan Basu on the occasion of his 65th birth anniversary.

than that employed for the 'valence-only' calculations. On the other hand intra-atomic double excitations normally require for their description a much larger basis space. Employment of such a large basis for each atom is impractical even for the smallest molecules. It is, therefore, desirable to find an approximate way of handling these excitations without bringing in anything larger than the molecular basis required at the 'valence-only' level. The work of Goodgame and Goddard (1984) addresses itself to this question by altering the value of some basic electron repulsion integrals such that the constituent atoms have the correct ionization potential and electron affinity. Besides its *ad hoc* nature, such a treatment runs into difficulty for those cases involving more than single charge transfers or those where the inter-shell correlation is important. In what follows we take a more direct route, namely re-express the molecular wavefunction in terms of the various component atomic functions and introduce the intra-atomic correlation in proportion to their relative weights.

Turning to single excitations, the fact that these excitations contribute significantly even if the reference function is optimized has important implications. Let us consider the state of an idealized homopolar system of the symmetry  ${}^1\Sigma_g^+$  described by the following wavefunction:

$$a(1/\sqrt{2})[(d\sigma_A d\pi_A^+)_{s=1} (d\sigma_B d\pi_B^-)_{s=1} + c \cdot c] + (b/2)[(d\sigma_A^2 + d\sigma_B^2)(d\pi_A^+ d\pi_B^- + c \cdot c)]. \quad (1)$$

An MCSCF process will obviously mix in single virtual excitations of the form

$$8^{-1/2}(d\sigma_A^2 + d\sigma_B^2)(d\pi_A'^+ d\pi_B^- + d\pi_A^+ d\pi_B'^- + c \cdot c). \quad (2)$$

The fact that single excitations contribute significantly even after the wavefunction is optimized imply that the contribution is coming through a 'uxu'-type mixing:

$$8^{-1/2}(d\sigma_A^2 - d\sigma_B^2)(d\pi_A'^+ d\pi_B^- - d\pi_A^+ d\pi_B'^- + c \cdot c), \quad (3)$$

which, obviously, cannot be eliminated by a generalized Brillouin's theorem 'process'. This is, in fact, substantiated by the calculations on  $\text{Cr}_2$  (Das and Jaffe 1984). One comes to the conclusion that the terms of category (a), in general, must be included even in the MCSCF framework. They can be regarded as truly molecular in the sense that they interact simultaneously with the constituents of the molecule.

On the other hand the intra-atomic correlation excitations remain specific with respect to their respective atoms even in the molecule. This is easily appreciated by considering the hydrogen molecule. If we write the  $\text{H}_2$  ( ${}^1\Sigma_g^+$ )-wavefunction in terms of localized orbitals as

$$a(s_A^2) + a(s_B^2) + b(s_A s_B), \quad (4)$$

a double excitation such as  $s_A^2 \rightarrow \phi_A^2$  mixes significantly only with the first term, while  $s_B^2 \rightarrow \phi_B^2$  only with the second. Thus the intra-atomic correlation contribution is easily seen to be given simply by  $a^2(\Delta E_A + \Delta E_B)$  to a good approximation, if  $\Delta E$  is the intra-atomic correlation in  $\text{H}^-$ . We generalize this approach by assuming that even in the molecular environment the orbitals (MO or PLO) are essentially of LCAO nature:

$$\phi_i = c_{iA} \phi_A + c_{iB} \phi_B.$$

Then it is easy to expand the molecular wavefunction as

$$\Psi = \omega^0 \Phi_A^0 \Phi_B^0 + \omega_{AB}^{(1)} \Phi_A^+ \Phi_B^- + \omega_{BA}^{(1)} \Phi_A^- \Phi_B^+ + \omega_{AB}^{(2)} \Phi_A^{++} \Phi_B^{--} + \omega_{BA}^{(2)} \Phi_A^{--} \Phi_B^{++} + \dots \quad (5)$$

It is easy to see that for a multiple bond rather high orders of ionic states can occur in this expansion. However, unlike the MO-description, PLO will certainly lead to a fast convergence. The corresponding intra-atomic correlation energies are approximated as

$$\Delta E_{\text{corr}} = (\omega^0)^2 [\Delta E_A + \Delta E_B] + (\omega_{AB}^1)^2 [\Delta E_A^+ + \Delta E_B^-] + \dots \quad (6)$$

### 3. Construction of the approximate MCSCF wavefunction

On the basis of the discussion above we shall consider three types of terms to be treated variationally in different orders of approximation. Firstly, the valence-only terms are treated exactly. The single excitation correlation terms are approximated by first restricting that the virtual orbital used for the promotion of one valence orbital cannot be used for the promotion of another. To simplify the problem of computation of vector-coupling coefficients for the singly excited configurations, the spin-coupling in them is required to be the same as the parent configurations. This is, of course, no real restriction when all the spin-couplings are present in the valence-only wavefunction. Thus for the single excitation  $\phi_i \rightarrow \phi_u$ , if  $\phi_i$  is singly occupied in the parent configuration,  $\phi_u$  will simply replace  $\phi_i$  with the spin-coupling left intact. If  $\phi_i$  is doubly-occupied,  $\phi_i$  and  $\phi_u$  will be singlet-coupled in the new configuration, all other couplings remaining unaltered. The matrix element between the parent and the resulting configurations is then

$$\langle 0|H|i \rightarrow u \rangle = \sqrt{n_i} \langle i|h|u \rangle + \sqrt{(1/n_i)} \sum_{j \neq i} \langle i|v_{ij}^j J_{jj}^{\text{op}} + v_{ij}^k K_{jj}^{\text{op}}|u \rangle, \quad (7)$$

where  $n_i$  is the occupancy of the orbital  $\phi_i$ ,  $v_{ij}$  and  $v_{ij}^k$  are the  $J$ - and  $K$ -vector-coupling coefficients for the diagonal term  $\langle 0|H|0 \rangle$  and  $J_{kl}^{\text{op}}$  and  $K_{kl}^{\text{op}}$  are the Coulomb and exchange operators:

$$J_{kl}^{\text{op}} \phi_i(\mathbf{r}) = \int \frac{\phi_k^*(\mathbf{r}') \phi_l(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' \cdot \phi_i(\mathbf{r})$$

$$K_{kl}^{\text{op}} \phi_i(\mathbf{r}) = \int \frac{\phi_k^*(\mathbf{r}') \phi_l(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' \cdot \phi_i(\mathbf{r}) \quad (8)$$

The matrix element between the two excitations  $\phi_i \rightarrow \phi_u$  and  $\phi_j \rightarrow \phi_v$  is

$$\langle 0; i \rightarrow u|H|0; j \rightarrow v \rangle = (n_i n_j)^{-1/2} [\langle i|v_{ij}^j J_{jv}^{\text{op}} + v_{ij}^k K_{jv}^{\text{op}}|u \rangle], \quad (9)$$

In the energy expression obtained by considering the above two groups of terms we add the third group, namely the correlation contribution given by (6). This will be our variational energy expression from which to obtain the MCSCF optimization equations, viz. the secular equations for the mixing coefficients and the Fock equations for both the valence and the virtual orbitals (see for example, Das 1981). For the atomic correlation corrections we use the experimental atomic energies along with the scf energies calculated with sufficiently accurate basis. In those cases where no experimental energies are available, it might be necessary to compute the atomic correlation energy theoretically.

The total energy with the single virtual excitations approximated as indicated above

can, therefore, be written as

$$\begin{aligned} \varepsilon = & A_0^2 \varepsilon_0 + 2A_0 \sum_i B_{ia} A_a \langle a; i \rightarrow u | H | a \rangle \\ & + \sum_{i,a} B_{ia}^2 \langle a; i \rightarrow u | H | a; i \rightarrow u \rangle, \end{aligned} \quad (10)$$

where

$$\varepsilon_0 = \sum A_a A_b H_{ab},$$

$H_{aa}$  including the intra-atomic correlation correction. We shall assume that the single excitations are small so we need consider them only in the lowest order; that is, we approximate the energy as

$$\begin{aligned} \varepsilon = & \varepsilon_0 + 2 \sum_{i,a} B_{ia} A_a \langle a; i \rightarrow u | H | a \rangle \\ & + \sum_{i,a} B_{ia}^2 [ \langle a; i \rightarrow u | H | a; i \rightarrow u \rangle - \varepsilon_0 ]. \end{aligned} \quad (11)$$

The optimization of  $B_{ia}$  gives

$$B_{ia} = - \frac{A_a \langle a; i \rightarrow u | H | a \rangle}{\langle a; i \rightarrow u | H | a; i \rightarrow u \rangle - \varepsilon_0}. \quad (12)$$

Thus

$$\varepsilon = \sum A_a A_b H'_{ab}, \quad (13)$$

where

$$H'_{ab} = H_{ab} - \delta_{ab} \sum_i \frac{\langle a; i \rightarrow u | H | a \rangle^2}{\langle a; i \rightarrow u | H | a; i \rightarrow u \rangle - \varepsilon_0}. \quad (14)$$

In order to avoid the destabilization effect of single excitations we optimize the valence orbitals without the orthogonalization constraints with respect to the virtual orbitals. The latter are, however, modified during the optimization process to insure mutual orthogonality. This is done as follows: Let  $\mathbf{c}$  be a valence vector and  $\mathbf{u}$  a virtual. Considering the variations in these vectors we have

$$\delta\varepsilon = 2(\delta\mathbf{c}^+ \mathbf{F}_c \mathbf{c}) + 2\delta\mathbf{u}^+ \mathbf{F}_u \mathbf{u}, \quad (15)$$

where  $\mathbf{F}_c$  and  $\mathbf{F}_u$  are the Fock operators. While  $\mathbf{F}_c$  has, in general, components coming from both  $\varepsilon_0$  as well as the single-excitation terms,  $\mathbf{F}_u$  has contribution only from the latter. Assuming that only the single excitation  $i \equiv (\mathbf{c} \rightarrow \mathbf{u})$  is selected:

$$\begin{aligned} \mathbf{F}_c \mathbf{c} & \equiv \mathbf{F}_{0,c} \mathbf{c} (1 - \sum_a B_{ia}^2) + \sum_a B_{ia} A_a \mathbf{F}_{ia}^0 \mathbf{u} + \sum_a B_{ia}^2 \mathbf{F}_{ia}^d \mathbf{c} \\ \mathbf{F}_c \mathbf{u} & \equiv - \sum_a B_{ia} A_a \mathbf{F}_{ia}^0 \mathbf{c} + \sum_a B_{ia}^2 \mathbf{F}_{ia}^d \mathbf{u} \end{aligned} \quad (16)$$

where  $\mathbf{F}_{0,c}$  is the contribution coming from  $\varepsilon_0$  and  $\mathbf{F}_{ia}^d$ ,  $\mathbf{F}_{ia}^d$  and  $\mathbf{F}_{ia}^0$  are the diagonal and off-diagonal contributions from the single excitation terms.

In order that  $\mathbf{u}$  stays orthogonal to  $\mathbf{c}$  to the first order in  $\delta\mathbf{c}$ , we must have

$$\delta\mathbf{u} = -(\mathbf{u}^+ \mathbf{S} \delta\mathbf{c}) \mathbf{c} \quad (17)$$

$\mathbf{S}$  being the overlap matrix. Hence

$$\delta\mathbf{u}^+ \mathbf{F}_u \mathbf{u} = - \langle \delta\mathbf{c} | \mathbf{S} \mathbf{u} \rangle \langle \mathbf{F}_u \mathbf{u} | \mathbf{c} \rangle \quad (18)$$

such that

$$\delta\varepsilon = \langle \delta\mathbf{c} | [\mathbf{F}_c - |\mathbf{S}\mathbf{u}\rangle \langle \mathbf{F}_u\mathbf{u}|] \mathbf{c} \rangle. \quad (19)$$

Thus the Fock equation for  $\mathbf{c}$  is

$$(\mathbf{F}_c - |\mathbf{S}\mathbf{u}\rangle \langle \mathbf{F}_u\mathbf{u}|) \mathbf{c} = \sum \lambda_j \mathbf{S}c_j \quad (20)$$

$\{\lambda_j\}$  being the Lagrangian multipliers.

#### 4. Matrix elements between the PLO-based configurations

##### 4.1 The vector-coupling problem for dimers

We adopt a new method of calculating the matrix elements where we take advantage of the partitioning of the occupation-space into the fragments  $A$  and  $B$ . We use the following theorem (Das 1982): If two spin-symmetrized functions of total spin  $s$  are formed as products  $|s_a \otimes s_b\rangle$  and  $|s'_a \otimes s'_b\rangle$  by combining the pairs of fragment spin-functions of spins  $s_a, s_b$  and  $s'_a, s'_b$  respectively, the matrix elements between these functions can be written as:

$$\begin{aligned} & \langle s'_a \otimes s'_b | H | s_a \otimes s_b \rangle \\ & = C_0 \langle s'_a s'_a, s'_b (-s'_b) | H | s_a s_a, s_b (s'_a - s'_b - s_a) \rangle \\ & \quad + C_1 \langle s'_a s'_a, s'_b (-s'_b) | H | s_a (s_a - 1), s_b (s'_a - s'_b - s_a + 1) \rangle, \end{aligned} \quad (21)$$

with

$$\begin{aligned} C_0 & = \langle S | s_a s_a, s_b (s'_a - s'_b - s_a) \rangle / \langle S | s'_a s'_a, s'_b (-s'_b) \rangle \\ C_1 & = \langle S | s_a (s_a - 1), s_b (s'_a - s'_b - s_a + 1) \rangle / \langle S | s'_a s'_a, s'_b (-s'_b) \rangle, \end{aligned} \quad (22)$$

where  $|sm\rangle$  denotes the spin function with spin  $s$  and spin-projection  $m$  and  $\langle S | s_1 m_1, s_2 m_2 \rangle$  are the Clebsch-Gordan coefficients.

We note that the matrix element is zero if  $|s'_a - s_a| > 1$  or  $|s'_b - s_b| > 1$ . We consider the four possible cases (all other cases being translatable into one of these):

$$\begin{aligned} & \text{(i) } s'_a = s_a, s'_b = s_b, \text{ (ii) } s'_a = s_a + \xi, s'_b = s_b + \xi, \xi = \frac{1}{2}, 1 \\ & \text{(iii) } s'_a = s_a + \xi, s'_b = s_a - \xi, \xi = \frac{1}{2}, 1 \text{ (iv) } s'_a = s_a, s'_b = s_b + 1 \end{aligned} \quad (23)$$

It is easily shown that except for the diagonal case (i), not more than one ' $m$ '-component of a fragment function is needed. Also it is necessary to consider the Slater determinants (SD) and their coefficients only for the spin-projections  $m = s, s-1$  and  $s-2$ . We give below the expressions for the matrix elements in each of the above cases:

$$\begin{aligned} & \text{(i) } \langle s_a \otimes s_b | H | s_a \otimes s_b \rangle \\ & = \langle s_a s_a, s_b (-s_b) | H | C_0 [s_a s_a, s_b (-s_b)] + C_1 [s_a s_a - 1, s_b (-s_b + 1)] \rangle, \\ & \text{(ii) } \langle s_a + \xi \otimes s_b + \xi | H | s_a \otimes s_b \rangle \\ & = C_0 \langle (s_a + \xi) (s_a + \xi), (s_b + \xi) - (s_b + \xi) | H | s_a, s_a, s_b (-s_b) \rangle, \\ & \text{(iii) } \langle s_a + \xi \otimes s_b - \xi | H | s_a \otimes s_b \rangle \\ & = C_0 \langle (s_a + \xi) (s_a + \xi), (s_b - \xi) - (-s_b + \xi) | H | s_a s_a, s_b (-s_b + 2\xi) \rangle, \\ & \text{(iv) } \langle s_a \otimes s_b + 1 | H | s_a \otimes s_b \rangle \\ & = C_1 \langle s_a s_a, (s_b + 1) (-s_b - 1) | H | s_a (s_a - 1), s_b (-s_b) \rangle. \end{aligned} \quad (24)$$

The computation of the vector-coupling coefficients of the matrix elements is carried out in the following steps:

(i) First we form (or take as input) the SD and their coefficients occurring in the fragment spin-functions of spin  $s$  and projection  $m = s$  for all spin-coupling types considered in a given calculation:

$$|ts\rangle = \sum_p C_{tp}(nsp) \quad (25)$$

where  $(nsp)$  is the  $p$ th SD with  $n$  open shells and  $s$ , the spin-projection and  $C_{tp}$  are the spin function expansion coefficients.

(ii) The matrix elements that involve only one of the fragments are calculated in a straightforward manner:

$$\langle ts|H|t's\rangle = \sum_{pq} C_{tp} C_{t'q} \langle nsp|H|n'sq\rangle. \quad (26)$$

(iii) For the matrix elements involving both the fragments, we first note that the coefficients  $C_{tp}$  for  $|tm\rangle$  are the same as those for  $|t, -m\rangle$ . Also in those instances where  $|tm\rangle$ ,  $m = s-1, s-2$  are used, the step-down operations are done in an outer DO-loop in order to make the innermost DO-loop efficient.

#### 4.2 Extension to multimers

We shall restrict ourselves in this work to what we shall call the fragment-pair correlation (FPC) model in which only those excitations are allowed that connect at most two fragments. While the double excitations are restricted to involve orbitals that belong to no more than two fragments, the single excitations between fragments may not be accompanied by a 'spin-flip'. Thus single excitations such as

$$(\phi_1 \phi_2 \phi_3)_{s_2} (\phi_4 \phi_5 \phi_6)_{s_3} \rightarrow (\phi_2 \phi_3)_{s_2 \pm \frac{1}{2}} (\phi_4^2 \phi_5 \phi_6)_{s_3 \pm \frac{1}{2}}$$

are allowed but not

$$(\phi_1 \phi_2 \phi_3)_{s_2} (\phi_4 \phi_5 \phi_6)_{s_3} \rightarrow (\phi_2 \phi_3)_{s_2 + \frac{1}{2}} (\phi_4^2 \phi_5 \phi_6)_{s_3 - \frac{1}{2}}$$

or,

$$(\phi_2 \phi_3)_{s_2 - \frac{1}{2}} (\phi_4^2 \phi_5 \phi_6)_{s_3 + \frac{1}{2}}$$

(the subscripts denoting the values of spins of the fragments).

In this model one can easily derive the following analog of (21) applicable to multimers. If the non-equivalently occupied fragments are 1 and 2 between the two states in question, one can write

$$\begin{aligned} & \langle s'_1 \otimes s'_2 \otimes s_3 \otimes \dots | H | s_1 \otimes s_2 \otimes s_3 \otimes \dots \rangle \\ &= \langle (s'_1 m'_1) (s'_2 m'_2) \dots | H | \sum_{m_1 m_2 \dots} a(m_1 m_2 \dots) (s_1 m_1) (s_2 m_2) \dots \rangle \end{aligned} \quad (27)$$

where all the  $m$ -values are the same on both sides, except for 1 and 2, which satisfy  $m'_1 + m'_2 = m_1 + m_2$ . The coefficients  $a(m_1, m_2, \dots)$  are given by

$$a(m_1 m_2 m_3 \dots) = C(m_1 m_2 m_3 \dots) / C'(m'_1 m'_2 m_3 \dots) \quad (28)$$

the  $C$ -coefficients being the expansion coefficients of the spin-symmetrized states.

It is easy to show that, in general, one can choose  $m_1 = s_1$  and  $m_2 = -s_2$ , regardless

of what spin-state is being considered. Thus in the FPC model the evaluation of the matrix elements for multimers follows essentially the same derivation as the dimers.

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