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Exponential transformation of molecular orbitals: A quadratically convergent SCF procedure. I. General formulation and application to closed-shell ground states

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A new formulation is proposed for obtaining the SCF wave functions. It is based on an exponential transformation of spin–orbitals which obviates the use of Lagrangian multipliers. A general method is developed for determining explicit expressions for the successive derivatives of the energy with respect to the new variables. The total energy and the wave function are obtained by an iterative procedure, the convergence of which is shown to be quadratic. The method itself provides information as to the Hartree–Fock stability — or instability — of the SCF solution. The method of exponential transformation of molecular orbitals is applicable to closed-shell systems, as well as to a large variety of open-shell systems. As an illustration of the procedure the results of *ab initio* calculations for ammonia, methane, formaldehyde, and aziridine are given.

I. INTRODUCTION

The SCF wave function is normally accepted as the appropriate wave function within the independent particle model to discuss the properties of molecules. It is also a convenient starting point for configuration interaction or perturbation expansion methods. It is not surprising, therefore, that considerable attention is still being given to the SCF procedure and the characteristics of its solution.

It is the purpose of this paper to present a new strategy for obtaining the SCF solution as well as verifying simultaneously whether the calculated wave function is a stable solution or not. Recently, indeed, the nature of the energy minimum obtained in SCF calculations when applying the variation principle to one-determinant wave functions has been investigated.[1-3] The factors that determine whether a one-determinant function can yield lower minima when the restrictions to the variations are removed have been pointed out, giving a better understanding of the stability or instability conditions of the SCF solutions. This point is particularly important for limited CI and perturbation calculations.

The idea of the method is to define a new set of unknowns to be used in place of the expansion coefficients of the molecular orbitals in the atomic orbital basis, in

such a way that the first and second derivatives of the energy with respect to the new variables can be obtained exactly. This can be achieved, following Levy,[4] by applying an exponential transformation to the molecular orbitals hereafter referred to as the ETMO–SCF method. It is then possible to carry out a quadratically convergent iterative procedure, similar to the Newton–Raphson method, which optimizes the orbitals variationally without use of Lagrangian multipliers. At the same time, the second derivative of the energy provides the desired information to assess the stability of the solution. The ETMO–SCF method is applicable to all systems in their ground state — or first excited states of a given symmetry — whose energy can be expressed in terms of one-electron and two-electron Coulomb and exchange integrals.

It should be emphasized from the very beginning that unoccupied orbitals play an essential role, in contrast to the usual formulation of the SCF problem. This restricts the method to the expansion SCF procedure, since there is no obvious way to define unoccupied orbitals in the framework of a numerical SCF procedure.

II. THE VARIATIONAL EQUATIONS

Before we discuss in detail the determination of the orbitals by means of the ETMO–SCF method it is convenient, for a better understanding of the following developments, to recall some key features of the usual expansion method. It will be assumed that all quantities

involved (coefficients, matrix elements, ...) can be written in real form.

A. Basic principles

Let the one-determinant wave function Ψ built from doubly occupied orbitals be an appropriate representation of a closed-shell $2N$-electron system:

$$\Psi = (2N!)^{-1/2} \det \| \phi_1(1)\bar{\phi}_1(2) \cdots \phi_N(2N-1)\bar{\phi}_N(2N) \| . \tag{1}$$

The variational approximation to the energy is given by

$$E(\Psi) = 2 \sum_i^{occ} \langle i|h|i \rangle + \sum_{i,j}^{occ} \{2(ii;jj) - (ij;ji)\} , \tag{2}$$

where i, j run over all occupied orbitals, and one- and two-electron integrals are defined by

$$\langle i|h|i \rangle = \int \phi_i(1)h(1)\phi_i(1) \, dv_1 , \tag{3}$$

$$(ij;kl) = \int\int \phi_i(1)\phi_k(2)\frac{1}{r_{12}}\phi_j(1)\phi_l(2) \, dv_1 dv_2 , \tag{4}$$

and h is the one-electron operator which comprises the nuclear field and kinetic energy operators.

The optimum choice of orbitals is obtained by minimizing the energy functional with respect to variation of the orbitals, i.e.,

$$\partial E(\Psi)/\partial \phi_i = 0 \quad (i = 1, 2 \ldots, N) , \tag{5}$$

subject to the constraints that orthonormality is preserved,

$$\langle i|j \rangle = \delta_{ij} \quad (i, j = 1, 2 \ldots, N) , \tag{6}$$

which implies that the total wave function Ψ is normalized.

The standard mathematical technique for solving this problem makes use of Lagrangian multipliers. For closed-shell systems the orbitals are the eigenfunctions of a one-electron eigenvalue equation

$$F\phi_i = \epsilon_i \phi_i . \tag{7}$$

The form of the operator F, namely,

$$F = h + \sum_j^{occ} (2J_j - K_j) , \tag{8}$$

was first given completely by Fock[5] and Slater[6] following the earlier work of Hartree,[7] and Eq. (7) is commonly called the Hartree–Fock equation. The Coulomb and exchange operators are defined as follows by their effect on an arbitrary function:

$$J_j(\mu)f(\mu) = \left\langle \phi_j(\nu) \left| \frac{1}{r_{\mu\nu}} \right| \phi_j(\nu) \right\rangle f(\mu) , \tag{9}$$

$$K_j(\mu)f(\mu) = \left\langle \phi_j(\nu) \left| \frac{1}{r_{\mu\nu}} \right| f(\nu) \right\rangle \phi(\mu) . \tag{10}$$

For molecules it is customary to use the so-called LCAO approximation. Following Hall[8] and Roothaan,[9] each molecular orbital is then expanded as a linear combination of a finite set of fixed basis functions χ_p,

$$\phi_i = \sum_{p=1}^{L} \chi_p c_{pi} , \tag{11}$$

where the χ_p's are atomic functions or linear combina-

tions of them. The molecular orbitals being linearly independent, the condition $L \geq N$ must be satisfied. The algebra becomes especially simple if one imposes the restriction $L = N$, which leads to an expression for the molecular ionization potentials in terms of quantities characteristic of the constituent atoms.[8] However, if it is desired to determine molecular orbitals in actual practice,[9] one must in general permit $L > N$.

If C is the matrix of elements c_{pi} whose columns c_i contain the expansion coefficients of the ϕ_i's, the variational problem to be solved is to determine the appropriate coefficients so that

$$\partial E(C)/\partial c_{pi} = 0 \quad (i = 1, \ldots, N) , \tag{12}$$

subject to the orthonormality condition

$$c_i^\dagger S c_j = \delta_{ij} , \tag{13}$$

where S is the overlap matrix between the basis functions. The energy is stationary against variation of c_{pi}'s provided that the equation

$$FC = SC\epsilon \tag{14}$$

is satisfied. It can be shown[9] that it is no loss of generality to assume that ϵ is a diagonal matrix with real diagonal elements ϵ_i; Eq. (14) then reduces to

$$Fc_i = \epsilon_i S c_i . \tag{15}$$

Equation (15) is called the LCAO–SCF equation; it is the finite expansion analog of the Hartree–Fock equation [Eq. (7)]. It should be noted that Eq. (15) has L solutions, i.e., $L-N$ solutions in addition to those which define the N occupied orbitals. These additional solutions yield the unoccupied or virtual orbitals; in general they are of no use in procedures dealing with Eq. (15) since their variation would leave the energy unchanged. However, we shall show that these virtual orbitals are essential to the ETMO–SCF method.

B. The variational problem in the ETMO–SCF method[10]

First proposed by Levy for obtaining the orbitals in MC–SCF wave functions,[4] the method of the exponential transformation of molecular orbitals will be presented here in its specific development for SCF calculations at the independent particle approximation level.

The basis used can be any set of L orthonormal and linearly independent functions. The orthonormality constraint represents no loss of generality since it does not affect the total space spanned by the orbitals. The molecular orbitals, occupied as well as virtual, are defined by their expansion coefficients as

$$\phi(X) = \Lambda \exp(X) , \tag{16}$$

where the exponential function is expressed in terms of the matrix elements x_{ij} by the usual power expansion; $\phi(X)$ is the row vector of the orbitals and Λ the row vector of the elements of the basis set $\{\lambda_i\}$. Obviously, the part of the matrix $\exp(X)$ corresponding to the expansion coefficients of the occupied MO's would be identical with the matrix C defined previously if $\{\lambda_i\}$ was the set of atomic functions. The variational equation [Eq. (12)] is then replaced by

$$\partial E(\mathbf{X})/\partial x_{ij} = 0 \ . \tag{17}$$

The unknowns of the problem are now the $(L \times L)$ matrix elements x_{ij} of X instead of the $(N \times L)$ matrix elements $c_{\mu i}$ of C.

In order to satisfy the orthonormality condition on the molecular orbitals, the matrix exp(X) must be unitary, i.e.,

$$[\exp(\mathbf{X})]^{\dagger} [\exp(\mathbf{X})] = [\exp(\mathbf{X})][\exp(\mathbf{X})]^{\dagger} = I \ . \tag{18}$$

This can be achieved by imposing the condition

$$\mathbf{X}^{\dagger} + \mathbf{X} = 0 \ , \tag{19}$$

which is a sufficient condition for Eq. (18) to be satisfied.[11]

The main advantage of Eq. (19) is that the orthonormality constraint on the orbitals is linear, instead of quadratic as in the method using Lagrangian multipliers. So, combining Eqs. (17) and (19), it can be included in the variational equation to be solved, i.e.,

$$\left(\frac{\partial}{\partial x_{ij}} - \frac{\partial}{\partial x_{ji}}\right) E(\mathbf{X}) = 0 \quad i > j \ . \tag{20}$$

The unknowns are now the $(x_{ij} - x_{ji})$ and the Lagrangian multipliers are no longer necessary. Indices i and j must run over the whole set of basis functions $\{\lambda_i\}$.

C. Method for solving the variational equations

We propose to use a quadratically convergent iterative process to determine the wave function $\Psi(\mathbf{X})$. The orbitals $\{\phi_i^{(n+1)}\}$ of the $(n+1)$th iteration are expanded in terms of the orbitals $\{\phi_i^{(n)}\}$ of the nth iteration. Therefore, at each step of the iterative process the orbitals $\{\lambda_i\}$ in Eq. (16) are different; they are replaced by the orbitals obtained as solutions of the preceding iteration. In our procedure, we have

$$\phi^{(n+1)} = \phi^{(n)} \exp(\mathbf{X}^{(n)}) \ . \tag{21}$$

The equations to be solved are

$$e'^{(n)}_{ij} + \sum_{k > l} e''^{(n)}_{ij,kl} x^{(n)}_{kl} = 0 \quad i > j \ , \quad x^{(n)}_{ij} + x^{(n)}_{ji} = 0 \ , \tag{22}$$

in which $e'^{(n)}_{ij}$ and $e''^{(n)}_{ij,kl}$ are the first and second derivatives of the energy calculated using the set of orbitals $\{\phi_i^{(n)}\}$,

$$e'^{(n)}_{ij} = \left[\left(\frac{\partial}{\partial x_{ij}} - \frac{\partial}{\partial x_{ji}}\right) E(\mathbf{X})\right]_{\Phi = \phi^{(n)}} , \tag{23}$$

$$e''^{(n)}_{ij,kl} = \left[\left(\frac{\partial}{\partial x_{ij}} - \frac{\partial}{\partial x_{ji}}\right)\left(\frac{\partial}{\partial x_{kl}} - \frac{\partial}{\partial x_{lk}}\right) E(\mathbf{X})\right]_{\Phi = \phi^{(n)}} . \tag{24}$$

It should be noted that the condition $\phi = \phi^{(n)}$ in Eqs. (23) and (24) is equivalent to setting X = 0 in Eq. (16) or Eq. (21). Consequently, the expressions giving the first and second derivatives of the energy are free of the infinite summations implied by use of the exponential function.

The computational scheme consists in using Eqs. (21) and (22) iteratively. The process, initiated by a complete set of occupied and virtual orbitals is repeated until both the difference between the $\{\phi_i^{(n)}\}$ and $\{\phi_i^{(n+1)}\}$

and the magnitude of the elements x_{kl} are less than some given thresholds (the theoretical convergence is reached for X = 0). The derivation of the first and second derivatives of the energy is described in Sec. III.

In practice, only a subsystem of Eq. (22) is solved. This modification is discussed more easily if the closed-shell and open-shell cases are considered separately. The closed-shell case is developed in Sec. IV below. The resulting wave function is equivalent, up to a unitary transformation, with that obtained by the traditional expansion method. This is shown in Appendix A.

III. EXPRESSION OF THE SUCCESSIVE DERIVATIVES OF THE ENERGY

The formalism presented in this section is applicable to open-shell as well as to closed-shell systems, being a detailed development for the case when the variational energy can be expressed as a sum over one-electron integrals and two electron Coulomb and exchange molecular integrals, namely,

$$E = \sum_i n_i \langle i | h | i \rangle + \sum_{i,j} n_{ij}(ii;jj) - n'_{ij}(ij;ji) \ . \tag{25}$$

For Eq. (25) to be as general as possible, we define n_i as the occupation number — equal to zero, one, or two — of orbital ϕ_i, and n_{ij} and n'_{ij} as pair-occupation factors to be determined for each specific case. Equation (25) describes the energy for open-shell systems whose wave functions are, in general, linear combinations of determinants.

The first and second derivatives of the energy in Eq. (22) are obtained as follows: For each iteration, orbitals $\phi_i, \phi_j \cdots$ in Eq. (25) are expressed as functions of X by a transformation from the initial orbitals, namely,

$$\phi_i(\mathbf{X}) = \sum_k \phi_k^{(n)} \exp(\mathbf{X})_{ki} \ . \tag{26}$$

Then the derivatives of the energy with respect to X are obtained analytically and evaluated at X = 0, which is equivalent to setting $\phi_i = \phi_i^{(n)}$.

The principle of the differentiation can be easily illustrated for the orbitals (see Appendix B for more details concerning energy itself). For convenience let Eq. (26) be rewritten as

$$|i(\mathbf{X})\rangle = \sum_k |k\rangle \exp(\mathbf{X})_{ki} \tag{27}$$

Expanding the exponential gives

$$|i(\mathbf{X})\rangle = |i\rangle + \sum_k |k\rangle x_{ki} + \frac{1}{2}\sum_{k,l} |k\rangle x_{kl}x_{li} + \cdots \ . \tag{28}$$

The first derivative of the latter expression with respect to a current element x_{ab} is

$$\frac{\partial}{\partial x_{ab}} |i(\mathbf{X})\rangle = |a\rangle\langle b|i\rangle + \frac{1}{2}|a\rangle x_{bi} + \frac{1}{2}\sum_k |k\rangle x_{ka}\langle b|i\rangle + \cdots \tag{29}$$

and the second derivative

$$\frac{\partial^2}{\partial x_{cd}\partial x_{ab}} |i(\mathbf{X})\rangle = \frac{1}{2}|a\rangle\langle b|c\rangle\langle d|i\rangle + \frac{1}{2}|c\rangle\langle d|a\rangle\langle b|i\rangle + \cdots \ . \tag{30}$$

So, one has

$$\left[\frac{\partial}{\partial x_{ab}}|i(\mathbf{X})\rangle\right]_{\mathbf{X}=0} = |a\rangle\langle b|i\rangle \ , \tag{31}$$

$$\left[\frac{\partial^2}{\partial x_{cd}\partial x_{ab}}|i(\mathbf{X})\rangle\right]_{\mathbf{X}=0} = \tfrac{1}{2}|a\rangle\langle b|c\rangle\langle d|i\rangle + \tfrac{1}{2}|c\rangle\langle d|a\rangle\langle b|i\rangle \ . \tag{32}$$

Keeping in mind the orthonormality of the basis set of MO's, including the skew symmetry of $\mathbf{X}$ in the process leads after some manipulations to the following general expressions for the energy derivatives.[12]

First derivative of the energy:

$$\left[\left(\frac{\partial}{\partial x_{ab}} - \frac{\partial}{\partial x_{ba}}\right)E(\mathbf{X})\right]_{\mathbf{X}=0} = 2\langle a|h|b\rangle(n_b - n_a) + 4\sum_j^{\text{occ}}\langle a|J_j|b\rangle(n_{bj} - n_{aj}) - \langle a|K_j|b\rangle(n'_{bj} - n'_{aj}) \ ; \tag{33}$$

Second derivative of the energy:

$$\left[\left(\frac{\partial}{\partial x_{cd}} - \frac{\partial}{\partial x_{dc}}\right)\left(\frac{\partial}{\partial x_{ab}} - \frac{\partial}{\partial x_{ba}}\right)E(\mathbf{X})\right]_{\mathbf{X}=0} = \left\{\langle a|h|d\rangle(n_a + n_d - 2n_b) + 2\sum_j^{\text{occ}}[\langle a|J_j|d\rangle(n_{aj} + n_{dj} - 2n_{bj}) - \langle a|K_j|d\rangle(n'_{aj} + n'_{dj} - 2n'_{bj})]\right\}\delta_{bc}$$

$$+ \left\{\langle b|h|c\rangle(n_b + n_c - 2n_a) + 2\sum_j^{\text{occ}}[\langle b|J_j|c\rangle(n_{bj} + n_{cj} - 2n_{aj}) - \langle b|K_j|c\rangle(n'_{bj} + n'_{cj} - 2n'_{aj})]\right\}\delta_{ad}$$

$$- \left\{\langle a|h|c\rangle(n_a + n_c - 2n_b) + 2\sum_j^{\text{occ}}[\langle a|J_j|c\rangle(n_{aj} + n_{cj} - 2n_{bj}) - \langle a|K_j|c\rangle(n'_{aj} + n'_{cj} - 2n'_{bj})]\right\}\delta_{bd}$$

$$- \left\{\langle b|h|d\rangle(n_b + n_d - 2n_a) + 2\sum_j^{\text{occ}}[\langle b|J_j|d\rangle(n_{bj} + n_{dj} - 2n_{aj}) - \langle b|K_j|d\rangle(n'_{bj} + n'_{dj} - 2n'_{aj})]\right\}\delta_{ac}$$

$$- 8(ab; cd)[(n_{ad} + n_{bc}) - (n_{ac} + n_{bd})] + 4[(bc; ad) + (bd; ac)][(n'_{ad} + n'_{bc}) - (n'_{ac} + n'_{bd})] \ , \tag{34}$$

where J_j and K_j are the Coulomb and exchange operators as defined in Eqs. (9)–(10). This relationship can be compared to the results obtained by Paldus and Cizek in their studies of the Hartree–Fock instability conditions.[1] Equation (34) is valid without exception since it does not assume that the Brillouin theorem is satisfied.

IV. THE ETMO–SCF METHOD FOR A CLOSED-SHELL GROUND STATE

The ground-state energy of a closed-shell system is obtained from Eq. (25) by taking the appropriate values for the occupation parameters of the molecular orbitals, i.e., $n_i = 0$ or 2 for empty and occupied orbitals, respectively, and $n_{ij} = \tfrac{1}{2}n_i n_j$, $n'_{ij} = \tfrac{1}{2}n_{ij}$ for all pairs of orbitals.

In the following we denote the orbitals occupied in the ground-state wave function by $o, o', o'', \ldots$, and the corresponding empty or virtual orbitals by $v, v', v'', \ldots$ Whenever possible, the results will be expressed in terms of the matrix elements of the Fock Hamiltonian for the electronic system, namely,

$$F = h + \sum_j^{\text{occ}}(2J_j - K_j) \ . \tag{35}$$

Applying Eq. (33) we obtain the three components of the first derivative,

$$e'_{vo} = 4\langle v|h|o\rangle + \sum_{o'}(2\langle v|J_{o'}|o\rangle - \langle v|K_{o'}|o\rangle) = 4\langle v|F|o\rangle \ , \tag{36}$$

$$e'_{oo'} = 0 \ , \tag{37}$$

$$e'_{vv'} = 0 \ . \tag{38}$$

These equations clearly show that a unitary transformation — here the rotation by means of $\exp(\mathbf{X})$ — in the subspace of the occupied [Eq. (37)] or virtual orbitals [Eq.

(38)] leaves the electronic energy unchanged.

Using the general expression of the second derivative [Eq. (34)] leads to

$$e''_{oo', o''o'''} = 0 \ , \tag{39}$$

$$e''_{vv', v''v'''} = 0 \ , \tag{40}$$

$$e''_{oo', vv'} = 0 \ , \tag{41}$$

$$e''_{vo', o''o} = -2\langle o|F|v\rangle\delta_{o'o''} \ , \tag{42}$$

$$e''_{vv', v''o} = 2\langle o|F|v\rangle\delta_{v'v''} \ , \tag{43}$$

$$e''_{vo, vo} = 4[\langle v|F|v\rangle - \langle o|F|o\rangle + 3(ov; ov) - (oo; vv)] \ , \tag{44}$$

$$e''_{vo, v'o} = 4[\langle v'|F|v\rangle + 3(vo; v'o) - oo; vv')] \ , \tag{45}$$

$$e''_{vo, vo'} = -4[\langle o'|F|o\rangle - 3(vo'; vo) + (oo'; vv)] \ , \tag{46}$$

$$e''_{vo, v'o} = 4[4(vo; v'o') - (vo'; v'o) - (o'o; v'v)] \ . \tag{47}$$

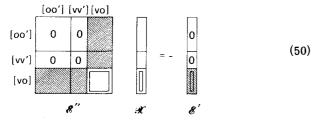The method for solving the set of linear equations

$$\sum_{k>l} e''_{ij,kl} x_{kl} = -e'_{ij} \quad i > j \tag{48}$$

subject to the constraint

$$x_{ij} + x_{ji} = 0 \tag{49}$$

can be discussed more easily in matrix form. The quantities x_{kl} and e'_{ij} are collected into column supervectors $\mathcal{X}$ and $\mathcal{E}'$ of elements $x_{[kl]}$ and $e'_{[ij]}$ and the four index quantities $e''_{ij,kl}$ are collected into a supermatrix $\mathcal{E}''$ of elements $e''_{[ij][kl]}$; Eq. (48) can then be represented

formally by

$$(50)$$

where the matrix and column vectors are partitioned according to the different possible pairs of occupied and virtual orbitals.

The $[oo']$ and $[vv']$ components of $\mathscr{E}''$ and $\mathscr{E}'$ indicated in Eq. (50) are always equal to zero according to Eqs. (38)–(41). Furthermore, according to Eqs. (36) and (42)–(43), the shaded areas become equal to zero when convergence is reached, so that $\det(\mathscr{E}'')$ is equal to zero and the system cannot be determined. Moreover, the system represented by Eq. (50) cannot be solved even before convergence. Although one cannot find a row or a column of $\det(\mathscr{E}'')$ with only zero elements before convergence, there are still not enough nonzero elements to avoid the singularity of $\mathscr{E}''$. In view of the structure of $\mathscr{E}''$ one would have

$$\det(\mathscr{E}'') \neq 0$$

only if the number of $[vo]$ elements was larger than the total number of $[oo']+[vv']$ elements, a situation which cannot hold. These difficulties can be overcome by reducing Eq. (50) to the $[vo]$ component and by putting the remaining components of $\mathscr{X}$ equal to zero. This solution leads to the subsystem

$$\sum_{v',o'} e''_{vo,\,v'o'}\,x_{v'o'} = -e'_{vo}\;,$$
$$x_{oo'} = x_{vv'} = 0\;,\tag{51}$$
$$x_{ov} + x_{vo} = 0\;.$$

Equations (51) must not be assumed at the beginning of the analysis. Initially the matrix X contains in general nonzero elements $x_{oo'}$ and $x_{vv'}$ which accomplish transformations of the occupied orbitals among themselves, or the virtual orbitals among themselves. Of course, the subspaces of the occupied and virtual orbitals do not depend on $x_{oo'}$ and $x_{vv'}$ at first order in the development of $\exp(X)$ and it may seem that these transformations are arbitrary. However, the elements $x_{oo'}$ and $x_{vv'}$ do contribute to the mixing between occupied and virtual orbitals at higher order, i.e., when the actual unitary transformation by $\exp(X)$ is performed. Therefore it would seem appropriate to determine $x_{oo'}$ and $x_{vv'}$ in an optimum way. Since this determination is impossible using Eq. (50) we have chosen $x_{oo'} = x_{vv'} = 0$. It remains to prove that the convergence of the process is still quadratic. This proof is given in Appendix C (see also Refs. 13 and 14).

In practice, the unitary transformation described by Eq. (21) is performed in an approximate way, namely,

$$\phi^{(n+1)} = \phi^{(n)}\,(1+X^{(n)})\tag{52}$$

and then the orthonormalization condition on the orbitals is restored iteratively by correcting the $C^{(n+1)}$ matrix

of the components of the $\phi_i^{(n+1)}$'s in the nonorthogonal atomic basis by

$$C_p^{(n+1)} \rightarrow C_{p+1}^{(n+1)} = \tfrac{1}{2}\,(3C_p^{(n+1)} - C_p^{(n+1)}\,S\,C_p^{(n+1)\dagger}\,C_p^{(n+1)})\,,\tag{53}$$

where S is the matrix of the nonorthogonality integrals between atomic orbitals. This process is quadratically convergent and is equivalent to the $S^{-1/2}$ symmetrical orthogonalization method.[4,15,16] It should be noted that the quadratic convergence rate of Eq. (51) is not altered since the rotation by $(1+X)$ followed by the reorthonormalization according to Eq. (53) is identical with the power expansion of $\exp(X)$ up to X^2.

The molecular orbitals thus obtained are taken as the new trial set and the iterative procedure is repeated until convergence.

V. THE USE OF MOLECULAR SYMMETRY IN THE ETMO–SCF METHOD

It is well established that group theory provides a powerful mean for simplifying the problem of finding SCF wave functions. This facility can also be used in the ETMO–SCF method.

We can choose the orbitals so that they fall into subsets of symmetry orbitals, carrying the various irreducible representations of the molecular point group. The system of the variational equations to be solved can then be reduced to a subsystem of lower dimension. This is due to the fact that the supermatrix of the second derivatives of the energy is block diagonal in these conditions. The situation can easily be visualized by considering the simple case of two irreducible representations Γ_i and Γ_j, namely,

$$(54)$$

It follows from the above equation that the shaded area of $\mathscr{X}$ is equal to zero. As a consequence, calculation of elements of the second derivative corresponding to the $\Gamma_i\Gamma_j \times \Gamma_i\Gamma_j$ area is not necessary.

Interestingly, the ETMO–SCF method provides an alternative way for taking symmetry into account by using symmetry equivalent excitation pairs of occupied and virtual orbitals. An excitation pair (occupied → virtual) will be equivalent to another pair of orbitals if they can be transformed into each other by applying a symmetry operation.

For example, in $NH_3\,(C_{3v})$ and using a minimal basis set, there are five occupied and three virtual orbitals, which amounts to solving Eqs. (50)–(51) in 15 dimensions. From the definition of symmetry equivalent excitation pairs, it is a straightforward matter to show that using localized orbitals, the 15 couples of orbitals can be classified into four groups:

Group I $(\phi_{1sN} \to \phi_{NH_1}^*);\;\; (\phi_{1sN} \to \phi_{NH_2}^*);\;\; (\phi_{1sN} \to \phi_{NH_3}^*)\;,$

Group II $(\phi_{NH_1} \to \phi_{NH_1}^*)$; $(\phi_{NH_2} \to \phi_{NH_2}^*)$; $(\phi_{NH_3} \to \phi_{NH_3}^*)$

Group III $(\phi_{\bar{N}} \to \phi_{NH_1}^*)$; $(\phi_{\bar{N}} \to \phi_{NH_2}^*)$; $(\phi_{\bar{N}} \to \phi_{NH_3}^*)$

Group IV $(\phi_{NH_1} \to \phi_{NH_2}^*)$; $(\phi_{NH_1} \to \phi_{NH_3}^*)$; $(\phi_{NH_2} \to \phi_{NH_1}^*)$

$(\phi_{NH_2} \to \phi_{NH_3}^*)$; $(\phi_{NH_3} \to \phi_{NH_1}^*)$; $(\phi_{NH_3} \to \phi_{NH_2}^*)$.

The first derivative of the energy has a unique value within each group and the second derivatives are now equal for all possible couples of excitation pairs between two given groups. So, the corresponding matrix elements need only to be computed once. The supervector and supermatrix in Eq. (50) are easily built using the symmetry properties of the excitation pairs. Solving the variational equations is then performed in the initial dimension as illustrated by the graph

$$(55)$$

where (●) represents the only computed element of a given area, all others being equal to that one. The conservation of symmetry equivalence between orbitals is automatically preserved along the search path. This way of considering symmetry is to be compared with the treatment proposed by Dupuis and King for evaluating atomic integrals.[17]

Using localized orbitals presents a number of supplementary advantages which should be underlined.

The initial guess of occupied and virtual bond orbitals can be obtained from any hybridization procedure. For example, the maximum overlap criterion[18] can be used to obtain fully localized bond orbitals.[19] Owing to the transferability of the localized SCF orbitals,[20] the initial guess can also be obtained by an appropriate cutoff of the localized MO's of a preceding calculation. The choice of localized MO's reduces the number of iterations to be done in any convergence method since the Fock matrix element between the occupied and virtual orbitals localized on the same chemical bond is nearly zero because the bond orbitals satisfy to a good approxi-

TABLE I. NH$_3$ (C_{3v}).

	S-SCF	ETMO-SCF	
Iterations	Total energy[a]	max$|C^{(n)} - C^{(n-1)}|$	Total energy
0	−55.850391		−55.850391
1	−55.914497	0.97×10^{-1}	−55.916000
2	−55.915778	0.10×10^{-2}	−55.916006
3	−55.915963	0.15×10^{-5}	...
4	−55.915998	0.17×10^{-10}	−55.916006
5	−55.916004		
6	−55.916006		
...	...		
...	...		
12	−55.916006		

[a]Atomic unit.

TABLE II. CH$_4$ (T_d).

	S-SCF	ETMO-SCF	
Iterations	Total energy[a]	max$|C^{(n)} - C^{(n-1)}|$	Total energy
0	−39.633274		−39.633274
1	−39.947447	0.16	−39.957825
2	−39.957645	0.13×10^{-1}	−39.958417
3	−39.958360	0.32×10^{-5}	...
4	−39.958413	0.80×10^{-10}	−39.958417
5	−39.958417		
...			
...			
12	−39.958417		

[a]Atomic unit.

mation a local Brillouin theorem. Moreover, interactions between bonds defined in distinct regions of space are weak.[19]

Once the stabilization of the wave function has been achieved the SCF MO's can be transformed easily according to any desired criterion of localization, since they are already localized. The canonical set of molecular orbitals can eventually be obtained by diagonalization of the ultimate Fock matrix.

VI. APPLICATION TO SOME MOLECULES

In order to illustrate the numerical aspects of the ETMO—SCF method for the determination of molecular wave functions, we present a few examples of results obtained for simple molecules of different sizes and symmetry: ammonia, methane, formaldehyde, and aziridine, which have been taken in their equilibrium geometries. The computations have been carried out using a basis of $7s$, $3p/3s$ Gaussian-type orbitals contracted to a minimal basis set.[21]

As a reference, we give simultaneously the convergence for the simplest method of successive diagonalization (hereafter referred to as S-SCF). In other words, the results presented in Tables I–IV have been obtained, for both methods, without any extrapolation or acceleration procedure.

Tables I–IV provide an illustration of the fundamental behavior of the ETMO–SCF method.

- The rate of convergence is quadratic in the sense of the Max norm.

TABLE III. H$_2$CO (C_{2v}).

	S-SCF	ETMO-SCF	
Iterations	Total energy[a]	max$|C^{(n)} - C^{(n-1)}|$	Total energy
0	−113.21257		−113.21257
1	−113.35940	0.22	−113.36444
2	−113.36600	0.27×10^{-1}	−113.36712
3	−113.36692	0.77×10^{-3}	...
4	−113.36708	0.34×10^{-6}	...
5	−113.36711	0.74×10^{-13}	−113.36712
6	−113.36712		
...			
...			
...			
...			
12	−113.36712		

[a]Atomic unit.

TABLE IV. $\overline{CH_2CH_2NH}$ (C_s).

Iterations	S-SCF Total energy[a]	ETMO-SCF max$|C^{(n)} - C^{(n-1)}|$	Total energy
0	-131.48933		-131.48933
1	-132.37077	0.25	-132.38727
2	-132.38849	0.70×10^{-1}	-132.39079
3	-132.39041	0.11×10^{-2}	-132.39081
4	-132.39072	0.16×10^{-5}	...
5	-132.39079	0.59×10^{-12}	-132.39081
6	-132.39080		
7	-132.39080		
8	-132.39081		
9	-132.39081		
...	...		
...	...		
23	-132.39081		

[a]Atomic unit.

- Two or three iterations only are necessary to achieve a stabilization of 10^{-6} a. u. in the total energy.

- Once the total energy is obtained, one supplementary iteration is enough to reach a stabilization of 5×10^{-8} in the absolute values of the molecular orbital expansion coefficients.

- At the same time, the eigenvalues of the second derivative matrix provide the desired information to assess the Hartree–Fock stability of the solution. If they are all positive (for NH_3 one has the four different eigenvalues 185.17, 26.07, 17.70, 5.92) this ensures that the energy cannot decrease in the vicinity of the calculated wave function, and then the SCF solution is said to be "stable." Of course, Hartree–Fock stability or instability are purely local properties. The general problem including double-well situations is beyond the scope of this paper, and the SCF procedure presented here is not the appropriate way to deal with it.[22]

Moreover, an important numerical result must be underlined, i. e. , the first derivative of the energy and the elements of the X matrix tend quadratically towards zero (Table V). This point is particularly useful for numerical applications of the ETMO method since the first derivative of the energy gives the slope of the search path towards the energy minimum. Thus, two iterations only are required to test whether the initial guess of trial functions provides a convergent starting point.

VII. DISCUSSION

Various methods have been proposed for solving the variational equations. Apart from numerical variational methods[23] which lead to a system of integrodif-

ferential equations, which cannot easily be solved except in the one-center case, most of the approaches to the problem are concerned with the orbital approximation.

The final step in any optimization process is normally the solution of a stationary value problem, subject to a variety of constraints. Because the equations are non-linear in the unknown coefficients iteration is necessary. The most widely used method of obtaining approximate solutions of the Hartree–Fock equation is to transform the system into a pseudoeigenvalue form, because an eigenvalue problem can easily be solved in general. In fact, there is no guarentee that the iterative method involving successive solution and adjustment of an eigenvalue problem will be convergent. However, in practice, with suitable trial vectors, it is possible to make the process converge at least for most closed-shell calculations and many open-shell cases as well. Many different iteration strategies have been proposed to improve convergence,[24] including quadratic procedures.[25]

On the other hand, there are the direct minimization techniques using "gradient" or "steepest descent" methods. The energy is regarded as a point on the hypersurface which represents the energy as a function of all the unknown variables. The coefficients of the orbitals are then changed in such a way as to obtain at each step of the process a maximum rate of descent on this surface.[26] Other attempts have been made by combining the steepest descent methods with perturbation treatments of an appropriate effective Fock matrix.[27] In that formulation, the convergence is dependent on step-length parameters whose optimum values can be estimated using various procedures.[26–28] The main advantage of these direct minimization methods is that they are applicable even when the variational problem cannot be replaced by an eigenvalue problem.

The principle of the method we present here is quite different. It relies on a mixing of occupied and virtual orbitals so as to satisfy the Brillouin theorem. Another approach of the same kind can be found in the direct determination of SCF orbitals by perturbation.[29]

The fundamental point of the method is the exponential transformation of the orbitals. This transformation leads to an explicit form of the successive derivatives of the energy and enable us to write the orthonormalization constraint as a linear condition in the unknowns instead of a quadratic one.

There is no longer the need to force the stationary value problem into an eigenvalue problem. It is replaced by the problem of finding the root of the first

TABLE V. Convergence of the first derivative of the energy and X matrix in the ETMO–SCF procedure.

Iterations	NH_3 max(e'_{vo})	max(x_{vo})	CH_4 max(e'_{vo})	max(x_{vo})	H_2CO max(e'_{vo})	max(x_{vo})	$\overline{CH_2CH_2NH}$ max(e'_{vo})	max(x_{vo})
0	0.15×10^{1}	0.40×10^{-1}	0.20×10^{1}	-0.76×10^{-1}	-0.28×10^{1}	-0.14	0.28×10^{1}	0.12
1	0.44×10^{-2}	0.74×10^{-3}	0.20×10^{-1}	-0.50×10^{-2}	-0.11	-0.31×10^{-1}	0.13	-0.54×10^{-1}
2	0.13×10^{-5}	0.60×10^{-6}	-0.17×10^{-4}	0.16×10^{-5}	0.16×10^{-2}	0.46×10^{-3}	0.47×10^{-2}	0.95×10^{-3}
3	-0.77×10^{-10}	0.99×10^{-11}	-0.29×10^{-9}	-0.40×10^{-10}	-0.13×10^{-5}	-0.39×10^{-6}	-0.29×10^{-5}	-0.11×10^{-5}
4					0.18×10^{-12}	0.50×10^{-13}	0.27×10^{-11}	0.59×10^{-12}

derivative of the energy. The method used is of the Newton–Raphson type which is particularly convenient since the exact values of the successive derivatives of the energy can easily be obtained. The iteration procedure which is carried out is then quadratically convergent. At the same time, the second derivative of the energy gives information on the stability, or instability, of the wave function along the search path without any supplementary manipulation.

Considering symmetry leads usually to several systems of lower dimensions in place of the initial system of equations. In the ETMO–SCF method, there is always one system to solve. The calculation can be performed in a reduced dimension by using symmetry adapted molecular orbitals or, if it is performed in the initial dimension, a minimum number of terms has to be calculated according to the definition of symmetry equivalent pairs of MO's. The approach adopted will be mainly a matter of taste — delocalized or localized orbitals and computational convenience. At that time, it should be recalled that each step of the ETMO method involves the evaluation of molecular integrals and the inversion of the matrix of the second derivatives of the energy, so that the computation time may be greater than for other procedures, even if the number of iterations is far smaller.

We believe that the simplicity of the approach described here, along with the explicit computational procedures and examples, will be helpful to the further development of ETMO methods. It is pertinent to acknowledge that since our paper was first submitted Dalgaard and Jorgensen[14] have published a general theoretical development for MC–SCF wave functions which contains our present treatment as a special case. Our program includes some of the features suggested in their paper. In particular, we have found that keeping the second derivative constant through several iterations is valid provided $\max|x_{uo}| < 10^{-1}$. The convergence is then no longer quadratic although it is very fast.[30]

Extension of the ETMO method to open-shell systems which should lead to much more important applications is now in progress. The effective Hamiltonian formalism necessary to obtain a restricted solution of the Hartree–Fock equations can be avoided and a solution to the convergence problems often encountered in this field is expected.

ACKNOWLEDGMENTS

APPENDIX A: EQUIVALENCE WITH THE ROOTHAAN METHOD

In the usual expansion formulation, the problem is to solve

$$\partial E(C)/\partial c_{pi} = 0 \quad \begin{array}{l}(p = 1, 2, \ldots L) \\ (i = 1, 2, \ldots N)\end{array} \tag{A1}$$

subject to the orthonormality constraint

$$C^t S C = I . \tag{A2}$$

In the ETMO–SCF method, the problem is to find a matrix X satisfying the system of equations

$$[\partial E(X)/\partial x_{kl}]_{X=0} = 0 \quad (k, l = 1, 2 \ldots L) , \tag{A3}$$

$$X + X^t = 0 . \tag{A4}$$

We shall prove here that if a set of linearly independent and orthonormal orbitals is such that Eqs. (A3) and (A4) are satisfied then these orbitals also satisfy Eqs. (A1) and (A2). In what follows it is implied that every derivative is computed for $X = 0$.

The basic equation for the ETMO–SCF procedure is

$$\phi^{(n+1)} = \phi^{(n)} \exp(X^{(n)}) . \tag{A5}$$

Let $C^{(n)}$ be the representative matrix of $\phi^{(n)}$ in the atomic orbital basis set $\{\chi_p\}$, of dimension L, and let $C^{(n+1)}$ be the representative matrix of $\phi^{(n+1)}$ in the same basis. Equation (A5) may be written as

$$c_{pi}^{(n+1)} = \sum_{j=1}^{L} c_{pj}^{(n)} \exp(X)_{ji} \quad (i, p = 1, 2 \ldots L) . \tag{A6}$$

Thus, Eq. (A3) becomes

$$\frac{\partial E(X)}{\partial x_{kl}} = \sum_{i=1}^{L} \sum_{p=1}^{L} \frac{\partial E(C^{(n+1)})}{\partial c_{pi}^{(n+1)}} \frac{\partial c_{pi}^{(n+1)}}{\partial x_{kl}} = 0 \quad (k, l = 1, 2, \ldots L). \tag{A7}$$

Taking the derivative of $c_{pi}^{(n+1)}$ with respect to x_{kl} in Eq. (A7), we have

$$\frac{\partial c_{pi}^{(n+1)}}{\partial x_{kl}} = \sum_{j=1}^{L} c_{pj}^{(n)} \frac{\partial \exp(X)_{ji}}{\partial x_{kl}} \quad (i, p, k, l = 1, 2 \ldots L) . \tag{A8}$$

where, on using the power expansion of the exponential function, one has

$$\frac{\partial \exp(X)_{ji}}{\partial x_{kl}} = \delta_{jk}\delta_{il} + \frac{1}{2} \sum_{m=1}^{L} (\delta_{jk}\delta_{ml}x_{li} + x_{jk}\delta_{mk}\delta_{il}) + \cdots . \tag{A9}$$

For $X = 0$, Eq. (A8) becomes

$$\frac{\partial c_{pi}^{(n+1)}}{\partial x_{kl}} = \delta_{ik}c_{pl}^{(n)} \quad (i, p, k, l = 1, 2 \ldots L) . \tag{A10}$$

Substituting Eq. (A10) in Eq. (A7) yields

$$\frac{\partial E(X)}{\partial x_{kl}} = \sum_{p=1}^{L} \frac{\partial E(C^{(n+1)})}{\partial c_{pk}^{(n+1)}} c_{pl}^{(n)} = 0 \quad (k, l = 1, 2 \ldots L) . \tag{A11}$$

But we note that $X = 0$ implies $C^{(n+1)} = C^{(n)}$ so that in the expression $[\partial E(C^{(n+1)})/\partial c_{pi}^{(n+1)}]_{X=0}$ we can replace $C^{(n+1)}$ by $C^{(n)}$ wherever $C^{(n+1)}$ appears. Thus we obtain

$$\left[\frac{\partial E(C^{(n+1)})}{\partial c_{pi}^{(n+1)}}\right]_{X=0} = \frac{\partial E(C^{(n)})}{\partial c_{pi}^{(n)}} \quad (i, p = 1, 2 \ldots L) . \tag{A12}$$

Using Eq. (A12), Eq. (A11) may be rewritten as

$$\left[\frac{\partial E(X)}{\partial x_{kl}}\right]_{X=0} = \sum_{p=1}^{L} \frac{\partial E(C^{(n)})}{\partial c_{pk}^{(n)}} c_{pl}^{(n)} = 0 \quad (k, l = 1, 2 \ldots L) . \tag{A13}$$

Thus, if a set of orthonormal orbitals satisfies the system of Eqs. (A3) and (A4), then it satisfies the set of

Eqs. (A13), too. But, from Eq. (A13) we can deduce the values of the derivatives $\partial E(\mathbf{C}^{(n)})/\partial c_{pk}^{(n)}$ for this set of orbitals. For that purpose we use the subset of Eqs. (A13) with fixed k as a system of linear equations in which the $\partial E(\mathbf{C}^{(n)})/\partial c_{pk}^{(n)}$'s ($k$ fixed, $p=1,2\ldots L$) are the unknowns and the $c_{pl}^{(n)}$'s ($l,p=1,2\ldots L$) are the coefficients. Since the orbitals under consideration are linearly independent we have

$$\det|\mathbf{C}^{(n)}| \neq 0 \; , \tag{A14}$$

and consequently Eq. (A13) implies

$$\partial E(\mathbf{C}^{(n)})/\partial c_{pk}^{(n)} = 0 \; .$$

In other words, Eq. (A3), which implies Eq. (A13), implies the condition of the usual expansion method at convergence.

APPENDIX B: DERIVATIVES OF THE ENERGY

We illustrate here the algebra which leads to the analytical formulas for the derivatives of the energy.

I. One-electron integrals

The expectation value of the one-electron operator (kinetic plus nuclear attraction) for an electron in ϕ_i is given by

$$\langle i(\mathbf{X})|h|i(\mathbf{X})\rangle = \langle i|h|i\rangle + 2\sum_k \langle i|h|k\rangle x_{ki} + \sum_{k,l}(\langle i|h|k\rangle x_{ki}x_{li} - x_{ik}\langle k|h|l\rangle x_{li}) + \cdots \; . \tag{B1}$$

Differentiating Eq. (B1) is performed by the same method as used for Eq. (28). Expanding Eq. (B1), taking account of the Hermitian nature of h and making use of the skew symmetry of X one has

$$\left(\frac{\partial}{\partial x_{ab}} - \frac{\partial}{\partial x_{ba}}\right)\langle i(\mathbf{X})|h|i(\mathbf{X})\rangle = 2\langle i|h|a\rangle\langle b|i\rangle - 2\langle i|h|b\rangle\langle a|i\rangle + \langle i|h|a\rangle x_{bi} - \langle i|h|b\rangle x_{ai} + \sum_k \langle i|h|k\rangle(x_{ka}\langle b|i\rangle - x_{kb}\langle a|i\rangle)$$

$$+ \sum_k (\langle i|a\rangle\langle b|h|k\rangle - \langle i|b\rangle\langle a|h|k\rangle)x_{ki} - \sum_k x_{ik}(\langle k|h|a\rangle\langle b|i\rangle - \langle k|h|b\rangle\langle a|i\rangle) + \cdots \; . \tag{B2}$$

Satisfying the orthonormality constraint on the molecular orbitals and setting $\mathbf{X}=0$ one obtains the expression to be used in e'_{ab},

$$\left[\left(\frac{\partial}{\partial x_{ab}} - \frac{\partial}{\partial x_{ba}}\right)\sum_i n_i\langle i(\mathbf{X})|h|i(\mathbf{X})\rangle\right]_{\mathbf{X}=0} = 2\langle a|h|b\rangle(n_b - n_a) \; . \tag{B3}$$

II. Two-electron integrals

Expanding the Coulomb integral yields

$$(i(\mathbf{X})i(\mathbf{X});j(\mathbf{X})j(\mathbf{X})) = (ii;jj) + 2\sum_k (\langle i|J_j|k\rangle x_{ki} + \langle j|J_i|k\rangle x_{kj}) + \sum_{k,l}(\langle i|J_j|k\rangle x_{ki}x_{li} + \langle j|J_i|k\rangle x_{ki}x_{lj})$$

$$- \sum_{k,l}(x_{ik}\langle k|J_j|l\rangle x_{li} + x_{jk}\langle k|J_i|l\rangle x_{lj}) - 4\sum_{k,l} x_{ik}(ki;jl)x_{lj} + \cdots \; . \tag{B4}$$

Then, upon differentiation one gets, for the total Coulomb energy,

$$\left[\left(\frac{\partial}{\partial x_{ab}} - \frac{\partial}{\partial x_{ba}}\right)\sum_{i,j} n_{ij}(i(\mathbf{X})i(\mathbf{X});j(\mathbf{X})j(\mathbf{X}))\right]_{\mathbf{X}=0} = 4\sum_j^{occ}\langle a|J_j|b\rangle(n_{bj} - n_{aj}) \; . \tag{B5}$$

Similarly, the exchange integral can be written

$$(i(\mathbf{X})j(\mathbf{X});j(\mathbf{X})i(\mathbf{X})) = (ij;ji) + 2\sum_k (\langle i|K_j|k\rangle x_{ki} + \langle j|K_i|k\rangle x_{kj}) + \sum_{k,l}(\langle i|K_j|k\rangle x_{ki}x_{li} + \langle j|K_i|k\rangle x_{ki}x_{lj})$$

$$- \sum_{k,l}(x_{ik}\langle k|K_j|l\rangle x_{li} + x_{jk}\langle k|K_i|l\rangle x_{lj}) - 2\sum_{k,l} x_{ik}[(kj;li) + (kl;ji)]x_{lj} + \cdots \; , \tag{B6}$$

so that

$$\left[\left(\frac{\partial}{\partial x_{ab}} - \frac{\partial}{\partial x_{ba}}\right)\sum_{i,j} n'_{ij}(i(\mathbf{X})j(\mathbf{X});j(\mathbf{X})i(\mathbf{X}))\right]_{\mathbf{X}=0} = 4\sum_j^{occ}\langle a|K_j|b\rangle(n'_{bj} - n'_{aj}) \; . \tag{B7}$$

The second derivatives of the energy are obtained in the same way by differentiating twice Eqs. (B1), (B4), and (B6).

APPENDIX C: CONVERGENCE OF THE METHOD

In order to prove that the procedure is quadratically convergent, one has to show that

$$\phi^{(n+1)} - \phi^{(n)} \sim (\phi^{(n)} - \phi^{(n-1)})^2 \tag{C1}$$

with

$$\phi^{(n)} = \phi^{(n-1)}\exp(\mathbf{X}) \tag{C2}$$

and

$$\phi^{(n+1)} = \phi^{(n)} \exp(Y) . \tag{C3}$$

The power expansion of $\exp(X)$ and $\exp(Y)$ leads to

$$\phi^{(n)} - \phi^{(n-1)} \sim X , \tag{C4}$$

$$\phi^{(n+1)} - \phi^{(n)} \sim Y , \tag{C5}$$

where X and Y are given respectively as the roots of

$$[e'_{vo}]^{\phi^{(n-1)}}_{X=0} = - \sum_{v',o'} [e''_{vo,v'o'}]^{\phi^{(n-1)}}_{X=0} \; x_{v'o'} , \tag{C6}$$

$$x_{oo'} = x_{vv'} = 0 , \tag{C7}$$

$$x_{vo} + x_{ov} = 0 , \tag{C8}$$

$$[e'_{vo}]^{\phi^{(n)}}_{Y=0} = - \sum_{v',o'} [e''_{vo,v'o'}]^{\phi^{(n)}}_{Y=0} \; y_{v'o'} , \tag{C9}$$

$$y_{oo'} = y_{vv'} = 0 , \tag{C10}$$

$$y_{vo} + y_{ov} = 0 , \tag{C11}$$

in which the superscript $\phi^{(n)}$ (respectively $\phi^{(n-1)}$) means that the derivatives are calculated with the $\phi^{(n)}$ (respectively $\phi^{(n-1)}$) vectors.

From Eqs. (C1), (C2), and (C3), one can deduce a direct relationship between $\phi^{(n+1)}$ and $\phi^{(n-1)}$

$$\phi^{(n+1)} = \phi^{(n-1)} \exp(Z) , \tag{C12}$$

which can be visualized as

$$
\begin{array}{c}
\overset{\exp(Z)}{\overline{\rule{4cm}{0pt}}} \\
\phi^{(n-1)} \xrightarrow{\exp(X)} \phi^{(n)} \xrightarrow{\exp(Y)} \phi^{(n+1)}
\end{array}
\tag{C13}
$$

with

$$\exp(Z) = \exp(X) \exp(Y) . \tag{C14}$$

Since making $Y=0$ in Eq. (C14) leads to $Z=X$, deriving the energy for $Y=0$ yields

$$[e'_{vo}]^{\phi^{(n)}}_{Y=0} = \sum_{k>l} [e'_{kl}]^{\phi^{(n-1)}}_{Z=X} \frac{\partial z_{kl}}{\partial y_{vo}} , \tag{C15}$$

where z_{kl} in the right-hand side of (C15) may belong to the z_{vo}, $z_{vv'}$, or $z_{oo'}$ components of Z. Expanding the first derivative of the energy for $Z=X$ as a function of x_{mn} in terms of a Taylor series around $X=0$ gives

$$[e'_{kl}]^{\phi^{(n-1)}}_{Z=X} = [e'_{kl}]^{\phi^{(n-1)}}_{Z=0} + \sum_{m>n}[e''_{kl,mn}]^{\phi^{(n-1)}}_{Z=0} \; x_{mn} + \sum_{m>n} \theta(x^2_{mn}). \tag{C16}$$

Keeping in mind that $Z=X$ at this level, we have to consider two cases according to the values taken by the indices k, l.

(i) $kl = oo'$ or vv'

We have

$$[e'_{kl}]^{\phi^{(n-1)}}_{Z=0} = 0 . \tag{C17}$$

In addition, since $x_{oo'}$ and $x_{vv'}$ are equal to zero [Eq. (C7)], the first summation in Eq. (C16) reduces to

$$\sum_{v,o} [e''_{kl,vo}]^{\phi^{(n-1)}}_{Z=0} \; x_{vo} .$$

Comparing Eqs. (42)–(43) with Eq. (36), it can be seen that the second derivative is either equal to zero or proportional to the first derivative of the energy. But, according to (C6), e' and x are of the same order of magnitude, so that

$$[e'_{kl}]^{\phi^{(n-1)}}_{Z=X} = \sum_{v>o} \theta(x^2_{vo}) . \tag{C18}$$

(ii) $kl = vo$

In that case, taking Eqs. (C6) and (C7) into account, Eq. (C16) becomes

$$[e'_{kl}]^{\phi^{(n-1)}}_{Z=X} = \sum_{v>o} \theta(x^2_{vo}) . \tag{C19}$$

Thus, in all cases, Eq. (C15) may be rewritten as

$$[e'_{vo}]^{\phi^{(n)}}_{Y=0} = \sum_{v>o} \theta(x^2_{vo}) \frac{\partial z_{kl}}{\partial y_{vo}} . \tag{C20}$$

Comparing with Eq. (C9), we obtain

$$Y \sim X^2 ,$$

which is the required condition for the method to converge quadratically.

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[30]The program is available from the authors and will be submitted to Q. C. P. E.