Towards a Calculation of the Electronic Structures of Macromolecules. I. Quadratically Convergent Method for a Direct Calculation of Localized Molecular Orbitals

Tatsuji Sano and Osamu Matsuoka*,†

Department of Applied Physics and Chemistry, The University of Electro-Communications, Chofu, Tokyo 182

†Department of Chemistry, Kyushu University, Ropponmatsu, Fukuoka 810

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A super configuration–interaction method is applied to a direct calculation of orthogonal localized molecular orbitals (LMO). Its iterative procedure converges quadratically, retaining the initial forms of the LMOs. When the basis sets of large sizes are employed for the calculation, Davidson's diagonalization method can be adopted beneficially, where the time-consuming four-index transformation of LMO integrals is replaced by simpler two-index transformations. Test calculations using double-zeta basis sets are reported in detail for H_2CO (formaldehyde). B_2H_6 (diborane), C_3H_4 (1-propyne [metylacetylene]), and cytosine. The implication of the method concerning macromolecular calculations is discussed.

The calculation of the electronic structures of macromolecules is one of the attractive fields to be investigated in quantum chemistry. Although macromolecules, such as proteins and nucleic acids, consist of hundreds or thousands of atoms as crystalline solids, they are non-periodic systems. This means that for macromolecules the methods fully developed in solid state physics might not be adoptable, and some new methodologies must be invented for them. In a series of studies we shall gradually develop methods that are suitable for such calculations. In the present paper we describe a method for the direct calculation of localized molecular orbitals (LMO). In contrast to the canonical molecular orbitals (CMO), which extend over all space, the LMOs spread only in limited space, and would work as building blocks for the construction of the wave functions of macromolecules. Also, their localized nature could be utilized for the calculations.

The methods of LMO calculations may be classified as direct and indirect. The indirect methods are usually employed, where the CMOs are calculated in the first, and then are transformed to the LMOs, so as to satisfy some localization criteria. Many indirect methods have been proposed, among which are the well-known ones of Foster–Boys,[1] Edmiston–Ruedenberg,[2] Magnasco–Perico,[3] and von Niessen.[4]

In the direct methods the LMOs are calculated directly without taking ways via CMOs. A few direct methods have been proposed which have not been extensively used mainly due to convergence difficulties inherent to their iterative procedures. The Adams–Gilbert method[5,6] is used to solve the Fock-like SCF equations in order to obtain nonorthogonal LMOs. Its modifications were proposed by Kunz[7] and Matsuoka.[8] Although Stoll, Wagenblast, and Preuss[9] used the Newton–Raphson method to obtain nonorthogonal orbitals, which could be localized when local bases were adopted, their method actually showed convergence difficulties. Peters[10] as well as Wilhite and Whitten[11] derived SCF equations for orthogonal LMOs. Daudey[12] calculated orthogonal LMOs using first-order perturbation theory. The LMOs obtained by their methods[10—12] depend on their initial forms, and do not explicitly satisfy such localization criteria as do the indirect methods[1—4] and the Adams–Gilbert methods.[5—8]

The indirect methods do not seem to be suitable for the calculations of macromolecules, since we must compute the CMOs before obtaining the LMOs. The direct methods seem to be more preferable, since we seek the LMOs in a target directly; also, in the course of the calculations we might advantageously use the localized nature of the orbitals. However, the iterative procedures of the direct methods hitherto proposed[5—12] showed a slow convergence, or, in most cases, encountered convergence difficulties.

In the present paper we propose a method for the direct calculation of orthogonal LMOs. It is essentially the super configuration–interaction (CI) method used in single- and multi-configuration SCF methods for CMOs,[13,14] and could be called the super-CI-LMO method. Its iterative process converges quadratically in contrast to other direct methods.[5—12] The obtained LMOs do not explicitly satisfy any localization criterion, and depend on the initial forms, as do some other direct LMO schemes,[9—12] but are still well-localized compared to the CMOs.

The next section describes a basic formalism of our quadratically convergent method for a direct calculation of orthogonal LMOs. It is then beneficially combined with Davidson's diagonalization method[15] in order to treat basis sets of large size. In the third section the results of test calcu-

lations are given for H_2CO (formaldehyde), B_2H_6 (diborane), C_3H_4 (1-propyne [metylacetylene]), and cytosine using double-zeta basis sets. In the last section a discussion concerning our super-CI-LMO method is presented, particularly concerning its significance in macromolecular calculations.

Quadratically-Convergent Iterative Method for Localized Molecular Orbitals

Super CI Formalism. Although our super-CI-LMO method could be formulated for any kind of molecules, in the present paper we consider only closed-shell molecules whose approximate wave functions can be described by a single-determinant consisting of doubly occupied LMOs $\phi_i (i=1,\cdots,N)$:

$$\Phi = [(2N)!]^{-1/2}\det|\phi_1(1)\alpha(1)\phi_1(2)\beta(2)\cdots\phi N(2N)\beta(2N)|. \quad (1)$$

In order to determine the LMO set in (1) we adopt essentially the same super CI formalism as that of Bacskay[14] which was developed to calculate CMOs. We expand the occupied LMOs $\{\phi_i\}$ in Eq. 1 and the virtual (unoccupied) molecular orbitals (MO) $\{\phi_a\}$ in terms of some starting occupied LMOs $\{\phi_i{}^0\}$ and virtual MOs $\{\phi_a{}^0\}$ as

$$\phi_i = \phi_i{}^0 + \sum_a X_{ia}\phi_a{}^0 \quad (2)$$

$$\phi_a = \phi_a{}^0 + \sum_i X_{ai}\phi_i{}^0. \quad (3)$$

We assume that since the MOs are orthogonal the expansion coefficients in Eqs. 2 and 3 are skew symmetric ($X_{ai}=-X_{ia}$). In the following we use suffices i and j to refer to the occupied orbitals and a and b to the virtual ones. Then, substituting Eqs. 2 and 3 into the wave function Eq. 1, we obtain, to the second order in $\{X_{ia}\}$,

$$\Phi = C_0\Phi_0 + \sum_{i,a} C_{ia}\Phi_{ia} + \sum_{i<j}\sum_{a,b} C_{ia}C_{jb}\Phi_{ia,jb}, \quad (4)$$

where Φ_0 is a normalized single-determinant of Eq. 1 expressed in terms of the starting LMOs $\{\phi_i{}^0\}$, and Φ_{ia} and $\Phi_{ia,jb}$ are singly and doubly excited wave functions with respect to the reference wave function Φ_0 (Eq. 19 in Ref. 14). The normalization of the wave function Eq. 4 requires that

$$|C_0|^2 + \sum_{i,a}|C_{ia}|^2 = 1. \quad (5)$$

The expansion coefficients in Eqs. 2 and 3 are related to those of Eq. 4 as

$$X_{ia} = C_{ia}/C_0 = -X_{ai}. \quad (6)$$

Minimization of the energy expectation value with respect to the coefficient vectors $\{C_0, C_{ia}\}$ of Eq. 4, subject to the normalization condition (Eq. 5) and the approximation that $|C_0|\approx 1$ and $|C_0| \gg |C_{ia}C_{jb}|$, lead to the following eigenvalue equation:[14]

$$\begin{bmatrix} H_{00} & \boldsymbol{H}_{01} \\ \boldsymbol{H}_{10} & \boldsymbol{H}_{11} \end{bmatrix}\begin{bmatrix} C_0 \\ \boldsymbol{C}_1 \end{bmatrix} = E\begin{bmatrix} C_0 \\ \boldsymbol{C}_1 \end{bmatrix}. \quad (7)$$

The matrix elements of Eq. 7 are given as follows:[14]

$$\begin{aligned} &H_{00} = E_0, \\ &(\boldsymbol{H}_{10})_{ia,0} = 2^{1/2}F_{ia}, \\ &(\boldsymbol{H}_{11})_{ia,jb} = E_0\delta_{ij}\delta_{ab} + \delta_{ij}F_{ab} - \delta_{ab}F_{ij} + P_{ia,jb}, \end{aligned} \quad (8)$$

where E_0 is the energy expectation value over the wave function Φ_0, $F_{ia}=\langle\phi_i{}^0|F|\phi_a{}^0\rangle$ is a component of the Brillouin vector, F being the Fock operator, and

$$P_{ia,jb} = 4[ia|jb] - [ij|ab] - [ib|ja], \quad (9)$$

$[i(1)a(1)|j(2)b(2)]$ etc. being two-electron integrals over the starting MOs in Eqs. 2 and 3. Also, the component of the eigenvector (C_0) is the CI coefficient in Eq. 4 and

$$(\boldsymbol{C}_1)_{ia} = 2^{1/2}C_{ia}. \quad (10)$$

The dimension of the eigenvalue Eq. 7 is $(N_{\mathrm{occ}}N_{\mathrm{virt}}+1)$, where N_{occ} and N_{virt} are the number of occupied and virtual MOs, respectively.

Thus, the computational procedure adopted for the direct determination of LMOs is iterative, and requires the following steps:

1. Obtain some starting orthogonal sets of occupied LMOs $\{\phi_i{}^0\}$ and virtual MOs $\{\phi_a{}^0\}$.
2. Compute the Hamiltonian matrix Eq. 8 and solve the eigenvalue Eq. 7 to obtain only the lowest eigenvalue and the corresponding CI coefficients $\{C_0, C_{ia}\}$.
3. Compute the expansion coefficients of the MOs, $\{X_{ia}\}$, through Eq. 6 and orthogonalize the occupied and virtual MOs $\{\phi_i, \phi_a\}$.
4. If the coefficient vectors $\{X_{ia}\}$, or, equivalently, Brillouin vectors $\{F_{ia}\}$, are sufficiently small, the computation may be terminated; otherwise, return to step (2) using the newly obtained MOs for the starting MOs in the next iteration.

Since this procedure considers an expansion of the energy expectation value up to the quadratic terms of the correction vectors $\{X_{ia}\}$, the convergence should be quadratic. This was actually substantiated by the test calculations described in the next section.

It should be noted that during iterative steps (1) through (4) the LMOs are not made to explicitly satisfy any localization criterion, and, thus, the obtained LMOs depend on the initial forms, as in some other direct methods.[9—12]

Incorporation of Davidson's Diagonalization Method. When the basis sets of large sizes are employed, the dimension of the eigenvalue Eq. 7 becomes so large that it is difficult to adopt the standard (e.g., the Householder's) methods for small dimensions. We thus adopted Davidson's diagonalization method[15] for very large eigenvalue problem, and modified step (2) of the previous subsection; we did not construct Hamiltonian matrix $\boldsymbol{H}$ in Eq. 8 explicitly, but, rather, directly formed a set of supervectors $\{\boldsymbol{Hb}_I\}$, where $\{\boldsymbol{b}_I\}$ are trial vectors for the eigenvalue Eq. 7. In this process the most time-consuming step is to form supervectors $\{\boldsymbol{Pb}_I\}$ from the trial vectors $\{\boldsymbol{b}_I\}$ and a two-electron supermatrix $\boldsymbol{P}$ over the MO bases (Eq. 9). However, we can adopt a similar algorithm as Bacskay's[14] in order to avoid a four-index transformation for the $\boldsymbol{P}$ matrix, and can construct them directly through three-step two-index transformations of two-electron integrals over the atomic-orbital bases. This process is also very similar to that adopted in the usual SCF process for constructing the Fock matrix from the two-electron integrals and the density matrix.

We further modified the original Davidson algorithm in order to adopt a direct CI-type scheme in the following way:

(1) We neglected the two-electron P integrals in the diagonal elements of the $\boldsymbol{H}_{11}$-matrix of Eq. 8, and formed a supervector $\boldsymbol{h}$ consisting of these approximate elements. Then, for trial vectors $\{\boldsymbol{b}_I, I=1,\cdots,L\}$ (step A of Ref. 15) we selected those vectors corresponding to the lowest eigenvalues of $\boldsymbol{h}$. We usually set L=4.

(2) When we computed the diagonal elements of the CI matrix in the denominator of a correction vector (ξ) (step D of Ref. 15), we also neglected the contribution from two-electron P integrals and made the approximation that $(\boldsymbol{H}_{11})_{ia,ia}\approx h_{ia}$. This approximation

made the computation of the correction vectors very fast with a very small loss of accuracy in the SCF coefficient vectors.

Test Calculations

We carried out several test calculations on small molecules in order to see the convergence behavior of our iterative method and the dependence of the obtained LMOs on their initial forms.

To obtain the initial LMOs we first generated approximate CMOs by diagonalization of approximate Fock matrices, which were constructed from the atomic-charge densities.[16] We then transformed them into the LMOs using the Pipek–Mezey localization method.[17] Their method attempts to minimize the mean number of atoms over which the LMOs spread (D) (Eq. 20 of Ref. 17), and is known to give almost the same LMOs as those of the Edmiston–Ruedenberg method.[2] The number (D) and the number of atoms over which each LMO extends (d) (Eq. 18 of Ref. 17) could give us a criterion concerning how the obtained LMOs would localize and depend on their initial forms.

We also calculated the initial approximate CMOs by a popular method of diagonalizing the matrices, which consisted of the kinetic-energy and the bare-nuclear attraction integrals. However, we found that they could not properly describe the ground-state wave functions, so that they could not produce the proper initial LMOs for some molecules. Hence, we do not report on these calculations.

In the iterative process we adopted symmetric orthogonalization method[18] in order to orthogonalize intermediate MOs. This method is known to least distort the original orbitals in the sense of the least-square deviation. The convergence of the iterative procedure was judged based on the energy differences of two successive iterations, and also by the norms of the Brillouin vector,

$$[\sum_{i,a} F_{ia}{}^2/N_F]^{1/2} = \varepsilon,$$

where N_F is the number of elements of a Brillouin vector

$$\{F_{ia} = \langle \phi_i | F | \phi_a \rangle\}.$$

We performed calculations on several molecules using basis sets of various sizes. However, we report here only on the results of H_2CO (formaldehyde), B_2H_6 (diborane), C_3H_4 (1-propyne), and cytosine using double-zeta basis sets. The basis sets are (3421/61) for B, C, N, and O[19] and (31) for H.[20] When we computed the LMOs, we did not consider the symmetries of the molecules.

We mention that our super CI-LMO method should in principle reproduce the total energies calculated using the CMOs, which was found to be true in the test calculations.

H_2CO and B_2H_6. For these molecules we used the standard Householder's method to solve the eigenvalue Eq. 7. Since the sizes of the adopted basis sets were 24 (H_2CO) and 32 (B_2H_6), the dimensions of the CI matrices were 129 and 193, respectively. We took the geometries from Ref. 17.

Table 1 collects the results for these molecules using dou-

Table 1. Convergence of Total Energies (E), Differences between Two Successive Total Energies (ΔE), Norms of Brillouin Vectors (ε), and Mean Atom Numbers over Which LMOs Extend (D)
All values are given in atomic units.

Molecule	Iteration	E	ΔE	ε	D[a]
H_2CO[b]	0	−144.76577039		1.25×10^{-1}	1.2711
	1	−144.99231626	2.3×10^{-1}	2.50×10^{-3}	1.3027
	2	−144.99399335	1.7×10^{-3}	1.56×10^{-5}	1.3049
	3	−144.99399343	8.0×10^{-8}	3.12×10^{-9}	1.3049
B_2H_6[b]	0	−84.45579133		6.38×10^{-2}	1.6500
	1	−84.50931601	5.3×10^{-2}	4.30×10^{-4}	1.6650
	2	−84.50938376	6.8×10^{-5}	4.08×10^{-7}	1.6652
	3	−84.50938376	$<10^{-8}$	5.59×10^{-13}	1.6652
C_3H_4[b]	0	−174.70403876		7.93×10^{-2}	1.5008
	1	−174.90893869	2.0×10^{-1}	2.01×10^{-3}	1.5207
	2	−174.91093730	2.0×10^{-3}	1.44×10^{-5}	1.5251
	3	−174.91093740	1.0×10^{-7}	9.48×10^{-10}	1.5251
C_3H_4[c]	0	−174.70403876		7.93×10^{-2}	1.5008
	1 (13)	−174.90893869	2.0×10^{-1}	2.01×10^{-3}	1.5207
	2 (11)	−174.91093730	2.0×10^{-3}	1.44×10^{-5}	1.5251
	3 (6)	−174.91093740	1.0×10^{-7}	6.90×10^{-8}	1.5251
Cytosine[c]	0	−748.49865486		5.51×10^{-2}	1.3911
	1 (12)	−749.14411808	6.5×10^{-1}	3.54×10^{-3}	1.3682
	2 (14)	−749.17622295	3.2×10^{-2}	8.90×10^{-5}	1.3618
	3 (11)	−749.17625726	3.4×10^{-5}	2.47×10^{-7}	1.3615
	4 (3)	−749.17625726	$<10^{-8}$	4.09×10^{-8}	1.3615

a) Mean atom numbers calculated by the Pipek–Mezey indirect method are 1.3009 (H_2CO), 1.6650 (B_2H_6), 1.5234 (C_3H_4), and 1.3572 (cytosine). b) Householder's method was used to solve CI matrix equation. c) Davidson's method was used to solve CI matrix equation. Number of micro-iterations needed are given in the parentheses.

ble-zeta basis sets. Judging from the differences in the total energies of two successive iterations (ΔE) and the norms of the Brillouin vectors (ε), the convergences are more or less quadratic. The mean atom number (D) do not change appreciably from the initial to the final values, which compare fairly well with those obtained by the indirect method[17] for the transformation of the CMOs.

Table 2 compares the change in the d values (atom numbers over which each LMO extends). The initial values change only slightly, and go to final values which are comparable to those obtained by the indirect method.[17]

C_3H_4. We took its geometry from Ref. 21 using the same numbering of the constituent atoms. Since the size of the double-zeta basis set was 38, the dimension of the eigenvalue Eq. 7 was 298. To solve the equation we used both the standard Householder's method and Davidson's method,

Table 2. Changes of d Values (Atom Numbers over Which Each LMO Extends) from Initial to Final Iteration
The d values obtained by the Pipek–Mezey indirect method are given by "Indirect".

Molecule	LMO	Initial	Final	Indirect
H_2CO	O1s	0.9964	0.9898	1.0002
	C1s	0.9971	0.9976	0.9976
	O lone pair [a]	1.0115	0.9830	0.9962
	O lone pair [b]	1.0388	1.0701	1.0584
	C–Hσ	1.6172	1.7855	1.7871
	O–Cσ	1.9160	1.9814	1.9694
	O–Cπ	1.7323	1.8488	1.8488
B_2H_6	B1s	0.9967	0.9967	0.9967
	B1–H1σ	1.9198	1.9218	1.9230
	B1–H5–B2σ	2.7997	2.7932	2.7850
C_3H_4	C11s	0.9918	0.9934	0.9933
	C21s	0.9935	0.9951	0.9950
	C31s	0.9964	0.9977	0.9978
	C1–C2σ	2.3222	2.1800	2.1415
	C1–C3σ	2.1330	1.9479	1.9436
	C2–H1σ	1.6427	1.8522	1.8553
	C3–H2σ	1.6704	1.8015	1.8020
	C3–H3σ	1.6705	1.8015	1.8021
	C1–C2π	1.9865	1.9583	1.9581
Cytosine	N1 lone pair	1.3422	1.2861	1.2878
	N3 lone pair	1.2554	1.0849	1.0482
	N7 lone pair	1.2423	1.1663	1.1700
	O8 lone pair [a]	1.0505	0.9993	0.9924
	O8 lone pair [b]	1.2081	1.0769	1.0740
	N1–C2σ	1.8182	1.7616	1.7898
	C2–N3σ	1.9422	1.7810	1.8225
	N3–C4σ	1.8831	1.8443	1.8676
	C4–C5σ	2.3241	2.0231	2.0079
	C5–C6σ	2.4700	2.0967	2.0103
	C6–N1σ	1.8648	1.8649	1.8753
	C2–O8σ	2.3213	2.1436	2.1253
	C4–N7σ	2.0625	1.9820	1.9718
	N3–C4π	2.1769	1.8506	1.8372
	C5–C6π	2.3429	2.0207	2.0084
	C2–O8π	1.6717	1.5342	1.5182

a) O–C direction. b) Perpendicular to O–C.

and compared the results. As Tables 1 and 2 show, the convergences are almost quadratic, and the obtained d values are comparable to those by the indirect method.[17] During the iterations both methods gave the same energies and the same D and d values. However, in the final iteration, the Brillouin norm by Davidson's method was slightly inferior to that of Householder's method. This is due to a slightly inaccurate estimation for the correction vectors (ξ) near to the SCF solutions, where both the numerators and denominators become very small (step D of Ref. 15).

In Davidson's method we needed around ten micro-iterations to solve the CI matrix Eq. 7; in each micro-iteration we had to form **Pb** supervectors using two-electron integrals stored in the file. However, we found that the overall iteration time needed for Davidson's method was shorter by two orders than that by Householder's method. There are some reasons for the superiority of Davidson's method. The main reason is that in his method we need to compute only the lowest eigenvalue of the CI matrix, so that we can simplify the associated process of forming the matrix, especially by adopting efficient three-step two-index transformations, as mentioned in the last section.

Cytosine. We adopted the same geometry and numbering of the constituent atoms as in Ref. 22. The size of the double-zeta basis set was 90, and the number of occupied MOs was 29, so that the dimension of the CI matrix (Eq. 7) was 1770. We adopted Davidson's method. As Tables 1 and 2 show, the convergence was almost quadratic, and the D and d values were comparable to those by the indirect method. Although the dimension of the eigenvalue equation was six times larger than the one in the case of C_3H_4, the number of micro-iterations were almost the same. This was also seen in other molecules.

Discussion and Conclusion

In the present paper our super-CI-LMO method for the direct calculation of LMOs was formulated for closed-shell molecules, and has been proved to work. Its iterative procedure converges quadratically, although all other direct methods[6–11] encountered convergence difficulties. Although the obtained LMOs depend on their initial forms, the test calculations showed that they retained the initial localized forms very well, and were close to those obtained by the indirect method for the transformation of CMOs. When we combined our method with Davidson's diagonalization method[15] to solve large eigenvalue problems, we found that his method *per se* needed around ten micro-iterations on the average, irrespective of the number of basis functions. Although the overall performance of Davidson's method is definitely superior to the standard Householder's method when using large basis sets, one might think that this will still become troublesome, since in every micro-iteration we have to form supervectors **Pb** from two-electron integrals. However, it seems that this can be overcome largely by algorithmic improvements, so as to reduce the number of micro-iterations. We shall report on these improvements in the following studies.

The significance of our method is not only the direct calculation of LMOs, but also the possibility to calculate the wave functions of macromolecules. If we applied the usual Hartree–Fock–Roothaan method[23] to macromolecules, we would have to overcome such problems as:

1. The computation of a huge number of molecular integrals;
2. Guessing good initial MOs or density matrices for the SCF iterations;
3. Solving the Fock equation of very large dimension; and
4. The convergency of SCF iterations.

Although we can now manage them fairly well, our method could do them more easily; if we utilize the localized nature of the LMOs, we would need fewer molecular integrals; we can compute very good LMOs for the subunits of a macromolecule by performing their SCF calculations; then, using them, we could guess good initial LMOs of the whole molecule. As our test calculations showed, we could replace solving the Fock equations with the super-CI eigenvalue equations; our method has been proven to converge quadratically.

In our next studies we shall test these conjectures and report on the improvements in our method to compute the wave functions of macromolecules.

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