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Efficient *ab initio* molecular-orbital approach to quasi-one-dimensional molecular crystals based on neighboring-interaction-localized molecular orbitals

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To obtain electronic states in molecular crystals efficiently, a quantum chemical method that utilizes the localization technique for providing the corresponding orbitals is presented. This localization technique enables us to diagonalize the large matrix for the entire system by means of eigenvalue problems for small dimensions of the number of molecules. To confirm the reliability of this treatment, the electronic states provided by this method were compared with those provided by the tight-binding method for periodic systems.

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Generally, electronic states in periodic systems are determined under periodic boundary conditions. This treatment is very useful for treating infinitely large systems such as one-dimensional polymers, and the *ab initio* molecular orbital (MO) method based on the Bloch functions has often been employed. The reliability of this treatment is doubtful in mesoscopic systems, because the crystal orbitals obtained by this method give band structures in the infinitely large limits of the system.

A theoretical method that is suitable for mesoscopic systems is urgently required because remarkable phenomena in mesoscopic systems have recently been reported. In dealing with a mesoscopic system, a method in which the size of the system is specified is preferable. In other words, a method that employs periodic boundary conditions is not suitable for mesoscopic systems. Conversely, use of the conventional MO method to calculate the electronic states of a mesoscopic system requires an enormous amount of time.

In this work, to avoid this difficulty, we present a convenient method that uses localized orbitals for molecular crystals. In this method, the matrices to be diagonalized are given with the dimension of the number of molecules in spite of the number of the basis sets included, facilitating the treatment of huge systems composed of large molecules. The localized orbitals are obtained by a procedure similar to that providing corresponding orbitals,[1] and consequently, small matrices that are divided from the large matrix of an entire system can be given efficiently. To ensure the reliability of this treatment, the total energy and charge density obtained by this localized orbital method are compared to those by the tight-binding (TB) method[2] for periodic systems.

Quasi-one-dimensional molecular chains in which periodicity is maintained are treated in this work. To begin with, the Fock matrix, based on molecular orbitals, is prepared as shown in Fig. 1. In this figure, a submatrix has the dimension of the molecular orbitals in a molecule, and the submatrices drawn with same patterns are identical because of the periodicity. This Fock matrix can also be represented as follows:

$$\boldsymbol{F}=\begin{pmatrix} \boldsymbol{F}_{11} & & & & & \\ \boldsymbol{F}_{21} & \boldsymbol{F}_{22} & & & & \\ \boldsymbol{F}_{31} & \boldsymbol{F}_{32} & \boldsymbol{F}_{33} & & & \\ \boldsymbol{F}_{41} & \boldsymbol{F}_{42} & \boldsymbol{F}_{43} & \boldsymbol{F}_{44} & & \\ \boldsymbol{F}_{51} & \boldsymbol{F}_{52} & \boldsymbol{F}_{53} & \boldsymbol{F}_{54} & \boldsymbol{F}_{55} & \\ \boldsymbol{F}_{61} & \boldsymbol{F}_{62} & \boldsymbol{F}_{63} & \boldsymbol{F}_{64} & \boldsymbol{F}_{65} & \boldsymbol{F}_{66} \end{pmatrix}. \qquad (1)$$

The diagonal submatrices (i.e., $\boldsymbol{F}_{11}, \boldsymbol{F}_{22}, \ldots, \boldsymbol{F}_{66}$) are already diagonalized in each matrix whose diagonal elements are given by the orbital energies in a molecule, and the off-diagonal submatrices are not diagonalized. The schematic representation of intermolecular interactions in this system is given in Fig. 2(a). In this system, only the two molecules in the periodic system are depicted in Fig. 2(a) to explain the nearest-neighbor interactions between molecules. Interactions from more than second-neighbor molecules exist; however, these interactions are not as strong as the nearest-neighbor interactions because of large distances. Therefore, transformation to a simplified system that includes no interactions between the different energy levels in the neighboring section is effective in order to divide the large matrix. The schematic representation of this system is given in Fig. 2(b).

In this simplified system, the matrix to be diagonalized is reduced to the small matrix that has the dimension of the number of molecules. We call this localized orbital the ‘‘neighboring-interaction-localized MO’’ (NILMO). The matrices that represent the nearest neighbor interactions correspond to the submatrices $\boldsymbol{F}_{21}, \boldsymbol{F}_{32}, \ldots, \boldsymbol{F}_{65}$ in Eq. (1), and thus we diagonalize only these submatrices to produce the

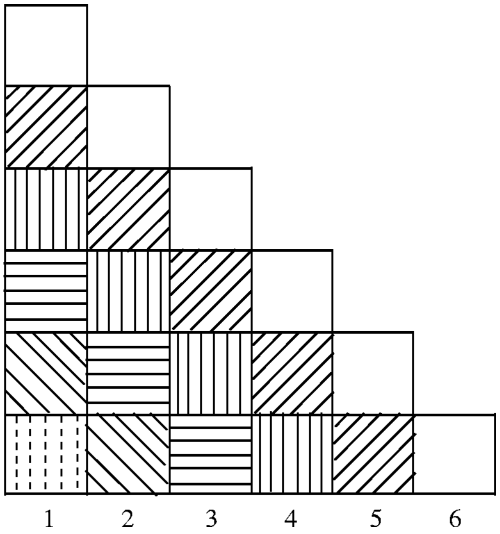

FIG. 1. Triangular Fock matrix in a system composed of six molecules. A small square block corresponds to a matrix of a molecule.

NILMO. Because these matrices are not symmetrical, we must use a procedure that provides the corresponding orbitals as follows:

$$\boldsymbol{U}^{\dagger}\boldsymbol{D}\boldsymbol{V}=\hat{d}, \tag{2}$$

where $\boldsymbol{U}$ and $\boldsymbol{V}$ are unitary matrices, $\boldsymbol{D}$ is a nonsymmetric matrix, and $\hat{\boldsymbol{d}}$ is a diagonal matrix. $\boldsymbol{U}$ and $\boldsymbol{V}$ are given by the diagonalization of $\boldsymbol{D}^{\dagger}\boldsymbol{D}$:

$$\boldsymbol{D}^{\dagger}\boldsymbol{D}\boldsymbol{V}=\boldsymbol{V}\hat{\boldsymbol{\lambda}}, \tag{3}$$

$$\boldsymbol{U}=\boldsymbol{D}\boldsymbol{V}\hat{\boldsymbol{\lambda}}^{-1/2}. \tag{4}$$

For the system whose Fock matrix is represented by Eq. (1), the above procedure corresponds to the unitary transformation $\boldsymbol{C}^{\dagger}\boldsymbol{F}\boldsymbol{C}$, where $\boldsymbol{C}$ is given by

$$\boldsymbol{C}=\begin{pmatrix} \boldsymbol{U} & & & & & \\ & \boldsymbol{V} & & & \boldsymbol{0} & \\ & & \boldsymbol{U} & & & \\ & & & \boldsymbol{V} & & \\ & \boldsymbol{0} & & & \boldsymbol{U} & \\ & & & & & V \end{pmatrix}. \tag{5}$$

However, in periodic systems, the diagonalization of only one matrix (e.g., $\boldsymbol{F}_{43}$) is sufficient to make the NILMO because of the periodicity. That is, the NILMO can be produced at one time without independently diagonalizing each submatrix and, therefore, the NILMO can be obtained very rapidly.

After this procedure, we can obtain the reduced matrix whose elements are composed of the same component of each submatrix. For example, the reduced matrix in the system given in Fig. 1 is

$$\boldsymbol{R}_i=\begin{pmatrix} (\boldsymbol{F}'_{11})_{ii} & & & & \\ (\boldsymbol{F}'_{21})_{ii} & (\boldsymbol{F}'_{22})_{ii} & & & \\ (\boldsymbol{F}'_{31})_{ii} & (\boldsymbol{F}'_{32})_{ii} & (\boldsymbol{F}'_{33})_{ii} & & \\ \vdots & \vdots & \vdots & \ddots & \\ (\boldsymbol{F}'_{61})_{ii} & (\boldsymbol{F}'_{62})_{ii} & (\boldsymbol{F}'_{63})_{ii} & & (\boldsymbol{F}'_{66})_{ii} \end{pmatrix}$$

$$(i=1,2,\ldots,k,k+1), \tag{6}$$

where $\boldsymbol{F}'$ represents the submatrix transformed by $\boldsymbol{U}$ and $\boldsymbol{V}$, and k corresponds to the level of the highest occupied molecular orbital (HOMO) in an isolated molecule. $\boldsymbol{R}_k$ and $\boldsymbol{R}_{k+1}$, which are the matrices for the highest occupied energy band and the lowest unoccupied energy band, respectively, are required to calculate the energy gap.

Except for the submatrices representing the nearest-neighbor interactions, the off-diagonal submatrices are not diagonal. However, the matrix elements in nondiagonal matrices are very small because the matrix elements in these matrices correspond to the long-range interactions. Therefore, a good approximation can be based on using only the diagonal elements in Eq. (6).

In the use of this treatment, we must pay attention to the range of the transformation, because diagonalization using Eq. (2) leads to an orbital mixing among molecular orbitals in an isolated molecule, and thus the concept of orbital energy is missed. That is to say, the diagonalization of the entire submatrix causes orbital mixing between occupied and unoccupied orbitals. Therefore, the range of transformation

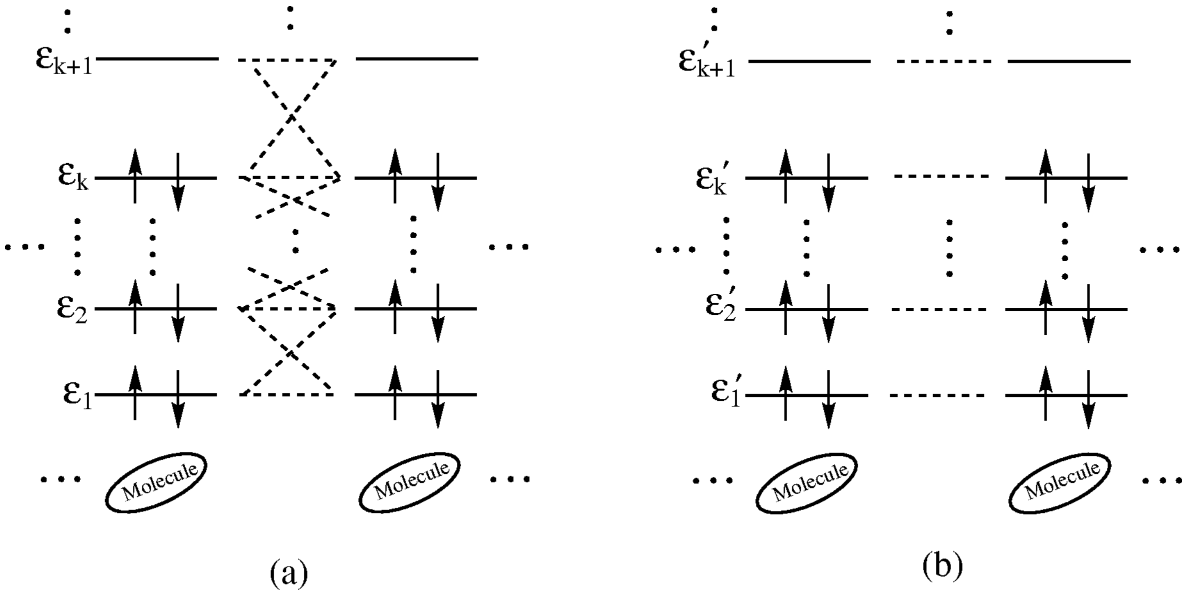

FIG. 2. Schematic representation of intermolecular interactions based on (a) the molecular orbitals and (b) the neighboring-interaction-localized molecular orbitals. The dashed lines between the molecular orbitals represent intermolecular interactions. This figure depicts only two molecules in a crystal.

TABLE I. Total energy per unit cell in ethylene stacking system and CPU time required for calculation. A unit cell is made up of two ethylene molecules.

Method	Total energy (a.u.)	Diff. (a.u.) [a]	CPU time (s)
NILMO(4) [b]	-154.10352	-0.00110	8.7
NILMO(6)	-154.10300	-0.00058	23.9
NILMO(8)	-154.10271	-0.00029	50.8
NILMO(10)	-154.10254	-0.00012	94.0
Tight binding	-154.10242		118.0

[a] Differences in total energies between the NILMO treatment and the tight-binding method.

[b] The number of molecules treated by NILMO calculation are indicated.

must be restricted to occupied orbitals. Moreover, HOMO should not be transformed, because the orbital energy of HOMO is necessary to estimate several physical properties. In addition, there is another matter that must be dealt with. Strictly speaking, several subdiagonal submatrices cannot necessarily be diagonalized by using this treatment, because the matrices $\boldsymbol{U}$ and $\boldsymbol{V}$ are not identical, and therefore $\boldsymbol{V}^\dagger \boldsymbol{D} \boldsymbol{U}$ is not necessarily a diagonal matrix. For example, in the system given in Eq. (1), $\boldsymbol{U}^\dagger \boldsymbol{F}_{21} \boldsymbol{V}$, $\boldsymbol{U}^\dagger \boldsymbol{F}_{43} \boldsymbol{V}$, and $\boldsymbol{U}^\dagger \boldsymbol{F}_{65} \boldsymbol{V}$ are diagonal, while $\boldsymbol{V}^\dagger \boldsymbol{F}_{32} \boldsymbol{U}$ and $\boldsymbol{V}^\dagger \boldsymbol{F}_{54} \boldsymbol{U}$ are not necessarily diagonal. The contributions from these off-diagonal elements in these matrices are treated using perturbation theory[3] in this work.

In a practical treatment, we need not prepare the entire matrices in the molecular crystal because of its periodicity. Preparation of only a few submatrices that represent intramolecular or intermolecular interactions are required [e.g., $\boldsymbol{F}_{33}$, $\boldsymbol{F}_{43}$, $\boldsymbol{F}_{52}$ in Eq. (1)]. Therefore, long-range interactions can easily be incorporated into the calculations. Finally, we can obtain eigenvectors in the entire system by the diagonalization of $k+1$ reduced matrices, given in Eq. (6).

This treatment was incorporated into the *ab initio* program package GAMESS (Ref. 4) and applied to the model crystals of quasi-one-dimensional stacking systems composed of ethylene or butadiene. The Hartree-Fock (HF) method was employed with the STO-3G basis set. The electronic properties and the central processing unit (CPU) times are discussed in comparison with the results obtained by the TB method.

The total energies in the ethylene and butadiene stacking systems are given in Tables I and II, respectively. The CPU times required for the calculations using an IBM RISC/6000 system are also listed. It can be seen from these tables that the NILMO method can reproduce reasonable total energies with shorter CPU times than can the TB method, and this treatment becomes advantageous with the size of molecules. Table III shows the Mulliken charges in the ethylene and butadiene systems. It confirms that the electronic charges obtained by the NILMO method are in good agreement with those obtained by the TB method.

TABLE II. Total energy per unit cell in butadiene stacking system and CPU time required for calculation. A unit cell is made up of two butadiene molecules.

Method	Total energy (a.u.)	Diff. (a.u.)	CPU time (s)
NILMO(4)	-305.95172	-0.00166	89.5
NILMO(6)	-305.95072	-0.00066	280.0
NILMO(8)	-305.95020	-0.00014	594.0
Tight binding	-305.95006		1131.9

TABLE III. Mulliken charges in ethylene stacking system and butadiene stacking system.

Method	C [a]	H [a]	C_α [b]	C_β [b]	H [b]
NILMO(6)	-0.1103	0.0552	-0.109	-0.054	0.052
Tight binding	-0.1105	0.0553	-0.107	-0.056	0.053

[a] Atom in ethylene.

[b] Atom in butadiene.

The band width of the highest occupied band (HOB) and the lowest unoccupied band (LUB) and the energy gap in the ethylene system are given in Table IV. NILMO(6) is employed in this calculation. In the estimation of the bandwidth and the energy gap, we need an extended matrix that can provide semicontinuous orbital energies, because NILMO(6) provides only six molecular orbitals in the HOB. Even if the reduced matrix is extended to a system composed of 100 molecules, the calculation is completed rapidly, because the matrix dimension is only 100. In this manner, we can efficiently obtain the bandwidth as well as the energy gap. In Table IV, however, some differences in the bandwidth of the HOB and the energy gap are recognized. The reason for these differences is as follows. In the NILMO treatment, to obtain the orbital energies in the HOB, the HOMO transformation must not be performed. Therefore, the intermolecular interactions between the HOMO and the other orbitals are not included in the reduced matrices. However, in a crystal composed of nondegenerated conjugated molecules, the orbital mixing between the π orbitals of one molecule and the π^* of neighboring molecules is negligible. Therefore, the differences shown in Table IV are caused by ignoring the interactions between the HOMO and the orbitals whose energies are lower than the HOMO. These interactions are easily incorporated into the calculation by extending the kth reduced matrix to one whose dimension is 2 or 3 times as large as the dimension of the matrix given in Eq. (6). Thus, the differences given in the bandwidth of the HOB and the energy gap will be improved, keeping the short CPU time.

The dependence of the intermolecular distance $r1$ on the total energy in the ethylene system is shown in Fig. 3. This

TABLE IV. Bandwidth and energy gap in the ethylene stacking system.

Method	Bandwidth of HOB (eV)	Bandwidth of LUB (eV)	E_g (eV)
NILMO(6)	3.69	2.82	12.93
Tight binding	3.53	2.82	13.08

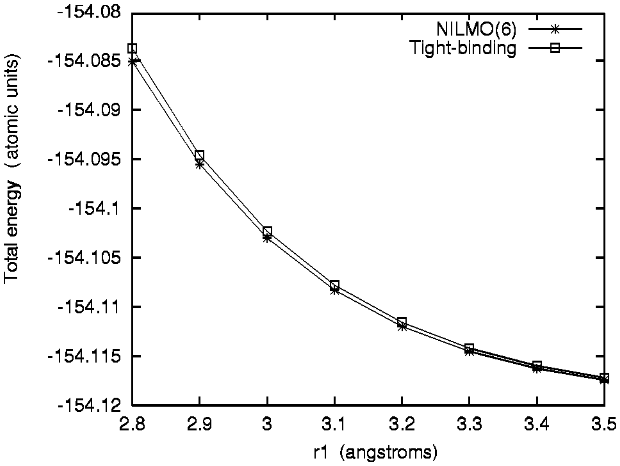

FIG. 3. Total energies in the ethylene stacking system obtained by using NILMO and the tight-binding method.

figure indicates the total energies obtained by NILMO(6) and the TB method. NILMO(6) is the calculation that includes intermolecular interaction from the nearest-neighbor section to the fifth-neighbor section. In the system with $r1 \geqslant 2.8$ Å, the total energies obtained by NILMO are in good agreement with those obtained by the TB method. This suggests that long-range interactions can be properly included in a NILMO transformation. If larger basis sets are used, we can obtain reliable results, retaining the advantages of NILMO, by extending to a larger system.

It is ascertained that this method can also be applicable for open-shell systems by treating α spin orbitals and β spin orbitals separately using the unrestricted Hartree-Fock (UHF) method. Furthermore, if the calculation using several Slater determinants is implemented, the CPU time may be slightly increased according to the number of the dimensions included. However, this condition is the same as the case using other methods. Therefore, the advantages of this method will be maintained.

Using the transformation of NILMO, we were able to obtain reliable results in a periodical molecular stacking system faster than by using the conventional TB method. This treatment, which does not use the periodic boundary condition, could be powerful for stacking systems of large molecules and is expected to become a convenient method of treating mesoscopic systems. In our laboratory, a theoretical treatment has been developed for modeling low-dimensional conductors in molecular crystals like naphthalene, TTF-TCNQ, and oligothiophene stacking systems.[5–9] This method can provide a relationship between the Peierls instability and intercolumnar interactions. The application of the present treatment to these systems could provide a powerful tool to design conducting materials at the level of the *ab initio* MO method. In the near future, we will present a method that is extended to treat the entire system, including the surface.

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[1] H. F. King, R. E. Stanton, H. Kim, R. E. Wyatt, and R. G. Parr, J. Chem. Phys. **47**, 1936 (1967).

[2] C. Pisani, R. Dovesi, and C. Roetti, *Hartree-Fock ab-initio Treatment of Crystalline Systems, Lecture Notes in Chemistry, Vol. 48* (Springer Verlag, Heidelberg, 1988).

[3] A. Imamura, Mol. Phys. **15**, 225 (1968).

[4] M. W. Schmidt, K. K. Baldridge, J. A. Boatz, S. T. Elbert, M. S. Gordon, J. H. Jensen, S. Koseki, N. Matsunaga, K. A. Nguyen, S. Su, T. L. Windus, M. Dupuis, and J. A. Montgomery, J. Comput. Chem. **14**, 1347 (1993).

[5] Y. Aoki and A. Imamura, J. Chem. Phys. **103**, 9726 (1995).

[6] Y. Aoki, T. Tada, and A. Imamura, Int. J. Quantum Chem. **64**, 325 (1997).

[7] T. Tada, Y. Aoki, and A. Imamura, Synth. Met. **95**, 169 (1998).

[8] T. Tada and Y. Aoki, Int. J. Quantum Chem. **86**, 401 (2002).

[9] T. Tada and Y. Aoki (unpublished).