

Million-Atom Molecular Dynamics Simulation by Order-N Electronic Structure Theory and Parallel Computation

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Parallelism of tight-binding molecular dynamics simulations is presented by means of the order-N electronic structure theory with the Wannier states, recently developed [J. Phys. Soc. Jpn. **69** (2000) 3773]. An application is tested for silicon nanocrystals of more than millions atoms with the transferable tight-binding Hamiltonian. The efficiency of parallelism is perfect, 98.8%, and the method is the most suitable to parallel computation. The elapse time for a system of 2×10^6 atoms is 3.0 min by a computer system of 64 processors of SGI Origin 3800. The calculated results are in good agreement with the results of the exact diagonalization, with an error of 2% for the lattice constant and errors less than 10% for elastic constants.

KEYWORDS: order-N method, parallel computation, tight-binding Hamiltonian, silicon nanocrystal
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1. Introduction

Accurate large-scale atomistic simulations are very important to investigate and to predict various properties of materials. For this purpose, the first principle electronic structure theories have been extended to calculations of the total energy and forces and the first principle molecular dynamics (MD) simulation or the Car–Parrinello method¹⁾ are now used quite widely in the condensed matter physics. However, the systems investigated by the first principle MD simulations are practically limited to much smaller size, at most, of hundreds atoms and much shorter time period of few tens pico-seconds. The other extreme is the classical MD simulations with short-range inter-atomic potentials which are applied to systems of millions or ten millions atoms with time period of a few hundreds pico-seconds.^{2,3)} Classical MD simulations are very useful to investigate nanoscale systems when accurate inter-atomic potentials can be used. Even so, applicability of classical MD simulations is limited to phenomena in which electronic process does not play an essential role.

Modern material technology is deeply involved in electronic processes. Then intense attention has been paid to the order-N method for the electronic structure calculations, whose computational cost increases in *linearly* proportion to the number of electrons.^{4,5)}

Novel order-N method is being developed on the basis of the Wannier states.^{6,7)} The Wannier states is formally defined with the unitary transformation of the occupied eigen states. Once we get true Wannier states $|\psi_j\rangle$, the density matrix can be defined as

$$\hat{\rho} = \sum_j^{\text{occ}} |\psi_j\rangle\langle\psi_j|. \quad (1)$$

The expectation value of any physical quantity X can be obtained with the density matrix or the Wannier states as

$$\langle\hat{X}\rangle = \text{Tr}[\hat{\rho}\hat{X}] = \sum_j^{\text{occ}} \langle\psi_j|\hat{X}|\psi_j\rangle. \quad (2)$$

If we put the localization constraint to construct approximate Wannier states with a loss of certain amount of accuracy,

then we can formulate the order-N method and reduce computational cost extremely. Using this order-N method, a system of 1.4×10^6 atoms was calculated by a single CPU standard workstation.⁸⁾

In the present paper we do parallel computation of the perturbation procedure of the order-N method, which we call the perturbative order-N method. We will estimate explicitly the memory size for the parallel computation and show that primitive parallelism achieves high performance in the perturbative order-N method. Silicon nanocrystals are calculated up to a system of 2,097,152 atoms, using SGI Origin 3800 system, and the efficiency of parallelism is analyzed. To test an accuracy and applicability for calculation of physical quantities, the lattice constant and elastic constants are calculated using cluster systems of up to 1,423,909 atoms. The usefulness and the limit of the perturbative order-N method will be discussed in detail.

2. Theoretical Backgrounds

2.1 The Wannier states

The Wannier states centered on the j -bond can be expressed as

$$|\psi_j\rangle = C_j^{(0)}|b_j\rangle + \sum_{i(\neq j)} C_j^{(i)}|a_i\rangle + \text{terms of farther distant bond sites}, \quad (3)$$

where $C_j^{(0)}$ is the mixing coefficient of the central bonding orbital $|b_j\rangle$ and $C_j^{(i)}$ is that of the anti-bonding orbital $|a_i\rangle$ on the neighboring i -bond.^{6,7)} The mixing of the bonding orbitals on the neighboring bonds are negligibly small due to the orthogonality and the completeness, because they contribute to other Wannier states.

For diamond structure crystals, we adopt the transferable Hamiltonian \hat{H} of Kwon *et al.*⁹⁾ The Hamiltonian includes the tight-binding interactions and the short-range repulsive interactions between ion cores. We truncate the hopping interactions at a distance halfway between the first and the second neighbor distances. If we denote sp^3 hybridized orbitals $|h_i\rangle$, the bonding orbital $|b_j\rangle$ and the anti-bonding orbital $|a_j\rangle$ are linear combinations of the two hybridized orbitals $(|h_i\rangle \pm |h_{i'}\rangle)/\sqrt{2}$.

In case of silicon crystals, the exact results for a system of 512 atoms are $|C_j^{(0)}|^2 = 0.938$ and $\sum_i |C_j^{(i)}|^2$ up to the second bond-steps is 0.995. On the other hand, by the first-order perturbation theory, the coefficients $C_j^{(i)}$ for the first bond-step can be given by an equation

$$\frac{C_j^{(i)}}{C_j^{(0)}} = \frac{\langle a_i | \hat{H} | b_j \rangle}{\epsilon_b - \epsilon_a}, \quad (4)$$

and this gives $|C_j^{(0)}|^2 = 0.934$.^{6,7)} Note that, in the first-order perturbation theory, $C_j^{(i)}$ does not vanish up to the second bond-steps.

2.2 Perturbative order-N method

The total energy in the tight-binding formalism is given as

$$E_{\text{tot}} = E_{\text{bs}} + E_{\text{rep}}, \quad (5)$$

where E_{bs} is the band structure (BS) energy and E_{rep} is the repulsive energy. On the basis of the Wannier states $|\psi_j\rangle$, the BS energy and its contribution to forces on the I atom (site \mathbf{R}_I) are written, with the tight-binding Hamiltonian \hat{H} , as⁶⁾

$$E_{\text{bs}} \equiv \text{Tr}[\hat{\rho}\hat{H}] = \sum_j^{\text{occ}} \langle \psi_j | \hat{H} | \psi_j \rangle \quad (6)$$

and

$$\mathbf{F}_I^{\text{bs}} \equiv \text{Tr} \left[\hat{\rho} \frac{\partial \hat{H}}{\partial \mathbf{R}_I} \right] = - \sum_j^{\text{occ}} \langle \psi_j | \frac{\partial \hat{H}}{\partial \mathbf{R}_I} | \psi_j \rangle. \quad (7)$$

We will calculate the Wannier states by using the perturbative treatment eqs. (3) and (4) and the density matrix should be given in the same equation as eq. (1) with calculated Wannier states $|\psi_j\rangle$. The computational cost of the procedure is linearly scales by the number of electrons N ,^{6,7)} and this procedure we call the perturbative order-N method.

When we use the variational procedure to obtain the Wannier states, the physical quantities should be calculated in a way consistent with the calculation of the Wannier states.^{6,7)} Therefore, the density matrix in the above eqs. (6) and (7) should be replaced by the optimal one $\tilde{\rho} = 2\hat{\rho} - \hat{\rho}^2$, and this procedure we call the variational order-N method.

It should be stressed that, once we can obtain Wannier states with a certain localization constraint, we do not introduce any other approximation in the present order-N method.

2.3 Linearly scaling property of perturbative order-N method

The Wannier states and the matrix elements of the Hamiltonian are given on the basis of the atomic orbitals $|\phi_{I\alpha}\rangle$. Then we can estimate the computational cost in the following way. Firstly the above physical quantities can be rewritten, by using the matrix elements of the Hamiltonian and the density matrix represented by the atomic orbitals, as

$$E_{\text{bs}} = \sum_I^{N_{\text{atom}}} \sum_{\Delta}^{N_{\text{loc}}} \sum_{\alpha}^{N_v} \sum_{\beta}^{N_v} \rho_{I\alpha(I+\Delta)\beta} \times \langle \phi_{I\alpha} | \hat{H} | \phi_{(I+\Delta)\beta} \rangle, \quad (8)$$

and

$$\mathbf{F}_I^{\text{bs}} = - \sum_J^{N_{\text{atom}}} \sum_{\Delta}^{N_{\text{loc}}} \sum_{\alpha}^{N_v} \sum_{\beta}^{N_v} \rho_{J\alpha(J+\Delta)\beta} \times \langle \phi_{J\alpha} | \frac{\partial \hat{H}}{\partial \mathbf{R}_I} | \phi_{(J+\Delta)\beta} \rangle. \quad (9)$$

The numbers N_{atom} , and N_v are those of atoms and atomic orbitals per atom, respectively. The number N_{loc} is that of interacting atoms in the local region around the central atom. The local region is defined, outside which the matrix elements of the tight-binding Hamiltonian vanish. In the diamond structure, $N_{\text{loc}} = 17$ including the central, the first and the second neighbor atoms.

From eqs. (8) and (9), the total computation time of the matrix elements are scaled by a factor $N_v \times N_v \times N_{\text{loc}} \times N_{\text{atom}}$, where the factor $N_v \times N_v$ is due to the cost for the quantum mechanical calculation. In the sp^3 minimal basis set, N_v is four. Therefore, we can calculate each Wannier state by a local procedure and the total computation cost is proportional to the number N_{atom} . The procedure is then the perfect order-N method.

Non-negligible amount of computation time is consumed in the calculation of the repulsive energy and forces. The part of the listing of the neighboring atoms is also important and its cost is not negligible for large systems. The above two parts are the same as in standard classical MD simulations and the computation time of these two parts are scaled by a factor $N_{\text{loc}} \times N_{\text{atom}}$. The computation time of the BS energy and forces costs, at least, $N_v \times N_v$ times more than those of the calculation of repulsive interactions and the listing of the neighboring atoms.

2.4 Allotment of Wannier states to processors, memory size and communication of data

Since the perturbative treatment is completely independent among the Wannier states, we can parallelize the computation with respect to several groups of the Wannier states. When we use N_{CPU} processors, each processor participates in the calculation of about N/N_{CPU} states among the total N Wannier states. For example, the calculation of $\{\langle \psi_j | \hat{H} | \psi_j \rangle\}$ and $\{\langle \psi_j | \frac{\partial \hat{H}}{\partial \mathbf{R}_I} | \psi_j \rangle\}_{j=j_{n-1}+1, \dots, j_n}$, ($j_n - j_{n-1} \simeq N/N_{\text{CPU}}$) is allotted to the n -th processor.

The matrix elements are not stored on memory because they require totally a large CPU memory. For example, the total memory size for the matrix elements $\{\langle \phi_{I\alpha} | \hat{H} | \phi_{(I+\Delta)\beta} \rangle\}$ can be estimated to be $8 \text{ (B)} \times 4^2 \times 17 \times 10^6 = 2.2 \text{ (GB)}$ for a system of 10^6 atoms. Therefore, we calculate the matrix elements when they are required and do not store them.

In the case of 10^6 atoms, the memory size for all atomic positions is $8 \text{ (B)} \times 3 \times 10^6 = 24 \text{ (MB)}$, that for the listing of the neighboring atoms is $4 \text{ (B)} \times 16 \times 10^6 = 64 \text{ (MB)}$, and that for the force is $8 \text{ (B)} \times 3 \times 10^6 = 24 \text{ (MB)}$. Then the total memory size for each processor is not large. In the present calculation, all processors have the same data of all atomic positions and no data are communicated among processors during the calculation of the Wannier states and contributions to the BS energy and forces.

After calculating contributions to the BS energy and forces in individual processor, we should sum up these elements. This procedure is accomplished by MPI-ALLREDUCE command in the Message Passing Interface

(MPI) in the present calculation. This is wasteful procedure with respect to the communication of the data because a large number of communicated data is not necessary, that is, null. Notwithstanding, the communication time would be relatively cheap expenses in the present work because there exist very heavy computations with respect to quantum mechanical freedoms.

The parallelism shown here is very primitive but keeps a high advantage to make an accurate estimation of memory size. It is exceptional that one can construct the algorithm of parallel computation in quantum mechanics with high performance shown in the next section.

3. Results and Discussions

3.1 Elapse time of one processor

We calculated four different systems of 4,096, 32,768, 262,144 and 2,097,152 atoms of Si crystals with the periodic boundary condition. Figure 1 shows the elapse time of one MD loop and one can see the almost perfect linearly scaling property. The elapse times for the calculation of the BS energy and forces are 97.44 %, 97.65%, 97.63% and 97.64% of the total elapse times in respective systems, which are larger than a factor $16/(16+1) = 0.941$, estimated simply in the case of $N_v \times N_v = 16$. Note that the small difference between two numbers 0.976 and 0.94 is very serious for the speed-up ratio discussed later. From these results, we can conclude that the tight-binding calculation is heavier by a factor 2.5 ($= \frac{0.976}{1-0.976} \times \frac{17-16}{16}$) than our naive estimation. This is very crucial difference in actual simulations, and quantum mechanical calculations are much heavier than the classical simulations even in the tight-binding calculation. One should parallelize firstly the part of the calculation of the BS energy and forces. In practice, we parallelize also the part of the calculation of the repulsive interaction energy. The parallelizable fraction P , the fraction of the elapse time of strictly parallelizable part among the whole elapse time in the case of one processor, reaches to 0.988. This high value of P would be impossible without the generic property of the linear scaling of the present method. Therefore, the perturbative order-N method is one of the most suitable procedures to the parallel computation.

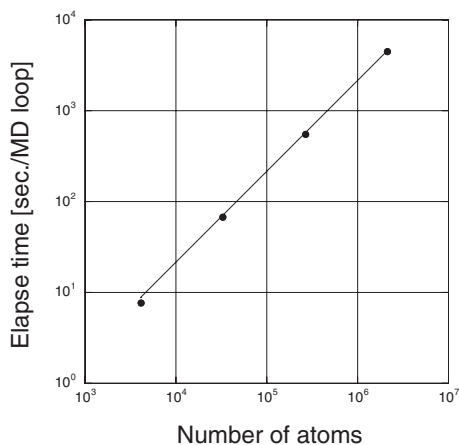


Fig. 1. The elapse time of one MD loop by using one processor for the systems of 4,096, 32,768, 262,144 and 2,097,152 atoms of Si crystals.

3.2 Speed-up ratio by parallelism

When we parallelize the computational program by using N_{CPU} processors, the speed-up ratio α_p is defined as the ratio of the elapse time $t_{N_{\text{CPU}}}$ of N_{CPU} processors and that t_1 of one processor as

$$\alpha_p \equiv \frac{t_1}{t_{N_{\text{CPU}}}}. \quad (10)$$

Let us assume that we can parallelize the part of the fraction P perfectly. In other words, we assume that the elapse time of this part can be reduced by a factor $1/N_{\text{CPU}}$. In such strictly parallelized case, the total elapse time can be minimized with the maximal speed-up ratio¹⁰⁾

$$(\alpha_p)_{\text{max}} = t_1 \times \left(\frac{1}{t_{N_{\text{CPU}}}} \right)_{\text{max}} \equiv \frac{1}{(1-P) + \frac{P}{N_{\text{CPU}}}}. \quad (11)$$

The high speed-up ratio is possible only for the high value of the parallelizable fraction P .

Figure 2 shows the observed speed-up ratio α_p by using MPI and the maximum one $(\alpha_p)_{\text{max}}$ with $P = 0.988$ as a function of the number of processors. Compared with the minimum elapse time $t_1/(\alpha_p)_{\text{max}}$, the present computation consumes 2% more for 32,768 atoms (8 processors), 18% more for 262,144 atoms (64 processors), and 45% more for 2,097,152 atoms (64 processors), respectively. In the case of 64 processors for 2,097,152 atoms, the communication cost is about 30% among whole elapse time. The cost of data communication increases with the number of the processors. The above analysis indicates that, when one uses a computer system of more than 200 processors for 2,097,152 atoms, the data communication process would consume the majority of the elapse time.

For a system of 2,097,152 atoms, the elapse time of one MD loop by one processor is 4565 s (76.1 min). When the time interval of one MD step corresponds to 3 fs in physical systems, a one pico second simulation needs 422 h (17.6 days) of CPU time by one processor. Such simulation becomes feasible when we use 128 processors.

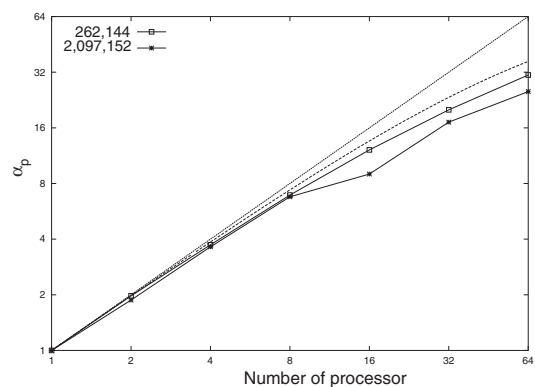


Fig. 2. The speed-up ratio α_p for systems of 262,144 and 2,097,152 atoms as a function of the number of processors. That for a system of 32,768 atoms locates slightly above that of 262,144 atoms. The dashed lines are the maximum speed-up ratio $(\alpha_p)_{\text{max}}$ of $P = 0.988$ and dotted lines are just $(\alpha_p)_{\text{max}} = N_{\text{CPU}}$ corresponding to $P = 1$. The observed deviation of the line of 2,097,152 atoms at 16 processors is due to the consumption of the elapse time in the data communication, presumably because of an ill balancing of the data size and the number of processors.

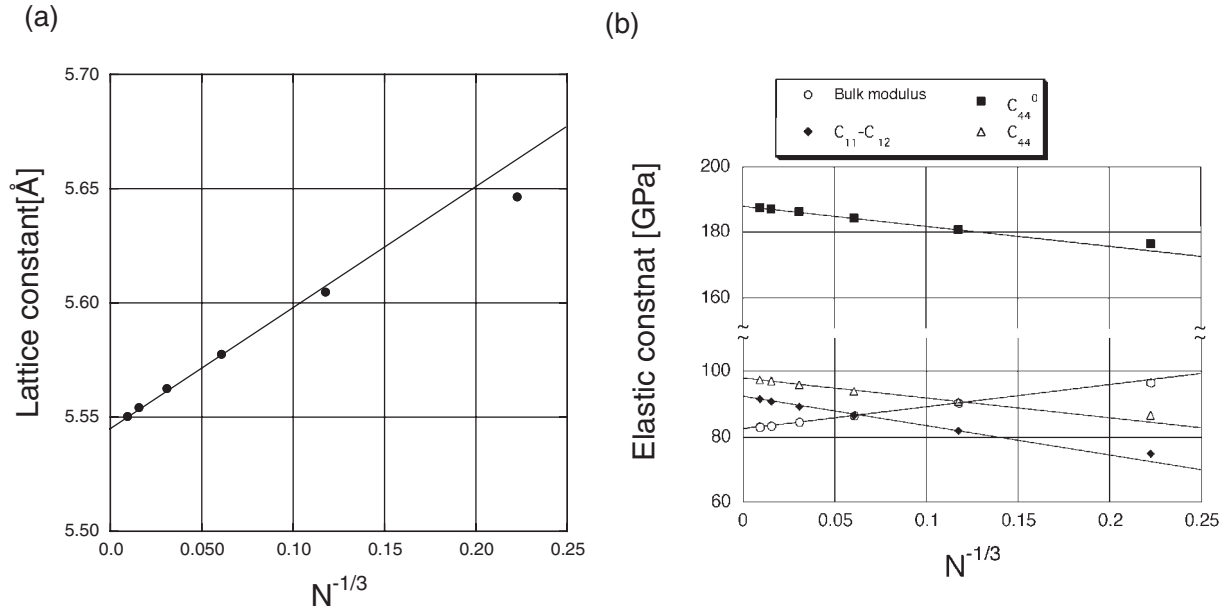


Fig. 3. The lattice constant (a) and elastic constants (b) as a function of $N^{-1/3}$, obtained by the perturbative method.

Table I. Lattice constant and elastic constants extrapolated to $N \rightarrow \infty$ systems are compared with those by the diagonalization method (Diag.), the first-principles calculation within the Local Density Approximation (LDA), and experiments (Exp.). The values in parentheses are errors against those with the diagonalization method. The elastic constant C_{44}^0 is that in a system where the internal displacement is not relaxed.

	Present work	Diag. ⁹⁾	LDA ¹²⁾	Exp.
Lattice constant (Å)	5.546 (2.19%)	5.427	5.431	5.429 ¹³⁾
Bulk modulus (GPa)	82.3 (6.05%)	87.6	93.0	97.8 ¹⁴⁾
$C_{11} - C_{12}$ (GPa)	92.3 (1.70%)	93.9	98.0	101.2 ¹⁴⁾
C_{44}^0 (GPa)	188.3 (5.14%)	198.5	111.0	
C_{44} (GPa)	97.9 (10.0%)	89.0	85.0	79.6 ¹⁴⁾

3.3 Calculations of elastic constants

The lattice constant and elastic constants are calculated in systems of several sizes of clusters of Si crystal of up to 1,423,909 atoms. The boundary condition is such that hybridized orbitals of the ideal sp^3 type are fixed on the surface atoms but surface atoms can move. Since the elastic constants are the linear response to small distortions, they may be expected to be reproduced by the first order perturbation calculations.

Figure 3 shows the calculated results with increasing the number of atoms N . The deviation can be scaled by $N^{-1/3}$ because it is the effects of the surface. The values extrapolated to $N \rightarrow \infty$ are summarized in Table I. The present results agree with those of the exact diagonalization method⁹⁾ within 10% error. The errors except for C_{44} are not more than the difference between results by the present tight-binding Hamiltonian (Diag.) and the LDA. The deviation of the shear modulus C_{44} is larger than those of the bulk modulus or $C_{11} - C_{12}$, since C_{44} is inherently complicated due to the rehybridization and the internal distortion^{11,12)} and this phenomena cannot be described very accurately by the first order perturbation of the Wannier states of fixed sp^3 hybrids. The discrepancy between the results with the order-N method and those with the diagonalization method originates from the localization constraint for constructing the Wannier states and the perturbation treatment in eqs. (3)

and (4). These restrictions are controllable and the discrepancy is not serious between the results by the present order-N method and the diagonalization method. This is a typical example of account balancing between the accuracy and the computational cost in the order-N method.

Much larger error is found in the value of C_{44}^0 of the tight-binding calculation itself, compared with that of the LDA calculation, which is a limitation of the present tight-binding Hamiltonian. One of the important works in future is the construction of more accurate tight-binding Hamiltonian from the first principle electronic structure calculations. Even if such sophisticated Hamiltonian is much complicated, it does not cause any serious difficulty in the calculation by the present order-N method, though it may increase the CPU times.

The bulk modulus originates from the energy change by a change of bond length, which is included in the dependence of the neighbor distances of the tight-binding parameters in the Hamiltonian. The origin of the elastic constants $C_{11} - C_{12}$ and C_{44} is more complex. In the present subsection, these elastic constants were evaluated quite accurately and this fact indicates the reliability of the present perturbation treatment. Since the Wannier states extent over the near neighbor bond sites, a change of the electronic energy through a change of the bond angle can be considered reasonably. The effect of deviation of bond angles is actually

treated in the wave functions of the Wannier states by the first order perturbation theory through eq. (3). Then the second order energy change corresponding to the elastic constants $C_{11} - C_{12}$ and C_{44} can be evaluated accurately, even though we use the unperturbed sp^3 hybrid orbitals as the basis functions. It should be noticed that one cannot formulate the order-N method based on the sp^3 hybrid orbitals, instead of the Wannier states as in the present paper.

3.4 The density matrix and the energy of the Wannier states by the perturbative method

The perturbative method was already analyzed in detail elsewhere,^{6,7)} and commented briefly in §2. In this subsection, we demonstrate additionally that the density matrix and the energy of the Wannier state can be reproduced accurately in the perturbative method. Furthermore, we will emphasize that the present order-N method will not introduce any numerical error except the error introduced by the approximation by a few terms instead of the infinite perturbation series.

For simplicity, we consider only nearest neighbor bond sites along a linear path with four sp^3 hybrid orbitals $|h_I\rangle$, $|h_{II}\rangle$, $|h_{III}\rangle$, $|h_{IV}\rangle$, where two orbitals $\{|h_I\rangle$ and $|h_{II}\rangle\}$ and $\{|h_{III}\rangle$ and $|h_{IV}\rangle\}$ are on the same bond sites and $\{|h_{II}\rangle$ and $|h_{III}\rangle\}$ are on the same atom. The phases of atomic orbitals are chosen so that two Wannier states centered on the two respective bond sites are written as

$$|\psi_1\rangle \approx \frac{C^{(0)}}{\sqrt{2}}(|h_I\rangle + |h_{II}\rangle) + \frac{C^{(1)}}{\sqrt{2}}(|h_{III}\rangle - |h_{IV}\rangle) + (\text{terms on other basis}), \quad (12)$$

$$|\psi_2\rangle \approx \frac{C^{(0)}}{\sqrt{2}}(|h_{III}\rangle + |h_{IV}\rangle) + \frac{C^{(1)}}{\sqrt{2}}(|h_{II}\rangle - |h_I\rangle) + (\text{terms on other basis}). \quad (13)$$

These forms are the one by the first order perturbation theory and we ignore the contributions from the second nearest bonds.

The one-body density matrix is given by

$$\rho = |\psi_1\rangle\langle\psi_1| + |\psi_2\rangle\langle\psi_2| + \text{other terms}. \quad (14)$$

The matrix elements on the sp^3 hybrid orbitals are calculated, with $|C^{(0)}|^2 = 0.934$ and $|C^{(1)}/C^{(0)}|^2 = 0.00904$ in the perturbative method, as follows;

$$\langle h_I|\rho|h_{II}\rangle = \frac{C^{(0)} C^{(0)}}{\sqrt{2} \sqrt{2}} + \frac{-C^{(1)} C^{(1)}}{\sqrt{2} \sqrt{2}} \approx 0.421 \quad (15)$$

$$\langle h_{II}|\rho|h_{III}\rangle = \frac{C^{(0)} C^{(1)}}{\sqrt{2} \sqrt{2}} + \frac{C^{(1)} C^{(0)}}{\sqrt{2} \sqrt{2}} \approx 0.088 \quad (16)$$

$$\langle h_I|\rho|h_{III}\rangle = \frac{C^{(0)} C^{(1)}}{\sqrt{2} \sqrt{2}} + \frac{-C^{(1)} C^{(0)}}{\sqrt{2} \sqrt{2}} \approx 0 \quad (17)$$

$$\langle h_I|\rho|h_{IV}\rangle = \frac{C^{(0)} - C^{(1)}}{\sqrt{2} \sqrt{2}} + \frac{-C^{(1)} C^{(0)}}{\sqrt{2} \sqrt{2}} \approx -0.088. \quad (18)$$

These estimated values are comparable with the exact values 0.439, 0.078, -0.008 and -0.071 , respectively. Though the first order perturbation theory is quite simple, the resultant values reproduce satisfactorily the exact ones. It is noticeable that the matrix element $\langle h_I|\rho|h_{III}\rangle$ is quite small, though

the corresponding hopping integral is finite ($\langle h_I|H|h_{III}\rangle = \beta_2 = -0.33$ eV). In case of $\langle h_I|\rho|h_{IV}\rangle$, this matrix element is not negligible, though the corresponding hopping integral is just zero. The above facts are caused by the interference of the two Wannier states, as in eqs. (17) and (18).

The energy of the Wannier state is given by

$$\begin{aligned} \varepsilon_{\text{WS}} &= \langle \psi_1|H|\psi_1\rangle \\ &\approx (|C^{(0)}|^2 + 6|C^{(1)}|^2)\varepsilon_h \\ &\quad + (|C^{(0)}|^2 - 6|C^{(1)}|^2)\beta_1 + 6 \cdot \frac{\beta_0}{2} C^{(0)}C^{(1)} \\ &\approx \varepsilon_b + 6 \cdot \frac{\beta_0}{2} C^{(0)}C^{(1)}, \end{aligned} \quad (19)$$

where ε_h and ε_b are the energies of the sp^3 hybridized orbitals and the bonding states on a one bond site, respectively, and β_0 and β_1 are the intra-atomic and inter-atomic hopping parameters ($\beta_0, \beta_1 < 0$);

$$\varepsilon_h \equiv \langle h_I|H|h_I\rangle = \frac{\varepsilon_s + 3\varepsilon_p}{4} = -0.413 \text{ eV}, \quad (20)$$

$$\varepsilon_b \equiv \langle b|H|b\rangle = \varepsilon_h + \beta_1 = -4.496 \text{ eV}, \quad (21)$$

$$\beta_0 \equiv \langle h_{II}|H|h_{III}\rangle = -\frac{\varepsilon_p - \varepsilon_s}{4} = -1.161 \text{ eV}, \quad (22)$$

$$\beta_1 \equiv \langle h_I|H|h_{II}\rangle = -4.083 \text{ eV}. \quad (23)$$

Here ε_s and ε_p are the energies of atomic s and p states, respectively. The factor six in eq. (19) is the number of the first nearest neighbor bond sites. The Wannier states energy is equal to twice of the band structure energy per bond site. The second term in eq. (19) is the energy gain of forming the Wannier state and evaluated as

$$6 \cdot \frac{\beta_0}{2} C^{(0)}C^{(1)} = -0.429 \text{ eV} \quad (24)$$

and the resulting value is ;

$$\varepsilon_{\text{WS}} = -4.496 - 0.429 = -4.925 \text{ eV}. \quad (25)$$

More careful calculation using the Wannier states constructed by the perturbative method gives a value of $\varepsilon_{\text{WS}} = -5.136$ eV and the exact value of the energy of the Wannier state by the present tight-binding Hamiltonian is $\varepsilon_{\text{WS}} = -5.083$ eV. Therefore, we conclude that the Wannier states constructed by the first order perturbation theory is accurate enough, both for the density matrix and the Wannier state energy. It should be noticed that the energy correction eq. (24) can be obtained also by the *second* order perturbation theory for the energy of the bonding orbit $|b_j\rangle$.

Since the energy ε_b is that of a simple bonding state $|b_j\rangle$ completely localizing on one bond site, the energy difference $\varepsilon_{\text{WS}} - \varepsilon_b$ is the energy gain of Wannier states due to its spatial extension in the system. In other words, the spatial behavior of the Wannier states is enough to describe energetic stability mechanism as eq. (19).

The numerical error for the Wannier state wave functions in the perturbative method is introduced by an approximation of a few terms instead of the perturbation series expansion in eq. (3) and this approximation is formally equivalent to the localization constraint to the Wannier states. The perturbative order-N method does not introduce

any additional error. This is also the case in the variational order-N method.

As discussed above, we do not introduce any additional approximation or error in the order-N method of the electronic structure calculations. In finite systems, the dangling bonds on surfaces are terminated by the localized sp^3 hybrid orbitals $|h_i\rangle$. Therefore, the Wannier states centered on bond sites of one bond-step inside from the surface miss a part of bonding and anti-bonding orbitals and this causes a relatively small error, compared with the energy stability of each Wannier state in eq. (24).

4. Conclusion

In a summary, we demonstrated the efficiency of parallelism of the perturbative order-N method in the large-scale tight-binding MD simulations. The method was shown to be the most profitable procedure for the parallel computation. The communication time is, even in the present case, much less than the time of the quantum mechanical calculations.

The perturbative order-N method may be hardly applied to systems with large distortion of lattices or bond breaking because the deviation from the unperturbed states becomes very large and, in the bond breaking process, the charge transfer and re-bonding are essentially important. In such cases we should start from the new basis set for the perturbation method. The other possible way is the one that we combine the perturbative order-N method with other methods for constructing basis states. The variational method can be associated with the perturbative order-N method and we can compose a hybrid order-N method. The hybrid order-N method can give electronic structures in the whole system and, more importantly, there is no discontinuous boundary in the connected region. The hybrid scheme of the perturbative and variational order N-methods has been already applied to the fracture propagation in Si nanocrystals with 1.4×10^6 atoms without parallelism.⁸⁾ The parallelized hybrid order-N method is a very essential method to pursue

tight-binding MD simulations for systems of millions atoms and the perturbative order-N method is the key technique in order to enlarge the size of the whole systems.

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