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O(N) Tight-Binding Algorithm for Large-Scale Molecular Dynamics Simulations

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Abstract

A parallel tight-binding molecular dynamics with an order-N $[O(N)]$ algorithm is implemented to perform large-scale simulation of nanostructured materials. The algorithm is based on the Fermi-operator expansion of an electronic energy and force, and we present its basic formalisms. Accuracy necessary for molecular-dynamics simulations can be obtained by a proper truncation in the expansion. Parallel efficiency on a parallel PC cluster shows nearly ideal scaling behavior with respect to the number of processors. Applicability of the method to a silicon-carbide system is examined.

1 INTRODUCTION

Recent advances in parallel computing technology have enabled one to perform atomistic simulations with the system sizes accessible experimentally, i.e. 1$\sim$100 nanometer [1]. In many cases, however, quantum simulations still suffer from its computational complexity which grows rapidly with increasing the number of electrons ($\sim N_{\rm el}^3$), and hence the range of system size in the simulations is limited around a few thousand atoms even on massive parallel computers. The order-N tight-binding (TB) algorithm, proposed recently by several groups [2], is one of the most promising approaches to *computer-aided design* of nanostructured materials such as semiconductor quantum devices [3] and nanophase ceramics [4]. Combining the method with accurate parameterizations of the tight-binding Hamiltonian and repulsive interactions between atoms, one can perform realistic quantum simulations of those materials in reasonable speed of computing.

In this report, we describe an order-N $[O(N)]$ algorithm of tight- binding molecular dynamics (TBMD) for insulators and semiconductors, proposed originally by Goedecker and Colombo

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[5]. Parallel efficiency of the algorithm on a PC-based parallel machine is presented. The method is applied to total-energy calculation of silicon carbide (SiC) crystals.

2 TBMD METHOD

2.1 TB Representation of the Total Energy

Given a system of $N_{\rm atom}$ atoms with $N_{\rm base}$ valence electrons each, one constructs an effective one-electron Hamiltonian, $\hat{H}$. The eigenstates, $|\Psi_n\rangle$, of the Hamiltonian are represented by a linear combination of atomic orbitals, $|\phi_{i\alpha}\rangle$, so called LCAO method, where i and α denote the indices of an atom and its orbital, respectively. The eigenstates and the eigenvalues, ϵ_n, of the Hamiltonian are then obtained by diagonalizing the Hamiltonian matrix,

$$H_{i\alpha j\beta} \equiv \langle\phi_{i\alpha}|\hat{H}|\phi_{j\beta}\rangle. \tag{1}$$

The band-structure energy is then obtained by

$$E_{\rm bs} = 2\sum_n \epsilon_n f_{\rm FD}\left(\frac{\epsilon_n - \mu}{k_{\rm B}T}\right), \tag{2}$$

where $f_{\rm FD}$, μ, $k_{\rm B}$, and T are the Fermi-Dirac distribution function, the Fermi energy, the Boltzmann constant, and an electronic temperature, respectively. The factor of two accounts for spin degeneracy in a closed-shell orbital.

The diagonalization of the Hamiltonian matrix requires the computation that scales as $(N_{\rm atom} \times N_{\rm base})^3$. Thus the ordinary TB method has a computational bottleneck similar to the one in other electronic-structure calculations such as the *ab initio* density-functional method [6].

By introducing the Fermi matrix,

$$F_{i\alpha j\beta} \equiv \langle\phi_{i\alpha}|f_{\rm FD}\left(\frac{\hat{H} - \mu}{k_{\rm B}T}\right)|\phi_{j\beta}\rangle, \tag{3}$$

the band-structure energy can be re-expressed as

$$E_{\rm bs} = 2{\rm Tr}[HF] = 2\sum_{i\alpha}\sum_{j\beta} H_{i\alpha j\beta}F_{j\beta i\alpha}. \tag{4}$$

The total energy of the system is then obtained by

$$E_{\rm tot} = \sum_i \frac{\mathbf{p}_i^2}{2m_i} + E_{\rm bs} + E_{\rm rep}, \tag{5}$$

where $\mathbf{p}_i$ represents the momentum of ith atom. $E_{\rm rep}$ is the repulsive term that takes into account the core-core interactions and neglected contributions in $E_{\rm bs}$ to the true electronic energy

such as a correction for double counting of electron-electron interaction. In a semiempirical TB approach, $E_{\rm rep}$ is determined by fitting with known properties such as elastic constants and phonon dispersions.

In a molecular-dynamics simulation, the force on each atom needs to be evaluated by differentiating $E_{\rm bs}$ and $E_{\rm rep}$ with respect to atomic coordinates. The Helmann-Feynman theorem [6] allows one to calculate the electronic term ($\mathbf{f}_i^{\rm bs}$) of the force as

$$-\mathbf{f}_i^{\rm bs} = 2{\rm Tr}[\frac{\partial H}{\partial \mathbf{r}_i}F]. \tag{6}$$

2.2 Fermi-operator Expansion with Chevyshev Polynomials

The various functions with a restricted range of variables can be approximated accurately by an interpolation with finite number of the Chevyshev polynomials defined as

$$T^{(m)}(x) \equiv \cos[m\cos^{-1}(x)] \tag{7}$$

for $-1 < x < 1$ ($m = 0, 1, ..., N_p$). They obey the recurrence relation

$$T^{(m)}(x) = 2xT^{(m-1)}(x) - T^{(m-2)}(x) \tag{8}$$

with $T^{(0)}(x) = 1$ and $T^{(1)}(x) = x$, and the orthogonality relation

$$\frac{2}{\pi}\int_{-1}^{1} dx \frac{T^{(m)}(x)T^{(n)}(x)}{\sqrt{1-x^2}} = \delta_{mn}. \tag{9}$$

The Chevyshev interpolation for a function $f(x)$ is given by

$$f(x) \approx f^{N_p} \equiv \frac{c_0}{2} + \sum_{m=1}^{N_p} c_m T^{(m)}(x), \tag{10}$$

and the expansion coefficient at mth order is

$$c_m = \frac{2}{\pi}\int_{-1}^{1} dx \frac{f(x)T^{(m)}(x)}{\sqrt{1-x^2}} = \frac{2}{N_p}\sum_{k=1}^{N_p} f(x_k)T^{(m)}(x_k), \tag{11}$$

where x_k is the kth root of $T^{(N_p)}(x) = 0$. Figure 1 depicts the Chevyshev interpolation of the Fermi-Dirac distribution function ($f_{\rm FD}$) in the case of $N_p = 100$. It shows that the interpolation reproduces the original function with reasonable accuracy even near $\epsilon = \mu$.

The Fermi matrix defined in Eq. (3) can also be approximated by the Chevyshev interpolation by replacing x with the matrix H in the above formulae and the polynomial $T^{(m)}$ thereby represents the corresponding matrix. Truncation at a finite N_p reduces the computational complexity of $O(N^3)$ in the exact diagonalization to $O(N^2)$ due to the finite number of matrix-matrix multiplication in Eq. (8). Further reduction of the complexity to $O(N)$ is

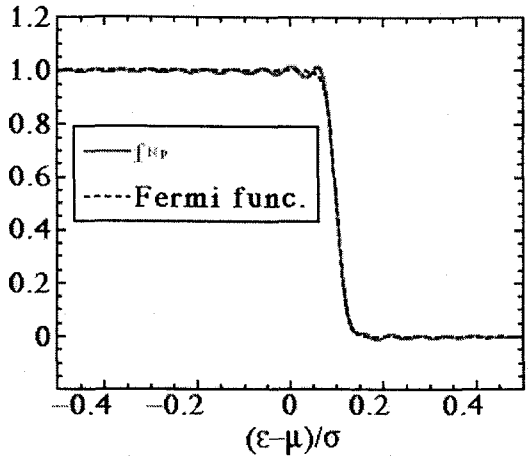

Fig. 1: Chevyshev interpolation of the Fermi-Dirac distribution function. ($N_p = 100, \mu = 0.1, \sigma = 0.01$)

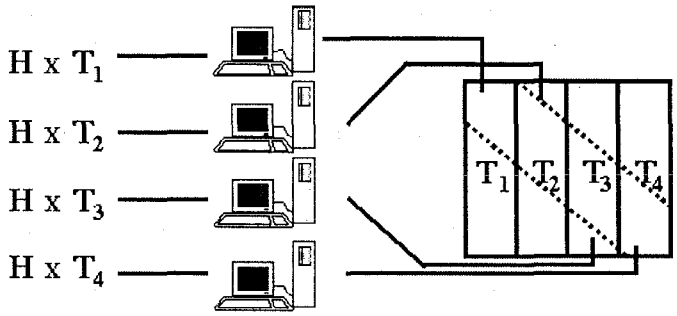

Fig. 2: Parallelization in matrix(H)-matrix(T) multiplication.

obtained by truncating the matrix(H)-matrix(T) multiplication at a physical distance between elements. This approximation is especially effective for insulators and semiconductors [5]. (The H matrix has an intrinsic nature of short-range interaction for these materials.)

This truncation in the matrix-matrix multiplication makes the code easy to be parallelized since the computation of the T matrix is independent of those for the other column. The parallelization is done simply by distributing the column of T over processors, as shown schematically in Fig. 2.

Using the Chevyshev interpolation, $E_{\rm bs}$ and the electronic occupation $n_{\rm el}$ are calculated approximately as

$$E_{\rm bs} = c_0 \sum_{i\alpha}\sum_{j\beta} H_{i\alpha j\beta} S_{j\beta i\alpha} + 2\sum_{m=1}^{N_p} c_m \sum_{i\alpha}\sum_{j\beta} H_{i\alpha j\beta} T^{(m)}_{j\beta i\alpha}, \tag{12}$$

$$n_{\rm el} = c_0 \sum_{i\alpha} S_{i\alpha i\alpha} + 2\sum_{m=1}^{N_p} c_m \sum_{i\alpha} T^{(m)}_{i\alpha i\alpha}, \tag{13}$$

where $S_{i\alpha j\beta}$ is the overlap integral between the atomic orbitals. In an orthogonal TB model, $S_{i\alpha j\beta} = \delta_{i\alpha j\beta}$. During the simulations, the Fermi energy (μ) needs to be adjusted so as to keep

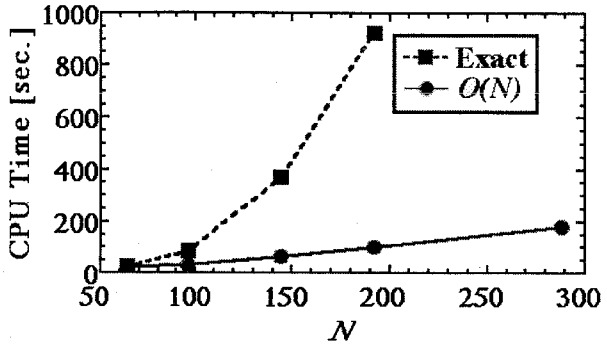

Fig. 3: CPU time vs. the total number of atoms. ($N_p = 50$)

the identity $n_{\rm el} = N_{\rm atom} \times N_{\rm base}$ (= the total number of electrons).

Figure 3 shows comparison between cpu times (on single processor) for calculating the band-structure energy of crystalline silicon at the diamond structure by the present method and those by the exact diagonalization. The TB parameters for the silicon crystal were taken from Ref. [7]. The figure clearly shows significant speedup in the $O(N)$ method over the exact method with cubic scaling.

3 APPLICATION TO SiC SYSTEM: EFFICIENCY, ACCURACY, AND PARALLELIZATION

We have applied the present method to silicon carbide (SiC) systems. Silicon carbide has attracted great deal of attention as an enabling material for a variety of new semiconductor devices in areas where silicon devices cannot effectively compete, including high-power high-voltage switching applications and high temperature electronics. Nanophase SiC has shown [8] unique properties such as high sinterability and enhanced toughness. Large-scale quantum simulation will be powerful tool to investigate theoretically microscopic processes in this material. The TB parameters for SiC have been taken from Ref. [9]. The TB model chosen is based on an sp^3 orthogonal basis set for valence electrons. It includes intra-atomic contribution to on-site terms of the Hamiltonian matrix in order to reproduce accurately the bulk properties such as the cohesive energy, the elastic constants, and the band structure at several polymorphs.

Figure 4 shows the total energy of the TB model for β-SiC (zincblende structure) as a function of the lattice parameter in the present method with $N_p = 50$ and that in the exact diagonalization. The largest error due to the truncation at 50th in the expansion is only on the order of 1% of the total energy under large variation of volume.

Parallel efficiency of the method has also been examined on our eight-node parallel machine

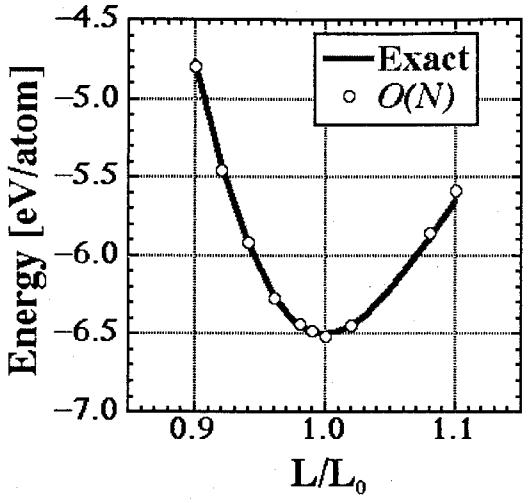

Fig. 4: Total energy per atom of β-SiC vs. lattice parameter. ($N_p = 50$; $L_0 = 4.43\text{Å}$)

consisting of PC clones (Pentium II 400 MHz ×4 + 450 MHz ×4 with 256MB SDRAM each) connected via a Fast Ethernet switch, shown in Fig. 5. Parallelization has been done using a High-performance Fortran (HPF) compiler. Figure 6 shows cpu time as a function of the number of processor in the calculations of $E_{\rm bs}$ of 64-atom system. Nearly ideal scaling can be achieved in the present method.

4 CONCLUDING REMARKS

We have implemented and examined the $O(N)$ TBMD algorithm for silicon carbide on the PC-based parallel machine. The code has been fully parallelized and the accuracy can be controlled by choosing the order of the Chevyshev polynomials. It has thus been shown that the present method was suitable for large-scale TBMD simulations of nanostructured materials.

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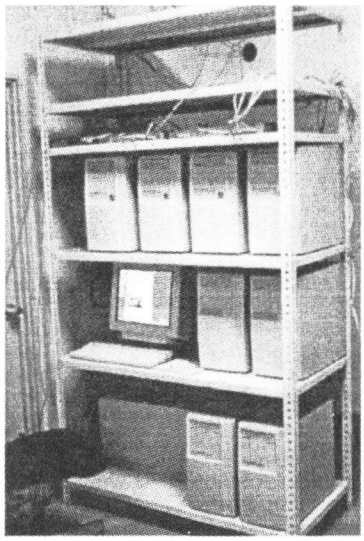

Fig. 5: Eight-node parallel PC cluster connected via Fast Ethernet switch.

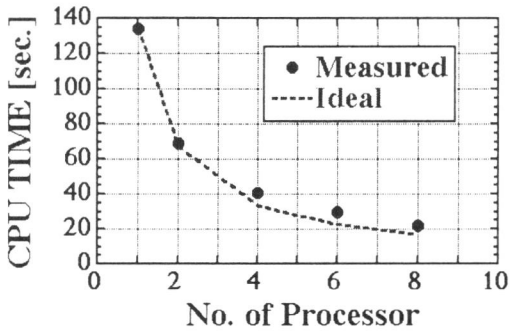

Fig. 6: CPU time vs. number of processor. ($N_p = 50$)

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