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Accuracy control in ultra-large-scale electronic structure calculations

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Abstract

Numerical aspects are investigated in ultra-large-scale electronic structure calculations. Accuracy control methods in process (molecular-dynamics) calculations are focused upon. Flexible control methods are proposed so as to control variational freedoms, automatically at each time step, within the framework of generalized Wannier state theory. The method is demonstrated in a silicon cleavage simulation with 10^2–10^5 atoms. The idea is of general importance among process calculations and is also used in Krylov subspace theory, which is another large-scale calculation theory.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Nowadays, one of most important scientific fields is the processing of nanostructures (structure on the scales of nanometers or tens of nanometers), particularly for the controllability of their structure and function. Electronic structure calculations for these purposes should be carried out with a large system (10^3 atoms or more) and over a meaningful timescale. For a decade, on the other hand, many calculation methods and related techniques have been proposed for handling such large systems; see the reviews [1, 2] and original works [3–22]. In these methodologies, a one-body density matrix or Green's function is calculated, instead of one-electron eigenstates, and the calculation is carried out with real-space representation. A physical quantity $\langle X \rangle$ is given as a trace form

$$\langle X \rangle = \mathrm{Tr}[\rho X] = \int \int \mathrm{d}\boldsymbol{r}\, \mathrm{d}\boldsymbol{r}' \rho(\boldsymbol{r}, \boldsymbol{r}') X(\boldsymbol{r}', \boldsymbol{r}) \tag{1}$$

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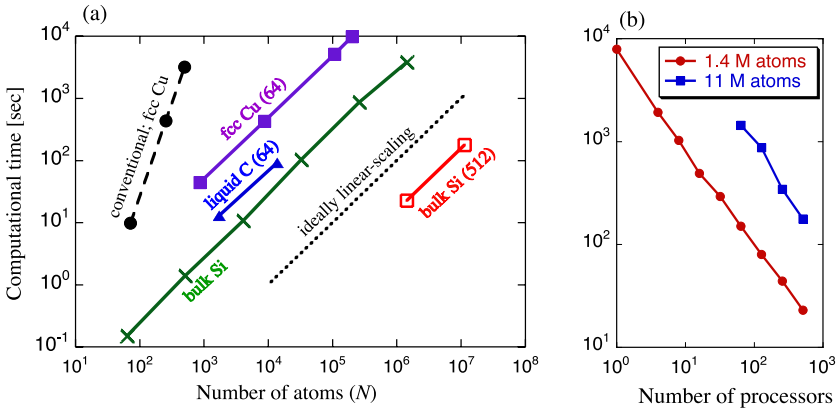

Figure 1. Computational time of ultra-large-scale calculation with up to 11 315 021 atoms. The times for our method are plotted for fcc Cu, liquid C and bulk Si. An optimal solver method is chosen for each system [21]; the Wannier state theory in the perturbative procedure is chosen for bulk silicon and the Krylov subspace theory is chosen for the other cases. (a) Comparison between materials. As reference data, the time for the conventional eigenstate calculation is also plotted for fcc Cu using a single CPU. See [15, 17, 21] for details. The computations were carried out using Intel or SGI CPUs. In parallel computation, the number of processors (CPU cores) is indicated inside the parentheses. (b) The time for bulk silicon with 1423 909 atoms and 11 315 021 atoms is measured as a function of processors using SGI origin 3800$^{\mathrm{TM}}$.

with the density matrix ρ. If the matrix $X(\boldsymbol{r}, \boldsymbol{r}')$ is of short range, the off-diagonal long-range component of the density matrix does not contribute to the physical quantity $\langle X \rangle$, which is crucial for the practical success of large-scale calculations [7].

In one of the above-mentioned works, we have developed a set of theories and program codes and applied them to silicon, carbon and metal systems with Slater–Koster-form Hamiltonians [15–17, 19–21]. These theories are constructed from the fundamental theory of the generalized Wannier state or Krylov subspace. An overview is given in [21]. Figure 1 demonstrates our methods with or without parallel computers, in which the computational cost is of 'order-N' or is linearly proportional to the system size (N), up to ten million atoms, and shows a satisfactory performance in parallel computation. We note that the electronic property, such as the density of states, is also calculated [16, 19, 21].

These large-scale-calculation methods have controlling parameters for calculating electronic freedoms, which gives the accuracy and computational cost. In the present paper, we will introduce flexible methods of controlling electronic freedoms for optimal computational cost, and this will be demonstrated within the framework of generalized Wannier state theory. The methods are crucial, particularly in a dynamical process or a molecular dynamics (MD) calculation. This paper is organized as follows. An overview of the theory and an example of silicon cleavage are given in section 2. Then the flexible control methods are introduced and demonstrated in section 3. We point out that similar flexible control methods are used in the Krylov subspace theory. Section 4 is devoted to concluding remarks.

2. Theoretical overview and examples

The calculations in this paper were carried out in the theoretical framework of the generalized Wannier state [23, 24, 3, 5, 25, 10, 26–29]. A physical picture of the generalized Wannier states $\{\phi_i^{(\mathrm{WS})}\}$ is the localized chemical wavefunction in condensed matter, such as a bonding orbital or a lone-pair orbital with a slight spatial extension or 'tail'. The suffix i of a wavefunction

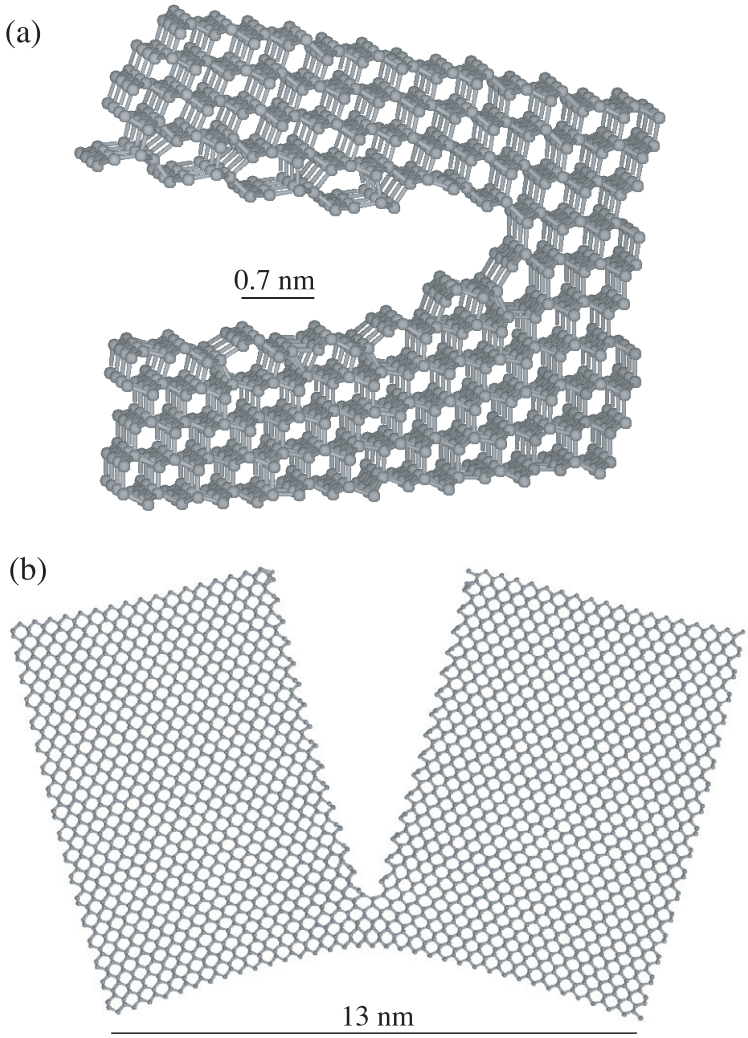

Figure 2. Simulation results of silicon cleavage. (a) A sample with 1112 atoms. The resultant cleaved surface shows a (111)-2 × 1 reconstruction and contains a step structure. (b) A sample with 10 368 atoms. The resultant cleaved surface shows a buckled (110) reconstruction.

$\phi_i^{(\mathrm{WS})}$ indicates the position of its localization center, such as the bond site. Their wavefunctions $\{\phi_i^{(\mathrm{WS})}\}$ are equivalent to the unitary transformation of occupied eigen-states, and the density matrix is given as

$$\rho(\boldsymbol{r}, \boldsymbol{r}') = \sum_{j=1}^{\mathrm{occ.}} \phi_j^{(\mathrm{WS})}(\boldsymbol{r})\phi_j^{(\mathrm{WS})}(\boldsymbol{r}') \tag{2}$$

where wavefunctions are described as real numbers. The Wannier state theory is suitable for large systems, particularly when a dominant number of wavefunctions are well localized. The present calculations were carried out using a variational procedure [10, 21, 29].

Hereafter, the silicon cleavage process is calculated with a transferable Hamiltonian in the Slater–Koster form [30]. Samples on the scale of nanometers or tens of nanometers are

cleaved under an external load. Figure 2 shows examples of the resultant cleaved samples that contain experimentally observed cleavage planes, (111) and (110) planes; in figure 2(a), the resultant sample contains a cleaved Si(111)-2 × 1 surface [17]. A pair of five- and seven-membered rings appears in the cleavage propagation direction (the $[2\bar{1}\bar{1}]$ direction), which forms the unit cell of the 2 × 1 structure called the Pandey structure [31–33]. As an interesting feature of the present result, the cleaved surface contains a step structure with a six-membered ring at the step edge, which is compared to experiments [17]. In detail, the sample consists of 1112 atoms and the periodic boundary condition is imposed, by eight atomic layers, in the direction perpendicular to the cleavage propagation direction. In the present case, an additional periodicity, by two atomic layers, is imposed as a constraint on the atomic structure. We note that the 2 × 1 structure appears even without the additional periodicity. See papers [17] for more details and results for larger samples with 10^5 atoms. In figure 2(b), the resultant cleaved surface is a buckled (110) surface that appears in textbooks in surface physics or papers such as [34, 35]. In detail, the sample consists of 10 368 atoms and the periodic boundary condition is imposed, by eight atomic layers, in the direction perpendicular to the cleavage propagation direction. The physical discussions on cleavage dynamics are found in [15, 17, 21] and references therein.

3. Flexible methods for accuracy control

3.1. Three methods in Wannier state theory

Here we describe the accuracy control methods [15, 17, 29] used in the above MD calculation. In generalized Wannier state theory, the region for localization constraint for each Wannier state is the variational freedom that governs the accuracy and computational cost. Therefore we will concentrate on the methods for setting the localization region for each wavefunction at each time step.

Here, three methods of accuracy control in the Wannier state calculation are proposed. Among all the methods, the localization constraint on each wavefunction $\phi_i^{(\mathrm{WS})}$ is imposed as a spherical region whose center is the weighted center of the wavefunction $\boldsymbol{r}_i^{(\mathrm{WS})} \equiv \langle\phi_i^{(\mathrm{WS})}|\hat{\boldsymbol{r}}|\phi_i^{(\mathrm{WS})}\rangle$. Therefore, the cutoff radius of the spherical region, denoted $R_i^{(\mathrm{WS})}$, mainly contributes to accuracy. We also denote $N_i^{(\mathrm{WS})}$ as the number of atoms inside the localization region of the ith Wannier state. Three methods for determinating the radius are used: (i) the 'constant cutoff' method (WS-CC method); (ii) the 'flexible control method at the first level' (WS-FC1 method); and (iii) the 'flexible control method at the second level' (WS-FC2 method). See below for an explanation of these methods.

The method is demonstrated in nanocrystalline silicon for an isolated cubic sample with 91 atoms [29]. The sample is thermally vibrated at 300 K and an additional slow constant-velocity motion is introduced for the atoms on the sample surface. As a result, the sample is stretched in the [001] direction with thermal vibration. Figure 3 shows the trajectory of the calculated stress σ. In figure 3(a), the results of three controlling methods for Wannier states are compared. Figure 3(a) also contains the result of a conventional eigen-state calculation as reference data, in which the temperature (level-broadening) parameter of $\tau = 0.1$ eV is used for the electronic system.

In the WS-CC method of figure 3, the radius is chosen to be a constant value of $R_i^{(\mathrm{WS})} = 2.5d_0$, where $d_0 (= 2.35$ Å) is the equilibrium bond length. This value is chosen for all Wannier states through the simulation. Without an external load, this radius sets the localization region of the Wannier states to about $N_i^{\mathrm{WS}} = 40$ atoms. We should say that the results with the CC method is expected to be rather poor, because the sample in the present MD simulation will

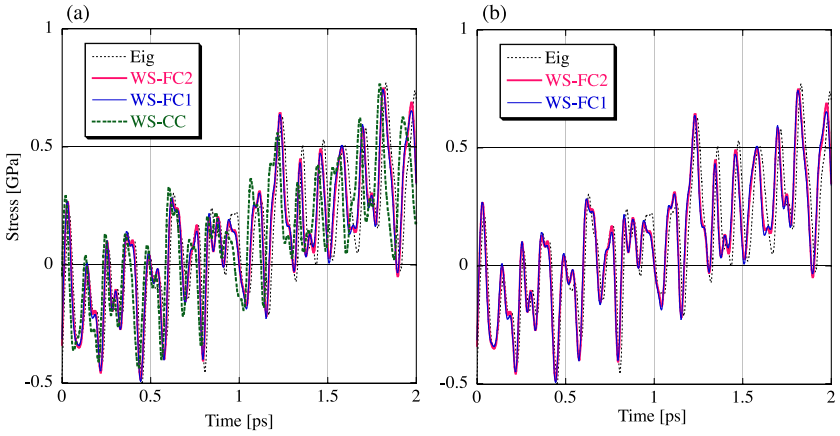

Figure 3. (a) The stress value for nanocrystalline silicon of 91 atoms with thermal vibration, in which the sample is stretched by a [001] uniaxial load. The calculations were carried out using the Wannier state method with (i) 'constant cutoff' (WS-CC), (ii) 'flexible control at the first level' (WS-FC1), and (iii) 'flexible control at the second level' (WS-FC2) methods. See the text for an explanation. The conventional eigen-state method (Eig) was also carried out as reference data. (b) The same data set as in (a) is plotted, but the data of the CC method are ignored so as to clarify significantly better agreement among the other methods.

be stretched by the external load and the number of atoms within the localization region tends to decrease during the MD simulation. This point will be confirmed numerically in the last paragraph of the present subsection.

A better method for accuracy control is to give the number of atoms in the localization region, N_i^{WS}, instead of a given radius $R_i^{(\mathrm{WS})}$, which realized flexible control for the localization radius. In this method, the radius $R_i^{(\mathrm{WS})}$ is chosen so that the localization region contains a given number, $N_i^{(\mathrm{WS,min})}$, of atoms or more. This method is called the flexible control method at the first level (the WS-FC1 method). In figure 3(a), we choose the value of $N_i^{(\mathrm{WS,min})} = 40$. In the results, the localization radius $R_i^{(\mathrm{WS})}$ may be different between Wannier states and the number of atoms within the localization region (N_i^{WS}) always satisfies $N_i^{(\mathrm{WS})} \geqslant N_i^{(\mathrm{WS,min})} = 40$.

Now we explain the third method for setting the localization region, called the flexible control method at the second level (the WS-FC2 method). In the program code, an iterative solution procedure is carried out for an equation of generalized Wannier states. See [10, 21, 29] for the explicit expression of the equation. Since the residual of the equation ($\delta\phi_i$) is well defined for each wavefunction $\phi_i^{(\mathrm{WS})}$, the accuracy of a calculated wavefuncion can be monitored rigorously by the residual norm $|\delta\phi_i|$. The residual norm vanishes when the calculated wavefuncion is exact ($|\delta\phi_i| \to 0$). When the wavefunction ϕ_i has a large residual norm $|\delta\phi_i|$, a larger number of atoms ($N_i^{(\mathrm{WS})}$) should be assigned inside the localization region so as to reduce the residual norm $|\delta\phi_i|$. In the present code, the assignment is carried out automatically for each wavefunction at each time step. In the calculation in figure 3(a), we classify all wavefunctions into three classes with different numbers $N_i^{(\mathrm{WS,min})} = 40, 60$ or 80. The classification procedure is carried out with the averaged value $\delta\phi_{\mathrm{av}}$ of the residual norm among all wavefunctions $\{|\delta\phi_i|\}$. If the residual norm of a wavefunction ($|\delta\phi_i|$) is almost the same as its averaged value ($|\delta\phi_i| \leqslant 1.2\delta\phi_{\mathrm{av}}$), the number $N_i^{(\mathrm{WS,min})}$ is set to be the small one ($N_i^{(\mathrm{WS,min})} = 40$). If the residual norm of a wavefunction ($|\delta\phi_i|$) is slightly larger than its averaged value ($1.2\delta\phi_{\mathrm{av}} \leqslant |\delta\phi_i| \leqslant 1.5\delta\phi_{\mathrm{av}}$), the number $N_i^{(\mathrm{WS,min})}$ is set to be the

middle one ($N_i^{(\mathrm{WS,min})} = 60$). If the residual norm of a wavefunction ($|\delta\phi_i|$) is larger than 150% of its averaged value ($1.5\delta\phi_{\mathrm{av}} \leqslant |\delta\phi_i|$), the number $N_i^{(\mathrm{WS,min})}$ is set to be the large one ($N_i^{(\mathrm{WS,min})} = 80$).

When the three control methods with Wannier states (the WS-CC, WS-FC1 and WS-FC2 methods) are compared, in figure 3(a), with reference data using the conventional eigen-state method, one finds that the flexible control methods (the FC1 and FC2 methods) are siginificantly better in accuracy than the CC method. This statement is clarified in figure 3(b), when the trajectories without that of the CC method show better agreement.

3.2. Discussions

Although the flexible control methods give, in general, better accuracy during the MD simulation than the CC method, any of the three methods (the WS-CC, WS-FC1 and WS-FC2 methods) is sufficient for discussing physical quantities in the present case. For example, the averaged gradient of figure 3 is proportional to the Young modulus in the [001] direction (E_{100}), because the stretching motion is realized within a constant velocity. The Young modulus is estimated, commonly between four calculation methods, to be $E_{100} \approx 100$ GPa, where the estimated value may include an error on the order of 10%. The estimated value is comparable with the experimental bulk value, $E_{100} \approx 130$ GPa, but deviates owing to the small system size. Satisfactory results are also given for the critical stress for cleavage; $\sigma_{\mathrm{c}} = 2.5$–3.0 GPa. Moreover, the cleavage propagation velocity (not shown) agrees well between the three Wannier state calculations and the eigen-state calculation. Note that a discussion on these quantities in nanocrystalline silicon is given in [15].

The WS-FC2 method is required in several simulations, and one example is the case of figure 2(a) or silicon cleavage with a Si(111)-2 $\times$ 1 cleaved surface; the elementary reconstruction process occurs among several bond sites including surface and subsurface layers [17] and a larger region is required for describing wavefunctions near the cleaved surface. Since the number of wavefunctions near the cleaved surface accounts for only a small fraction (typically 10%) of the total number of wavefunctions, the total computational cost of the FC2 method is moderate when compared with the CC method.

Finally, we note that similar flexible control is also used in the Krylov subspace theory, which is another theory for large-scale calculation theory; see the appendix of [21].

4. Concluding remarks

In this paper, we have focused on methods for accuracy control in dynamical process or MD simulation. Flexible control methods are proposed so as to realize large-scale process (MD) calculation, in which the electronic freedoms are determined optimally at each time step.

Since the nature (or electronic structure) of a physical system can change during a dynamical process, the flexible control methods proposed here are crucial, generally, in large-scale calculations, when one would like to achieve proper balance between accuracy and computational cost.

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References

[1] Galli G 2000 *Phys. Status Solidi* b **217** 231
[2] Wu S Y and Jayamthi C S 2002 *Phys. Rep.* **358** 1
[3] Mauri F, Galli G and Car R 1993 *Phys. Rev.* B **47** 9973
[4] Li X-P, Nunes R W and Vanderbilt D 1993 *Phys. Rev.* B **47** 10891
[5] Ordejón P, Drabold D A, Grumbach M P and Martin R 1993 *Phys. Rev.* B **48** 14646
[6] Goedecker S and Colombo L 1994 *Phys. Rev. Lett.* **73** 122
[7] Kohn W 1996 *Phys. Rev. Lett.* **76** 3168
[8] Hoshi T and Fujiwara T 1997 *J. Phys. Soc. Japan* **66** 3710
[9] Roche S and Mayou D 1997 *Phys. Rev. Lett.* **79** 2518
[10] Hoshi T and Fujiwara T 2000 *J. Phys. Soc. Japan* **69** 3773
[11] Ozaki T and Terakura K 2001 *Phys. Rev.* B **64** 195126
[12] Tsuruta K, Totsuji H and Totsuji C 2001 *Phil. Mag. Lett.* **81** 357
[13] Soler J M, Artacho E, Gale J D, García A, Junquera J, Ordejón P and Sánchez-Portal D 2002 *J. Phys.: Condens. Matter* **14** 2745
[14] Bowler D R, Miyazaki T and Gillan M J 2002 *J. Phys.: Condens. Matter* **14** 2781
[15] Hoshi T and Fujiwara T 2003 *J. Phys. Soc. Japan* **72** 2429
[16] Takayama R, Hoshi T and Fujiwara T 2004 *J. Phys. Soc. Japan* **73** 1519
[17] Hoshi T, Iguchi Y and Fujiwara T 2005 *Phys. Rev.* B **72** 075323
[18] Skylaris C-K, Haynes P D, Mostofi A A and Payne M C 2005 *J. Chem. Phys.* **122** 084119
[19] Takayama R, Hoshi T, Sogabe T, Zhang S-L and Fujiwara T 2006 *Phys. Rev.* B **73** 165108
[20] Hoshi T, Takayama R, Iguchi Y and Fujiwara T 2006 *Physica* B **376/377** 975
[21] Hoshi T and Fujiwara T 2006 *J. Phys.: Condens. Matter* **18** 10787
[22] Ozaki T 2006 *Phys. Rev.* B **74** 245101
[23] Kohn W 1973 *Phys. Rev.* B **7** 4388
[24] Kohn W 1993 *Chem. Phys. Lett.* **208** 167
[25] Marzari N and Vanderbilt D 1997 *Phys. Rev.* B **56** 12847
[26] Hoshi T and Fujiwara T 2001 *Surf. Sci.* **493** 659
[27] Andersen O K, Saha-Dasgupta T and Ezhov S 2003 *Bull. Mater. Sci.* **26** 19
[28] Geshi M, Hoshi T and Fujiwara T 2003 *J. Phys. Soc. Japan* **72** 2880
[29] Hoshi T 2003 *Doctor Thesis* School of Engineering, University of Tokyo, Tokyo
[30] Kwon I, Biswas R, Wang C Z, Ho K M and Soukoulis C M 1994 *Phys. Rev.* B **49** 7242
[31] Pandey K C 1981 *Phys. Rev. Lett.* **47** 1913
[32] Ancilotto F, Andreoni W, Selloni A, Car R and Parrinello M 1990 *Phys. Rev. Lett.* **65** 3148
[33] Csányi G, Albaret T, Payne M C and DeVita A 2004 *Phys. Rev. Lett.* **93** 175503
[34] Pérez R and Gumbsch P 2000 *Phys. Rev. Lett.* **84** 5347
[35] Stekolnikov A A, Furthmüller J and Bechstedt F 2002 *Phys. Rev.* B **65** 115318