Nano-Scale Simulation by the Use of Supercomputer Electronic Structure Calculation of Materials

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Abstract

This paper presents NEC's developments in simulation technologies for nano-scale phenomena based on the principles of quantum mechanics and High Performance Computing (HPC) technologies. The procedure using the Schrödinger equation to obtain real physical quantities is briefly introduced, and applications of nano-scale simulations to explore catalysis and nano-carbon are presented. The necessity of using HPC in large-scale simulations is also discussed.

Keywords

quantum mechanics, Schrödinger equation, density functional theory, catalysis, nano carbon, HPC

1. Introduction

As stated by the National Nanotechnology Initiative (NNI), Nanotechnology is "the understanding and control of matter at dimensions of roughly 1 to 100 nanometers."* Indeed, precise 'understanding' of phenomena at such scales will help us to make useful predictions for real applications of nanotechnologies. Atomic scale simulations based on quantum mechanics are indispensable for this purpose and NEC has developed nano-scale simulation technology with the use of High Performance Computing (HPC).

In this paper, the fundamentals of nano-scale simulation together with NEC's recent developments in simulation techniques are presented in Section 2 and applications in catalysis and nano-carbon are presented in Section 3. The essential contribution of HPC technology in large scale simulation will also be discussed in Section 4. Finally, future issues and conclusions will be presented in Sections 5 and 6, respectively.

2. Fundamentals of Nano-Scale Simulations and NEC's Recent Developments in Simulation Techniques

Properties of materials such as conductivity, optical properties and formation energy can be derived from electronic structures obtained as solutions of the Schrödinger equations of electron wave functions. Here we introduce band-structure calculations based on the density functional theory (DFT), which efficiently approximates complicated interactions of many electrons, and based on the pseudo-potentials which mimic interactions of valence electrons and ions. Within DFT, the Schrödinger equation turns out to be the Kohn-Sham equation[1] which is,

$$H_{KS}\psi_n^{KS} = \varepsilon_n^{KS}\psi_n^{KS} \qquad \cdots\cdots (1)$$

Here H_{KS} is the 'Kohn-Sham Hamiltonian' and ψ_n^{KS} and ε_n^{KS} are Kohn-Sham wave functions and eigenvalues. This equation and eigenvalues are obtained by the Euler's equation to minimize the total energy expressed in equation (2) with respect to the set $\{\psi_n^{KS}\}$.

$$E_{total} = \sum_{\varepsilon_n \le \varepsilon_F} \int \psi_n^{KS*}(\vec{r})\left(-\frac{\nabla^2}{2}\right)\psi_n^{KS}(\vec{r})d\vec{r} + \frac{1}{2}\iint \frac{\rho(r)\rho(r')}{|\vec{r}-\vec{r}'|}d\vec{r}\,d\vec{r}'$$
$$+ \int E_{XC}[\rho(\vec{r})]\rho(\vec{r})d\vec{r} + \sum_n \iint \psi_n^{KS}(\vec{r})\sum_I v_I^{ps}(\vec{r},\vec{r}')\psi_n^{KS}(\vec{r}')d\vec{r}\,d\vec{r}'$$
$$+ \sum_I \int \frac{Z_I\rho(\vec{r})}{|\vec{r}-\vec{R}_I|}d\vec{r} + \sum_{I\neq J}\frac{Z_I Z_J}{|\vec{R}_I-\vec{R}_J|} \qquad \cdots\cdots (2)$$

Minimization is done within the constraint of keeping the total number of electrons of the system. Thus the eigenvalues are the Lagrange multipliers of the Euler's equation. In equation (2), the first term is a sum of electron kinetic energies while the second and third terms are the Hartree and exchange-correlation interactions of electrons. The DFT treats the exchange-correlation interactions as a mean-field potential for a single electron, which is a function of the charge density. The fourth term expresses the non-local part of the pseudopotentials, and the fifth and the last terms are electron-ion and ion-ion interactions. Equation (2) gives the enthalpy of the material of the subject in a given atomic position and the volume of

*See NNI's home page as http://www.nano.gov/html/facts/whatIsNano.html

the unit cell. By computing the enthalpies under different atomic positions and the volumes, one can obtain the potential energy surface for chemical reactions, phase diagrams, activation barriers for atomic diffusions, etc.

The above technique is based on the adiabatic approximation where electrons are assumed to immediately follow the motions of ions. However, this approximation becomes invalid when they are subjected to molecular dynamics under electronic excitation. Photo-chemical reactions are examples of this situation, in which we can apply the time-dependent density functional theory (TDDFT)[2] with the time-dependent Kohn-Sham equation below.

$$i\hbar\frac{d\psi_n(\vec{r},t)}{dt} = H_{KS}(\vec{r},t)\psi_n(\vec{r},t) \quad \cdots\cdots (3)$$

Solution of this equation is obtained by integrating equation (3) through the time-axis within the self-consistent relation between time-dependent Hamiltonian and the time-dependent wave functions. NEC has developed the computer code FPSEID (éf-psái-dí:)[3], which stands for First-Principles Simulation tool for Electron Ion Dynamics and efficiently treats equation (3) by using the Suzuki-Trotter split operator method[4]. By combining the equation (3) with the classical Newton's equations of ionic motion, we can perform reasonably approximated molecular dynamics under electronic excitation.

3. Application to Material Researches

NEC researches materials for key devices of high-performance energy storage/products and electronics/optics. In this paper, two topics of applications by the nano-scale simulations are introduced. The first is an effort toward designing catalysis for accelerating electro-chemical reactions inside the fuel cells. The other one is a study of an intrinsic property of carbon nanotubes which are potential non-linear optical devices. Both results were produced by using the Earth Simulator with the support of the JAMSTEC/Earth Simulator Center*.

3.1 Exploration of Catalysis for Future Fuel Cells

For efficient and environmentally friendly energy sources, a search of advanced catalysts for the electro-chemical reaction is highly demanded with a smart selection of elements and/or smart designing of clusters.

*See, http://www.es.jamstec.go.jp/esc/eng/index.html

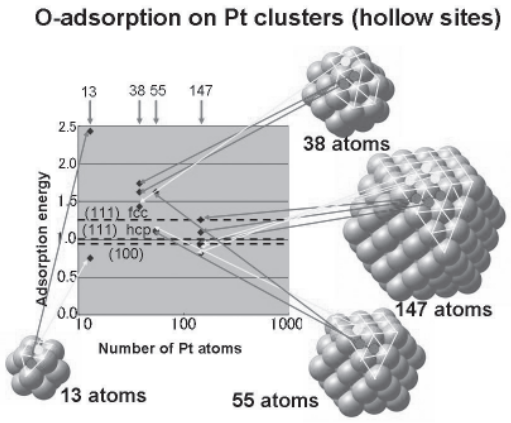

Fig. 1 Size and position dependence of O atom adsorption energy on Pt clusters obtained by DFT calculations. Note that the lateral axis is in a logarithmic scale. Dotted lines are those on several surfaces of the bulk Pt.

Clusters of catalytic metal increase their ratio of chemically active atoms on their surfaces to those in the bulk, as their sizes decrease. Minimizing Pt clusters is a leading guideline for the development of catalysts for fuel cells. Thus, first principles calculations based on DFT are important because the results could provide information for finding the minimum size at which Pt clusters can be used as a catalyst. **Fig. 1** shows how oxygen adsorption energies on hollow sites of Pt clusters depend on their size. (All calculations were performed by using a DFT code 'STATE' [5].) When the cluster size reaches 147 atoms, the adsorption energies on several facets of the cluster are almost equal to those on the corresponding (100) and (111) surfaces of bulk Pt.

In addition to the size effect, this calculation also shows a significant enhancement of the reactivity of the edge atoms of the clusters. Such a trend seen in oxygen adsorption is also seen in the case of hydrogen adsorption on these clusters[6].

This theoretical result provides an important guideline for designing future catalysis even without Pt atoms considering the optimum shapes of clusters toward higher ratio of edge-atoms to others.

3.2 Hot Carrier Dynamics in Carbon Nanotubes

Carbon nanotubes can be used as optical limiting devices applied to the mode-rocked laser[7]. The lifetime of the optically-excited carriers determines the on-to-off switching frequencies. If the lifetime is too long, the recovery from 'on' state to 'off' state is too slow, while if the lifetime is too short, the quantum efficiency of optical excitation is too low. Therefore,

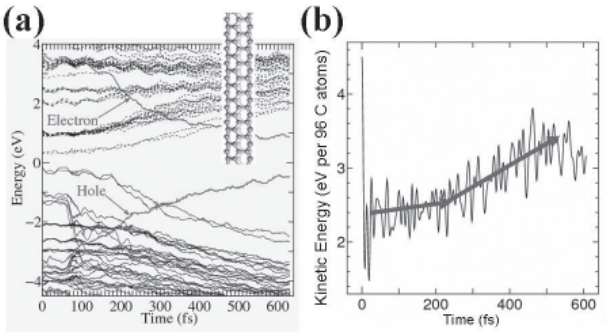

Fig. 2 Time-evolution of (a) one-electron energy levels of excited electron-hole pair, and (b) the corresponding time-evolution of the kinetic energies of 96 carbon atoms in the unit cell used in the present simulation of a (3,3) nanotube. Arrows are guides to eyes. The inset in (a) is a structure of the (3,3) nanotube.

the design of proper lifetime is important as well as the clarification of decay dynamics of excited carriers in order to improve the performance of optical limiting devices.

Fig. 2(a) shows simulated decay dynamics of an optically excited pair of electrons and holes in a (3,3) nanotube. (The calculation was performed by the code FPSEID[3] using the TDDFT and MD simulation.) This result shows rapid decrease of the electron-hole energy gap within 600fs.

The time-evolution of kinetic energy of a nanotube lattice is shown in **Fig. 2(b)**. At the beginning of the simulation, there is a significant fluctuation due to thermal instability in the simulation. But later than 30fs, the simulation shows a clear turning point at 230fs, after which the increase of kinetic energy is accelerated. This behavior means that the excitation energy is distributed to unexcited electrons before the turning point and that the excitation energy is converted into kinetic energy of each carbon atom after the turning point.

This interpretation is confirmed by repeating the simulations with different initial temperatures of the lattice. The lower beginning temperature of the lattice causes the delay of the turning point, but once the kinetic energies of the carbon atoms start to increase, the rates of the energy transfer into the lattice are higher at lower temperatures[8]. These results are consistent with the thermo-dynamic interpretation of 'heat-flow.'

4. High Performance Computing (HPC) Technology for Large Scaled Simulations

As we have shown in this paper, nano-scale simulations are a powerful tool for accelerating the R&D cycles of materials research needed for advances in nano-technology. In order to

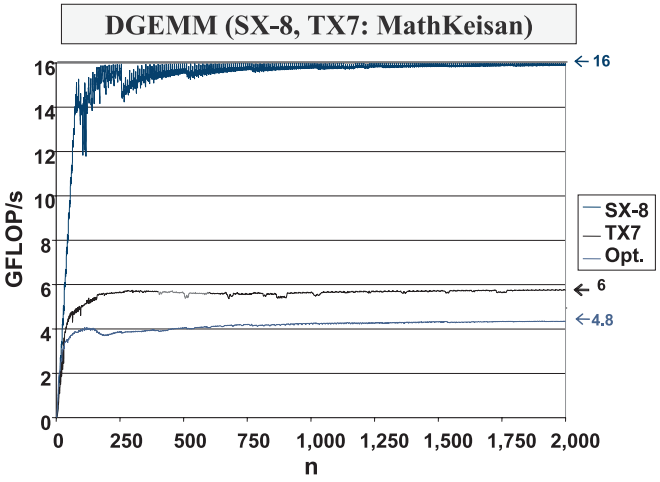

Fig.3 Comparison of performance for running DGEMM matrix operation code (part of NEC's MathKeisan numerical library) for different architectures (NEC SX-8; vector machine, TX7 and Opt; scalar machines). Lateral axis *n* means the size of the matrix treated in running the code.

approach realities with complex situations, the model assumed in simulation must have a sufficiently large size. The number of electrons N and the number of grids in real- and reciprocal-spaces M_{mesh} to express wave functions respectively increase linearly in proportion to volume. Thus the required number of floating point operations and the memory capacity, which are in proportion to the product of N and M_{mesh}, rapidly grow in sharp contrast to those needed for simulating the continuum or fluid behaviors, in which the size of simulations are namely determined only by M_{mesh}.

For large-scale simulations, a sufficiently high computing capability is required even with the use of large core-memories. The NEC's High Performance Computing (HPC) technology based on vector processors is tailored to this requirement, thus providing unparallel performance regardless of the sizes of the numerical simulations. **Fig. 3** shows the performance of the NEC's vector parallel computer (SX-8) in comparison to other scalar systems in running the DGEMM matrix operation code as part of the NEC's proprietary numerical library Math Keisan, which computes the products of large-sized matrices. Such a type of calculation is one of the most frequent operations in solving the equations of DFT. One can immediately note that a highly sustained performance can be maintained on the NEC SX-8 for a wide range of matrix sizes, while scalar machines show performance saturation with increased matrix dimensions particularly for the larger matrix sizes.

NEC continues to provide parallel computing systems based on vector architecture in order to achieve a highly sustained

performance for large-scale simulations, which will make nano-scale simulations feasible for complicated realities.

5. Future Aspects of Nano-Scale Simulations

Nano-scale simulations will be performed at larger scales to cope with the complicated processes of real devices. For example, the electrochemical reactions at a liquid/electrode interface under an applied electric field are subjects of basic research aimed at realizing efficient power supply by fuel cells. On the other hand, electro-optical devices based on nano-carbons must be designed with a precise knowledge of the electronic properties of such nano-carbons when contacted with other electrodes under electric fields for device operation. Thus the necessary computing capability will inevitably be increased with the growing demand for sophisticated modeling, which requires a higher computation performance, as well as an efficient way to bridge both microscopic and macroscopic phenomena. NEC will continue to develop nano-scale simulation technology as a fundamental component of nano-technology.

6. Concluding Remarks

This paper has introduced the fundamentals of nano-scale simulation, together with NEC's recent developments in simulation techniques. Applications are presented for catalyses useful for fuel cells and for carbon nanotubes as possible optical limiting devices. NEC is committed to developing nano-scale simulation technologies in order to efficiently meet increasingly complicated demands by fully capitalizing on HPC technologies.

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