Can *ab initio* simulation really predict properties of materials prior to actually carrying out the experiments?

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Abstract. In the present paper, all-electron full-potential *ab initio* simulation method with mixed-basis is introduced and several typical examples are indicated which successfully show the possibility of predicting properties of materials prior to actually carrying out the experiments. We have used the *ab initio* calculation to extract energy parameters, and apply them to cluster variation and direct methods, which bridge the limited space of *ab initio* treatment to real complex materials. To overcome the limited computer power, we have also developed parallel processing codes and tested their efficiencies.

Keywords. Materials design; *ab initio*; cluster variation method; direct method; parallel processing.

1. Introduction

In recent years, materials design based only on experiments have come up against a stone wall. Since according to industrial requirement for materials having increasingly higher physical and chemical properties, materials to be developed have become complex and/or need to be atomistically controlled. There the number of combination of elements explodes and necessary time and expenditure for experimental studies become tremendous. Therefore, there is a necessity to introduce a fundamentally new method of computer simulation to predict materials structures and properties on computer prior to actually carrying out the experiments.

By using the largest supercomputing system available, it is possible to calculate band structure in a system that contains several hundreds of atoms in a unit cell. This size is good enough to discuss industrially useful materials and it is possible to ascertain physical properties of materials in detail. To relax the system completely with the first-principles local density approximation (LDA) calculations, the present day supercomputer power is not enough. It is limited up to 10 atoms in a unit cell. Normally we assume some symmetries and try to relax around these symmetries. The first-principles molecular dynamics is also limited up to several picosec in time duration. Although some chemical reactions do occur within this time and it is possible to simulate dynamic behaviour of these reactions, most of the chemical and physical processes take far more time and it is not possible to trace these processes.

In this paper, the following have been discussed. (i) all-electron full-potential *ab initio* simulation method, with mixed-basis introduced to show the possibility of prediction of properties of materials using the present day state-of-art theoretical method, (ii) since by using

only the first-principles calculations, the size and the time duration to be treated are limited, cluster variation method (CVM) and direct method which enable handling of more realistic systems have been indicated and (iii) to overcome the present limitations of simulation based on used approximations, three 'beyond the present theories' concepts have been discussed.

2. All-electron full-potential *ab initio* simulation method with mixed-basis

In this section the computational scheme in an all-electron full-potential mixed-basis approach is described briefly. The mixed-basis approach was originally introduced in the *ab initio* calculation of transition metal elements by Louie *et al* (1979) in order to treat efficiently the spatial locality and asymmetry of 3d orbitals with limited number of basis functions. It is a technique to expand the wave functions in terms of both plane waves (PW) and atomic orbitals (AO). They applied the mixed-basis approach in the pseudopotential formalism. The pseudopotential scheme allows one to replace a strong electron-ion Coulomb potential with a soft potential, which is smooth inside a sphere of core region.

However, it has often been pointed out that the description of wave functions only with PWs is not easy particularly for 2p orbitals in the second-row elements and 3d orbitals in the transition metal elements, even if an efficient pseudopotential is used. But, in our all-electron mixed-basis approach, both PWs and AOs are used to expand the true wave functions, including the core.

The all-electron mixed-basis approach for band structure calculations has been successfully applied to similar experimental results of aligned C₆₀ on Cu (111) (see figure 1) (Maruyama *et al* 1995) and to fcc and sc C₆₀

(see figure 2) (Gu *et al* 1994a, b; Ohno *et al* 1996a). It has been applied also to dynamics (see figure 3) (Ohno *et al* 1996b, c; Ohtsuki *et al* 1998). In the mixed-basis formalism, the basis is composed of both plane waves (PW) and atomic orbitals (AO). Because AOs are not orthogonal to the PWs, it is necessary to orthogonalize the basis at each iteration step. Once the orthogonalization process is adopted, the main algorithm for updating the wave function becomes formally the same as that of the original PW approach. The exchange-correlation potential is evaluated in real space under the local density approximation. In the present formalism, the charge density and the self-consistent potential are evaluated either in real space (for AO-related part) in terms of a spherical coordinate centred at every atom or in Fourier space (for PW-related part). We use the fast Fourier transformation several times in each iteration.

Once the potential is determined, the Hamiltonian matrix elements have to be evaluated. In the potential matrix elements, there are three types of combinations: PW–PW, PW–AO, and AO–AO. As in the PW approach, herein as well it is not necessary to register the PW–PW matrix elements in computer memory, because the PW–PW block does not change after the diagonal transformation. The other combinations PW–AO and AO–AO are conveniently calculated in the real space inside each atomic sphere. Atomic spheres are chosen so as not to

overlap each other, i.e. nonoverlapping sphere is assumed for the present calculation.

3. More than the standard *ab initio* calculation

For performing the *ab initio* calculation by supercomputer, for the above samples it takes 50 h of CPU time with 1 GB of main memory. This size is the limitation in standard conditions of supercomputer time sharing. To study more complex systems with larger number of atoms with quantum theory, there are several attempts such as tight-binding modelling. These model the potential and normal function nicely around the region where the potential is determined. In this chapter however more sophisticated methods, by using the results of *ab initio* calculation, to apply to more complex systems are introduced.

3.1 Cluster variation method

The standard *ab initio* LDA calculation gives us information on the ground state total energy and stable structure of the materials with physicochemical properties. It is necessary to study thermodynamic properties to reveal dynamic behaviours of materials at finite tempe-

Figure 1. Upper three figures show STM images of C₆₀ self-organized on Cu (111) surface around the gap. (a), (b) and (c) indicate different bias voltages corresponding to different excitations. Lower three figures are the results of the mixed-basis *ab initio* calculation, which can explain the reason of the observed patterns in the above figures (symmetries of charge distribution is determined by the electronic state).

rature. To this aim, cluster variation method (CVM) has been used to determine the phase diagram by estimating the free energy by using the energy parameters for clusters in complex systems.

CVM can also be applied to determine site preference of ternary additions in alloys. We have studied the site preferences of transition metals in Ni_3Al and other important alloy systems (Sluiter and Kawazoe 1995).

Figure 2. Isosurface of partial charge density (PCD) distribution. (a) represents PCD composed of the highest 12 occupied molecular orbital (HOMO, h_u) bands, while (b) PCD of the lowest 12 unoccupied molecular orbital (LUMO, l_u) bands.

Another application of CVM is to study the dynamic behaviour of the interface. The Al–Al₃Li system has been studied as an example (Sluiter *et al* 1996). We have used a supercell that consists of 38 fcc cubes in the calculation including (100) interface boundary (IPB). A part of the obtained results is shown in figure 4. It clearly shows that at the IPB the Li concentration varies from one phase to another. At 400 K the thickness of this variation is about 4 lattice constants and it is a linear function of temperature.

Figure 3. Snapshots of the Li insertion process to C₆₀. At the initial kinetic energy of 5–20 eV, Li atom can penetrate into C₆₀ through hexagon of carbon atoms on the C₆₀ surface and get trapped closed to the cage. This atom inclusion fullerene is expected to be a stable high-*T_c* material.

Figure 4. Li concentration averaged over (100) planes parallel to the IPB as a function of distance (in units of the lattice constant) at 400 K. The solid and dotted lines are drawn for the eye.

3.2 Direct method

There is a direct method, to treat problems in materials science based on the *ab initio* calculations (Parlinski *et al* 1997). This has been recently invented to study phonon dispersions and phase transitions in crystalline solids.

The calculation of phonon frequencies of the crystal is one of the fundamental subjects to study phase stability, phase transition, and thermodynamics. Another *ab initio* calculation, linear response method, has difficulty in determining phonon dispersions, since the dielectric matrix must be calculated in terms of electronic eigenfunctions of perfect crystal (King-Smith and Needs 1990).

In the direct method (Parlinski *et al* 1997), the dynamical matrix is constructed using cumulant force constants determined numerically by Hellman-Feynman force and it is solved to obtain phonon dispersions.

We have successfully applied the direct method to study the structural phase transition in cubic ZrO₂. The force constants are determined from the Hellman-Feynman forces induced by displacement of atoms in a 2 × 2 × 2 fcc supercell. The calculated phonon dispersions in figure 5 show clearly a soft mode at X point, which corresponds to the experimentally confirmed cubic to tetragonal structural phase transition.

4. Beyond the present approximations

Most of the text books on solid state physics start with the statement that the adiabatic Born–Oppenheimer (BO) approximation is good enough, since nucleus is almost 2,000 times heavier than electron. However, it is not so

Figure 5. Calculated phonon dispersions of ZrO₂ in the cubic structure. At the X point it clearly indicates the existence of soft mode, which corresponds to a structural phase transition observed experimentally for this material.

simple in some cases. For example, to simulate chemical reactions, we should consider that the reactions depend strongly on temperature and many branches occur with variety of branching ratios. This means that the reaction is not happening only on the BO surface (beyond BO). The above-mentioned insertion process of Li into C_{60} is also the case, since Li passes the C_{60} very rapidly. Recently, supercritical water (water under high pressure and at high temperature) has attracted strong attention, since it is very reactive to be able to resolve even polyethylene terephthalate (PET) bottles. This is very important for recycling of materials. This special phase of water has been studied extensively experimentally as well as theoretically. The understanding of the supercritical water is not yet completed. Especially, theoretical treatment has been limited only within classical molecular dynamics. To study the fundamental behaviour of this extraordinarily reactive water, 'beyond BO' theory is important, since under such conditions, protons vibrate very strongly and electron clouds are separated from the nucleus.

To overcome the present level of BO approximation, we have tested three Fermion systems H^- and H_2^+ almost analytically and have obtained that the quantization of kinetic energies of proton is essential to discuss these quantum systems (Farajian *et al.*, to be published).

Since present day standard local density approximation (LDA) and/or generalized gradient approximation (GGA) is known to be accurate only for the ground states without degeneracy, we should consider including excited states as well to obtain really meaningful simulation results that could be compared with most of the other experiments, such as the band gap in semiconductor. To this aim we are considering to include GW approximation (Green function-vertex method, or quasi particle treatment) into our first principles band calculation and molecular dynamics code.

The last 'go beyond' story is to solve the time-dependent Schrödinger equation as it is. This approach can be named beyond Car-Parrinello (CP), since it does not use any fictitious mass in the formulation. We have tested this approach for the Li inclusion procedure into C_{60} , since for this case variational force is calculated as a derivative of time.

5. Conclusions

An LDA code with all-electron full-potential mixed-basis formulation is introduced and typical examples of the results, by using the program, indicate that it is really one of the best existing *ab initio* codes within LDA and GGA and that it can treat molecular dynamics far better than full potential augmented plane wave (FLAPW) method. Despite using *ab initio* calculation, it still has

limitations to treat real materials having interesting properties, since only up to several hundreds of atoms in a unit cell can be handled even by the largest computer systems. Cluster variation method and direct method help to fill in this gap. We have applied these methods to simulate dynamical behaviours of complex materials.

It is true that the first-principles calculation has no phenomenological parameters, but it has a lot of approximations such as LDA. We are trying to overcome this drawback by expanding the standard approximation by 'beyond BO', 'beyond LDA', and 'beyond CP'. These new levels of theories are expected to function to simulate more realistically the physical and chemical behaviours of materials.

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