Development of First-Principles Simulation of Material Structure and Electronic Properties

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Abstract

I discuss the grand challenges in first-principles material simulation and briefly review two of our trials to solve them. The first one is the development of the transcorrelated method, a correlated wave function theory applicabl to condensed matter. The second one is a general scheme for calculating lattice thermal conductivity.

1 Introduction

First-principles electronic structure calculation based on the density functional theory (DFT) is widely used not only in the analysis of material structure and its electronic state but also for theoretical prediction of material properties. As the scope of its application expands, however, we find there are many problems still remaining.

Firstly, accuracy and reliability of total energy and energy spectrum obtained by the present DFT are sometimes insufficient for the research of strongly correlated electronic systems, spin states or magnetic orders, optical properties, structure of molecular crystals and so on. Although there have been reported various succesful attemps such as combination of DFT, downfolding techniques and accurate simulation of simplified model Hamiltonian for low-energy electrons, first-principles method, which is general in the sense of DFT, is still missing.

Secondly, calculable system size is quite limited despite advances in massively parallel supercomputers. This is because the computational cost of DFT essentially scales as order N^3 with N being the number of atoms. So-called order-N methods have been developed for large-scale structural simulations, but calculation of the energy spectrum needs additional process with high calculation load.

Thridly, researh on non-equilibrium dynamics often needs large-scale and long-time dynamical simulation, or otherwise requires some ingenuity. Chemical reaction, thermal transport and structure formation like crystal growth are such examples.

Finally, prediction of material structure is a very important challenge considering increasing importance of computer simulations in new material development. Recent activities on materials informatics have further increase its importance.

For years, we have developed various methods with collaborators to tackle the problems mentioned above. In this article, I briefly review two important methods among them. The developments were mainly done by Masayuki Ochi (Section 2) and Terumasa Tadano (Section 3).

2 Wave-function theory for condensed matter

Wave function theory (WFT) is not often applied to first-principles calculation of condensed matter, since the Hartree-Fock (HF) method, virtually the only available method except for quantum Monte Carlo methods, fails to describe finite density of states at the Fermi level of metals and seriously overestimates the band gap of semiconductors. WFT-based approaches are, however, systematically improvable and this is a great advantage against the density functional theory (DFT). Therefore some groups have been revisiting WFT to go beyond the present DFT calculation.

The transcorrelated (TC) method first developed by S.F. Boys and N.C. Handy [1, 2] is a unique approach to correlated electrons with Slater-Jastrow-type many-body wavefunctions. In TC, by using similarity transformation of the Hamiltonian with the Jastrow factor, HF-like self-consistent-field (SCF) equations called TC-SCF equations are derived for one-electron wave functions in the Slater determinant together with their orbital energies, which are very helpful for intuitive understanding of the electronic state of matter. Thus we have so far developed the TC method for periodic systems [3, 4, 5, 6, 7, 8, 9, 10, 11].

In the TC method, a many-body wavefunction of the system Ψ is formally factorized as $\Psi = F\Phi$. $F = \exp(-\sum_{i,j(\neq 1)} u(x_i, x_j))$ is a Jatrow factor representing two-body electron correlation and Φ is defined as $\Phi = \Psi/F$. The eigenstate equation for the total Hamiltonian $\mathcal{H}$, $\mathcal{H}\Psi = E\Psi$ leads $\mathcal{H}_{\mathrm{TC}}\Phi = E\Phi$ with $\mathcal{H}_{TC} \equiv F^{-1}\mathcal{H}F$. Note that this is just a similarity transformation and mathematically exact. The Jastrow factor has been widely used in the variational Monte Carlo method for correlated electrons with variations of the Jastrow function $u(x, x')$. In our study we usually adopt a simple form:

$$u(x, x') = \frac{A}{|\mathbf{r} - \mathbf{r}'|}\left\{1 - \exp\left(-\frac{|\mathbf{r} - \mathbf{r}'|}{C_{\sigma,\sigma'}}\right)\right\}, \quad (1)$$

$$A = \sqrt{\frac{V}{4\pi N}} \times \sqrt{1 - \frac{1}{\varepsilon}}, \quad (2)$$

$$C_{\sigma,\sigma'} = \sqrt{2A}(\sigma = \sigma'), \sqrt{A}(\sigma \neq \sigma'), \quad (3)$$

where V and N are the volume of the cell and the number of electrons, respectively, and ε is the static dielectric constant. Improvement of u is discussed in Ref.[7]. The transcorrelated Hamiltonian $\mathcal{H}_{\mathrm{TC}}$ is a non-Hermitian and contains effective two-body and three-body interactions.

Then we use the HF approximation and adopt a single Slater determinant of one-electron wavefunction $\phi_i(\mathbf{r})$ $(i = 1 - N)$ for the manybody function Φ. The TC-SCF equation for $\phi_i(\mathbf{r})$ is similar to the HF-SCF equation, with which $\phi_i(\mathbf{r})$ in the Slater determinant can be optimized for the Jastrow function F:

$$\begin{aligned}
&\left(-\frac{1}{2}\nabla_1^2 + v_{\mathrm{ext}}(x_1)\right)\phi_i(x_1) \\
&+\sum_{j=1}^{N}\int dx_2 \phi_j^*(x_2) v_{\mathrm{2body}}(x_1, x_2) \\
&\qquad \times det[\phi_i(x_1), \phi_j(x_2)] \\
&-\frac{1}{2}\sum_{j=1}^{N}\sum_{k=1}^{N}\int dx_2 dx_3 \phi_j^*(x_2)\phi_k^*(x_3) \\
&\qquad \times v_{\mathrm{3body}}(x_1, x_2, x_3) \\
&\times det[\phi_i(x_1), \phi_j(x_2)\, \phi_k(x_3)] = \sum_{j=1}^{N}\epsilon_{ij}\phi_j(x_1). \quad (4)
\end{aligned}$$

Here $v_{\mathrm{ext}}(x_1)$ is the external potenial from nuclei or pseudopotentials. v_{2body} and v_{3body} are effective two-body and three-body potentials derived from the Jastrow function u:

$$\begin{aligned}
&v_{\mathrm{2body}}(x_1, x_2) = \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \\
&+\frac{1}{2}\sum_{i=1}^{2}[\nabla_i^2 u(x_1, x_2) - (\nabla_i u(x_1, x_2))^2 \\
&\qquad +2\nabla_i u(x_1, x_2) \cdot \nabla_i], \quad (5) \\
&v_{\mathrm{3body}}(x_1, x_2, x_3) \\
&= \nabla_1 u(x_1, x_2) \cdot \nabla_1 u(x_1, x_3)
\end{aligned}$$

$$+\nabla_2 u(x_2,x_1)\cdot\nabla_2 u(x_2,x_3)$$
$$+\nabla_3 u(x_3,x_1)\cdot\nabla_3 u(x_3,x_2). \qquad (6)$$

The orbital energy matrix ϵ_{ij} can be made triangular (by orbital orthogonalization) or diagonal (by biorthogonal formulation), when Koopmans' theorem holds for the diagonal elements. Since $\mathcal{H}_{\rm TC}$ preserves the crystal symmetry of the original Hamiltonian $\mathcal{H}$, we can obtain band structure of the crystal with taking account of the electron correlation through F.

To solve the TC-SCF equation and to calculate the total energy, we need to evaluate three-body integrals for $v_{\rm 3body}$. Since each term of $v_{\rm 3body}$ is a product of two-body functions, computational cost for the three-body integrals can be reduced to the order of two-body integrals in the HF method [6]. Thanks to this algorithm, computational cost of the TC method has come to be within the reach of supercomputers or PC clusters.

So far we have shown that the TC method is actually a good and alternative approach to condensed matter: it is applicable to metals in principle [3], much improves the HF band structure of semiconductors [4, 6, 7], and is compatible with post-HF methods such as the configuration interaction method for calculating photo-excitation spectrum including the excitonic effect [5, 8] and also Møller-Plesset perturbation theory [9]).

Very recently, we have developed a new iterative scheme to solve the TC-SCF equations to further reduce the comutational cost and memory [10], which enabled us to apply the TC method with biorthogonal formalism to a transition metal oxide ZnO for the first time. Calculated band gap, valence band width and position of the narrow 3d band were in better agreement with experimental data than several other conventional methods including the G_0W_0 method (see Table 1) [11].

3 Anharmonic phonons and lattice thermal conductivity

Lattice thermal conductivity is a key parameter in the figure of merit for thermoelectric materials. It is also important from the viewpoint of device technology, since thermal management is necessary to avoid thermal breakdown of nano-scale devices. Therefore, it is highly desirable for material and device development to calculate it from first principles.

Lattice thermal conductivity can be evaluated by molecular dynamic simulation (MD) with Kubo formula, non-equilibrium MD with Fourier's law, or by Boltzman transport equation (BTE) usually with the single-mode relaxation-time approximation (RTA). MD needs large simulation cell comparable with phonon-scattering length and long-time simulation corresponding to the relaxation time of phonons. Since the phonon-scattering length and the relaxation time can reach 10^{-9}s and 10^{-6}m, respectively, in some cases, it is difficult to use first-principles MD except for materials with low thermal conducltivity or at high temperature [21]. It should also be noted that we cannot easily check and assure the appropriateness of the calculation condition of MD.

On the other hand, by BTE with the single-mode RTA, the lattice thermal conductivity can be accurately estimated by the following formula:

$$\kappa_L^{\mu,\nu}(T)=\frac{1}{\Omega N}\sum_{\mathbf{q},\mu}c_{\mathbf{q}}(T)v_{\mathbf{q}}^{\mu}v_{\mathbf{q}}^{\nu}\tau_{\mathbf{q}}(T). \qquad (7)$$

Here, Ω is the volume of the unit cell, $c_{\mathbf{q}}$, $v_{\mathbf{q}}$ and $\tau_{\mathbf{q}}$ are the constant-volume specific heat, the group velocity, and the relaxation time of phonons with wave vector $\mathbf{q}$, respectively. N is the mumber of q points. The relaxation time $\tau_{\mathbf{q}}=[2\Gamma_{\mathbf{q}}(\omega_{\mathbf{q}})]^{-1}$ can be calculated by

$$\begin{aligned}\Gamma_{\mathbf{q}}(\omega)=\frac{\pi}{2N}\sum_{\mathbf{q}',\mathbf{q}''}\frac{\hbar|\Phi(-\mathbf{q},\mathbf{q}',\mathbf{q}'')|^2}{8\omega_{\mathbf{q}}\omega_{\mathbf{q}'}\omega_{\mathbf{q}''}}\\ \times[(n_{\mathbf{q}'}+n_{\mathbf{q}''}+1)\delta(\omega-\omega_{\mathbf{q}'}-\omega_{\mathbf{q}'})\\ -2(n_{\mathbf{q}'}-n_{\mathbf{q}''})\delta(\omega-\omega_{\mathbf{q}'}+\omega_{\mathbf{q}'})],\end{aligned} \qquad (8)$$

Table 1: Characteristic values in the band structure of ZnO obtained by various first-principles methods and experiments. All values are in eV. (Ref.[11])

	Band gap	O2p bottom	Zn3d average/bottom
LDA	0.7	$\cdots$	$\cdots/-5.8$
HSE03[a]	2.1	-4.9	$\cdots/-6.5$
G_0W_0 (LDA)[b]	2.4	-5.2	$\cdots/-6.5$
G_0W_0 (HSE03)	3.2[a], 3.46[c]	$\cdots$	-6.21[c]$/-7.2$[a]
AFQMC[d]	3.26(16)	$\cdots$	$\cdots$
VMC[e]	3.8(2)	$\cdots$	$\cdots$
HF	11.4	-5.7	$-9.1/-9.9$
Biorthogonal TC	3.1	-5.1	$-9.3/-9.7$
Expt.	3.4[f]	-5.3[f], -5.2[g]	-7.5[c,h], -8.6[i], -8.81[g]/–

[a]Ref.[12], [b]Ref.[13], [c]Ref.[14], [d]Ref.[15], [e]Ref.[16], [f]Ref.[17], [g]Ref.[18], [h]Ref.[19], [i]Ref.[20].

where the three-phonon scattering matrix element $\Phi(-\mathbf{q},\mathbf{q}',\mathbf{q}'')$ is calculated from third-order force constants in the potential energy function of atoms. As the third-order force constants are considered to be short-range, they can be calculated with a periodic cell containing relatively small number of atoms. Although we need to use many $\mathbf{q}$-points in eq.(8), we can easily check the convergence of calculation in the BTE-RTA approach. Another advantage of the BTE-RTA approach is that, once we know $\Phi(-\mathbf{q},\mathbf{q}',\mathbf{q}'')$, temperature dependence of the thermal conductivity is easily obtained from the same $\Phi(-\mathbf{q},\mathbf{q}',\mathbf{q}'')$. Furthermore mode-dependent analysis of the phonon relaxation can be easily done by eq.(8). These are the reason we often use the BTE-RTA approach instead of MD.

To get anharmonic force constants we developed a general and efficient method based on a first-principles molecular dynamics simulation: the simulation cell typically contains a few tens of atoms and the simulation time is of the order of 10^{-12}s. The third-order force constants derived from the simulation were then used for calculation of the lattice thermal conductivity of various materials (see Fig. 1)[22, 23, 24]. It should be noted that a wide range of lattice thermal conductivity including the temperature dependence is accurately calculated with the present scheme.

The calculation of $SrTiO_3$ shown in Fig. 1 is a special case to be mentioned. $SrTiO_3$ exhibits phase transformation at 105 K and has cubic symmetry above the transition temperature. Frequencies of some phonon modes are calculad to be imaginary with the cubic structure, showing that the cubic phase is not stable statically and has highly anharmonic potential energy surface. In this case we cannot use eqs.(7)-(8) as they are. Thus we introduced the self-consistent-phonon (SCPH) approach to calculate phonon frequencies realized by thermal fluctuation. With the method, we succeeded in quantitative calculation of temperature-dependent *real* phonon frequencies as observed in experiments, and with these frequencies, we obtained the lattice thermal conductivity of $SrTiO_3$ in Fig. 1, which agreed well with experiments [24, 25].

The simulation software named ALAMODE developed by T. Tadano is published as an open source software [26].

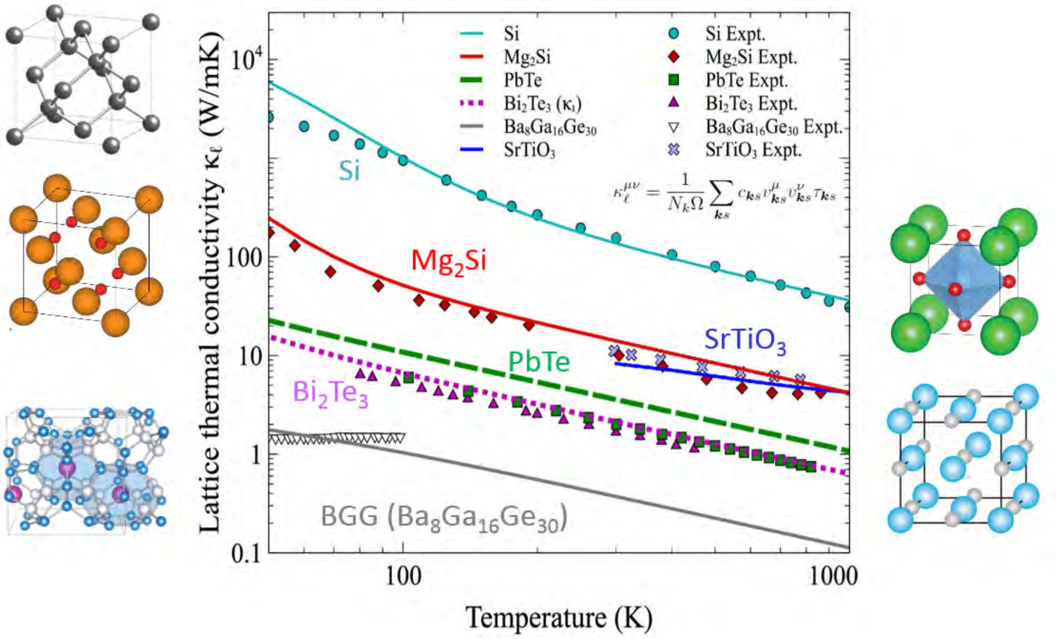

Figure 1: Temperature dependence of the lattice thermal conductivity of various materials obtained by simulation withom BTE-RTA (lines) and by experiments (symbols). (See Refs.[22,23,24] and references therein.)

4 Summary

Supported by rapidly advancing computers, first-principles material simulation is nowadays an indispensable tool for material science. As the simulation extends its application, however, we have come to face with its limitations and challenges. After summarizing the challenges in four direction in the introduction, I reviewed two of our trials to solve some of the challenges. Firstly I reviewed the idea and recent development of the transcorrelated method. It is the wave function theory for correlated electronic systems, which enables us to calculte not only the total energy but also the electronic energy spectrum accurately. Secondly I reviewed the method to calculate lattice thermal conductivity. It is general, accurate and applicable to even a high-symmetry crystal realized by thermal fluctuation at high tempetature. Itroduction of the SCPH approach further expands the scope of its application.

Acknowledgement

The development and calculation reviewed in this article are partly done using the facilities of the Supercomputer Center, Institute for Solid State Physics, The University of Tokyo.

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