論文の内容の要旨

論文題目　Derivation of Static Low-Energy Effective Models by *ab initio* Downfolding Method, and Its Improvement
（第一原理ダウンフォールディング法による低エネルギー有効模型の導出とその改良）

平山　元昭

The quantum state calculation for the real material from microscopic basis has been a central subject of theoretical condensed-matter physics for a long time. In particular, the density functional theory (DFT) [1] has been playing a major role as the tool for the calculation and prediction of the microscopic nature of the real material. In the realistic calculation, the local density approximation (LDA) [2] and generalized gradient approximation (GGA) offer reliable results in spite of the simplified correlation effect, and hence, is used in the wide range of the microscopic science from solid-state physics to biological chemistry.

However, the approximation of the correlation effect in the LDA and the GGA becomes inappropriate in the strongly correlated systems, such as transition metal compounds, rare earth compounds, and molecular organic conductors. Moreover, because the DFT/LDA is essentially the theory for the ground-state, there is no clear theoretical justification of describing the excited states.

To overcome the weakness such as the evaluation of the correlation effect in the first principle calculation, a hybrid method of multiscale *ab initio* scheme for correlated electrons (MACE) has been under intensive investigation in recent years [3]. In the general framework of MACE, the global band structure is obtained by *e.g.* the DFT, and next, the bands far away from the Fermi level are renormalized into the bands near the Fermi level by the constrained random phase approximation (cRPA) [4]. Derived *ab initio* low-energy models are solved by high-accuracy solvers, such as variational Monte Carlo (VMC)[5], path-integral renormalization group (PIRG), and dynamical mean field theory (DMFT). This hybrid scheme has been applied to a wide variety of materials; semiconductors, transition metals, transition metal-oxides, molecular organic conductors, and iron-based layered superconductors [5,6].

Quantitative accuracies of obtained physical quantities in comparison to experimental results support the validity of the framework of MACE. However, as I will discuss below, some serious problems, which make qualitative difference to the result, still exist in this framework.

In this thesis, I propose new basis for *ab initio* downfolding method, and also enable to calculate the systems, which is difficult to deal only with the DFT/LDA, in the first principle framework. In particular, I propose the way to eliminate the major problems inherent in the conventional downfolding method, and establish the downfolding method as the high accuracy calculation. Moreover, I extend the applicable

materials to the *ab initio* downfolding method, and make it possible to calculate the low-energy effective model for a variety of systems. According to these purposes, I study some themes about MACE.

First, I develop MACE for transition-metal-oxide heterostructure and interface, and determine the parameters of the low-energy effective model. By separating Ti t_{2g} bands near the Fermi level from the global Kohn–Sham (KS) bands of $LaAlO_3$ (LAO)/$SrTiO_3$ (STO), which are highly entangled with each other, I am able to calculate the parameters of the low-energy effective model of the interface with the help of cRPA. In the heterostructure of LAO/STO, the on-site energies of the Ti t_{2g} orbitals in the 1st layer is about 650 meV lower than those in the second layer, which makes the localization of the electron to the interface. In the 1st layer, the transfer integral of the Ti t_{2g} orbital is nearly the same as that of bulk STO, while the effective screened Coulomb interaction becomes about 10% larger than that of bulk STO. The differences in the parameters from bulk STO decrease rapidly with increasing distance from the interface. Next, I calculate the band structure of the interface of LAO/STO, where LAO layer is deposited on STO, with the lattice relaxation. The instability of the electric potential from polar LAO layer $(LaO)^{+1}$-$(AlO_2)^{-1}$ is absorbed by the lattice relaxation, the carrier doping to the interface is suppressed compared to the case without the lattice relaxation. In spite of the atomic displacement, the parameter at the interface is nearly the same as that of the heterostructure. My present versatile method enables us to derive effective *ab initio* low-energy models from the semi-infinite systems such as the transition-metal-oxide interface, where the band structures of the interface and the bulk region are highly entangled with each other, and to study interfaces of strongly correlated electron systems from first principles.

Next, I propose the method to overcome the double-counting problem of the low-energy degree of freedom, and also renormalize the frequency dependence of the effective interaction, which is usually neglected in the conventional low-energy effective model. Moreover, I calculate the derived low-energy effective model by using unrestricted Hartree-Fock approximation (UHF) and the VMC. This is the main study in my thesis.

In the conventional downfolding method, double counting of the electron correlation between the low-energy states exsists, and the frequency-dependence of the effective Coulomb interaction U is ignored in the standard approach. In this work, I reexamin the derivation of the low-energy effective models. I propose an improved formalism free from the double-counting of electron correlation in the low-energy degrees of freedom. In this approach, the exchange-correlation energy in the LDA is replaced with the self-energy corrections coming from the eliminated high-energy degrees of freedom. As well as such replacement, I also renormalize the frequency-dependent part of the partially screened interaction. Moreover, I introduce the self-interaction correction of the low-energy degree of freedom to this formalism, because the compensation of the self-interaction between the direct and exchange terms partially collapses by the subtraction of the low-energy correlation. I apply the formalism to $SrVO_3$ as well as to iron-based superconductors, LaFeAsO, FeSe and FeTe. The resultant bandwidths of the

effective models are nearly the same as those of the previous downfolding formalism because of striking cancellations. In $SrVO_3$, the bandwidths of the V t_{2g} orbitals without the double counting increase by about 30% from that of the LDA. After renormalizing the quasiparticle by the self-energy originated from the frequency-dependent part of U, the resultant bandwidth eventually decreases to 2.57 eV (LDA: 2.58 eV, GW approximation: 2.03 eV). In the non-degenerate multi-band materials such as LaFeAsO, FeSe, and FeTe, the momentum dependent self-energy effects yield modifications of the band structures and relative shifts of orbital-energy levels of the effective models. Next, I calculate the derived low-energy effective model of the iron-based superconductors, LaFeAsO, FeSe and FeTe, by the UHF and the VMC. I introduce the dimensional downfolding effect [7] to the obtained effective interaction, and calculate the derived effective model as the two-dimensional one. For example, FeTe shows an antiferromagnetic bicollinear (AFB) order, which is actually observed in the experiment, in my resultant model, although an antiferromagnetic stripe (AFS) order is more stable than the AFB order in the conventional parameter, where the one-body parameter is estimated as the expectation value of the LDA Hamiltonian. From my formalism, the validities of some existing low-energy model calculations are confirmed, and at the same time, the necessity of the introduction of those improvements becomes apparent especially in the non-degenerate multi-band materials.

[1] P. Hohenberg and W. Kohn: Phys. Rev. **136** (1964) B864.

[2] W. Kohn and L. J. Sham: Phys. Rev. **140** (1965) A1133.

[3] M. Imada and T. Miyake: J. Phys. Soc. Jpn. **79** (2010) 112001.

[4] F. Aryasetiawan, *et al.*: Phys. Rev. B **70** (2004) 195104.

[5] T. Misawa, K. Nakamura, and M. Imada: J. Phys. Soc. Jpn. **80** (2011) 023704.

[6] T. Miyake, K. Nakamura, R. Arita, and M. Imada: J. Phys. Soc. Jpn. **79** (2010) 044705.

[7] K. Nakamura, Y, Yoshimoto, Y. Nohara, and M. Imada: J. Phys. Soc. Jpn. **79** (2010) 123708