Fundamental knowledge of first-principles calculation

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In this tutorial talk, the fundamentals of first-principles calculation are briefly reviewed for beginners. The theoretical framework of first-principles calculation, i.e. so-called density-functional theory was established by Hohenberg and Kohn[1]. They probed that the ground-state energy of an inhomogeneous electron gas can be expressed as a functional of the electron density $n(\boldsymbol{r})$ and the energy functional takes its minimum value for the correct ground-state. The advantage of the theory is that we need no explicit expression for the wave function of an interacting electron system. The density-functional theory gives us a firm base for understanding the complex interacting electron systems. However, no one knows an explicit expression of the energy functional. A practical method treating an interacting electron system was proposed by Kohn and Sham[2] on the basis of the density-functional theory. They reduced the many-body problem of interacting electron systems to self-consistent equations, i.e. Kohn-Sham equations, for single electron in an effective potential, which contains exchange and correlation terms. They assumed that the exchange and correlation potentials depend only on the electron density at the position where the potential is acting. We usually adopt the explicit form of the exchange and correlation potentials for a homogeneous electron gas. This is called local density approximation (LDA). The treatment enables us to obtain the ground state energy as well as the energy band-structure of complex systems such as molecules and solids. However, there are drawbacks originated from the LDA; overestimation of cohesive energy and hence underestimation of inter-atomic distances, underestimation of band gap of semiconductors or insulators including Mott-Hubbard insulators caused by electron correlation effect, underestimation of exchange splitting of spin-up and down bands in magnetic materials, and so on. Some of these drawbacks can be overcome by improved treatments of the exchange and correlation potentials; i.e. generalized gradient approximation[3], self-interaction correction[4], LDA+U method[5], self-energy correction including GW approximation[6] and dynamical mean-field approximation[7], and so on. Typical examples calculated with use of these approaches are presented and the shortcoming of them will be discussed.

Reference

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