

Chapter 2

Methodology of Quantum Mechanics/Atomic Simulations

Abstract Methodology for electronic structure calculations is overviewed. We place focus on first-principles calculation method based on the density-functional theory, which is most widely used for calculations of multiphysics in nanostructures. We explain the formulation for first-principles calculation method using pseudopotentials, which is a common practice in this field. Relatively advanced calculation methods including Beyond LDA approaches are also covered. Semi-empirical electronic structure calculation methods and empirical atomistic models are briefly introduced as well.

Keywords First-principles • Density-functional theory • Electronic structure calculation • Atomic model simulation

2.1 Method for Electronic Structure Calculation

Theoretical methods to obtain the electronic structure in solids and molecules have relatively a long history, which started in 1920s. In various fields, different methods suitable for each purpose have been proposed and improved. Needless to say, behind the advance of the increasingly sophisticated methods is the remarkable improvement of computational proficiency, which has enabled complicated and large-scale calculations.

Theories to obtain the electronic structure are basically based on the Schrödinger equation. When the method does not require empirical parameters and the calculation can be performed in a purely theoretical manner, it is called a first-principles calculation. “Ab initio” (Latin word meaning “from the beginning”) is often used as a word equivalent to “first-principles” but there is a controversy whether these two words are exchangeable (see Appendix). It should be noted that first-principles (ab initio) calculations do *not* mean that no approximation is employed. Although first-principles calculations are basically regarded as rigorous and reliable and one can usually obtain the fundamental properties of materials in a good accuracy, one should well understand the introduced approximations and their limitations.

There are a number of theoretical methods for electronic structure calculation. It is out of the scope of this book to cover all the methods proposed thus far. Classification of the methods may also be difficult because they are intermingled in the process of development. In this chapter, therefore, we explain about only some methods that are important and often used for the evaluation of the property of solids. Here we basically focus on the pseudopotential method with plane wave basis calculation scheme based on the density-functional theory (DFT) [1] which is mainly used for first-principles calculations for multiphysics of nanostructures introduced in the following chapters, while some of other methods are briefly covered.

2.1.1 Fundamental Approximations for Electronic Structure Calculation

In the electronic structure calculation, two fundamental approximations are usually employed: Born–Oppenheimer (adiabatic) and independent-electron approximations [2].

The adiabatic approximation assumes that electrons always take the ground state at any given configuration of atoms. In other words, the electron state is optimized fast enough to immediately follow varying atom configuration. This approximation is reasonable considering the fact that the mass of an electron is about three orders of magnitude lighter than that of an atom unless the change in atom configuration is extremely rapid. With this approximation, one can treat the behavior of electrons and that of atoms separately and independently, i.e., the electron state (and any physical quantity associated with it) can be obtained as the optimal solution to the given atom configuration, which is treated as a fixed environment.

An electron receives not only Coulomb interaction with its nucleus but also Coulomb and exchange–correlation interactions with other electrons. However, it is tremendously difficult to rigorously treat and solve the many-body problem of electrons. A way to circumvent this obstacle is to substitute the many-body interaction with a one-electron effective potential, i.e., it is regarded as a one-electron problem in a potential that represents contributions from other electrons. While this concept, which is called the independent-electron approximation, seems to be a rather drastic and bold approximation, it is often employed in most of the electron structure calculation methods, and it usually leads to successful results in various problems.

2.1.2 Hartree–Fock Method

The Hartree–Fock (HF) method [3] has been developed mainly for the electronic structure calculation of molecules or cluster systems. The molecular orbital

(MO) method calculation, which expresses wave functions with molecular orbitals (localized functions around atoms), is often performed based on the HF method. Here, the concept of the HF method is briefly explained.

Electrons are fermions, which are described by Fermi–Dirac statistics and follow the Pauli exclusion principle. Therefore, restrictions are imposed on the form of many-electron wave functions. We denote $\xi_i \equiv (\mathbf{r}_i, \sigma_i)$, where \mathbf{r}_i is the coordinate of electron i and $\sigma_i (= \pm 1)$ its spin coordinate. The wave function of a N -electron system is written as $\Psi(\xi_1, \xi_2, \dots, \xi_N)$. The wave function must change its sign when coordinates of two electrons are exchanged, i.e.,

$$\Psi(\dots \xi_i \dots \xi_j \dots) = -\Psi(\dots \xi_j \dots \xi_i \dots) \quad (2.1)$$

Now we express the wave function with one-electron orbitals, $\phi_{a_1}(\xi), \phi_{a_2}(\xi), \dots$, as

$$\Psi_N(\xi_1, \dots, \xi_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_{a_1}(\xi_1) & \phi_{a_2}(\xi_1) & \cdots & \phi_{a_N}(\xi_1) \\ \phi_{a_1}(\xi_2) & \phi_{a_2}(\xi_2) & & \vdots \\ \vdots & & \ddots & \\ \phi_{a_1}(\xi_N) & & \cdots & \phi_{a_N}(\xi_N) \end{vmatrix} \quad (2.2)$$

This expression, called the Slater determinant, meets the Pauli exclusion principle. The exchange of two electrons alters the sign of wave function, meaning that electrons repel each other even without Coulomb interaction. While the many-electron state can in general be expressed as a linear combination of Slater determinants, the HF approximation uses one determinant. In the HF approximation, the one-electron Schrödinger equation (called the HF equation) becomes

$$-\frac{\hbar}{2m} \nabla^2 \Psi_i + V_H^i(\mathbf{r}_i) \Psi_i = \varepsilon_i \Psi_i \quad (2.3)$$

$$\begin{aligned} V_H^i(\mathbf{r}_i) = & -e^2 \sum_{\alpha} \frac{Z_{\alpha}}{|\mathbf{r}_i - \mathbf{R}_{\alpha}|} + e^2 \sum_{j \neq i} \int \frac{|\Psi_j(\mathbf{r}'_j)|^2}{|\mathbf{r}_i - \mathbf{r}'_j|} d\mathbf{r}'_j \\ & - e^2 \sum_{j \neq i} \left[\int \frac{\Psi_j^*(\mathbf{r}'_j) \Psi_i(\mathbf{r}_i)}{|\mathbf{r}_i - \mathbf{r}'_j|} d\mathbf{r}'_j \right] \Psi_j(\mathbf{r}_j) \delta_{\sigma_i \sigma_j} \end{aligned} \quad (2.4)$$

The second and third terms of the effective potential (V_H) are electron–electron Coulomb interaction and exchange interaction, respectively.

2.1.3 Density-functional Theory

Another approach to electronic structure calculation that started being used actively in 1970s is based on the density-functional theory (DFT) [1], which originates in the work by Hohenberg and Kohn (1964) that showed the total energy of a system can be expressed as a functional of charge density (ρ)

$$E_{\text{tot}} = \int V_{\text{ext}}(r)\rho(r)dr + T[\rho] + E_{ee}[\rho] \quad (2.5)$$

where V_{ext} is the external potential (potential of the nucleus ion), T the kinetic energy functional, and E_{ee} the electron–electron interaction functional. A practical calculation method was presented by Kohn and Sham (1965). According to the Kohn–Sham (KS) theory [4], one is to solve one-electron eigenvalue problem (Kohn–Sham equation)

$$[T + V_{\text{ext}} + V_H + V_{\text{XC}}]\psi_i(r) = \varepsilon_i\psi_i(r) \quad (2.6)$$

where V_H is the Hartree (Coulomb) potential and V_{XC} the exchange–correlation potential (details will be described in the next section). The energy functional in the Kohn–Sham theory is described as

$$E_{\text{tot}} = T[\rho(r)] + \int V_{\text{ext}}(r)\rho(r)dr + \frac{1}{2} \iint \frac{\rho(r)\rho(r')}{|r - r'|} dr' dr + E_{\text{XC}}[\rho(r)] \quad (2.7)$$

The ground state can be therefore obtained by optimizing wave functions so that corresponding charge density minimizes the total energy. In other words, DFT is a charge density-based theory, while the HF method is a wave-function-based one.

Usually, the KS equation is written in the matrix form and solution (eigenvalues and eigenvectors) is found by an iterative method. As the Hamiltonian terms contain the contribution of charge density of electrons, solving the KS equation cannot be done only once but a so-called self-consistent loop (SCL) calculation is needed, i.e., the Hamiltonian is constructed with a provisional charge density distribution (ρ_{in}), and the KS equation is solved to obtain ψ , from which charge density is renewed (ρ_{out}). Then the created charge density constructs the new Hamiltonian, and this process is repeated until the equation becomes self-consistent ($\rho_{\text{in}} = \rho_{\text{out}}$).

Electronic structure calculation for crystals (periodic structures) is sometimes called “electronic band structure calculation.” Various theoretical methods for band calculation have been proposed and developed. All-electron calculation methods, which obtain the states of both valence and core electrons, will be only briefly introduced in Sect. 2.2.8. Electronic band structure calculation based on DFT is also conducted with a plane wave basis set, where the pseudopotential method is usually employed to (explicitly) treat valence electrons only. One of the advantages

of such approach is its suitability for the calculation of forces exerted on atoms due to the Hellmann–Feynman theorem [5], which enables efficient structural optimization and obtains mechanical properties such as stress tensor and elastic constants. This approach is widely used owing to sophisticated simulation packages including VASP [6], CASTEP [7], ABINIT [8], and PWSCF [9]. The detail of the calculation method of DFT with pseudopotentials will be described in the next section.

2.2 First-Principles Calculation with Plane Wave Basis Set

In this section, we describe the DFT calculation method using a plane wave basis set. Hartree atomic units (Table 2.1) are used in the following description of the formalism. For the sake of brevity, we assume the nonmagnetic case without spin polarization unless otherwise stated.

The plane wave basis is not suitable for expressing wave functions with many nodes. The plane wave basis DFT calculations are therefore usually performed with employing the pseudopotential method, which makes the effective potential remarkably softer to reduce the basis set required to represent wave functions. For pseudopotential methods, see later section.

2.2.1 Kohn–Sham Equation

In DFT, the Kohn–Sham equation

$$[T + V_{\text{ext}} + V_{\text{H}} + V_{\text{XC}}]\psi_i(\mathbf{r}) = \varepsilon_i\psi_i(\mathbf{r}) \quad (2.8)$$

is to be solved to find the wave vector (eigenvector), $\psi_i(\mathbf{r})$, and the corresponding energy level (eigenvalue), ε_i , of one-electron state (i). T is the operator of the kinetic energy of the electron

$$T[\rho(\mathbf{r})] = \sum_i^{\text{occ}} \left\langle \psi_i \left| -\frac{1}{2} \nabla^2 \right| \psi_i \right\rangle \quad (2.9)$$

Table 2.1 Hartree and Rydberg atomic units and SI unit

	Hartree (a.u.)	Rydberg (a.u.)	SI
Mass	1	$\frac{1}{2}$	$9.10965 \times 10^{-31} \text{ kg}$
Time	1	$\frac{1}{2}$	$2.41889 \times 10^{-17} \text{ s}$
Energy	1	2	$4.35982 \times 10^{-18} \text{ J}$
Length	1	1	$5.29177 \times 10^{-11} \text{ m}$
Force	1	2	$8.23892 \times 10^{-8} \text{ N}$

and the charge density ρ is obtained as

$$\rho(\mathbf{r}) = 2 \sum_i^{\text{occ}} |\psi_i(\mathbf{r})|^2 \quad (2.10)$$

Here “occ” means that the summation ranges over the occupied electron states. The other three terms ($V_{\text{eff}} \equiv V_{\text{ext}} + V_{\text{H}} + V_{\text{HC}}$) are the effective one-electron potential. V_{ext} represents the interaction between the electron and the “core ion,” which consists of the nucleus and the surrounding core electrons in the framework of the pseudopotential method (see Sect. 2.2.4). V_{H} represents the electron–electron (Coulomb) interaction

$$V_{\text{H}} = \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' \quad (2.11)$$

which is also called Hartree term. V_{XC} is the exchange–correlation potential

$$V_{\text{XC}} = \frac{\delta E_{\text{XC}}[\rho(\mathbf{r})]}{\delta \rho(\mathbf{r})} \quad (2.12)$$

where all quantum effect is included. The exact exchange–correlation functional ($E_{\text{XC}} = E_{\text{C}} + E_{\text{X}}$; E_{C} and E_{X} are the correlation and the exchange energies, respectively) is not known, and an approximation must be introduced to write this term (see, e.g., Sect. 2.2.2).

2.2.2 Local Density Approximation

To solve the Kohn–Sham equation, it is required to determine the exchange–correlation functional form. This is, however, a many-electron term and it is hardly possible to come up with the exact solution for general cases. The local density approximation (LDA) [4] was introduced to give a major breakthrough to this problem. LDA assumes that the gradient of the charge density with respect to space is modest and writes

$$E_{\text{XC}}[\rho(r)] = \int \varepsilon_{\text{XC}}(\mathbf{r}) \rho(\mathbf{r}) d\mathbf{r} \quad (2.13)$$

where $\varepsilon_{\text{XC}}(\mathbf{r})$ is the exchange–correlation energy density, which is the sum of the exchange (ε_{X}) and correlation (ε_{C}) energy densities, i.e.,

$$\varepsilon_{\text{XC}}(\mathbf{r}) = \varepsilon_{\text{X}}(\mathbf{r}) + \varepsilon_{\text{C}}(\mathbf{r}) \quad (2.14)$$

The exchange–correlation potential is then

$$V_{\text{XC}} = \frac{\delta E_{\text{XC}}[\rho(\mathbf{r})]}{\delta \rho} = \varepsilon_{\text{XC}}(\mathbf{r}) + \rho(\mathbf{r}) \frac{\delta \varepsilon_{\text{XC}}(\mathbf{r})}{\delta \rho(\mathbf{r})} \quad (2.15)$$

Although LDA is a rather bold approximation, it has been empirically known that the approximation works well for various cases. The reason for this was intensively discussed by Gunnarsson [10]. To perform analysis of magnetic materials, LDA was extended to the spin-polarized case, where majority and minority spins do not take an identical state. This is called the local spin density approximation (LSDA). Denoting the opposite spins by + and −, the Kohn–Sham equation becomes as follows:

$$\left[-\frac{1}{2} \nabla^2 + V_{\text{eff}}^{\pm}(\mathbf{r}) \right] \psi_i^{\pm}(\mathbf{r}) = \varepsilon_i^{\pm} \psi_i^{\pm}(\mathbf{r}) \quad (2.16)$$

$$V_{\text{eff}}^{\pm}(\mathbf{r}) = V_{\text{ext}}(\mathbf{r}) + V_{\text{H}}(\mathbf{r}) + V_{\text{XC}}^{\pm}(\mathbf{r}) \quad (2.17)$$

$$V_{\text{XC}}^{\pm}(\mathbf{r}) = \frac{\delta E_{\text{XC}}}{\delta \rho^{\pm}(\mathbf{r})} \quad (2.18)$$

Here,

$$\rho(\mathbf{r}) = \rho^{+}(\mathbf{r}) + \rho^{-}(\mathbf{r}) \quad (2.19)$$

$$\rho^{\pm}(\mathbf{r}) = \sum_i^{\text{occ}} |\psi_i^{\pm}(\mathbf{r})|^2 \quad (2.20)$$

The exchange–correlation energy reads

$$E_{\text{XC}}[\rho^{+}, \rho^{-}] = \int \rho(\mathbf{r}) \varepsilon_{\text{XC}}\{\rho^{+}(\mathbf{r}), \rho^{-}(\mathbf{r})\} d\mathbf{r} \quad (2.21)$$

Various expressions for the exchange and correlation energies have been suggested thus far [11]. Here we introduce an example, which is one of the most commonly used functions. In the following expressions, superscripts P and F denote paramagnetic and ferroelectric states, respectively. Kohn, Sham, and Gaspar gave an approximation for the exchange energy density as [4, 12]

$$\varepsilon_{\text{X}}^{\text{P}} = -\frac{3}{4\pi} \left(\frac{9\pi}{4} \right)^{1/3} \frac{1}{r_s} \quad (2.22)$$

and

$$\varepsilon_{\text{X}}^{\text{F}} = 2^{1/3} \varepsilon_{\text{X}}^{\text{P}} \quad (2.23)$$

where

$$r_s = \left(\frac{3}{4\pi\rho(\mathbf{r})} \right)^{1/3} \quad (2.24)$$

A functional form for the correlation energy density was proposed by Perdew and Zunger [13] based on the results of Monte Carlo calculations of electron gas by Ceperley and Alder [14] as

$$\varepsilon_C^i(\mathbf{r}) = \begin{cases} -\frac{\gamma^i}{1 + \beta_1^i \sqrt{r_s} + \beta_2^i r_s} & (r_s > 1) \\ A^i \ln r_s + B^i + C^i r_s \ln r_s + D^i r_s & (r_s \leq 1) \end{cases} \quad (2.25)$$

where $i = \text{P or F}$. The parameters are given as follows: $\gamma^{\text{P}} = -0.07115$, $\beta_1^{\text{P}} = 1.0529$, $\beta_2^{\text{P}} = 0.3334$, $A^{\text{P}} = 0.01555$, $B^{\text{P}} = -0.024$, $C^{\text{P}} = 0.001$, $D^{\text{P}} = -0.0116$, $\gamma^{\text{F}} = -0.04215$, $\beta_1^{\text{F}} = 1.3981$, $\beta_2^{\text{F}} = 0.2611$, $A^{\text{F}} = 0.007775$, $B^{\text{F}} = -0.01345$, $C^{\text{F}} = 0.00035$, and $D^{\text{F}} = -0.0024$. For the spin polarization $\zeta (\equiv (\rho^+ - \rho^-)/\rho)$ between 0 and 1, the energy densities can be obtained using the spin interpolation formula by von Barth and Hedin [15], i.e.,

$$\varepsilon_{\text{XC}}(\zeta) = \varepsilon_{\text{XC}} + f(\zeta)(\varepsilon_{\text{XC}}^{\text{F}} - \varepsilon_{\text{XC}}^{\text{P}}) \quad (2.26)$$

$$f(\zeta) = \frac{(1 + \zeta)^{4/3} + (1 - \zeta)^{4/3} - 2}{2^{4/3} - 2} \quad (2.27)$$

LDA (LSDA) has been and still is widely used due to its good performance in spite of the simplicity. Nevertheless, it is known that the approximation does not work well for some cases. Some of the nontrivial, well-known problems are listed below [16].

- (1) LDA tends to underestimate the lattice constant. (In general, however, this trait is not considered to be fatal because the deviation from the experimental value can be restricted within 1% in most cases.)
- (2) Structure and magnetism of 3D transition metals cannot be reproduced well. For instance, the hcp (paramagnetic) structure of Fe is evaluated as the most stable state, as opposed to the bcc structure with the ferromagnetic state in reality.
- (3) The band gap energy of semiconductors and insulators tends to be underestimated.

2.2.3 Generalized Gradient Approximation

Generalized gradient approximation (GGA) [17, 18], which is to take into account the spatial gradient of charge density, is a natural and reasonable extension of LDA. The exchange–correlation energy in GGA is expressed as

$$E_{\text{XC}}[\rho^+, \rho^-] = \int f\{\rho^+, \rho^-, \nabla\rho^+, \nabla\rho^-\} d\mathbf{r} \quad (2.28)$$

GGA tends to improve various energy evaluations including total energies and structural energy differences. Evaluation of magnetism can be improved in some cases. In GGA, interatomic bonds are evaluated to be softer than in LDA, which leads to (over)correction to the underestimation of lattice constants by LDA.

Among GGA, functionals being used most frequently are PW91 proposed by Perdew and Wang [19], and PBE by Perdew et al. [18]. Omitting the details of its derivation, explicit forms of the PBE functional are given below. The correlation energy is given by

$$E_C^{\text{PBE}}[\rho^+, \rho^-] = \int \rho [e_c^{\text{LDA}}(r_s, \zeta) + H(r_s, \zeta, t)] d\mathbf{r} \quad (2.29)$$

where $r_s = (3/4\pi\rho)^{1/3}$ is the Wigner–Seitz radius, $\zeta = (\rho^+ - \rho^-)/\rho$ is the relative spin polarization, and $t = |\nabla\rho|/2\phi k_s \rho$ is a dimensionless density gradient ($\phi(\zeta) = [(1+\zeta)^{2/3} + (1-\zeta)^{2/3}]/2$, $k_s = \sqrt{4k_F/\pi a_0}$). The gradient contribution is given by

$$H = \left(\frac{e^2}{a_0}\right) \gamma \phi^3 \ln \left\{ 1 + \frac{\beta}{\gamma} t^2 \left[\frac{1 + At^2}{1 + At^2 + A^2 t^4} \right] \right\} \quad (2.30)$$

$$A = \frac{\beta}{\gamma} \left[\exp \left\{ \frac{-\varepsilon_c^{\text{LDA}} a_0}{\gamma \phi^3 e^2} \right\} - 1 \right]^{-1} \quad (2.31)$$

$$(e =, a_0 =, \beta = 0.066725, \gamma = (1 - \ln 2)/\pi^2)$$

The exchange energy is written as

$$E_X^{\text{PBE}} = \int \rho [\varepsilon_X^{\text{LDA}}(\rho) + F_X(s)] d\mathbf{r} \quad (2.32)$$

$$F_X(s) = 1 + \kappa - \kappa / (1 + \mu s^2 / \kappa) \quad (2.33)$$

$$(\kappa = 0.804)$$

2.2.4 Pseudopotential Method and Norm-Conserving Pseudopotential

Potentials that electrons feel basically have a deep valley around the nucleus. Wave functions have therefore many nodes, which makes it impractical to represent such wave functions with plane wave basis sets. The pseudopotential method is to circumvent this problem by dealing with only valence electrons and constructing “effective” (pseudo-)potentials created by the nucleus and the core electrons (see Fig. 2.1). Core electrons, chemically inert, are considered to be fixed (frozen-core approximation), and only the Schrödinger equation for valence electrons is solved.

Pseudopotentials are constructed from the solution of the all-electron Schrödinger equation for an isolated atom and are put in use for condensed matters. Thus, it is essential for the pseudopotentials to possess good transferability (i.e., reliability of the potential when being put in different environment). In addition, the pseudopotentials are desired to be sufficiently “soft” so that only small basis sets are required.

The norm-conserving pseudopotential (NCPP) method was proposed by Hamann et al. [20], and various potentials were constructed with modifications later on [21–25]. NCPPs are constructed to meet the following conditions (ψ_l^{AE} and ϵ_l^{AE} are the wave function and the energy (eigenvalue) of the all-electron calculation, respectively. ψ_l^{PS} and ϵ_l^{PS} are the pseudo wave function and the corresponding (pseudo) energy, respectively):

- (1) Pseudo wave functions (ψ_l^{PS} , where l is the angular momentum) are nodeless.
- (2) Pseudo wave functions are identical with all-electron wave functions (ψ_l^{AE}) outside the core radius, r_{cl} .
- (3) Energies (eigenvalues) of the pseudo wave functions, ϵ_l^{PS} , are identical with all-electron energies (ϵ_l^{AE}).
- (4) The integral of pseudo charge density (norm of pseudo wave functions) inside the cutoff sphere is identical with that of true charge density, namely

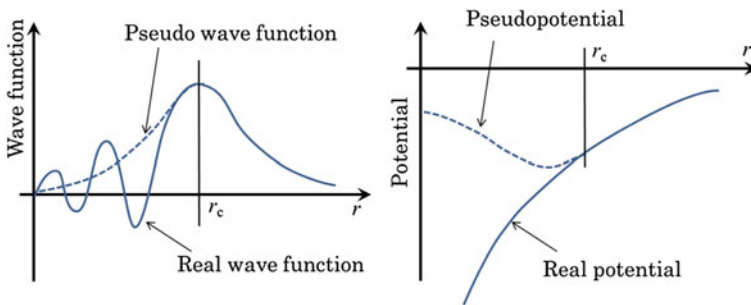


Fig. 2.1 Schematics explaining pseudopotential method

$$\int_0^{r_{cl}} |r\psi_l^{PS}(r)|^2 dr = \int_0^{r_{cl}} |r\psi_l^{AE}(r)|^2 dr \quad (2.34)$$

The following identity is obtained.

$$\left[-\frac{1}{2} r^2 \psi(r)^2 \frac{d}{d\varepsilon} \frac{d}{dr} \ln \psi(r) \right]_{r_{cl}}^0 = \int_0^{r_{cl}} r^2 \psi(r)^2 dr \quad (2.35)$$

The left-hand side is unchanged between ψ_l^{AE} and ψ_l^{PS} if the above condition (4) is satisfied, i.e., the logarithmic derivative of the radial wave function, which describes the scattering property of electrons by the ion, is correct. This ensures the transferability of NCPPs.

2.2.5 Hamiltonian in NCPP

Here we show the Hamiltonian operator in the matrix form within the framework of the NCPP method [26]. Consider an object (crystal) cell, whose primitive translation vectors are $\mathbf{a}_1, \mathbf{a}_2$, and \mathbf{a}_3 . The reciprocal lattice is given as

$$\mathbf{G} = m_1 \mathbf{b}_1 + m_2 \mathbf{b}_2 + m_3 \mathbf{b}_3 \quad (2.36)$$

with

$$\mathbf{b}_1 = 2\pi \frac{\mathbf{a}_2 \times \mathbf{a}_3}{\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)} \quad (2.37)$$

$$\mathbf{b}_2 = 2\pi \frac{\mathbf{a}_3 \times \mathbf{a}_1}{\mathbf{a}_2 \cdot (\mathbf{a}_3 \times \mathbf{a}_1)} \quad (2.38)$$

$$\mathbf{b}_3 = 2\pi \frac{\mathbf{a}_1 \times \mathbf{a}_2}{\mathbf{a}_3 \cdot (\mathbf{a}_1 \times \mathbf{a}_2)} \quad (2.39)$$

and m_1, m_2 , and m_3 are integers. We use the notation of a plane wave

$$|\mathbf{k} + \mathbf{G}\rangle = \frac{1}{\sqrt{\Omega}} \exp[i(\mathbf{k} + \mathbf{G}) \cdot \mathbf{r}] \quad (2.40)$$

where \mathbf{k} is a sampling point in the Brillouin zone. Plane waves are orthonormal as

$$\langle \mathbf{k} + \mathbf{G} | \mathbf{k} + \mathbf{G}' \rangle = \frac{1}{\sqrt{\Omega}} \int_{\Omega} \exp[i(\mathbf{G} - \mathbf{G}') \cdot \mathbf{r}] d\mathbf{r} = \delta_{\mathbf{G}\mathbf{G}'} \quad (2.41)$$

(Ω is the volume of the entire crystal.) The wave function that has the n th eigenvalue for \mathbf{k} , $\psi_{kn}(\mathbf{r})$, is expanded into the plane wave basis as

$$\psi_{kn}(\mathbf{r}) = \sum_{\mathbf{G}} C_{\mathbf{k}+\mathbf{G}}^n |\mathbf{k} + \mathbf{G}\rangle \quad (2.42)$$

Practically, the summation ranges over all \mathbf{G} 's with $\frac{1}{2}|\mathbf{k} + \mathbf{G}|^2$ smaller than a certain value (the cutoff value for plane waves). The charge density is given by

$$\rho(\mathbf{r}) = \sum_{\mathbf{G}} \sum_{\mathbf{G}'} \sum_n^{\text{occ}} \sum_k f_n f_k \frac{1}{\Omega} C_{\mathbf{k}+\mathbf{G}'}^{n*} C_{\mathbf{k}+\mathbf{G}}^n \exp[i(\mathbf{G} - \mathbf{G}') \cdot \mathbf{r}] \quad (2.43)$$

where f_n and f_k indicate the weight of each \mathbf{k} -point and the occupation number of the energy level n , respectively.

In the plane wave basis formalism, the Kohn–Sham equation becomes the eigenvalue problem whose eigenvectors are the expansion coefficients written as

$$\sum_{\mathbf{G}'} H_{\mathbf{k}+\mathbf{G}, \mathbf{k}+\mathbf{G}'} C_{\mathbf{k}+\mathbf{G}'}^n = \varepsilon_{kn} C_{\mathbf{k}+\mathbf{G}}^n \quad (2.44)$$

where ε_{kn} is the eigenvalue for the n th state of the sampling point \mathbf{k} .

Here we show the elements of the Hamiltonian matrix

$$H_{\mathbf{k}+\mathbf{G}, \mathbf{k}+\mathbf{G}'} = \langle \mathbf{k} + \mathbf{G} | -\frac{1}{2} \nabla^2 + v_{\text{eff}}(\mathbf{r}) | \mathbf{k} + \mathbf{G}' \rangle \quad (2.45)$$

The kinetic energy term is

$$\langle \mathbf{k} + \mathbf{G} | -\frac{1}{2} \nabla^2 | \mathbf{k} + \mathbf{G}' \rangle = \frac{1}{2} |\mathbf{k} + \mathbf{G}|^2 \delta_{\mathbf{G}\mathbf{G}'} \quad (2.46)$$

The term for the Coulomb interaction with the ion core is split into the local term (V_{loc}), which is independent of the angular momentum, and the angular-dependent nonlocal term (V_{nlloc}). The local term

$$\begin{aligned} & \langle \mathbf{k} + \mathbf{G} | V_{\text{loc}}^{\text{pp}}(\mathbf{r}) | \mathbf{k} + \mathbf{G}' \rangle \\ &= \frac{1}{\Omega} \int_{\Omega} V_{\text{loc}}^{\text{pp}}(r) \exp[-i(\mathbf{k} + \mathbf{G}) \cdot \mathbf{r}] \exp[i(\mathbf{k} + \mathbf{G}') \cdot \mathbf{r}] d\mathbf{r} \\ &= V_{\text{loc}}^{\text{pp}}(\mathbf{G} - \mathbf{G}') \end{aligned} \quad (2.47)$$

is given by the coefficients of the Fourier transformation of $V_{\text{loc}}^{\text{pp}}(\mathbf{r})$, i.e.

$$V_{\text{loc}}^{\text{pp}}(\mathbf{G}) = \frac{1}{\Omega_a} \sum_a \exp(-i\mathbf{G} \cdot \mathbf{r}_a) V_a^{\text{pp},\text{loc}}(\mathbf{G}) \quad (2.48)$$

$$V_a^{\text{pp},\text{loc}}(\mathbf{G}) = \int_{\Omega} V_a^{\text{pp},\text{loc}}(r) \exp(-\mathbf{G} \cdot \mathbf{r}) d\mathbf{r} \quad (2.49)$$

Here, Ω_a is the volume of the simulation cell, and $V_a^{\text{pp},\text{loc}}(r)$ and \mathbf{r}_a are the local pseudopotential and the position of atom a , respectively. The nonlocal part is

$$\begin{aligned} \langle \mathbf{k} + \mathbf{G} | V_{\text{nl}}^{\text{pp}}(\mathbf{r}) | \mathbf{k} + \mathbf{G}' \rangle &= \frac{1}{\Omega_a} \sum_a \exp[-i(\mathbf{G} - \mathbf{G}') \cdot \mathbf{r}_a] V_a^{\text{pp},\text{nl}}(\mathbf{k} + \mathbf{G}, \mathbf{k} + \mathbf{G}') \\ &= V_{\text{nl}}^{\text{pp}}(\mathbf{k} + \mathbf{G}, \mathbf{k} + \mathbf{G}') \end{aligned} \quad (2.50)$$

Here,

$$\begin{aligned} V_{\text{nl}}^{\text{pp}}(\mathbf{k} + \mathbf{G}, \mathbf{k} + \mathbf{G}') &= 4\pi \sum_l (2l+1) P_l(\cos \omega) \\ &\times \int V_{a,l}^{\text{pp},\text{nl}}(r) j_l(|\mathbf{k} + \mathbf{G}|r) j_l(|\mathbf{k} + \mathbf{G}'|r) r^2 dr \end{aligned} \quad (2.51)$$

$V_{a,l}^{\text{pp},\text{nl}}(r)$ is the nonlocal pseudopotential of atom a for angular momentum l , P_l the Legendre polynomial, and j_l the spherical Bessel function. ω is the angle between $\mathbf{k} + \mathbf{G}$ and $\mathbf{k} + \mathbf{G}'$.

The Fourier transformation of the charge density reads

$$\rho(\mathbf{r}) = \sum_{\mathbf{G}} \rho(\mathbf{G}) \exp(i\mathbf{G} \cdot \mathbf{r}) \quad (2.52)$$

$$\rho(\mathbf{G}) = \frac{1}{\Omega} \int \rho(\mathbf{r}) \exp(-i\mathbf{G} \cdot \mathbf{r}) d\mathbf{r} \quad (2.53)$$

The Coulomb term meets the Poisson equation,

$$\nabla^2 V_{\text{coul}}(\mathbf{r}) = -4\pi\rho(\mathbf{r}) \quad (2.54)$$

therefore

$$\nabla^2 V_{\text{coul}}(\mathbf{r}) = -4\pi \sum_{\mathbf{G}} \rho(\mathbf{G}) \exp(i\mathbf{G} \cdot \mathbf{r}) \quad (2.55)$$

Thus, we get

$$V_{\text{coul}}(\mathbf{r}) = 4\pi \sum_{\mathbf{G}} \frac{\rho(\mathbf{G})}{|\mathbf{G}|^2} \exp(i\mathbf{G} \cdot \mathbf{r}) \quad (2.56)$$

and its Fourier transformation becomes

$$\begin{aligned} V_{\text{coul}}(\mathbf{G}) &= \frac{1}{\Omega} \int_{\Omega} 4\pi \sum_{\mathbf{G}'} \frac{\rho(\mathbf{G}')}{|\mathbf{G}'|^2} \exp(i\mathbf{G}' \cdot \mathbf{r}) \exp(-i\mathbf{G} \cdot \mathbf{r}) d\mathbf{r} \\ &= 4\pi \frac{\rho(\mathbf{G})}{|\mathbf{G}|^2} \end{aligned} \quad (2.57)$$

The corresponding element of the Hamiltonian matrix therefore becomes

$$\begin{aligned} \langle \mathbf{k} + \mathbf{G} | V_{\text{coul}}(\mathbf{r}) | \mathbf{k} + \mathbf{G}' \rangle &= \frac{1}{\Omega} \int_{\Omega} V_{\text{coul}}(\mathbf{r}) \exp(-i\mathbf{G} \cdot \mathbf{r}) \exp(i\mathbf{G}' \cdot \mathbf{r}) d\mathbf{r} \\ &= V_{\text{coul}}(\mathbf{G} - \mathbf{G}') \end{aligned} \quad (2.58)$$

In the same manner, the exchange–correlation term can be obtained as

$$\langle \mathbf{k} + \mathbf{G} | \mu_{\text{XC}}(\mathbf{r}) | \mathbf{k} + \mathbf{G}' \rangle = \mu_{\text{XC}}(\mathbf{G} - \mathbf{G}') \quad (2.59)$$

Summarizing the above equations, we get

$$\begin{aligned} H_{\mathbf{k} + \mathbf{G}, \mathbf{k} + \mathbf{G}'} &= \frac{1}{2} |\mathbf{k} + \mathbf{G}|^2 \delta_{\mathbf{G}\mathbf{G}'} + V_{\text{loc}}^{\text{pp}}(\mathbf{G} - \mathbf{G}') \\ &\quad + V_{\text{nlloc}}^{\text{pp}}(\mathbf{k} + \mathbf{G}, \mathbf{k} + \mathbf{G}') + V_{\text{coul}}(\mathbf{G} - \mathbf{G}') \\ &\quad + \mu_{\text{XC}}(\mathbf{G} - \mathbf{G}') \end{aligned} \quad (2.60)$$

2.2.6 Ultrasoft Pseudopotential Method

Softer pseudopotentials require smaller basis sets, leading to the improvement in calculation efficiency. The ultrasoft pseudopotential (USPP) scheme proposed by Vanderbilt [27] succeeded in making substantially soft potentials without sacrificing calculation accuracy by removing the norm-conserving condition and introducing augmentation charges. A scheme to include more than one reference energies in the construction of pseudopotential for better transferability was also suggested. This “multireference energy” scheme can be applied to the NCPP method in principle, but such an approach was employed in few studies.

Based on all-electron calculations, pseudo wave functions ($\tilde{\psi}_i$) are constructed so that the scattering properties are correct for reference energy levels. For a given angular momentum l , more than one energy levels, ε_i , are chosen. Pseudo wave functions are constructed under the generalized norm-conserving condition as follows.

$$Q_{ij} = \langle \psi_i | \psi_j \rangle_R - \langle \tilde{\psi}_i | \tilde{\psi}_j \rangle_R = 0 \quad (2.61)$$

Here $\langle \psi_i | \psi_j \rangle_R$ denotes the integral of $\psi_i^*(r) \psi_j(r)$ inside the sphere with a radius of R . Now, projector functions $|\beta_i\rangle = \sum_j (B^{-1})_{ji} \langle \chi_j |$ are defined, which are dual to the pseudofunctions $|\tilde{\psi}_i\rangle$ (i.e., $\langle \beta_i | \tilde{\psi}_j \rangle = \delta_{ij}$). Then, the nonlocal pseudopotential operator can be chosen as

$$V_{NL} = \sum_{i,j} B_{ij} |\beta_i\rangle \langle \beta_j| \quad (2.62)$$

The generalized norm-conserving condition $Q_{ij} = 0$ is not necessary if we accept the generalized eigenvalue problem where the overlapping operator

$$S = 1 + \sum_{i,j} Q_{ij} |\beta_i\rangle \langle \beta_j| \quad (2.63)$$

Then the nonlocal pseudopotential operator is redefined with $D_{ij} \equiv B_{ij} + \varepsilon_j Q_{ij}$ as

$$V_{NL} = \sum_{i,j} D_{ij} |\beta_i\rangle \langle \beta_j| \quad (2.64)$$

Here we get the following relation

$$\langle \tilde{\psi}_i | S | \tilde{\psi}_j \rangle_R = \langle \psi_i | \psi_j \rangle_R \quad (2.65)$$

Thus, the pseudofunctions are the solution of the generalized eigenvalue problem ($H = T + V_{\text{loc}} + V_{\text{NL}}$)

$$(H - \varepsilon_i S) |\tilde{\psi}_i\rangle = 0 \quad (2.66)$$

Though B is no longer Hermitian due to the removal of the generalized norm-conserving condition, the hermiticity of the pseudo-Hamiltonian is restored because D and Q are Hermitian operators. Valence charge density is written as

$$\rho(\mathbf{r}) = \sum_i^{\text{occ}} \tilde{\psi}_i^*(\mathbf{r}) \tilde{\psi}_i(\mathbf{r}) + \sum_{i,j} \rho_{ij} Q_{ji}(\mathbf{r}) \quad (2.67)$$

where

$$\rho_{ij} \equiv \sum_k^{\text{occ}} \langle \beta_i | \psi_k \rangle \langle \psi_k | \beta_j \rangle \quad (2.68)$$

$$Q_{ij}(r) \equiv \psi_i^*(r) \psi_i(r) - \tilde{\psi}_i^*(r) \tilde{\psi}_i(r) \quad (2.69)$$

The advantage of the removal of the generalized norm-conserving condition is that the pseudofunction construction should only meet the requirement that the pseudofunctions should only be smoothly connected to all-electron functions at a radius of R ; therefore, the core radius can be much larger than that of NCPPs without sacrificing accuracy (accuracy can be retained by introducing the auxiliary function Q and the overlapping operator S) [28]. In fact, the logarithmic derivative of the wave function is conserved as

$$-\frac{1}{2}(r\tilde{\psi}_i(r))^2 \frac{d}{d\varepsilon_i} \frac{d}{dr} \ln \tilde{\psi}_i(r) \Big|_R = \langle \tilde{\psi}_i | \tilde{\psi}_i \rangle_R + Q_{ii} = \langle \psi_i | \psi_i \rangle_R \quad (2.70)$$

$$-\frac{1}{2}(r\psi_i(r))^2 \frac{d}{d\varepsilon_i} \frac{d}{dr} \ln \psi_i(r) \Big|_R = \langle \psi_i | \psi_i \rangle_R \quad (2.71)$$

2.2.7 Projector-augmented Wave Method

The projector-augmented wave (PAW) method proposed by Blöchl [29] is another solution to the problem that wave functions are sharp in the core region requiring a substantial number of plane waves. In PAW, a linear transformation operator, \hat{T} , is introduced to efficiently describe wave function features that are largely different between core and interstitial regions.

The operator \hat{T} transforms an smooth auxiliary function, $|\psi_i\rangle$, to the true all-electron Kohn–Sham single-particle wave function, $|\psi_i\rangle$

$$|\psi_i\rangle = \hat{T} |\tilde{\psi}_i\rangle \quad (2.72)$$

Then we get a transformed Kohn–Sham equation,

$$\hat{T}^\dagger H \hat{T} = \varepsilon_i \hat{T}^\dagger \hat{T} |\hat{\psi}_i\rangle \quad (2.73)$$

which is to be solved instead of the ordinary Kohn–Sham equation. The transformation operator is determined so that the auxiliary function as the solution of the above equation becomes smooth. \hat{T} has only to affect the core region, so we define

$$\hat{T} = 1 + \sum_a \hat{T}^a \quad (2.74)$$

where a is an atom index. \hat{T}^a is an atom-centered transformation, which has no effect outside augmentation spheres with a radius of r_c^a , i.e., $|\mathbf{r} - \mathbf{R}^a| > r_c^a$. Augmentation spheres do not overlap with each other. In the augmentation sphere, the true wave function is expanded to partial waves, ϕ_j^a . For each partial wave, a smooth auxiliary wave, $\tilde{\phi}_j^a$, is defined, and the following condition is required.

$$|\phi_j^a\rangle = (1 + \hat{T}^a) |\tilde{\phi}_j^a\rangle \quad (2.75)$$

ϕ_j^a and $\tilde{\phi}_j^a$ coincide with each other outside the augmentation sphere. Now, the smooth wave function $|\tilde{\psi}_i\rangle$ is expanded with the smooth partial waves as

$$|\tilde{\psi}_i\rangle = \sum_j P_{ij}^a |\tilde{\phi}_j^a\rangle; |\mathbf{r} - \mathbf{R}^a| < r_c^a \quad (2.76)$$

Recalling $|\phi_j^a\rangle = \hat{T} |\tilde{\phi}_j^a\rangle$, we can make the following expansion with the same coefficients,

$$|\psi_i\rangle = \hat{T} |\tilde{\psi}_i\rangle = \sum_j P_{ij}^a |\phi_j^a\rangle; |\mathbf{r} - \mathbf{R}^a| < r_c^a \quad (2.77)$$

The linearity of the transformation operator gives

$$P_{ij}^a = \langle \tilde{p}_j^a | \tilde{\psi}_i \rangle \quad (2.78)$$

\tilde{p}_j^a is called a smooth projector function.

The projector function must satisfy the following completeness relation,

$$\sum_j |\tilde{\phi}_j^a\rangle \langle \tilde{p}_j^a| = 1; |\mathbf{r} - \mathbf{R}^a| < r_c^a \quad (2.79)$$

which implies that the projector function must be orthonormal to the smooth partial waves within the augmentation sphere ($\langle p_j^a | \tilde{\phi}_k^a \rangle = \delta_{jk}; |\mathbf{r} - \mathbf{R}^a| < r_c^a$). Using the completeness relation, we get

$$\hat{T}^a = \sum_j \hat{T}^a |\tilde{\phi}_j^a\rangle \langle \tilde{p}_j^a| = \sum_j \left(|\phi_j^a\rangle - |\tilde{\phi}_j^a\rangle \right) \langle \tilde{p}_j^a| \quad (2.80)$$

and therefore

$$\hat{T} = 1 + \sum_a \sum_j \left(|\phi_j^a\rangle - |\tilde{\phi}_j^a\rangle \right) \langle \tilde{p}_j^a| \quad (2.81)$$

The all-electron Kohn–Sham wave function can be obtained as

$$\psi_i(\mathbf{r}) = \tilde{\psi}_i(\mathbf{r}) + \sum_a \sum_j \left(\phi_j^a(\mathbf{r}) - \tilde{\phi}_j^a(\mathbf{r}) \right) \langle \tilde{p}_j^a | \hat{\psi}_i \rangle \quad (2.82)$$

By this decomposition, the original wave function is divided to the auxiliary wave function (smooth everywhere) and the contribution including fast oscillation (affecting limited region in space). It is the advantage of the introduction of the transformation operator to be able to treat the two functions independently.

2.2.8 All-Electron Method

Besides the pseudopotential approach, there exist calculation methods to obtain the states of all electrons (core and valence electrons). One of the methods that have been widely used for all-electron (including both valence and core electrons) calculation has its origin in the APW (augmented plane wave) method proposed by Slater (1937) [30]. In APW, wave functions are represented by plane waves for interstitial region that are connected to wave functions of (atomic) core region. The potential of the core region is approximated with muffin-tin-type functions. LAPW (linearized APW) developed by Anderson (1975) [31] enabled efficient calculation by linearizing radial wave functions with respect to energy, with which the calculation can be solved as a generalized eigenvalue problem. To lift the restriction of spherical wave functions due to the muffin-tin approximation, it was further developed to FLAPW (full-potential LAPW) [32]. WIEN2k [33] is a well-known simulation package for calculations based on FLAPW.

There is also a lineage of the KKR method [34], which was originally proposed by Koringa (1947), Kohn, and Rostoker (1954). This is also called the Green function method, as the method defines the one-particle Green function of the Kohn–Sham equation. Calculation of wave functions and eigenvalues is circumvented, and charge density or local density of states can be obtained directly through the Green function. It has been confirmed by many studies that results obtained by KKR and APW exhibit good agreement with each other.

2.2.9 Beyond LDA and GGA

While DFT calculations with LDA and GGA have enjoyed much success, it is also known that there are a number of problems that cannot be addressed with these approximations. Attempts to eliminate these problems, which are often called “Beyond LDA and GGA,” include the $+U$ method (often called DFT + U , LDA + U or GGA + U as well) [35], the GW approximation [36], and DFT–HF hybrid functionals [16]. In general, these advanced methods require much increased computational resources or introduction of additional, adjustable parameters.

It has been known that the “standard” DFT calculation with LDA or GGA can fail dramatically in materials containing electrons with strong correlation, whose ground state is characterized by pronounced localization of electrons. A typical and serious problem is the substantial underestimation of the band gap energy. This is because the approximate exchange–correlation functionals do not cancel out the electronic self-interaction, which makes charge density portions associated with one atom repel each other, in the Hartree (Coulomb) term, resulting in over-delocalized valence electrons. The $+U$ approach is based on the Hubbard model, which considers the interaction between electrons within the same atom (on-site Coulomb interaction), and corrects the self-interaction error in the standard DFT that tends to overly delocalize the metal d and f states. In the $+U$ approach, the strength of the on-site interactions is described by parameters U and J , which represent on-site Coulomb and on-site exchange contributions, respectively. These parameters can be evaluated by ab initio calculations, but usually determined empirically (i.e., treated as adjustable parameters) to reproduce experimental results. One of the main advantages of this method is that computational cost is not much different from the standard DFT calculation.

If we denote the m th energy level in the Kohn–Sham equation of a N -electron system as $\epsilon_M^{(N)}$, the actual (experimental) energy gap is $E = \epsilon_{N+1}^{(N+1)} - \epsilon_N^{(N)}$. In a standard DFT calculation, however, the gap is obtained as $E_{\text{DFT}} = \epsilon_{N+1}^{(N)} - \epsilon_N^{(N)}$, resulting in the underestimation by $\Delta = \epsilon_{N+1}^{(N+1)} - \epsilon_{N+1}^{(N)}$. The GW approximation is a way to correct this discrepancy based on the quantum theory of many-body system. In the approximation, Δ is written as the product between the one-particle Green’s function (G) and the screened Coulomb interaction (W), $\Delta = iGW$, where G and W are obtained using the HF approximation. It has been shown that GW can remarkably improve the evaluation of the band gap energy for the cases where LDA works to some extent (e.g., the band gap is underestimated but not completely closed). A major disadvantage of GW is the requirement of tremendous increase in computational cost.

As explained in Sect. 2.1.2, the exchange interaction is correctly implemented in the HF method. One way to circumvent the problem of inaccurate representation of the exchange energy in the standard DFT is therefore to incorporate a portion of exact exchange from the HF method. The exact exchange functional in HF is written as

$$E_X^{\text{HF}} = -\frac{1}{2} \sum_{i,j} \iint \psi_i^*(\mathbf{r}_1) \psi_j^*(\mathbf{r}_1) \frac{1}{r_{12}} \psi_i(\mathbf{r}_2) \psi_j(\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2 \quad (2.83)$$

where $\psi(\mathbf{r})$ is one-electron Bloch states of the system. The most popular B3LYP functional (standing for “Becke, three-parameter, Lee-Yang-Parr”) writes the hybrid exchange–correlation functional as $E_{XC}^{\text{B3LYP}} = E_X^{\text{LDA}} + a_0(E_X^{\text{HF}} - E_X^{\text{LDA}}) + a_X(E_X^{\text{GGA}} - E_X^{\text{LDA}}) + E_C^{\text{LDA}} + a_C(E_C^{\text{GGA}} - E_C^{\text{LDA}})$, where a_0 , a_X and a_C are parameters. The DFT–HF hybrid functional method also requires substantial increase in computational effort.

2.2.10 Evaluation of Physical Quantities

The total energy of the system, E_{tot} , is expressed as

$$E_{\text{tot}} = \sum_k \sum_n^{\text{occ}} \varepsilon_{kn} - \frac{1}{2} \int V_{\text{coul}}(r) \rho(r) dr + \int [\varepsilon_{\text{xc}}(r) - \mu_{\text{xc}}(r)] \rho(r) dr + E_{\text{Ewald}} \quad (2.84)$$

where E_{Ewald} is the Ewald summation representing interaction between nuclei (ions). In the NCPP formalism, we get

$$\begin{aligned} E_{\text{tot}} = & \frac{1}{2} \sum_k f_k \sum_n^{\text{occ}} f_n \sum_G |k+G|^2 |C_{k+G}^n|^2 + \Omega_a \sum_G V_{\text{loc}}^{\text{pp}}(G) \rho(-G) \\ & + \sum_k f_k \sum_n^{\text{occ}} f_n \sum_G \sum_{G'} C_{k+G}^{n*} C_{k+G'}^n V_{\text{nloc}}^{\text{pp}}(k+G, k+G') \\ & + \frac{1}{2} \Omega_a \sum_G V_{\text{coul}}(G) \rho(-G) \\ & + \Omega_a \sum_G \varepsilon_{\text{xc}}(G) \rho(-G) + E_{\text{Ewald}} \end{aligned} \quad (2.85)$$

Considering the fact that the diverging terms $V_{\text{loc}}^{\text{pp}}(G)|_{G=0}$ and $V_{\text{coul}}(G)|_{G=0}$ offset with the diverging term in E_{Ewald} , we obtain

$$\begin{aligned}
 E_{\text{tot}} = & \frac{1}{2} \sum_k f_k \sum_n^{\text{occ}} f_n \sum_G |k+G|^2 |C_{k+G}^n|^2 + \Omega_a \sum_{G \neq 0} V_{\text{loc}}^{\text{pp}}(G) \rho(-G) \\
 & + \sum_k f_k \sum_n^{\text{occ}} f_n \sum_G \sum_{G'} C_{k+G}^{n*} C_{k+G'}^n V_{\text{nloc}}^{\text{pp}}(k+G, k+G') \\
 & + \frac{1}{2} \Omega_a \sum_{G \neq 0} V_{\text{coul}}(G) \rho(-G) \\
 & + \Omega_a \sum_G \varepsilon_{\text{xc}}(G) \rho(-G) + E'_{\text{Ewald}} + \sum_a \frac{\alpha_a Z_a}{\Omega_a}
 \end{aligned} \tag{2.86}$$

Here, Z_a is the number of valence electrons of each atom and α_0 is given by

$$\alpha_a = \int_{\Omega_a} \left(V_a^{\text{pp,loc}}(r) - \left(-\frac{Z_a}{r} \right) \right) d\mathbf{r} = 4\pi \int_0^\infty r^2 \left(V_a^{\text{pp,loc}}(r) + \frac{Z_a}{r} \right) dr \tag{2.87}$$

E'_{Ewald} is the Ewald sum subtracted by the diverging term, given as

$$\begin{aligned}
 E'_{\text{Ewald}} = & \sum_a \sum_{a'} Z_a Z_{a'} \sum_{G \neq 0} \frac{2\pi}{\Omega_a |G|^2} \exp[-i\mathbf{G} \cdot (\mathbf{r}_a - \mathbf{r}_{a'})] \exp\left(-\frac{|G|^2}{4\gamma^2}\right) \\
 & + \frac{1}{2} \sum_a \sum_{a'} Z_a Z_{a'} \sum_R \frac{\text{erfc}(|\mathbf{r} + \mathbf{r}_{a'} - \mathbf{r}_a| \gamma)}{|\mathbf{r} + \mathbf{r}_{a'} - \mathbf{r}_a|} - \sum_a \frac{Z_a^2 \gamma}{\sqrt{\pi}} - \frac{Z^2 \pi}{2\Omega_a \gamma^2}
 \end{aligned} \tag{2.88}$$

where γ is a parameter such that the series expansion converges fast and $Z = \sum_a Z_a$.

The force exerted on atom a , \mathbf{F}_a , is given as the derivative of the total energy with respect to \mathbf{r}_a ,

$$\begin{aligned}
 \mathbf{F}_a = & -\frac{\partial E_{\text{tot}}}{\partial \mathbf{r}_a} = -\frac{1}{\Omega_a} \sum_k f_k \sum_n^{\text{occ}} f_n \sum_G \sum_{G'} C_{k+G}^{n*} C_{k+G'}^n i(\mathbf{G}' - \mathbf{G}) \exp[-i(\mathbf{G} - \mathbf{G}')] \\
 & \cdot \mathbf{r}_a \times [V_a^{\text{pp,loc}}(\mathbf{G} - \mathbf{G}') + V_a^{\text{pp,nloc}}(\mathbf{k} + \mathbf{G}, \mathbf{k} + \mathbf{G}')] - \frac{\partial E'_{\text{Ewald}}}{\partial \mathbf{r}_a}
 \end{aligned} \tag{2.89}$$

The last term can be written as

$$\begin{aligned}
\frac{\partial E'_{\text{Ewald}}}{\partial \mathbf{r}_a} = & - \sum_{a'} Z_a Z_{a'} \frac{4\pi}{\Omega_a} \sum_{\mathbf{G} \neq 0} \frac{\mathbf{G}}{|\mathbf{G}|^2} \sin\{\mathbf{G} \cdot (\mathbf{r}_a - \mathbf{r}_{a'})\} \exp\left(-\frac{|\mathbf{G}|^2}{4\gamma^2}\right) \\
& + \sum_{a'} Z_a Z_{a'} \sum_{\mathbf{R}} \frac{\mathbf{R} + \mathbf{r}_{a'} - \mathbf{r}_a}{|\mathbf{R} + \mathbf{r}_{a'} - \mathbf{r}_a|^3} \\
& \times \left\{ \text{erfc}(|\mathbf{R} + \mathbf{r}_{a'} - \mathbf{r}_a|\gamma) \right. \\
& \left. - |\mathbf{R} + \mathbf{r}_{a'} - \mathbf{r}_a|\gamma \frac{\partial \text{erfc}(|\mathbf{R} + \mathbf{r}_{a'} - \mathbf{r}_a|\gamma)}{\partial (|\mathbf{R} + \mathbf{r}_{a'} - \mathbf{r}_a|\gamma)} \right\}
\end{aligned} \tag{2.90}$$

The local term can be rewritten as below for faster calculation,

$$\begin{aligned}
& - \frac{1}{\Omega_{at}} \sum_k f_k \sum_n^{\text{occ}} f_n \sum_G \sum_{G'} C_{k+G}^{n*} C_{k+G'}^n i(\mathbf{G}' - \mathbf{G}) \exp[-i(\mathbf{G} - \mathbf{G}') \cdot \mathbf{r}_a] V_a^{\text{pp,loc}}(\mathbf{G} - \mathbf{G}') \\
& = - \frac{1}{\Omega_{at}} \sum_k f_k \sum_n^{\text{occ}} f_n \sum_G \sum_{G'} C_{k+G}^{n*} C_{k+G'}^n i(-\mathbf{G}') \exp[-i\mathbf{G}' \cdot \mathbf{r}_a] V_a^{\text{pp,loc}}(\mathbf{G}') \\
& = \sum_G \rho(-\mathbf{G}) i\mathbf{G} \exp(-i\mathbf{G} \cdot \mathbf{r}_a) V_a^{\text{pp,loc}}(\mathbf{G})
\end{aligned} \tag{2.91}$$

The global stress exerted on the simulation box (supercell), $\sigma_{\alpha\beta}(\alpha, \beta = x, y, z)$, is calculated as the derivative of the total energy with respect to strain. Using $S_a(\mathbf{G}) = \exp(-i\mathbf{G} \cdot \mathbf{r}_a)$, the global stress is expressed as

$$\begin{aligned}
\sigma_{\alpha\beta} = & \frac{1}{\Omega_a} \frac{\partial E_{\text{tot}}}{\partial \varepsilon_{\alpha\beta}} = - \frac{1}{\Omega_a} \sum_k f_k \sum_n^{\text{occ}} f_n \sum_G |C_{k+G}^n|^2 (k+G)_\alpha (k+G)_\beta \\
& - \frac{1}{\Omega_a} \sum_{G \neq 0} \sum_a S_a(\mathbf{G}) \left[\frac{\partial V_a^{\text{pp,loc}}(\mathbf{G})}{\partial (G^2)} 2G_\alpha G_\beta \right. \\
& + V_a^{\text{pp,loc}}(\mathbf{G}) \delta_{\alpha\beta} \left. \right] \rho(-\mathbf{G}) \\
& + \sum_k f_k \sum_n^{\text{occ}} f_n \sum_G \sum_{G'} \sum_l \sum_a S_a(\mathbf{G} - \mathbf{G}') C_{k+G}^{n*} C_{k+G'}^n \frac{\partial}{\partial \varepsilon_{\alpha\beta}} \left[\frac{1}{\Omega_a} V_{a,l}^{\text{pp,nloc}}(k+G, k+G') \right] \\
& + \frac{1}{2} \sum_{G \neq 0} V_{\text{coul}}(\mathbf{G}) \rho(-\mathbf{G}) \left(\frac{2G_\alpha G_\beta}{G^2} - \delta_{\alpha\beta} \right) + \delta_{\alpha\beta} \sum_G [\varepsilon_{\text{xc}}(\mathbf{G}) - \mu_{\text{xc}}(\mathbf{G})] \rho(-\mathbf{G}) \\
& + \frac{1}{\Omega_a} \frac{\partial E_{\text{Ewald}}}{\partial \varepsilon_{\alpha\beta}} - \delta_{\alpha\beta} \frac{Z}{\Omega_a} \sum_a \alpha_a
\end{aligned} \tag{2.92}$$

The Ewald term becomes

$$\begin{aligned} \frac{\partial E_{\text{Ewald}}}{\partial \varepsilon_{\alpha\beta}} &= \frac{2\pi}{\Omega_a} \sum_{G \neq 0} \frac{1}{G^2} \exp\left(-\frac{G^2}{4\gamma^2}\right) \left| \sum_a Z_a \exp(iG \cdot r_a) \right|^2 \\ &\times \left[\frac{2G_\alpha G_\beta}{G^2} \left(\frac{G^2}{4\gamma^2} + 1 \right) - \delta_{\alpha\beta} \right] \\ &+ \frac{1}{2} \gamma \sum_a \sum_{a'} \sum_R Z_a Z_{a'} H'(D\gamma) \frac{D_\alpha D_\beta}{D^2} \Big|_{D=R+r_{a'}-r_a} + \frac{Z^2 \pi}{2\Omega_a \gamma^2} \delta_{\alpha\beta} \end{aligned} \quad (2.93)$$

where $H'(x) = \frac{\partial \text{erfc}(x)}{\partial x} - \frac{\text{erfc}(x)}{x}$.

A practical scheme to evaluate local energy and local stress was established by Shiihara et al. [37] within the framework of the stress density developed by Filippetti and Fiorentini [38]. With the method, one can evaluate the distribution of energy and stress in a system containing nonuniform structure, such as surfaces and grain boundaries. Energy density ($e_{\text{tot}}(\mathbf{r})$) and stress density ($\tau_{\alpha\beta}(\mathbf{r})$) are defined as integrands of macroscopic total energy and stress tensor, respectively, as

$$E_{\text{tot}} = \int_V e_{\text{tot}}(\mathbf{r}) d\mathbf{r} \quad (2.94)$$

$$\sigma_{\alpha\beta} = \frac{1}{V} \frac{\partial E_{\text{tot}}}{\partial \varepsilon_{\alpha\beta}} = \frac{1}{V} \int_V \tau_{\alpha\beta}(\mathbf{r}) d\mathbf{r} \quad (2.95)$$

where V is the total volume of the supercell and $\varepsilon_{\alpha\beta}$ is strain tensor. Therefore, local energy and local stress for partial region indicated by i can be defined, respectively, as

$$E_{\text{tot}}(i) = \int_{V_i} e_{\text{tot}}(\mathbf{r}) d\mathbf{r} \quad (2.96)$$

$$\sigma_{\alpha\beta}(i) = \frac{1}{V_i} \int_{V_i} \tau_{\alpha\beta}(\mathbf{r}) d\mathbf{r} \quad (2.97)$$

where V_i indicates partial volume. The local values are not well defined because the expressions can contain functions that are gauge-dependent, which integrates to zero over V but does not over V_i . The gauge dependency stems from the fact that local energy density can be defined in symmetric and asymmetric expressions. The former is

$$e_{\text{kin},S}(\mathbf{r}) = \frac{1}{2} \sum_i f_i \nabla \psi_i^*(\mathbf{r}) \cdot \nabla \psi_i(\mathbf{r}) \quad (2.98)$$

and the latter is

$$e_{\text{kin},AS}(\mathbf{r}) = -\frac{1}{2} \sum_i f_i \psi_i^*(\mathbf{r}) \nabla^2 \psi_i(\mathbf{r}) \quad (2.99)$$

where ψ_i is a valence wave function and f_i is an occupation number. If we take partial region i such that the symmetric and asymmetric expressions coincide, local energy can be described in a well-defined form. It was shown that the differences between the symmetric and asymmetric expressions for local energy and local stress are proportional to $\nabla^2 \rho$ and $\nabla_\alpha \nabla_\beta \rho$, respectively. Thus, the conditions of gauge dependence for e_{tot} and $\tau_{\alpha\beta}$ are

$$\int_{V_i} \nabla^2 \rho(\mathbf{r}) d\mathbf{r} = 0 \quad (2.100)$$

and

$$\int_{V_i} \nabla_\alpha \nabla_\beta \rho(\mathbf{r}) d\mathbf{r} = 0 \quad (2.101)$$

respectively. As practical ways to divide a supercell to meet the above conditions, Shiihara et al. established a layer-by-layer and Bader integral methods [37].

2.3 Semi-empirical and Empirical Theories for Nanostructure Properties

2.3.1 Semi-empirical Calculation of Electronic State

One of the major disadvantages in the first-principles electronic state calculation is that the calculation requires tremendous computer resources, which severely limits the size of simulation objects. It is already challenging to handle a system consisting of thousands of atoms with a laboratory-class cluster server. When a relatively large simulation cell is required to investigate, e.g., properties of materials with defects, it can be a reasonable way to choose a method of semi-empirical electronic structure calculation, where the Schrödinger equation is solved but with empirically constructed functions and parameters.

The tight-binding (TB) method is a most widely used MO method for semi-empirical electronic structure calculation [39, 40]. The method is based on the assumption that electrons are strongly bound to atoms which they belong to so that they cannot move to other orbitals. In that sense, the method is opposite to free-electron models. Hopping of electron states between different orbitals is, however, allowed to some extent because orbitals are slightly overlapped. It should

be noted here that different definitions of the TB method seem to exist. Nevertheless, the TB method is in most cases considered to be equivalent to the extended Hückel method, where electron–electron interaction is neglected but overlapping (hopping) integral between different orbitals is considered. In usual TB calculations, the self-consistent loop calculation is not performed.

We write the atomic orbital α of the a th atom positioned at \mathbf{r}_a as $\phi_{a\alpha}(\mathbf{r} - \mathbf{r}_a)$. The wave function Ψ^i of electron state i is written as

$$\Psi^i = \sum_{a,\alpha} C_{a\alpha}^i \phi_{a\alpha}(\mathbf{r} - \mathbf{r}_a) \quad (2.102)$$

The Hamiltonian is written with the potential from atom a , V_a , as

$$H = -\frac{1}{2} \nabla^2 + \sum_a V_a(\mathbf{r} - \mathbf{r}_a) \quad (2.103)$$

The Hamiltonian matrix element therefore becomes

$$\begin{aligned} H_{a\alpha b\beta} &= \int \phi_{a\alpha}(\mathbf{r} - \mathbf{r}_a) H \phi_{b\beta}(\mathbf{r} - \mathbf{r}_b) d\mathbf{r} \\ &= \int \phi_{a\alpha}(\mathbf{r} - \mathbf{r}_a) \left\{ -\frac{1}{2} \nabla^2 + \sum_k V_k(\mathbf{r} - \mathbf{r}_k) \right\} \phi_{b\beta}(\mathbf{r} - \mathbf{r}_b) d\mathbf{r} \\ &= \int \phi_{a\alpha}(\mathbf{r} - \mathbf{r}_a) \left\{ -\frac{1}{2} \nabla^2 + V_a(\mathbf{r} - \mathbf{r}_a) + V_b(\mathbf{r} - \mathbf{r}_b) \right\} \phi_{b\beta}(\mathbf{r} - \mathbf{r}_b) d\mathbf{r} \\ &\quad + \int \phi_{a\alpha}(\mathbf{r} - \mathbf{r}_a) \left\{ \sum_{k \neq a,b} V_k(\mathbf{r} - \mathbf{r}_k) \right\} \phi_{b\beta}(\mathbf{r} - \mathbf{r}_b) d\mathbf{r} \end{aligned} \quad (2.104)$$

The last term (the three-center integral) is neglected in conventional TB calculations, which is called the two-center approximation. The Hamiltonian matrix elements (also called the resonance integral) under the two-center approximation are calculated by the direction cosine of atom pairs and parameters, which is shown by Slater and Koster (Slater–Koster table, see Table 2.2) [40]. The overlap integral is defined as

$$S_{a\alpha b\beta} = \int \phi_{a\alpha}(\mathbf{r} - \mathbf{r}_a) \phi_{b\beta}(\mathbf{r} - \mathbf{r}_b) d\mathbf{r} \quad (2.105)$$

and then the generalized eigenvalue problem

Table 2.2 Slater–Koster table (only part). l, m, n are direction cosine from atom a to atom b

$H_{as,bs}$	$= V_{s,s}$	$= V_{ss\sigma}$
H_{as,bp_x}	$= V_{s,x}$	$= lV_{sp\sigma}$
H_{ap_x,bp_x}	$= V_{x,x}$	$= l^2 V_{pp\sigma} + (1 - l^2) V_{pp\pi}$
H_{ap_x,bp_y}	$= V_{x,y}$	$= lm(V_{pp\sigma} - V_{pp\pi})$
H_{ap_x,bp_z}	$= V_{x,z}$	$= ln(V_{pp\sigma} - V_{pp\pi})$

$$\mathbf{H}\mathbf{C} = \mathbf{E}\mathbf{S}\mathbf{C} \quad (2.106)$$

is solved to obtain eigenvalues (energy levels) and eigenfunctions (wave functions).

In a system with periodic boundaries, basis functions are constructed by taking the Bloch sum for a \mathbf{k} -point as follows.

$$\psi_{a\alpha,\mathbf{k}}(\mathbf{r}) = \frac{1}{\sqrt{N}} \sum_l \exp[i\mathbf{k} \cdot (\mathbf{r}_a + \mathbf{R}_l)] \psi_{a\alpha}(\mathbf{r} - \mathbf{r}_a - \mathbf{R}_l) \quad (2.107)$$

Here, \mathbf{r}_a is the position vector of atom a in the fundamental cell, l the index for cells, and \mathbf{R}_l is the translation vector for cell l . N is the number of periodically arranged cells (N is infinity but will be canceled out later). An individual Hamiltonian for each \mathbf{k} -point is constructed, and its eigenvalue problem is to be solved. Diagonal and nondiagonal terms are written as

$$\begin{aligned} H_{a\alpha,a\alpha}^{\mathbf{k}} &= \int \psi_{a\alpha,\mathbf{k}}^*(\mathbf{r}) H \psi_{a\alpha,\mathbf{k}}(\mathbf{r}) d\mathbf{r} \\ &= \sum_l \exp[i\mathbf{k} \cdot \mathbf{R}_l] \int \psi_{a\alpha,\mathbf{k}}^*(\mathbf{r} - \mathbf{r}_i) H \psi_{a\alpha,\mathbf{k}}(\mathbf{r} - \mathbf{r}_i - \mathbf{R}_l) d\mathbf{r} \end{aligned} \quad (2.108)$$

and

$$\begin{aligned} H_{a\alpha,b\beta}^{\mathbf{k}} &= \int \psi_{a\alpha,\mathbf{k}}^*(\mathbf{r}) H \psi_{b\beta,\mathbf{k}}(\mathbf{r}) d\mathbf{r} \\ &= \sum_l \exp[i\mathbf{k} \cdot (\mathbf{r}_j + \mathbf{R}_l - \mathbf{r}_i)] \\ &\quad \int \psi_{a\alpha,\mathbf{k}}^*(\mathbf{r} - \mathbf{r}_i) H \psi_{b\beta,\mathbf{k}}(\mathbf{r} - \mathbf{r}_j - \mathbf{R}_l) d\mathbf{r} \end{aligned} \quad (2.109)$$

respectively.

The total energy of a system, E_{tot} , is given as the sum of the band energy, E_{TB} , and the repulsive energy, E_{rep} ,

$$E_{\text{tot}} = E_{TB} + E_{\text{rep}} \quad (2.110)$$

Here, the band energy is the sum of the energy eigenvalues of occupied states,

$$E_{TB} = 2 \sum_i^{\text{occ}} E^i \quad (2.111)$$

The repulsive energy is often given as the form of simple pairwise functions.

As an example, a set of TB parameters (function forms for \mathbf{H} and \mathbf{S}) for silicon atoms by Kohyama [41] is presented below.

$$E_{\text{rep}} = \frac{1}{2} \sum_{j \neq i} \sum_i \varphi(r_{ij}) \quad (2.112)$$

$$\varphi(r_{ij}) = A_{ij} S(r_{ij}) r_{ij}^{-v} \quad (2.113)$$

$$V_{ll'm} = \eta_{ll'm} S(r_{ij}) r_{ij}^{-v} \quad (2.114)$$

$$S(r_{ij}) = \{1 + \exp[\mu(r_{ij} - R_c)]\}^{-1} \quad (2.115)$$

where r_{ij} is the separation between atoms i and j , and η , v , and μ are parameters. A_{ij} is defined as

$$A_{ij} = b_0 - b_1(Z_i + Z_j) \quad (2.116)$$

Z_i is the effective coordination number of atom i

$$Z_i = \sum_{j \neq i} \exp[-\lambda_1(r_{ij} - R_i)^2] \quad (2.117)$$

$$R_i = \sum_{j \neq i} r_{ij} \exp(-\lambda_2 r_{ij}) \left[\sum_{j \neq i} \exp(-\lambda_2 r_{ij}) \right]^{-1} \quad (2.118)$$

R_c , b_0 , b_1 , λ_1 , and λ_2 are parameters. In addition, the diagonal elements of the Hamiltonian (on-site terms) are constants given as parameters.

2.3.2 Atomistic Modeling Using Empirical Interatomic Potential

To obtain electronic structure and evaluate related physical properties, it is basically needed to solve the Schrödinger equation. However, some relatively sophisticated interatomic models include terms that represent the structure of electrons, e.g., charge density, so that the models can evaluate physical properties determined by the electron structure, such as magnetism and ferroelectricity. These approaches may be a solution of problems that require a very large number of atoms and therefore cannot be addressed by electron structure calculations.

The shell model [42] is a crude model to mimic charge polarization around atoms by pairs of cation and anion particles (a cation–anion pair corresponds to an atom and surrounding charge). In this way, one can simulate changes in atom positions and charge polarization by optimizing the structure of the particles

according to the environment. It has been demonstrated that the model works for perovskites to reproduce ferroelectricity.

The dipole potential model by Tangney and Scandolo [43] is originated in the same idea to represent charge polarization around atoms but in a slightly different way. The TS model incorporates electrostatic dipole vectors assigned to atoms. Because of the similarity in the fundamental concepts, there seems to be no significant difference in the two models except technical matters in computation.

An interatomic model was developed by Dudarev and Derlet [44] to represent the effect of magnetism in Fe. The model, which describes potential energy of atoms within the framework of the embedded atom method (EAM) [45], was constructed so that the effect of paramagnetic–ferromagnetic transition on potential energy difference is represented by employing an additional term in the embedding energy function.

Though abovementioned empirical atomistic models have enjoyed successful representation of the objective properties they are designed for, such approaches are available only for a limited variety of properties. For example, electrostatic calculations are necessary for the evaluation of the band gap energy, even for qualitative analysis.

2.4 Conclusion

This chapter gave an overview of methods for computational analysis of solid materials. To evaluate physical properties originated in electron states, it is necessary to perform electron structure calculations, which usually require solving the Schrödinger equation. Currently, *ab initio* DFT seems to be the method of choice for solid materials, especially for problems of multiphysics because with the approach one can evaluate various properties, both mechanical and physical, with an excellent accuracy. In fact, a growing number of researches are being conducted using the approach not only due to the reliability of the theory *par se* but also due to software packages available on the market or for free, which still keep being developed with incorporating new methods that improve the prediction accuracy and the computational efficiency. Owing to seemingly everlasting advance of computational power, it will presumably keep getting easier to deal with larger models (simulation cell containing a large number of atoms) that are necessary to address problems of complex structures.

It is also indispensable, however, to employ other methods that are not *ab initio*-based but computationally efficient when necessary. In a theoretical approach with numerical simulations, a typical pitfall is producing artifacts due to the limitation of cell size, i.e., if the property in question has a strong size effect, setting up a sufficiently large simulation cell should be prioritized than conducting rigorous electronic structure calculations. One should always be aware of the theoretical

background of the computational method and its drawbacks as there is no versatile method. It should also be noted that computational methods for electronic structure calculations are making a rapid progress. Present challenges referred to in this chapter may be addressed in the near future.

Appendix: First-Principles and Ab Initio

The term “ab initio” is often used as a synonym of “first-principles,” as is found in many scientific papers. Rigorously speaking, however, they have different meanings. Ab initio, meaning “from the beginning” in Latin, is calculation of electron states using no empirical parameters where the usage of only fundamental physical constants, such as Planck constant, electron mass, elementary charge, are allowed. The term “ab initio” should be used when the calculation is wave-function-based theories as opposed to DFT, which is density-based. Thus, it is strange to say “ab initio DFT” although it is not rare to find such combination of the terms in scientific reports. To be exact, when a DFT calculation is done without empirical parameters, it should be called “first-principles DFT.” However, in this book, we do not stick to the slight difference of the meaning between “ab initio” and “first-principles,” and we accept the use of “ab initio” for DFT calculations.

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