

Chapter 2

Theoretical Methods and Approximations

This chapter describes the theoretical approaches and approximations used in standard first principles calculations. First, the Born Oppenheimer approximation is stated. Next, an overview of the basic formulation of density functional theory (DFT) is given, underlying its merits in describing various materials and their properties, but also pointing out the aspects which need further improvements. The Kohn–Sham ansatz, which provides a means of calculating properties of many-body system using independent-particle methods, is presented along with practical schemes for solving the resulting Kohn–Sham equations. Finally, the DFT+U method and its implementation within a pseudopotential-plane wave framework are introduced.

2.1 Born Oppenheimer Approximation

The adiabatic approximation of Born and Oppenheimer allows one to treat the electrons and nuclei of a real system separately as a consequence of the large mass difference between them [1]. Being much lighter than the ions, the electrons move in a solid much faster than the nuclei, which makes it possible to consider the electronic configuration as completely relaxed in its ground state at each position of the ions during their motion. Thus the nuclei can be treated adiabatically, leading to a separation of the electronic and nuclear degrees of freedom in the many-body wavefunction. The only exception to this are the lightest elements (especially H), where the ions require quantum mechanical treatments. Although the Born Oppenheimer approximation provides a major simplification to the complicated many-body problem by transforming it into the solution of the electronic dynamics in some frozen configuration of nuclei, further approximations are required to perform efficient and accurate total energy calculations. These include *density functional theory* (DFT) to model the electron–electron

interactions, *pseudopotential theory* to describe the electron–ion interactions, and *supercell approach* to model systems with aperiodic geometries.

2.2 Density Functional Theory

Since its theoretical foundation in the mid-1960s [2], DFT of Hohenberg and Kohn has demonstrated a large predictive power in first principles studies of the study of the ground state properties of real materials. Its conceptual advantage lies in reformulating the problem of an interacting electron gas under an external (ionic) potential in terms of the ground state electronic charge density, thereby bypassing the necessity to calculate the many-body electron wavefunctions. The N particle system of interacting particles with $3N$ degrees of freedom is reduced to a significantly more tractable problem, which deals with a function (density) of only three variables. The many-body effects incorporated in the exchange-correlation potential are typically approximated within either the local density approximation or the generalized gradient approximation. The formulation applies to any system of interacting particles in an external potential $V_{\text{ext}}(\mathbf{r})$, including any problem of electrons and fixed nuclei, where the Hamiltonian can be written as

$$H = - \sum_i \frac{\hbar^2}{2m_e} \nabla_{\mathbf{r}_i}^2 + \sum_i V_{\text{ext}}(r_i) + \frac{e^2}{2} \sum_{i \neq j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} + \sum_{i \neq j} \frac{Z_i Z_j e^2}{|\mathbf{R}_i - \mathbf{R}_j|} \quad (2.1)$$

The first term in this equation corresponds to the kinetic energy of the interacting electrons, the second term is the external potential acting on the electrons due to the ions, the third term is the electron Coulomb interaction, and the last term is the interaction energy of the nuclei. The latter is called Madelung energy and, as far as the electron degrees of freedom are concerned, is simply a constant. For such a system, Hohenberg and Kohn demonstrated a one-to-one correspondence between the external potential and the ground state density $n(\mathbf{r})$, which allows to express the former as a functional of the latter. Since the Hamiltonian is thus fully determined (except for a constant shift of the energy), it follows that all properties of the system can be found given only the ground state density $n(\mathbf{r})$. This result allowed Hohenberg and Kohn to further prove the existence of an energy functional of the density $E[n(\mathbf{r})]$, which assumes its minimum value for the correct ground state density. For practical purposes, it is convenient to write this energy functional $E[n(\mathbf{r})]$ in terms of a contribution due to the external potential acting on the particles and a universal functional $F[n(\mathbf{r})]$ representing both the kinetic energy and the Coulomb interaction,

$$E[n(\mathbf{r})] = \int V_{\text{ext}}(\mathbf{r}) n(\mathbf{r}) d\mathbf{r} + F[n(\mathbf{r})] \quad (2.2)$$

The minimization of energy functional $E[n(\mathbf{r})]$ with respect to the charge density with the constraint of fixed number of electrons gives the ground state energy and the ground state charge density from which all other physical properties can be extracted. It should be pointed out, however, that in spite of the universality of $F[n(\mathbf{r})]$ no explicit expressions for this functional are known to date.

In 1965, Kohn and Sham readdressed the problem of minimizing the Hohenberg-Kohn density functional (Eq. 2.2) directly with an improved strategy that maps the original interacting problem into an auxiliary non-interacting one [3]. This is achieved by expressing the charge density $n(\mathbf{r})$ as

$$n(\mathbf{r}) = \sum_i |\psi_i(\mathbf{r})| \quad (2.3)$$

where ψ_i 's are the single-particle wavefunctions for the non-interacting electron gas with ground state charge density $n(\mathbf{r})$, and the sum is over all occupied single-particle states.

The $F[n(\mathbf{r})]$ functional is now expressed as

$$F[n(\mathbf{r})] = T_s[n(\mathbf{r})] + \frac{e^2}{2} \int \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}d\mathbf{r}' + E_{xc}[n(\mathbf{r})] \quad (2.4)$$

where the first term corresponds to the kinetic energy of a non-interacting electron gas at the same density $n(\mathbf{r})$, the second term is the classical Coulomb interaction energy (the Hartree term), and the last term $E_{xc}[n(\mathbf{r})]$ represents the quantum mechanical exchange-correlation energy. This term accounts for the differences between the non-interacting fictitious system and the real interacting one, collecting the contributions from the non-classic electrostatic interaction and the differences in their corresponding kinetic energies. The success of the Kohn-Sham approach ultimately lies in the fact that $E_{xc}[n(\mathbf{r})]$, which contains the many-body contributions, is a small fraction of the total energy, and although not known exactly, it can be *approximated* surprisingly well. These approximations, discussed in Sect. 2.3, are at present the strength and the limitation of DFT, providing efficient yet not exact reformulation of the quantum mechanical problem, respectively.

If the energy functional defined in Eq. 2.2 and Eq. 2.4 is now varied with respect to the wavefunctions ψ_i 's subject to the orthonormality constraint, the following set of Schrodinger equations is obtained

$$\left[-\frac{\hbar^2}{2m_e} \nabla_{\mathbf{r}}^2 + v_{\text{eff}}(\mathbf{r}, n(\mathbf{r})) \right] \psi_i(\mathbf{r}) = \varepsilon_i \psi_i(\mathbf{r}) \quad (2.5)$$

where the effective potential $v_{\text{eff}}(\mathbf{r}, n(\mathbf{r}))$ is given as

$$v_{\text{eff}}(\mathbf{r}, n(\mathbf{r})) = V_{\text{ext}}(\mathbf{r}) + e^2 \int \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + \frac{\delta E_{xc}[n(\mathbf{r})]}{\delta n(\mathbf{r})} \quad (2.6)$$

Equations 2.5 and 2.6 are called the Kohn–Sham equations and have to be solved self-consistently because of the dependence of $v_{\text{eff}}(\mathbf{r})$ on $n(\mathbf{r})$. It should be emphasized here that the Kohn–Sham procedure introduces a one-body Hamiltonian representing a single-particle electron in the mean field created by the nuclei and by all other electrons. However, it assigns no formal interpretation to the calculated orbitals and the eigenvalues. Indeed, the sum of the single-particle Kohn–Sham eigenvalues does not give the total electronic energy because this would overestimate the effect of the electron–electron interactions in the Hartree energy and in the exchange–correlation energy. More specifically, the Kohn–Sham eigenvalues are not the energies of the single-particle electron states, but rather the derivatives of the total energy with respect to the occupation numbers of these states [4]. The only exception is the highest eigenvalue in a finite system (atomic or molecular), which represents the unrelaxed ionization [5].

2.3 Approximations for the Exchange–Correlation Energy Functional

In principle, the solution of the Kohn–Sham equations would yield the exact ground state energy of the interacting electron gas problem. However, as mentioned earlier, the exact exchange–correlation functional $E_{\text{xc}}[n(\mathbf{r})]$ for an inhomogeneous interacting electron gas is not known for general $n(\mathbf{r})$. To proceed further, approximations to this functional are required. The most common and extensively tested approximation is the local density approximation (LDA), in which $E_{\text{xc}}[n(\mathbf{r})]$ for the inhomogeneous system is constructed from a parametrized form of the exchange–correlation energy density of the homogeneous electron gas $\epsilon_{\text{xc}}^{\text{hom}}$ [3],

$$E_{\text{xc}}[n(\mathbf{r})] = \int \epsilon_{\text{xc}}(\mathbf{r})n(\mathbf{r})d\mathbf{r} \quad (2.7)$$

and

$$\frac{\delta E_{\text{xc}}[n(\mathbf{r})]}{\delta n(\mathbf{r})} = \frac{\partial [n(\mathbf{r})\epsilon_{\text{xc}}(\mathbf{r})]}{\partial n(\mathbf{r})} \quad (2.8)$$

with $\epsilon_{\text{xc}}(\mathbf{r}) = \epsilon_{\text{xc}}^{\text{hom}}[n(\mathbf{r})]$. Several parametrizations for the exchange–correlation energy of a homogeneous electron gas exist in the literature. They are based on Monte Carlo simulations and many-body perturbation theory, and use interpolation formulas to link exact results for the exchange–correlation energy of high-density electron gases and those corresponding to the intermediate and low-density electron systems [3, 6, 7, 8, 9]. Because of the local nature of the exchange–correlation energy functional within the LDA, this approach is expected to be valid for systems with slowly varying electron density such as simple metals or intrinsic semiconductors. In all other cases, the LDA is indeed unpredictable and its justification relies mainly on its ability to reproduce experimental ground state properties of

many solids, especially covalent or metallic. Although recent work has shown that the success of LDA can be partially attributed to the fact that the LDA gives the correct sum rule for the exchange-correlation hole (that is, there is a total electronic charge of one electron excluded from the neighborhood of a given electron), there is no general argument explaining why it works remarkably well [10, 11, 12].

In spite of the success of the LDA in capturing the exchange-correlation effects in many systems, the approximation generally overestimates the cohesive energies of solids and predicts shorter equilibrium bond lengths than found experimentally. Errors in the structural properties calculated within the LDA are usually small for crystals with covalent or metallic bonds, but it is well known that the hydrogen bond cannot be described accurately within this approximation. These shortcomings have led to the development of various generalized gradient approximations (GGAs) with marked improvement over the LDA in many cases [13, 14]. In the GGA, the $E_{xc}[n(\mathbf{r})]$ is a functional density as well as its local spatial variations:

$$E_{xc}^{GGA}[n(\mathbf{r})] = \int \epsilon_{xc}^{GGA}(n(\mathbf{r}), |\nabla n(\mathbf{r})|) n(\mathbf{r}) d\mathbf{r} \quad (2.9)$$

The approximation usually gives a better description of the structural properties of real materials (in particular, the binding energies) as compared to the LDA. It is expected to work better in the case of inhomogeneous systems, like transition metals, where the LDA typically fails. Several expressions of the exchange energy density in the GGA formulation are available in the literature; two of most popular are the Perdew–Wang-91 (PW91) and the Perdew–Burke–Ernzerhof (PBE) functionals [5, 11]. Although both functionals produce similar results in the calculations of lattice constants, bulk moduli, and atomization energies, they can lead to numerical differences when surface effects are present. In this thesis, both the PW91 and the PBE formulations of the GGA will be used.

2.4 Periodic Systems: Bloch’s Theorem

In the previous section it was established that certain observables of the many-body problem can be mapped into equivalent observables in an effective single-particle system. In spite of the great simplification of the original problem, two difficulties still remain for practical and efficient computations: a wavefunction must be calculated for each of the $\sim 10^{23}$ number of electrons in the system, and the correct description of the electronic wavefunctions, extending over the entire solid, requires an infinite basis set. To overcome both problems, calculations involving periodic systems are performed using Bloch’s theorem to describe the electronic wavefunctions.

The theorem states that in a solid characterized by the periodic potential $V(\mathbf{r} + \mathbf{R}) = V(\mathbf{r})$, where $\mathbf{R}$ is a direct lattice vector, the electronic wavefunction can be written as the product of a cell-periodic part and a wave-like part

$$\psi_{n\mathbf{k}}(\mathbf{r}) = \exp[i\mathbf{k} \cdot \mathbf{r}] u_{n\mathbf{k}}(\mathbf{r}) \quad (2.10)$$

where $\mathbf{k}$ is a vector in the first Brillouin zone (BZ) of the reciprocal lattice, n is the band index classifying states corresponding to the same $\mathbf{k}$ -vector, and $u_{n\mathbf{k}}(\mathbf{r})$ is a function with the periodicity of the unit cell, i.e., $u_{n\mathbf{k}}(\mathbf{r} + \mathbf{R}) = u_{n\mathbf{k}}(\mathbf{r})$. This cell-periodic part can be expanded using a discrete set of plane waves whose wave vectors are reciprocal lattice vectors of the crystal,

$$u_{n\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{G}} c_{\mathbf{k},n}(\mathbf{G}) \exp[i\mathbf{G} \cdot \mathbf{r}] \quad (2.11)$$

Effectively, the single-particle wavefunction can be expressed as a sum of plane waves,

$$\psi_{\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{G}} c_{\mathbf{k},n}(\mathbf{G}) \exp[i(\mathbf{k} + \mathbf{G}) \cdot \mathbf{r}] \quad (2.12)$$

Electronic states are allowed only at the set of $\mathbf{k}$ points imposed by the boundary conditions. The density of these $\mathbf{k}$ points is proportional to volume of the solid, but only a finite number of electronic states are occupied at each $\mathbf{k}$ point. By virtue of Bloch's theorem, the infinite number of wavefunctions of an extended system is now represented by a finite number of electronic wavefunctions at an infinite set of $\mathbf{k}$ points.

2.5 k-Point Sampling

The calculation of many physical quantities such as the total energy of a solid requires integration of functions with Bloch vector $\mathbf{k}$ performed over the BZ. Using the symmetry of the crystal, the integration can be conveniently confined in a smaller region of the BZ, the irreducible wedge of the Brillouin zone (IBZ). The approach can be further improved by the use of the special k-point integration techniques, which allow to perform reciprocal space integrations with a finite number of $\mathbf{k}$ -vectors in the IBZ. For example, in a total energy calculation, after obtaining the single-particle wavefunctions, $\psi_{\mathbf{k}n}(\mathbf{r})$, one has to construct the corresponding charge density $n(\mathbf{r})$ first summing over bands and then integrating over the BZ. The typical practice for this integration is to replace it by discrete sum over a few carefully chosen special $\mathbf{k}$ points. That is,

$$n_{\mathbf{k}}(\mathbf{r}) = 2 \sum_n |\psi_{\mathbf{k}n}(\mathbf{r})|^2 \quad (2.13)$$

$$n(\mathbf{r}) = \frac{\Omega}{(2\pi)^3} \int n_{\mathbf{k}}(\mathbf{r}) d\mathbf{k} \approx \sum_{i=1}^N \omega(k_i) n_{\mathbf{k}_i}(\mathbf{r}) \quad (2.14)$$

where $\mathbf{k}_i \in \text{IBZ}$ and $\omega(\mathbf{k}_i)$ is the relative weight associated with $\mathbf{k}_i$. Several schemes to construct these points have been proposed in the literature with the sampling accuracy easily checked by the convergence tests involving denser sets of $\mathbf{k}$ points [15, 16, 17].

2.6 Plane Waves, Pseudopotentials, and the Projector Augmented Wave Method

As shown in Eq. 2.12, the single-particle wavefunctions at each $\mathbf{k}$ point in the BZ of a given crystal can be expanded in a discrete set of plane waves. In principle, an infinite plane wave basis set is required to expand these wavefunctions. However, in practical calculations this set is truncated by an energy cutoff E_{cut} such that only plane waves with kinetic energy $\frac{\hbar^2}{2m}|\mathbf{k} + \mathbf{G}|^2$ less than E_{cut} are included. The choice of E_{cut} affects the accuracy of the calculations and should be carefully checked with simple convergence tests, i.e. the physical results obtained from the calculations should be converged with respect to this cutoff.

When plane waves are used as a basis set, the Kohn–Sham equations take on a particularly simple form

$$\sum_{\mathbf{G}'} \left[\frac{\hbar^2}{2m_e} |\mathbf{k} + \mathbf{G}|^2 \delta_{\mathbf{G}\mathbf{G}'} + v_{\text{eff}}(\mathbf{G} - \mathbf{G}') \right] c_n(\mathbf{k} + \mathbf{G}') = \varepsilon_{\mathbf{k}n} c_n(\mathbf{k} + \mathbf{G}) \quad (2.15)$$

Solution of the Hamiltonian matrix in Eq. 2.15 proceeds by conventional diagonalization techniques, taking advantage of the Fast Fourier Transformations. Since the size of the matrix is determined by the choice of E_{cut} , its diagonalization can be formidable for systems that contain both valence and core electrons. This is because a very large number of plane waves are required to expand the tightly bound core orbitals and to follow the rapid oscillations of the wavefunctions of the valence electrons in the core region. To circumvent this problem the pseudopotential approximation [18, 19], which allows the electronic wavefunctions to be expanded using a much smaller number of plane wave basis states, is widely used. The approximation is based on the assumption that most physical and chemical properties of a system depend, to a very good approximation, only on the distribution of the valence electrons, while the ionic cores (the nuclei and the most internal electronic cloud) can be considered as frozen in their atomic configurations. The strong ionic core potential is thus replaced by a weaker pseudopotential acting on a set of nodeless pseudowavefunctions rather than the true valence wavefunctions.

In addition to reducing the number of plane wave basis sets needed to expand the electronic wavefunctions, the pseudopotential approximation has many other advantages. The removal of the core electrons, which contribute most to the total energy of the system (typically a thousand times more than the valence electrons),

means that the total energy differences between various ionic configurations will be taken between much smaller numbers. This relaxes the required accuracy for the total energy calculations as compared to the all-electron calculations. In addition, the relativistic effects can be easily incorporated into the potential while treating the valence electrons non-relativistically.

In this work, the projector augmented wave (PAW) method of Blöchl [20], combining the advantages of full potential augmented plane wave approach (by keeping the nodal structure of the wavefunctions inside the core) and the simplicity and numerical efficiency of pseudopotentials, will be used. The computational times for such calculations are slightly higher than for pseudopotentials, while the accuracy is at the level of most accurate full potential linear augmented plane wave methods since PAW provides access to the full charge and spin density. The method is based on a mapping between the true valence wavefunctions $\psi_n(\mathbf{r})$ with their complete nodal structure and the smooth auxiliary wavefunctions $\tilde{\psi}_n(\mathbf{r})$ having a rapidly convergent plane wave expansion via a linear transformation T ,

$$|\psi_n\rangle = \hat{T}|\tilde{\psi}_n\rangle \quad (2.16)$$

The transformation is assumed to be unity except for a sphere centered on the nucleus (so-called augmentation region), whose cutoff radius r_c^a should be chosen such that there is no overlap between neighboring augmentation spheres. The transformation can be written as

$$\hat{T} = 1 + \sum_a \hat{T}^a \quad (2.17)$$

where a is an atom index. All physical quantities like $\langle\psi_n|A|\psi_n\rangle$ can be easily calculated in the pseudo Hilbert space representation $\langle\tilde{\psi}_n|\tilde{A}|\tilde{\psi}_n\rangle$ (with $\tilde{A} = \hat{T}^\dagger A \hat{T}$) rather than directly from the true wavefunctions. Similarly, the variational principle for the total energy,

$$\frac{\partial E[\hat{T}|\tilde{\psi}]}{\partial \langle\tilde{\psi}|} = \varepsilon \hat{T}^\dagger \hat{T}|\tilde{\psi}\rangle \quad (2.18)$$

gives an equivalent of the KS equations for the pseudowavefunctions, and so the calculations for the ground state can now be carried out in the pseudo Hilbert space, which can be efficiently spanned by the plane wave expansion. For more details, please refer to Appendix C.

2.7 Aperiodic Structures

Most of the standard electronic structure algorithms rely on the periodic nature of the studied systems for actual calculations. Semi-periodic structures such as surfaces are typically modeled using a slab geometry, in which a number of bulk

layers separated by a vacuum region are repeated periodically. This approach allows the use of standard methods described in the previous sections to model surfaces, provided that a large vacuum region and a sufficient number of bulk layers are used in the calculations to ensure that the introduced artificial periodicity does not affect the physical results.

Relative structural stabilities of various atomic arrangements on a given surface can be analyzed using well-established formalisms in terms of chemical potentials of the relevant species [21]. For a bare surface, for example, the surface formation energy E_{surf} is written as

$$E_{\text{surf}} = E_{\text{surf}}^{\text{tot}} - \sum_i \mu_i N_i \quad (2.19)$$

where $E_{\text{surf}}^{\text{tot}}$ is the total energy of the slab, N_i is the number of atoms of type i in the slab, and μ_i is the corresponding chemical potential. Assuming that the surface is in equilibrium with the bulk, which sets the upper limits on the μ_i 's, a phase diagram can be calculated to determine stabilities of different surfaces as a function of stoichiometry.

2.8 DFT+U

In spite of the great success of DFT in predicting the fundamental properties of molecules and materials, there still exist classes of systems and phenomena for which current forms of the theory fail or are inadequate. These include the strongly correlated electron materials, such as actinides and middle-to-late transition metal oxides, which contain electrons in d or f shells. The d and f electrons are inherently localized on each metal atom resulting in large intra-atomic exchange and Coulomb energies [22]. The conventional DFT with approximate exchange and correlation does not properly remove the fictitious electron self-interaction; as a consequence, the electron–electron repulsion is predicted to be too large. To reduce this repulsion energy, the electrons incorrectly delocalize, causing invalid predictions such as giving a metallic ground state for FeO and a small band gap for MnO, whereas these materials are believed to be wide gap insulators.

Since its introduction more than two decades ago, the DFT+U method by Anisimov and coworkers has remained to be the most efficient method to describe strong correlations of electrons confined in an atomic region [23, 24, 25]. In this method, the interactions between electrons localized on the same atomic centers (the on-site interactions) are described with a Hartree Fock (HF)-like formalism, while the remaining interactions are treated within DFT [22]. In real calculations, the on-site interaction energy is obtained from a parameterized Hamiltonian (coming from the Hubbard Hamiltonian), rather than from an explicit HF calculation. This Hamiltonian includes the average Coulomb and exchange interactions between electrons of the same angular momentum that are localized on the same atom, labeled as U_I and J_I , respectively. The index I denotes the atomic center on

which the electrons are localized, and l represents their angular momentum. The accuracy of the DFT+U calculations lies in selecting appropriate values for the U and J parameters, which are system-specific. These values can be treated as tunable parameters chosen to reproduce known properties of the system of interest (empirical approach) or can be extracted from constrained DFT calculations.

The energy functional within the DFT+U framework can be written as

$$E^{\text{DFT+U}}[n(r), n_{llm\sigma}] = E^{\text{DFT}}(n) + E^{\text{on-site}}[n_{llm\sigma}] - E^{dc}[n_{ll\sigma}] \quad (2.20)$$

where $E^{\text{DFT+U}}$ is the total energy of the system, E^{DFT} is the DFT energy of the system based on the total electron density $n(\mathbf{r})$, $E^{\text{on-site}}$ is the HF energy arising from on-site interactions between localized electrons, and E^{dc} is the double counting term which corrects for contributions to the total energy that are included in both E^{DFT} and $E^{\text{on-site}}$. The $E^{\text{on-site}}$ term depends on the number of electrons that occupy localized orbitals centered on atom I and is described by angular momentum l , magnetic number m , and spin σ . These atom-centered, localized orbitals consist of spherical harmonics multiplied by a radial function selected to accurately represent the electronic states of the non-spin-polarized atom. The occupation numbers $n_{llm\sigma}$ can be obtained by projecting the Kohn–Sham DFT orbitals for the total system onto a set of these localized orbitals, while the n_{llm} term corresponds to the total number of electrons for a given spin and angular momentum that are localized on I, i.e. $n_{ll\sigma} = \sum_m n_{llm\sigma}$.

To evaluate Eq. 2.20, the form of $E^{\text{on-site}}$ and E^{dc} must be decided. One approach is to use the rotationally invariant formulation proposed by Dudarev *et al.* [26], which yields the following expression for the total energy functional

$$E^{\text{DFT+U}}[n(r), n_{llm\sigma}] = E^{\text{DFT}}(n) + \sum_{llm\sigma} \frac{U_{ll} - J_{ll}}{2} (n_{llm\sigma} - n_{llm\sigma}^2) \quad (2.21)$$

The first term on the right-hand side of this equation corresponds to the DFT energy obtained using the total electron density and includes the on-site interactions. The second term corrects for the first term by driving the system toward electron densities in which the localized states have occupation numbers of either 0 or 1 ($n_{llm\sigma}$ lies between 0 and 1) [22]. This approach has been shown to lead to an improved description of the electronic structure of many strongly correlated electron systems and will be used in this thesis in the calculations involving rare-earth elements.

References

1. Hohenberg, P., Kohn, W.: Zur Quantentheorie der Molekeln. Ann. Phys. (Leipzig) **84**, 456 (1927)
2. Hohenberg, P., Kohn, W.: Inhomogeneous electron gas. Phys. Rev. **136**(3B), B864–B871 (1964)

3. Kohn, W., Sham, L. J.: Self-consistent equations including exchange and correlation effects. *Phys. Rev.* **140**(4A), A1133–A1138 (1965)
4. Janak, J.F.: Proof that $\frac{\partial E}{\partial n_i} = \varepsilon$ in density-functional theory. *Phys. Rev. B.* **18**(12), 7165–7168 (1978)
5. Perdew, J.P., Parr, R.G., Levy, M., Balduz, J.L.: Density-functional theory for fractional particle number: derivative discontinuities of the energy. *Phys. Rev. Lett.* **49**(23), 1691–1694 (1982)
6. Wigner, E.: On the interaction of electrons in metals.: *Phys. Rev.* **46**(11), 1002–1011 (1934)
7. Vosko, S.H., Wilk, L., Nusair, M.: Accurate spin-dependent electron liquid correlation energies for local spin-density calculations—a critical analysis. *Can. J. Phys.* **58**, 1200 (1980)
8. Ceperley, D.M., Alder, B.J.: Ground state of the electron gas by a stochastic method. *Phys. Rev. Lett.* **45**(7), 566–569 (1980)
9. Perdew, J.P., Zunger, A.: Self-interaction correction to density-functional approximations for many-electron systems. *Phys. Rev. B.* **23**(10), 5048–5079 (1981)
10. Harris, J., Jones, R.O.: The surface energy of a bounded electron gas. *J. Phys. F Metal Phys.* **4**, 1170–1186 (1974)
11. Gunnarsson, O., Lundqvist, B.I.: Exchange and correlation in atoms, molecules, and solids by the spin-density-functional formalism. *Phys. Rev. B* **13**(10), 4274–4298 (1976)
12. Langreth, D.C., Perdew, J.P.: Exchange-correlation energy of a metallic surface: wave-vector analysis. *Phys. Rev. B.* **15**(6), 2884–2901 (1977)
13. Perdew, J.P., Burke, K., Ernzerhof, M.: Generalized gradient approximation made simple. *Phys. Rev. Lett.* **77**(18), 3865–3868 (1996)
14. Perdew, J.P., Wang, Y.: Accurate and simple analytic representation of the electron-gas correlation energy. *Phys. Rev. B* **45**(23), 13244–13249 (1992)
15. Chadi, D.J., Cohen, M.L.: Special points in the Brillouin zone. *Phys. Rev. B* **8**(12), 5747–5753 (1973)
16. Monkhorst, H.J., Pack, J.D.: Special points for Brillouin-zone integrations. *Phys. Rev. B* **13**(12), 5188–5192 (1976)
17. Evarestov, R.A., Smirnov, V.P.: Special points of the Brillouin-zone and thier use in the solid-State theory. *Phys. Status Solidi B* **119**, 9–40 (1983)
18. Phillips, J.C.: Energy-band interpolation scheme based on a pseudopotential. *Phys. Rev.* **112**(3), 685–695 (1958)
19. Yin, M.T., Cohen, M.L.: Theory of ab initio pseudopotential calculations. *Phys. Rev. B* **25**(12), 7403–7412 (1982)
20. Blöchl, P.E.: Projector augmented-wave method. *Phys. Rev. B* **50**(24), 17953–17979 (1994)
21. Qian, G.X., Martin, R.M., Chadi, D.J.: First-principles study of the atomic reconstructions and enegies of Ga- and As-stabilized GaAs(100) surfaces. *Phys. Rev. B* **38**(11), 7649–7663 (1988)
22. Mosey, N.J., Carter, E.: Ab initio evaluation of Coulomb and exchange parameters for DFT+U calculations. *Phys. Rev. B* **57**, 1505–1509 (1998)
23. Anisimov, V.I., Zaanen, J., Andersen, O.K.: Band theory and Mott insulators: Hubbard U instead of Stoner I. *Phys. Rev. B* **44**(3), 943–954 (1991)
24. Anisimov, V.I., Solovyev, I.V., Korotin, M.A., Czyzyk, M.T., Sawatzky, G.A.: Density-functional theory and NiO photoemission spectra. *Phys. Rev. B* **48**(23), 16929–16934 (1993)
25. Solovyev, I.V., Dederichs, P.H., Anisimov, V.I.: Corrected atomic limit in the local-density approximation and the electronic structure of impurities in Rb. *Phys. Rev. B* **50**(23), 16861–16871 (1994)
26. Dudarev, S.L., Botton, G.A., Savrasov, S.Y., Humphreys, C.J., Sutton, A.P.: Electron-energy loss spectra and the structural stability of nickel oxide: An LSDA+U study. *Phys. Rev. B* **57**, 1505–1509 (1998)

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Walkosz, W.

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