

Chapter 2

Theoretical Methods

If in some cataclysm all scientific knowledge were to be destroyed and only one sentence passed on to the next generation of creatures, what statement would contain the most information in the fewest words? I believe it is the atomic hypothesis that all things are made of atoms, little particles that move around in perpetual motion, attracting each other when they are a little distance apart, but repelling upon being squeezed into one another. In that one sentence, you will see there is an enormous amount of information about the world, if just a little imagination and thinking are applied.

Richard P. Feynman

2.1 Methods for Electronic Structure Calculation

Density functional theory provides an efficient and robust method for (approximately) solving the many-body Schrödinger equation of quantum mechanics. Solving this equation is one of the central problems in solid states physics and quantum chemistry since they are potentially able to provide some fundamental understanding as well as predict, in some instances, the properties of atoms, molecules and solids, enabling to describe a large variety of experimental observations.

Matters around us is made of atoms which differ from each other for the number of electrons and protons. By using these informations about a specific atomic structure, one can study how the particles interact in matters (described in the Schrödinger equation) and thus be potentially able to explain most of the properties of materials. Developing theoretical approaches and computational methods that can accurately describe the interaction between many particles in condensed matter and complex molecules is a challenge in theoretical physics and chemistry. A review of the most common methods currently used along with their strengths and limitations is given.

2.1.1 The Schrödinger Equation

Macroscopic systems are well described by classical mechanics. For instance, the motion of classical particles is governed by the Newton's second law:

$$F = ma = m \frac{d^2x}{dt^2} \quad (2.1)$$

On a particle moving with an acceleration a acts a force F that is given by the product of its mass and its acceleration. The force is also related to the second derivative in time of the position of the particle, $x(t)$. If the position of the particle at a certain time, its mass and the force acting on it (i.e. its current state) is known, then the evolution of the position of the particle can be predicted. Hence, given the exact knowledge of the present state of a classical-mechanical system, one can predict its future state.

This principle is not valid when one deals with microscopic particles, such as electrons or protons. In this case, a quantum mechanical formalism [1] is needed to describe the state of the microscopic system. In fact, the Heisenberg uncertainty principle shows that we can not determine simultaneously the exact position and momentum of a microscopic particle. But to describe the state of a quantum mechanical system, one need to postulate the existence of a function of the particle's coordinates, so called wave function Ψ .

In general, the wave function Ψ is also a function of time, $\Psi = \Psi(x, t)$. The wave function contains all the information of the system and once we know it, we can predict all the properties of the system. An example is given by the Born postulate:

$$|\Psi(x)|^2 dx \quad (2.2)$$

is the probability density, i.e. the probability at time t of finding the particle in the region between x and $x + dx$.

In order to predict the properties of the quantum mechanical system, an equation that describes how the wave function changes with time is needed, similarly to the second Newton's law in classical systems. For one particle in one-dimensional system, this equation postulates

$$-\frac{\hbar}{i} \frac{\delta \Psi(x, t)}{\delta t} = -\frac{\hbar^2}{2m} \frac{\delta^2 \Psi(x, t)}{\delta x^2} + V(x, t) \Psi(x, t) \quad (2.3)$$

This is known as the time-dependent Schrödinger equation and contains $i = \sqrt{-1}$, m is the mass of the particle, $V(x, t)$ the potential energy of the system and $\hbar$ the reduced Planck constant.

If we restrict ourselves to a system with constant potential energy function, then the system can exist in a number of stationary states of fixed energy E and is described by the time-independent Schrödinger equation:

$$-\frac{\hbar^2}{2m} \frac{d^2\psi(x)}{dx^2} + V(x)\psi(x) = E\psi(x) \quad (2.4)$$

where $\psi(x)$ is only dependent on the spatial coordinate.

By introducing the Hamiltonian, so called the quantum mechanical energy operator

$$\hat{H} = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + V(x) \quad (2.5)$$

and extending the problem to many-particles systems, we obtain the many-particles Schrödinger equation [1]:

$$\hat{H}\psi = E\psi. \quad (2.6)$$

To calculate the properties of a physical quantum mechanical system, one needs to solve Eq. 2.6 where ψ are the eigenfunctions of $\hat{H}$ and E represent the eigenvalues of the Schrödinger equation. But an analytical solution to this equation is possible only for systems consisting of two particles, so called two-body systems. For larger systems, as in the case of a multi-electron atom or molecule, the equation can only be solved numerically. Besides that, another trouble in the case of the many-electron problem is represented by the number of particles. If one want to investigate a system consisting of 1 cm^3 of copper, the number of atoms to be taken into account is in the order of 10^{21} . The total number of interacting particles in this system is given by the number of nuclei and electrons which is roughly one order of magnitude larger than the number of atoms. Then, the wavefunction ψ will depend on a number of variables 3 times larger than the number of interacting particles (because it is a three dimensional system), i.e about 10^{23} variables. Solving Eq. 2.6 with such a huge number of variables would be impossible or very time consuming even for a modern HPC.

Approximations are thus unavoidable and a compromise between computational time and accuracy of calculations is needed.

2.1.2 The Wave Function Approach

The first two approximations used, aim to reduce the Schrödinger equation (SE) for the true many-body wavefunction in a set of independent one electron Schrödinger equations that can be solved numerically.

To have a clear physical meaning of these approximations, one can reformulate the Hamiltonian energy operator in terms of kinetic and potential energy operators:

$$\begin{aligned} \hat{H} &= \underbrace{\hat{T}_e + \hat{T}_n}_{\text{kinetic}} + \underbrace{\hat{V}_{en} + \hat{V}_{ee} + \hat{V}_{nn}}_{\text{potential}} \\ &= \sum_i -\frac{\hbar^2}{2m} \Delta_i^2 + \sum_I -\frac{\hbar^2}{2M_I} \Delta_I^2 \end{aligned}$$

$$+ \sum_i \sum_I \frac{Z_I e^2}{|\mathbf{r}_i - \mathbf{R}_I|} + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} + \frac{1}{2} \sum_{I \neq J} \frac{Z_I Z_J e^2}{|\mathbf{R}_I - \mathbf{R}_J|} \quad (2.7)$$

The first two terms correspond to the kinetic energies of the electrons and of the nuclei, the other three ones are the potential energies describing the electron–nuclei, electron–electron and nuclei–nuclei Coulombic interactions. $(\mathbf{r}_i)$ and $(\mathbf{R}_I)$ are the coordinates of the electrons and of the nuclei, respectively. Δ^2 is the Laplace operator.

Born and Oppenheimer [2] exploited the *Adiabatic principle* to decouple the ionic part of the SE from the electronic one. The significant difference existing between the mass of the nucleus and the electron one leads to the fact that electrons are moving much faster than nuclei and hence they adapt immediately their positions to any change in the positions of the ions. So, the motion of electrons is determined by the motion of the other electrons and the “frozen” position of the nuclei, which act as an external potential ($\hat{V}_{en}$) for the electrons. The total wave function, dependent on the positions of the nuclei and electrons, can then be divided in two parts:

$$\Psi(\mathbf{r}, \mathbf{R}) = \chi_n(\mathbf{R}) \psi_e(\mathbf{r}; \mathbf{R}) \quad (2.8)$$

where ψ_e is the electron wave function dependent on the positions of the electrons (variables $\mathbf{r}$) and on the position of the nuclei as parameters $(\mathbf{R})$. Thus one can solve the quantum problem for electrons at several fixed positions of nuclei and calculate the corresponding electron total energy E_e . This energy can then be used as external potential for solving the quantum problem for nuclei.

Focusing on the former more complex problem, the adiabatic approximation allows one to reduce the Hamiltonian for the electron subsystem as:

$$\begin{aligned} \hat{H}_e &= \underbrace{\sum_i -\frac{\hbar^2}{2m} \Delta_i^2 - \sum_i \sum_I \frac{Z_I e^2}{|\mathbf{r}_i - \mathbf{R}_I|}}_{\sum_i h(\mathbf{r}_i)} + \underbrace{\frac{1}{2} \sum_{i \neq j} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|}}_{\frac{1}{2} \sum_{i \neq j} v(\mathbf{r}_i, \mathbf{r}_j)} \\ &= \sum_i h(\mathbf{r}_i) + \frac{1}{2} \sum_{i \neq j} v(\mathbf{r}_i, \mathbf{r}_j); \end{aligned} \quad (2.9)$$

since the kinetic energy of the nuclei is zero when the nuclei are considered at fixed position, while the nuclei–nuclei Coulombic potential is constant and does not influence the total electron energy. The first term $h(\mathbf{r}_i)$ in Eq. 2.9 is the single-electron operator, so called because it depends on the position of the single electron; the second term $v(\mathbf{r}_i, \mathbf{r}_j)$ takes into account the inter-electron interaction and depends on the coordinates of the single electron and of all other electrons at the same time. Due to the latter, the many-electrons SE can not be still solved exactly because the exact electron wave function can not be written down as a product of mono-electronic wave functions.

2.1.2.1 The Hartree–Fock Method

The inter-electron interaction can be neglected leading to the formulation of the *Independent Model* (IM), which is a simplistic approximation of the SE. In this case, the exact wave function can be written down as a product of mono-electronic wavefunctions:

$$\Psi^{IM} = \prod_i \psi_i(\mathbf{r}_i) \quad (2.10)$$

$\psi_i(\mathbf{r}_i)$ are the eigenfunctions of the one electron SE:

$$h_i(\mathbf{r}_i)\psi_i(\mathbf{r}_i) = \varepsilon_i \psi_i(\mathbf{r}_i). \quad (2.11)$$

The one-electron SE equation for the i th electron is independent from that of all other electrons in the system, because h_i is given by the sum of the electronic kinetic energy and the Coulomb potential related to the ion–electron interaction for the i th electron, with no electron–electron terms. In the IM, the total Hamiltonian is therefore given by the sum of the single electron Hamiltonian:

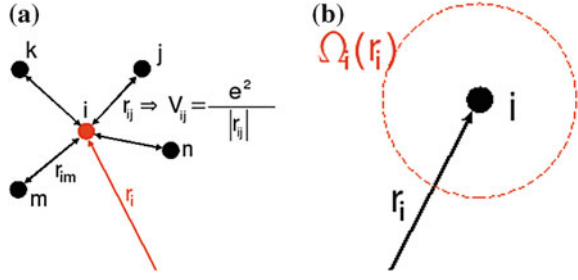
$$H^{IM} = \sum_i h(\mathbf{r}_i) \quad (2.12)$$

Unfortunately, neglecting the inter-electron interaction term is a too crude approximation and leads to significant errors in the resolution of the SE. Hence, a different approach is needed to account for this interaction. There are two main approaches that can handle this problem, the Hartree–Fock (HF) and the DFT theories, which distinguish themselves by the different solutions adopted to approximate the potential energy of the electron–electron interaction. The Hartree–Fock theory is based on the Slater determinant *ansatz*:

$$\Psi = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_1(\mathbf{r}_1) & \psi_1(\mathbf{r}_2) & \dots & \psi_1(\mathbf{r}_N) \\ \psi_2(\mathbf{r}_1) & \psi_2(\mathbf{r}_2) & \dots & \psi_2(\mathbf{r}_N) \\ \vdots & \vdots & & \vdots \\ \psi_N(\mathbf{r}_1) & \psi_N(\mathbf{r}_2) & \dots & \psi_N(\mathbf{r}_N) \end{vmatrix}, \quad (2.13)$$

which is a general formulation of the wave function of the IM, accounting for the anti-symmetrized product of N spin orbitals (N = total number of electrons) due to the Pauli principle. Contrary to the IM, the Hartree–Fock method does not neglect the electron–electron interaction term $v_i(\mathbf{r}_i, \mathbf{r}_j)$ (see Eq. 2.9), but replaces it with a potential $\Omega_i(\mathbf{r}_i)$ which is exactly the same as the inter-electron interaction potential of the i th electron in the field of all other electrons, depending only on the coordinates of the i th electron. Thus, this method introduces the electron–electron interaction as an average (*self-consistent*) field of the other electrons. This is illustrated in Fig. 2.1.

Fig. 2.1 The electron in an interacting system (a) and in the average field (b). **a** e–e interacting system. **b** Hartree approximation



The effective potential $\Omega(\mathbf{r})$ is chosen such that the wave function Ψ , corresponding to N independent electrons, minimize the ground state energy of the system described by a set of one electron SE:

$$[h(\mathbf{r}) + \Omega(\mathbf{r})] \psi_i(\mathbf{r}) = \varepsilon_i \psi_i(\mathbf{r}). \quad (2.14)$$

In other words, the potential $\Omega(\mathbf{r})$ corresponding to the true electron–electron interacting potential is found by minimizing the ground state energy and equivalently by solving the problem:

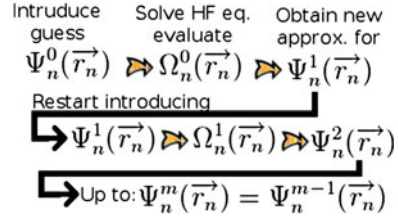
$$\int \Psi^* \hat{H} \Psi d(\mathbf{r}) \equiv \langle \Psi | \hat{H} | \Psi \rangle \longrightarrow \min. \quad (2.15)$$

This is possible through the *variational theorem* which asserts that: ‘Given a system whose Hamiltonian operator $\hat{H}$ is time independent and whose lowest-energy eigenvalue is E_0 , any normalized well-behaved function Ψ that satisfy the boundary condition of the problem, will be an eigenfunction with corresponding eigenvalue $E > E_0$.’

With the introduction of the Slater determinant, of the Hamiltonian as a sum of the single-electron operator $h(\mathbf{r})$ and of the effective potential $\Omega(\mathbf{r})$ in the problem 2.15, one can satisfy the condition of minimum ground state energy by using the Lagrange multiplier ε_i [3, 4]. The resulting expression in the form of eigenvalue equations, called Hartree–Fock equations, is:

$$\left\{ \underbrace{-\frac{\hbar^2}{2m} \Delta_i^2 + V_{en}(\mathbf{r})}_{h(\mathbf{r})} + \underbrace{2 \sum_{j=1}^{N/2} \int \frac{e^2 |\psi_j(\mathbf{r}')|^2}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}'}_{V_c(\mathbf{r})} \right\} \psi_i(\mathbf{r}) - \underbrace{\left\{ \sum_{j=1}^{N/2} \int \frac{e^2 \psi_j^*(\mathbf{r}') \psi_i(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' \right\}}_{V_x(\mathbf{r})} \psi_j(\mathbf{r}) = \varepsilon_i \psi_i(\mathbf{r}). \quad (2.16)$$

Fig. 2.2 Self consistent field method



In fact, this equation is the one electron SE in which the electron interaction potential ($V_{ee}(\mathbf{r}_i, \mathbf{r}_j)$) is replaced by the self-consistent (or Hartree) potential $\Omega(\mathbf{r})$ which contains the Coulombic potential (V_c) from all electrons (with both spin directions) and the exchange potential from all electrons with same spin (V_x). Thus the Hartree–Fock equation can be simply re-written as:

$$\left[h(\mathbf{r}) + \underbrace{V_c(\mathbf{r}) + V_x(\mathbf{r})}_{\Omega_i(\mathbf{r})} \right] \psi_i(\mathbf{r}) = \varepsilon_i \psi_i(\mathbf{r}). \quad (2.17)$$

Note that $V_c(\mathbf{r})$ contains the interaction of an electron at the position $\mathbf{r}$ with itself, i.e. the self-interaction term. This term is cancelled in the HF equation by an equal term in $V_x(\mathbf{r})$.

Starting with a guess wave function ψ_n^0 , a set of independent equations in the form of 2.16 is iteratively solved to produce the final eigenvalues and eigenvectors (see Fig. 2.2). Note that the iterative procedure is also called Self-Consistent Field method (SCF). In practice, this task is very complex for a many-electrons system (such as solids and molecules) and the Hartree–Fock approach has to be reformulated to be mathematically/computationally tractable. Roothaan expressed the Hartree–Fock orbitals as a linear expansion in M known basis functions:

$$\psi_i(\mathbf{r}) = \sum_k^M C_{ki} \varphi_k(\mathbf{r}) \quad (2.18)$$

where, C_{ki} are the coefficients and $\varphi_k(\mathbf{r})$ the basis functions of the system. The introduction of the basis functions in Eq. 2.16 allows one to formulate the Hartree–Fock equations as a matrix equation in the form of:

$$\mathbf{F} \cdot \mathbf{C} = \mathbf{S} \cdot \mathbf{C} \cdot \mathbf{E} \quad (2.19)$$

where $\mathbf{F}$, is the Fock matrix. It is a matrix of one electron Hamiltonian equations corresponding to the left side terms of Eq. 2.16; $\mathbf{S}$ is the overlap matrix taking into account the overlap between the basis functions (which are not in general orthogonal) and $\mathbf{E}$ and $\mathbf{C}$ are the eigenvalues and eigenvectors, respectively [3].

The Hartree–Fock problem is reduced to a linear algebra problem, which may be solved by matrix techniques [5]. Note that the basis set expansion represents an additional approximation. In fact, an exact expansion of the wave functions would require an infinite set of basis functions. In practical, a finite set of K basis functions is used, which is a compromise between the computational cost and the error with respect to the exact Hartree–Fock energy.

2.1.3 Density Functional Theory

The Hartree–Fock–Roothaan method is very efficient and allows one to reduce the many-body original problem (which was represented by coupled differential equations) to a matrix equation which can be efficiently treated by computer calculators. However, the wavefunction approach does not reduce the number of variables with respect to the original multi-atomic problem. In fact, the study of 1 cm^3 of Cu proposed before, still depends on $N = 10^{23}$ variables which leads to a number of parameters in the Hartree–Fock matrix equation 2.19 in the range p^{3N} , $3 \leq p \leq 10$. Solving a matrix equation in space with so many dimensions is likely impossible. This is the so called “Exponential Wall” [6] that the wavefunction approach meets when the many body system becomes too large. Besides that, the correlation energy, which is defined as the difference between the exact ground state solution of the SE and the exact HF solution, is often the cause of a poor description of the interaction energy in many molecules and solids.

The alternative approach, called *Density Functional Theory*, allows reducing the number of parameters sensibly and involves an interacting density rather than independent particles (which is the case of the HF method).

2.1.3.1 The Hohenberg–Kohn Theorems

The Density Functional Theory finds its origin in the work of Thomas and Fermi [7], where they described the interaction of the electron cloud present in an atom as a non-interacting electron gas placed in an external potential. They formulated the energy of the gas based on the sum of the kinetic energy, the external potential and the local exchange-correlation energy (terms added successively by Dirac in order to obtain a better approximation). All these terms depend on the electronic density $n(\mathbf{r})$ [4]. Finally, using a variational principle, they formulated the expression of the energy of the system. The Thomas–Fermi (TF) approach is an oversimplified model that works only on single atoms (because it does not account for the deformation of the electronic cloud present in solids and molecules due to the formation of chemical bonds). However, it built-up up a working basis that led to the formulation by Kohn and Hohenberg of the two main theorems which constitute the foundation of the Density Functional Theory [8]:

Theorem 1 (Hohenberg–Kohn I) *Every observable of a stationary quantum mechanical system (including energy) can be calculated in principle exactly, from the ground state density $n(\mathbf{r})$ alone.*

Theorem 2 (Hohenberg–Kohn II) *A universal functional for the energy $E(n)$ in terms of the density $n(\mathbf{r})$ can be defined, valid for any external potential $V_{ext}(\mathbf{r})$:*

$$E_{V_{ext}}[n] = F_{HK}[n] + \int n(\mathbf{r})V_{ext}(\mathbf{r})d\mathbf{r}; \quad (2.20)$$

For any particular $V_{ext}(\mathbf{r})$, the exact ground state energy of the system is the global minimum value of this functional, and the density $n(\mathbf{r})$ that minimizes the functional is the exact ground state density $n_0(\mathbf{r})$

$F_{HK}[n]$ is the Hohenberg–Kohn universal functional of n that returns the kinetic and electron–electron part of the total energy.

The second term of the functional 2.20 is the equivalent of the electron–nucleus interaction potential V_{en} in the Born–Oppenheimer Hamiltonian 2.7, but expressed as a functional of the electronic density.

Therefore, the energy (and all other property) of a system is completely determined by a unique electronic ground state density. Assuming that an analytical expression for the energy exists, minimizing the latter will provide the ground state density of the system (and hence all the relative properties associated to it).

2.1.3.2 Kohn–Sham Method

In order to exploit the two Hohenberg–Kohn theorems and find the ground state density of the system, an analytical formulation of the universal functional for the energy $E(n)$ is needed. The ingenuity of the method developed by Kohn–Sham (KS) consists in the formulation of the Hohenberg–Kohn universal functional in two separated terms for the independent particle Kinetic energy and the Hartree one, including the remaining entities in an exchange–correlation functional $E_{xc}[n]$ (which can reasonably be approximated as a local functional of the density). The Hohenberg–Kohn expression for the ground state energy functional is reformulated as:

$$E_{KS} = T_s[n] + \int n(\mathbf{r})V_{ext}(\mathbf{r})d\mathbf{r} + E_{Hartree}[n] + E_{xc}[n] \quad (2.21)$$

The exact ground state density of a N -electrons system which minimizes the universal functional of Eq. 2.21 is:

$$n(\mathbf{r}) = \sum_{i=1}^N \psi_i^*(\mathbf{r})\psi_i(\mathbf{r}) \quad (2.22)$$

where the single-particle wave functions ψ_i are solutions of the Kohn–Sham Schrödinger-like equations:

$$\hat{H}_{KS}(\mathbf{r})\psi_i(\mathbf{r}) = \epsilon_i\psi_i(\mathbf{r}); \quad (2.23)$$

with $\hat{H}_{KS}$ that can be expressed as:

$$\hat{H}_{KS} = \hat{T}_s + \hat{V}_{Hartree} + \hat{V}_{ext} + \hat{V}_{xc}. \quad (2.24)$$

Equation 2.23 can be obtained by minimizing the energy functional of Eq. 2.21 with respect to the density $n(\mathbf{r})$ and then applying the Lagrange multiplier method [4]. We will give below an analytical expression for each of the terms in Eq. 2.21.

$T_s[n]$ is defined as the kinetic energy of a non-interacting system with density $n(\mathbf{r})$.

$$T_s = \frac{1}{2} \sum_{i=1}^N |\Delta\psi_i|^2. \quad (2.25)$$

In fact, to be able to obtain an analytical expression for the kinetic energy of the many-body interacting system, Kohn and Sham proposed an *ansatz*: to assume that the ground state density of the original interacting system is equal to that of some chosen non-interacting system. This leads to independent-particle equations (in the form of 2.23) that can be numerically solved with all the many-body terms included into the exchange-correlation functional E_{xc} .

The classical Coulomb interaction energy (electron–electron interaction) is defined as:

$$E_{Hartree} = \frac{1}{2} \int \int \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}d\mathbf{r}'. \quad (2.26)$$

The electron–nucleus interaction energy has been defined in Eq. 2.21. If one expresses the electron–nucleus interaction as the interaction between electrons captured in a small volume $d(r_i)$ and nuclei of charge Z_j , the electron–nucleus term can be formulated as:

$$E_{en}[n] = \int n(\mathbf{r}_i) \sum_j \frac{Z_j}{|\mathbf{R}_{ij}|} d(\mathbf{r}_i) \longrightarrow E_{en}[n] = \int n(\mathbf{r}) V_{ext}(\mathbf{r}) d(\mathbf{r})$$

Finally, the exchange-correlation functional $E_{xc}[n]$ can be approximated as a local or near local functional of the density:

$$E_{xc}[n] = \int n(\mathbf{r}) \epsilon_{xc}(n(\mathbf{r})) d\mathbf{r}. \quad (2.27)$$

where $\epsilon_{xc}([n], \mathbf{r})$ is an energy per electron at point $\mathbf{r}$ that depends only upon the density $n(\mathbf{r})$ in some neighborhood of point $\mathbf{r}$. More details about the approximation techniques to find an analytical form of E_{xc} will be given in the next section.

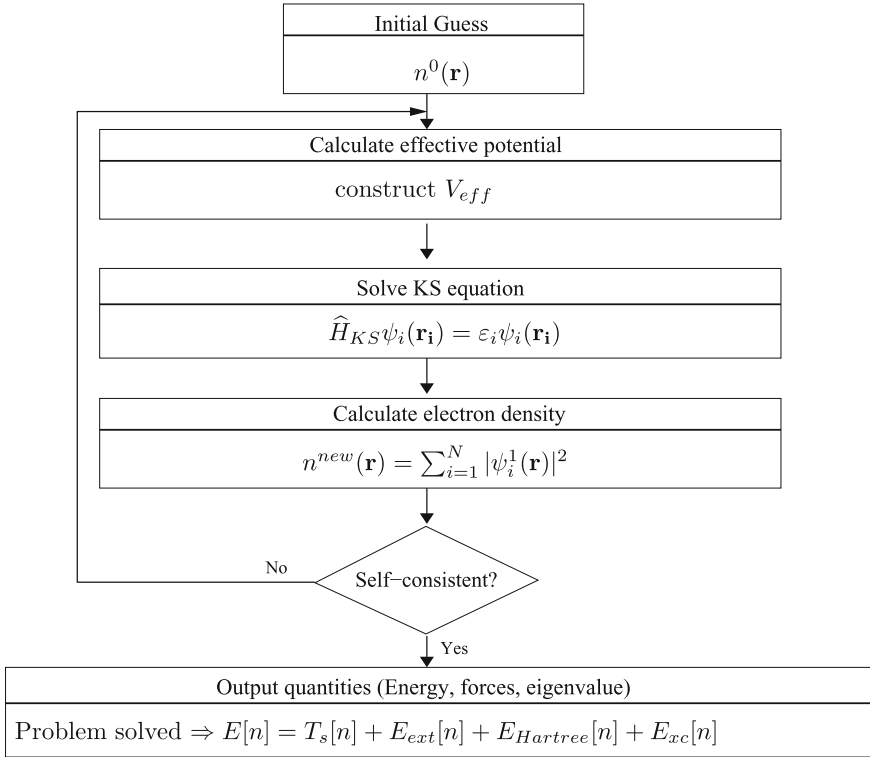


Fig. 2.3 Self-consistent Kohn–Sham equations

The energy terms 2.26–2.27 have an explicit dependence on the density n , hence they can be included in an *effective potential*:

$$V_{eff}(\mathbf{r}) = V_{ext}(\mathbf{r}) + \frac{\delta E_{Hartree}}{\delta n(\mathbf{r})} + \frac{\delta E_{xc}}{\delta n(\mathbf{r})}. \quad (2.28)$$

The Kohn–Sham single particle Hamiltonian of Eq. 2.23 can then be reformulated as:

$$\left[-\frac{\hbar^2}{2m} \Delta_i^2 + V_{eff}(\mathbf{r}) \right] \psi_i(\mathbf{r}) = \epsilon_i \psi_i(\mathbf{r}). \quad (2.29)$$

To find the eigenstates of the Kohn–Sham Hamiltonian, an iterative method is needed. Similarly to the self-consistent HF method, by introducing a guess density n^0 into the Eq. 2.28, one can evaluate the effective potential $V_{eff}(\mathbf{r})$, which in turn leads to the resolution of the set of independent Kohn–Sham equations 2.29. The resulting wavefunction is then used to construct a new density n which can be used again for the calculation of a new effective potential. This iterative resolution of the self-consistent Kohn–Sham equation is illustrated in Fig. 2.3.

2.1.4 Additional Approximations in DFT

A crucial approximation in the Kohn–Sham approach, illustrated above, is the exchange-correlation energy, which is expressed as a functional of the density n . This energy term includes all the quantities not explicitly accounted for in the independent-particle kinetic energy and Hartree term. Unfortunately, an analytical form for E_{xc} is unknown and its exact value can be calculated only for very simple systems. However, E_{xc} can be reasonably approximated as a local or near local functional of the density.

2.1.4.1 The Local Density Approximation and the Generalized-Gradient Approximation

In the local density approximation, the original non-uniform system is considered as close as to an homogeneous electron gas. In an uniform electron gas, the electrons move into a distribution of positive background charges such that total system is electrically neutral (similar to the case of electrons evolving in a metal). In such a homogeneous problem, the SE can be solved numerically and the exchange-correlation energy can be evaluated. The value of $E_{xc}(n)$ for the non-uniform system is then approximated by the exchange-correlation energy of the homogeneous gas with the same local density n of the original system, and expressed as in Eq. 2.27.

If the exchange-correlation energy density of the homogeneous gas ϵ_{xc}^{hom} is written as the sum of the exchange and correlation term, the exchange-correlation energy of the original system can be expressed as:

$$E_{xc}^{LDA}[n] = \int n(\mathbf{r}) \left[\epsilon_x^{hom}(n(\mathbf{r})) + \epsilon_c^{hom}(n(\mathbf{r})) \right] d(\mathbf{r}) \quad (2.30)$$

The exchange energy of the homogeneous gas is given by a simple analytic form [4]. An expression for the correlation energy can be obtained by interpolating the values obtained from numerical simulations [9] of an homogeneous electron gas with different values of the electronic density in between the high- and low-density limit. For these cases also analytical expressions of the correlation energy are known [4, 10, 11]. In its ‘simple’ form, the LDA is able to describe accurately quasi all the elements of the periodic table. It however leads to a slight overbidding of atoms in solids together with an underestimation of the energy band gap by typically 50–100 % with respect to the experimental value in semiconductors and insulators. An approach to improve the LDA is to include a functional of the magnitude of the gradient density $|\nabla n|$ as well as the density n in the formulation of E_{xc} . Thus, in the so called generalized gradient approximation (GGA), the exchange-correlation functional can be defined as:

$$E_{xc}^{GGA}[n] = \int n(\mathbf{r}) \epsilon_x^{hom}(n) F_{xc}(n, |\nabla n|) d(\mathbf{r}). \quad (2.31)$$

Several forms for F_{xc} have been proposed, including the three widely used forms of Becke(B88) [12], Perdew and Wang (PW91) [13], and Perdew, Burke and Enzerhof (PBE) [14]. Most of the other approximations proposed lead to a value of F_{xc} that falls between those obtained by the B88, PW91 and PBE.

GGA reduces the binding energy of LDA, but sometimes overcorrects LDA. As a matter of fact, the structural parameters obtained by GGA are typically few percent larger than experimental values. The GGA band gap is usually in between the LDA and experimental value, but it is typically still underestimated. Finally, both LDA and GGA can not describe properly properties such as strong electron correlations and long-range van der Waals interactions.

2.1.4.2 Hybrid and Non Local Functionals

Although the E_{xc} energy can be approximated as a local or near local functional of the density, hybrid functionals exploit the fact that the Kohn–Sham approach provides also orbitals from which an exact exchange energy may be constructed. In fact, the exchange term in the HF Eq. 2.16 represents an exact estimation of the Pauli exclusion and self-interaction effects (even if it neglects any other electron correlation effect). Thus, the exact exchange energy (from HF theory), can be mixed or “hybridized” with the exchange-correlation energy derived by other approximations (i.e. LDA or GGA), to obtain results which are in better agreement with experimental results.

The first hybrid functional was the “half-and-half” form from Becke [15]

$$E_{xc} = \frac{1}{2}(E_x^{HF} + E_{xc}^{DFA}), \quad (2.32)$$

where DFA denotes an LDA or GGA functional. This first version of hybrid functional included half of the Hartree–Fock exchange energy and half of the exchange-correlation energy calculated by a DFT approach. Later, Becke presented the “B3P91” [15, 16], a parametrized form of exchange-correlation functional which mixed, by three parameters, the Hartree–Fock exchange, the exchange functional of Becke (B88), and the correlation from Perdew and Wang (PW91). This last term was substituted by the correlation from Lee, Yang and Parr (LYP) [17] in the popular hybrid functional B3LYP [18]. Other two popular hybrid functionals are the PBE0 [19] and the HSE [20]. The former mixes the PBE functional with the Hartree–Fock exchange:

$$E_{xc} = \frac{1}{4}E_x^{HF} + \frac{3}{4}E_x^{PBE} + E_c^{PBE}. \quad (2.33)$$

The HSE exchange-correlation functional is based on a screening Coulomb potential. The screened Coulomb potential is used to split the Coulomb operator into short range (SR) and long range (LR) components. This allows one to accelerate the spatial decay of the HF exchange which is highly system dependent, and in the case of extended system limits the computational efficiency of the PBE0 hybrid functional.

Focusing on the exchange part of the expression 2.33, we can express the PBE0 exchange energy as:

$$E_x = aE_x^{HF} + (1 - a)E_x^{PBE}, \quad (2.34)$$

where the mixed coefficient $a = 1/4$ was used in the Eq. 2.33.

All terms can be split into their short and long range components:

$$E_x = aE_x^{HF,SR}(\omega) + aE_x^{HF,LR}(\omega) + (1 - a)E_x^{PBE,SR}(\omega) + E_x^{PBE,LR}(\omega) - aE_x^{PBE,LR}(\omega), \quad (2.35)$$

where ω is an adjustable parameter for partitioning the full $1/r$ Coulomb potential into the short and long range components as:

$$\frac{1}{r} = \underbrace{\frac{erfc(\omega r)}{r}}_{SR} + \underbrace{\frac{erf(\omega r)}{r}}_{LR}. \quad (2.36)$$

Thus, the Coulomb potential is substituted with a screened potential by using the error function in Eq. 2.36, since it leads to computational advantages in evaluating the short range HF exchange integrals [20].

Numerical tests indicate that the HF and PBE LR exchange contributions to the functional in Eq. 2.35 are rather small and tend to cancel each other. One can neglect these terms, obtaining the HSE hybrid density functional in the form:

$$E_{xc}^{HSE} = aE_x^{HF,SR}(\omega) + (1 - a)E_x^{PBE,SR}(\omega) + E_x^{PBE,LR}(\omega) + E_c^{PBE}. \quad (2.37)$$

Both the popular generalized gradient approximation (GGA) or hybrid exchange-correlation functionals mentioned previously, do not accurately describe the dispersion (Van der Waals) interactions. A way to take into account dispersion, within DFT, is the introduction of a non-local exchange-correlation functional. For example, in the non-local Van der Waals density functional (vdW-DF) [21] the non-local correlation is calculated so that the exchange-correlation energy has the form:

$$E_{xc} = E_x^{GGA} + E_c^{LDA} + E_c^{nl}, \quad (2.38)$$

where E_x^{GGA} is the GGA exchange energy (particularly obtained with the revised version of the PBE) [22]. E_c^{LDA} accounts for the local correlation energy obtained within the local density approximation (LDA), and E_c^{nl} is the non-local correlation energy. The latter is based on long-range interacting electron densities modeled by an approximate dielectric function.

2.1.4.3 Basis Sets and the Role of Reciprocal Space

To be computationally tractable, the wavefunctions of the K-S equations 2.23 have to be expressed in term of basis functions (similar to the approach developed in the

Roothaan method (2.18). There are several possible choices for the basis functions, including localized basis sets, plane waves and atomic spherical methods. Each of these choices has advantages and pitfalls. In fact, the ideal basis set should be efficient, meaning that one need to sum a relatively low number of basis functions to accurately describe the wave functions; and unbiased, i.e. not dependent on a specific type of solutions and nuclear position.

Localized basis sets provide an intuitive description of the electronic structure, because they expand the wavefunction as a linear combination of localized atomic-like orbital. A localized basis function can be expressed as:

$$\varphi_{Iln}(\mathbf{r}) = R_{Iln}(|\mathbf{r}_I|)Y_{lm}(\hat{\mathbf{r}}_I), \quad (2.39)$$

where l is the quantum number of the orbital angular momentum and m the magnetic quantum number. I is the index of the atom where the orbital is centered and $(\hat{\mathbf{r}})$ is the radius of the spherical harmonics Y_{lm} , which is a well defined (fixed) term. The first term (R_{Iln}) is the radial part and it is defined by the type of atomic orbitals. For instance, in the Gaussian Type Orbitals (GTO), the radial part has the form:

$$R_{Iln}(|\mathbf{r}|_I) = N r^l e^{-\alpha r^2}, \quad (2.40)$$

with N a normalization constant.

Other popular type of localized atomic orbitals are the Slater Type Orbitals (STO) and Numerical Atomic Orbitals (NAO), which are used in the SIESTA (DFT) code [23]. The localized atomic orbitals are usually very efficient, particularly if a high accuracy is not requested, but they are very biased.

A type of basis set which has the characteristic to be unbiased is based on plane waves. Such basis sets have a quite simple form and naturally benefit from the periodicity of the crystalline solids. In fact, one can re-define the Kohn–Sham equations in the reciprocal space, taking advantage of the peculiar form of plane waves.

If we consider a crystal with dimensions $L_1 = N_1|\mathbf{a}_1|$, $L_2 = N_2|\mathbf{a}_2|$, and $L_3 = N_3|\mathbf{a}_3|$, with $\mathbf{a}_i$ being the primitive vectors of the lattice (shown in Fig. 2.4 a), one can define the wave vector $\mathbf{k}$ in the reciprocal space as:

$$\mathbf{k} = \frac{n_1}{N_1}\mathbf{b}_1 + \frac{n_2}{N_2}\mathbf{b}_2 + \frac{n_3}{N_3}\mathbf{b}_3. \quad (2.41)$$

where n_i are integers and $\mathbf{b}_i$ the primitive vectors of the reciprocal lattice, satisfying the relation:

$$\mathbf{b}_i \cdot \mathbf{a}_j = 2\pi\delta_{ij}, \quad (2.42)$$

where δ_{ij} is the Kronecker delta.

According to the Bloch's theorem [24], a complete set for the one-electron SE and their eigenvalues $\varepsilon_i(\mathbf{k})$ occur for $\mathbf{k}$ -values within the so called first Brillouin zone (BZ), illustrated in Fig. 2.4b for a face-centered cubic cell. This zone coincides with the Wigner-Seitz cell of the reciprocal lattice, which is defined by the planes

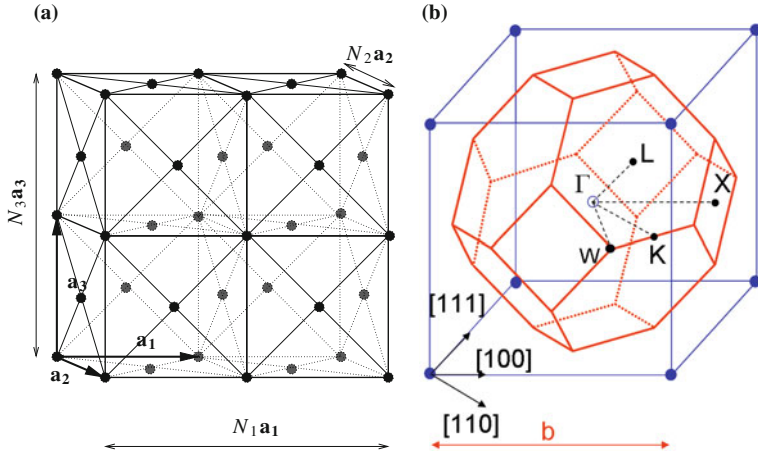


Fig. 2.4 Face center cubic cell (a) and corresponding first Brillouin zone (b). **a** Real space. **b** Reciprocal space

that correspond to the perpendicular bisectors of the vectors from the origin to the reciprocal lattice point.

Thus, by imposing the periodic boundary conditions on the crystal and following Bloch's theorem, the wavefunctions can be written as:

$$\psi_{j,\mathbf{k}}(\mathbf{r}) = f_{j,\mathbf{k}}(\mathbf{r})e^{i\mathbf{k}\mathbf{r}}, \quad (2.43)$$

where j , denotes the discrete band index, f_j is a function that takes into account the lattice periodicity and the last term is the plane wave.

Due to the periodicity of the reciprocal lattice, two waves with wave vector $\mathbf{k}$ are equivalent if they differ by a reciprocal lattice vector, which is defined from 2.41 as:

$$\mathbf{G} = m_1 \mathbf{b}_1 + m_2 \mathbf{b}_2 + m_3 \mathbf{b}_3, \quad (2.44)$$

where m_i is an integer. Since $f_j(\mathbf{r})$ of Eq. 2.43 has the same periodicity as the lattice, it can be written as a Fourier transform:

$$f_j(\mathbf{r}) = \sum_{\mathbf{G}} C_{j,\mathbf{G}} \times \frac{1}{\sqrt{\Omega}} e^{i\mathbf{G}\mathbf{r}} \quad (2.45)$$

and the wavefunctions can be rewritten as:

$$\psi_{j,\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{G}} C_{\mathbf{G}}^{j,\mathbf{k}} \times \frac{1}{\sqrt{\Omega}} e^{i(\mathbf{G}+\mathbf{k})\mathbf{r}}, \quad (2.46)$$

with Ω the volume of the primitive cell.

Similarly, the potential felt by the electrons in the crystal (V_{eff}) contained in the one-electron Kohn–Sham equation (2.29), is also periodic and can be rewritten using the Bloch’s theorem as:

$$V_{eff}(\mathbf{r}) = \sum_m V_{eff}(\mathbf{G}_m) e^{i\mathbf{G}_m \cdot \mathbf{r}} \quad (2.47)$$

and the KS equation becomes [4]:

$$\sum_{m'} \left\{ -\frac{\hbar^2}{2m} |\mathbf{k} + \mathbf{G}_m|^2 \delta_{m,m'} + V_{eff}(\mathbf{G}_m - \mathbf{G}_{m'}) \right\} C_{i,\mathbf{k}+\mathbf{G}_{m'}} = \varepsilon_i C_{i,\mathbf{k}+\mathbf{G}_m}, \quad (2.48)$$

where $\mathbf{K}_m = \mathbf{k} + \mathbf{G}_m$ and $\mathbf{K}_{m'} = \mathbf{k} + \mathbf{G}_{m'}$, satisfying the relation:

$$\langle \mathbf{K}_m | \mathbf{K}_{m'} \rangle = \delta_{m,m'}. \quad (2.49)$$

Therefore, to obtain the total energy of a system, the Fourier transform of the wavefunction has to be computed and its coefficients $C_{i,\mathbf{k}+\mathbf{G}_m}$ evaluated using the self-consistent approach. The problem of solving the KS equations is “reduced” to a matrix eigenvalue problem, similarly to the case of the Roothaan’s method.

Despite the Bloch’s theorem, the number of plane-wave basis required to expand the wavefunction is in principle still infinite due to the infinite term required by the Fourier transform. In practice, the set of plane waves is restricted to those ones whose kinetic energy is less than a cut-off value E_{cut} . For all values of ($\mathbf{G}$) included in the expansion, one has:

$$\frac{\hbar^2 |\mathbf{k} + \mathbf{G}|^2}{2m} \leq E_{cut} \quad (2.50)$$

Thus, to be sure that a proper value of E_{cut} has been chosen, the convergence of the obtained total energy with respect to the basis set has to be carefully checked in the DFT calculations.

The computation of the total energy or any physical property also typically requires the evaluation of a set of other operators over the wavefunction in the Brillouin zone. For instance, the electronic density $n(\mathbf{r})$ is given by:

$$n(\mathbf{r}) = \frac{\Omega}{2\pi^3} \int_{BZ} n_{\mathbf{k}}(\mathbf{r}) d^3\mathbf{k},$$

$$with \quad n_{\mathbf{k}} = \sum_{i=1}^N |\psi_{i,\mathbf{k}}(\mathbf{r})|^2 \quad (2.51)$$

In principle, the integral 2.51 can be computed exactly but it is computationally very demanding to integrate over the full Brillouin zone. In practice, one replaces the continuous integral by a weighted sum over a discrete set of $\mathbf{K}$ -points. This set

of $\mathbf{K}$ -points (called Monkhorst–Pack grid) is generated by an uniform mesh which samples the function ($n(\mathbf{r})$ in the example above) in the Brillouin zone. Similarly to the case of the E_{cut} energy, the minimum number of $\mathbf{K}$ -points necessary to obtain accurate results, has to be tested by checking the convergence of the total energy as well as other properties of the solid under investigation (e.g. the electronic density of states).

The main drawback of the plane-wave basis set method is the number of basis functions required to accurately represent the Kohn–Sham orbitals. In fact, plane waves methods are not so efficient with respect to atomic orbital methods, but their computational cost can be reduced if they are combined with pseudopotentials. Plane waves and pseudopotential approximations are the main recipe of DFT codes such as Quantum Espresso [25] and Abinit [26].

Finally, atomic spheres methods are the most accurate methods within DFT, but they are computationally very expensive. The most popular atomic spheres method is based on the Augmented Plane Waves (APW), introduced by Slater [27]. In the APW, the smoothly varying part of the wavefunctions between the atoms is represented by plane waves, while the rapidly varying part near the nuclei is represented by a radial function times spherical harmonics (similarly to the localized atomic wavefunctions).

2.1.4.4 Pseudopotentials

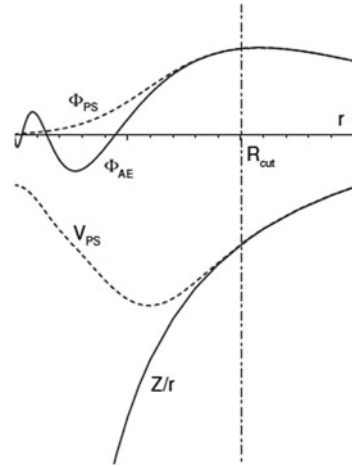
The fundamental idea of a pseudopotential consists in replacing the strong Coulomb interaction between the nucleus and the tightly bond core electrons by a special constructed potential mimicking their effect on the valence electrons. This pseudopotential is generated during an all-electron calculation and then used to describe the properties of the valence electrons, since the core states remain almost unchanged (i.e. do not participate in chemical bond formation in the material). Using this approach, we strongly reduce the number of electrons (and hence the dimension of the basis set) used in the computations.

For instance, the electrons of germanium are divided into a set of core electrons $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10}$ and four valence electrons $4s^2 4p^2$. Only the latter are included in the calculations through the pseudopotential, which leads to the same atomic valence energy without having to treat the core states explicitly.

The behavior of a pseudopotential is illustrated in Fig. 2.5. It is constructed such that it matches the true potential outside a given radius designated by the core radius (r_c). Similarly, each pseudo-wavefunction matches the corresponding true wavefunction beyond this point in space. The region that presents the rapid oscillations of the wavefunctions (close to the nucleus), due to the action of the strong potential present, is then neglected. Thanks to this approach, less plane-waves are required to approximate the (pseudo-)wavefunction.

Two major families of pseudopotentials are usually used: norm-conserving (NC) pseudopotentials and ultrasoft (US) pseudopotentials. NC pseudopotentials guarantee two properties for the pseudo-wavefunction: it is nodeless and, when normalized, it is identical to the true valence wave function beyond the core radius r_c . They are

Fig. 2.5 Pseudopotential and pseudo-wavefunction: illustration of an atomic all-electron (AE) wave function (solid line) and the corresponding atomic pseudo-wave (PS) function (dashed line) together with the respective external coulomb potential and pseudopotential [28]



constructed in two steps from the results of an all-electrons atom calculation. First, the full potential at large r is smoothly merged into a parametrized potential inside a radius r_c . The parameter is adjusted to reproduce the valence eigenvalue, and hence eigenfunction for $r > r_c$. The norm is then corrected by the addition of a short-range term to this eigenfunction [29, 30]. Several other methods to efficiently generate NC pseudopotentials, which should be as smooth as possible, have been developed, including Troullier–Martins [31] and Goedecker–Hartwigsen–Hutter–Teter [32, 33] pseudopotentials. There are two competing characteristics of pseudopotentials:

- Accuracy and transferability which are typically linked to a small cutoff radius but also to “hard” potentials. In fact, pseudopotentials have to mimic as much as possible the true potentials in the region near the atom.
- Smoothness of the pseudo-wavefunctions: large cutoff radius and “soft” potentials allow one to reduce the number of basis functions describing the wavefunctions.

In US pseudopotentials firstly developed by Vanderbilt, the second aim is achieved by relaxing the norm-conservation constraint, so that the pseudo-wavefunctions can be constructed in such a way as to optimize smoothness [34]. The price to pay, is that the Fourier representation of the KS equation (2.48) becomes more complicated. Firstly, when the electron density is calculated, one needs to add back the part of the electron distribution to compensate the difference between the all-electron wave function and the US (pseudo-)wavefunction (the so-called augmentation charges). Then, due to the relaxation of the normconserving condition, the eigenstates $\psi_{j,\mathbf{k}}$ will be not orthonormal and an overlap matrix has to be introduced. Due to these modifications, additional terms in the force calculation have to be also evaluated. Nevertheless, the additional computational effort, which is required by these modifications, is compensated by the reduction of the plane wave cut-off energy, and in many cases, particularly for elements in which the valence electrons are strongly

localized in the ionic core region, the US pseudo-potential approach results into a gain in computational cost.

Generally, taking into account explicitly for the valence electrons alone in the calculations, allows one to have accurate results. In fact, the core electrons do not participate in the chemical bond, they are strongly localized around the nucleus, and their wavefunctions overlap only very little with the core electron wave functions from neighboring atoms. Due to that, one can assume the core electrons to be “frozen” in the so called frozen-core approximation. However, in few specific cases, there is a significant overlap between core and valence wave-functions, hence considering the valence electrons alone is not enough to compute the properties of the molecule or solid. The pseudopotential of these atoms need to include some “semi-core” states as valence electrons. This is for instance the case of transition metals such as molybdenum, where the 4s and 4p semi-core electrons are typically explicitly treated in the pseudopotential as valence electrons [35].

2.1.5 Phonons from DFT

Many properties of materials can be determined by variations of the total energy of the system. This is also the case for the vibrational properties of solids.

In Sect. 2.1.2, we have shown how Born and Oppenheimer decoupled the vibrational and electronic degrees of freedom in a solid, by using the *adiabatic principle*. The lattice vibrations can be determined by the eigenvalue of the SE, whose Hamiltonian is given by the contribution of the kinetic energy of the nuclei (T_n term of the total Hamiltonian described in the Eq. 2.7) and the ground-state energy $E(\mathbf{R})$ of a system of N interacting electrons moving in the field of fixed nuclei. This is often referred as the Born–Oppenheimer energy surface and is the eigenvalue of the Hamiltonian:

$$H_R = \sum_i -\frac{\hbar^2}{2m} \Delta_i^2 - \sum_i \sum_l \frac{Z_l e^2}{|\mathbf{r}_i - \mathbf{R}_l|} + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} + V_{nn}(\mathbf{R}), \quad (2.52)$$

which is equal to the electron Hamiltonian defined in Eq. 2.9, where the nuclear electrostatic energy $V_{nn}(\mathbf{R})$ was neglected.

The force F acting on an atom i of the system, at position $\mathbf{R}_i$, is given by:

$$F_i = M_i \frac{\delta^2 u_i[\mathbf{R}_i]}{\delta t^2} = -\frac{\delta E(\mathbf{R})}{\delta \mathbf{R}_i}, \quad (2.53)$$

where u_i denotes the displacement of the atom i , M_i its mass and $E(\mathbf{R})$ is the Born–Oppenheimer energy surface. The equilibrium geometry of the system is determined by the condition that the force acting on individual nuclei vanish:

$$F_i \equiv -\frac{\delta E(\mathbf{R})}{\delta \mathbf{R}_i} = 0. \quad (2.54)$$

The vibrational frequencies ω of the atoms are then determined by the eigenvalues of the Hessian of the Bohn–Oppenheimer energy surface, scaled by the nuclear masses, the so called dynamical matrix (D):

$$D_{ij}(\mathbf{r}) = \frac{1}{\sqrt{M_i M_j}} \sum_i \frac{\delta^2 E(\mathbf{R})}{\delta \mathbf{R}_i \delta \mathbf{R}_j}. \quad (2.55)$$

The Hessian of the Bohn–Oppenheimer energy surface

$$C_{ij} \equiv \frac{\delta^2 E(\mathbf{R})}{\delta \mathbf{R}_i \delta \mathbf{R}_j} \quad (2.56)$$

is often referred as the matrix of the *interatomic force constants* (IFCs).

2.1.5.1 Density Functional Perturbation Theory

The equilibrium geometry and the vibrational properties of a system can thus be obtained by computing the second order derivative of the Born–Oppenheimer energy surface [36, 37], which from Eq. 2.53 is also given by first order derivative of the forces acting on each atom of the system. This force can be calculated by applying the Hellman-Feynman theorem [38, 39] on the Born–Oppenheimer Hamiltonian H_R , which states that the first derivative of the eigenvalues of a Hamiltonian is given by the expectation value of the derivative of the Hamiltonian. Thus, the force acting on the i th nuclei can be rewritten as:

$$F_i \equiv -\frac{\delta E(\mathbf{R})}{\delta \mathbf{R}_i} = -\int n(\mathbf{r}) \frac{\delta V_{en}(\mathbf{r})}{\delta \mathbf{R}_i} d\mathbf{r} - \frac{\delta V_{nn}(\mathbf{R})}{\delta \mathbf{R}_i}, \quad (2.57)$$

where V_{en} is the electron–nuclei interaction defined in Eq. 2.7, also called the external potential in the Kohn–Sham approach. $n(\mathbf{R})$ is the ground-state electron charge density for the nuclear configuration $\mathbf{R}$:

$$n(\mathbf{R}) = N \int |\Psi(\mathbf{R})(\mathbf{r}, \mathbf{r}_2, \dots, \mathbf{r}_N)|^2 d\mathbf{r}_2 \dots d\mathbf{r}_N. \quad (2.58)$$

An explicit expression for the IFCs can be then obtained by differentiating the force with respect to the nuclear coordinates:

$$\frac{\delta^2 E(\mathbf{R})}{\delta \mathbf{R}_i \delta \mathbf{R}_j} = \int \frac{\delta n(\mathbf{r})}{\delta \mathbf{R}_j} \frac{\delta V_{en}(\mathbf{r})}{\delta \mathbf{R}_i} d\mathbf{r} + \int n(\mathbf{r}) \frac{\delta^2 V_{en}(\mathbf{r})}{\delta \mathbf{R}_i \delta \mathbf{R}_j} d\mathbf{r} + \frac{\delta^2 V_{nn}(\mathbf{R})}{\delta \mathbf{R}_i \delta \mathbf{R}_j}. \quad (2.59)$$

Thus, the calculation of the IFCs requires the knowledge of the ground-states charge density $n(\mathbf{r})$, and its linear response to a distortion of the nuclear geometry, $\delta n(\mathbf{r})/\delta \mathbf{R}_i$. The former can be obtained by a typical self-consistent DFT procedure, while the latter can be evaluated by linearizing the Eq. 2.22 for the ground-state density:

$$\frac{\delta n(\mathbf{r})}{\delta \mathbf{R}_i} = 4Re \sum_{n=1}^{N/2} \psi_n^*(\mathbf{r}) \frac{\delta \psi_n(\mathbf{r})}{\delta \mathbf{R}_i}. \quad (2.60)$$

Similarly, the derivative of the Kohn–Sham orbitals $\delta \psi_n(\mathbf{r})/\delta \mathbf{R}_i$ is obtained by linearization of the kohn–Sham equation 2.29:

$$(H_{KS} - \epsilon_n) \frac{\delta \psi_n(\mathbf{r})}{\delta \mathbf{R}_i} = - \left(\frac{\delta V_{eff}(\mathbf{r})}{\delta \mathbf{R}_i} - \frac{\delta \epsilon_n}{\delta \mathbf{R}_i} \right) \psi_n(\mathbf{r}), \quad (2.61)$$

where

$$\frac{\delta V_{eff}(\mathbf{r})}{\delta \mathbf{R}_i} = \frac{\delta V_{en}(\mathbf{r})}{\delta \mathbf{R}_i} + e^2 \int \frac{1}{\mathbf{r} - \mathbf{r}'} \frac{\delta n(\mathbf{r}')}{\delta \mathbf{R}_i} d\mathbf{r}' + \int \frac{\delta V_{xc}(\mathbf{r})}{\delta n(\mathbf{r}')} \frac{\delta n(\mathbf{r}')}{\delta \mathbf{R}_i} d\mathbf{r}' \quad (2.62)$$

is the first order derivative of the effective potential 2.28 and $\delta \epsilon_n/\delta \mathbf{R}_i$ is the first order derivative of the Kohn–Sham eigenvalue, ϵ_n .

The Eqs. 2.60–2.62 form a set of self-consistent linear equations which are solved in a way very similar to the self-consistent DFT illustrated in Fig. 2.3. Summarizing, the purpose of the density functional perturbation theory (DFPT) is to calculate the response of the electronic density to an external perturbation, knowing the ground-state of the unperturbed system (obtained by the Kohn–Sham approach). The response of the electronic density is then used to calculate the second derivative of the total energy and so the IFCs, which will give the vibrational frequencies of the lattice. The Hohenberg–Kohn theorem (2) establishes a correspondence between the external potential of a system V_{en} and the ground-state density $n(\mathbf{r})$. Similarly, the derivative of the external potential is linked to the derivative of the ground-state density. Thus, the (guess) derivative of the electronic density $\delta n(\mathbf{r})/\delta \mathbf{R}_i$ corresponding to a perturbed potential, is introduced in the Eq. 2.62 and the derivative of the effective potential $\delta V_{eff}(\mathbf{r})/\delta \mathbf{R}_i$ obtained, is then used in the Eq. 2.61. The solution of the latter allows one to obtain the derivative of the Kohn–Sham orbitals $\delta \psi_n(\mathbf{r})/\delta \mathbf{R}_i$, which are then used to calculate a new derivative of the density; the process is then self-consistently iterated. This approach is the basis of the DFPT [40–42] implemented in several DFT codes, including Quantum Espresso.

One needs to solve the self-consistent linear system described above, by using several perturbations (the number of perturbations are 3 times the number of atoms N_{at}) at a fixed $\mathbf{q}$ vector to obtain the dynamical matrix

$$D_{ij}(\mathbf{q}) = \frac{1}{\sqrt{M_i M_j}} \sum_i \frac{\delta E[\mathbf{R}]}{\delta \mathbf{R}_i \delta \mathbf{R}_j} e^{i\mathbf{q}(\mathbf{R}_j - \mathbf{R}_i)}. \quad (2.63)$$

This is the Fourier transform of real-space IFCs, scaled by the mass matrix. By diagonalizing this dynamical matrix one obtains $3 \times N_{at}$ frequencies $\omega(\mathbf{q})$. Then, by repeating this procedure for several $\mathbf{q}$ vectors, one can plot $\omega(\mathbf{q})$ as a function of $\mathbf{q}$, so the called phonon dispersion. Practically, it is more convenient to adopt a different approach that requires the calculation of the dynamical matrix in a smaller set of $\mathbf{q}$ points. In fact, the dynamical matrix in real space can be written as:

$$D_{ij} = \frac{\Omega}{(2\pi)^3} \int D_{ij}(\mathbf{q}) e^{-i\mathbf{q}(\mathbf{R}_j - \mathbf{R}_i)} d\mathbf{q}^3. \quad (2.64)$$

One can use the properties of the discrete Fourier transform and sample the integral in a uniform mesh of $\mathbf{q}$ points. This will give the IFCs at any $\mathbf{q}$ point, even if not explicitly included in the DFT calculations. This approach is valid if the dynamical matrix is a sufficiently smooth function of $\mathbf{q}$ and the IFCs decays sufficiently rapidly in real space.

Note that in this section the density functional perturbation theory has been treated with the specific aim of determining the lattice dynamics of crystalline systems. However, the perturbation theory can be used more generally, within the density functional framework, to obtain the response function of a system to a perturbation. This is very useful, since many physical properties are derivative of the total energy of the system with respect to perturbations, which include, besides the atomic displacements used above, also homogeneous external field, such as an electric field. The derivative of the total energy, and more generally of any quantities, may be then obtained by the response of a generic physical quantity, e.g. the Kohn–Sham orbitals $\psi(\mathbf{r})$, the Kohn–Sham energy E , or the electronic density $n(\mathbf{r})$, to a perturbation.

2.1.5.2 Frozen phonons

An alternative approach to calculate the vibrational properties of a crystal is the *frozen phonons* technique [43], in which the second derivative of the energy is expressed as:

$$\frac{\delta F_i}{\delta R_i} = -\frac{\delta^2 E[\mathbf{R}]}{\delta \mathbf{R}_i^2} \quad (2.65)$$

and the derivative of the force is calculated using the finite-difference method (providing that the displacement of the atoms is small enough). A force matrix is built by perturbing a specific atom, with the other atoms fixed at their equilibrium position, and by cycling on all the atoms: the forces on all atoms, once diagonalized, provides the dynamical matrix. For this reason, the method is also called *small displacement method*. In the frozen-phonon approach, the calculation of the dynamical matrix at a generic point of the BZ, presents an additional difficulty. The distortions applied to the crystal are taking place in real space, thus not defining a specific $\mathbf{q}$ vector. Moreover, the crystal loses the original periodicity and an enlarged unit cell, so called supercell, is required for the calculation of the IFCs at any $\mathbf{q} \neq 0$. A suitable

supercell for a perturbation of wave-vector $\mathbf{q}$ must be large enough to accommodate $\mathbf{q}$ as one of the reciprocal-lattice vector.

The main advantage of this technique is that no specific code is needed for its implementation, but it can be straightforwardly implemented using any tool able to calculate the force acting on the atoms of the crystal. On the other hand, for the modelling of specific system, supercells are needed, independently of the method used for the calculation of the vibrational modes. For example, the modelling of a defective semiconductor or an amorphous material requires a supercell approach. In such cases, the frozen phonon technique can be more favourable with respect to the DFPT method.

2.1.5.3 Non Resonant Raman Cross Section

Within DFT, the Raman and infra-red cross sections in molecules and solids can be determined. Infra-red cross sections are proportional to the square of the polarization induced by a phonon mode, which can be calculated by considering a macroscopic electric field in the crystal [36, 37]. The resonant Raman cross section is quite difficult to compute, since it requires the determination of excited states. On the other hand, off-resonance Raman cross section can be more easily calculated within DFT.

In non resonant Stokes Raman spectra of harmonic solids, the peak intensities I^ν can be computed as:

$$I^\nu \propto |\mathbf{e}_i \cdot \mathbf{A} \cdot \mathbf{e}_s|^2 \frac{1}{\omega_\nu} (n_\nu + 1), \quad (2.66)$$

where $\mathbf{e}_i$ ($\mathbf{e}_s$) is the polarization of the incident (scattered) radiation, $n_\nu = [\exp(\hbar\omega_\nu/k_B T) - 1]^{-1}$, T is the temperature, and

$$A_{lm}^\nu = \sum_{k\gamma} \frac{\delta^3 \xi^{el}}{\delta E_l \delta E_m \delta u_{k\gamma}} \frac{w_{k\gamma}^\nu}{\sqrt{M_\gamma}}, \quad (2.67)$$

with ξ^{el} the electronic energy of the system, E_l the l th Cartesian component of a uniform electric field, $u_{k\gamma}$ the displacement of the γ th atom in the k th direction, M_γ the atomic mass, and $w_{k\gamma}^\nu$ the orthonormal vibrational eigenmode ν .

In addition to the vibrational frequency, the third-order derivative of the energy of the system with respect to two electric fields and one atomic displacement is needed to compute the non-resonant Raman intensity. The latter can be obtained directly from higher-order perturbation theory. M. Lazzeri and F. Mauri [44] used the second order derivative of the electronic density with respect to a uniform electric field to obtain the third-order derivative of the total energy and, hence, the Raman intensity. This approach is also implemented in the Quantum Espresso code.

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