

Chapter 2

Approximations to the Ground State

In this chapter, approximations to calculating the ground state of a many-body system with electronic Hamiltonian $\hat{H}_e$ as discussed in the previous section are considered. Unlike the methods introduced briefly in the last chapter, the method discussed here avoids any explicit representation of the many-electron wavefunction, but will instead be making use of the electron density of the system defined via

$$\rho(\mathbf{r}) = \langle \Psi | \hat{\rho}(\mathbf{r}) | \Psi \rangle = \int \prod_{i=2} d^3 r_i |\Psi(\mathbf{r}, \mathbf{r}_2, \dots, \mathbf{r}_N)|^2. \quad (2.1)$$

One can readily see the advantage of such a treatment. While the many-body wavefunction is a $3N$ -dimensional function, the electron density is a 3-dimensional function and thus potentially much easier to treat. For convenience, the spin dependence of the wavefunction is dropped in the entire chapter and only reintroduced where necessary.

2.1 Density-Functional Theory

In this section the main theorems that lead to the establishment of density-functional theory (DFT) are discussed. The electron Hamiltonian $\hat{H}_e$ of an interacting many-electron system is considered under the assumption that the ground state of $\hat{H}_e$ is non-degenerate. The Hamiltonian can be divided into three parts (ignoring the constant term due to ion-ion interactions that does not influence the solutions to the eigenstates):

$$\hat{H}_e = \hat{T} + \hat{V}_{\text{ee}} + \hat{V}_{\text{ext}} \quad (2.2)$$

where

$$\hat{V}_{\text{ext}} = \sum_i V_{\text{ext}}(\mathbf{r}_i) = - \sum_{i,A} \frac{Z_A}{|\mathbf{r}_i - \mathbf{R}_A|} \quad (2.3)$$

the static external potential due to the ions acting on the electrons and $\hat{T}$ and $\hat{V}_{ee}$ are the kinetic energy term and the electron-electron interaction. Note that $\hat{T} + \hat{V}_{ee}$ is the same for any N -electron system. Therefore $\hat{H}_e$ and thus $|\Psi_0\rangle$ must be completely determined by N and $V_{\text{ext}}(\mathbf{r})$. Furthermore, because $|\Psi_0\rangle$ is a functional of N and $V_{\text{ext}}(\mathbf{r})$, the ground state density of the system, $\rho_0(\mathbf{r})$, is equally a functional of N and $V_{\text{ext}}(\mathbf{r})$.

2.1.1 Hohenberg–Kohn Theorem

In 1964, Hohenberg and Kohn [1] proved two crucial theorems that form the starting point of density-functional theory:

- There exists a one-to-one mapping between the external potential $V_{\text{ext}}(\mathbf{r})$ of the interacting quantum system and the ground state density $\rho_0(\mathbf{r})$.
- For all v -representable¹ densities $\rho(\mathbf{r})$, there exists a unique functional $E[\rho(\mathbf{r})]$ such that the exact ground state energy is the global minimum of $E[\rho(\mathbf{r})]$.

The first Hohenberg–Kohn theorem can be proven by assuming that there exists a second external potential $V'_{\text{ext}}(\mathbf{r})$ with ground state wavefunction $|\Psi'_0\rangle$ that produces the same ground state density $\rho_0(\mathbf{r})$. One therefore considers two different Hamiltonians $\hat{H}_e = \hat{T} + \hat{V}_{ee} + \hat{V}_{\text{ext}}$ and $\hat{H}'_e = \hat{T} + \hat{V}_{ee} + \hat{V}'_{\text{ext}}$ with ground state energies $E_0 = \langle \Psi_0 | \hat{H}_e | \Psi_0 \rangle$ and $E'_0 = \langle \Psi'_0 | \hat{H}'_e | \Psi'_0 \rangle$. Using the variational principle it is clear that

$$E_0 < \langle \Psi'_0 | \hat{H}_e | \Psi'_0 \rangle = \langle \Psi'_0 | \hat{H}'_e | \Psi'_0 \rangle + \langle \Psi'_0 | (\hat{H}_e - \hat{H}'_e) | \Psi'_0 \rangle \quad (2.4)$$

$$E'_0 < \langle \Psi_0 | \hat{H}'_e | \Psi_0 \rangle = \langle \Psi_0 | \hat{H}_e | \Psi_0 \rangle + \langle \Psi_0 | (\hat{H}'_e - \hat{H}_e) | \Psi_0 \rangle \quad (2.5)$$

Given that both systems have the same ground state density, the terms $\langle \Psi'_0 | (\hat{H}_e - \hat{H}'_e) | \Psi'_0 \rangle$ and $\langle \Psi_0 | (\hat{H}'_e - \hat{H}_e) | \Psi_0 \rangle$ can both be written in terms of $\rho_0(\mathbf{r})$ to give

$$E_0 < E'_0 + \int \rho_0(\mathbf{r}) [V_{\text{ext}}(\mathbf{r}) - V'_{\text{ext}}(\mathbf{r})] d^3r \quad (2.6)$$

$$E'_0 < E_0 - \int \rho_0(\mathbf{r}) [V_{\text{ext}}(\mathbf{r}) - V'_{\text{ext}}(\mathbf{r})] d^3r \quad (2.7)$$

from which immediately follows that

$$E_0 + E'_0 < E'_0 + E_0 \quad (2.8)$$

which is a contradiction. Thus if two systems have the same ground state density, their external potentials must be identical (to within a constant) and vice versa. Therefore,

¹A density $\rho_\alpha(\mathbf{r})$ is v -representable, iff it is the ground state density of a system with some external potential $V_{\text{ext}}^\alpha(\mathbf{r})$. See later in this section for more details on the question of v -representability.

there exists a one-to-one mapping between the external potential and the ground state density of the system.

To consider the second theorem, it is first necessary to address some of the implications of the first theorem. Since the ground state density uniquely determines the external potential and the external potential uniquely defines the electronic Hamiltonian of the system, it must be possible to express any ground state property of the many-body system as a unique functional of the ground state density. Now consider a set of all densities $\{\rho_v\}$, each of which is the ground state density to some external potential $V_v(\mathbf{r})$ and thus $\{\rho_v\}$ uniquely defines the set of many-body wavefunctions $\{|\Psi_v\rangle\}$. These densities are referred to as v -representable since for them the one-to-one mapping to the potential exists. Since the wavefunction is uniquely defined for the v -representable density, the functional $F[\rho_v] = \langle \Psi_v | \hat{T} + \hat{V}_{ee} | \Psi_v \rangle$ must be uniquely defined as well. Thus for the v -representable densities there exists a unique energy functional $E[\rho_v]$ such that

$$\begin{aligned} E[\rho_v] &= \langle \Psi_v | \hat{H}_e | \Psi_v \rangle = \langle \Psi_v | \hat{T} + \hat{V}_{ee} | \Psi_v \rangle + \langle \Psi_v | \hat{V}_{\text{ext}} | \Psi_v \rangle \\ &= F[\rho_v] + \int d^3r V_{\text{ext}}(\mathbf{r})\rho_v(\mathbf{r}) \end{aligned} \quad (2.9)$$

for some electronic Hamiltonian $\hat{H}_e$ with external potential $\hat{V}_{\text{ext}}$.

Now consider some v -representable density ρ_v with associated potential $V_v(\mathbf{r})$ and wavefunction $|\Psi_v\rangle$ acting on the Hamiltonian $\hat{H}_e$ with arbitrary external potential V_{ext} . Using both the variational principle and the considerations above one finds that

$$\langle \Psi_v | \hat{H}_e | \Psi_v \rangle = F[\rho_v] + \int d^3r V_{\text{ext}}(\mathbf{r})\rho_v(\mathbf{r}) = E[\rho_v] \geq E_0 \quad (2.10)$$

where equality is only reached if $\rho_v = \rho_0$. Thus, in principle it is possible to find the ground state energy of any system defined by the electronic Hamiltonian $\hat{H}_e$ by minimising the functional $E[\rho_v]$ over the set of all v -representable densities $\{\rho_v\}$. However the Hohenberg–Kohn theorems do not specify how the minimisation should be carried out in practice given that, for an arbitrary density, it is generally not known if it is v -representable.

2.1.2 Levy Constrained Search Method

The problem of carrying out the minimisation of the energy functional suggested by Hohenberg and Kohn without relying on v -representability has been addressed by Levy [2]. It turns out that to prove the second statement of the Hohenberg–Kohn theorem, it is not necessary to make a reference to v -representability at all. Following Levy it is possible to define the functional $F[\rho]$ as

$$F[\rho] = \min_{|\Psi\rangle \rightarrow \rho} \langle \Psi | \hat{T} + \hat{V}_{\text{ee}} | \Psi \rangle. \quad (2.11)$$

Thus $F[\rho]$ is defined via the minimum of the expectation value of $(\hat{T} + \hat{V}_{\text{ee}})$, where the minimisation is carried out with respect to all many-electron wavefunctions $|\Psi\rangle$ that yield the electron density ρ .

Now consider the many-electron wavefunction $|\Psi_{[\rho]}\rangle$ that produces the density ρ and minimizes $F[\rho]$. The expectation value of the Hamiltonian $\hat{H}_e$ with external potential V_{ext} and ground state energy E_0 , under the redefinition of $E[\rho]$ via the new definition of $F[\rho]$ can then be written as

$$\begin{aligned} \langle \Psi_{[\rho]} | \hat{H}_e | \Psi_{[\rho]} \rangle &= \langle \Psi_{[\rho]} | \hat{T} + \hat{V}_{\text{ee}} | \Psi_{[\rho]} \rangle + \langle \Psi_{[\rho]} | \hat{V}_{\text{ext}} | \Psi_{[\rho]} \rangle \\ &= F[\rho] + \int d^3r V_{\text{ext}}(\mathbf{r})\rho(\mathbf{r}) = E[\rho] \geq E_0 \end{aligned} \quad (2.12)$$

where the last statement follows necessarily from the variational principle and equality only holds if $|\Psi_{[\rho]}\rangle = |\Psi_0\rangle$. The statement holds for all densities that can be generated by an N -particle wavefunction, a condition that is referred to as N -representability and that is much less restrictive than v -representability. Now consider $F[\rho_0]$ and the ground-state wavefunction $|\Psi_0\rangle$. Clearly $|\Psi_0\rangle$ is one of the many-electron wavefunctions yielding ρ_0 over which $F[\rho]$ is minimised. From Eq. (2.11) it therefore follows that

$$\begin{aligned} F[\rho_0] &\leq \langle \Psi_0 | \hat{T} + \hat{V}_{\text{ee}} | \Psi_0 \rangle \\ \Rightarrow F[\rho_0] + \int d^3r V_{\text{ext}}(\mathbf{r})\rho_0(\mathbf{r}) &\leq \langle \Psi_0 | \hat{H}_e | \Psi_0 \rangle \\ \Rightarrow E[\rho_0] &\leq E_0 \end{aligned} \quad (2.13)$$

From the two inequalities, it directly follows that $E[\rho] \geq E[\rho_0] = E_0$ such that minimising $E[\rho]$ with respect to all ρ that are N -representable yields the ground state energy of the system. It has been shown [3, 4] that the condition of N -representability is easily met for arbitrary, normalisable, differentiable densities and that it poses no real restriction on the validity of the central Hohenberg–Kohn theorem as the problem of v -representability does.

2.1.3 Kohn–Sham Theory

While the Hohenberg–Kohn theorems prove the existence of a functional $E[\rho]$ that, if minimised, yields the ground state density and energy of the many-electron system, the exact form of $F[\rho]$ is unknown and has to be approximated.

The main strategy to achieve approximations is to split $F[\rho]$ into independent particle and mean field contributions and unknown many-body contributions. One therefore writes

$$F[\rho] = T_s[\rho] + E_H[\rho] + E_{xc}[\rho] \quad (2.14)$$

where $T_s[\rho]$ is the kinetic energy of a system of N non-interacting particles of density ρ and $E_H[\rho]$ is the Hartree energy (see Sect. 1.2.9), the mean-field electron interaction energy due to a system of N particles with density ρ . E_{xc} is the exchange-correlation energy and contains all many-body effects not included in $T_s[\rho]$ and $E_H[\rho]$, such that

$$E_{xc}[\rho] = T[\rho] - T_s[\rho] + E_{ee}[\rho] - E_H[\rho] \quad (2.15)$$

Since this is just a simple rewriting of the original statement, both $E_{xc}[\rho]$ and $T_s[\rho]$ are generally not known and suitable approximations have to be found. It is to be hoped that the many-body corrections introduced through E_{xc} are small. However, the kinetic energy contributions through $T_s[\rho]$ are generally not small and good approximate treatments become crucial. Several approximations have been known long before the development of density-functional theory, most notably the Thomas–Fermi kinetic energy functional [5, 6]

$$T_{TF}[\rho] = \frac{3}{10} \left(3\pi^2 \right)^{\frac{2}{3}} \int d^3r [\rho(\mathbf{r})]^{\frac{5}{3}} \quad (2.16)$$

and the von Weizsäcker kinetic energy functional [7]

$$T_W[\rho] = \frac{3}{10} \left(3\pi^2 \right)^{\frac{2}{3}} \int d^3r [\rho(\mathbf{r})]^{\frac{5}{3}} + \frac{1}{8} \int d^3r \frac{\nabla \rho(\mathbf{r}) \cdot \nabla \rho(\mathbf{r})}{\rho(\mathbf{r})}. \quad (2.17)$$

While in the Thomas–Fermi model, the kinetic energy per infinitesimal unit volume is constant and only dependent on the density at that point, the von Weizsäcker functional adds a correction term depending on the gradient of $\rho(\mathbf{r})$. It can be shown that the von Weizsäcker functional is exact for 1- or 2-electron systems [8] and constitutes a lower bound to $T_s[\rho]$ for an N -electron system. Other, higher order corrections to $T_W[\rho]$ can be introduced but in general the deviation of these approximate kinetic energy functionals from the true, independent particle kinetic energy functional $T_s[\rho]$ is significant [8].

A way to avoid any approximations to $T_s[\rho]$ was introduced by Kohn and Sham [9]. It consists of a remapping of the problem of N interacting electrons to a fictitious system of non-interacting electrons in an effective potential producing the same ground-state density. It exploits the fact that for a set of N non-interacting electrons with single-particle wavefunctions $\{\psi_i(\mathbf{r})\}$ producing the density ρ , $T_s[\rho]$ is simply given by

$$T_s[\rho] = T_s[\{\psi_i[\rho]\}] = - \sum_i^{N/2} \langle \psi_i | \nabla^2 | \psi_i \rangle \quad (2.18)$$

and is thus exactly known (here it is assumed that the system in question is spin-degenerate and thus every single-particle state ψ_i is doubly occupied). In order to arrive at the Kohn–Sham equations, it is possible to minimize the energy functional of a system in external potential $V_{\text{ext}}(\mathbf{r})$. The stationarity condition at the minimum can be written as:

$$\frac{\delta}{\delta \rho(\mathbf{r})} \left[T_s[\rho] + E_H[\rho] + E_{\text{xc}}[\rho] + \int d^3r V_{\text{ext}}(\mathbf{r})\rho(\mathbf{r}) - \mu \left(\int d^3r \rho(\mathbf{r}) - N \right) \right] = 0 \quad (2.19)$$

where the Lagrange multiplier μ is introduced to constrain the density to integrate to N . It follows that

$$\frac{\delta T_s[\rho]}{\delta \rho(\mathbf{r})} + V_{\text{KS}}(\mathbf{r}) = \mu \quad (2.20)$$

with

$$V_{\text{KS}}(\mathbf{r}) = \int d^3r' \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + \frac{\delta E_{\text{xc}}[\rho]}{\delta \rho(\mathbf{r})} + V_{\text{ext}}(\mathbf{r}). \quad (2.21)$$

However, Eq. (2.20) has the form of a noninteracting system of particles moving in an effective potential $V_{\text{KS}}(\mathbf{r})$. Thus the problem of finding the ground state density of the system is mapped to solving the single particle Schrödinger equation for a set of $N/2$ single-particle states $\psi_i(\mathbf{r})$ with

$$\left[-\frac{1}{2} \nabla^2 + \hat{V}_{\text{KS}} \right] |\psi_i\rangle = \epsilon_i |\psi_i\rangle. \quad (2.22)$$

The electron density of the system is then defined via the sum of the single particle densities

$$\rho(\mathbf{r}) = 2 \sum_i^{N/2} |\psi_i(\mathbf{r})|^2 \quad (2.23)$$

and the total energy of the system can be written as

$$\begin{aligned} E[\rho] &= T_s[\{\psi_i[\rho]\}] + E_H[\rho] + E_{\text{xc}}[\rho] + \int d^3r V_{\text{ext}}(\mathbf{r})\rho(\mathbf{r}) \\ &= 2 \sum_i^{N/2} \langle \psi_i | \hat{H}_{\text{KS}} | \psi_i \rangle - \frac{1}{2} E_H[\rho] - \int d^3r \rho(\mathbf{r}) V_{\text{xc}}(\mathbf{r}) + E_{\text{xc}}[\rho] \\ &= 2 \sum_i^{N/2} \epsilon_i - \frac{1}{2} E_H[\rho] - \int d^3r \rho(\mathbf{r}) V_{\text{xc}}(\mathbf{r}) + E_{\text{xc}}[\rho] \end{aligned} \quad (2.24)$$

$$= E_{\text{BS}}[\rho] - E_{\text{dc}}[\rho]. \quad (2.25)$$

Here, the effective Kohn–Sham Hamiltonian $\hat{H}_{\text{KS}}$ has been introduced and the ground state energy is written in terms of the bandstructure energy E_{BS} of single particle

energy eigenvalues ϵ_i and some double counting terms that are obtained from comparing to the full energy functional of the density.

Since the Kohn–Sham effective potential in (2.22) is dependent on the density, which is in turn defined via the Kohn–Sham single particle orbitals $\{|\psi_i\rangle\}$, the problem has to be solved self-consistently. This is done by starting with a guess for the ground-state density of the system which defines the Kohn–Sham potential and a set $\{|\psi_i\rangle\}$. These orbitals define a new density and the process can be iterated until the change between incoming and outgoing density vanishes.²

Thus in order to gain a good representation of the kinetic energy functional, the problem of minimising $E[\rho]$ with respect to ρ is recast into iteratively solving for $N/2$ orthogonal single particle states $|\psi_i\rangle$. This reformulation comes at a computational cost. While minimising $E[\rho]$ directly does scale linearly with size of the system, finding the solutions to (2.22) generally scales as $\mathcal{O}(N^3)$ with system size, due to the orthogonality constraints on the $N/2$ Kohn–Sham single-particle orbitals. However, while there has been an intense research effort over the last decades in trying to find better purely density-based approximations to $T_s[\rho]$ for orbital-free DFT approaches (OF-DFT) [8, 11], to this point none of them can achieve accuracies comparable to Kohn–Sham DFT over a wide range of different systems. For this reason Kohn–Sham DFT has been the more widely used flavour of DFT over the last decades.

While the Kohn–Sham eigenstates $|\psi_i\rangle$ are those of a fictitious noninteracting system in an effective potential that are introduced purely in order to gain a representation of the kinetic energy functional, they are often being taken to have some physical meaning attached to them. In particular, it is often found that Kohn–Sham eigenvalues are in reasonably good agreement with experimentally obtained band-structures of the real system. Strictly speaking however, only the Kohn–Sham energy of the highest occupied orbital has a physical meaning attached to it, as for the exact DFT functional it corresponds to the ionisation energy of the system following Koopmans’ theorem [12].

2.1.4 Exchange-Correlation Functionals

So far, the form of the functional $E_{xc}[\rho]$, the term in which all the many-body effects of exchange and correlation are collected that are ignored in $T_s[\{\psi_i[\rho]\}]$ and $E_H[\rho]$ has not been addressed. The exact functional form of $E_{xc}[\rho]$ is unknown and a number of properties that $E_{xc}[\rho]$ must obey suggest that it cannot be easily stated as a simple functional of the density [13]. Therefore in practice, DFT cannot provide an exact solution to the many-body problem and the results obtained are dependent on the way $E_{xc}[\rho]$ is approximated.

²In practice, a naive approach of using the outgoing density to define the Kohn–Sham potential is unlikely to yield convergence in real systems. For calculations in real systems, sophisticated density mixing schemes are used that take into account the densities of previous iterations to define a new one (see for example [10] for details).

The simplest possible approximation of $E_{xc}[\rho]$ is the local density approximation (LDA), where it is assumed that the exchange-correlation energy at an infinitesimal volume element d^3r is the same as that of a homogeneous electron gas with uniform density $\rho = \rho(\mathbf{r})$. Thus

$$E_{xc}[\rho] = \int d^3r \epsilon_{xc}[\rho(\mathbf{r})] \rho(\mathbf{r}) \quad (2.26)$$

$$V_{xc}(\mathbf{r}) = \epsilon_{xc}[\rho(\mathbf{r})] + \rho(\mathbf{r}) \left. \frac{d\epsilon[\rho]}{d\rho} \right|_{\rho=\rho(\mathbf{r})} \quad (2.27)$$

The exchange energy of the homogeneous electron gas is fully known, while for the correlation energy, analytic forms for the high and low density limit are known [14]. These limits are extrapolated over the whole density range by fitting to data obtained by very accurate quantum Monte-Carlo calculations [15]. Different fittings have yielded a number of different LDA functionals in recent years [14, 16, 17]. LDA is very appealing due to its simplicity and generally yields good results for a wide range of different materials and molecules.

While the LDA functionals have turned out to yield very good results in a variety of systems and have been used extensively by physicists, total energies calculated for molecular systems are often not good enough for the purposes of quantum chemists. As a result, DFT was not a widely used method in quantum chemistry until the next class of functionals, the gradient-corrected functionals (GGA functionals) were introduced [18]. In order to deal with rapidly changing electron densities such as encountered close to the nucleus,³ GGA functionals treat the exchange-correlation energy as

$$E_{xc}^{GGA}[\rho] = \int d^3r \epsilon_{xc}^{GGA}[\rho(\mathbf{r}), |\nabla\rho(\mathbf{r})|] \rho(\mathbf{r}) \quad (2.28)$$

and different analytic forms and fittings to the homogeneous electron gas have again led to a vast variety of different functionals of this type [19–21]. GGA functionals do improve significantly on total energies and some structural properties like bond lengths in some covalently bonded systems, but in many regards have the same failures as LDA functionals and do not deliver a universal improvement over a wide range of systems.

The main failure of many simple density-based exchange correlation functionals is the so-called self-interaction error. This error can be quantified by considering a system with a single electron. Since there is only one electron, the electron-electron interaction is required to strictly vanish. In the DFT framework, this means that the Hartree potential of a single electron is required to exactly cancel the exchange-correlation

³This is mainly the case for quantum chemistry all-electron DFT methods, since they need to explicitly treat core electrons that are confined to the region close to the nucleus. These core electrons are ignored in pseudopotential approaches (see Sect. 2.2.6) often used in solid-state physics community, making the electron density smoother.

functional. In essence, the requirement states that the asymptotic $1/r$ dependence of the Hartree potential must be cancelled by a $1/r$ dependence of the exchange-correlation potential. For most (semi)-local functionals depending only locally on ρ (or $|\nabla\rho|$), this simple property is violated. Note that the Hartree–Fock method discussed in Sect. 1.2.9 does not suffer from this type of self interaction error as the Hartree potential exactly cancels the exchange potential for a single electron.

The self-interaction error in most commonly used DFT functionals causes ionisation energies to be severely underestimated. This can be understood by considering that in the limit that an electron is moved far away from an arbitrary nucleus, it should be feeling a simple $1/r$ potential of the nucleus screened by all other valence electrons. However, in DFT treatments the self-interaction error screens the potential, causing it to decay faster, which leads to underestimated ionisation energies.

To address some of the shortcomings of (semi)-local functionals, a third class of functionals named hybrid functionals [22, 23] has been introduced. In hybrid functionals, a certain fraction of non-local Hartree–Fock exchange is added to a GGA-type exchange-correlation functional to yield better results in systems where the (semi)-local exchange correlation functionals perform poorly. However, while hybrid functionals often perform better in systems where non-local effects are important, they still do not produce the correct long-range behaviour for V_{xc} and are, unlike the pure Hartree–Fock method, not self-interaction free. They also come with significant increase in computational cost as V_{xc} is no longer a simple functional of the density but has a dependence on individual Kohn–Sham orbitals. Furthermore, just as (semi)-local functionals, hybrid functionals generally do not reproduce correct binding curves for systems that are bound by van der Waals type interactions which arise from non-local correlation effects.⁴

2.2 From Theory to Practical Method

In Sect. 2.1 the theoretical foundation of density-functional theory was outlined. Over the last thirty years, intense research has been invested into transforming the theory into a practical method that can be used routinely for calculating energies and structural properties of any system. In this section, some of the main techniques used by most modern DFT-codes in order to facilitate routine calculations on a variety of systems are discussed.

⁴These non-local correlation effects can be introduced into the DFT framework by making use of van der Waals density functionals, which have been shown to give realistic binding curves in many systems where van der Waals effects are important (see [24]).

2.2.1 Bloch's Theorem, Brillouin Zones and Periodic Boundary Conditions

Consider a crystalline solid with a translational symmetry defined by the primitive lattice vectors $\mathbf{a}_i$. From this it follows that the external potential of the ions V_{ext} follows the same periodicity, i.e.

$$V_{\text{ext}}(\mathbf{r} + n_i \mathbf{a}_i) = V_{\text{ext}}(\mathbf{r}) \text{ for } n_i \in \mathbb{Z}, i \in \{1, 2, 3\} \quad (2.29)$$

It follows that

$$V_{\text{KS}}(\mathbf{r} + \mathbf{R}) = V_{\text{KS}}(\mathbf{r}) \quad (2.30)$$

where

$$\mathbf{R} = n_1 \mathbf{a}_1 + n_2 \mathbf{a}_2 + n_3 \mathbf{a}_3 \text{ for } n_1, n_2, n_3 \in \mathbb{Z} \quad (2.31)$$

and thus that the effective single particle Hamiltonian $\hat{H}_{\text{KS}}$ possesses the same translational symmetry as the lattice since the kinetic energy is translation-invariant. Consider now the translation operator $\hat{T}_{\mathbf{R}}$ that translates the system by $\mathbf{R}$. Since the Hamiltonian is invariant under translations by $\mathbf{R}$, $\hat{H}_{\text{KS}}$ and $\hat{T}_{\mathbf{R}}$ commute and therefore have a common set of eigenfunctions. From this consideration it immediately follows that $\psi_i^{\text{KS}}(\mathbf{r} + \mathbf{R})$ can be written as

$$\psi_i^{\text{KS}}(\mathbf{r} + \mathbf{R}) = C(\mathbf{R}) \psi_i^{\text{KS}}(\mathbf{r}) \quad (2.32)$$

for some complex function $C(\mathbf{R})$. Given that translating the Kohn–Sham eigenfunction by $\mathbf{R}$ cannot change the normalisation of that wavefunction, it is found that $|C(\mathbf{R})|^2 = 1$ and that therefore

$$C(\mathbf{R}) = e^{i\theta(\mathbf{R})}. \quad (2.33)$$

Considering that

$$\hat{T}_{\mathbf{R}} \hat{T}_{\mathbf{R}'} \psi_j^{\text{KS}}(\mathbf{r}) = \hat{T}_{\mathbf{R}'} \hat{T}_{\mathbf{R}} \psi_j^{\text{KS}}(\mathbf{r}) = \hat{T}_{\mathbf{R}+\mathbf{R}'} \psi_j^{\text{KS}}(\mathbf{r}) = \psi_j^{\text{KS}}(\mathbf{r} + \mathbf{R} + \mathbf{R}') \quad (2.34)$$

it follows that

$$\hat{T}_{\mathbf{R}} \psi_j^{\text{KS}}(\mathbf{r}) = \psi_j^{\text{KS}}(\mathbf{r} + \mathbf{R}) = e^{i\mathbf{k} \cdot \mathbf{R}} \psi_j^{\text{KS}}(\mathbf{r}) \quad (2.35)$$

for some wavevector $\mathbf{k}$.

Equivalently one can state that the eigenfunctions of the Hamiltonian can be written as

$$\psi_{j\mathbf{k}}^{\text{KS}}(\mathbf{r}) = e^{i\mathbf{k} \cdot \mathbf{r}} u_j(\mathbf{r}) \quad (2.36)$$

where the function $u_j(\mathbf{r})$ has the same periodicity as the external potential. This can be seen by considering $\psi_{j\mathbf{k}}^{\text{KS}}(\mathbf{r} + \mathbf{R})$ and finding that

$$\psi_{j\mathbf{k}}^{\text{KS}}(\mathbf{r} + \mathbf{R}) = e^{i\mathbf{k} \cdot (\mathbf{r} + \mathbf{R})} u_j(\mathbf{r} + \mathbf{R}) = e^{i\mathbf{k} \cdot \mathbf{R}} e^{i\mathbf{k} \cdot \mathbf{r}} u_j(\mathbf{r}) = e^{i\mathbf{k} \cdot \mathbf{R}} \psi_{j\mathbf{k}}^{\text{KS}}(\mathbf{r}). \quad (2.37)$$

The two statements in (2.35) and (2.37) are known as Bloch's theorem [25].

Before continuing, one has to consider the appropriate boundary conditions for the problem at hand. It is assumed that the crystal considered here is made up of a number of N_j primitive unit cells in each of the three dimensions. An appropriate set of boundary conditions comes in the form of Born-von Karman boundary conditions that are imposed on the crystal supercell made up of N_j copies of the unit cell in all j direction. Let $\mathbf{o}$ denote the point of origin of the crystal, from which a number of N_j primitive unit cells get repeated in each of the three directions. One then requires that

$$\psi_i^{\text{KS}}(\mathbf{o} + \sum_j^3 \mathbf{a}_j N_j) = \psi_i^{\text{KS}}(\mathbf{o}) \quad (2.38)$$

To obey the boundary condition, it is required that $\mathbf{k} \cdot (\sum_j^3 \mathbf{a}_j N_j) = 2\pi l$ for some integer l . From this it simply follows that

$$\mathbf{k} = \sum_{j=1}^3 \frac{m_j}{N_j} \mathbf{b}_j \quad \text{for } N_j, m_j \in \mathbb{Z} \quad (2.39)$$

with the primitive reciprocal lattice vectors defined as

$$\mathbf{b}_i \cdot \mathbf{a}_j = 2\pi \delta_{ij}. \quad (2.40)$$

One can now use the above definitions to define an arbitrary reciprocal lattice vector $\mathbf{G}$ as

$$\mathbf{G} = m_1 \mathbf{b}_1 + m_2 \mathbf{b}_2 + m_3 \mathbf{b}_3 \quad \text{for } m_1, m_2, m_3 \in \mathbb{Z}. \quad (2.41)$$

Note that from Bloch's theorem it follows that $\psi_{i\mathbf{k}}(\mathbf{r}) = \psi_{i[\mathbf{k}+\mathbf{G}]}(\mathbf{r})$ and thus it is sufficient to limit the range of allowed $\mathbf{k}$ -vectors to $-\frac{1}{2} \leq \frac{m_j}{N_j} \leq \frac{1}{2}$ in order to obtain the full solution of the system. The reciprocal space to which $\mathbf{k}$ is limited by introducing this range to the allowed values of m_j is known as the first Brillouin zone and it contains all information of the entire system. From the above considerations it can be seen that the first Brillouin zone contains exactly $N_1 \times N_2 \times N_3$ discrete allowed values for $\mathbf{k}$, and thus there are as many $\mathbf{k}$ -points to be considered as there are primitive unit cells in the crystal supercell.

To solve for $|\psi_{i\mathbf{k}}\rangle$ one can then use the second formulation of Bloch's theorem (2.37) to act onto the Hamiltonian, which yields

$$\hat{H}_{\mathbf{k}}^{\text{KS}} |u_{i\mathbf{k}}\rangle = \epsilon_i |u_{i\mathbf{k}}\rangle \quad (2.42)$$

under the boundary condition $u_{i\mathbf{k}}(\mathbf{r} + \mathbf{R}) = u_{i\mathbf{k}}(\mathbf{r})$, where the effective Kohn–Sham Hamiltonian now has a $\mathbf{k}$ -dependence that can be expressed as⁵

$$\hat{H}_{\mathbf{k}} = -\frac{1}{2}(\mathbf{i}\mathbf{k} + \nabla)^2 + V_{\text{KS}}(\mathbf{r}). \quad (2.43)$$

An important special point in the Brillouin zone is the Γ -point corresponding to $\mathbf{k} = 0$. From the above Eq. (2.43) it can be seen that at this point, the eigenfunctions of the Hamiltonian can be chosen to be real.

Therefore, in order to calculate the properties of a crystal consisting of a number of unit cells, it is sufficient to solve (2.42) in a single unit cell for all allowed $\mathbf{k}$ in the first Brillouin zone. The total energy of the system is then defined via a discrete sum over eigenenergies in $\mathbf{k}$ -space. In case of an infinite crystal, $N_i \rightarrow \infty$, $\mathbf{k}$ becomes continuous in the Brillouin zone and the Kohn–Sham eigenenergies form continuous bands in $\mathbf{k}$ -space. For practical calculations however, one still only considers a discrete number of $\mathbf{k}$ -states and the integral over the Brillouin zone is approximated as a discrete sum. If enough discrete points are used, the integral is well converged and the result obtained is equivalent to that of the infinite system.

From the above considerations it also follows that one does not have to choose the primitive unit cell in real space to solve for the Bloch functions $|u_{i\mathbf{k}}\rangle$. It is equally valid to consider larger real space cells made up of a number of primitive unit cells. While this increases the computational cost of solving for $\{|u_{i\mathbf{k}}\rangle\}$ it means that fewer discrete points $\mathbf{k}$ are required to achieve converged energies for the infinite crystal.

2.2.2 Wannier Functions

Consider an infinite crystal with Bloch functions $|\psi_{i\mathbf{k}}\rangle$ as defined in (2.37). Let index i label an *isolated* Bloch function associated with an energy band $\epsilon_i(\mathbf{k})$ that does not possess any degeneracies with any other Bloch band for any value of $\mathbf{k}$. It is then possible to define a localised, orthonormal real space function $w_n(\mathbf{r} - \mathbf{R})$ such that [26]

$$|w_{n\mathbf{R}}\rangle = \frac{V}{(2\pi)^3} \int d^3k e^{-i\mathbf{k}\cdot\mathbf{R}} |\psi_{i\mathbf{k}}\rangle \quad (2.44)$$

and, conversely

$$|\psi_{i\mathbf{k}}\rangle = \sum_{\mathbf{R}} e^{i\mathbf{k}\cdot\mathbf{R}} |w_{n\mathbf{R}}\rangle \quad (2.45)$$

where V is the volume of the real space primitive unit cell. This function is referred to as a Wannier function. In a normal infinite crystal, there is generally some band crossing and thus degeneracies in $\mathbf{k}$ -space. In this scenario one defines a set

⁵Here, it is assumed that V_{KS} is fully local, which is not the case depending on whether non-local pseudopotentials are used in order to remove the core electrons from the effective Hamiltonian.

of J generalised Wannier functions for a set of J *composite* bands, that have some degeneracies amongst each other but not with any other band, via Eq. (2.44). This establishes a connection between generalised Wannier functions and generalised Bloch states via Eq. (2.45) such that the generalised Bloch states are no longer eigenfunctions of the Hamiltonian at $\mathbf{k}$ but are transformed to the eigenstates by a single unitary transformation defined by a matrix of size $J \times J$ [26]. Consider an insulator with some number of occupied bands N_{occ} . By definition, the set of N_{occ} bands forms a composite set of bands, not sharing any degeneracies in $\mathbf{k}$ -space with unoccupied bands. It is therefore possible to define a set of N_{occ} generalised localised Wannier functions spanning the same space as the N_{occ} eigenstates $|\psi_{i\mathbf{k}}\rangle$.

There is some arbitrariness in defining Wannier functions which follows from the fact that there is a freedom in the choice of phase of Bloch functions $|u_{i\mathbf{k}}\rangle$. In practice this freedom of choice can be expressed as a unitary matrix of dimensions $N_{\text{occ}} \times N_{\text{occ}}$ for a composite set of N_{occ} bands of such that

$$|u_{i\mathbf{k}}\rangle \rightarrow \sum_{j=1}^{N_{\text{occ}}} U_{ji}^{\{\mathbf{k}\}} |u_{j\mathbf{k}}\rangle. \quad (2.46)$$

Given the arbitrariness of the phase of $|u_{i\mathbf{k}}\rangle$ it can be chosen such that the spread of the resulting Wannier functions is minimised, leading to maximally localised generalised Wannier functions. It is this feature of maximal localisation that makes Wannier functions interesting for a number of applications, including linear-scaling approaches as discussed in Sect. 2.3.

The asymptotic localisation of Wannier functions has been discussed for a number of years [26]. While it had long been proven that Wannier functions and generalised Wannier functions are exponentially localised in 1D [27, 28], in 3D the proof only existed for isolated bands [28, 29]. Recently, it has been shown that generalised Wannier functions spanning the composite bands corresponding to the occupied states in a 3D insulator with time-reversal symmetry are exponentially localised [30].

2.2.3 Basis Functions

The most effective way of solving the Kohn–Sham Hamiltonian for its eigenstates depends on the type of system of interest. In most cases, it is beneficial to represent $|\psi_i^{\text{KS}}\rangle$ in some underlying set of basis functions $\{\phi_\alpha\}$ such that

$$|\psi_i^{\text{KS}}\rangle = \sum_{\alpha} a_i^{\alpha} |\phi_{\alpha}\rangle \quad (2.47)$$

for some complex coefficients a_i^{α} . For the case of a periodic crystal discussed above, a natural choice are plane waves of the form

$$\phi_{\mathbf{G}}(\mathbf{r}) = \frac{1}{\sqrt{V}} e^{i\mathbf{G} \cdot \mathbf{r}}. \quad (2.48)$$

Expanding the eigenfunction of the $\mathbf{k}$ -dependent Hamiltonian $\hat{H}_{\mathbf{k}}$ in terms of $\phi_{\mathbf{G}}(\mathbf{r})$ ensures that $u_{i\mathbf{k}}(\mathbf{r})$ obeys the periodic boundary conditions by construction. Obtaining the eigenfunctions at a certain $\mathbf{k}$ -point in the Brillouin zone reduces to finding the lowest $N/2$ eigenstates of a matrix with the elements

$$H_{\mathbf{k}}^{\mathbf{G},\mathbf{G}'} = \langle \phi_{\mathbf{G}} | \hat{H}_{\mathbf{k}} | \phi_{\mathbf{G}'} \rangle \quad (2.49)$$

Plane waves have the convenient property that they form an orthonormal basis that gives an unbiased sampling of the entire space. Furthermore, the action of the kinetic energy operator of the Kohn–Sham Hamiltonian onto a plane wave is trivial to evaluate. The accuracy of the plane wave expansion of the eigenfunctions is controlled by a single parameter $\mathbf{G}_{\max}$, the maximum reciprocal lattice vector $\mathbf{G}$ included in the basis. Given that the plane wave $|\phi_{\mathbf{G}_{\max}}\rangle$ has a kinetic energy associated with it that can simply be written as $|\mathbf{G}_{\max}|^2/2$, the basis set size is often specified via a kinetic energy cutoff. This defines the maximum kinetic energy the Kohn–Sham electrons are allowed to have and thus provides a physically motivated, systematically improvable accuracy of the basis set representation.

While plane-waves form a very effective basis in an infinite solid in periodic boundary conditions, they are not a suitable choice for isolated molecules.⁶ In this scenario, the most efficient basis sets come in the form of localised, atom-centered functions, that are generally non-orthogonal. Common choices include Gaussian functions or pseudoatomic orbitals. The non-orthogonality of the basis functions transforms the Kohn–Sham eigenvalue equations into generalised eigenvalue equations of the form

$$\mathbf{H}_{\text{KS}}^{\phi} \mathbf{a}_i = \epsilon_i \mathbf{S}^{\phi} \mathbf{a}_i \quad (2.50)$$

where

$$\begin{aligned} \left(H_{\text{KS}}^{\phi} \right)_{\alpha\beta} &= \langle \phi_{\alpha} | \hat{H}_{\text{KS}} | \phi_{\beta} \rangle \\ S_{\alpha\beta}^{\phi} &= \langle \phi_{\alpha} | \phi_{\beta} \rangle \end{aligned} \quad (2.51)$$

and $\mathbf{a}_i$ forms the coefficient vector of Kohn–Sham state $|\psi_i^{\text{KS}}\rangle$. The localisation of the basis functions allows for efficient calculations on systems of isolated molecules. Furthermore, far fewer basis functions are generally needed to represent the eigenstates of the Hamiltonian compared to the plane-wave basis. However, localised basis sets of the form discussed here do not generally offer the systematic convergence proper-

⁶This is mainly due to the fact that the treatment of a molecule in periodic boundary conditions requires the explicit inclusion of vacuum into the unit cell to avoid interaction between periodic images of the system. Since plane waves provide a uniform description of the entire unit cell, they are ineffective in this scenario, as they sample the vacuum to the same degree as the molecule.

ties of plane-wave basis sets and require special techniques to treat problems arising from non-orthogonality. Furthermore, any localised basis set is naturally unsuited to represent very delocalised Kohn–Sham states. This issue will become important in the discussion of excited states.

2.2.4 Fast-Fourier Transforms and Ewald Summation

In Sect. 2.2.1 it is pointed out that to obtain the DFT eigenstates of an infinite, periodic system, it is sufficient to solve for the functions $|u_{i\mathbf{k}}\rangle$ in a single primitive real space unit cell for some discrete mesh of points $\mathbf{k}$ confined to the first Brillouin zone in reciprocal space. The periodicity of the Kohn–Sham potential allows for the use of a number of special techniques to speed up calculations. For every density $\rho(\mathbf{r})$ constructed in the self-consistent solution to the Kohn–Sham equations, a new Kohn–Sham potential has to be constructed. For semi-local exchange-correlation functionals, the application of the Hartree potential $V_H(\mathbf{r})$ to a certain Kohn–Sham band is normally the most computationally demanding term to calculate. For a given density, the Hartree potential is simply the convolution of the density with the Coulomb potential in real space

$$V_H(\mathbf{r}) = \int d^3r' \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}. \quad (2.52)$$

The density must have the same periodicity as the lattice and can thus be expanded using a plane wave basis as defined in Sect. 2.2.3. The density in real space and the basis set coefficients $\rho(\mathbf{G})$ are related by a simple Fourier transform. However, in reciprocal space, the convolution in (2.52) reduces to a simple product⁷

$$V_H(\mathbf{G}) = \frac{4\pi\rho(\mathbf{G})}{\Omega|\mathbf{G}|^2} \quad (2.53)$$

where Ω denotes the unit cell volume. Fast-Fourier Transforms (FFTs) [31] allow to change between reciprocal space and real space in a computational effort scaling as $\mathcal{O}(N \log(N))$ with unit cell size, allowing for very efficient calculations of the Hartree potential.

Another term that does need to be evaluated to calculate the total energy per unit cell of the system is the electrostatic energy related to the ion-ion interaction associated with a single unit cell of the crystal.

$$E_{\text{ion-ion}} = \frac{1}{2} \sum_A \sum_{B \neq A} \sum_{\mathbf{R}} \frac{Z_A Z_B}{|\mathbf{R}_A - \mathbf{R}_B + \mathbf{R}|} \quad (2.54)$$

⁷The $|\mathbf{G}|=0$ component is excluded from the calculation as the overall system is taken to be charge neutral and the term is cancelled by analogous terms in the ion-ion and electron-ion interactions.

Here, the first two sums run over all the ions in the unit cell, $\mathbf{R}_A$ and $\mathbf{R}_B$ denote the positions of ion A and B and $\mathbf{R}$ denotes a real space lattice vector. The sum over $\mathbf{R}$ runs over an infinite number of real space lattice vectors and accounts for all possible interactions between the primitive unit cell and the infinite number of periodic repeats. Since the Coulomb potential falls off slowly with distance, the sum over $\mathbf{R}$ converges very slowly and is inefficient to evaluate for practical purposes. A more efficient approach comes in the form of the Ewald summation technique [32], where the Coulomb interaction $1/r$ is split into a long range and a short range part such that

$$\frac{1}{r} = \frac{\operatorname{erfc}(\alpha r)}{r} + \frac{\operatorname{erf}(\alpha r)}{r} \quad (2.55)$$

for some Ewald splitting parameter α . This allows the sum over $\mathbf{R}$ to be split into a short range part converging rapidly in real space and a long range part converging rapidly in reciprocal space, yielding a much more efficient computational scaling of $\mathcal{O}(N^2)$ with the number of ions in the unit cell. In principle, the computational effort that can be made to scale as good as $\mathcal{O}(N \log(N))$ with the number of ions in the unit cell if FFTs are used.⁸

2.2.5 Iterative Eigensolvers

Once the KS potential is constructed, the lowest $N_{\text{occ}}/2$ eigenstates of H_{KS} have to be found in the iterative solution of the Kohn–Sham equations. In case of an isolated system where the KS states are expanded in a relatively small number of localised basis functions $\{\phi_\alpha\}$, it is often possible to directly construct the Hamiltonian matrix $\mathbf{H}_{\text{KS}}^\phi$ and use standard linear-algebra methods to diagonalise it. For localised basis functions, the asymptotic scaling of the construction of the Hamiltonian is linear with system size (provided (semi)-local approximations to the exchange–correlation potential are used), while the diagonalisation techniques generally scale as $\mathcal{O}(N_\phi^3)$ with the number of basis functions N_ϕ .

In an infinite crystal, where plane waves form an appropriate basis set as discussed in Sect. 2.2.3, the computational cost of this direct approach of solving the Kohn–Sham equations is often prohibitive. In a plane wave basis N_ϕ is given by

$$N_\phi \approx \frac{V}{2\pi^2} \frac{|\mathbf{G}_{\text{max}}|^3}{\sqrt{(2^3)}} \quad (2.56)$$

which is generally much larger than the size of localised basis sets. For large cell volumes, it can become prohibitive to construct, store and diagonalise $\hat{H}_{\mathbf{k}}^{\mathbf{G}, \mathbf{G}'}$. The

⁸Given that the Ewald summation has to be only carried out once at the beginning of a calculation, it is often (eg. in the ONETEP method) considered to be unnecessary to calculate it in linear-scaling effort since it does not provide a bottleneck for practical calculations.

explicit construction of $H_{\mathbf{k}}^{\mathbf{G},\mathbf{G}'}$ also scales as $\mathcal{O}(N_{\phi}^2)$ as the plane waves are delocalised over the entire unit cell. Furthermore, since $N_{\text{occ}}/2 \ll N_{\phi}$, direct diagonalisation of $H_{\mathbf{k}}^{\mathbf{G},\mathbf{G}'}$ yields a large number of eigenstates that are not needed for the self-consistent solution of the KS equations.

The above problems can be avoided by using an iterative eigensolver. Since solving for a subset of eigenvalues of large matrices is a standard problem in computational science, a variety of different algorithms exist that vary in convergence properties and memory requirements [33]. Among the most popular in electronic structure theory are the Davidson [34] and Conjugate Gradients algorithms [35], which are based on minimising the Rayleigh quotient

$$\rho(\mathbf{x}) = \sum_i^{N_{\text{occ}}/2} \frac{\mathbf{x}_i^{\dagger} \mathbf{H}_{\text{KS}}^{\phi} \mathbf{x}_i}{\mathbf{x}_i^{\dagger} \mathbf{S}^{\phi} \mathbf{x}_i} \quad (2.57)$$

under the constraint

$$\mathbf{x}_i^{\dagger} \mathbf{S}^{\phi} \mathbf{x}_j = \delta_{ij} \quad (2.58)$$

where $\mathbf{H}_{\text{KS}}^{\phi}$ is again the Hamiltonian in some basis set representation ϕ , $\{\mathbf{x}_i\}$ is a set of approximate eigenvectors and $\mathbf{S}^{\phi}$ is the overlap matrix of the basis set. Minimising (2.57) with respect to $\{\mathbf{x}_i\}$ yields the lowest $N_{\text{occ}}/2$ eigenstates of $\mathbf{H}_{\text{KS}}^{\phi}$. A main feature of iterative methods is that to perform the minimisation it is sufficient to know the action of the Hamiltonian on an arbitrary trial vector $\mathbf{x}$. Thus in practice, one never has to explicitly calculate or store $\mathbf{H}_{\text{KS}}^{\phi}$, which is prohibitive for large basis set representations. For localised basis sets, $\mathbf{H}_{\text{KS}}^{\phi}$ is sparse and computing $\mathbf{H}_{\text{KS}}^{\phi} \mathbf{x}_i$ can be made to scale linearly with the number of basis functions. However, keeping $\{\mathbf{x}_i\}$ orthogonal has a computational complexity of $\mathcal{O}(2N_{\phi}(N_{\text{occ}}/2)^2)$ associated with it,⁹ leading to a still overall cubic scaling with system size when solving the Kohn–Sham equations.

2.2.6 Norm-Conserving Pseudopotentials

Close to the ionic core, the Coulomb potential diverges and the Kohn–Sham valence wavefunctions are known to show rapid oscillations in order to fulfil the orthogonality requirement to the core wavefunctions. This causes numerical problems in representing these states, especially when plane wave basis sets are used. To resolve the rapid oscillations close to the ionic core, very high kinetic energy cutoffs are required, making basis sets prohibitively large for practical calculations. To address this issue, plane-wave DFT codes generally make use of pseudopotentials.

⁹The computational complexity corresponds to that of the Gram-Schmidt method, a commonly used technique to orthonormalise a set of vectors.

In the pseudopotential method, the chemically inert core electrons are removed from the calculation and the bare ionic potential is replaced by a soft pseudopotential that reproduces the effect of the core electrons on the valence wave functions outside a certain cutoff region, while yielding smooth valence wave functions inside the core region. Since the core electrons to a good approximation do not take part in chemical bonding, a well constructed pseudopotential produces the right behaviour of Kohn–Sham valence wavefunctions outside the core regions no matter what chemical environment the ion is placed in.

Pseudopotentials are generally generated by solving a radial Kohn–Sham equation of the form

$$\left[-\frac{1}{2} \frac{d^2}{dr^2} + \frac{l(l+1)}{r^2} + V_{\text{KS}}[\rho](r) \right] r R_{nl}(r) = \epsilon_{nl} r R_{nl}(r) \quad (2.59)$$

for each atomic species in isolation. Here, l determines the angular momentum quantum number, $R_{nl}(r)$ are the radial wavefunctions and $\rho(r)$ is the radial density associated with the sum of the occupied wavefunctions $R_{nl}(r)$. For the purpose of this work, only norm-conserving pseudopotentials are considered. These so-called norm-conserving pseudopotentials have a number of desirable features which can be summarised as [36]:

- The valence pseudo-wavefunctions generated from the pseudopotentials should contain no nodes. This is to ensure computational efficiency, as nodes are generally associated with high kinetic energy components that are to be avoided to keep the required plane-wave basis set as small as possible.
- The radial all-electron wavefunction of a valence state n is equal to the radial pseudo wavefunction outside a given core cutoff region defined by r_c :

$$R_{nl}^{\text{AE}}(r) = R_{nl}^{\text{PS}}(r) \text{ for } r > r_c \quad (2.60)$$

- The charge enclosed in the core region must be equal for both the all-electron and the pseudo wavefunction such that:

$$\int_0^{r_c} |R_{nl}^{\text{AE}}(r)|^2 r^2 dr = \int_0^{r_c} |R_{nl}^{\text{PS}}(r)|^2 r^2 dr \quad (2.61)$$

This is the definition of “norm-conserving” when referring to pseudopotentials.

- Both the pseudo Kohn–Sham wavefunction and the all-electron wavefunction have the same eigenvalue associated with them

$$\epsilon_{nl}^{\text{AE}} = \epsilon_{nl}^{\text{PS}} \quad (2.62)$$

In general, there exists a tradeoff between the “softness” and the transferability of a generated normconserving pseudopotential. While large core region cutoffs r_c lead to very soft pseudopotentials that produce valence Kohn–Sham wavefunctions

representable by only few plane waves, harder pseudopotentials with small r_c are much more reliable when being transferred to different chemical environments.

2.2.7 Projector Augmented-Wave Formalism

While the norm-conserving pseudopotential approach is relatively simple and intuitive, it comes with a number of drawbacks. First, many transition metals require the explicit treatment of semi-core states as valence states in order to achieve satisfactory agreements with experimental data, resulting in very hard pseudopotentials. Second, any access to the all-electron density and the full all-electron wavefunctions is lost in the pseudopotential approach. The projector augmented-wave (PAW) formalism [37] has been developed to address these issues by defining a linear transformation τ that maps soft pseudo (PS) Kohn–Sham wavefunctions onto their all-electron (AE) equivalents such that

$$|\psi\rangle = \tau|\tilde{\psi}\rangle \quad (2.63)$$

Here, quantities with a tilde denote quantities associated with the PS Hilbert space. Given that the all-electron wavefunctions outside the core region are smooth quantities, we require the AE wavefunctions and the pseudo-wavefunctions to differ only inside the core regions of the ions. Inside these augmentation regions, the operator is expanded by defining AE partial waves $\{|\varphi_i\rangle\}$ that are linked to PS partial waves $\{|\tilde{\varphi}_i\rangle\}$ by the operator τ inside the augmentation region. It is required that $|\varphi_i\rangle = |\tilde{\varphi}_i\rangle$ outside the augmentation region and that $\{|\tilde{\varphi}_i\rangle\}$ is a set of numerically convenient smooth functions. The partial waves are generally written in terms of a radial function expressible on a radial grid around the atoms within the augmentation region and a spherical harmonic, such that

$$\varphi_j(\mathbf{r}) = \frac{\varphi_{n_j, L_j}(r)}{r} S_{L_j, M_j}(\hat{\mathbf{r}}). \quad (2.64)$$

The linear transformation τ can then be written as

$$\tau = 1 + \sum_i (|\varphi_i\rangle - |\tilde{\varphi}_i\rangle) \langle \tilde{p}_i| \quad (2.65)$$

where $\langle \tilde{p}_i|$ are fixed projector functions for each partial wave. The projector functions are required to fulfil the completeness and orthonormality conditions

$$\sum_i |\tilde{\varphi}_i\rangle \langle \tilde{p}_i| = 1 \quad (2.66)$$

$$\langle \tilde{p}_i | \tilde{\varphi}_j \rangle = \delta_{ij}. \quad (2.67)$$

The full mapping between the AE wavefunction and the PS wavefunction can thus be expressed as

$$|\psi\rangle = |\tilde{\psi}\rangle + \sum_i (|\varphi_i\rangle - |\tilde{\varphi}_i\rangle) \langle \tilde{p}_i | \tilde{\psi} \rangle. \quad (2.68)$$

As required, the AE wavefunction reduces to the PS wavefunction outside the augmentation spheres around the ions, while inside the spheres the soft part is replaced by an all-electron part defined via the projectors $\langle \tilde{p}_i |$ and the AE partial waves $|\varphi_i\rangle$.

Using the linear operator τ the Kohn–Sham eigenvalues of the all-electron Hamiltonian can be expressed as

$$\frac{\langle \tilde{\psi}_i | \tau^\dagger \hat{H}^{\text{KS}} \tau | \tilde{\psi}_i \rangle}{\langle \tilde{\psi}_i | \tau^\dagger \tau | \tilde{\psi}_i \rangle} = \epsilon_i^{\text{KS}}. \quad (2.69)$$

Therefore, in order to obtain the all-electron Kohn–Sham eigenvalues, it is sufficient to solve the Kohn–Sham equations for the smooth pseudo-wavefunctions and an effective transformed Hamiltonian $\tilde{H} = \tau^\dagger \hat{H}_{\text{KS}} \tau$, where the pseudo-wavefunctions need to obey a modified orthonormality condition $\langle \tilde{\psi}_i | \tau^\dagger \tau | \tilde{\psi}_j \rangle = \delta_{ij}$. The power of the formalism lies in the fact that all-electron quantities like the total all-electron energy and bandstructure are directly accessible while one only has to solve for the smooth pseudo Kohn–Sham eigenstates which are conveniently expressed by plane wave functions.

2.3 Linear-Scaling Density-Functional Theory

As seen in Sect. 2.1.3, in order to achieve an accurate representation of the kinetic energy functional, one has to introduce $N_{\text{occ}}/2$ orthogonal eigenstates $|\psi_i^{\text{KS}}\rangle$ of a fictitious non-interacting system. Solving the Kohn–Sham equations self-consistently for these eigenstates introduces an asymptotic scaling of $\mathcal{O}(N^3)$ with the number of electrons due to the orthonormality constraint. This unfavourable scaling places severe limitations on the sizes of systems that can be studied using conventional Kohn–Sham DFT. For this reason there has been a long-lasting research effort into methods that show a *linear* asymptotic scaling with system size [38, 39], while retaining the accuracy of orbital-based DFT.¹⁰ In the following, some of the main concepts of a particular class of linear-scaling DFT methods, namely methods based on the single-particle density matrix, are introduced. The discussion presented here is limited to systems with a finite band gap.

¹⁰As mentioned earlier, OF-DFT trivially obtains an $\mathcal{O}(N)$ scaling with system size but, due to the approximation of the kinetic energy functional, lacks the accuracy of Kohn–Sham approaches.

2.3.1 The Single-Particle Density Matrix

The most successful subset of linear-scaling DFT methods over the recent years relies on the use of the single-particle density matrix. Since the orthogonality constraint on the Kohn–Sham orbitals poses a major problem for linear-scaling methods, one has to give up the use of individual Kohn–Sham states in favour of a collective representation. The single-particle Kohn–Sham density matrix can be introduced as

$$\rho^{\{v\}}(\mathbf{r}, \mathbf{r}') = \sum_i^{N_{\text{occ}}/2} \psi_i^{\text{KS}*}(\mathbf{r}) \psi_i^{\text{KS}}(\mathbf{r}') \quad (2.70)$$

such that the KS density of the system can be written as $\rho(\mathbf{r}) = 2\rho^{\{v\}}(\mathbf{r}, \mathbf{r})$. In order to be a valid density matrix of an independent particle Kohn–Sham system, $\rho^{\{v\}}(\mathbf{r}, \mathbf{r}')$ has to obey two conditions that directly follow from Eq. (2.70):

$$\int d^3r'' \rho^{\{v\}}(\mathbf{r}, \mathbf{r}'') \rho^{\{v\}}(\mathbf{r}'', \mathbf{r}') = \rho^{\{v\}}(\mathbf{r}, \mathbf{r}') \quad (2.71)$$

$$2 \int d^3r \rho^{\{v\}}(\mathbf{r}, \mathbf{r}) = N_{\text{occ}}. \quad (2.72)$$

The first condition is known as the idempotency condition [40] and follows directly from the orthogonality of the Kohn–Sham states. The second condition is a normalisation constraint that ensures that the density associated with the single-particle density matrix integrates to the number of (valence)-electrons in the system. Therefore, in solving for the density matrix rather than the individual KS eigenstates, the orthonormality constraint on the eigenstates can be dropped and replaced by the idempotency and normalisation constraints of the density matrix.

2.3.2 Localised Representation and Non-orthogonality

While the collective representation of KS states in terms of a density matrix avoids the orthogonality constraint on individual eigenstates in favour of a single idempotency constraint, this approach can only lead to efficient algorithms if the density matrix can be represented in an efficient basis. In linear-scaling approaches, the density matrix is generally expanded in a set of localised, non-orthogonal orbitals or support functions $\{\phi_\alpha\}$. One then writes

$$\rho^{\{v\}}(\mathbf{r}, \mathbf{r}') = \sum_{\alpha\beta} \phi_\alpha^*(\mathbf{r}) P^{\{v\}\alpha\beta} \phi_\beta(\mathbf{r}') \quad (2.73)$$

where $\mathbf{P}^{(v)}$ is the ground state KS density matrix in the representation of localised orbitals. While for isolated molecular systems, it is always possible to choose a localised representation in the form of Eq. (2.73), the validity of the expression for infinite systems in periodic boundary conditions crucially depends on the existence of exponentially localised Wannier functions in those systems. As established in Sect. 2.2.2, in an insulating system the valence Kohn–Sham states form a composite band for which a set of exponentially localised Wannier functions can be constructed. From this it directly follows that a representation of the form of Eq. (2.73) is generally possible even in periodic systems, as long as the system in question is insulating. Note that while the formal justification for the localised representation in (2.73) originates from the existence of Wannier functions, the support functions $\{\phi_\alpha\}$ are generally not chosen to be Wannier functions constructed as described in Sect. 2.2.2, since that construction would require the self-consistent solution of the KS equations for all KS eigenstates. In most methods, more generalised localised functions like atom-centered pseudoatomic orbitals are chosen [41, 42] in order to represent the valence density matrix. This results in the fact that the set of support functions chosen in order to obtain a good representation of $\rho^{(v)}(\mathbf{r}, \mathbf{r}')$ is generally larger than the minimal set of Wannier functions necessary to span the occupied subspace.

Since the localised support functions are generally non-orthogonal, it is convenient to introduce a differentiation between covariant and contravariant tensorial quantities. Quantities with subscript greek letters are taken to be covariant quantities, while superscript greek letters are contravariant quantities. The covariant and contravariant support functions form a dual set such that $\langle \phi_\alpha | \phi^\beta \rangle = \delta_\alpha^\beta$. The overlap matrix $S_{\alpha\beta}^\phi = \langle \phi_\alpha | \phi_\beta \rangle$ is an example of a covariant quantity, while $\mathbf{P}^{(v)}$ and the inverse of the overlap matrix $(S^\phi)^{-1}$ are contravariant quantities. In this sense Eq. (2.73) is an example of a contraction between contravariant and covariant tensor quantities. In the following sections, a repeated greek index on a contra- and covariant quantity will be taken to mean a contraction of the form (2.73) and any explicit sums over localised orbitals are dropped (for more details on the tensorial nature of non-orthogonal basis sets in electronic structure theory, see [43, 44]).

2.3.3 Density Matrix DFT

The self-consistent solution of the Kohn–Sham equations can be replaced by a single energy minimisation in the density matrix formalism. Choosing the localised support functions as a representation for the single-particle Kohn–Sham Hamiltonian, the bandstructure energy $E_{\text{BS}}[\rho]$ can be written as

$$E_{\text{BS}}[\rho] = 2\text{Tr} \left[\mathbf{P}^{(v)} \mathbf{H}_{\text{KS}}^\phi \right] \quad (2.74)$$

Therefore, by using the variational principle, carrying out a direct minimisation of the bandstructure energy with respect to $\mathbf{P}^{(v)}$

$$E_{\text{BS}}[\rho_0] = \min_{\mathbf{P}^{(v)}} 2\text{Tr} \left[\mathbf{P}^{(v)} \mathbf{H}_{\text{KS}}^\phi \right] \quad (2.75)$$

subject to the constraints

$$\left(P^{\{v\}} S^\phi P^{\{v\}} \right)^{\alpha\beta} = P^{\{v\}\alpha\beta} \quad (2.76)$$

$$2\text{Tr} \left[\mathbf{P}^{(v)} \mathbf{S}^\phi \right] = N_{\text{occ}} \quad (2.77)$$

yields the Kohn–Sham ground state density ρ_0 and the ground state energy of the system without any reference to individual Kohn–Sham states and their orthogonality. Note however that $\mathbf{H}_{\text{KS}}^\phi$ is dependent on the Kohn–Sham density and thus on the density matrix. Thus the minimisation has to be performed self-consistently, just like in standard Kohn–Sham approaches. Self-consistency can be achieved by minimizing $E_{\text{BS}}[\rho_0]$ for a fixed $\mathbf{H}_{\text{KS}}^\phi$. The resulting idempotent, normalised $\mathbf{P}^{(v)}$ generates a new ρ and thus a new $\mathbf{H}_{\text{KS}}^\phi$ and the optimisation can be repeated until self-consistency is reached.

The normalisation constraint to the density matrix can be incorporated into the minimisation scheme by considering the grand potential Ω rather than the band structure energy [45]

$$\Omega[\mathbf{P}^{(v)}] = 2\text{Tr} \left[\mathbf{P}^{(v)} \left(\mathbf{H}_{\text{KS}}^\phi - \mu \mathbf{S}^\phi \right) \right] \quad (2.78)$$

and minimising it at fixed chemical potential μ . However, carrying out the minimisation while simultaneously enforcing the idempotency constraint on the ground state density matrix requires special numerical techniques and algorithms to ensure the stability of the minimisation procedure, which is discussed in the next sections.

2.3.4 Purification and Penalty Functionals

As was pointed out by McWeeny [40], it is possible to drive a near idempotent density matrix to idempotency using a purification scheme. Consider the functional $Q[\mathbf{P}^{(v)}]$ defined as the square of the deviation from idempotency of $\mathbf{P}^{(v)}$:

$$Q[\mathbf{P}^{(v)}] = \text{Tr} \left[\left(\mathbf{P}^{(v)} \mathbf{S}^\phi \mathbf{P}^{(v)} \mathbf{S}^\phi - \mathbf{P}^{(v)} \mathbf{S}^\phi \right)^2 \right] \quad (2.79)$$

The functional is necessarily positive-semidefinite and strictly vanishes for idempotent $\mathbf{P}^{(v)}$. Differentiating the scalar quantity $Q[\mathbf{P}^{(v)}]$ with respect to $\mathbf{P}^{(v)}$ one obtains the covariant gradient:

$$\frac{\partial Q[\mathbf{P}^{(v)}]}{\partial \mathbf{P}^{(v)}} = 4\mathbf{S}^\phi \mathbf{P}^{(v)} \mathbf{S}^\phi \mathbf{P}^{(v)} \mathbf{S}^\phi \mathbf{P}^{(v)} \mathbf{S}^\phi - 6\mathbf{S}^\phi \mathbf{P}^{(v)} \mathbf{S}^\phi \mathbf{P}^{(v)} \mathbf{S}^\phi + 2\mathbf{S}^\phi \mathbf{P}^{(v)} \mathbf{S}^\phi \quad (2.80)$$

The covariant gradient can be changed into a contravariant gradient with the same tensorial properties as $\mathbf{P}^{(v)}$ by multiplying the above expression from the left and right with the inverse overlap matrix. Using the contravariant gradient as a steepest descent direction for improving a trial guess $\mathbf{P}_n^{(v)}$, $\mathbf{P}_{n+1}^{(v)}$ can be written as

$$\mathbf{P}_{n+1}^{(v)} = 3\mathbf{P}_n^{(v)} \mathbf{S}^\phi \mathbf{P}_n^{(v)} - 2\mathbf{P}_n^{(v)} \mathbf{S}^\phi \mathbf{P}_n^{(v)} \mathbf{S}^\phi \mathbf{P}_n^{(v)} \quad (2.81)$$

It is then in principle possible to find the DFT ground state energy by performing a two-step approach of alternatingly minimising $\Omega[\mathbf{P}^{(v)}]$ and $Q[\mathbf{P}^{(v)}]$. However, this approach is potentially numerically unstable and an alternative method comes in the form of including the effect of $Q[\mathbf{P}^{(v)}]$ into the ground state energy minimisation via a penalty functional. Consider the effective total energy functional introduced by Kohn [46]

$$F_1[\mathbf{P}^{(v)}] = \Omega[\mathbf{P}^{(v)}] + \alpha \left[Q[\mathbf{P}^{(v)}] \right]^{\frac{1}{2}} \quad (2.82)$$

where α is some positive constant. The functional $F_1[\mathbf{P}^{(v)}]$ has a true minimum for the idempotent ground state density matrix. This follows from the fact that the energy is non-variational with respect to changes in the occupancies of $\mathbf{P}^{(v)}$ due to the presence of the square root. The square root causes the functional to have a branch point at the correct occupancy, which causes issues for standard conjugate gradient minimisation schemes [47, 48].

The alternative to the Kohn functional is to consider [48]

$$F_2[\mathbf{P}^{(v)}] = \Omega[\mathbf{P}^{(v)}] + \alpha Q[\mathbf{P}^{(v)}]. \quad (2.83)$$

This functional does not contain any branch points and is easy to minimise with standard iterative techniques. However, the missing branch point causes F_2 to only have a minimum at an approximately idempotent density matrix $\mathbf{P}'^{(v)}$, with $\mathbf{P}'^{(v)}$ approaching the correct idempotent ground state density matrix as $\alpha \rightarrow \infty$. The error in the occupancies of $\mathbf{P}^{(v)}$ can be shown to be proportional to α^{-1} , causing significant errors in the bandstructure energy for practical values of α . However, it is possible to derive a correction term to the energy due to the imperfect idempotency such that [48]

$$E_{\text{BS}}[\rho_0] \approx E_{\text{BS}}[\mathbf{P}'^{(v)}] - 2\alpha \text{Tr} \left[\mathbf{P}'^{(v)} \mathbf{S}^\phi \left(1 - \mathbf{P}'^{(v)} \mathbf{S}^\phi \right)^2 \left(1 - 2\mathbf{P}'^{(v)} \mathbf{S}^\phi \right) \right]. \quad (2.84)$$

2.3.5 The LNV Method

While enforcing the density matrix idempotency with penalty functionals causes a number of problems in standard minimisation approaches, it was shown by Li, Nunes and Vanderbilt [45] that these issues can be largely avoided. In the LNV method, one introduces a trial or auxiliary density matrix $\mathbf{L}^{\{v\}}$ such that

$$\mathbf{P}^{\{v\}} = 3\mathbf{L}^{\{v\}}\mathbf{S}^\phi\mathbf{L}^{\{v\}} - 2\mathbf{L}^{\{v\}}\mathbf{S}^\phi\mathbf{L}^{\{v\}}\mathbf{S}^\phi\mathbf{L}^{\{v\}} \quad (2.85)$$

i.e. $\mathbf{P}^{\{v\}}$ is the first order idempotency corrected version of $\mathbf{L}^{\{v\}}$ following Eq. (2.81). Now, one considers the grand potential Ω to be a function of $\mathbf{L}^{\{v\}}$ such that

$$\Omega[\mathbf{L}^{\{v\}}] = \text{Tr} \left[\left(3\mathbf{L}^{\{v\}}\mathbf{S}^\phi\mathbf{L}^{\{v\}} - 2\mathbf{L}^{\{v\}}\mathbf{S}^\phi\mathbf{L}^{\{v\}}\mathbf{S}^\phi\mathbf{L}^{\{v\}} \right) \left(\mathbf{H}_{\text{KS}}^\phi - \mu\mathbf{S}^\phi \right) \right]. \quad (2.86)$$

The functional $\Omega[\mathbf{L}^{\{v\}}]$ has a *local* minimum where $\mathbf{P}^{\{v\}}$ corresponds to the idempotent Kohn–Sham ground state density of the system. The global minimum is characterised by a runaway solution where the occupancies of states below and above the Fermi level approach positive and negative infinity respectively. However, as long as a near idempotent density matrix is used as an input guess, with occupancies close to 0 and 1, standard iterative minimisation techniques applied to Eq. (2.86) yield the idempotent ground state density matrix corresponding to the Hamiltonian $\mathbf{H}_{\text{KS}}^\phi$.

2.3.6 Linear-Scaling DFT

In the previous sections it was shown that density matrix DFT avoids the source $\mathcal{O}(N^3)$ scaling of standard Kohn–Sham DFT by replacing the orthonormality of Kohn–Sham states with the idempotency of the single-particle density matrix. However, regardless of whether idempotency is achieved via a penalty functional minimisation or the LNV method, it generally involves the multiplication of density matrices. Since $\{\phi_\alpha\}$ and thus the dimensions of $\mathbf{L}^{\{v\}}$ or $\mathbf{P}^{\{v\}}$ grow linearly with system size, the computational effort in computing matrix products of the form $\mathbf{L}^{\{v\}}\mathbf{S}^\phi\mathbf{L}^{\{v\}}$ generally scales as $\mathcal{O}(N^3)$ with system size, suggesting that the density matrix formalism does not in fact yield any improvement in scaling over the conventional KS-DFT method.

However, the considerations that prove the existence of maximally localised Wannier functions for a set of composite bands (see Sect. 2.2.2) also show that the single particle density matrix corresponding to the same set of composite bands in a crystal with inversion symmetry decays exponentially with distance [28], such that

$$\lim_{|\mathbf{r}-\mathbf{r}'| \rightarrow \infty} e^{\epsilon A|\mathbf{r}-\mathbf{r}'|} \rho^{\{v\}}(\mathbf{r}, \mathbf{r}') = 0 \quad (2.87)$$

for some $0 < \epsilon < 1$. Thus in an insulator, the Kohn–Sham single particle density matrix decays exponentially with distance and the rate of the exponential decay A is a function of the band gap [49]. Since the density matrix is represented by localised functions, it follows that in the case of insulators $\mathbf{L}^{\{v\}}$ and $\mathbf{P}^{\{v\}}$ are sparse for sufficiently large system sizes. In the limit of large enough systems, the resulting matrices of all matrix products required in the energy minimisation become sparse and all matrix operations can be performed in $\mathcal{O}(N)$ effort.

Linear-scaling DFT calculations are thus possible if the explicit calculation of individual Kohn–Sham states is abandoned in favour of a collective representation through the single particle density matrix and if the sparsity of the density matrix is exploited. The nature of the density matrix representation means that some quantities readily accessible in Kohn–Sham DFT like the Kohn–Sham bandstructure of the system are inaccessible in the linear-scaling formulation, although they can generally be obtained in a single $\mathcal{O}(N^3)$ post-processing step of diagonalising the Kohn–Sham Hamiltonian.

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