

LINEAR SCALING ELECTRONIC STRUCTURE METHODS

Christine Bolliger

Responsibility and supervision:
Prof. Daniel Kressner

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Contents

0	Introduction	1
1	Density functional theory	3
1.1	The electronic Schrödinger equation	3
1.2	Hohenberg-Kohn theory	5
1.3	Kohn-Sham approach	7
2	Plane wave basis sets	11
2.1	Structure of crystals	11
2.2	The Bloch theorem	14
2.3	Pseudopotential approximation	16
2.4	Matrix diagonalization procedure	16
3	O(N) strategies	19
3.1	Density matrix	19
3.2	Locality	20
3.3	Fermi operator expansion	21
3.4	Fermi operator projection	22
4	The density matrix minimization approach	23
4.1	Purification function	23
4.2	Conjugate gradient minimization	24
A	abinit input files	27
	Bibliography	33

List of Figures

Structure optimization.	5
1.1 The Fermi function.	8
2.1 A fraction of a silicon crystal and its primitive vectors.	12
2.2 Wigner-Seitz cell of a $2d$ structure.	12
2.3 Supercell of the H_2 molecule.	13
2.4 Matrix diagonalization procedure.	17
4.1 The McWeeny purification function.	24

Chapter 0

Introduction

Solving the quantum-mechanical equations for many-electron systems is a highly non-trivial task which is feasible only by means of various approximations, such as the approximation of the Hamiltonian by considering a coulombic potential only and the Born-Oppenheimer approximation. In most cases (such as Hartree-Fock and density functional methods), the wave function is approximated by an independent-electron approach.

But even with these approximations, solving the equations analytically is impossible and the numerical solution needs a high computational effort. The computer time needed scales at least cubically (in density functional theory) with the number of electrons involved. Thus by considering very large systems, the solution cannot be found within a reasonable amount of time even with the most powerful computers. To this end, various methods have been developed that have a linear scaling of the computer time with respect to the number of electrons. In general, they have a larger prefactor, thus they are suitable for very large systems, but for smaller systems standard techniques perform better.

The purpose of this thesis is to review the essentials of linear scaling methods and in particular the density matrix minimization approach in density functional theory.

Chapter 1

Density functional theory

1.1 The electronic Schrödinger equation

A system of M nuclei and N electrons is considered. The nuclei are treated as structureless particles with charge Z_α and spin σ_α , which is already an approximation (no nuclear physics).

The *time-dependent Schrödinger equation (TDSE)* for the system reads

$$\hat{H}(t)\tilde{\Psi}(\tau, \nu, t) = i\hbar \frac{\partial \tilde{\Psi}(\tau, \nu, t)}{\partial t} \quad (1.1)$$

where

$\tau = \{\tau_1, \dots, \tau_N\}$ is a $4N$ -dimensional electronic coordinate and spin vector, and $\nu = \{\nu_1, \dots, \nu_M\}$ is a $4M$ -dimensional nuclear coordinate and spin vector.

Assuming a *time-independent Hamiltonian* $\hat{H}(t) = \hat{H}$ yields the *time-independent Schrödinger equation (TISE)*:

$$\hat{H}\Psi(\tau, \nu) = E\Psi(\tau, \nu) . \quad (1.2)$$

$\Psi(\tau, \nu)$ is the stationary wave function defined by

$$\tilde{\Psi}(\tau, \nu, t) = \Psi(\tau, \nu)e^{-\frac{iEt}{\hbar}} , \quad (1.3)$$

where $\hbar = \frac{h}{2\pi}$ and h is Planck's constant.

As a further approximation, only coulombic interactions are included, while neglecting relativistic effects, magnetic interactions (spin-spin, spin-orbit and orbit-orbit) and non-electromagnetic forces (e.g. strong, weak and gravitational interactions). The system is isolated and thus no interaction with external fields is included, yielding a Hamiltonian of pure electrostatic interaction (in atomic units):

$$\begin{aligned} \hat{H} = & - \sum_i^N \frac{1}{2} \nabla_i^2 - \sum_I^M \frac{1}{2M_I} \nabla_I^2 \\ & + \sum_i^N \sum_{j>i}^N \frac{1}{r_{ij}} - \sum_i^N \sum_I^M \frac{Z_I}{r_{iI}} + \sum_I^M \sum_{J>I}^M \frac{Z_I Z_J}{r_{IJ}} , \end{aligned} \quad (1.4)$$

where M_I is the mass, Z_I the charge and \mathbf{r}_I the position of nucleus I , \mathbf{r}_i denotes the position of electron i , and $r_{\alpha\beta} = |\mathbf{r}_\alpha - \mathbf{r}_\beta|$ the distance between two positions.

The so-called *Born-Oppenheimer approximation* decouples the movement of the electrons and the nuclei. Knowing that electrons are more than 10^4 times lighter than nuclei and thus they move more than 10^4 times faster, the problem can be decomposed into an electronic and a nuclear problem, as follows:

- *Electronic problem.* From the point of view of the electrons, the nuclei are quasi motionless, hence the kinetic energy of the nuclei can be neglected (moreover, the repulsion between the nuclei is not included, since this is a constant energy shift which does not depend on the positions of the electrons):

$$\hat{H}_e = - \sum_i^N \frac{1}{2} \nabla_i^2 + \sum_i^N \sum_{j>i}^N \frac{1}{r_{ij}} - \sum_i^N \sum_I^M \frac{Z_I}{r_{iI}}, \quad (1.5)$$

yielding the electronic Schrödinger equation for a given nuclear configuration ν :

$$\hat{H}_e \Psi_{e,k}(\tau; \nu) = V_k(\nu) \Psi_{e,k}(\tau; \nu). \quad (1.6)$$

Solving the electronic problem gives a set of electronic energy levels $\{V_k(\nu)\}$.

- *Nuclear problem.* As the electrons relax instantaneously to the movement of the nuclei, in the Schrödinger equation the electronic part of the Hamiltonian can be replaced by the electronic energy levels $V_k(\nu)$:

$$\hat{H}_n = - \sum_I^M \frac{1}{2M_I} \nabla_I^2 + \sum_I^M \sum_{J>I}^M \frac{Z_I Z_J}{r_{IJ}} + V_k(\nu), \quad (1.7)$$

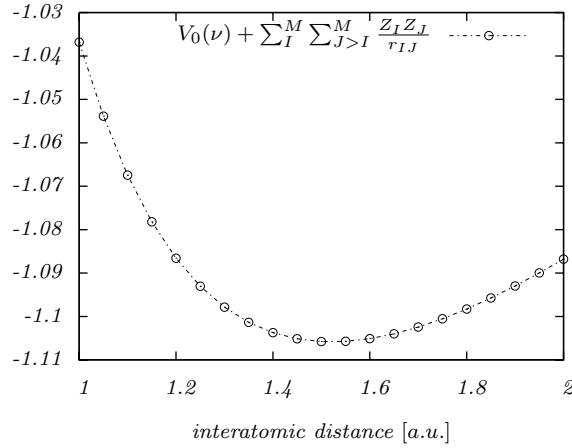
and the nuclear Schrödinger equation reads:

$$\hat{H}_n \Psi_{n,kl}(\nu) = E_{kl}(\nu) \Psi_{n,kl}(\nu). \quad (1.8)$$

Combining the results of the electronic and the nuclear problem yields the solution of the TISE $\hat{H}\Psi(\tau, \nu) = E\Psi(\tau, \nu)$ within the Born-Oppenheimer approximation:

$$\Psi(\tau, \nu) = \Psi_{e,k}(\tau; \nu) \Psi_{n,kl}(\nu) \quad (1.9)$$

Example 1.1 (H_2 molecule).



The electronic Schrödinger equation was solved for different interatomic distances yielding the effective potential for the nuclei.

From now on, only the electronic Schrödinger equation (for a given nuclear configuration) is considered, and it will be written as $\hat{H}\Psi(\mathbf{r}_1, s_1, \mathbf{r}_2, s_2, \dots, \mathbf{r}_N, s_N) = E\Psi(\mathbf{r}_1, s_1, \mathbf{r}_2, s_2, \dots, \mathbf{r}_N, s_N)$ for convenience.

1.2 Hohenberg-Kohn theory

The electronic Schrödinger equation can be solved by means of the variational principle. For a numerical solution, the wave function has to be expanded in a series of basis functions. However, as the wave function is a function of $4N$ variables, this leads to a high-dimensional problem. There is another formulation available, the density functional theory, where all calculations are based on the electron density, a function of only 3 variables, rather than the full wave function. The formal basis for the density functional theory was derived by Hohenberg and Kohn [5].

The ground state of a quantum system is completely determined by its wave function Ψ_0 , which is an eigenfunction of the Hamiltonian of the system with energy E_0 , i.e. the energy and all properties are determined by the Hamiltonian.

The (electronic) Hamiltonian consists of three parts

$$\hat{H} = \hat{T} + \hat{V}_{ee} + \hat{V}_{\text{ext}}, \quad (1.10)$$

the kinetic energy

$$\hat{T} = -\sum_i^N \frac{1}{2} \nabla_i^2, \quad (1.11)$$

the electron-electron interaction

$$\hat{V}_{ee} = \sum_i^N \sum_{j>i}^N \frac{1}{r_{ij}} \quad (1.12)$$

and the external potential (the attraction of the nuclei)

$$\hat{V}_{\text{ext}} = \sum_i v(\mathbf{r}_i) = -\sum_i^N \sum_I^M \frac{Z_I}{r_{iI}}, \quad (1.13)$$

which is a purely local function.

Definition 1.1 (Electron density). *The electron density is defined as*

$$\begin{aligned} \rho(\mathbf{r}) &= N \int \Psi^*(\mathbf{r}, s_1, \mathbf{r}_2, s_2, \dots, \mathbf{r}_N, s_N) \\ &\quad \times \Psi(\mathbf{r}, s_1, \mathbf{r}_2, s_2, \dots, \mathbf{r}_N, s_N) ds_1 ds_2 \dots ds_N d\mathbf{r}_2 \dots d\mathbf{r}_N, \end{aligned} \quad (1.14)$$

where $\Psi(\mathbf{r}, s_1, \mathbf{r}_2, s_2, \dots, \mathbf{r}_N, s_N)$ is the wave function of the system which is, according to the Pauli principle, antisymmetric under interchange of any two electrons, and it is assumed to be normalized: $\langle \Psi | \Psi \rangle = \int \Psi^* \Psi ds_1 d\mathbf{r}_1 \dots ds_N d\mathbf{r}_N = 1$. Thus it holds $\int \rho(\mathbf{r}) d\mathbf{r} = N$.

The **basic Hohenberg-Kohn theorem** states that *the ground state electron density determines – within an additional constant – the external potential.*

There is a unique correspondence between the ground state density of a system and the external potential which fixes – together with the number of electrons, that can be obtained from ρ by integration – the Hamiltonian of the system and all its properties.

Thus the energy can, in principle, be expressed as a functional of the electron density:

$$\begin{aligned} E[\rho] &= \langle \Psi[\rho] | \hat{H} | \Psi[\rho] \rangle \\ &= \langle \Psi[\rho] | (\hat{T} + \hat{V}_{ee}) | \Psi[\rho] \rangle + \langle \Psi[\rho] | \sum_i v(\mathbf{r}_i) | \Psi[\rho] \rangle \\ &= \int \Psi^*[\rho] (\hat{T} + \hat{V}_{ee}) \Psi[\rho] ds_1 d\mathbf{r}_1 \dots ds_N d\mathbf{r}_N \\ &\quad + \sum_i \int \Psi^*[\rho] v(\mathbf{r}_i) \Psi[\rho] ds_1 d\mathbf{r}_1 \dots ds_N d\mathbf{r}_N \\ &= F[\rho] + \int \rho(\mathbf{r}) v(\mathbf{r}) d^3r. \end{aligned} \quad (1.15)$$

Definition 1.2 (v -representability). *A density is called v -representable if it can be obtained from an antisymmetric wave function that corresponds to the ground state of a Hamiltonian for which we know the number of electrons, the type of interaction between the electrons and which contains some kind of local external potential.*

It is, however, a difficult task to check whether a given density is generated by an external potential or not, i.e. if it is v -representable or not.

Theorem 1.3 (Hohenberg-Kohn variational principle). *The energy functional $E[\rho]$ takes its minimum for the true ground state electron density, i.e. for all v -representable $\tilde{\rho}$ it holds*

$$\Rightarrow E[\rho(\mathbf{r})] \leq E[\tilde{\rho}(\mathbf{r})]. \quad (1.16)$$

However, if one wants to apply the HK variational principle, one has to make sure that all trial densities belong to the class of v -representable functions.

Levy [7] stated in 1979 that the minimization can be performed over all N -representable densities as well (densities that can be represented by any antisymmetric, normalized N -particle wave function). Fortunately, every "reasonable" positive function is N -representable.

The variational principle for the energy functional, together with the constraint $\int \rho(\mathbf{r}) d\mathbf{r} = N$, leads to the *Euler-Lagrange equation*:

$$\delta \left\{ E[\rho] - \mu \left[\int \rho(\mathbf{r}) d^3r - N \right] \right\} = 0 \quad (1.17)$$

$$\mu = \frac{\delta E[\rho]}{\delta \rho(\mathbf{r})} = v(\mathbf{r}) + \frac{\delta F[\rho]}{\delta \rho(\mathbf{r})},$$

with Lagrange multiplier μ which corresponds to the chemical potential.

Thomas-Fermi and related approaches approximate $F[\rho]$ by means of certain model systems. However, in practice, this approach leads to rather crude approximations for the kinetic energy and the exchange energy.

1.3 Kohn-Sham approach

Kohn and Sham [6] proposed a different approach. The central assertion of the Kohn-Sham approach is:

Assumption 1.4 (Kohn-Sham). *For every interacting system with ground state density ρ , there exists a non-interacting system S with the same ground state density $\rho_s = \rho$.*

(Unfortunately, it turns out that this is not the case in general, but exceptions are rare.)

The Kohn-Sham assumption indicates that we can express the density of the interacting system in terms of the one-electron functions $\{\Psi_i\}$ forming a Slater-determinant which is the ground state wave function for a non-interacting system S with some kind of local external potential $v_{\text{eff}}(\mathbf{r})$:

- *The non-interacting system.*

$$\hat{H}_s = \hat{T}_s + \hat{V}_s = \sum_i^N \hat{h}_i = \sum_i^N \left[-\frac{1}{2} \nabla_i^2 + v_{\text{eff}}(\mathbf{r}_i) \right] \quad (1.18)$$

The ground state wave function of a non-interacting system is a Slater determinant composed of the one-electron functions Ψ_i (the so-called *Kohn-Sham orbitals*) with the lowest eigenvalues ϵ_i obtained from the one-electron equation:

$$\left[-\frac{1}{2} \nabla^2 + v_{\text{eff}}(\mathbf{r}) \right] \Psi_i(\mathbf{r}) = \epsilon_i \Psi_i(\mathbf{r}). \quad (1.19)$$

The ground state density that can be obtained from the one-electron functions (a closed-shell system is assumed) by

$$\rho_s(\mathbf{r}) = 2 \sum_{i=1}^{\infty} f(\epsilon_i) |\Psi_i(\mathbf{r})|^2 \quad (1.20)$$

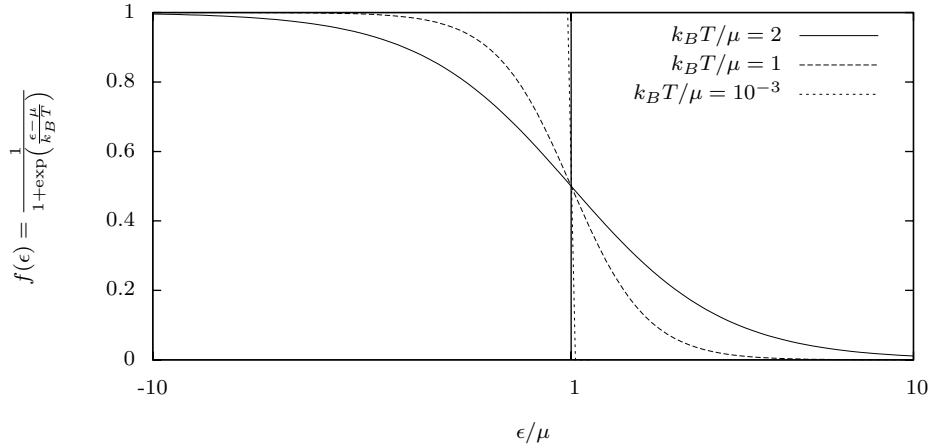


Figure 1.1. The Fermi function. At $T = 0$, it corresponds to a step function.

at a finite temperature T , where f is the Fermi function (cf. Figure 1.1):

$$f(\epsilon) = \frac{1}{1 + \exp\left(\frac{\epsilon - \mu}{k_B T}\right)}, \quad (1.21)$$

μ is the chemical potential (Fermi level) and k_B the Boltzmann constant. At $T = 0$, this simplifies to

$$\rho_s(\mathbf{r}) = 2 \sum_{i=1}^{N/2} |\Psi_i(\mathbf{r})|^2. \quad (1.22)$$

In the latter case, the energy of this system is the sum of the one-electron energies:

$$\begin{aligned} E_s[\rho] &= 2 \sum_{i=1}^{N/2} \epsilon_i = 2 \sum_{i=1}^{N/2} \langle \Psi_i | -\frac{1}{2} \nabla^2 + v_{\text{eff}}(\mathbf{r}) | \Psi_i \rangle \\ &= 2 \sum_{i=1}^{N/2} \langle \Psi_i | -\frac{1}{2} \nabla^2 | \Psi_i \rangle + 2 \sum_{i=1}^{N/2} \langle \Psi_i | v_{\text{eff}}(\mathbf{r}) | \Psi_i \rangle \\ &= \sum_{i=1}^{N/2} \int |\nabla \Psi_i(\mathbf{r})|^2 d\mathbf{r} + 2 \sum_{i=1}^{N/2} \int v_{\text{eff}}(\mathbf{r}) |\Psi_i(\mathbf{r})|^2 d\mathbf{r} \\ &= T_s[\rho] + \int v_{\text{eff}}(\mathbf{r}) \rho(\mathbf{r}) d\mathbf{r}, \end{aligned} \quad (1.23)$$

where $T_s[\rho]$ is the kinetic energy.

The ground state density obtained from the solution of (1.19) is also the solution of the Euler-Lagrange equation of this system

$$\mu_s = \frac{\delta T_s[\rho]}{\delta \rho(\mathbf{r})} + v_{\text{eff}}(\mathbf{r}). \quad (1.24)$$

Note that in so doing the Euler-Lagrange equation (1.24) can be solved even though the explicit form of the functional derivative of $T_s[\rho]$ is not known.

- *The interacting system.*

The energy of the interacting system can be rewritten as

$$E[\rho] = T_s[\rho] + V_{\text{ext}}[\rho] + J[\rho] + E_{\text{xc}}[\rho] \quad (1.25)$$

where

$$\begin{aligned} T_s[\rho] &\stackrel{(1.23)}{=} \sum_{i=1}^{N/2} \int |\nabla \Psi_i(\mathbf{r})|^2 d\mathbf{r}, \\ V_{\text{ext}}[\rho] &= \int \rho(\mathbf{r}) v(\mathbf{r}) d^3r, \\ J[\rho] &= \frac{1}{2} \int \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}', \\ E_{\text{xc}}[\rho] &= V_{\text{ee}}[\rho] - J[\rho] + T[\rho] - T_s[\rho]. \end{aligned} \quad (1.26)$$

The Euler-Lagrange equation reads as

$$\mu = \frac{\delta T_s[\rho]}{\delta \rho(\mathbf{r})} + v(\mathbf{r}) + v_{\text{coul}}(\mathbf{r}) + v_{\text{xc}}(\mathbf{r}), \quad (1.27)$$

where

$$\begin{aligned} v_{\text{coul}}(\mathbf{r}) &= \frac{\delta J[\rho]}{\delta \rho(\mathbf{r})} = \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}', \\ v_{\text{xc}}(\mathbf{r}) &= \frac{\delta E_{\text{xc}}[\rho]}{\delta \rho(\mathbf{r})}. \end{aligned} \quad (1.28)$$

Defining

$$v_{\text{eff}}(\mathbf{r}) = v(\mathbf{r}) + v_{\text{coul}}(\mathbf{r}) + v_{\text{xc}}(\mathbf{r}), \quad (1.29)$$

we obtain exactly the same Euler-Lagrange equation as in the case of the non-interacting system (1.24). The solution of this equation is, as already pointed out, the density obtained by (1.20), with the one-electron functions that belong to the lowest eigenvalues of (1.19).

But note that, although the density has been obtained by the one-electron functions, they have no physical meaning, in particular the energy of the interacting system is not the sum of the eigenvalues! To see this, we compare the energy of the non-interacting system (1.23)

$$\begin{aligned} E_s[\rho] &= 2 \sum_{i=1}^{N/2} \epsilon_i = T_s[\rho] + \int v_{\text{eff}}(\mathbf{r})\rho(\mathbf{r}) d\mathbf{r} \\ &= T_s[\rho] + \int v(\mathbf{r})\rho(\mathbf{r}) d\mathbf{r} + \int \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' \\ &\quad + \int v_{\text{xc}}(\mathbf{r})\rho(\mathbf{r}) d\mathbf{r} \end{aligned} \quad (1.30)$$

to the energy of the interacting system

$$E[\rho] = T_s[\rho] + \int v(\mathbf{r})\rho(\mathbf{r}) d\mathbf{r} + \frac{1}{2} \int \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' + E_{\text{xc}}[\rho] \quad (1.31)$$

and obtain

$$E[\rho] = 2 \sum_{i=1}^{N/2} \epsilon_i - \frac{1}{2} \int \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' - \int v_{xc}(\mathbf{r})\rho(\mathbf{r}) d\mathbf{r} + E_{xc}[\rho]. \quad (1.32)$$

One may ask what has been gained by this formulation, since the explicit energy functional is still not known (the unknown parts have just been put into the exchange-correlation functional $E_{xc}[\rho]$). The advantage of the Kohn-Sham approach is that by explicitly separating out the independent-particle kinetic energy and the long-range coulombic term, the remaining exchange-correlation functional $E_{xc}[\rho]$ can reasonably be approximated by a local functional of the density, i.e.

$$E_{xc}[\rho] = \int \rho(\mathbf{r})\epsilon_{xc}(\mathbf{r}) d\mathbf{r}, \quad (1.33)$$

thus

$$\frac{\delta E_{xc}[\rho]}{\delta \rho(\mathbf{r})} = \epsilon_{xc}(\mathbf{r}). \quad (1.34)$$

Approximations of ϵ_{xc} are obtained by LDA (local density approximation) [15] or GGA (generalized gradient approximation) [14].

Summary (Kohn-Sham approach)

1. Use an approximation for $E_{xc}[\rho]$.
2. Solve $[-\frac{1}{2}\nabla_i^2 + v(\mathbf{r}) + v_{coul}(\mathbf{r}) + \epsilon_{xc}(\mathbf{r})] \Psi_i = \epsilon_i \Psi_i$ for the $N/2$ lowest eigenvalues to obtain the Kohn-Sham orbitals Ψ_i .
3. Obtain the ground state density from $\rho_s(\mathbf{r}) = 2 \sum_{i=1}^{N/2} |\Psi_i(\mathbf{r})|^2$ (for $T = 0$).
4. Now the ground state energy can be calculated:

$$E[\rho] = 2 \sum_{i=1}^{N/2} \epsilon_i - \frac{1}{2} \int \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' - \int v_{xc}(\mathbf{r})\rho(\mathbf{r}) d\mathbf{r} + E_{xc}[\rho].$$

Chapter 2

Plane wave basis sets

The electronic Schrödinger equation is solved, in the Kohn-Sham approach (c.f. p.10), by solving the independent particle Schrödinger equation

$$\underbrace{\left[-\frac{1}{2}\nabla^2 + v_{\text{eff}}(\mathbf{r}) \right]}_{\hat{H}_{\text{eff}}} \Psi_i(\mathbf{r}) = \epsilon_i \Psi_i(\mathbf{r}) \quad (2.1)$$

numerically by expanding the eigenfunctions in a series of basis functions. In this chapter the expansion in a plane wave basis set is considered. To proceed, we need the definition of the Bravais lattice and the reciprocal lattice.

2.1 Structure of crystals

In a crystal, the positions of the nuclei are repeated periodically in space, and thus all properties follow the same periodicity. The set of all translations that map the crystal onto itself, written as

$$\mathbf{T}(\mathbf{n}) = \sum_i n_i \mathbf{a}_i, \quad (2.2)$$

where the vectors $\{\mathbf{a}_i\}$ are the primitive vectors defining the *unit cell*, forms the *Bravais lattice*. Positions and types of atoms in the primitive cell are called the *basis*.

The *Wigner-Seitz cell* of a lattice is a special kind of unit cell, it is defined by the planes that are the perpendicular bisectors from the origin to all lattice points (cf. Figure 2.2). It is the most compact unit cell that is symmetric around the origin.

As an example, consider the silicon crystal. In Figure 2.1, a fraction of a silicon crystal is shown. The primitive vectors are

$$\begin{aligned} \mathbf{a}_1 &= a(0, 1/2, 1/2) \\ \mathbf{a}_2 &= a(1/2, 0, 1/2) \\ \mathbf{a}_3 &= a(1/2, 1/2, 0) \end{aligned} \quad (2.3)$$

and the basis is

$$\begin{aligned} \mathbf{r}_0 &= (0, 0, 0) \\ \mathbf{r}_1 &= \frac{1}{4}(\mathbf{a}_1 + \mathbf{a}_2 + \mathbf{a}_3). \end{aligned} \quad (2.4)$$

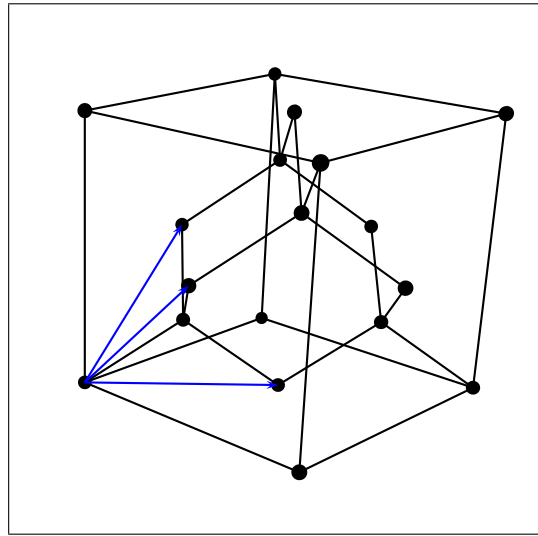


Figure 2.1. *A fraction of a silicon crystal and its primitive vectors.*

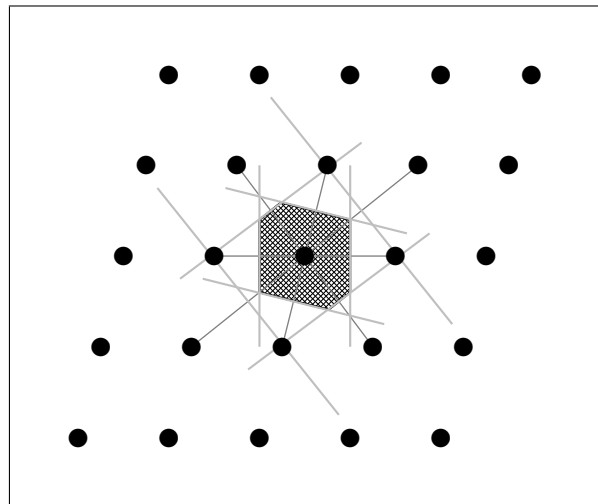


Figure 2.2. *Wigner-Seitz cell of a 2d structure.*

In this framework, also isolated molecules can be considered, by considering an infinitely large unit cell. However, in practice, this is not possible, and so-called *supercells* are introduced, for which periodic boundary conditions are applied. The size of the supercell has to be chosen large enough such that the influence of the artificial copies of the molecule is negligible. This is tested by increasing its volume until the energy has converged. The supercell of a H_2 molecule is illustrated in Figure 2.3, and in Example 2.1, the convergence of the energy with respect to the size of the supercell is presented.

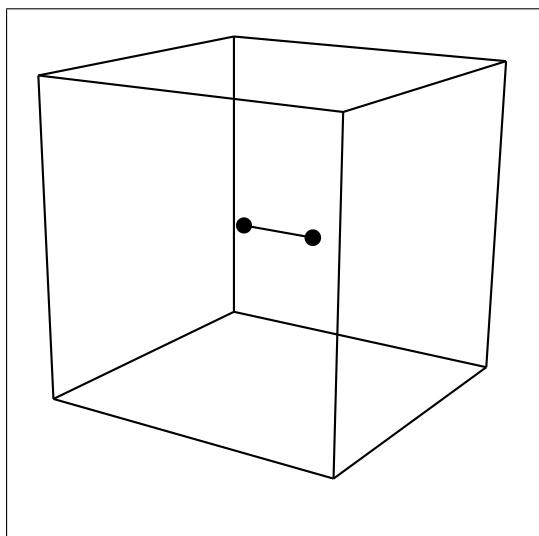


Figure 2.3. Supercell of the H_2 molecule.

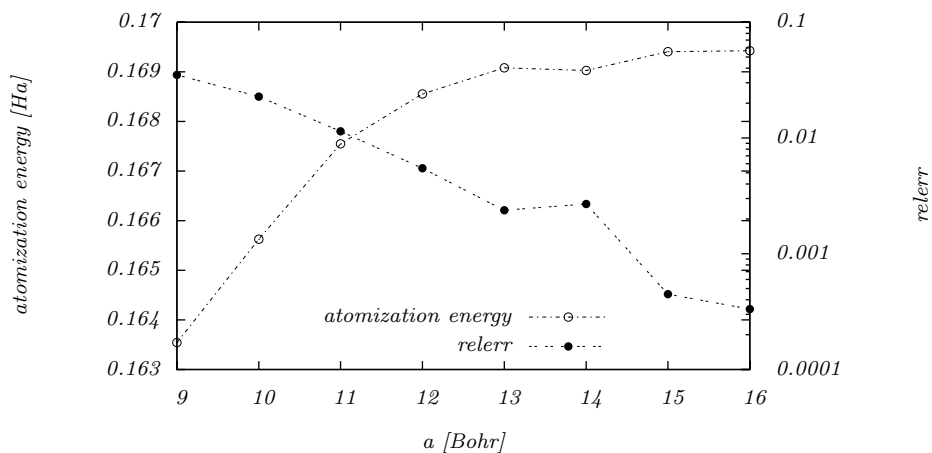
The *reciprocal lattice* is defined as the set of \mathbf{q} that satisfy the condition

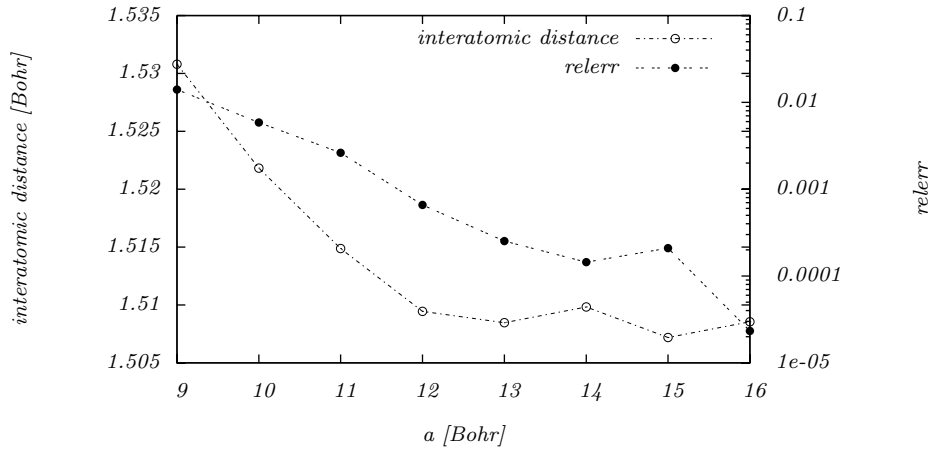
$$\mathbf{q} \cdot \mathbf{a}_j = 2\pi \times \text{integer} . \quad (2.5)$$

The (first) *Brillouin zone* is the Wigner-Seitz cell of the reciprocal lattice.

Example 2.1 (Isolated molecule).

Convergence study of the size of the supercell (cf. figure 2.3) for an isolated H_2 molecule with respect to the atomization energy and the interatomic distance. The size of the supercell is varied from $9 \times 9 \times 9 \text{ Bohr}^3$ to $16 \times 16 \times 16 \text{ Bohr}^3$. The relative error is calculated with respect to the value obtained from the $40 \times 40 \times 40 \text{ Bohr}^3$ supercell.





2.2 The Bloch theorem

In a crystal, the effective potential is a periodic function, i.e. invariant under all lattice translations $v_{\text{eff}}(\mathbf{r} + \mathbf{T}(\mathbf{n})) = v_{\text{eff}}(\mathbf{r})$, where $\mathbf{T}(\mathbf{n}) = \sum_i n_i \mathbf{a}_i$ and the vectors $\{\mathbf{a}_i\}$ are the primitive vectors defining the unit cell with volume Ω_{cell} . The crystal under consideration consists of $N_1 \times N_2 \times N_3$ cells.

It follows that also the Hamiltonian is invariant under lattice translations and thus the eigenfunctions have to be periodic too and can be expanded in the complete set of Fourier components

$$\Psi_i(\mathbf{r}) = \sum_{\mathbf{q}} c_{i,\mathbf{q}} |\mathbf{q}\rangle, \quad (2.6)$$

where $|\mathbf{q}\rangle$ are the (orthonormal) plane wave basis functions

$$|\mathbf{q}\rangle = \frac{1}{\sqrt{\Omega}} \exp(i\mathbf{q} \cdot \mathbf{r}). \quad (2.7)$$

Inserting (2.6) into (2.1) and multiplying from the left by $\langle \mathbf{q}' |$ leads to the discrete formulation

$$\sum_{\mathbf{q}} \langle \mathbf{q}' | \hat{H}_{\text{eff}} | \mathbf{q} \rangle c_{i,\mathbf{q}} = \epsilon_i \sum_{\mathbf{q}} \langle \mathbf{q}' | \mathbf{q} \rangle c_{i,\mathbf{q}} = \epsilon_i c_{i,\mathbf{q}'}. \quad (2.8)$$

As the plane waves are eigenfunctions of the momentum operator, for the first part of the matrix element $\langle \mathbf{q}' | \hat{H}_{\text{eff}} | \mathbf{q} \rangle$ it holds

$$\langle \mathbf{q}' | -\frac{1}{2} \nabla^2 | \mathbf{q} \rangle = \frac{1}{2} \langle \mathbf{q}' | \hat{\mathbf{p}}^2 | \mathbf{q} \rangle = \frac{1}{2} \mathbf{q}^2 \delta_{\mathbf{q},\mathbf{q}'}. \quad (2.9)$$

Expressing the effective potential in a Fourier series yields (by summing over all vectors \mathbf{G}_m of the reciprocal lattice)

$$\begin{aligned}
v_{\text{eff}}(\mathbf{r}) &= \sum_m v_{\text{eff}}(\mathbf{G}_m) \exp(i\mathbf{G}_m \cdot \mathbf{r}) \\
\langle \mathbf{q}' | v_{\text{eff}}(\mathbf{r}) | \mathbf{q} \rangle &= \sum_m v_{\text{eff}}(\mathbf{G}_m) \langle \mathbf{q}' | \exp(i\mathbf{G}_m \cdot \mathbf{r}) | \mathbf{q} \rangle \\
&= \sum_m v_{\text{eff}}(\mathbf{G}_m) \frac{1}{\Omega} \int_{\Omega} \exp(i(\mathbf{G}_m - (\mathbf{q}' - \mathbf{q})) \cdot \mathbf{r}) d\mathbf{r} \\
&= \sum_m v_{\text{eff}}(\mathbf{G}_m) \delta_{\mathbf{G}_m, \mathbf{q}' - \mathbf{q}}
\end{aligned} \tag{2.10}$$

Thus for the matrix element we get

$$\langle \mathbf{q}' | \hat{H}_{\text{eff}} | \mathbf{q} \rangle = \frac{1}{2} \mathbf{q}^2 \delta_{\mathbf{q}, \mathbf{q}'} + \sum_m v_{\text{eff}}(\mathbf{G}_m) \delta_{\mathbf{G}_m, \mathbf{q}' - \mathbf{q}} . \tag{2.11}$$

It vanishes unless \mathbf{q} and \mathbf{q}' differ by a reciprocal lattice vector, so we can uniquely define $\mathbf{q} = \mathbf{k} + \mathbf{G}_m$ and $\mathbf{q}' = \mathbf{k} + \mathbf{G}_{m'}$ for a \mathbf{k} in the Brillouin zone, and the Schrödinger equation for any given $\mathbf{k} \in BZ$ can be written as

$$\sum_{m'} H_{m, m'}(\mathbf{k}) c_{i, m'}(\mathbf{k}) = \epsilon_i(\mathbf{k}) c_{i, m}(\mathbf{k}) , \tag{2.12}$$

where

$$\begin{aligned}
H_{m, m'}(\mathbf{k}) &= \langle \mathbf{k} + \mathbf{G}_m | \hat{H}_{\text{eff}} | \mathbf{k} + \mathbf{G}_{m'} \rangle \\
&= \frac{1}{2} |\mathbf{k} + \mathbf{G}_m|^2 \delta_{m, m'} + v_{\text{eff}}(\mathbf{G}_m - \mathbf{G}_{m'}) , \\
\Psi_{i, \mathbf{k}} &= \sum_m c_{i, m}(\mathbf{k}) | \mathbf{k} + \mathbf{G}_m \rangle .
\end{aligned} \tag{2.13}$$

The Schrödinger equation is defined for each \mathbf{k} separately and thus eigenfunctions can be found for each \mathbf{k} in the Brillouin zone. This was a simple derivation of the Bloch theorem:

Theorem 2.1 (Bloch theorem). *Each eigenfunction of the Schrödinger equation (2.13) for a given \mathbf{k} is given by*

$$\Psi_{i, \mathbf{k}} = \exp(i\mathbf{k} \cdot \mathbf{r}) u_{i, \mathbf{k}}(\mathbf{r}) , \tag{2.14}$$

where $u_{i, \mathbf{k}}(\mathbf{r})$ is a cell-periodic function.

To calculate properties of a crystal, an integration over the Brillouin zone has to be performed. In particular, the electron density reads as (cf. (1.20))

$$\rho(\mathbf{r}) = \sum_i \frac{N_{\text{cells}}}{\Omega_{BZ}} \int f(\epsilon_{i, \mathbf{k}}) \rho_{i, \mathbf{k}}(\mathbf{r}) d\mathbf{k} , \text{ where } \rho_{i, \mathbf{k}}(\mathbf{r}) = 2 |\Psi_{i, \mathbf{k}}(\mathbf{r})|^2 , \tag{2.15}$$

where N_{cells} is the number of primitive cells in the crystal, Ω_{BZ} is the volume of the Brillouin zone and $f(\epsilon_{i, \mathbf{k}})$ is the Fermi function, cf. (1.21).

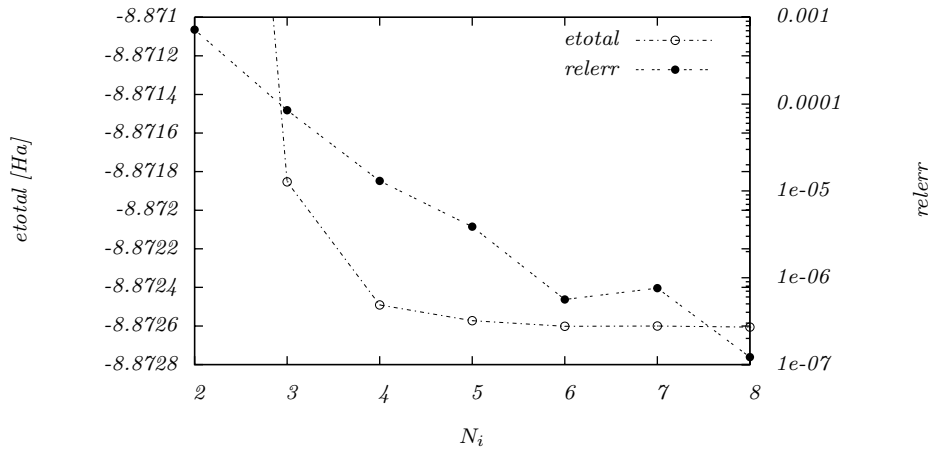
For a numerical integration, Monkhorst and Pack [11] proposed the following grid of \mathbf{k} points:

$$\mathbf{k}_{n_1, n_2, n_3} = \sum_{i=1}^3 \frac{2n_i - N_i - 1}{2N_i} \mathbf{q}_i, \quad (2.16)$$

where the \mathbf{q}_i are the primitive vectors of the reciprocal lattice.

Example 2.2 (k-point sampling).

Convergence study of the total energy with respect to the sampling of the Brillouin zone. The number of sampling points is varied from $2 \times 2 \times 2$ to $8 \times 8 \times 8$. The relative error is calculated with respect to the total energy obtained with $16 \times 16 \times 16$ sampling points.



2.3 Pseudopotential approximation

The valence electron wave functions typically have rapid oscillations in the core region. Since plane waves are not well suited to these oscillations, it needs a very large number of these basis functions to expand the wave functions of the valence electrons in these regions.

Pseudopotentials are an ansatz to solve this problem: In the pseudopotential approximation, the core electrons are removed, and the strong ionic potential is replaced by a weaker pseudopotential that includes the ion and the core electrons (cf [4]).

Potentials are defined by two different approaches: Most modern pseudopotential calculations are based on "ab initio" potentials that are constructed to fit the valence properties of the atom, but also empirical pseudopotential methods are known.

2.4 Matrix diagonalization procedure

In Figure 2.4, the computational procedure using conventional matrix diagonalization techniques is presented. Since the ground-state electron density enters the potential, a self-consistent procedure is required: First, a trial density is chosen as input. Then the effective potential is calculated with that trial density. The Hamiltonian matrix for each of the \mathbf{k} values in the Brillouin zone needed for numeric integration is calculated and the corresponding Schrödinger equations are solved by

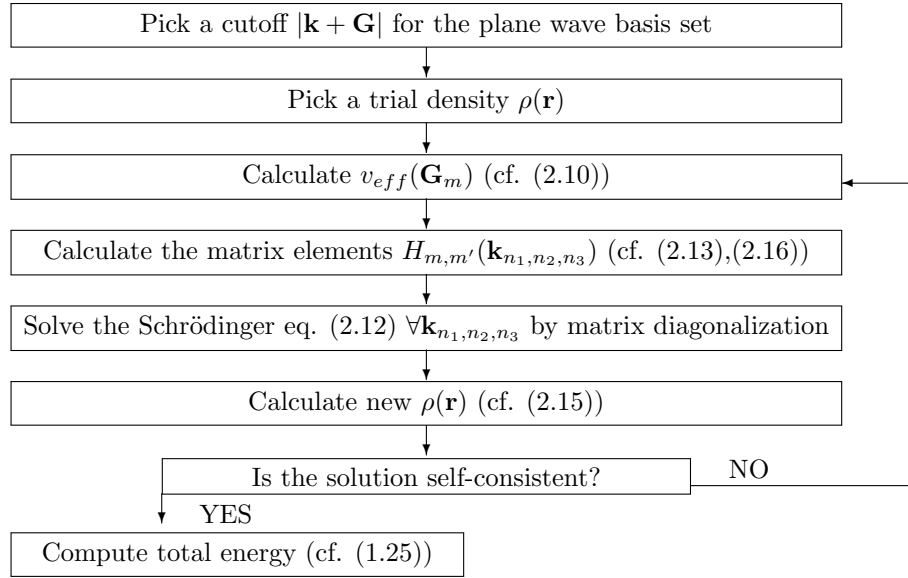


Figure 2.4. *The ordinary computational procedure using matrix diagonalization.*

matrix diagonalization. From the eigenvectors of the Hamilton matrices, the electron density is calculated and used as a new input density. This process is iterated until self-consistence.

This procedure has certain drawbacks, in particular because all eigenvalues of the Hamiltonian are calculated, whereas only the lowest ones are actually used for the calculation of the density (at least at $T = 0$).

Chapter 3

O(N) strategies

Many $O(N)$ algorithms are based on the density matrix due to its decay properties.

3.1 Density matrix

Definition 3.1 (Density matrix). *The (spinless) density matrix is defined as*

$$\begin{aligned} \rho(\mathbf{r}, \mathbf{r}') = N \int & \Psi^*(\mathbf{r}, s_1, \mathbf{r}_2, s_2, \dots, \mathbf{r}_N, s_N) \\ & \times \Psi(\mathbf{r}', s_1, \mathbf{r}_2, s_2, \dots, \mathbf{r}_N, s_N) ds_1 ds_2 \dots ds_N d\mathbf{r}_2 \dots d\mathbf{r}_N, \end{aligned} \quad (3.1)$$

with the same assumptions as in Definition 1.1.

For non-interacting particles (such as in the Kohn-Sham approach), the density matrix reads as

$$\rho(\mathbf{r}, \mathbf{r}') = \sum_{i=1}^{\infty} f(\epsilon_i) \Psi_i^*(\mathbf{r}) \Psi_i(\mathbf{r}') \quad (3.2)$$

for finite temperatures and

$$\rho(\mathbf{r}, \mathbf{r}') = \sum_{i=1}^{N/2} \Psi_i^*(\mathbf{r}) \Psi_i(\mathbf{r}') \quad (3.3)$$

for $T = 0$, respectively.

In a closed-shell system, the electron density $\rho(\mathbf{r})$ can be obtained from the diagonal elements of the density matrix:

$$\rho(\mathbf{r}) = 2\rho(\mathbf{r}, \mathbf{r}) . \quad (3.4)$$

At $T = 0$, the density matrix is a projection operator onto the space of occupied states, which satisfies the idempotency constraint:

$$\int \rho(\mathbf{r}, \mathbf{r}'') \rho(\mathbf{r}'', \mathbf{r}') d\mathbf{r}'' = \rho(\mathbf{r}, \mathbf{r}') . \quad (3.5)$$

The density matrix operator in the non-interacting case reads as:

$$\hat{\rho} = \sum_{i=1}^{\infty} f(\epsilon_i) |\psi_i\rangle \langle \psi_i| = f(\hat{H}) , \quad (3.6)$$

which is, in space representation, simply the density matrix (3.2):

$$\langle \mathbf{r} | \hat{\rho} | \mathbf{r}' \rangle = \sum_{i=1}^{\infty} f(\epsilon_i) \Psi_i^*(\mathbf{r}) \Psi_i(\mathbf{r}') = \rho(\mathbf{r}, \mathbf{r}') \quad (3.7)$$

The eigenvectors of the density matrix operator are the eigenvectors $|\psi_j\rangle$ of the Hamiltonian with eigenvalues $f(\epsilon_j)$:

$$\hat{\rho} |\psi_j\rangle = \sum_{i=1}^{\infty} f(\epsilon_i) |\psi_i\rangle \langle \psi_i | \psi_j \rangle = \sum_{i=1}^{\infty} f(\epsilon_i) |\psi_i\rangle \delta_{ij} = f(\epsilon_j) |\psi_j\rangle . \quad (3.8)$$

For numerical calculations, a finite dimensional basis $\{\phi_i(\mathbf{r})\}$ is introduced and the corresponding approximations of the density matrix and the Hamiltonian are:

$$\begin{aligned} \rho_{i,j} &= \int \int \phi_i(\mathbf{r})^* \rho(\mathbf{r}, \mathbf{r}') \phi_j(\mathbf{r}') d\mathbf{r} d\mathbf{r}' , \\ H_{i,j} &= \int \phi_i(\mathbf{r})^* \left[-\frac{1}{2} \nabla^2 + v_{\text{eff}}(\mathbf{r}) \right] \phi_j(\mathbf{r}) d\mathbf{r} . \end{aligned} \quad (3.9)$$

3.2 Locality

In contrast to traditional chemistry, quantum chemistry is a non-local theory. However, the principle of nearsightedness introduced by Kohn [17] ensures that many important properties can be found without calculating the eigenstates and using only local information. It is the physical basis of the existence of computational methods scaling linearly with the number of electrons. This principle is a consequence of wave-mechanical destructive interference, and it states that in equilibrium systems consisting of many quantum mechanical particles moving in an external potential v_{eff} local electronic properties depend significantly on the effective potential only at nearby points.

As an example, the density matrix $\rho(\mathbf{r}, \mathbf{r}')$ is diagonally dominant and its off-diagonal elements decay with increasing distance from the diagonal:

$$\rho(\mathbf{r}, \mathbf{r}') \rightarrow 0 \text{ as } |\mathbf{r} - \mathbf{r}'| \rightarrow \infty . \quad (3.10)$$

As pointed out by Goedecker [1], the decay properties are different in insulators and metals. In a metallic system at zero temperature, the density matrix decays only algebraically with respect to $|\mathbf{r} - \mathbf{r}'|$

$$\rho(\mathbf{r}, \mathbf{r}') \propto k_F \frac{\cos(k_F |\mathbf{r} - \mathbf{r}'|)}{|\mathbf{r} - \mathbf{r}'|^2} , \quad (3.11)$$

where $k_F = |\mathbf{k}_F|$ and \mathbf{k}_F is the Fermi wave vector. In insulators at zero temperature, the decay is exponentially, namely: For any \mathbf{r} and for any \mathbf{s} inside the primitive cell, there exist constants C and γ such that

$$C \exp(-\gamma |\mathbf{r}|) \geq |F(\mathbf{s}, \mathbf{s} - \mathbf{r})| . \quad (3.12)$$

Due to this rapid decay, a localization region can be introduced outside of which the density matrix is assumed to vanish. To obtain linear scaling, the basis set has to be chosen such that the matrix elements $\rho_{i,j}$ reflect the decay properties of $\rho(\mathbf{r}, \mathbf{r}')$, which is possible only when the basis set consists of localized functions.

As for the purely local one-electron Hamilton operator $\hat{H}_{\text{eff}} = [-\frac{1}{2}\nabla^2 + v_{\text{eff}}(\mathbf{r})]$ in the independent-particle approximation, its representation in any localized basis is sparse since $\langle \phi_i | \hat{H}_{\text{eff}} | \phi_j \rangle$ is nonzero only if ϕ_i and ϕ_j have a non-vanishing overlapping region.

Examples for localized basis sets are atom-centered Gaussian-type functions or approximations of exponentially localized Wannier functions.

Wannier functions are a unitary transformation of Kohn-Sham orbitals:

$$\Psi_n^{\text{new}}(\mathbf{r}) = \sum_{m \text{ occ}} U_{n,m} \Psi_m(\mathbf{r}), \quad (3.13)$$

where U is a unitary $N \times N$ matrix (only $T = 0$ is considered). Since the occupied orbitals are eigenfunctions of the density matrix with eigenvalue one, the same is valid for the transformed functions, and they can be used to build the density matrix as well:

$$\rho(\mathbf{r}, \mathbf{r}') = \sum_{m \text{ occ}} \Psi_m^*(\mathbf{r}) \Psi_m(\mathbf{r}') = \sum_n \Psi_n^{\text{new}*}(\mathbf{r}) \Psi_n^{\text{new}}(\mathbf{r}'). \quad (3.14)$$

Any set of functions that span the space of occupied space are called Wannier functions. The usual way to define the Wannier functions in an insulating crystal is:

$$W_n(\mathbf{r} - \mathbf{R}) = \frac{\Omega_{\text{cell}}}{(2\pi)^3} \int_{BZ} d\mathbf{k} \exp(-i\mathbf{k}\mathbf{R}) \Psi_{n,\mathbf{k}}(\mathbf{r}). \quad (3.15)$$

For crystalline solids such a transformation can be used to generate exponentially localized Wannier functions.

In the following some important linear scaling methods based on the density matrix are outlined, cf. [1]. In the next chapter the density matrix minimization method is presented in a more detailed fashion.

3.3 Fermi operator expansion

In the Fermi operator expansion method an approximation $p(H) \approx f(H)$ of the expression for the density matrix (cf. Section 3.1)

$$\rho = f(H) = \frac{1}{1 + \exp\left(\frac{H-\mu}{k_B T}\right)} \quad (3.16)$$

is calculated.

In the *Chebyshev Fermi operator expansion*, the density matrix is approximated by a Chebyshev polynomial representation:

$$p(H) = \frac{c_0}{2} I + \sum_{j=1}^{n_{pl}} c_j T_j(H), \quad (3.17)$$

where the Chebyshev polynomials fulfill the recursion relation

$$\begin{aligned} T_0(H) &= I, \\ T_1(H) &= H, \\ T_{j+1}(H) &= 2HT_j(H) - T_{j-1}(H). \end{aligned} \quad (3.18)$$

The coefficients of the expansion have to be chosen such that the polynomial $p(\epsilon)$ approximates $f(\epsilon)$ for scalar ϵ .

Since the Chebyshev polynomials are defined only in the interval $[-1, 1]$, the Hamiltonian first has to be scaled and shifted.

In the *rational Fermi operator expansion*, a rational representation of the density matrix is used:

$$p(H) = \sum_{\nu} \frac{w_{\nu}}{H - z_{\nu}} . \quad (3.19)$$

The parameters w_{ν} and z_{ν} can be obtained, for example, from the discretization of the contour integral

$$f(\epsilon) = \frac{1}{2\pi i} \oint \frac{dz}{\epsilon - z} = \begin{cases} 1 \\ 0 \end{cases} \quad (3.20)$$

which is 1 if ϵ is inside the area enclosed by the contour and 0 otherwise and thus represents the Fermi function at $T = 0$ if the integration path contains all energies of the occupied states.

Once the parameters are known, expression (3.19) can be evaluated by solving

$$(H - z_{\nu})F_{\nu} = I \quad (3.21)$$

for all ν and building the sum

$$\rho = \sum_{\nu} w_{\nu} F_{\nu} . \quad (3.22)$$

3.4 Fermi operator projection

The Fermi operator expansion method computes the full density matrix, which is sometimes inefficient when the number of basis functions per atom is very large. The Fermi operator projection method uses another approach which is based on the fact that the density matrix is a projector onto the space of occupied orbitals (in the zero temperature case). Once the expansion parameters of (3.17) or (3.19) are known, the density matrix operator is applied on a set of trial functions to generate a set of functions that span the space of occupied states, i.e. Wannier functions.

In the case of rational expansion, the generation of the Wannier functions \tilde{W}_n from the trial functions \tilde{V}_n is calculated by solving:

$$\begin{aligned} (H - z_{\nu})\tilde{W}_{n,\nu} &= \tilde{V}_n , \\ \tilde{W}_n &= \sum_{\nu} w_{\nu} \tilde{W}_{n,\nu} . \end{aligned} \quad (3.23)$$

Chapter 4

The density matrix minimization approach

In the density matrix minimization approach, the approximations of the density matrix and the Hamiltonian in a discrete basis (3.9) are needed: The energy of the non-interacting system (1.19) is

$$E_s = \sum_{i=1}^{\infty} f(\epsilon_i) \epsilon_i , \quad (4.1)$$

which can be written as a trace:

$$E_s = \text{Tr } f(H)H = \text{Tr } \rho H . \quad (4.2)$$

Therefore the density matrix can be obtained by minimizing E_s under the constraint of a fixed number of electrons $N - \sum_{i=1}^{\infty} f(\epsilon_i) = N - \text{Tr } \rho = 0$. However, it is more convenient to work at a fixed chemical potential μ and to consider the grand potential

$$\Omega_s = E_s - \mu N = \text{Tr } \rho(H - \mu I) , \quad (4.3)$$

thus eliminating the explicit constraint on the number of electrons. The Lagrange multiplier μ corresponds to the chemical potential. However, the idempotency constraint still needs to be included.

4.1 Purification function

If (4.3) is minimized without constraint, we will end up with runaway solutions where eigenvalues corresponding to states below the Fermi level μ tend to $-\infty$, and eigenvalues corresponding to states above the Fermi level will go to $+\infty$, which is of course not a physical solution.

Li, Nunes and Vanderbilt [8] proposed a method to obtain the density matrix at $T = 0$ by using the idempotency property which is equivalent to require the occupation numbers (eigenvalues) to be 1 for occupied states (below the Fermi level) and 0 for unoccupied states (above the Fermi level).

The idea is to restrict the eigenvalues to the interval $[0, 1]$, since in this case the minimization of (4.3) yields the correct result.

To do so, a purification function is introduced, the "McWeeny purification function" $3x^2 - 2x^3$ (cf. Figure 4.1). It maps idempotent matrices onto themselves,

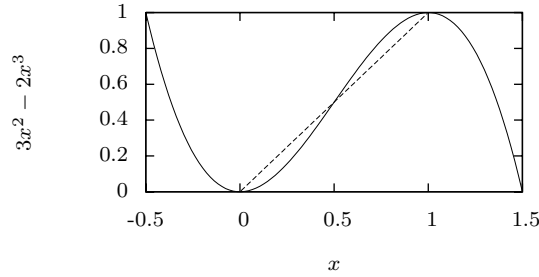


Figure 4.1. The McWeeny purification function.

since in this case $\rho^2 = \rho$. If ρ is a trial matrix which is only nearly idempotent, then $3\rho^2 - 2\rho^3$ is a purified version which is even closer to exact idempotency, since the eigenvalues of the original matrix that are close to zero (one) are even closer to zero (one) for the transformed matrix. The new eigenvalues lie in the interval $[0, 1]$ as long as the old eigenvalues were not outside the interval $[-0.5, 1.5]$. So, instead of the grand potential, we minimize a modified version:

$$\Omega_s = \text{Tr}(3\rho^2 - 2\rho^3)(H - \mu I) . \quad (4.4)$$

Starting with an initial density matrix with occupation numbers in the interval $[0, 1]$, the minimization procedure should not lead to a runaway solution. For the minimization of the grand potential, we need the gradient:

$$\begin{aligned} \frac{\partial \Omega_s}{\partial \rho} = & 3[\rho(H - \mu I) + (H - \mu I)\rho] \\ & - 2[\rho^2(H - \mu I) + \rho(H - \mu I)\rho + (H - \mu I)\rho^2] . \end{aligned} \quad (4.5)$$

Note that in the case of the true ground state density, the modified version equals the original grand potential, and the gradient vanishes (since $\rho = f(H)$ is a function of H and thus they commute).

4.2 Conjugate gradient minimization

To minimize a function $f(x)$, one can use iterative methods:

Let $x^{(k)}$ be the current approximation of \hat{x} and $d^{(k)}$ the search direction. The new approximation $x^{(k+1)}$ is then obtained by minimization of $\phi(x)$ along the line $x^{(k)} + \alpha_k d^{(k)}$, such that:

$$\left. \frac{\partial f(x^{(k)} + \alpha d^{(k)})}{\partial \alpha} \right|_{\alpha=\alpha_k} = 0 . \quad (4.6)$$

In the method of *steepest descent*, one searches for the minimum in the direction of the negative gradient:

$$\begin{aligned} d^{(k)} &= g^{(k)} \\ g^{(k)} &= - \nabla_x f(x)|_{x=x^{(k)}} , \end{aligned} \quad (4.7)$$

such that consecutive search directions are orthogonal to each other:

$$\begin{aligned} \left. \frac{\partial f(x^{(k)} + \alpha d^{(k)})}{\partial \alpha} \right|_{\alpha=\alpha_k} &= \sum_i \left. \frac{\partial f(x)}{\partial x_i} \right|_{x=x^{(k+1)}} g_i^{(k)} \\ &= \sum_i g_i^{(k+1)} g_i^{(k)} = g^{(k+1)T} g^{(k)} \stackrel{(4.6)}{=} 0. \end{aligned} \quad (4.8)$$

To introduce the *conjugate gradient method*, we consider now a quadratic function of the form

$$f(x) = \frac{1}{2} x^T A x - x^T b, \quad (4.9)$$

where A is hermitian and positive definite, i.e. $x^T A x > 0 \forall x : x \neq 0$.

The following ansatz for the search directions is chosen: The first search direction corresponds to the negative gradient, and all following search directions are chosen such that they are mutually conjugate with respect to A , that means they are "A-orthogonal":

$$\langle d^{(i)}, d^{(j)} \rangle_A = d^{(i)*} A d^{(j)} = 0, \quad i \neq j. \quad (4.10)$$

With the ansatz:

$$d^{(k)} = g^{(k)} + \beta_k d^{(k-1)}, \quad \text{where } g^{(k)} = -\nabla f(x) \quad (4.11)$$

this yields

$$\beta_k = -\frac{g^{(k+1)*} A d^{(k)}}{d^{(k)*} A d^{(k)}} \quad \text{for } k \neq 0, \quad \beta_0 = 0. \quad (4.12)$$

The Polak-Ribiere formula [16] is equivalent to this formulation:

$$\beta_k = \frac{(g^{(k+1)} - g^{(k)})^* g^{(k+1)}}{g^{(k)*} g^{(k)}} \quad \text{for } k \neq 0, \quad \beta_0 = 0. \quad (4.13)$$

This formula is now used not only for quadratic forms, but for any kind of formula for which one searches the minimum.

We apply the conjugate gradient method on the modified grand potential (4.4):

```

ρ₀ ← ρguess                                ▷ cf. Comment 2
G₀ ← H₀ ← -∂Ωs/∂ρ (ρ₀)                    ▷ cf. (4.5)
for it = 0, ..., itmax do
  ρi+1 ← ρi + λiHi                          ▷ cf. Comment 1
  determine μ                                ▷ cf. Comment 2, (4.14)
  Gi+1 ← -∂Ωs/∂ρ (ρi+1)                    ▷ cf. (4.5)
  γi ←  $\frac{\text{Tr}(G_{i+1} - G_i) \cdot G_{i+1}}{\text{Tr} G_i \cdot G_i}$                 ▷ Polak-Ribière formula (4.13)
  Hi+1 ← Gi+1 + γiHi
end for

```

Some comments:

1. Line minimization: $\Omega(\rho_i + \lambda H_i)$ is cubic with respect to λ , thus finding the minimum corresponds to finding the zeros of a quadratic form.
2. Since the chemical potential is not known in advance (it corresponds to the highest occupied energy level at zero temperature), Millam and Scuseria [10] proposed to reset μ in every step such that the gradient is traceless

$$\mu = -\text{Tr} (3\rho H + 3H\rho - 2\rho^2 H - 2\rho H\rho - 2H\rho^2) / N, \quad (4.14)$$

and thus the number of electrons (the trace of the density matrix) is conserved in every step:

$$\text{Tr } \rho_{i+1} = \text{Tr}(\rho_i + \gamma_i H_i) = \text{Tr } \rho_i + \gamma_i \text{Tr } H_i = \text{Tr } \rho_i . \quad (4.15)$$

Of course the initial guess of the density matrix has to yield the correct number of electrons (which can be obtained by scaling, if necessary).

To ensure linear scaling, the basis functions need to be localized, as pointed out in the previous section. Then the sparsity of the density matrix is conserved during the iteration.

Appendix A

abinit input files

The present examples have been calculated by the use of the `abinit` code [3, 2], www.abinit.org, that is based on pseudopotentials and planewaves.

Example 1.1 (From the `abinit` tutorial.)

```
# H2 molecule in a big box
#
# In this input file , the location of the information on this or that line
# is not important : a keyword is located by the parser , and the related
# information should follow .
# The "#" symbol indicates the beginning of a comment : the remaining
# of the line will be skipped .
ndtset 21
xcart:
  -0.5 0.0 0.0
  0.5 0.0 0.0
xcart+
  -0.025 0.0 0.0
  0.025 0.0 0.0
nband 1
#-----

#Definition of the unit cell
acell 10 10 10 # The keyword "acell" refers to the
               # lengths of the primitive vectors (in Bohr)

#Definition of the atom types
ntypat 1      # There is only one type of atom
znucl 1      # The keyword "znucl" refers to the atomic number of the
             # possible type(s) of atom. The pseudopotential(s)
             # mentioned in the "files" file must correspond
             # to the type(s) of atom. Here, the only type is Hydrogen
             .

#Definition of the atoms
natom 2      # There are two atoms
typat 1 1    # They both are of type 1, that is , Hydrogen

#Definition of the plane-wave basis set
ecut 10.0    # Maximal plane-wave kinetic energy cut-off , in Hartree

#Definition of the k-point grid
nkpt 1      # Only one k point is needed for isolated system ,
            # taken by default to be 0.0 0.0 0.0

#Definition of the SCF procedure
nstep 10     # Maximal number of SCF cycles
tol dfe 1.0d-6 # Will stop when, twice in a row, the difference
              # between two consecutive evaluations of total energy
```

```

diemac 2.0          # differ by less than toldfe (in Hartree)
                   # Although this is not mandatory, it is worth to
                   # precondition the SCF cycle. The model dielectric
                   # function used as the standard preconditioner
                   # is described in the "dielng" input variable section.
                   # Here, we follow the prescriptions for molecules
                   # in a big box

```

Results (extracted from the abinit output file):

```

# d      etotal
1 -1.0368223891E+00
1.05 -1.0538645432E+00
1.1 -1.0674504851E+00
1.15 -1.0781904896E+00
1.2 -1.0865814785E+00
1.25 -1.0930286804E+00
1.3 -1.0978628207E+00
1.35 -1.1013539124E+00
1.4 -1.1037224213E+00
1.45 -1.1051483730E+00
1.5 -1.1057788247E+00
1.55 -1.1057340254E+00
1.6 -1.1051125108E+00
1.65 -1.1039953253E+00
1.7 -1.1024495225E+00
1.75 -1.1005310614E+00
1.8 -1.0982871940E+00
1.85 -1.0957584181E+00
1.9 -1.0929800577E+00
1.95 -1.0899835223E+00
2 -1.0867972867E+00

```

Example 2.1 (From the abinit tutorial, modified.)

```

# H2 molecule in a big box
#
# This file to optimize the H2 bond length, compute the associated total
# energy, then to compute the total energy of the isolated H atom.
# Here, a double loop has been used.
#
ndtset 18  utdset 9 2

#Definition of the unit cell and ecut,
#for which one will have to make a convergence study
  acell1? 9 9 9
  acell2? 10 10 10
  acell3? 11 11 11
  acell4? 12 12 12
  acell5? 13 13 13
  acell6? 14 14 14
  acell7? 15 15 15
  acell8? 16 16 16
  acell9? 40 40 40
  ecut 10

#First dataset : find the optimal bond length of H2, and associated total
  energy
  natom?1 2          # There are two atoms
  ionmov?1 3         # Use the modified Broyden algorithm
  ntime?1 10         # Maximum number of Broyden "timesteps"
  tolmxf?1 5.0d-4    # Stopping criterion for the geometry optimization
  : when

```

```

# the residual forces are less than tolmxf, the
# Broyden
# algorithm can stop
xcart?1 -0.7 0.0 0.0 # The starting values of the
          0.7 0.0 0.0 # atomic coordinates
toldff?1 1.0d-8 # Will stop the SCF cycle when, twice in a row,
# the difference between two consecutive
# evaluations of
# forces differ by less than toldff (in Hartree/
# Bohr)
nband?1 1 # Just one band

#Second dataset : get the total energy of the isolated atom
natom?2 1 # There is one atom
nspol?2 2 # Spin-polarized calculation
noccpt?2 2 # Allow occupation numbers to be set by hand
nband?2 1 1 # Number of bands for spin up and spin down
occ?2 1.0 0.0 # Occupation numbers for spin up state and spin
down state.
toldfe?2 1.0d-10 # Will stop the SCF cycles when, twice in a row,
# the difference between two consecutive
# evaluations
# of total energy differ by less than toldfe (in
# Hartree)
xcart?2 0.0 0.0 0.0 # The atom is located at the origin
spinat?2 0.0 0.0 1.0 # Initialisation of spin

#Definition of the atom types
ntypat 1 # There is only one type of atom
znucl 1 # The keyword "znucl" refers to the atomic number of the
# possible type(s) of atom. The pseudopotential(s)
# mentioned in the "files" file must correspond
# to the type(s) of atom. Here, the only type is Hydrogen
.

#Definition of the atoms
typat 1 1 # For the first dataset, both numbers will be read,
# while for the second dataset, only one number will be
# read

#Definition of the k-point grid
nkpt 1 # Only one k point is needed for isolated system,
# taken by default to be 0.0 0.0 0.0

#Definition of the SCF procedure
nstep 20 # Maximal number of SCF cycles
#toldfe is no more defined, as toldff is used above...
diemac 2.0 # Although this is not mandatory, it is worth to
# precondition the SCF cycle. The model dielectric
# function used as the standard preconditioner
# is described in the "dielng" input variable section.
# Here, we follow the prescriptions for molecules
# in a big box

```

Results (extracted from the abinit output file):

```

# acell d/2 eh eh2
9.000000000E+00 -7.6539544910E-01 -4.7394116070E-01 -1.1114240079E+00
1.000000000E+01 -7.6090955106E-01 -4.7010531520E-01 -1.1058360646E+00
1.100000000E+01 -7.5743827221E-01 -4.6859731320E-01 -1.1047427543E+00
1.200000000E+01 -7.5472306662E-01 -4.6767804802E-01 -1.1039109449E+00
1.300000000E+01 -7.5423438678E-01 -4.6748802746E-01 -1.1040562185E+00
1.400000000E+01 -7.5491642761E-01 -4.6743724199E-01 -1.1039012769E+00
1.500000000E+01 -7.5359545251E-01 -4.6727185267E-01 -1.1039503586E+00
1.600000000E+01 -7.5427419294E-01 -4.6735895176E-01 -1.1041439326E+00
4.000000000E+01 -7.5447247224E-01 -4.6736983269E-01 -1.1042220955E+00

```

Example 2.2 (From the abinit tutorial, modified.)

```

# Crystalline silicon : computation of the total energy
# Convergence with respect to the number of k points.

ndtset 8

#Definition of the k-point grids
kptopt 1          # Option for the automatic generation of k points, taking
                  # into account the symmetry
nshiftk 4
shiftk 0.5 0.5 0.5 # These shifts will be the same for all grids
        0.5 0.0 0.0
        0.0 0.5 0.0
        0.0 0.0 0.5

ngkpt1 2 2 2      # Definition of the different grids
ngkpt2 3 3 3
ngkpt3 4 4 4
ngkpt4 5 5 5
ngkpt5 6 6 6
ngkpt6 7 7 7
ngkpt7 8 8 8
ngkpt8 16 16 16

getwfk -1         # This is to speed up the calculation, by restarting
                  # from previous wavefunctions, transferred from the old
                  # to the new k-points.

#Definition of the unit cell
acell 3*10.18     # This is equivalent to 10.18 10.18 10.18
rprim 0.0 0.5 0.5 # FCC primitive vectors (to be scaled by acell)
        0.5 0.0 0.5
        0.5 0.5 0.0

#Definition of the atom types
ntypat 1          # There is only one type of atom
znucl 14          # The keyword "znucl" refers to the atomic number of the
                  # possible type(s) of atom. The pseudopotential(s)
                  # mentioned in the "files" file must correspond
                  # to the type(s) of atom. Here, the only type is Silicon.

#Definition of the atoms
natom 2           # There are two atoms
typat 1 1         # They both are of type 1, that is, Silicon.
xred              # This keyword indicate that the location of the atoms
                  # will follow, one triplet of number for each atom
        0.0 0.0 0.0 # Triplet giving the REDUCED coordinate of atom 1.
        1/4 1/4 1/4 # Triplet giving the REDUCED coordinate of atom 2.

#Definition of the planewave basis set
ecut 8.0          # Maximal kinetic energy cut-off, in Hartree

#Definition of the SCF procedure
nstep 20          # Maximal number of SCF cycles
toldfe 1.0d-15    # Will stop when, twice in a row, the difference
                  # between two consecutive evaluations of total energy
                  # differ by less than toldfe (in Hartree)
diemac 12.0       # Although this is not mandatory, it is worth to
                  # precondition the SCF cycle. The model dielectric
                  # function used as the standard preconditioner
                  # is described in the "dielng" input variable section.
                  # Here, we follow the prescription for bulk silicon.

```

Results (extracted from the *abinit* output file):

```

# N_i etotal
2 -8.8662238960E+00
3 -8.8718529095E+00
4 -8.8724909739E+00
5 -8.8725723303E+00

```

6 -8.8726017432E+00
7 -8.8725999849E+00
8 -8.8726056405E+00
16 -8.8726067215E+00

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