

Density functional theory

5.1 Introduction

In the previous chapter we saw how the many-electron problem can be treated in the Hartree–Fock formalism in which the solution of the many-body Schrödinger equation is written in the form of a Slater determinant. The resulting HF equations depend on the occupied electron orbitals, which enter these equations in a nonlocal way. The nonlocal potential of Hartree–Fock is difficult to apply in extended systems, and for this reason there have been relatively few applications to solids; see however ref. 33.

Most electronic structure calculations for solids are based on density functional theory (DFT), which results from the work of Hohenberg, Kohn and Sham.^{34,35} This approach has also become popular for atoms and molecules. In the density functional theory, the electronic orbitals are solutions to a Schrödinger equation which depends on the electron density rather than on the individual electron orbitals. However, the dependence of the one-particle Hamiltonian on this density is in principle nonlocal. Often, this Hamiltonian is taken to depend on the *local* value of the density only – this is the *local density approximation* (LDA). In the vast majority of DFT electronic structure calculations for solids, this approximation is adopted. It is, however, also applied to atomic and molecular systems.³⁶

In this chapter we describe the density functional method for electronic structure calculations. In the present section, the physical interpretation of the density functional equations is first described and the formal derivations are given. In the next section the local density approximation is considered. An application to the ground state of the helium atom will be described in some detail in section 5.3. Finally, some results obtained using density functional theory will be discussed in section 5.3.3. For further reading, there are many reviews and books available, see for example refs. 36–38.

5.1.1 Density functional theory – physical picture

In density functional theory, an effective independent particle Hamiltonian is arrived at, leading to the following Schrödinger equation for one-electron spin-orbitals:

$$\left[-\frac{1}{2}\nabla^2 - \sum_n \frac{Z_n}{|\mathbf{r} - \mathbf{R}_n|} + \int d^3r' n(\mathbf{r}') \frac{1}{|\mathbf{r} - \mathbf{r}'|} + V_{xc}[n](\mathbf{r}) \right] \psi_k(\mathbf{r}) = \varepsilon_k \psi_k(\mathbf{r}). \quad (5.1)$$

The first three terms in the left hand side of this equation are exactly the same as those of Hartree–Fock, Eq. (4.30), namely the kinetic energy, the electrostatic interaction between the electrons and the nuclei, and the electrostatic energy of the electron in the field generated by the total electron density $n(\mathbf{r})$. The fourth term contains the many-body effects, lumped together in an exchange–correlation potential. The main result of density functional theory is that there exists a form of this potential, depending only on the electron density $n(\mathbf{r})$, which yields the *exact* ground state energy and density. Unfortunately, this exact form is not known, but there exist several approximations to it, as we shall see in section 5.2. The dependence of the independent particle Hamiltonian on the density only is in striking contrast with Hartree–Fock theory, where the Hamiltonian depends on the individual orbitals. The solutions of Eq. (5.1) must be self-consistent in the density, which is given by

$$n(\mathbf{r}) = \sum_{k=1}^N |\psi_k(\mathbf{r})|^2, \quad (5.2)$$

where the sum is over the N spin-orbitals ψ_k having the lowest eigenvalues ε_k in (5.1) – N is the number of electrons in the system.

The total energy of the many-electron system is given by

$$E = \sum_{k=1}^N \varepsilon_k - \frac{1}{2} \int d^3r d^3r' n(\mathbf{r}) \frac{1}{|\mathbf{r} - \mathbf{r}'|} n(\mathbf{r}') + E_{xc}[n] - \int d^3r V_{xc}[n](\mathbf{r}) n(\mathbf{r}) \quad (5.3)$$

where the parameters ε_k are the eigenvalues occurring in Eq. (5.1) and E_{xc} is the exchange correlation energy. The exchange correlation potential $V_{xc}[n]$ which occurs in (5.1) is the functional derivative of this energy with respect to the density:

$$V_{xc}[n](\mathbf{r}) = \frac{\delta}{\delta n(\mathbf{r})} E_{xc}[n]. \quad (5.4)$$

Although the energy parameters ε_k are not, strictly speaking, one-electron energies they are often treated as such for comparison with spectroscopy experiments according to an extended version of Koopman's theorem (see problem 5.4). The wave functions ψ_k also have no individual meaning but are used to construct the total charge density. This again contrasts with Hartree–Fock where the one-electron spin-orbitals have a definite interpretation: they are the constituents of the many-electron wave function.

Equations (5.1) and (5.2) are solved in an iterative self-consistency loop, which is started by choosing an initial density $n(\mathbf{r})$, constructing the Schrödinger equation (5.1) from it, solving the latter and calculating the resulting density from (5.2). Then a new Schrödinger equation is constructed and so on, until the density does not change appreciably any more.

In both DFT and Hartree–Fock theory, the electrons move in a background composed of the Hartree and external potentials. In addition to this, the exchange term in Hartree–Fock accounts for the fact that electrons with parallel spin avoid each other as a result of the exclusion principle (exchange hole) – opposite spin pairs do not feel this interaction. In DFT, the exchange correlation potential not only includes exchange effects but also correlation effects due to the Coulomb repulsion between the electrons (*dynamic correlation* effects). In HF, the exchange interaction is treated exactly, but dynamic correlations are neglected. DFT is in principle exact, but we do not know the exact form of the exchange correlation potential – both exchange and dynamic correlation effects are in practice treated approximately.

It is essential that the exchange correlation energy is given in terms of the electron density only and contains no explicit dependence on the external potential – in our case the potential due to the atomic nuclei. As we shall see in section 5.2, a local approximation for the exchange correlation energy occurring in the DFT equation (5.1) is usually made, thereby simplifying the implementation significantly with respect to Hartree–Fock with its complicated nonlocal exchange term.

*5.1.2 Density functional formalism and derivation of the Kohn–Sham equations

For a many-electron system, the Hamiltonian is given by

$$H = \sum_i \left[-\frac{1}{2} \nabla_i^2 + V_{\text{ext}}(\mathbf{r}_i) \right] + \frac{1}{2} \sum_{\substack{i,j; \\ i \neq j}} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}. \quad (5.5)$$

V_{ext} is an external potential which, in the systems which are of interest to us, is the Coulomb attraction by the static nuclei.

In chapter 3 we have seen how the ground state can be found by varying the energy functional with respect to the wave function. Now consider carrying out this variational procedure in two stages: first – for a given electron density – minimise with respect to the wave functions consistent with this density, and then minimise with respect to the density. Denoting by $\min_{\Psi|n}$ a minimisation with respect to the wave functions Ψ which are consistent with the density $n(\mathbf{r})$, we can write

$$E[n] = \min_{\Psi|n} \langle \Psi | H | \Psi \rangle \quad (5.6)$$

and it will be clear that the ground state of the many-electron Hamiltonian can be found by minimising the functional $E[n]$ with respect to the density, subject to the constraint

$$\int d^3r n(\mathbf{r}) = N \quad (5.7)$$

where N is the total number of electrons.

Now consider a separation of the Hamiltonian into the Hamiltonian H_0 of the homogeneous electron gas (with external potential $V_{\text{ext}} \equiv 0$), and the external potential:

$$H = H_0 + V_{\text{ext}}(\mathbf{r}). \quad (5.8)$$

In this case we can write $E[n]$ as

$$E[n] = \min_{\Psi|n} \left[\langle \Psi | H_0 | \Psi \rangle + \int d^3r V_{\text{ext}}(\mathbf{r})n(\mathbf{r}) \right]. \quad (5.9)$$

If we minimise the term in square brackets for a given density $n(\mathbf{r})$, the second term is a constant so that we do not have to include it in the minimisation:

$$E[n] = \min_{\Psi|n} [\langle \Psi | H_0 | \Psi \rangle] + \int d^3r V_{\text{ext}}(\mathbf{r})n(\mathbf{r}). \quad (5.10)$$

Writing

$$F[n] = \min_{\Psi|n} [\langle \Psi | H_0 | \Psi \rangle] \quad (5.11)$$

we see that $E[n]$ can be written as

$$E[n] = F[n] + \int d^3r V_{\text{ext}}(\mathbf{r})n(\mathbf{r}) \quad (5.12)$$

and $F[n]$ does obviously not depend on the external potential. We shall now use these general statements to treat our problem of interacting electrons in an external potential. Summarising the results obtained so far, we have:

- The ground state density can be obtained by minimising the energy functional (5.6).
- If we split the Hamiltonian H into a homogeneous one, H_0 , and the external potential, the energy functional can be split into a part $F[n]$, which is defined in (5.11) and which is independent of the external potential, and the functional $\int d^3r V_{\text{ext}}(\mathbf{r})n(\mathbf{r})$.

The problem with treating the many-electron system lies in the electron-electron interaction. In fact, for both interacting and noninteracting electron systems the form of the functional $E[n]$ is unknown, but the ground state energy for noninteracting electrons can be solved for trivially, and we can use this to tackle the problem of interacting electrons. In the noninteracting case, $E[n]$ has a kinetic contribution and a contribution from the external potential V_{ext} :

$$E[n] = T[n] + \int d^3r n(\mathbf{r})V_{\text{ext}}(\mathbf{r}). \quad (5.13)$$

Variation of E with respect to the density leads to the following equation:

$$\frac{\delta T[n]}{\delta n(\mathbf{r})} + V_{\text{ext}}(\mathbf{r}) = \lambda n(\mathbf{r}), \quad (5.14)$$

where λ is the Lagrange parameter associated with the restriction of the density to yield the correct total number of electrons, N . The form of $T[n]$ is unknown, but we know that the ground state of the system can be written as a Slater determinant with spin-orbitals satisfying the single-particle Schrödinger equation:

$$\left[-\frac{1}{2}\nabla^2 + V_{\text{ext}}(\mathbf{r}) \right] \psi_k(\mathbf{r}) = \varepsilon_k \psi_k(\mathbf{r}). \quad (5.15)$$

The ground state density is then given by

$$n(\mathbf{r}) = \sum_{k=1}^N |\psi_k(\mathbf{r})|^2 \quad (5.16)$$

where the spin-orbitals ψ_k are supposed to be normalised so that the density satisfies the correct normalisation to the number of particles N . Using the above analysis, taking $T[n]$ for the functional $F[n]$, we immediately see that the kinetic energy functional T is independent of the potential V_{ext} . Summarising, we have:

- The energy functional of a noninteracting electron gas can be split into a kinetic functional $T[n]$, and a functional representing the interaction with the external potential, $\int d^3r V_{\text{ext}}(\mathbf{r})n(\mathbf{r})$. The kinetic functional does not depend on the external potential.
- The exact solution of the noninteracting electron gas is given in terms of the eigenfunction solutions of the IP Hamiltonian; see Eq. (5.15).

The energy functional for a many-electron system with electronic interactions included can be written in the form

$$E[n] = T[n] + \int d^3r n(\mathbf{r})V_{\text{ext}}(\mathbf{r}) + \frac{1}{2} \int d^3r \int d^3r' n(\mathbf{r}') \frac{1}{|\mathbf{r} - \mathbf{r}'|} n(\mathbf{r}) + E_{\text{xc}}[n], \quad (5.17)$$

where the last term, the exchange correlation energy, contains, by definition, all the contributions not taken into account by the first three terms which represent the kinetic energy functional of the *noninteracting* electron gas, the external and the Hartree energy respectively. It is important to note that we have made no approximations so far but moved all the unknown correlations into E_{xc} , which depends on the density n rather than on the explicit form of the wave function because all the other terms in (5.17) depend on the density. For the interacting electron gas it is not clear that the kinetic energy and the electron–electron interaction can be written as a sum of two terms depending on the density only; therefore the kinetic functional for *noninteracting* electrons, which depends only on the density, has been split off and the remaining part of the kinetic energy has been moved into E_{xc} . Varying this equation with respect to the density, we obtain

$$\frac{\delta T[n]}{\delta n(\mathbf{r})} + \frac{\delta E_{\text{xc}}[n]}{\delta n(\mathbf{r})} + \int d^3r' n(\mathbf{r}') \frac{1}{|\mathbf{r} - \mathbf{r}'|} + V_{\text{ext}}(\mathbf{r}) = \lambda n(\mathbf{r}). \quad (5.18)$$

This equation has the same form as (5.14), the only difference being the potential replaced by a more complicated one, the ‘effective potential’:

$$V_{\text{eff}}(\mathbf{r}) = V(\mathbf{r}) + \frac{\delta E_{\text{xc}}[n]}{\delta n(\mathbf{r})} + \int d^3r' n(\mathbf{r}') \frac{1}{|\mathbf{r} - \mathbf{r}'|}. \quad (5.19)$$

The analogue of Eq. (5.15) now becomes

$$\left[-\frac{1}{2} \nabla^2 + V_{\text{eff}}(\mathbf{r}) \right] \psi_k(\mathbf{r}) = \varepsilon_k \psi_k(\mathbf{r}). \quad (5.20)$$

Comparing Eqs. (5.20) and (5.17), we see that adding the eigenvalues ε_k of the occupied states does not lead to the total energy as the Hartree energy is overestimated by a factor of 2, and there is a further difference in the exchange correlation term, so that we have all together:

$$E = \sum_{k=1}^N \varepsilon_k - \frac{1}{2} \int d^3r d^3r' n(\mathbf{r}) \frac{1}{|\mathbf{r} - \mathbf{r}'|} n(\mathbf{r}') + E_{xc}[n] - \int d^3r V_{xc}[n(\mathbf{r})]n(\mathbf{r}). \quad (5.21)$$

where V_{xc} is defined in (5.4). The density functional procedure is now given by Eqs. (5.16), (5.19), (5.20) and (5.21). These equations were first derived by Kohn and Sham.³⁵

We have already mentioned that the exact form of the exchange correlation potential is not known. This energy is a functional of the density, but there may be an additional explicit dependence on the external potential. Such a dependence would imply that each physical system has its own particular exchange correlation energy functional. That the exchange correlation potential does not have such a dependence follows immediately from the argument given at the beginning of this section [Eqs. (5.8–5.12)] by separating the external potential off the Hamiltonian and taking the remaining contributions to the energy functional for $F[n]$. This shows that the exact exchange correlation potential, which should work for *all* materials, is simply a functional of the density. In practice we have to use approximations for E_{xc} , as the exact form of this functional is unknown, and our approximation might be better for some materials than for others. The final conclusion can then be formulated as follows:

- If we split the energy functional according to (5.17), the term $E_{xc}[n]$ into which we have moved all the terms we do not have under control, is independent of the external potential.
- The minimisation problem of the energy functional can be carried out using the Kohn–Sham equations (5.20) together with the constraint (5.16).

5.2 The local density approximation

The difference between the Hartree–Fock and density functional approximation is the replacement of the HF exchange term by the exchange correlation energy E_{xc} which is a functional of the density. The exchange correlation potential is a functional derivative of the exchange correlation energy with respect to the local density, and for a homogeneous electron gas, this will

depend on the value of the electron density. For a nonhomogeneous system, the value of the exchange correlation potential at the point \mathbf{r} depends not only on the value of the density at \mathbf{r} but also on its variation close to \mathbf{r} , and it can therefore be written as an expansion in the gradients to arbitrary order of the density:

$$V_{xc}[n](\mathbf{r}) = V_{xc}[n(\mathbf{r}), \nabla n(\mathbf{r}), \nabla(\nabla n(\mathbf{r})), \dots]. \quad (5.22)$$

Apart from the fact that the exact form of the energy functional is unknown, inclusion of density gradients makes the solution of the DFT equations rather difficult, and usually the *Ansatz* is made that the exchange correlation energy leads to an exchange correlation potential depending on the value of the density in \mathbf{r} only and not on its gradients – this is the *local density approximation* (LDA):

$$E_{xc} = \int d^3r \epsilon_{xc}[n(\mathbf{r})]n(\mathbf{r}) \quad (5.23)$$

where $\epsilon_{xc}[n]$ is the exchange correlation energy per particle of an homogeneous electron gas at density n . The local density approximation is exact for an homogeneous electron gas, so it works well for systems in which the electron density does not vary too rapidly. We shall briefly discuss the various forms used for the exchange correlation energy density in the local density approximation, $\epsilon_{xc}[n(\mathbf{r})]$, and refer to the literature for more details.^{36,39,40}

The exchange effects (denoted by the subscript ‘x’) are usually included in a term based on calculations for the homogeneous electron gas¹⁸ giving the following form for the exchange energy in density functional theory:

$$\epsilon_x[n(\mathbf{r})] = \text{Const.} \times n^{1/3}(\mathbf{r}) \quad (5.24)$$

which we have already encountered at the end of section 4.5.1. The value for the constant is found as $-3/4(3/\pi)^{1/3}$.

For open-shell systems the spin-up and -down densities n_+ and n_- are usually taken into account as two independent densities in the exchange correlation energy according to a natural extension of the DFT formalism.³⁶ In local density approximation (now called local spin density approximation), the exchange is given as

$$E_x[n_+, n_-] = -\text{Const.} \int d^3r \left[n_+^{4/3}(\mathbf{r}) + n_-^{4/3}(\mathbf{r}) \right], \quad (5.25)$$

with $\text{Const.} = 3/2(3/4\pi)^{1/3}$ in accordance with the closed-shell prefactor in (5.24). As is to be expected for an exchange coupling, this expression contains interactions between parallel spin pairs only.

In addition to exchange, there is a contribution from the dynamic correlation effects (due to the Coulomb interaction between the electrons) present in the exchange correlation potential, and several local density parametrisations of this interaction have been proposed. A successful one is a parametrised version of the correlation energy obtained in quantum Monte Carlo simulations of the homogeneous electron gas at different densities.^{40,41} Other parametrisations have been presented by Von Barth and Hedin⁴² and Gunnarson and Lundqvist.⁴³ These dynamic correlations represent couplings between both parallel and opposite spin pairs.

In calculations of the electronic structure, the DFT-LDA approach has turned out very successfully. In some systems, however, it leads to noticeable deviations or even failures – some stable negative ions such as H^- , O^- and F^- are predicted to be unstable for example. Many improvements on LDA have therefore been proposed. One of these consists of taking gradients of the density into account in the exchange correlation energy whose form is motivated by calculations taking many-electron effects into account.³⁹

Another approach focuses on the self-interaction present in the Hartree energy which contains Coulomb couplings between an electron and its own charge distribution. This overestimation of the electron–electron interaction should be cancelled by the exchange correlation term, which – in LDA – succeeds only partially in doing so (although in the hydrogen atom for example, 95% of the self-interaction is cancelled by the exchange correlation). It is possible to add these corrections afterward to the exchange correlation potential,⁴⁰ which, however, introduces a dependence of the exchange correlation on the individual orbitals, ψ_k , instead of a dependence on the density only. Both the gradient-correction and self-interaction methods lead to important improvements in calculations of physical properties.³⁶

5.3 A density functional program for the helium atom

In this section we describe the construction of a program for the calculation of the ground state of the helium atom within the local density approximation. As the two electrons occupy the 1s-orbital, the density and hence the Hartree potential is radially symmetric and we exploit this symmetry in spatial integrations. Instead of using basis functions, we solve the radial Schrödinger equation directly, just as we have done in the first chapter for calculating scattering cross sections. The program is set up in three steps. First, we use a simple integration algorithm and combine this with an interpolation routine in order to find the stationary states of hydrogen-like atoms. Second, a routine

for obtaining the Hartree potential from the (radial) electronic density is added. At this point the results should compare with those obtained in the previous chapter using Gaussian basis functions. Finally, the exchange correlation potential is added and we have a fully self-consistent local density program.

5.3.1 Solving the radial equation

To solve the radial Schrödinger equation you can use the Numerov algorithm which is discussed in section A.7.1.4 and which has been used for the scattering program in chapter 2. However, we also have to solve other differential equations and integrals, and in order to avoid complications we shall not require the $O(h^6)$ accuracy of Numerov's algorithm – hence you can also use the simpler Verlet/Stoermer algorithm of section A.7.1.3. It is of course possible and recommended to use library routines throughout the program. For integrating the radial Schrödinger equation, a nonuniform grid is often used which is dense near the nucleus where the Coulomb potential diverges – see problem 5.1. For the hydrogen atom, the radial equation for $l = 0$ reads (in atomic units)

$$\left[-\frac{1}{2}\nabla^2 - \frac{1}{r} \right] u(r) = Eu(r) \quad (5.26)$$

where $u(r)$ is given as $rR(r)$, $R(r)$ being the radial wave function. For the hydrogen atom we know that the solution for the ground state is given by $E = -0.5$ a.u. and $u(r) \propto re^{-r}$, and this enables us to test our programs. The energy eigenvalues can be found by integrating the radial Schrödinger equation from some large radius r_{\max} inward to $r = 0$ and checking whether the solution vanishes there. The procedure is analogous to that described in problem A.4. You should first check whether indeed for $E = -0.5$ a.u. the radial solution vanishes at $r = 0$. Note that for the regular solutions [$u(0) = 0$] we are looking for, the divergence of the potential near the origin causes no problems in the integration routine as long as it is not evaluated at $r = 0$.

For the starting values at r_{\max} you can either substitute the exact values $u(r_{\max}) = r_{\max} \exp(-r_{\max})$ and similarly for $u(r_{\max} - h)$, but it is also possible to take $u(r_{\max})$ equal to 0 and $u(r_{\max} - h)$ equal to a very small value. It is interesting to play around varying the starting conditions and the value of r_{\max} in order to get a feeling for how the accuracy is affected by these.

To arrive at a program which determines the spectrum for you, you must couple the integration routine to a root-finding scheme and apply it to the value of u at the origin. Although it is in principle possible to solve for the energy derivative of u alongside the determination of u itself, we assume here that

the integration routine does not provide energy derivatives. Therefore a library root-finding routine must not use the derivative and the same holds for one you write yourself. In the latter case, the secant method is appropriate; see section A.3. You will have to supply the boundaries between which the root must lie when using the program.

– Programming exercise – *Combine the integration routine and the root-finding routine into a method for finding the $l = 0$ states of a radial potential.*

Check Test your program for the hydrogen atom.

5.3.2 Including the Hartree potential

We now describe an extension of the hydrogen program to the helium case, which implies having a nuclear potential $-2/r$ in the Hamiltonian and requires some treatment of the electron–electron interaction. In this section we take the latter into account in the same way as in section 4.3.2, that is by a so-called Hartree potential which is the electrostatic potential generated by the charge distribution following from the wave function. This potential is given by

$$V_H(\mathbf{r}) = \int d^3r' n_s(\mathbf{r}') \frac{1}{|\mathbf{r} - \mathbf{r}'|}. \quad (5.27)$$

Here, n_s stands for the density of a *single* orbital – the total charge density is twice as large as a result of summation over the spin. The proper Hartree potential is therefore twice as large but half of it consists of the self-interaction which we have subtracted off because this can easily be done for the helium case (see also the end of section 4.3.1). Rather than solving for this potential by calculating the integral (5.27) directly, we shall find it by solving Poisson's equation:

$$\nabla^2 V_H(\mathbf{r}) = -4\pi n_s(\mathbf{r}). \quad (5.28)$$

Using the radial symmetry of the density and defining $U(r) = rV_H(r)$, this equation reduces to the form

$$\frac{d^2}{dr^2} U(r) = -4\pi r n_s(r). \quad (5.29)$$

This is an ordinary second order differential equation which can be solved again using Verlet's algorithm (or a library routine). Note that it is necessary to normalise the radial wave function before integrating Poisson's equation! If you take for the normalisation

$$\int dr u^2(r) = \int dr r^2 R^2(r) = 1, \quad (5.30)$$

you have already included a factor 4π into the density (arising from the angular integrations) and the factor 4π in Poisson's equation drops out:

$$U''(r) = -\frac{u^2(r)}{r}. \quad (5.31)$$

We shall use the normalisation (5.30) throughout this section.

The solution of Eq. (5.31) contains two integration constants which have to be fixed by the boundary conditions. We take $U(0) = 0$ as the first boundary condition. Elementary electrostatics then leads to the second condition

$$V'_H(r_{\max}) = \frac{q_{\max}}{r_{\max}^2}, \quad (5.32)$$

where q_{\max} is the electron charge contained in a sphere of radius r_{\max} :

$$q_{\max} = \int_0^{r_{\max}} dr u^2(r). \quad (5.33)$$

For large r_{\max} , q_{\max} is the total electron charge. If there is no charge beyond r_{\max} , q_{\max} does not depend on r_{\max} , and we have $U(r_{\max}) = q_{\max}$. When carrying out the numerical integration, we take for the first starting condition $U(0) = 0$. The second starting condition, for $U(h)$, is not known at the beginning – we take $U(h) = h$. As the solution $U(r) = \alpha r$ solves the homogeneous differential equation, $U''(r) = 0$, we can add this solution to the numerical solution found, with α taken such as to satisfy the end condition $U(r_{\max}) = q_{\max}$, without violating the starting condition $U(0) = 0$.

– Programming exercise – *Add an extra integration to your program which solves Eq. (5.31).*

It is useful to check for the correctness by using the hydrogen atom as an example. The normalised ground state density [in the sense of (5.30)], found at $E = -0.5$ a.u., is $4e^{-2r}$ and we must solve

$$U''(r) = -4re^{-2r}, \quad (5.34)$$

with the boundary conditions $U(0) = 0$, $U(\infty) = 1$:

$$U(r) = -(r+1)e^{-2r} + 1. \quad (5.35)$$

Check Check whether your program produces these results.

The next step is to make the program self-consistent. This is done by adding the Hartree potential to the nuclear potential and solving for the eigenstate again. You repeat this process until the energy does not change appreciably between subsequent steps. The total energy is given by

$$E = 2\varepsilon - \int dr V_H(r)u^2(r). \quad (5.36)$$

The Hartree correction arises because the Hartree energy is quadratic in the density.

Check Try to reproduce the results for the helium Hartree–Fock calculation in section 4.3.2. In fact, the present method is more accurate as the wave functions are not restricted to linear combinations of four Gaussians. For an integration step $h = 0.01$ (in the Verlet algorithm) you will find for the eigenvalue of the radial Schrödinger equation the value -0.923 a.u. and for the Hartree correction 1.0155 a.u., so that the total energy amounts to $E = -2.861$ a.u., in good agreement with the result obtained in the previous chapter. The experimental value is -2.903 a.u.

5.3.3 The local density exchange potential

The aim of the exercise has not yet been achieved: we must calculate the energy and eigenvalues in the density functional formalism within the local density approximation. Remember that in density functional theory, the density which gives rise to the Hartree potential is the *full* density $n(\mathbf{r})$, i.e. the density of the two electrons, and in the previous section we have subtracted off the self-interaction contribution, leading to a reduction by a factor of 2 of the Hartree potential. Multiplying the Hartree potential by a factor 2 in the previous program yields very poor results and therefore we hope that the exchange potential will correct for the self-interaction. As we have noted above, a

popular form of the local density exchange potential is the one based on a treatment of the exchange hole in a homogeneous electron gas and is given by

$$V_x(\mathbf{r}) = \text{Const.} \times n^{1/3}(\mathbf{r}) \quad (5.37)$$

where the constant is given as

$$\text{Const.} = - \left(\frac{3}{\pi} \right)^{1/3}. \quad (5.38)$$

Here, again the *full* density is to be taken in the right hand side of (5.37) and this is twice the single electron density arising from the radial Schrödinger equation since we have two electrons. Therefore, in terms of the radial eigenfunctions u normalised as in (5.30), our exchange potential reads

$$V_x(\mathbf{r}) = - \left[\frac{3u^2(r)}{2\pi^2 r^2} \right]^{1/3} \quad (5.39)$$

which, for the s-states under consideration, depends only on the radial coordinate r . The total energy is given by

$$E = 2\varepsilon - \int dr V_H(r)u^2(r) + \frac{1}{2} \int dr u^2(r)V_x(r). \quad (5.40)$$

The extension of your program to a local density version is now straightforward: instead of adding only the Hartree potential to the nuclear attraction, you take twice this potential and add the exchange potential to it. The self-consistency loop remains unaltered.

– Programming exercise – *Extend your Hartree–Fock program to include the exchange potential.*

Check If your program is correct, it should give the following values for the energies: $\varepsilon = -0.52$ and $E = -2.72$ atomic units.

Obviously the result is inferior to Hartree–Fock as the exchange potential is included only in an approximate way. Improvement is possible by considering an exchange correlation potential based on an interpolation of quantum Monte Carlo results by Ceperley and Alder,⁴⁴ and it yields a ground state energy of $E = -2.83$ atomic units⁴⁰ which is an important improvement with respect to -2.72 , although it is still worse than the HF result of -2.86 a.u. Implementation of this is straightforward and will be done in problem 5.3.

Table 5.1: Lattice constants and cohesive energies for diamond, Si and Ge. Atomic units are used. Data taken from ref. 36.

	Lattice constant		Cohesion energy	
	DFT	Expt.	DFT	Expt.
Diamond	6.807	6.740	7.58	7.37
Si	10.30	10.26	4.84	4.64
Ge	10.69	10.68	4.02	3.85

Table 5.2: Energies in a.u. for various atoms. Data taken from ref. 36.

Atom	HF	DFT	Expt.
Li	-7.433	-7.353	-7.479
C	-37.702	-37.479	-37.858
O	-74.858	-74.532	-75.113

5.4 Applications and results

In numerous calculations for atoms, molecules and solids the DFT-LDA approach has been very successful. In this section we quote some results which have been taken from the review by Jones and Gunnarson.³⁶

The original applications were to the ground state properties of solids, and some typical results are shown in table 5.1. Results for atoms and molecules are often better than HF (tables 5.2 and 5.3). Interpretation of the Kohn–Sham eigenvalues as excitation energies works surprisingly well in many solids, where the energy bands frequently agree with those measured in photo-emission for example (see problem 5.4). But we should be cautious about interpreting ψ_k and ε_k as anything other than auxiliary quantities for constructing the ground state energy and density. There are several examples where interpretation of ε_k as excitation energies goes drastically wrong – band gaps in semiconductors and insulators are almost invariably too small, and this should not surprise us as the DFT is designed to give the ground state only. The inclusion of self-interaction corrections, mentioned in the previous subsection, gives better results for these gaps – remember these corrections introduce dependence of the Hamiltonian on individual orbitals instead of the density only and are therefore incompatible with DFT.

Table 5.3: Binding energies in a.u. for diatomic molecules. Data taken from ref. 36.

Atom	HF	DFT	Expt.
H ₂	3.64	4.91	4.75
C ₂	0.79	7.19	6.32
O ₂	1.28	7.54	5.22

Exercises

- 5.1 [C] Instead of the regular grid which was used in the helium program of section 5.3, it is better to use a grid with a step size which grows from a very small value near the nucleus to larger values in the valence region, because the wave function will oscillate more rapidly near the nucleus as a result of the deep Coulomb potential. Consider a grid with grid points given by the following formula:

$$r_j = r_p [\exp(j\delta) - 1], \quad j = 0, 1, \dots, j_{\max}.$$

The grid point with $j = 0$ coincides with the nucleus and the grid runs up to a radius r_{\max} which fixes the value of the prefactor r_p to

$$r_p = r_{\max} / [\exp(\delta j_{\max}) - 1].$$

The grid is defined by the number of grid points j_{\max} , by the outermost point r_{\max} and by the parameter δ which determines how much the grid constant near the nucleus differs from that near r_{\max} . All these three values must be specified and then the prefactor r_p can be determined.

- (a) Show that, in terms of j , the radial Schrödinger equation

$$\frac{d^2}{dr^2} u(r) = [V(r) - E] u(r)$$

transforms into

$$\frac{d^2}{dj^2} u(j) - \delta \frac{d}{dj} u(j) = r_p^2 \delta^2 e^{2j\delta} [V(j) - E] u(j),$$

where $u(j) = u(r_j)$.

- (b) Write a general integral $\int_0^{r_{\max}} f(r) dr$ as an integral over j .

- (c) [C] Transform all integrals and differential equation methods in the density functional program to the nonhomogeneous grid defined above. Compare the accuracies of the two versions.
- (d) Show that the first derivative occurring in the radial Schrödinger equation in terms of j above can be transformed away by writing $u(j) = v(j) \exp(\delta j/2)$. Show that the resulting equation for v reads

$$\frac{d^2}{dj^2}v(j) - \frac{\delta^2}{4}v(j) = r_p^2 \delta^2 e^{2j\delta} [V(j) - E]v(j).$$

- (e) [C] Numerov's algorithm (see section A.7.1.4) can be used for solving this differential equation. Try this out for the ground state of the hydrogen atom and show that the numerical error scales as $1/N^4$ as is expected (see problem A.3). Note that when the number of points is doubled, δ should be decreased by a factor of 2.

5.2 [C] The Hartree energy

$$E_H = \int d^3r \int d^3r' \frac{n(\mathbf{r}')n(\mathbf{r})}{|\mathbf{r} - \mathbf{r}'|}$$

overestimates the classical electrostatic energy of the electrons because it includes interactions of the electrons with themselves – these are the so-called self-interactions. In Hartree–Fock theory, this spurious effect is cancelled by the exchange energy. In density functional theory, the exchange correlation energy does not ensure this cancellation *a priori* and we can only hope that it cancels the self-interaction as much as possible. In order to see to what extent the exchange correlation potential succeeds in doing so, we consider the hydrogen atom in DFT (of course, DFT was designed for many-electron systems, but its validity is not *a priori* restricted to systems containing more than one electron). In the hydrogen atom, we find a nonvanishing Hartree and exchange correlation energy, which can easily be evaluated with our DFT program for helium.

Change the nuclear charge back to $Z = 1$ and make sure that the density used in the Hartree and exchange correlation energies is evaluated for the single electron (i.e. not multiplied by 2 as in the helium case). Evaluate both energies for the exact solution of the hydrogen atom.

You should find that the exchange correlation energy compensates about 80% of the self-interaction. For better exchange correlation energies, a value of 96% can be found – see the following problem and ref. 40. See also ref. 17 for more examples.

5.3 [C] The Slater exchange potential

$$V_x = - \left(\frac{3}{\pi} \right)^{1/3} n^{1/3}(\mathbf{r})$$

is based on the exchange energy in a homogeneous electron gas.²¹ It is quite a crude approximation, and a refinement can be made using quantum Monte Carlo results obtained by Ceperley and Alder.^{40,41,44} This leads to a parametrised correlation energy which should be *added* to the Slater term given above. The parametrisation is given in terms of the parameter r_s which is related to the density n according to

$$n = \frac{3}{4\pi r_s^3}.$$

The parametrisation is split into two parts: $r_s \geq 1$ and $r_s < 1$. We need an expression for the correlation energy parameter ϵ_c defined by

$$E_c = \int d^3r n(\mathbf{r}) \epsilon_c(n) n(\mathbf{r}).$$

- (a) Show that from this an expression for the correlation potential V_c can be derived according to

$$V_c(r_s) = \left(1 - \frac{r_s}{3} \frac{d}{dr_s} \right) \epsilon_c(r_s).$$

- (b) [C] A parametrised form of ϵ_c is given by the following expressions. For $r_s \geq 1$ we have

$$\epsilon_c = \gamma / (1 + \beta_1 \sqrt{r_s} + \beta_2 r_s)$$

and for $r_s > 1$

$$\epsilon_c = A \ln r_s + B + C r_s \ln r_s + D r_s.$$

From this, we obtain the following expressions for the correlation potential:

$$V_c(r_s) = \epsilon_c \frac{1 + \frac{7}{6} \beta_1 \sqrt{r_s} + \beta_2 r_s}{1 + \beta_1 \sqrt{r_s} + \beta_2 r_s}$$

for $r_s \geq 1$ and

$$V_c(r_s) = A \ln r_s + B - A/3 + \frac{2}{3} C r_s \ln r_s + (2D - C) r_s / 3.$$

The values of the parameters A , B etc. depend on whether we are dealing with the polarised (all spins same z component) or unpolarised case. For both cases, the values are given in the following table:

Parameters for correlation energy		
	Unpolarised	Polarised
A	0.0311	0.01555
B	-0.048	-0.0269
C	0.0020	0.0014
D	-0.0116	-0.0108
γ	-0.1423	-0.0843
β_1	1.0529	1.3981
β_2	0.3334	0.2611

Use this parametrisation in your helium density functional theory program (unpolarised). You should find an energy $E = -2.83$ atomic units, to be compared with -2.72 without this correction.

- (c) [C] Use the polarised parametrisation for the hydrogen program of the previous problem. You should find an energy $E = -0.478$ a.u.
- (d) [C] It is also possible to combine the self-energy correction with the correlation energy. You should consult the paper by Perdew and Zunger, ref. 40, if you intend to do this. This results in an energy $E = -2.918$ a.u., which is only 0.015 a.u. off the experimental value.

5.4 In this problem, we consider a generalisation of Koopman's theorem (see section 4.5.3) to the density functional formalism. To this end, we consider the spectrum $\{\varepsilon_i\}$ and the corresponding eigenstates of the Kohn–Sham Hamiltonian. We want to consider excitations from the ground state, which means that we do not fill the N lowest levels of the Kohn–Sham spectrum, but skip some levels. In fact we focus on singly ionised systems, which means that instead of filling the lowest N levels of the Kohn–Sham spectrum, we leave level j unoccupied. This results in a change in the total density:

$$n_I(\mathbf{r}) = n(\mathbf{r}) + \delta n(\mathbf{r})$$

where the index I stands for the ionised system.

We want to compare total energies for the full and for the ionised system. The total energy for the full system containing N electrons is given by

$$E(N) = \sum_{i=1}^N \varepsilon_i - \frac{1}{2} \int d^3r d^3r' \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} - \int d^3r n(\mathbf{r})V_{xc}(\mathbf{r}) + E_{xc}[n].$$

The levels ε_i arise from taking the matrix elements $\langle \psi_i | H(N) | \psi_i \rangle$. As a result of the change in density, both the Hamiltonian occurring in these matrix elements and the remaining terms in the energy expression change.

Show that, to linear order in $\delta n(\mathbf{r})$, the effect of the change in the Hamiltonian occurring in these matrix elements is precisely compensated by the change in the remaining terms in the energy expression so that we obtain

$$E(N) - E(N - 1) = \varepsilon_j$$

where $E(N - 1)$ is the total energy if the level j remains unoccupied.

Hint: the change in the exchange correlation energy $E_{xc}[n]$ is given by the expression

$$\delta E_{xc}[n] = \int d^3r \delta n(\mathbf{r}) \frac{\delta E_{xc}[n]}{\delta n(\mathbf{r})} = \int d^3r V_{xc}[n](\mathbf{r}) |\psi_j|^2$$

where ψ_j denotes the j -th orbital.

Unless j is the highest level, the DFT formalism does not provide an interpretation of a system in which we skip levels when filling the spectrum. Therefore, this version of Koopman's theorem does not seem justified for excitation from lower lying states. It is, however, frequently used in interpreting excitation spectra, and often with success.

Solving the Schrödinger equation in periodic solids

In the previous chapter we encountered density functional theory (DFT) which is extensively used for calculating the electronic structure of periodic solids. Aside from DFT, carefully designed potentials often allow for obtaining accurate electronic structures by simply solving the Schrödinger equation without going through the self-consistency machinery of DFT. In both approaches it is necessary to solve the Schrödinger equation and the present chapter focuses on this problem, although some comments on implementing a DFT self-consistency loop will be made.

The large number of electrons contained in a macroscopic crystal prohibits a direct solution of the Schrödinger equation for such a system. Fortunately, the solid has periodic symmetry in the bulk, and this can be exploited to reduce the size of the problem significantly, using *Bloch's theorem*, which enables us to replace the problem of solving the Schrödinger equation for an infinite periodic solid by that of solving the Schrödinger equation in a unit cell with a series of different boundary conditions – the so-called *Bloch boundary conditions*. Having done this, there remains the problem that close to the nuclei, the potential diverges, whereas it is weak when we are not too close to any of the nuclei (interstitial region). We can take advantage of the fact that the potential is approximately spherically symmetric close to the nuclei, but further away the periodicity of the crystal becomes noticeable. These two different symmetries render the solution of the Schrödinger equation in periodic solids difficult. In this chapter we consider an example of an electronic structure method, the augmented plane wave (APW) method, which uses a spatial decomposition of the wave functions: close to the nuclei they are solutions to a spherical potential, and in the interstitial region they are plane waves satisfying the appropriate Bloch boundary conditions.

It is possible to avoid the problem of the deep potential altogether by replacing it by a weaker one, which leaves the interesting physical properties