

A 1 Introduction to Density-Functional Theory

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1 Introduction

The description of the chemical and physical properties of materials requires a quantum mechanical treatment of the many-particle system of electrons and nuclei with their basic electrostatic Coulomb interactions. Even if the more massive nuclei are regarded as classical particles and if the fast moving electrons are treated non-relativistically, this requires the solution of the Schrödinger equation of $3N$ spatial variables and N spin variables. Since the number N of electrons is usually large (even for small molecules N is often larger than 100 and for solids $N \approx 10^{23}$), it is obvious that the solution cannot be obtained without approximation. It is also obvious that the many-electron wavefunction obtained as the solution of the Schrödinger equation is a much too complicated object, if one wants to understand and predict material properties.

In the last decades density-functional theory has emerged as a powerful alternative. Density-functional theory formally reduces the many-electron problem to a single-electron problem and uses the electron density distribution $n(\underline{r})$ as the elementary quantity instead of the many-electron wavefunction. The idea goes back to Thomas [1] and Fermi [2] who, shortly after the basic publications of Schrödinger and Heisenberg, already in 1927 obtained a heuristic description of the many-electron system completely in terms of the electronic density. The Thomas-Fermi method can be considered as the conceptual root of density-functional theory. Almost 40 years later in 1964, Hohenberg and Kohn [3] were then able to prove their famous theorem, which states that the ground-state properties of the many-particle system are uniquely determined by the ground-state particle density $n(\underline{r})$. This theorem provides the fundamental justification of modern density-functional theory and has motivated an enormous number of applications primarily in the electron theory of atoms, molecules and solids, but also in the physics of liquids [4] and in nuclear physics [5].

It is the aim of this chapter to introduce the basic concepts of density-functional theory and to discuss its apparent success for practical applications. The consideration will be simplified by the restriction to a non-relativistic, non-spin-polarized, time-independent many-electron system at zero temperature, which has a non-degenerate ground state Ψ described by the Schrödinger equation

$$\begin{aligned}\hat{H}\Psi &= \left[\hat{T} + \hat{U} + \hat{V}_{ext} \right] \Psi \\ &= \left[-\frac{\hbar^2}{2m} \sum_i^N \nabla_i^2 + \sum_{i < j}^N \sum_j^N U(\underline{r}_i, \underline{r}_j) + \sum_i^N v_{ext}(\underline{r}_i) \right] \Psi = E\Psi\end{aligned}\tag{1}$$

Here $U(\underline{r}, \underline{r}') = e^2|\underline{r} - \underline{r}'|^{-1}$ is the electron-electron interaction and $v_{ext}(\underline{r})$ the static external potential due to the interaction of the electrons with the atomic nuclei. The kinetic energy operator \hat{T} and the interaction operator \hat{U} are universal in the sense that they are the same for any system, while v_{ext} is system dependent or non-universal.

The plan of this chapter is the following. After introducing the Thomas-Fermi approximation as a historical density-functional method, the main principles of modern density-functional theory, the Hohenberg-Kohn theorem and the Kohn-Sham method of mapping the complicated many-electron system to an effective single-electron system, are explained. It is then discussed that approximations for the exchange-correlation part of the density functional can be derived, which are useful for practical applications. Finally, two techniques are considered, which have received increasing attention in recent years. These are the method of coupling-constant integration as a tool to find and understand approximate exchange-correlation functionals and the

method of constraints as a tool to extend the applicability of density-functional theory from ground states to the states of lowest energy compatible with the constraints.

Remark: Extensions of density functional to non-degenerate ground states, to spin-polarized and relativistic electron systems, to excited states and finite temperatures, to time-dependent and to superconducting situations are possible and will be partly covered in other chapters.

1.1 Thomas-Fermi Approximation (1927)

The starting point for the Thomas-Fermi method is the non-interacting system of N electrons in volume V with the density $n = N/V$ and the Fermi energy E_F , which is connected to the radius k_F of the Fermi sphere by

$$k_F = \sqrt{\frac{2m}{\hbar^2} E_F}. \quad (2)$$

In terms of k_F , the density n and the kinetic energy T can be written as

$$n = \frac{1}{3\pi^2} k_F^3 \quad (3)$$

and as

$$T = \frac{3}{5} N E_F = \frac{3}{5} N \frac{\hbar^2}{2m} k_F^2. \quad (4)$$

The kinetic energy density $t = T/V$ follows from (4) by use of (3) as

$$t = \frac{1}{5\pi^2} \frac{\hbar^2}{2m} k_F^5 = \frac{3}{5} (3\pi^2)^{2/3} \frac{\hbar^2}{2m} n^{5/3}. \quad (5)$$

The Thomas-Fermi method applies this relation locally for each point in the inhomogeneous interacting electron system and approximates the kinetic energy as

$$T = \int t(\underline{r}) d\underline{r} \approx \frac{3}{5} (3\pi^2)^{2/3} \frac{\hbar^2}{2m} \int n^{5/3}(\underline{r}) d\underline{r}. \quad (6)$$

By this approximation the kinetic energy can be calculated directly from the density without requiring the knowledge of the many-electron wavefunction. This knowledge is also unnecessary for the calculation of the energy contribution arising from the interaction with the external potential. This contribution is given by the expectation value $\langle \Psi | \hat{V}_{ext} | \Psi \rangle$ and can exactly be determined from the density by formula (56) given in the appendix. The electron-electron interaction energy U , given by the expectation value $\langle \Psi | \hat{U} | \Psi \rangle$, can be calculated by

$$U = \frac{e^2}{2} \int \frac{n_2(\underline{r}, \underline{r}')}{|\underline{r} - \underline{r}'|} d\underline{r} d\underline{r}', \quad (7)$$

which follows from formula (58) given in the appendix by using $U(\underline{r}, \underline{r}') = e^2 |\underline{r} - \underline{r}'|^{-1}$. Thus also the calculation of U does not require the full many-electron wavefunction, but only the pair density $n_2(\underline{r}, \underline{r}')$. In the Thomas-Fermi method the interaction energy (7) is approximated by replacing the pair density $n_2(\underline{r}, \underline{r}')$ with the product of the densities $n(\underline{r})$ and $n(\underline{r}')$. This leads to

$$U \approx \frac{e^2}{2} \int \frac{n(\underline{r}) n(\underline{r}')}{|\underline{r} - \underline{r}'|} d\underline{r} d\underline{r}'. \quad (8)$$

The total energy E for the electron system in the external potential v_{ext} is thus approximated by

$$E \approx \frac{3}{5}(3\pi^2)^{2/3} \frac{\hbar^2}{2m} \int n^{5/3}(\underline{r}) d\underline{r} + \frac{e^2}{2} \int \frac{n(\underline{r})n(\underline{r}')}{|\underline{r} - \underline{r}'|} d\underline{r} d\underline{r}' + \int n(\underline{r}) v_{ext}(\underline{r}) d\underline{r}, \quad (9)$$

which represents a functional $E[n(\underline{r})]$ of the density. Here the word functional is used in its initial meaning originating in the calculus of variation and describes a function that takes functions as its argument; that is, a function whose domain is a set of functions.

The ground-state density and energy can be obtained from (9) by variation over all possible densities with the condition $\int n(\underline{r}) d\underline{r} = N$, which is taken into account by using a Lagrange parameter μ . From

$$\delta \left\{ E[n(\underline{r})] + \mu \left[N - \int n(\underline{r}) d\underline{r} \right] \right\} = 0 \quad (10)$$

one obtains the integral form of the Thomas-Fermi equation as

$$(3\pi^2)^{2/3} \frac{\hbar^2}{2m} n^{2/3}(\underline{r}) + e^2 \int \frac{n(\underline{r}')}{|\underline{r} - \underline{r}'|} d\underline{r}' + v_{ext}(\underline{r}) - \mu = 0. \quad (11)$$

The usual differential form (13) of the Thomas-Fermi equation follows from (11) by introducing the induced potential via

$$e^2 \int \frac{n(\underline{r}')}{|\underline{r} - \underline{r}'|} d\underline{r}' = v_{ind}(\underline{r}) \quad \text{or} \quad \nabla^2 v_{ind}(\underline{r}) = -4\pi e^2 n(\underline{r}) \quad (12)$$

and by using the induced potential as the basic variable. This leads to

$$\nabla^2 v_{ind}(\underline{r}) = -\frac{4e^2}{3\pi} \left[\frac{2m}{\hbar^2} (\mu - v_{ext}(\underline{r}) - v_{ind}(\underline{r})) \right]^{3/2}. \quad (13)$$

Remark: It has been shown that the heuristically obtained density functional (9) of the Thomas-Fermi approximation is inaccurate for most applications, for instance, it does not give the shell structure of the atoms, it makes the atoms smaller with larger nuclear charge and it does not lead to binding of molecules and solids. The largest source of errors is the use of the free-electron approximation for the kinetic energy $T[n(\underline{r})]$, which should be replaced by a better functional. This has been achieved in the density-functional theory of Hohenberg, Kohn, and Sham [3, 6], which also provides a fundamental justification for the use of the density as the elementary variable to describe the many-electron system.

2 Density-Functional Theory

2.1 Hohenberg-Kohn Theorem (1964)

Since the electron-electron interaction is known (Coulomb potential), the external potential completely determines the Hamiltonian of the many-electron system. Thus it also completely determines the ground-state wavefunction and the ground-state density of the many-electron system. This means that a unique mapping exists from the external potential to the ground-state density and that the ground-state density is a uniquely determined functional of the external potential $n_0[v_{ext}(\underline{r})]$.

The first statement of the Hohenberg-Kohn theorem is that the mapping from the external potential to the ground-state density is invertible up to a trivial additive constant in the potential. This means that the external potential is a uniquely determined functional of the ground-state density: $v_{ext}[n_0(\underline{r})]$. Consequently, since every wavefunction Ψ (not only the ground-state wavefunction!) is trivially a functional $\Psi[v_{ext}(\underline{r})]$ of the external potential, the wavefunction Ψ is also a functional $\Psi[v_{ext}[n_0(\underline{r})]]$ of the ground-state density. Thus every quantum mechanical observable, i. e. every expectation value $\langle \Psi | \hat{O} | \Psi \rangle$ is a functional of the ground-state density. The second statement of the Hohenberg-Kohn theorem is that a unique functional $E[n(\underline{r})]$ of the electron density $n(\underline{r})$ exists, which under the condition $\int n(\underline{r}) d\underline{r} = N$ obtains its minimum for the ground-state density $n_0(\underline{r})$ and gives the ground-state energy as $E_0 = E[n_0(\underline{r})]$. The proof of the Hohenberg-Kohn theorem for non-degenerate ground states is simple and proceeds by reductio ad absurdum. It is shown that a contradiction arises if one assumes that two different ground states $\Psi_0 \neq \Psi_0'$ (arising from two different potentials $v \neq v' + \text{const}$) lead to the same ground-state density $n_0(\underline{r})$. The proof is based on the Rayleigh-Ritz principle for the ground-state energy, which is given by $E_0 = \langle \Psi_0 | \hat{H}_v | \Psi_0 \rangle$ assuming a normalized wavefunction as everywhere in this chapter. The Rayleigh-Ritz principle leads to

$$E_0 < \langle \Psi_0' | \hat{H}_v | \Psi_0' \rangle = \langle \Psi_0' | \hat{H}_{v'} + v - v' | \Psi_0' \rangle = E_0' + \int n_0(\underline{r}) [v(\underline{r}) - v'(\underline{r})] d\underline{r}, \quad (14)$$

where the strict inequality is a consequence of the restriction to non-degenerate ground states. Analogously one obtains

$$E_0' < E_0 + \int n_0(\underline{r}) [v'(\underline{r}) - v(\underline{r})] d\underline{r}. \quad (15)$$

The addition of (14) and (15) leads to a cancellation of the integrals, which contain the same density by assumption, with the result $E_0 + E_0' < E_0' + E_0$. This is clearly a contradiction and the assumption that the densities are equal cannot be true. Consequently, two different potentials cannot lead to the same ground-state density, which means that the ground-state density uniquely determines the external potential and, as explained above, all stationary observables of the many-electron systems.

Unfortunately, for most physical properties it is not known how they can be calculated directly from the ground-state density. Therefore, the second part of the Hohenberg-Kohn theorem, which is the minimum principle for the ground-state energy E_0 , is of particular importance. According to Levy [7] the unique energy functional $E[n(\underline{r})]$ can be defined as the minimum over all wavefunctions, which deliver the density $n(\underline{r})$,

$$E[n(\underline{r})] = \min_{\Psi \rightarrow n} \langle \Psi | \hat{T} + \hat{U} + \hat{V}_{ext} | \Psi \rangle \quad (16)$$

and can be written as

$$E[n(\underline{r})] = F[n(\underline{r})] + \int n(\underline{r}) v_{ext}(\underline{r}) d\underline{r}. \quad (17)$$

Here the simple functional dependence on v_{ext} is explicitly displayed. The functional

$$F[n(\underline{r})] = \min_{\Psi \rightarrow n} \langle \Psi | \hat{T} + \hat{U} | \Psi \rangle \quad (18)$$

is universal, which means that it does not depend on v_{ext} and is the same for all systems described by the Schrödinger equation (1). From (16) one obtains

$$E[n(\underline{r})] = \langle \Psi_n^{min} | \hat{T} + \hat{U} + \hat{V}_{ext} | \Psi_n^{min} \rangle \geq E_0, \quad (19)$$

where Ψ_n^{min} is defined as the wavefunction, which delivers the minimum, and where the inequality follows from the Rayleigh-Ritz minimum principle for the ground-state energy E_0 . If the ground-state wavefunction Ψ_0 is used in (16), one obtains

$$E[n_0(\underline{r})] \leq \langle \Psi_0 | \hat{T} + \hat{U} + \hat{V}_{ext} | \Psi_0 \rangle = E_0 , \quad (20)$$

where it has been used that the ground-state wavefunction delivers the ground-state energy and where the inequality follows from (16), because $E[n_0(\underline{r})]$ is defined as the minimum over all wavefunctions, which give the ground-state density $n_0(\underline{r})$, and one of these wavefunctions is the ground-state wavefunction Ψ_0 . Since (19) is valid for any density, it is also valid for the ground-state density. This leads to $E[n_0(\underline{r})] \geq E_0$, which together with (20) shows $E_0 = E[n_0(\underline{r})]$ and establishes the minimum principle

$$E_0 = \min_n E[n(\underline{r})] . \quad (21)$$

Here the minimization is over all densities which arise from antisymmetric wavefunctions for N electrons. This variational principle can be used to determine the ground-state density $n_0(\underline{r})$ and energy E_0 provided that the functional $F[n(\underline{r})]$ can be defined explicitly, which is, however, only possible approximately.

2.2 Kohn-Sham Equations (1965)

The theory discussed above has transformed the formidable problem of finding the minimum of $\langle \Psi | \hat{H} | \Psi \rangle$ with respect to the $3N$ -dimensional trial function Ψ into the seemingly trivial problem of finding the minimum of $E[n(\underline{r})]$ with respect to the three-dimensional trial function $n(\underline{r})$. However, since the explicit form of the functional $F[n(\underline{r})]$ is not known, the theory seems to be rather abstract and of little use. Here, the idea of Kohn and Sham [6], the introduction of a fictitious auxiliary non-interacting electron system with an effective external potential $v_{eff}(\underline{r})$ is of unique importance. This effective potential is constructed in such a way that the density of the auxiliary non-interacting system equals the density of the interacting system of interest. The Hohenberg-Kohn theorem (applied for $U \equiv 0$) guarantees the one-to-one correspondence between the densities and the effective potentials. While the functional $F[n(\underline{r})]$ in (17) and (18) is universal with respect to the external potential, it evidently depends on the interaction U . For $U \equiv 0$ the functional $F[n(\underline{r})]$ reduces to the kinetic energy functional $T_s[n(\underline{r})]$ of non-interacting electrons and the total-energy functional can be written as

$$E_s[n(\underline{r})] = T_s[n(\underline{r})] + \int n(\underline{r}) v_{eff}(\underline{r}) d\underline{r} . \quad (22)$$

The Hohenberg-Kohn variational principle (21) then leads to the Euler-Lagrange equation

$$\frac{\delta}{\delta n(\underline{r})} \left\{ E_s[n(\underline{r})] + \mu \left[N - \int n(\underline{r}) d\underline{r} \right] \right\} = \frac{\delta T_s[n(\underline{r})]}{\delta n(\underline{r})} + v_{eff}(\underline{r}) - \mu = 0 , \quad (23)$$

where similarly as for the derivation of the Thomas-Fermi equation (10) a Lagrange parameter μ is used to guarantee the charge conservation $N = \int n(\underline{r}) d\underline{r}$. Equation (23) provides an exact way to calculate the ground-state density $n(\underline{r})$ provided that the potential $v_{eff}(\underline{r})$ is known, since the functional $T_s[n(\underline{r})]$ for the kinetic energy of non-interacting electrons can be implicitly

constructed by using single-particle wavefunctions (orbitals) $\varphi_i(\underline{r})$, which allows to represent $n(\underline{r})$ and T_s in the form

$$n(\underline{r}) = \sum_i^{occ} |\varphi_i(\underline{r})|^2 \quad \text{and} \quad T_s[n(\underline{r})] = \sum_i^{occ} \int \varphi_i^*(\underline{r}) \left(-\frac{\hbar^2}{2m} \nabla_{\underline{r}}^2 \right) \varphi_i(\underline{r}) d\underline{r}, \quad (24)$$

where i denotes both the spatial as well as the spin quantum numbers and where the sum is over the lowest N (occupied) eigenstates to respect the Pauli principle. The variation of $E[n(\underline{r})]$ with respect to the orbitals leads to the Kohn-Sham equations

$$\left[-\frac{\hbar^2}{2m} \nabla_{\underline{r}}^2 + v_{eff}(\underline{r}) - \mu \right] \varphi_i(\underline{r}) = \epsilon_i \varphi_i(\underline{r}), \quad (25)$$

where the ϵ_i represent Lagrange parameters, which guarantee that the orbitals are normalized as $(\varphi_i, \varphi_i) = 1$. To apply this scheme, a useful expression for the effective potential $v_{eff}(\underline{r})$ must be found. The important achievement of Kohn and Sham was the suggestion to write equation (17) as

$$E[n(\underline{r})] = T_s[n(\underline{r})] + \int n(\underline{r}) v_{ext}(\underline{r}) d\underline{r} + \frac{e^2}{2} \int \frac{n(\underline{r}) n(\underline{r}')}{|\underline{r} - \underline{r}'|} d\underline{r} d\underline{r}' + E_{xc}[n(\underline{r})]. \quad (26)$$

Here the last term is the so-called exchange-correlation energy functional defined as

$$E_{xc}[n(\underline{r})] = F[n(\underline{r})] - T_s[n(\underline{r})] - \frac{e^2}{2} \int \frac{n(\underline{r}) n(\underline{r}')}{|\underline{r} - \underline{r}'|} d\underline{r} d\underline{r}' \quad (27)$$

As before, $T_s[n(\underline{r})]$ is the kinetic energy functional (24) of non-interacting electrons. The variational principle applied to (26) gives

$$\frac{\delta T_s[n(\underline{r})]}{\delta n(\underline{r})} + v_{ext}(\underline{r}) + e^2 \int \frac{n(\underline{r}')}{|\underline{r} - \underline{r}'|} d\underline{r}' + \frac{\delta E_{xc}[n(\underline{r})]}{\delta n(\underline{r})} - \mu = 0. \quad (28)$$

This equation is formally identical with the Euler-Lagrange equation (23) of the non-interacting electron system with the effective potential

$$v_{eff}(\underline{r}) = v_{ext}(\underline{r}) + e^2 \int \frac{n(\underline{r}')}{|\underline{r} - \underline{r}'|} d\underline{r}' + v_{xc}[n(\underline{r})](\underline{r}), \quad (29)$$

where the exchange-correlation potential is defined as

$$v_{xc}[n(\underline{r})](\underline{r}) = \frac{\delta E_{xc}[n(\underline{r})]}{\delta n(\underline{r})}. \quad (30)$$

Equations (24) and (25) are the famous Kohn-Sham equations, which are probably the most important equations of density-functional theory. Since the effective potential depends on the density via (29) and the density on the effective potential via (24) and (25), these equations must be solved self-consistently. This can be achieved by iteration: starting from a trial density the effective potential is determined by (29), for which the equations (24) and (25) are solved to determine a new density. This process is repeated until the new density equals the previous one. In order to damp possible increasing oscillations in the iteration process, it can be necessary to use only a part of the output density and to mix it with the input density in the iterations. From the behavior of the eigenvalues of the functional derivative $f(\underline{r}, \underline{r}') = \delta E[n(\underline{r})]/\delta n(\underline{r}')$ it can be shown [8] that the iteration process always converges to a stable solution if the mixing parameter is small enough, but many iterations may be required.

2.3 Approximations for the Exchange-Correlation Energy Functional

The density-functional theory presented above is exact in principle, however the density functionals $E_{xc}[n(\underline{r})]$ and $v_{xc}[n(\underline{r})]$, in which all complications of the many-particle problem are hidden, are not exactly known and must be approximated. The widespread use of density-functional theory in calculating physical and chemical properties arises from the fact that approximations for E_{xc} and v_{xc} have been found which are both simple and accurate enough for practical applications. A rather simple and remarkably good approximation is the so-called local density approximation (LDA), which replaces the exact functional E_{xc} by

$$E_{xc}^{LDA}[n(\underline{r})] = \int n(\underline{r}) \epsilon_{xc}^{LDA}(n(\underline{r})) d\underline{r}, \quad (31)$$

where $\epsilon_{xc}^{LDA}(n)$ is a function (not a functional) of the density. This function is used in (31) locally at each point \underline{r} with the value $n = n(\underline{r})$ of the density at this point. For a homogeneous interacting electron system with constant density, equation (31) gives the exact result for the exchange-correlation energy and the function $\epsilon_{xc}^{LDA}(n)$ in (31) can be determined by quantum mechanical many-body calculations. The exchange part of $\epsilon_{xc}^{LDA}(n)$ is given by

$$\epsilon_x(n) = -\frac{3}{4} \frac{e^2}{\pi} k_F = -\frac{3}{4} e^2 \left(\frac{3}{\pi} \right)^{1/3} n^{1/3} \quad (32)$$

and can be obtained by the Hartree-Fock method, which neglects correlation, but takes into account exchange. The exchange potential in the Kohn-Sham equations follows from (32) as

$$v_x(n) = \frac{d}{dn}(n\epsilon_x(n)) = -e^2 \left(\frac{3}{\pi} \right)^{1/3} n^{1/3}. \quad (33)$$

The correlation part of $\epsilon_{xc}^{LDA}(n)$ is more difficult to calculate. Accurate results for the correlation part of $\epsilon_{xc}^{LDA}(n)$ have been obtained by the quantum Monte Carlo method [9] and reliable parameterizations for these results are available [10, 11].

For systems with more inhomogeneous densities, the integrand in (31) can be generalized by taking into account dependences on the gradient of the density

$$E_{xc}^{GGA}[n(\underline{r})] = \int f(n(\underline{r}), \nabla n(\underline{r})) d\underline{r}. \quad (34)$$

While the input ϵ_{xc}^{LDA} in (31) is unique, the function f in (34) is not and many different forms have been suggested incorporating a number of known properties of the exact functional, for instance limit and scaling behaviors, or empirical parameters. A well tested numerical approximation is the generalized gradient approximation (GGA) [12, 13], which for instance, improves the cohesive energies and lattice constants of the 3d transition metals. Recently, so-called meta-GGA functionals [14, 15] were proposed, where besides the local density and its gradient also other variables are introduced, for instance the kinetic energy density of the Kohn-Sham orbitals

$$E_{xc}^{GGA}[n(\underline{r})] = \int f(n(\underline{r}), \nabla n(\underline{r}), \tau(\underline{r})) d\underline{r} \quad \text{with} \quad \tau(\underline{r}) = \sum_i^{occ} |\nabla \varphi_i(\underline{r})|^2. \quad (35)$$

By the additional flexibility in (35) it has been possible to improve the accuracy compared to (34) for some physical properties without worsening the results for others. Another possibility

to improve the exchange-correlation functional has been suggested by Becke [16]. These so-called hybrid functionals use a fraction of exact exchange

$$E_{xc}^{hyb} = aE_x^{KS} + (1 - a)E_x^{GGA} + E_c^{GGA}, \quad (36)$$

where E_x^{KS} is the exact exchange calculated with the Kohn-Sham orbitals and the constant $a \approx 0.28$ is an empirical parameter. Unlike LDA and GGA, which are explicit functionals of the density, meta-GGA's and hybrid functionals also depend explicitly on the Kohn-Sham orbitals. Nevertheless, they are still density functionals, since by (25) the orbitals are functionals of the effective potential and therefore by virtue of the Hohenberg-Kohn theorem functionals of the density.

2.4 Applications

Although the Hohenberg-Kohn-Sham density-functional theory provides a formally exact and computationally efficient scheme for electronic-structure calculations, it took more than ten years before it became widely used in solid state theory at the late 1970's. The main obstacle was the form of the exchange-correlation functional, which, available in its local density approximation (LDA), was believed to be good only for spatially slowly varying densities, a condition hardly ever met for real electronic systems. Nevertheless, the LDA has proved to be remarkably accurate in describing the ground-state properties for a wide variety of systems. Out of the many thousands applications one particular example of early calculations [18, 19] is chosen here to illustrate that the LDA can lead to rather good results. Figure 1 displays calculated values and experimental results for the Wigner-Seitz radius as a measure of the equilibrium lattice constant, the cohesive energy, and the bulk modulus of the transition metals of the third and fourth series of the periodic system. The agreement with experiment is rather good, in particular for the fourth series and for the trends along both series. It should be noted in this context that for the calculations the only input specific to each metal was its atomic number and the choice of a fcc or bcc lattice structure. Part of the differences seen in the middle of the third series is caused by the magnetism of these elements, which was not taken into account by ignoring spin-polarization. Early spin-polarized calculation for some selected metals can be found, for instance in Ref. [20]. Including spin-polarization improves the lattice constants and bulk moduli for the magnetic metals, but worsens the cohesive energies mainly due to energy errors arising from the LDA description of the $3d$ atoms.

Because of these errors density-functional theory was rarely used in chemistry, where energetics are generally more important than in solid state theory. Only in the early 1990's with the advent of the GGA, which was quite successful to improve binding energies, atomic energies, and also bond-length and angles, density-functional theory became an accepted method for large scale applications in quantum chemistry. The introduction of hybrid functionals further increased the usefulness of density-functional theory for quantum chemical calculations. By 1998, because it allowed to consider systems unattainable by traditional quantum chemistry methods, density-functional theory had become so successful and popular among quantum chemists that half of the Nobel prize in chemistry went to Walter Kohn "for his development of density-functional theory" [17].

Remark: The treatment of exchange-correlation effects in the LDA and in its improvements discussed above is not appropriate for systems for which the electron system of slowly varying density is a fundamentally incorrect starting point. Examples are: Van der Waals (or polariza-

tion) energies between non-overlapping systems, density tails evanescent into the vacuum near the surfaces of bounded electron systems, or strongly correlated electron systems.

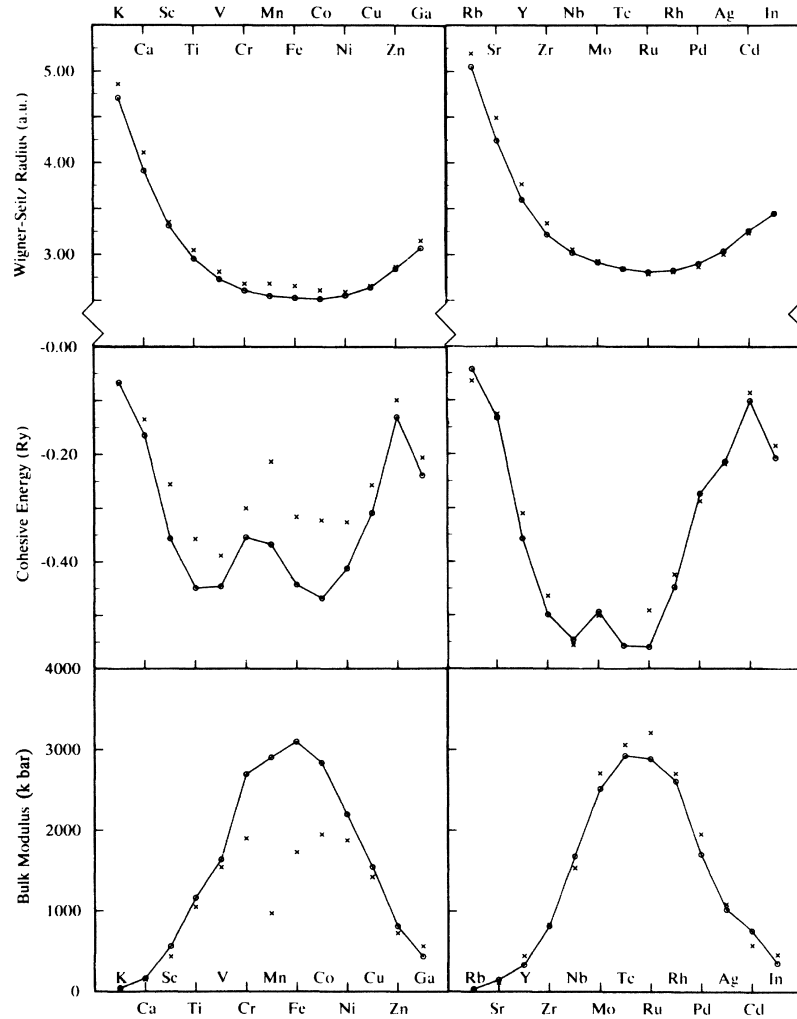


Fig. 1: Calculated Wigner-Seitz radius, cohesive energy, and bulk modulus for metallic elements of the third and fourth series of the periodic system (from Ref. [18]). Measured values are indicated by crosses. The calculations employ the muffin-tin approximation and ignore spin-polarization.

3 Coupling-Constant Integration

An important concept in the development of density functionals is the method of coupling-constant integration [21–23], also known as the adiabatic-connection approach [24], which provides intuitive and physical insight into the exchange and correlation energies and guidance for the approximation of their density functionals. The method is based on the introduction of a fictitious many-electron system with a scaled electron-electron interaction $\lambda U(\underline{r}, \underline{r}')$, $0 \leq \lambda \leq 1$ and a fictitious external potential v_λ , which is chosen such that for all λ in the interval (0,1) the

corresponding density equals the physical density

$$n_\lambda(\underline{r}) \equiv n_{\lambda=1}(\underline{r}) = n(\underline{r}) . \quad (37)$$

This procedure represents an interpolation between the non-interacting system ($\lambda = 0$) with the effective Kohn-Sham potential v_{eff} and the physical system ($\lambda = 1$) with the true external potential v_{ext} . The Hellmann-Feynman theorem can be used to obtain the λ derivative of the ground-state energy as

$$\frac{dE_0(\lambda)}{d\lambda} = \frac{d}{d\lambda} \langle \Psi_\lambda | \hat{H}_\lambda | \Psi_\lambda \rangle = \langle \Psi_\lambda | \frac{d\hat{H}_\lambda}{d\lambda} | \Psi_\lambda \rangle = \langle \Psi_\lambda | U | \Psi_\lambda \rangle + \frac{d}{d\lambda} \int n(\underline{r}) v_\lambda(\underline{r}) d\underline{r} , \quad (38)$$

where Ψ_λ denotes the ground-state wavefunction for the Hamiltonian \hat{H}_λ (with potential v_λ and interaction $\lambda U(\underline{r}, \underline{r}')$). By integration over the λ interval (0,1) one obtains

$$E[n(\underline{r})] - E_s[n(\underline{r})] = \int_0^1 \langle \Psi_\lambda | U | \Psi_\lambda \rangle d\lambda + \int n(\underline{r}) [v_{ext}(\underline{r}) - v_{eff}(\underline{r})] d\underline{r} , \quad (39)$$

where it was used that $E(\lambda = 1)$ is the ground-state energy $E[n(\underline{r})]$ of the physical system with external potential $v_{ext} = v_{\lambda=1}$ and $E(\lambda = 0)$ is the ground-state energy $E_s[n(\underline{r})]$ of the non-interacting system with the effective potential $v_{eff} = v_{\lambda=0}$. If (26) and (22) are used, the difference of the energies on the left-hand side of (39) can be written as

$$E[n(\underline{r})] - E_s[n(\underline{r})] = \frac{e^2}{2} \int \frac{n(\underline{r})n(\underline{r}')}{|\underline{r} - \underline{r}'|} d\underline{r} d\underline{r}' + E_{xc}[n(\underline{r})] + \int n(\underline{r}) [v_{ext}(\underline{r}) - v_{eff}(\underline{r})] d\underline{r} \quad (40)$$

and the exchange-correlation functional is explicitly obtained as

$$E_{xc}[n(\underline{r})] = \int_0^1 \langle \Psi_\lambda | U | \Psi_\lambda \rangle d\lambda - \frac{e^2}{2} \int \frac{n(\underline{r})n(\underline{r}')}{|\underline{r} - \underline{r}'|} d\underline{r} d\underline{r}' . \quad (41)$$

According to (59) given in the appendix, the expectation value in (41) can be written in terms of the pair density, which leads to

$$E_{xc}[n(\underline{r})] = \int_0^1 \frac{e^2}{2} \int \frac{n_2^\lambda(\underline{r}, \underline{r}')}{|\underline{r} - \underline{r}'|} d\underline{r} d\underline{r}' d\lambda - \frac{e^2}{2} \int \frac{n(\underline{r})n(\underline{r}')}{|\underline{r} - \underline{r}'|} d\underline{r} d\underline{r}' . \quad (42)$$

Here the pair density explicitly depends on the interaction strength λ , while the density is independent of λ by construction. With the pair-correlation function, given by $n_2^\lambda(\underline{r}, \underline{r}') = n(\underline{r})g_\lambda(\underline{r}, \underline{r}')n(\underline{r}')$, the last equation can be written as

$$E_{xc}[n(\underline{r})] = \frac{e^2}{2} \int \frac{n(\underline{r})n(\underline{r}')}{|\underline{r} - \underline{r}'|} \left[\int_0^1 (g_\lambda(\underline{r}, \underline{r}') - 1) d\lambda \right] d\underline{r} d\underline{r}' \quad (43)$$

or as

$$E_{xc}[n(\underline{r})] = \frac{e^2}{2} \int n(\underline{r}) \frac{n_{xc}(\underline{r}, \underline{r}' - \underline{r})}{|\underline{r} - \underline{r}'|} d\underline{r} d\underline{r}' \quad (44)$$

with

$$n_{xc}(\underline{r}, \underline{r}' - \underline{r}) = n(\underline{r}') \int_0^1 (g_\lambda(\underline{r}, \underline{r}') - 1) d\lambda . \quad (45)$$

Here n_{xc} can be understood as the exchange-correlation hole and E_{xc} as the interaction energy between the electronic density $n(\underline{r})$ and the hole. The hole is created by three effects: (i) self-interaction correction, which guarantees that the electron does not interact with itself, (ii) the Pauli exclusion principle, which keeps electrons of equal spin apart in space, and (iii) the Coulomb repulsion, which keeps any two electrons apart in space. Effects (i) and (ii) are responsible for the exchange energy, which is present even for $\lambda = 0$, while effect (iii) is responsible for the correlation energy, which arises only for $\lambda \neq 0$. By use of equation (59) given in the appendix one obtains that the hole is normalized

$$\int n_{xc}(\underline{r}, \underline{r}' - \underline{r}) d\underline{r}' = -1, \quad (46)$$

which reflects the total screening of an electron at \underline{r} due to the combined effect of the Pauli principle and the electron-electron interaction.

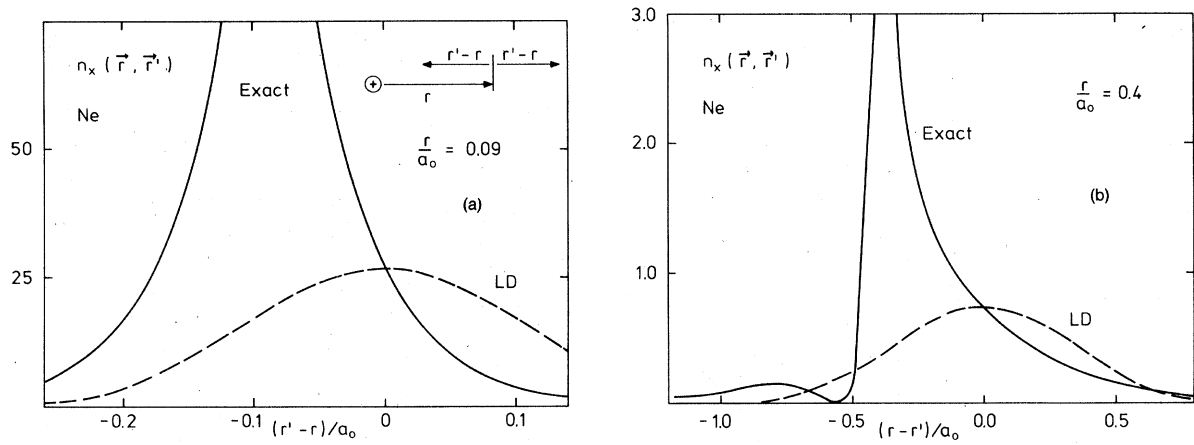


Fig. 2: The exchange hole around an electron at \underline{r} in the neon atom shown as function of distance from the electron along a line connecting the electron and the nucleus for two different positions of the electron 0.09 and 0.4 Bohr radii away from the nucleus (from Ref. [25]). Solid lines are for the exact hole and dashed lines for the LDA hole.

For the use of (44), which is an exact quantum mechanical result, it is important to realize that the Coulomb interaction $1/|\underline{r} - \underline{r}'|$ only depends on the distance $|\underline{r} - \underline{r}'|$ between the particles. This can be exploited by a change of variable $\underline{r}'' = \underline{r}' - \underline{r}$. In terms of \underline{r}'' , equation (44) can be written as

$$E_{xc}[n(\underline{r})] = \frac{e^2}{2} \int n(\underline{r}) \frac{n_{xc}(\underline{r}, \underline{r}'')}{r''} d\underline{r} d\underline{r}'', \quad (47)$$

which by integration over the angles of \underline{r}'' leads to

$$E_{xc}[n(\underline{r})] = \frac{e^2}{2} \int n(\underline{r}) 4\pi \bar{n}_{xc}(\underline{r}, r'') r'' dr'' d\underline{r}, \quad (48)$$

where $\bar{n}_{xc}(\underline{r}, r'')$ is defined as the spherical average of $n_{xc}(\underline{r}, \underline{r}'')$. Similarly (46) can be transformed into

$$\int 4\pi \bar{n}_{xc}(\underline{r}, r'') r''^2 dr'' = -1. \quad (49)$$

Together (48) and (49) show that the exchange-correlation energy depends on the first moment of a function for which the second moment is exactly known. Since (48) and (49) are valid for any external potential, they are of course also valid for the homogeneous electron system with a constant external background potential. Since the LDA exactly describes the homogeneous electron system, this means that these equations are exactly satisfied in the LDA. This observation has been used by Gunnarsson, Jonson and Lundqvist [25] to explain the unexpected quantitative success of LDA density-functional calculations. These authors have argued that the success arises from the fact that only the spherical average is used in (48) so that distortions of the hole due to inhomogeneities are averaged out and from the fact that the LDA hole satisfies the sum rule (46). The effect of the spherical averaging is illustrated in Figs. 2 and 3, where results for the exchange-only limit of the hole are shown for the neon atom. The actual shape of the exchange hole in Fig. 2 is poorly represented by the LDA exchange hole (the true exchange hole in an atom has a maximum at the nucleus whereas the LDA hole is centered at the electron). However, the spherical averages in Fig. 3, which really enter in (48), are in much better agreement.

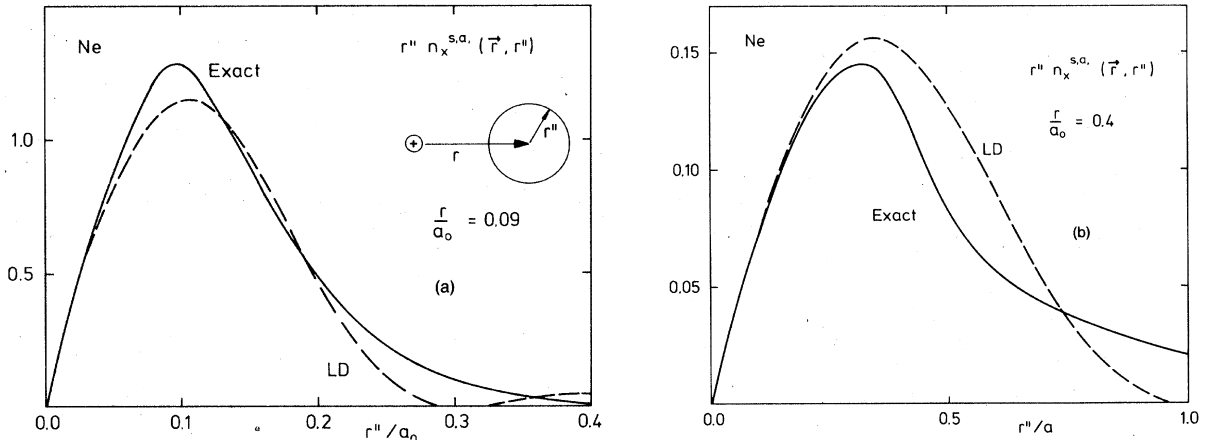


Fig. 3: Spherical average of the exchange hole in the neon atom (from Ref. [25]). The average is multiplied by r'' so that the area under each curve is directly proportional to the integral over r'' , which enters in (48). Note that the integral of r'' times the curves is the same for the exact and the LDA hole because of the sum rule (49).

Thus the adiabatic connection formula (44) provides strong arguments to understand why the LDA works so well for systems even far from the limit of constant density and why it was so difficult to improve upon the LDA by relaxing this limit in gradient expansions. Only after it had been realized that any successful exchange-correlation functional should obey physical constraints like sum rules and scaling behaviors as the ones imposed by the adiabatic connection formula, it became possible in the late 1980's to develop functionals like the GGA with improved accuracy.

4 Constrained Density-Functional Theory

Already the formal development of density-functional theory in Sec. 2 contains constraints in the minimization procedures. For instance, in (16) the minimization is constrained to wave-

functions Ψ with the correct density $n(\underline{r})$ and in (10) and (23) the variation is constrained to charge conserving densities. The basic idea of constrained density-functional theory [26] is to extend this concept to quite arbitrary constraints. The energy of the lowest state compatible with a constraint can then be found by a modified energy functional. One example considered in Ref. [26] is the modified energy functional

$$\tilde{E}[n(\underline{r})] = E[n(\underline{r})] + v \left[N_V - \int_V n(\underline{r}) d\underline{r} \right]. \quad (50)$$

Here $E[n(\underline{r})]$ is the usual functional (17) and the constraint, guaranteed by the Lagrange parameter v , describes that the local volume V exactly contains N_V electrons. The minimization of (50) with respect to $n(\underline{r})$ leads to an additional potential v in the Kohn-Sham equations, which is constant in the volume V and zero otherwise. This potential must be adjusted such that the resulting density $n_v(\underline{r})$ gives exactly N_V electrons in the volume V . Instead of calculating the energy from the functional $\tilde{E}[n_v(\underline{r})]$, it is computationally much easier to calculate directly the energy difference with respect to a reference state N_0 , for instance the ground state. This can be done by the Hellmann-Feynman theorem

$$\frac{dE(N_V)}{dN_V} = v \quad \Rightarrow \quad \Delta E(N_V) = \int_{N_0}^{N_V} v(N') dN', \quad (51)$$

which only requires the knowledge of the potential $v(N')$. Physically, the potential v can be viewed as the “force” necessary to constrain the system to the desired state and ΔE as the “strain energy” of the system.

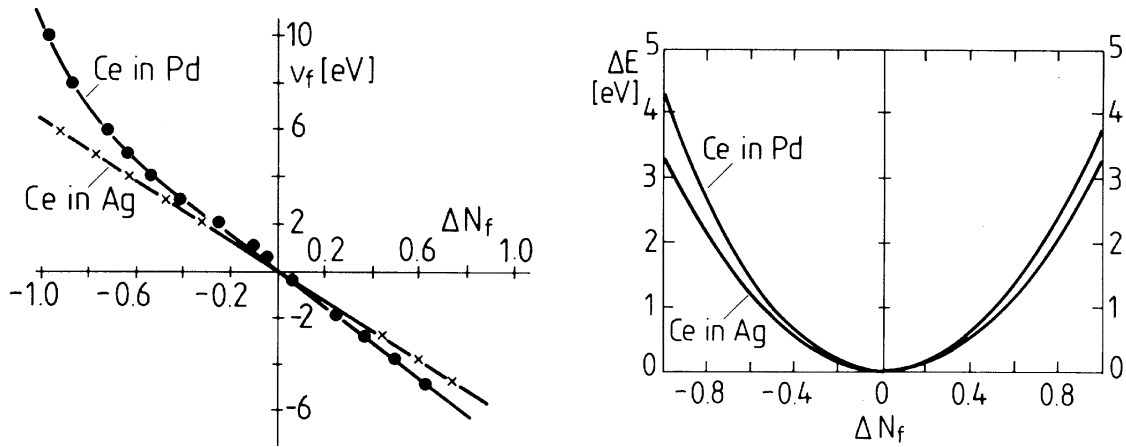


Fig. 4: The Lagrange parameter v_f (left), which controls the f occupation N_f and the energy difference $\Delta E(N_f)$ (right) for Ce impurities in Pd and Ag as function of ΔN_f (from Ref. [26]).

Instead of constraining the total number of electrons in volume V to a desired number, it is more interesting to constrain the partial number of electrons of a particular angular-momentum character. This has been used in Ref. [26] for a first fully self-consistent calculation of the screened Coulomb interaction parameter (the Hubbard U) for the Ce $4f$ electrons of Ce impurities in Pd and Ag crystals. The Lagrange parameter, which enforces the desired number N_f of f electrons in the Ce impurity cell, is a projection potential v_f acting only on the $l = 3$ angular momentum components of the wavefunction in the considered impurity cell. The spd electrons in this cell as well as all other electrons in neighboring cells can freely relax to minimize

the energy, describing in this way an optimally screened excitation. The results of Ref. [26] for the self-consistently determined potential v_f and energy difference $\Delta E(N_f)$ are shown in Fig. 4 as function of $\Delta N_f = N_f - N_f^0$, where $N_f^0 = 1.18$ and $N_f^0 = 1.25$ are the calculated ground-state values for the f occupation in the Ce impurity cells in Pd and Ag. Fig. 4 shows a nearly linear dependence of v_f on ΔN_f and consequently by integration an almost quadratic dependence of $\Delta E(N_f)$ on ΔN_f . The values of the Coulomb interaction calculated by $U_f = \Delta E(N_f + 1) + \Delta E(N_f - 1)$ have been obtained as 8.1 eV for Ce in Pd and as 6.6 eV for Ce in Ag, which is in reasonable agreement with experimental and other theoretical estimates [26].

Remark: Constrained LDA calculations provide presently probably one of the best ways to determine the value of the Coulomb interaction parameter U , which can be used in methods for strongly correlated electrons as in the dynamical mean field theory (DMFT) or in the LDA+ U method. However, a significant uncertainty remains, since the constraint is not defined unambiguously and depends, for instance, on the volume V chosen in (50) or on the shape of the orbitals in basis-set methods.

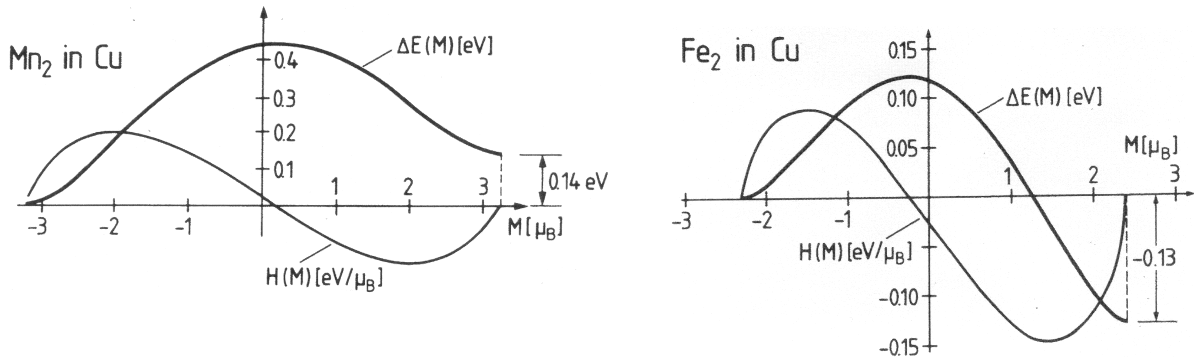


Fig. 5: Magnetic interaction energy $\Delta E(M)$ and constraining magnetic field $H(M)$ for pairs of Mn and Fe impurities on nearest neighbor sites in a Cu crystal (from Ref. [27]). Note that the energies involved in these calculations are several orders of magnitude smaller than the individual energies of the antiferromagnetic and ferromagnetic configurations.

The constrained density-functional approach is also of particular importance for magnetic systems, since it allows to fix the local magnetic moments in the atomic unit cells and to calculate the resulting energies. These energies can then be mapped to effective Hamiltonians describing only the contracted degrees of freedom of the local moments. For instance, for small deviations from the ground state, the energy difference is quadratic in the changes of the moments

$$\Delta E \approx \frac{1}{2} \sum_{i,j} \sum J_{ij} \Delta M_i \Delta M_j, \quad (52)$$

which provides a method to calculate the exchange-coupling constants J_{ij} within density-functional theory. An early application [27] to magnetic systems is the calculation of interaction energy differences between the ferromagnetic and antiferromagnetic configuration of impurity pairs in metals. In these calculations the local magnetic moment of one of the impurities is constrained to an arbitrary value M and the lowest energy $E(M)$ compatible with this constraint is determined by a modified functional similar to (50) given by

$$\tilde{E}[n(\underline{r}), m(\underline{r})] = E[n(\underline{r}), m(\underline{r})] + H \left[M - \int_{V_1} m(\underline{r}) d\underline{r} \right], \quad (53)$$

where the Lagrange parameter H is a constraining magnetic field, which is constant in cell V_1 and vanishes elsewhere. This field is chosen such that the integral of the magnetization density $m(\underline{r})$ over the cell V_1 gives the desired value of the moment. Similar to (51) the energy difference is given by

$$\Delta E(M) = \int_{M_0}^M H(M') dM', \quad (54)$$

where M_0 is the moment of the reference state. For instance in Fig. 5, the reference state is the antiferromagnetic configuration, for which the moment M_0 of one impurity is negative and opposite to the moment of the second impurity. This reference state with calculated moments of $M = -3.22\mu_B$ and $M = -2.31\mu_B$ (for Mn and Fe pairs) corresponds to the left minima of the $\Delta E(M)$ curves in Fig. 5. The right minima of the $\Delta E(M)$ curves correspond to the ferromagnetic configuration with calculated moments $M = 3.20\mu_B$ and $M = 2.40\mu_B$ (for Mn and Fe pairs). Both the antiferromagnetic and the ferromagnetic configurations are stable as the minima of the energies with vanishing constraining field H indicate. Near $M \approx 0$ the $\Delta E(M)$ curves have maxima indicating unstable nearly non-magnetic states. The energy differences between the ferromagnetic and antiferromagnetic configuration are 0.14 eV for Mn and -0.13 eV for Fe pairs such that the antiferromagnetic state is more stable for the Mn pair and the ferromagnetic state is more stable for the Fe pair. Note that whereas the energy and field curves depend on the choice of the constraint, for instance the volume V_1 , the resulting energy differences between both configurations are independent of the choice of the constraint. Instead of varying the absolute magnitude of the moment also its direction can be constrained. This requires a transversal field perpendicular to the direction of the moment and will be discussed in more detail by Bihlmayer in chapter *Magnetism in Density Functional Theory* (A2).

Remark: The constrained density-functional approach discussed above provides a generalization of earlier ideas for discrete systems. For instance, by constraining the symmetry of the wavefunction one obtains the theorem of Gunnarsson and Lundqvist [23], which establishes density-functional theory for the lowest state of each symmetry, and by constraining the occupation n_i of a certain atomic orbital i one can rederive Janak's formula $\epsilon_i = \partial E / \partial n_i$ [28] or, in the integrated form, Slater's transition state [29].

Appendix

The expectation values $\langle \Psi | \hat{V}_{ext} | \Psi \rangle$ and $\langle \Psi | \hat{U} | \Psi \rangle$ can be written in terms of the density $n(\underline{r})$ and the pair density $n_2(\underline{r}, \underline{r}')$. This can be shown as follows. By using the representation of the density as expectation value of the density operator

$$n(\underline{r}) = \langle \Psi | \hat{n} | \Psi \rangle = \int |\Psi(\underline{r}_1, \dots, \underline{r}_N)|^2 \sum_i^N \delta(\underline{r} - \underline{r}_i) d\underline{r}_1 \dots d\underline{r}_N \quad (55)$$

one obtains

$$\begin{aligned} \int n(\underline{r}) v_{ext}(\underline{r}) d\underline{r} &= \int |\Psi(\underline{r}_1, \dots, \underline{r}_N)|^2 \sum_i^N \delta(\underline{r} - \underline{r}_i) v_{ext}(\underline{r}_i) d\underline{r}_1 \dots d\underline{r}_N d\underline{r} \\ &= \int |\Psi(\underline{r}_1, \dots, \underline{r}_N)|^2 \sum_i^N v_{ext}(\underline{r}_i) d\underline{r}_1 \dots d\underline{r}_N \\ &= \langle \Psi | \hat{V}_{ext} | \Psi \rangle, \end{aligned} \quad (56)$$

where first $v_{ext}(\underline{r})$ has been replaced by $v_{ext}(\underline{r}_i)$ because of the δ function and then the result $\int \delta(\underline{r} - \underline{r}_i) d\underline{r} = 1$ was used. Similarly by using the representation of the pair density as expectation value of the two-particle density operator

$$n_2(\underline{r}, \underline{r}') = \langle \Psi | \hat{n}_2 | \Psi \rangle = \int |\Psi(\underline{r}_1, \dots, \underline{r}_N)|^2 \sum_{i \neq j}^N \sum^N \delta(\underline{r} - \underline{r}_i) \delta(\underline{r}' - \underline{r}_j) d\underline{r}_1 \dots d\underline{r}_N \quad (57)$$

one obtains

$$\begin{aligned} \int n_2(\underline{r}, \underline{r}') U(\underline{r}, \underline{r}') d\underline{r} d\underline{r}' &= \int |\Psi(\underline{r}_1, \dots, \underline{r}_N)|^2 \sum_{i \neq j}^N \sum^N \delta(\underline{r} - \underline{r}_i) \delta(\underline{r}' - \underline{r}_j) \\ &\quad \times U(\underline{r}_i, \underline{r}_j) d\underline{r}_1 \dots d\underline{r}_N d\underline{r} d\underline{r}' \\ &= 2 \int |\Psi(\underline{r}_1, \dots, \underline{r}_N)|^2 \sum_{i < j}^N \sum^N U(\underline{r}_i, \underline{r}_j) d\underline{r}_1 \dots d\underline{r}_N \\ &= 2 \langle \Psi | \hat{U} | \Psi \rangle, \end{aligned} \quad (58)$$

where the double sum over $i \neq j$ has been replaced by twice the double sum over $i < j$. It is also useful to note that the density $n(\underline{r})$ is connected to an integral of the pair density by

$$\int n_2(\underline{r}, \underline{r}') d\underline{r}' = (N - 1) n(\underline{r}), \quad (59)$$

which can be established by using the identity

$$\sum_{i \neq j}^N \sum^N \int \delta(\underline{r}' - \underline{r}_j) d\underline{r}' = \sum_{i \neq j}^N \sum^N = (N - 1) \sum_i^N \quad (60)$$

in equation (58).

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