

Density Functional Theory - Important Concepts

Strictly speaking, none of the fundamental principles from density functional theory (DFT) has been used up to now. Instead of adding DFT exchange and correlation energies, we used the exact exchange result of the Fock term from Hartree-Fock's theory, which cancelled exactly half of the Hartree energy in case of the Helium atom.

Theoretically, when using the "correct/exact" exchange-correlation DFT functional we could calculate the exact total energy. Unfortunately, the functional is unknown and we have to cope with approximations, and as we will see soon, even then we cannot always find analytic expressions but have to be content with parameterizations.

- Formulate the basic idea behind the Hohenberg-Kohn theorem. What are the fundamental equations associated with this theorem? In particular, what universal form does the total energy functional $E[n]$ take and how is this related to the minimum principle? What stationary condition on the universal functional $F[n]$ follows from this principle?

Optional: Express the kinetic energy, external potential and two-particle interaction operators in their second quantized form.

Optional: Show that, independent of using the 1st vs. 2nd quantized external potential operator, the same expression for the corresponding energy is obtained when taking the scalar product with a N particle wave function.

Solution:

Many-Body Formalism and 2nd Quantization

This section follows mainly the text book of Engel and Dreizler [1], especially §2.1 and §3.1.

Since in *density* functional theory the leading protagonist is the electronic number or charge density, $\rho(\mathbf{x}) = (-e)n(\mathbf{x})$, we should have a quick look on how this quantity is build in the context of the so called second quantization.

In general, $n(\mathbf{x})$ can be calculated from a N -particle wave function $|\Psi^N\rangle \in \Lambda_N \mathcal{H}$ by virtue of

$$n(\mathbf{x}) = N \int d^3 \mathbf{x}_2 \dots \int d^3 \mathbf{x}_N (\Psi^N)^*(\mathbf{x}, \mathbf{x}_2, \dots, \mathbf{x}_N) \Psi^N(\mathbf{x}, \mathbf{x}_2, \dots, \mathbf{x}_N), \quad (1)$$

and has to integrate to the total number of electrons

$$N = \int d^3 \mathbf{x} n(\mathbf{x}). \quad (2)$$

The time-independent Schrödinger equation applies to the many-body wave function as usual,

$$\hat{\mathcal{H}}^N |\Psi^N\rangle = E |\Psi^N\rangle, \quad (3)$$

where the standard Hamiltonian for N particles takes the form¹

$$\hat{\mathcal{H}}^N = \hat{T}^N + \hat{V}_{\text{ext}}^N + \hat{W}^N. \quad (4)$$

¹In this section, we add for clarity the superscript \hat{O}^N to operators acting on N -particle wave functions. Later we drop N for better readability since in DFT we usually do not leave \mathcal{H}^N .

Here, \hat{T} denotes the kinetic energy (one-particle) operator²

$$\mathcal{Q}(\hat{T}) = \int d^3\mathbf{x} \hat{\psi}^\dagger(\mathbf{x}) \left(-\frac{\hbar^2}{2m} \Delta \right) \hat{\psi}(\mathbf{x}), \quad \hat{T}^N = \mathcal{Q}(\hat{T}) \upharpoonright_{\mathcal{H}^N} = \sum_{i=1}^N \frac{|\hat{\mathbf{p}}_i|^2}{2m}. \quad (5)$$

The multiplicative external (one-particle) potential energy operator is given in terms of a time-independent function v_{ext} by virtue of

$$\mathcal{Q}(\hat{V}_{\text{ext}}) = \int d^3\mathbf{x} \hat{\psi}^\dagger(\mathbf{x}) v_{\text{ext}}(\mathbf{x}) \hat{\psi}(\mathbf{x}), \quad \hat{V}_{\text{ext}}^N = \mathcal{Q}(\hat{V}_{\text{ext}}) \upharpoonright_{\mathcal{H}^N} = \sum_{i=1}^N v_{\text{ext}}(\hat{\mathbf{x}}_i). \quad (6)$$

By contrast, \hat{W} denotes a general two-particle interaction operator determined by an interaction kernel $w(\mathbf{x}, \mathbf{x}')$ in the following manner:

$$\mathcal{Q}(\hat{W}) = \frac{(-e)^2}{2} \int d^3\mathbf{x} \int d^3\mathbf{x}' \hat{\psi}^\dagger(\mathbf{x}) \hat{\psi}^\dagger(\mathbf{x}') w(\mathbf{x}, \mathbf{x}') \hat{\psi}(\mathbf{x}') \hat{\psi}(\mathbf{x}), \quad (7)$$

$$\hat{W}^N = \mathcal{Q}(\hat{W}) \upharpoonright_{\mathcal{H}^N} = \frac{(-e)^2}{2} \sum_{\substack{i,j=0 \\ i \neq j}} \sum_{\substack{i,j=0 \\ i < j}} w(\hat{\mathbf{x}}_i, \hat{\mathbf{x}}_j) = (-e)^2 \sum_{\substack{i,j=0 \\ i < j}} w(\hat{\mathbf{x}}_i, \hat{\mathbf{x}}_j), \quad (8)$$

where $w(\mathbf{x}, \mathbf{x}')$ is not further specified except for symmetry $w(\mathbf{x}, \mathbf{x}') = w(\mathbf{x}', \mathbf{x})$, but usually takes the form of the Coulomb interaction kernel,

$$w(\mathbf{x}, \mathbf{x}') = v_c(\mathbf{x} - \mathbf{x}') = \frac{1}{4\pi\epsilon_0} \frac{1}{|\mathbf{x} - \mathbf{x}'|}, \quad (9)$$

when dealing with electron-electron interaction.

Density Operator

The density operator is defined by

$$\hat{n}(\mathbf{x}) = \hat{\psi}^\dagger(\mathbf{x}) \hat{\psi}(\mathbf{x}), \quad \hat{n}(\mathbf{x}) \upharpoonright_{\mathcal{H}^N} = \sum_{i=1}^N \delta^3(\mathbf{x} - \hat{\mathbf{x}}_i). \quad (10)$$

where $\hat{\psi}(\mathbf{x})$ is the Schrödinger field operator

$$\hat{\psi}^{(\dagger)}(\mathbf{x}) := \hat{a}^{(\dagger)}(|\mathbf{x}\rangle) \quad (11)$$

that acts on a N -particle wave function as

$$\langle \mathbf{x}_2, \dots, \mathbf{x}_N | \hat{\psi}(\mathbf{x}) \Psi^N \rangle = (\hat{\psi}(\mathbf{x}) \Psi^N)(\mathbf{x}_2, \dots, \mathbf{x}_N) \quad (12)$$

$$= \sqrt{N} \Psi^N(\mathbf{x}, \mathbf{x}_2, \dots, \mathbf{x}_N), \quad (13)$$

and thus transforms a state $|\Psi^N\rangle \in \mathcal{H}^N$ into $|\Psi^{N-1}\rangle \in \mathcal{H}^{N-1}$, because it annihilates a position state as defined above via the generic annihilator. You should think of the argument \mathbf{x} as being

²The deduction of the N -particle Hilbert space restricted operators from their general second quantized form is rather involved (cf. [2, §6h]), so we will only state the well-known expressions for both in each case.

externally set to a specific value and is thus not a dynamic variable of Ψ anymore, which leaves Ψ with $(N - 1)$ remaining dynamic variables.

Equation (1) is recovered by constructing the expectation value of the density operator,

$$n(\mathbf{x}) = \langle \Psi^N | \hat{n}(\mathbf{x}) | \Psi^N \rangle, \quad (14)$$

and either inserting eq. (12) into

$$n(\mathbf{x}) = \langle \hat{\psi}(\mathbf{x}) \Psi^N | \hat{\psi}(\mathbf{x}) \Psi^N \rangle_{\mathcal{H}^{N-1}} \quad (15)$$

with

$$\mathbb{1}_{\mathcal{H}^{N-1}} = \int d^3 \mathbf{x}_2 \dots \int d^3 \mathbf{x}_N |\mathbf{x}_2, \dots, \mathbf{x}_N\rangle \langle \mathbf{x}_2, \dots, \mathbf{x}_N|, \quad (16)$$

or, for the first quantized version, by first evaluating the scalar product in (14) in position space and afterwards inserting the second form in (10):

$$\begin{aligned} & \langle \Psi^N | \hat{n}(\mathbf{x}) | \Psi^N \rangle_{\mathcal{H}^N} \\ &= \int d^3 \mathbf{x}_1 \dots \int d^3 \mathbf{x}_N \sum_{i=1}^N \delta^3(\mathbf{x} - \mathbf{x}_i) (\Psi^N)^*(\mathbf{x}_1, \dots, \mathbf{x}_N) \Psi^N(\mathbf{x}_1, \dots, \mathbf{x}_N). \end{aligned} \quad (17)$$

The action of a function of the position operator evaluated in position space is analogous to the one-particle version³, $\langle \mathbf{x} | f(\hat{\mathbf{x}}) | \psi \rangle = f(\mathbf{x}) \psi(\mathbf{x})$, such that the Dirac-delta will then simply set the i -th coordinate to \mathbf{x} for each term. Because of the antisymmetry of the wave function w.r.t. the coordinates we obtain N -times the same expression, thus leading back to eq. (1).

External potential

The expectation value of $\langle \hat{V}_{\text{ext}} \rangle = E_{\text{ext}}$ in the 2nd quantized formalism is simply

$$\langle \Psi^N | \mathcal{Q}(\hat{V}_{\text{ext}}) | \Psi^N \rangle = \int d^3 \mathbf{x} v_{\text{ext}}(\mathbf{x}) \langle \Psi^N | \hat{n}(\mathbf{x}) | \Psi^N \rangle \quad (18)$$

$$= \int d^3 \mathbf{x} v_{\text{ext}}(\mathbf{x}) n(\mathbf{x}). \quad (19)$$

On the other hand, for the 1st quantized variant follows under utilization of eq. (1) and the complete antisymmetry of the many-body wave function Ψ^N :

$$\begin{aligned} \langle \Psi^N | \hat{V}_{\text{ext}} | \Psi^N \rangle &\stackrel{(6)}{=} \sum_{i=1}^N \langle \Psi^N | v_{\text{ext}}(\hat{\mathbf{x}}_i) | \Psi^N \rangle \\ &= \sum_{i=1}^N \int d^3 \mathbf{x}_1 \dots \int d^3 \mathbf{x}_N v_{\text{ext}}(\mathbf{x}_i) (\Psi^N)^*(\mathbf{x}_1, \dots, \mathbf{x}_N) \Psi^N(\mathbf{x}_1, \dots, \mathbf{x}_N) \\ &= N \int d^3 \mathbf{x} \int d^3 \mathbf{x}_2 \dots \int d^3 \mathbf{x}_N v_{\text{ext}}(\mathbf{x}) (\Psi^N)^*(\mathbf{x}, \mathbf{x}_2, \dots, \mathbf{x}_N) \Psi^N(\mathbf{x}, \mathbf{x}_2, \dots, \mathbf{x}_N) \\ &\stackrel{(1)}{=} \int d^3 \mathbf{x} v_{\text{ext}}(\mathbf{x}) n(\mathbf{x}), \end{aligned} \quad (20)$$

which is obviously identical to the former result.

³ $\hat{A} = \sum_n a_n |n\rangle \langle n|$, $f(\hat{A}) = \sum_n f(a_n) |n\rangle \langle n|$, $\hat{x} = \int d^3 \mathbf{x}' \mathbf{x}' | \mathbf{x}' \rangle \langle \mathbf{x}' |$, $\langle \mathbf{x} | \hat{x} | \psi \rangle = \int d^3 \mathbf{x}' \mathbf{x}' \langle \mathbf{x} | \mathbf{x}' \rangle \langle \mathbf{x}' | \psi \rangle = \mathbf{x} \psi(\mathbf{x})$

Hohenberg-Kohn Theorem

The Hohenberg-Kohn theorem now states for a N -particle ground state $|\Psi_0\rangle := |\Psi_0^N\rangle$ and corresponding ground state density $n_0(\mathbf{x})$ according to eq. (1) (cf. [1, §2.1]):

1. The quantities v_{ext} , Ψ_0 and n_0 uniquely determine each other (v_{ext} only up to a constant),

$$v_{\text{ext}}(\mathbf{x}) \xLeftrightarrow{\text{SGL}} |\Psi_0\rangle \iff n_0(\mathbf{x}) = \langle \Psi_0 | \hat{n}(\mathbf{x}) | \Psi_0 \rangle \quad (21)$$

i.e. the ground state is a unique functional of the ground state density,

$$|\Psi_0\rangle = |\Psi[n_0]\rangle, \quad (22)$$

where no explicit form for v_{ext} is required. Hence, $|\Psi[n]\rangle$ is called *universal*.

2. Consequently, any ground state observable has to be a functional of the density as well,

$$O[n] = \langle \Psi[n] | \hat{O} | \Psi[n] \rangle, \quad (23)$$

which is in particular true for the ground state energy, i.e. the expectation value of the Hamiltonian evaluated in the N -particle ground state⁴,

$$E[n] := \langle \Psi[n] | \hat{\mathcal{H}} | \Psi[n] \rangle = F[n] + \int d^3\mathbf{x} v_{\text{ext}}(\mathbf{x}) n(\mathbf{x}), \quad (24)$$

with

$$F[n] := \langle \Psi[n] | \hat{T} + \hat{W} | \Psi[n] \rangle \quad (25)$$

as the universal part. Note, that v_{ext} enters exactly once in $E[n]$, namely in the non-universal part. In fact, this functional can be regarded as a first optimization step where for a given density, the energy

$$E[n] = \min_{|\Psi\rangle \rightarrow n(\mathbf{x})} \langle \Psi | \hat{\mathcal{H}} | \Psi \rangle = \langle \Psi[n] | \hat{\mathcal{H}} | \Psi[n] \rangle \quad (26)$$

is minimized within the subset of wave functions yielding the required density.

3. There exists a (second) minimum principle for $E[n]$ with respect to the density:

$$E[n_0] < E[n'_0] \quad \forall n'_0 \neq n_0 \iff E_0 = \min_n E[n], \quad (27)$$

where n_0 is the ground state density corresponding to v_{ext} and the ground state $|\Psi_0\rangle$, and n'_0 another ground state associated with a different v'_{ext} and consequently, because of the statement in (21), a different ground state $|\Psi'_0\rangle$.

Following the minimum principle (27), the functional derivative has to vanish for the true ground state density,

$$\left. \frac{\delta E[n]}{\delta n(\mathbf{x})} \right|_{n=n_0} = 0. \quad (28)$$

This is, however, a highly simplified approach to the minimum principle where the allowed densities are always subject to the normalization condition eq. (2). The question if this functional derivative exists in the first place is non-trivial and beyond the scope of this exercise. The keyword associated with this issue is *interacting v -representability* and has been discussed

⁴Multiply (3) with $\langle \Psi^N |$ and insert (4).

thoroughly by Levy and Lieb (see e.g. [1, §2.3] for a more detailed discussion), representing a far more mathematical access.

A third approach often found in text books on DFT (e.g. [3, §7.2.1]) is postulating the existence of the functional derivative of $E[n]$ (and so $F[n]$) w.r.t. a density $n(\mathbf{x}) = n_0(\mathbf{x}) + \eta\delta n(\mathbf{x})$ near the true ground state density n_0 and using a functional Taylor expansion of $E[n]$ around $n = n_0$,

$$E[n] = E[n_0] + \int d^3\mathbf{x} \left. \frac{\delta E[n]}{\delta n(\mathbf{x})} \right|_{n=n_0} [n(\mathbf{x}) - n_0(\mathbf{x})] + \mathcal{O}(\delta n^2), \quad (29)$$

which is (using eq. (24)) equivalent to

$$E[n_0 + \eta\delta n] - E[n_0] = \eta \int d^3\mathbf{x} \left(\frac{\delta F[n]}{\delta n(\mathbf{x})} + v_{\text{ext}}(\mathbf{x}) \right) \delta n(\mathbf{x}) + \mathcal{O}(\delta n^2). \quad (30)$$

The last equation gives a reason why the functional derivative has to vanish: In case it would not, the energy could always be lowered by appropriately choosing the sign of η .

In any of these cases, the condition

$$\frac{\delta F[n]}{\delta n(\mathbf{x})} = -v_{\text{ext}}(\mathbf{x}) \quad (31)$$

follows for the universal functional $F[n]$ from the minimum principle in one or another way.

- What is the basic concept behind the Kohn-Sham approach? Formulate their ansatz for the universal functional $F[n]$. What is the exchange-correlation energy? Sketch the connection of Kohn-Sham's ansatz to the implications of Hohenberg-Kohn's theory.

Solution:

Kohn-Sham Effective Single Particle Equations

We consider a non-interacting N -particle system, i.e. a system of the form eq. (4) with $\hat{W} = 0$ and a multiplicative external single-particle (= effective Kohn-Sham) potential $v_s \neq v_{\text{ext}}$. The N -particle ground state is assumed to be non-degenerate and of the form

$$|\Phi_0\rangle := |\Phi_0^N\rangle = |\text{SL}(\varphi_1, \dots, \varphi_N)\rangle \quad (32)$$

and

$$\langle \mathbf{x}_1, \dots, \mathbf{x}_N | \Phi_0 \rangle = \Phi_0(\mathbf{x}_1, \dots, \mathbf{x}_N) = \frac{1}{\sqrt{N!}} \det(\varphi_i(\mathbf{x}_k)) \quad (33)$$

with

$$\langle \varphi_i | \varphi_j \rangle = \delta_{ij}, \quad (34)$$

i.e. a Slater determinant constructed of the energetically lowest solutions of the single-particle Schrödinger equation,

$$\left(-\frac{\hbar^2}{2m} \Delta + v_s(\mathbf{x}) \right) \varphi_i(\mathbf{x}) = \varepsilon_i \varphi_i(\mathbf{x}). \quad (35)$$

Note, that these orbitals (= single particle wave functions) are density functionals themselves. By construction, we have $\varepsilon_1 \leq \dots \leq \varepsilon_N = \varepsilon_F \leq \varepsilon_{N+1} \leq \dots$, where the Fermi energy is identified with the eigenvalue of the highest occupied single-particle level (cf. [1, §3.1]).

Under these conditions, the expression for the density (eq. (1)) simplifies to

$$n_{0s}(\mathbf{x}) = \sum_{i=1}^N \varphi_i^*(\mathbf{x}) \varphi_i(\mathbf{x}). \quad (36)$$

or equivalently⁵,

$$n_{0s}(\mathbf{x}) = \sum_i \Theta(\varepsilon_F - \varepsilon_i) \varphi_i^*(\mathbf{x}) \varphi_i(\mathbf{x}). \quad (37)$$

According to the Hohenberg-Kohn theorem, the ground state of this non-interacting system has to be again a unique functional of the corresponding ground state density, i.e. $|\Phi_0\rangle = |\Phi[n_{0s}]\rangle$, and so has the energy (cf. eq. (24)),

$$E_s[n] = \langle \Phi[n] | \hat{T} | \Phi[n] \rangle + \int d^3\mathbf{x} v_s(\mathbf{x}) n(\mathbf{x}). \quad (38)$$

Following the same arguments as in the interacting case, we find that this functional has the same properties (e.g. the existence of a minimum principle), but is not identical to eq. (24).

Applying the minimum principle (eq. (27)) to $E_s[n]$ leads in the non-interacting case to the stationary condition

$$\left. \frac{\delta E_s[n]}{\delta n(\mathbf{x})} \right|_{n=n_0} = 0 \iff \left. \frac{\delta T_s[n]}{\delta n(\mathbf{x})} \right|_{n=n_0} = -v_s(\mathbf{x}), \quad (39)$$

where the kinetic energy functional $T_s[n]$ represents the expectation value of the kinetic energy operator, but not evaluated in the state $|\Psi\rangle$ but in its non-interacting equivalent $|\Phi\rangle$,

$$T_s[n] = \langle \Phi[n] | \hat{T} | \Phi[n] \rangle = \sum_i \Theta(\varepsilon_F - \varepsilon_i) \int d^3\mathbf{x} \varphi_i^*(\mathbf{x}) \left(-\frac{\hbar^2}{2m} \Delta \right) \varphi_i(\mathbf{x}). \quad (40)$$

Note, that in DFT this constitutes a non-trivial functional⁶, since $\varphi_i(\mathbf{x}) = \varphi_i[n](\mathbf{x})$ per Hohenberg-Kohn theorem.

The essential assumption of Kohn and Sham was, that the ground state density of this auxiliary system (with a yet to be determined effective Kohn-Sham potential v_s) is simultaneously the ground state density of the interacting system (eq. (4)), i.e. $n_0(\mathbf{x}) \equiv n_{0s}(\mathbf{x})$. If such an auxiliary system (a.k.a. Kohn-Sham system) exists in the first place is subject to the question of *noninteracting v -representability* (cf. [1, §3.2]) and exceeds the scope of this exercise. However, taking for granted that the earlier assumption is correct, we decompose the universal functional $F[n]$ (and thus $E[n]$) according to Kohn-Sham in a more convenient fashion:

$$F[n] = T_s[n] + E_H[n] + E_{xc}[n]. \quad (41)$$

The classical Hartree energy introduced in the last equation should already be familiar,

$$E_H[n] = \frac{(-e)^2}{2} \int d^3\mathbf{x} \int d^3\mathbf{x}' n(\mathbf{x}) v_c(\mathbf{x}, \mathbf{x}') n(\mathbf{x}') = \frac{1}{2} \int d^3\mathbf{x} v_H(\mathbf{x}) n(\mathbf{x}), \quad (42)$$

⁵In case of finite temperature $T > 0$, the Heaviside step function $\Theta(x - x_0)$ is replaced by the Fermi-Dirac distribution in many DFT codes. Definition Heaviside function: $\Theta: \mathbb{R} \rightarrow \{0, 1\}$, $x \mapsto (0: x < 0, 1: x \geq 0)$

⁶By contrast, in the Thomas-Fermi theory this functional is modelled using the homogeneous interaction-free fermion gas, i.e. $n(\mathbf{x}) \propto k_f^3$ and $\epsilon \propto k_f^2$, such that $E_{\text{kin}} \approx \int d^3\mathbf{x} n(\mathbf{x}) \epsilon_{\text{kin}}(\mathbf{x}) = C_f \int d^3\mathbf{x} n^{5/3}(\mathbf{x})$, with $C_f \approx 2.8712$ [4, §3.1].

and the kinetic energy is given by eq. (40). By contrast, the so called exchange-correlation functional $E_{xc}[n]$ is unknown and just said to “absorb[...] all the complicated many-body effects not contained in T_s, E_H and E_{ext} ” [1, p. 61].⁷ In fact, it is *defined* by eq. (41) and is thus a universal density functional just like $F[n]$. It can also be written more suggestively as

$$E_{xc}[n_0] = \langle \Psi_0 | \hat{T} + \hat{W} | \Psi_0 \rangle - T_s[n_0] - E_H[n_0]. \tag{43}$$

By inserting eq. (39) and eq. (41) into the stationary condition of the interacting system (eq. (28)), we find an expression for the yet unknown effective Kohn-Sham potential,

$$v_s[n_0](\mathbf{x}) = v_H[n_0](\mathbf{x}) + v_{xc}[n_0](\mathbf{x}) + v_{ext}(\mathbf{x}), \tag{44}$$

where v_{xc} is the functional derivative of the Kohn-Sham energy with respect to the density,

$$v_{xc}[n_0](\mathbf{x}) = \left. \frac{\delta E_{xc}[n]}{\delta n(\mathbf{x})} \right|_{n=n_0}. \tag{45}$$

Obviously, this so called Kohn-Sham potential is a functional of the density itself. In fact, the solutions of the single-particle Schrödinger equation (35) determine the orbitals $\varphi_i(\mathbf{x})$ that construct the density via eq. (36), which is passed to eq. (44) to build the Kohn-Sham potential. This set of equations is known as Kohn-Sham (effective single particle) equations and because of their nonlinearity, they have to be solved iteratively. The connection of the Kohn-Sham ansatz and the Hohenberg-Kohn theorem is sketched in fig. 1.

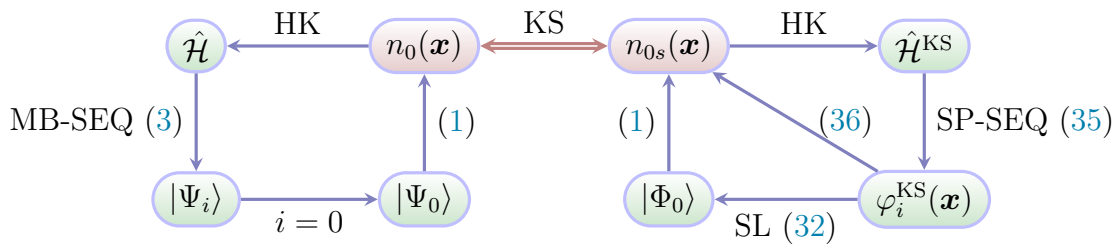


Figure 1: Scheme combining the Hohenberg-Kohn theorem with the Kohn-Sham equations. In the left hand side, the density n_0 determines the Hamiltonian $\hat{\mathcal{H}}$ that, by virtue of the many-body Schrödinger equation, leads to the many-bmany-body states $|\Psi_i\rangle$ and in particular the ground state $|\Psi_0\rangle$. The density build from this wave function shall now be identical to the one of the right hand side, where per density functionals the effective single-particle Hamiltonian $\hat{\mathcal{H}}^{KS}$ is constructed, leading via the single-particle Schrödinger equation to the Kohn-Sham orbitals $\varphi_i^{KS}(\mathbf{x})$. An auxiliary many-body wave function $|\Phi_0\rangle$ in the form of a single Slater determinant can be constructed or the Kohn-Sham orbitals can be used directly to finally come back to the density $n_{0s} = n_0$.

The great advantage of Kohn and Sham’s formulation is, that it is no longer necessary to approximate the entire universal functional $F[n]$, but only its exchange-correlation part (and its functional derivative v_{xc}). Since E_{xc} is usually smaller than E_H , the errors in approximating E_{xc} will hopefully have only a small impact on the result of e.g. solid-state calculations.

⁷Interestingly, the other three energy contributions usually dominate over the exchange-correlation energy. Thus, even when completely ignoring E_{xc} , we obtain qualitatively good results, e.g. when calculating band structures or just the plain total energy. Unfortunately, this will not work in the case of helium, as we verified in the last exercise.

- The exchange-correlation energy defined in the last problem is not identical to the one from quantum chemistry. In fact, it is not even identical to the difference between the full interaction energy of the interacting system and its classical counterpart. Find the reason.

Solution: A proof is straight forward (cf. [1, Eq. 3.27-3.31]): Let

$$E_{xc}^{|\Psi_0\rangle} = \langle \Psi_0 | \hat{W} | \Psi_0 \rangle - E_H[n_0] \quad (46)$$

be the difference between the quantum mechanical and the classical interacting energy and E_{xc}^{DFT} defined by eq. (43). The difference between the two xc-energies,

$$E_{xc}^{\text{DFT}} - E_{xc}^{|\Psi_0\rangle} = \langle \Psi_0 | \hat{T} | \Psi_0 \rangle - \langle \Phi_0 | \hat{T} | \Phi_0 \rangle, \quad (47)$$

originates in the difference between the kinetic energy of the interacting and non-interacting system and will not vanish since in general $|\Psi_0\rangle \neq |\Phi_0\rangle$.⁸⁹ Empirical studies on closed-subshell atoms showed, that this difference is of the same order of magnitude as the complete correlation energy (cf. [1, p. 62]). Note that $E_{xc}^{|\Psi_0\rangle} \neq E_{xc}^{\text{QC}}$ in general.

- For practical purposes, the “total energy” (= energy functional) is calculated differently than suggested by the Kohn-Sham energy functional, because the latter involves a differentiation of the KS orbitals per Laplace operator in $T_s[n]$. Work around this annoyance by eliminating the kinetic energy functional using the single-particle Schrödinger equation.

Solution: Inserting eq. (35) into eq. (40) yields

$$\begin{aligned} T_s[n] &= \sum_{i=1}^N \int d^3\mathbf{x} \varphi_i^*(\mathbf{x}) (\varepsilon_i - v_s(\mathbf{x})) \varphi_i(\mathbf{x}) \\ &= \sum_{i=1}^N \varepsilon_i - \int d^3\mathbf{x} v_s(\mathbf{x}) n(\mathbf{x}), \end{aligned} \quad (48)$$

where in the last step, we have used the normalization of the KS orbitals. Replacing T_s in eq. (41) and subsequently in eq. (24) we find an alternative way to calculate the total energy:

$$E = \sum_{i=1}^N \varepsilon_i - \int d^3\mathbf{x} (v_{\text{ext}} + v_H + v_{xc})(\mathbf{x}) n_0(\mathbf{x}) + E_{\text{ext}} + E_H + E_{xc}. \quad (49)$$

This result may be simplified using the definitions in eq. (18) and eq. (42) for E_{ext} and E_H , leading to (cf. [5, Eq. 2.16], [1, Eq. 3.52])

$$E_0 = \sum_{i=1}^N \varepsilon_i - E_H[n_0] + E_{xc}[n_0] - \int d^3\mathbf{x} v_{xc}[n_0](\mathbf{x}) n_0(\mathbf{x}). \quad (50)$$

Apparently, this not only saves us from calculating second derivatives of KS orbitals, but also eliminates the need to explicitly calculate the external energy. Note, that the exchange-correlation energy and integral over its potential do not cancel each other since from eq. (45) does not necessarily follow a form of $E_{xc}[n]$ like e.g. in eq. (18).

Finally note, that it is common practice to decompose E_{xc} into a pure exchange E_x and a remaining correlation part E_c . A more detailed treatment of this concept will be content of the next exercise sheet.

⁸⁹In fact one can show that $\langle \Phi_0 | \hat{T} | \Phi_0 \rangle = \inf_{\Psi \rightarrow n_0} \langle \Psi | \hat{T} | \Psi \rangle$ and $\langle \Phi_0 | \hat{T} | \Phi_0 \rangle \leq \langle \Psi_0 | \hat{T} | \Psi_0 \rangle$ thus $E_{xc}^{\text{DFT}} \geq E_{xc}^{|\Psi_0\rangle}$. Engel and Dreizler state the difference with $\Delta E_{xc} = 2.903724$ a.u. for the non-relativistic helium calculation and 0.0737 a.u. for beryllium. The magnitude of ΔE_{xc} is thus found to be in the typical range of the correlation energy. [1, p. 62].

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