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# 1 Density functional theory (DFT)

## 1.1 Introduction

Density functional theory is an alternative to ab initio methods for solving the non-relativistic, time-independent Schrödinger equation  $\mathcal{H}|\Phi\rangle = E|\Phi\rangle$ . The ab initio approach is to assume that the wave function of the system may be decomposed into single electron wave functions. However, for a system with  $N$  electrons this means there are  $3N$  continuous variables necessary to be fitted. Assuming that  $3 \leq p \leq 10$  parameters per variable are required to yield a fit of reasonable accuracy, this means that  $p^{3N}$  parameters must be optimized for an  $N$  electron system. Although this is a great oversimplification this *exponential wall* does exist and limits the traditional wave function methods to molecules with a small number of chemically active electrons:  $N \approx \mathcal{O}(10)$ . This problem shall be overcome by DFT, which is expressed in terms of the density  $n(\mathbf{r})$  in the Hohenberg-Kohn formulation and in terms of  $n(\mathbf{r})$  and the single-particle wave functions  $\psi_j(\mathbf{r})$  in the Kohn-Sham formulation.

## 1.2 Thomas Fermi (TF) theory

Since the early 1920s this theory was used to roughly compute the electronic energy based on electron density distributions. However, it did not predict chemical binding and therefore was of almost no use for questions of chemistry and material science. It did, however, consider interacting electrons moving in an external potential  $v(\mathbf{r})$  and provided an implicit relation between  $v(\mathbf{r})$  and the density distribution  $n(\mathbf{r})$ :

$$n(\mathbf{r}) = \gamma(\mu - v_{eff}(\mathbf{r}))^{3/2}; \quad \gamma = \frac{1}{3\pi^2} \left( \frac{2m}{\hbar^2} \right)^{3/2} \quad (1)$$

$$v_{eff}(\mathbf{r}) = v(\mathbf{r}) + \int \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' \quad (2)$$

Here  $\mu$  is the chemical potential and the first equation is based on the expression  $n = \gamma(\mu - v)^{3/2}$  for the density of a uniform, non-interacting, degenerate electron gas in a constant external potential. The second term in the second equation is the classically computed electrostatic potential, also referred to as the Hartree potential  $v_H$ . Despite the fact that TF theory was a rough solution to the many-electron Schrödinger equation, it was unclear whether there was a strict connection between them and whether knowledge of the groundstate density  $n(\mathbf{r})$  alone uniquely determined the system. This mystery was solved by Hohenberg and Kohn.

## 1.3 The Hohenberg Kohn theorem

**The Hohenberg Kohn theorem.** *The groundstate density  $n(\mathbf{r})$  of a bound system of interacting electrons in some external potential  $v(\mathbf{r})$  determines this potential uniquely.*

### 1.3 The Hohenberg Kohn theorem

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*Proof.* The proof is given for a non-degenerate groundstate, but may easily be expanded to degenerate groundstates as well. Let  $n(\mathbf{r})$  be the non-degenerate groundstate density of  $N$  electrons in the potential  $v_1(\mathbf{r})$ , corresponding to the groundstate  $\Phi_1$  and the energy  $E_1$ . Then:

$$E_1 = \langle \Phi_1 | \mathcal{H}_1 | \Phi_1 \rangle = \int v_1(\mathbf{r}) \mathbf{n}(\mathbf{r}) \mathbf{d}\mathbf{r} + \langle \Phi_1 | (\mathbf{T} + \mathbf{U}) | \Phi_1 \rangle,$$

where  $\mathcal{H}_1$  is the total Hamiltonian corresponding to  $v_1$  and  $T$  and  $U$  are the kinetic and interaction energy operators. Note that the external potential  $v_1$  is a multiplicative operator with respect to  $\Phi$ . Now assume that there exists a second potential  $v_2(\mathbf{r})$ , *not* equal to  $v_1(\mathbf{r}) + \text{constant}$ , with groundstate  $\Phi_2$ , necessarily  $\neq e^{i\theta} \Phi_1$ , which gives rise to the same  $n(\mathbf{r})$ . Then

$$E_2 = \int v_2(\mathbf{r}) \mathbf{n}(\mathbf{r}) \mathbf{d}\mathbf{r} + \langle \Phi_2 | (\mathbf{T} + \mathbf{U}) | \Phi_2 \rangle.$$

Since  $\Phi_1$  is assumed to be non-degenerate, the variational principle (Rayleigh-Ritz minimal principle) for  $\Phi_1$  gives rise to the following inequality:

$$\begin{aligned} E_1 < \langle \Phi_2 | \mathcal{H}_1 | \Phi_2 \rangle &= \int v_1(\mathbf{r}) \mathbf{n}(\mathbf{r}) \mathbf{d}\mathbf{r} + \langle \Phi_2 | (\mathbf{T} + \mathbf{U}) | \Phi_2 \rangle \\ &= E_2 + \int [v_1(\mathbf{r}) - v_2(\mathbf{r})] \mathbf{n}(\mathbf{r}) \mathbf{d}\mathbf{r} \end{aligned} \quad (3)$$

Analogously

$$E_2 \leq \langle \Phi_1 | \mathcal{H}_2 | \Phi_1 \rangle = E_1 + \int [v_2(\mathbf{r}) - v_1(\mathbf{r})] \mathbf{n}(\mathbf{r}) \mathbf{d}\mathbf{r} \quad (4)$$

where  $\leq$  is used since non-degeneracy of  $\Phi_2$  was not assumed. Adding equations (3) and (4) leads to the contradiction:

$$E_1 + E_2 < E_1 + E_2$$

This shows that the assumption of the existence of a second potential  $v_2(\mathbf{r})$ , which is unequal to  $v_1(\mathbf{r}) + \text{constant}$  but yet yields the the same  $n(\mathbf{r})$ , must be wrong.  $\square$

Since  $n(\mathbf{r})$  determines both  $N$  and  $v(\mathbf{r})$  it gives us the full  $\mathcal{H}$  and  $N$  for the electronic system. Therefore  $n(\mathbf{r})$  implicitly determines *all* properties of the system derivable from solving the Schrödinger equation for  $\mathcal{H}$ .

## 1.3 The Hohenberg Kohn theorem

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### 1.3.1 N- and v-representability

A question that may arise immediately linked to the HK theorem is how one knows, after having minimized a given density, whether this density is a density arising from an antisymmetric  $N$ -body wave function (N-representability) and whether it actually corresponds to the ground-state density of a potential  $v(\mathbf{r})$  (v-representability). It has been shown that any non-negative function can be written in terms of some  $\Phi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)$ , so  $N$  representability is not a problem. However, for v-representability no general solution exists, but the constrained search algorithm of Levy and Lieb shows that this is irrelevant for the proof above.

### 1.3.2 Applications of DFT

- Since  $v(\mathbf{r})$  depends on a set of parameters - lattice constants or nuclei positions - the energy may be minimized with respect to these quantities yielding molecular geometries and sizes, lattice constants, charge distributions etc.
- By looking at the change in energy with respect to these parameters one may calculate compressibilities, phonon spectra, bulk moduli (solids) and vibrational frequencies (molecules).
- Comparison of the energy of a composite system (e.g., a molecule) with its constituent systems (e.g., individual atoms) gives dissociation energies
- Calculating the total energy with an electron more or less yield electron affinities and ionization energies. Note: within the local density and generalized gradient approximations the  $(N + 1)^{\text{st}}$  electron is too weakly bound or even unbound. The asymptotic potential obtained decays exponentially and not as  $1/r$ , so the binding of negative ions is strongly suppressed. Self-interaction corections or other fully non-local functionals are needed to improve this behavior.
- One can calculate forces from the derivative of the total energy with respect to the nuclear coordinates using the Hellmann-Feynman theorem.

It is now clear, that in principle it is sufficient to express the total energy of the system in terms of the density and minimize this functional to obtain the groundstate energy, density and wave function. The total energy of a typical molecule or solid is given by:

$$E(n) = T(n) + U(n) + V(n) = T(n) + U(n) + \int n(\mathbf{r})v(\mathbf{r}) d^3\mathbf{r} \quad (5)$$

Here  $T$  is the kinetic energy of the electrons,  $U$  the potential energy due to the interaction between them and  $V$  the potential energy from an external potential  $v$ , usually the electrostatic potential of the nuclei, which are taken to be fixed in space (Born-Oppenheimer approximation). Only this potential is easy to treat since it is a multiplicative operator. For the others a universal density functional is known at this point, but a possible treatment are the Kohn-Sham equations.

### 1.4 The Kohn-Sham equations

The idea of the Kohn-Sham approach is to reintroduce a special type of wave functions (single particle orbitals) into the formalism, to treat the kinetic and interaction energy terms. In this approach the energy is taken to be composed of the following terms:

$$E(n) = T(n) + U(n) + V(n) = T_s\{\phi_i(n)\} + U_H(n) + E_{xc}(n) + V(n) \quad (6)$$

Here the kinetic energy is split into two contributions:

$$T(n) = T_s(n) + T_c(n)$$

$T_s$  stands for the kinetic energy of non-interacting particles of density  $n$  with  $s$  denoting 'single particle' and  $T_c$  being the remainder with  $c$  denoting 'correlation'. The interaction energy  $U$  is approximated by the classical electrostatic interaction or Hartree energy  $U_H$ . The new energy term  $E_{xc}$  stands for a correction of these approximation due to exchange (x) and correlation (c) effects, i.e. is given by  $E_{xc} = (T - T_s) + (U - U_H) = T_c + (U - U_H)$ . It is often decomposed as  $E_{xc} = E_x + E_c$ , where  $E_x$  is the exchange energy due to the Pauli principle (antisymmetry) and  $E_c$  is due to correlations ( $T_c$  is then a part of  $E_c$ ).

#### 1.4.1 The kinetic energy of non-interacting particles $T_c$

For non-interacting particles, the kinetic energy is nothing other than the sum of the kinetic energies of each particle. Written in terms of wave functions that is:

$$T_s(n) = -\frac{\hbar^2}{2m} \sum_i^N \int \phi_i^*(\mathbf{r}) \nabla^2 \phi_i(\mathbf{r}) d^3\mathbf{r} \quad (7)$$

$T_s(n) = T_s[\{\phi_i(n)\}]$  is an explicit orbital functional, but only an implicit density functional, due to the dependence of the wave functions on the density. Because  $T_s$  is defined as the expectation value of the kinetic energy operator  $\hat{T}$  with the Slater determinant arising from the density  $n$ , i.e.  $T_s(n) = \langle \Phi(n) | \hat{T} | \Phi(n) \rangle$ , all consequences of antisymmetrization (exchange) are described by employing a determinantal wave function in defining  $T_s$ . Hence,  $T_c$ , the difference between  $T_s$  and  $T$  is a pure correlation effect.

#### 1.4.2 The Hartree energy $U_H$

The classical electrostatic interaction energy (Hartree energy) as well as the mean field result  $U_H$  in terms of density is given by

$$U_H = \frac{q^2}{2} \int d^3r \int d^3r' \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \quad (8)$$

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### 1.4.3 The exchange energy $E_x$

Since the exchange energy correction stems purely from the interaction potential, it may be written in terms of single-particle orbitals as:

$$E_x[\{\phi_i(n)\}] = -\frac{q^2}{2} \sum_{jk} \int d^3r \int d^3r' \frac{\phi_j^*(\mathbf{r})\phi_k^*(\mathbf{r}')\phi_j(\mathbf{r}')\phi_k(\mathbf{r})}{|\mathbf{r} - \mathbf{r}'|} \quad (9)$$

where a single term in the sum corresponds to the energy of exchanging molecule  $j$  located at  $\mathbf{r}$  with molecule  $k$  located at  $\mathbf{r}'$ . No exact expression in terms of the density is known. The exchange energy therefore describes the energy lowering due to antisymmetrization, i.e. the tendency of electrons with like spin to avoid each other, giving rise to the so-called 'exchange-hole'. It also corrects the Hartree term (8) for the self-interaction (see eqn. 10).

### 1.4.4 The correlation energy $E_c$

The correlation energy is the difference between the full ground-state energy obtained from the correct many-body wave function and the one obtained from the Hartree-Fock or Kohn-Sham Slater determinant. Recalling the interpretation of the wave function as probability amplitude, the product form of the many-body wave function corresponds to treating the probability amplitude of a many-electron system as a product of the probability amplitudes of individual electrons (the orbitals). This is only the same, when the individual electrons are independent. Clearly this is not the case, so such wave functions neglect the fact, that due to Coulombic interaction, electrons try to avoid each other. The correlation energy is therefore the additional energy lowering obtained in a real system due to the mutual avoidance of the interacting electrons. To understand the correlation for interaction energy, let us take another look at the corresponding operator written in two perfectly equivalent ways:

$$\hat{U} = \sum_{i < j} \frac{q^2}{|\mathbf{r} - \mathbf{r}'|} = \frac{q^2}{2} \int d^3r \int d^3r' \frac{\hat{n}(\mathbf{r})\hat{n}(\mathbf{r}') - \hat{n}(\mathbf{r})\delta(\mathbf{r} - \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \quad (10)$$

The operator character is only carried by the density operators  $\hat{n}$  (in occupation number representation) and the term with the delta function subtracts out the interaction of a charge with itself (which is taken care of by the  $ij$  in the other case). The expectation value of this operator  $U = \langle \Phi | \hat{U} | \Phi \rangle$  involves the expectation value of a product of density operators  $\langle \Phi | \hat{n}(\mathbf{r})\hat{n}(\mathbf{r}') | \Phi \rangle$ , which in the Hartree term (8) is replaced by a product of expectation values, each of the form  $n(\mathbf{r}) = \langle \Phi | \hat{n}(\mathbf{r}) | \Phi \rangle$ . This replacement amounts to a mean field approximation, which neglects quantum fluctuations. Therefore, the correlation energy accounts for the energy lowering due to quantum fluctuations, i.e. the 'correlation hole', which arises because electrons with unlike spins try to coordinate their movement to minimize their Coulomb energy. The other significant part of the correlation energy is due to the difference  $T_c$  between non-interacting and interacting kinetic energies.

## 1.4 The Kohn-Sham equations

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### 1.4.5 Nomenclature and properties regarding $E_{xc}$

- Since both exchange and correlation tend to keep electrons apart, the term 'electron hole' was coined, describing the region of reduced probability for encountering a second electron in the vicinity of a given reference electron.
- Both exchange and correlation energies give negative contributions, which leads to an upper bound of 0 for the energy correction, the lower one given by the Lieb-Oxford bound:  $E_{xc} \geq -1.68 \int d^2r n(\mathbf{r})^{4/3}$
- In the one electron limit  $E_c(n^{(1)}) = 0$  and  $E_x(n^{(1)}) = -U_H(n^{(1)})$ , where  $n^{(1)}$  is a one-electron density. Note: this is satisfied by HF, but not by standard LDA and GGA functionals.

### 1.4.6 The Kohn-Sham equations

To get the groundstate energy, i.e. to minimize eqn. (6) with respect to the density, one cannot directly minimize with respect to  $n$ , since  $T_s$  is written as an orbital functional. Instead, Kohn and Sham proposed the following scheme for indirect minimization. To minimize  $E$  with respect to density means, we want:

$$0 = \frac{\delta E[n]}{\delta n(\mathbf{r})} = \frac{\delta T_s[n]}{\delta n(\mathbf{r})} + \frac{\delta V[n]}{\delta n(\mathbf{r})} + \frac{\delta U_H[n]}{\delta n(\mathbf{r})} + \frac{\delta E_{xc}[n]}{\delta n(\mathbf{r})} = \frac{\delta T_s[n]}{\delta n(\mathbf{r})} + v(\mathbf{r}) + \mathbf{v}_H(\mathbf{r}) + \mathbf{v}_{xc}(\mathbf{r}) \quad (11)$$

As a consequence of eqn. (5)  $\frac{\delta V}{\delta n} = v(\mathbf{r})$ , which is nothing other than the external potential due to the fixed nuclei, the lattice or a truly external field. The term  $\frac{\delta U_H}{\delta n}$  yields the Hartree potential introduced in eqn. (1). The term  $\frac{\delta E_{xc}}{\delta n}$  can only be calculated after an approximation has been chosen, but nevertheless we can call the result  $v_{xc}$ . Now consider this brilliant idea: look at a system of non-interacting particles moving in the arbitrary potential  $v_s(\mathbf{r})$ . For this system the minimization condition is:

$$0 = \frac{\delta E_s[n]}{\delta n(\mathbf{r})} = \frac{\delta T_s[n]}{\delta n(\mathbf{r})} + \frac{\delta V_s[n]}{\delta n(\mathbf{r})} = \frac{\delta T_s[n]}{\delta n(\mathbf{r})} + v_s(\mathbf{r})$$

The density solving this Euler equation is  $n_s(\mathbf{r})$ . Comparison with eqn. (11) shows that both minimizations have the same solution  $n_s(\mathbf{r}) = \mathbf{n}(\mathbf{r})$ , if we choose:

$$v_s(\mathbf{r}) = v(\mathbf{r}) + \mathbf{v}_H(\mathbf{r}) + \mathbf{v}_{xc}(\mathbf{r}) \quad (12)$$

Therefore we can calculate the density of an interacting many-body system in the potential  $v(\mathbf{r})$ , described by a many-body Schrödinger equation, by simply solving the equations of a noninteracting single-body system in the potential  $v_s(\mathbf{r})$ , given by:

## 1.5 Construction of exchange functionals

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$$\left[ -\frac{\hbar^2}{2m}\nabla^2 + v_s(\mathbf{r}) \right] \phi_i(\mathbf{r}) = \epsilon_i \phi_i(\mathbf{r}) \quad (13)$$

This yields orbitals that reproduce the density  $n(\mathbf{r})$  of the original system via:

$$n(\mathbf{r}) = \mathbf{n}_s(\mathbf{r}) = \sum_i^N f_i |\phi_i(\mathbf{r})|^2, \quad (14)$$

where  $f_i$  is the occupation of the  $i^{\text{th}}$  orbital. Equations (12) to (14) are the celebrated Kohn-Sham equations. They replace the problem of minimizing  $E(n)$  (and originally of solving the corresponding many-body Schrödinger equation) by that of solving a noninteracting Schrödinger equation. The solution to this nonlinear problem is usually found by starting with an initial guess for  $n(\mathbf{r})$ , calculating the corresponding  $v_s(\mathbf{r})$  and then solving the differential equation 13 for the  $\phi_i$ . From these a new density is calculated using eqn. (14) and the process is restarted until reasonable convergence is reached.

## 1.5 Construction of exchange functionals

### 1.5.1 Local density approximation (LDA)

The general idea of LDA is to take the known result for a homogeneous system and apply it locally to a non-homogeneous system. The exchange energy of a homogeneous system is known to be:

$$e_x^{\text{hom}}(n) = -\frac{3q^2}{4} \left( \frac{3}{\pi} \right)^{1/3} n^{4/3}$$

So in the LDA one takes:

$$E_x^{\text{LDA}}(n) = -\frac{3q^2}{4} \left( \frac{3}{\pi} \right)^{1/3} \int n(\mathbf{r})^{4/3} d^3\mathbf{r} \quad (15)$$

Expressions for  $E_c^{\text{LDA}}(n)$  are parametrizations of highly precise Quantum Monte Carlo (QMC) calculations for the electron liquid.

### 1.5.2 Gradient expansion approximation (GEA)

In this case one tries to systematically calculate gradient corrections of the form  $|\nabla n(\mathbf{r})|$ ,  $|\nabla n(\mathbf{r})|^2$ ,  $\nabla^2 n(\mathbf{r})$  etc. to the LDA to take into account the rate of density variation in the system. The lowest order correction to the LDA exchange energy is given by the Weizsäcker term:

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$$E_x^{GEA(2)}(n) = E_x^{LDA}(n) - \frac{10q^2}{432\pi(3\pi^2)^{1/3}} \int d^3r \frac{|\nabla n(\mathbf{r})|^2}{n(\mathbf{r})^{4/3}} \quad (16)$$

In practice, low-order gradient corrections almost never improve the LDA results and higher-order corrections are exceedingly difficult to calculate.

### 1.5.3 Generalized gradient approximation (GGA)

It was a major breakthrough, when it was realized that instead of power-series-like systematic gradient expansions one could experiment with more general functions of  $n(\mathbf{r})$  and  $\nabla n(\mathbf{r})$ , which need not proceed order by order. Such functionals have the general form:

$$E_{xc}^{GGA}(n) = \int d^3r f(n(\mathbf{r}), \nabla \mathbf{n}(\mathbf{r})) \quad (17)$$

The most popular GGAs are PBE (denoting the functional proposed in 1996 by Perdew, Burke and Ernzerhof) and BLYP (denoting the combination of the exchange functional by Becke and the correlation functional of Lee, Yang and Parr, both in 1988). GGAs give reliable results for chemical bonds, but mostly fail for van der Waals or dispersion interactions.

### 1.5.4 Hybrid functionals

One of the most popular functionals in quantum chemistry today is B3LYP, which combines the LYP GGA for correlation with Becke's three-parameter hybrid functional B3 for exchange. The latter mixes a fraction of Hartree-Fock exchange into the DFT exchange functional. This mixing involves a certain amount of empiricism and optimization for selected classes of molecules.

### 1.5.5 Meta-GGA

These functionals depend, in addition to the density and its derivatives, also on the Kohn-Sham kinetic-energy density  $\tau(\mathbf{r})$ .

$$\tau(\mathbf{r}) = \frac{\hbar^2}{2\mathbf{m}} \sum_{\mathbf{i}} |\nabla \phi_{\mathbf{i}}(\mathbf{r})|^2 \quad (18)$$

The exchange-correlation energy is therefore written as  $E_{xc}[n(\mathbf{r}), \nabla \mathbf{n}(\mathbf{r}), \tau(\mathbf{r})]$ . The additional degree of freedom is then used to satisfy additional constraints on  $E_{xc}$ , such as a self-interaction correlation functional, etc. In recent test, Meta-GGAs have performed favorably even when compared to the best GGAs.