

# Density Functional Theory

## 1 Introduction

The notes below provide some, hopefully concise, information on the basic aspects of density functional theory, and make visible a link with Hartree-Fock. It is standard theory, largely based on the more comprehensive treatment that can be found in, amongst others, the following excellent textbooks on electronic structure theory:

- E. Kaxiras, Atomic and Electronic Structure of Solids, Cambridge University Press (2003).
- J. Kohanoff, Electronic Structure Calculations for Solids and Molecules, Theory and Computational Methods, Cambridge University Press (2006).
- R.M. Martin, Electronic Structure, Basic Theory and Practical Methods, Cambridge University Press (2004).

The Kohanoff book is used with this course, and offers also information from the molecular perspective. The other two books have a strong emphasis on condensed matter physics, and are recommended to the interested reader for background information.

## 2 Recap Hartree-Fock

Life always starts with a Hamiltonian:

$$H = - \sum_i \frac{\hbar^2}{2m_e} \nabla_i^2 + \sum_i V_{\text{ext}}(\mathbf{r}_i) + \frac{e^2}{2} \sum_{i,j(i \neq j)} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}$$

Here  $V_{\text{ext}}$  is the external potential. In general it is the Coulomb potential of the (bare) nuclei. The repulsive Coulomb energy of the nuclei amongst each other has been left out. To convert to a.u.:  $\hbar = 1$ ,  $m_e = 1$ ,  $e = 1$ .

In HF the Ansatz for the wave functions is a Slater determinant, i.e. it is an antisymmetric wave function by construction:<sup>1</sup>

$$\Psi^{HF} = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_1(\mathbf{r}_1) & \psi_2(\mathbf{r}_1) & \psi_3(\mathbf{r}_1) & \dots \\ \psi_1(\mathbf{r}_2) & \psi_2(\mathbf{r}_2) & \psi_3(\mathbf{r}_2) & \dots \\ \psi_1(\mathbf{r}_3) & \psi_2(\mathbf{r}_3) & \psi_3(\mathbf{r}_3) & \dots \\ \dots & \dots & \dots & \dots \end{vmatrix} \quad (1)$$

Using this Ansatz in the expectation value for the Hamiltonian yields an energy expression:

$$\begin{aligned} \langle \Psi^{HF} | H | \Psi^{HF} \rangle = & \sum_i \langle \psi_i | -\frac{\hbar^2}{2m_e} \nabla_i^2 + V_{\text{ext}} | \psi_i \rangle + \frac{e^2}{2} \sum_{i,j(i \neq j)} \langle \psi_i(\mathbf{r}) \psi_j(\mathbf{r}') | \frac{1}{|\mathbf{r} - \mathbf{r}'|} | \psi_i(\mathbf{r}) \psi_j(\mathbf{r}') \rangle \\ & - \frac{e^2}{2} \sum_{i,j(i \neq j)} \langle \psi_i(\mathbf{r}) \psi_j(\mathbf{r}') | \frac{1}{|\mathbf{r} - \mathbf{r}'|} | \psi_j(\mathbf{r}) \psi_i(\mathbf{r}') \rangle \end{aligned}$$

---

<sup>1</sup>It is easiest to consider here that the  $|\psi_i\rangle$  are the spin orbitals, just as in our HF story before. In the next section we will consider only spatial orbitals and include the spin degeneracy with appropriate factors 2. Hence, in the double summations in the equation above we do not yet have the factor 2 in front of the  $K_{ij}$ .

Here we assume  $|\Psi^{HF}\rangle$  is normalized. Minimizing the above expression (well, assuming a stationary point) with the constraint  $\langle \delta\psi_i | \psi_i \rangle = 0$  gives the eigenvalue equations:<sup>2</sup>

$$\left[ -\frac{\hbar^2}{2m_e} \nabla_i^2 + V_{\text{ext}} + V_i^H \right] \psi_i(\mathbf{r}) - e^2 \sum_{j(j \neq i)} \langle \psi_j(\mathbf{r}') | \frac{1}{|\mathbf{r} - \mathbf{r}'|} | \psi_i(\mathbf{r}') \rangle \psi_j(\mathbf{r}) = \epsilon_i \psi_i(\mathbf{r})$$

The  $\epsilon_i$  are the Lagrange multipliers. Note that the factor 1/2 in front of the double summations has disappeared in the single summation here (double counting!).

The Hartree-part of the potential is:

$$V_i^H = e^2 \int \frac{\rho(\mathbf{r}') - \rho_i(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' \quad , \quad \rho(\mathbf{r}') = \sum_i \rho_i(\mathbf{r}') = \sum_i \psi_i^*(\mathbf{r}') \psi_i(\mathbf{r}')$$

Note that we have absorbed into  $\rho$  also the charge density  $\rho_i$  of particle  $i$  itself. So  $\rho$  is now the chargedensity due to all electrons, i.e. independent of  $i$ . However, particle  $i$  does not “feel” its own charge, so we have to correct and subtract  $\rho_i$ .

For the exchange (Fock) part of the eigenvalue equation we can write:

$$-e^2 \int \sum_{j(j \neq i)} \frac{\psi_j^*(\mathbf{r}') \psi_i(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \times \overbrace{\frac{\psi_i^*(\mathbf{r}) \psi_i(\mathbf{r})}{\psi_i^*(\mathbf{r}) \psi_i(\mathbf{r})}}^1 \psi_j(\mathbf{r}) d\mathbf{r}' = -e^2 \int \frac{\rho_i^X(\mathbf{r}, \mathbf{r}') - \rho_i(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' \psi_i(\mathbf{r})$$

Here we first multiplied with 1. Next we recognize an exchange of  $\mathbf{r}$  and  $\mathbf{r}'$  in the  $\psi_i$  and  $\psi_j$  in the 4 red  $\psi$ 's in the numerator. If we “normalize” this with the density of the denominator, we have defined a charge density  $\rho^X$  that accounts for the exchange (hence the “X”). We’re not there yet. Next we include in  $\rho^X$  the self-exchange (i.e. lift the restriction on  $j \neq i$  in the summation). We make an error, and correct by subtracting the self-exchange, which is just the density  $\rho_i$ .

Finally:

$$\left[ -\frac{\hbar^2}{2m_e} \nabla_i^2 + V_{\text{ext}} + e^2 \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' - e^2 \int \frac{\rho_i^X(\mathbf{r}, \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' \right] \psi_i(\mathbf{r}) = \epsilon_i \psi_i(\mathbf{r}) \quad (2)$$

Note that everything is cast into the form of one operator working on  $|\psi_i\rangle$ . The interactions with charges  $\rho_i(\mathbf{r}')$  cancel. The exchange part involves a complicated *non-local* chargedensity  $\rho_i^X$  that depends on  $i$ , i.e. it is an *orbital dependent* potential.

Now let’s have a glimpse at the density functional theory that comes later. There we’ll also have some kind of orbitals, and Kohn-Sham equations of a similar form... the first 3 terms of the KS equations are just as above. The 4th term, in practice, often is a much simpler expression, in general not dependent on  $i$ .<sup>3</sup>

### 3 Uniform electron gas

In the uniform electron gas we have electrons and a uniform compensating background charge as our external potential  $\rho_{\text{ext}} = -\rho(\mathbf{r}') = \text{constant}$ . So the 2nd and 3rd terms in Eq. 2 just cancel, and we have:<sup>4</sup>

$$\left[ -\frac{\hbar^2}{2m_e} \nabla^2 - e^2 \int \frac{\rho_{\mathbf{k}}^X(\mathbf{r}, \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' \right] \phi_{\mathbf{k}}(\mathbf{r}) = \epsilon_{\mathbf{k}} \phi_{\mathbf{k}}(\mathbf{r})$$

To solve this, we first (temporarily) remove the exchange part from the Hamiltonian. Remains a system with non-interacting particles, i.e. the Hamiltonian is nothing more than the kinetic energy.

<sup>2</sup>This is just the HF equation but now written down for the full spin-orbitals.

<sup>3</sup>Cf. the computer exercise on the H atom: in (2) the hydrogen feels the interaction with its own charge. In HF that is exactly compensated by the “self-exchange”, in practical DFT the cancellation is only partial.

<sup>4</sup>Here we best make the step from spin orbitals  $|\psi_i\rangle$  to spatial orbitals  $|\phi_{\mathbf{k}}\rangle$ . For each  $|\phi_{\mathbf{k}}\rangle$  we have two spin orbitals:  $|\phi_{\mathbf{k}}\rangle|\alpha\rangle$  and  $|\phi_{\mathbf{k}}\rangle|\beta\rangle$ . The “exchange charge density”  $\rho_{\mathbf{k}}^i$  only describes the exchange between orbitals with identical spin. In our case it is independent of spin.

See the werkcollege for details. The eigenfunctions are plane waves (we normalized in a volume  $\Omega$ , we assume  $\Omega \rightarrow \infty$ ):

$$\phi_{\mathbf{k}}(\mathbf{r}) = \frac{1}{\sqrt{\Omega}} e^{i\mathbf{k}\cdot\mathbf{r}}$$

$\mathbf{k}$  and  $\mathbf{r}$  are 3D vectors. The eigenvalue spectrum is just the free-electron parabola:

$$\epsilon_{\mathbf{k}} = \frac{\hbar^2 k^2}{2m_e}$$

Next we re-introduce the exchange (Fock) part. The eigenfunctions are still plane waves. To make that credible, we have this operator work on  $|\phi_{\mathbf{k}}\rangle$ :

$$\begin{aligned} -e^2 \int \frac{\rho_{\mathbf{k}}^X(\mathbf{r}, \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' \phi_{\mathbf{k}}(\mathbf{r}) &= -e^2 \int \sum_{\mathbf{k}'}^{\text{occ}} \frac{\phi_{\mathbf{k}}(\mathbf{r}') \phi_{\mathbf{k}'}^*(\mathbf{r}) \phi_{\mathbf{k}}(\mathbf{r}) \phi_{\mathbf{k}'}^*(\mathbf{r}')}{\phi_{\mathbf{k}}(\mathbf{r}) \phi_{\mathbf{k}}^*(\mathbf{r})} \frac{1}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' \frac{e^{i\mathbf{k}\cdot\mathbf{r}}}{\sqrt{\Omega}} \stackrel{\text{a}}{=} \\ -e^2 \int d\mathbf{r}' \int \frac{\Omega}{(2\pi)^3} d\mathbf{k}' \frac{\Omega}{\Omega^2} \frac{e^{i(\mathbf{k}\cdot\mathbf{r}' - \mathbf{k}\cdot\mathbf{r} + \mathbf{k}'\cdot\mathbf{r} - \mathbf{k}'\cdot\mathbf{r}')}}{e^{i(\mathbf{k}\cdot\mathbf{r} - \mathbf{k}\cdot\mathbf{r})}} \frac{1}{(2\pi)^3} \int d\mathbf{q} \frac{4\pi}{q^2} e^{i\mathbf{q}\cdot(\mathbf{r} - \mathbf{r}')} \frac{e^{i\mathbf{k}\cdot\mathbf{r}}}{\sqrt{\Omega}} &\stackrel{\text{b}}{=} \\ -\frac{4\pi e^2}{(2\pi)^3} \int d\mathbf{k}' \int d\mathbf{q} \frac{1}{q^2} \left\{ \frac{1}{(2\pi)^3} \int d\mathbf{r}' e^{-i(\mathbf{k} - \mathbf{k}')\cdot(\mathbf{r} - \mathbf{r}') + i\mathbf{q}\cdot(\mathbf{r} - \mathbf{r}')} \right\} \frac{e^{i\mathbf{k}\cdot\mathbf{r}}}{\sqrt{\Omega}} &\stackrel{\text{c}}{=} \\ -\frac{4\pi e^2}{(2\pi)^3} \int d\mathbf{k}' \left\{ \int d\mathbf{q} \frac{1}{q^2} \delta(\mathbf{q} - (\mathbf{k} - \mathbf{k}')) \right\} \frac{e^{i\mathbf{k}\cdot\mathbf{r}}}{\sqrt{\Omega}} &\stackrel{\text{d}}{=} \\ \left[ -\frac{4\pi e^2}{(2\pi)^3} \int d\mathbf{k}' \frac{1}{|\mathbf{k} - \mathbf{k}'|^2} \right] \frac{e^{i\mathbf{k}\cdot\mathbf{r}}}{\sqrt{\Omega}} \end{aligned}$$

So the plane wave remains an eigenfunction. At “a” we converted the  $\mathbf{k}'$  summation into an integral (blue), and inserted a Fourier representation of  $1/|\mathbf{r} - \mathbf{r}'|$  (red). The  $\mathbf{q}$  integral runs over the whole 3D “Fourier” space. At “b” we reshuffled stuff, being careful not to put integrands to the wrong sides of the integrals. At “c” we used a delta-function representation (see werkcollege) and integrate over the  $\mathbf{q}$  at “d”.

The final quantity in [...] is just a function of  $\mathbf{k}$ . The integral can be done:

$$-\frac{4\pi e^2}{(2\pi)^3} \int_{|\mathbf{k}'| < k_F} d\mathbf{k}' \frac{1}{|\mathbf{k} - \mathbf{k}'|^2} = -\frac{e^2}{\pi} k_F F(k/k_F) \quad , \quad F(x) = 1 + \frac{1 - x^2}{2x} \ln \left| \frac{1 + x}{1 - x} \right|$$

The Fermi wave vector  $k_F$  separates occupied ( $|\mathbf{k}| = k < k_F$ ) from unoccupied states ( $|\mathbf{k}| = k > k_F$ ). For the eigenvalue one obtains a correction to the free electron value:

$$\epsilon_{\mathbf{k}} = \frac{\hbar^2 k^2}{2m_e} - \frac{e^2}{\pi} k_F F(k/k_F)$$

Note the “-”: the function  $F$  always yields positive numbers, so the exchange gives rise to an eigenvalue lowering. On the Fermi sphere ( $x = 1$ )  $F$  has pathological behaviour: it does not diverge (physical), but its derivative does (unphysical). So no gap opens, but  $d\epsilon/dk$ , which is associated with a velocity (no proof) is pathological. In fact, for metals in general HF is problematic, but that need not bother us, as we’re usually dealing with molecules.

Our aim is the energy:

$$E_{\text{HF}} = \frac{\Omega}{(2\pi)^3} \int_{|\mathbf{k}| < k_F} d\mathbf{k} \left\{ 2 \frac{\hbar^2 k^2}{2m_e} - \frac{2}{2} e^2 k_F F(k/k_F) \right\}$$

The red factor 2 accounts for spin, the blue factor 2 corrects for double counting (cf. the HF lectures). You’ve done the first integral yourself, the second is more dreadful, but can also be done. The final result is:

$$\frac{E_{\text{HF}}}{N} = \frac{3}{5} \epsilon_F - \frac{3}{4} \frac{e^2 k_F}{\pi}$$

Here we have divided by the total number of (occupied) states  $N$ . From the werkcollege you know that  $k_F^3/(3\pi^2) = N/\Omega = n$ , where we have defined  $n$  as the density. This allows to express the exchange contribution to the energy per electron as a function of the density:

$$\frac{E^X}{N} = -\frac{3}{4} e^2 \sqrt[3]{\frac{3}{\pi}} n^{1/3} \quad (3)$$

## 4 Density Functional Theory, basics

You can construct the electron density from the wave function:<sup>5</sup>

$$n(\mathbf{r}) = \rho(\mathbf{r}) = N \int \Psi^*(\mathbf{r}, \mathbf{r}_2, \dots, \mathbf{r}_N) \Psi(\mathbf{r}, \mathbf{r}_2, \dots, \mathbf{r}_N) d\mathbf{r}_2 \dots d\mathbf{r}_N$$

Now we briefly derive the basic theorems of Hohenberg & Kohn from the 1960's. These provide the rigid foundations of density functional theory (DFT). The upshot will be that the ground state energy<sup>6</sup> is a functional of the (charge) density. A "functional" is a recipe that yields a number for each function (here the density function) that you put in. The ground state density  $n(\mathbf{r})$  itself is a function of the position. It just depends on 3 variables, so provides - in principle - a much simpler description of the system than the wave function.

First (theorem I) we want to establish that the external potential is unique for a given ground state (g.s.) density.<sup>7</sup> In other words, we want to establish the existence of the mapping  $n(\mathbf{r}) \rightarrow V_{\text{ext}}(\mathbf{r})$ : you make up some function  $n(\mathbf{r})$ , then the external potential that yields that function is unique.<sup>8</sup>

Suppose there are 2 different external potentials for the same g.s. density  $n(\mathbf{r})$ . For the normalized g.s. wavefunctions:

$$E = \langle \Psi | H | \Psi \rangle \quad \text{and} \quad E' = \langle \Psi' | H' | \Psi' \rangle$$

Apply the variational principle twice (at "RR", i.e. Rayleigh-Ritz), and convert Hamiltonians by swapping the external potentials:<sup>9</sup>

$$\begin{aligned} E &\stackrel{\text{RR}}{<} \langle \Psi' | H | \Psi' \rangle = \langle \Psi' | H + \overbrace{V' - V}^0 | \Psi' \rangle = \langle \Psi' | H' + V - V' | \Psi' \rangle = E' + \langle \Psi' | V - V' | \Psi' \rangle \\ E' &\stackrel{\text{RR}}{<} \langle \Psi | H' | \Psi \rangle = \langle \Psi | H' + \underbrace{V - V'}_0 | \Psi \rangle = \langle \Psi | H + V' - V | \Psi \rangle = E - \langle \Psi | V - V' | \Psi \rangle \end{aligned}$$

We used:  $H^{(l)} = T + W + V^{(l)}$  with  $T$  the kinetic energy operator,  $W$  the electron-electron repulsion and  $V$  and  $V^{(l)}$  the external potentials. Now add:

$$E + E' < E + E' + \langle \Psi' | V - V' | \Psi' \rangle - \langle \Psi | V - V' | \Psi \rangle$$

The densities  $n(\mathbf{r})$  and  $n'(\mathbf{r})$  are identical, but the matrix elements depend on the density only, i.e.:

$$\langle \Psi | V | \Psi \rangle = \int n(\mathbf{r}) V(\mathbf{r}) d\mathbf{r}$$

But we have assumed the densities to be unique, so the matrix elements of  $V - V'$  cancel, i.e.

$$E + E' < E + E'$$

which disqualifies our assumption that  $V$  and  $V'$  are different. Proof complete.

Note that now we have the following mapping:

$$n(\mathbf{r}) \rightarrow V_{\text{ext}} \rightarrow \Phi \rightarrow n(\mathbf{r})$$

Next (theorem II) we want to establish that there exists an energy functional that depends on the density and attains its minimum for the ground state density (given an external potential  $V_{\text{ext}}$ ). This minimum should be the ground state energy.

<sup>5</sup>Sloppy about spin again...

<sup>6</sup>and more...

<sup>7</sup>It is unique except for an additive constant:  $V_{\text{ext}}$  and  $V_{\text{ext}} + C$  ( $C$  is a constant) obviously yield the same  $n(\mathbf{r})$ . The corresponding energies also differ with the same constant  $C$ .

<sup>8</sup>Remember: the external potential is that felt by the electrons from their surroundings, i.e. in molecular systems it is the Coulomb potential of the nuclei.

<sup>9</sup>Here we assume the ground state is non-degenerate. A generalization for degenerate ground states exists.

Define a functional of the density (we call it  $\tilde{n}$ , to discriminate it from the fixed density  $n(\mathbf{r})$  that corresponds to the  $V_{\text{ext}}$  that defines our Hamiltonian):

$$E[\tilde{n}(\mathbf{r})] = \langle \Psi[\tilde{n}] | T + W | \Psi[\tilde{n}] \rangle + \int \tilde{n}(\mathbf{r}) V_{\text{ext}} d\mathbf{r}$$

Here  $|\psi[(\tilde{n})]\rangle$  is the g.s. wave function for  $\tilde{V}_{\text{ext}}$ , i.e. the external potential that corresponds to (in principle) another system and that has  $\tilde{n}$  as ground state density. The RR variational principle then says:

$$\langle \Psi[\tilde{n}] | H | \Psi[\tilde{n}] \rangle \geq \langle \Psi[n] | H | \Psi[n] \rangle ,$$

because  $\Psi[\tilde{n}]$  is not the g.s. of  $H$ . The equality pertains to the g.s. wave function. Now re-write with the functional:

$$E[\tilde{n}(\mathbf{r})] = \langle \Psi[\tilde{n}] | H | \Psi[\tilde{n}] \rangle \geq \langle \Psi[n] | H | \Psi[n] \rangle = E[n(\mathbf{r})]$$

which is the variational principle for the density functional, i.e. the g.s. density minimizes our functional yielding the g.s. energy. Now the existence of density function theory has been established. We have a beautiful result, but we do not know how to calculate the matrix element of  $T + W$  directly from the density (we can always take a detour, via the the wave function, but then we do not gain anything). In fact, this important unknown part of the functional is given a separate symbol in many textbooks:

$$F[n(\mathbf{r})] = \langle \Psi[n] | T + W | \Psi[n] \rangle \quad (4)$$

Attacking this problem requires the re-introduction of orbitals, leading to the Kohn-Sham equations, and approximations.

## 5 Density Functional Theory, the Kohn-Sham equations and the Local Density Approximation

A major problem in (4) is the kinetic energy.<sup>10</sup> The solution, by Kohn & Sham, is to think  $n(\mathbf{r})$  to be made from a set of non-interacting orbitals,

$$n(\mathbf{r}) = \sum_i^{\text{occ}} |\phi_i(\mathbf{r})|^2 , \quad (5)$$

but for the orbitals  $T$  can be calculated:

$$T^{\text{non-int}}[n(\mathbf{r})] = \sum_i^{\text{occ}} \langle \phi_i | \frac{p^2}{2m_e} | \phi_i \rangle$$

For the Kohn-Sham orbitals we use here the same symbols as for the *different* orbitals in the HF Ansatz in (1). Note they are not the same!

The term with “ $W$ ” is the electron-electron repulsion. We split it into a part that we can easily calculate and a remainder. The easy part is the electrostatic interaction of the charge density with itself (the “Hartree” part, where we include the artificial self-interaction). Then for  $F$  we have:

$$F[n(\mathbf{r})] = T^{\text{non-int}}[n(\mathbf{r})] + \frac{e^2}{2} \iint \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' + E^{\text{XC}}[n(\mathbf{r})] \quad (6)$$

Here  $E^{\text{XC}}[n(\mathbf{r})]$  is still unknown:

- It has to repair for the error made by approximating the kinetic energy with  $T^{\text{non-int}}[n(\mathbf{r})]$
- It has to account for the exchange and correlation contribution to  $\langle \Phi[n] | W | \Phi[n] \rangle$ .

---

<sup>10</sup>The Thomas-Fermi model offers an expression the kinetic energy only depending on the density, but an extension to an accurate expression for molecules and solids in general is very problematic.

- It has to compensate for the artificial self-interaction in the Hartree term, i.e. it should exhibit the “self-exchange” that exactly cancels the Coulomb self-repulsion (cf. the HF discussion above).

Of course, we hope  $E^{\text{XC}}[n(\mathbf{r})]$  is small... it has to be approximated. We’ll return to that later.

First, from the functional (6) we now go to “Schrödinger”-like, eigenvalue equations by requiring a stationary (in fact extremal) total energy ( $\delta E[n] = 0$ ) under the constraint that the orbitals are normalized. These are the *Kohn-Sham equations*:

$$\left[ \frac{-\hbar^2}{2m_e} \nabla^2 + V(\mathbf{r}) + e^2 \int \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + v_{\text{XC}}[n(\mathbf{r})] \right] \phi_i(\mathbf{r}) = \epsilon_i \phi_i(\mathbf{r}) \quad (7)$$

$$\text{where } v_{\text{XC}}[n(\mathbf{r})] = \frac{\delta E_{\text{XC}}[n(\mathbf{r})]}{\delta n(\mathbf{r})} \quad (8)$$

Provided a suitable and simple form for the exchange correlation potential  $v_{\text{XC}}$  is known, this system of eigenvalue equations is even easier to solve than the HF equations. Like for HF, these equations have to be solved self-consistently, as the potential experienced by the orbitals also depends on the orbitals *via* (5). With the  $|\phi_i\rangle$  expanded in a basis, the  $|\phi_i\rangle$  can be solved for by straightforward diagonalization, but the feed-back system requires a repeated diagonalization and careful mixing of the chargedensities (i.e. potential) until (5) and (7) are simultaneously satisfied.<sup>11</sup>

Now we want to use the knowledge on the uniform electron gas to devise an approximate expression for the exchange part in  $E^{\text{XC}}[n(\mathbf{r})]$ . We suppose that *locally*, i.e. in an infinitesimal volume  $d\mathbf{r}$ , our system has the same energy per electron as the uniform electron gas. For the exchange energy  $dE^{\text{X}}$  in that volume  $d\mathbf{r}$ :

$$dE^{\text{X}} = (E^{\text{X}} \text{ per electron}) \times (\# \text{ electrons in } d\mathbf{r}) = \epsilon_{\text{X}}^{\text{LDA}}[n] \times n(\mathbf{r}) d\mathbf{r}$$

This is the essence of the *local density approximation* (LDA), for the exchange. We know  $\epsilon_{\text{X}}^{\text{LDA}}[n]$  for the uniform electron gas: It is given by (3). Inserting (3) and integrating over whole space yields:

$$E_{\text{X}}^{\text{LDA}}[n(\mathbf{r})] = \int \epsilon_{\text{X}}^{\text{LDA}}[n] n(\mathbf{r}) d\mathbf{r} = -\frac{3}{4} e^2 \sqrt[3]{\frac{3}{\pi}} \int n(\mathbf{r})^{4/3} d\mathbf{r}$$

Its functional derivative:

$$v_{\text{X}}^{\text{LDA}} = -e^2 \sqrt[3]{\frac{3}{\pi}} n(\mathbf{r})^{1/3}$$

To complete the LDA we use a similar Ansatz of a local (energy) density  $\epsilon_{\text{C}}^{\text{LDA}}$  for the correlation. It can be extracted from numerically exact results that have been obtained for the uniform electron gas (in the quantum Monte Carlo study of Cerperley and Alder). A parametrization has been made by (among others) Perdew and Zunger (1981).

A few remarks are in order:

- The Hartree-term has an artificial self-interaction. It is only imperfectly canceled by the approximate LDA XC functional.
- A local functional, such as the LDA cannot capture physical phenomena that are inherently non-local such as the van der Waals interaction.
- In making the LDA, one implicitly assumes the that density is slowly varying in space. In fact, that is a bad approximation in general (That it works nevertheless, has to do with a spherical averaging, see below).

---

<sup>11</sup>In (7) one fixes  $n(\mathbf{r})$  in the Kohn-Sham Hamiltonian (in brackets “[...]”). This is the “input” density  $n^{\text{in}}(\mathbf{r})$ . After solving, the orbitals  $\phi_i(\mathbf{r})$  go into (5) to yield the output density  $n^{\text{out}}(\mathbf{r})$ . Next  $n^{\text{out}}(\mathbf{r})$  should to into (7) again, and the procedure be repeated until self-consistency is reached, i.e.  $n^{\text{out}}(\mathbf{r}) = n^{\text{in}}(\mathbf{r})$ . In practice that would lead to an instability in the feed-back system, and the density diverges instead of converges. To prevent this, only a fraction of the output density is “mixed” in with the old input density to obtain the new input density. Tuning the feedback system into efficient convergence is a real art. Most electronic structure programs provide defaults, but those are often insufficient for difficult systems.

- The KS scheme outlined above is based on the variational principle. However, beware that you can obtain energies below the real ground state energy, because the functional used is *approximate*. Unlike HF, you are not guaranteed to obtain an upper boundary on the ground state energy.
- DFT is not a “wave function” method. The orbitals are the result of the creative genius of Kohn and Sham, but formally they cannot be identified with the real wave function (although often in practice...). Whether DFT is an “*ab initio*” method, has been, and maybe still is, controversial. Many approximate exchange-correlation functionals are from “first-principles”, in so far that no experimental data are used in their construction (e.g. the LDA, one of the least accurate functionals). However, also semi-empirical functionals exist, where parameters of the functional have been fitted in order to reproduce experimental data.

## 5.1 Spin: the Local Spin Density Approximation, LSDA

The Hartree part of the KS Hamiltonian is not affected by spin (just add  $\alpha$  and  $\beta$  densities to get the total). The kinetic-energy is also trivial, the  $\alpha$  and  $\beta$  parts (say the “up” and “down” parts) can be treated separately. However, in the XC part they are not independent. The spin-generalization of the LDA is:

$$E_{XC}^{\text{LSDA}}[n^\uparrow(\mathbf{r}), n^\downarrow(\mathbf{r})] = \int \overbrace{(n^\uparrow(\mathbf{r}) + n^\downarrow(\mathbf{r}))}^{n(\mathbf{r})} \epsilon_{XC}^{\text{LSDA}}[n^\uparrow(\mathbf{r}), n^\downarrow(\mathbf{r})] d\mathbf{r}$$

The energy density  $\epsilon_{XC}^{\text{LSDA}}[n^\uparrow, n^\downarrow]$  is a functional of both densities. It can also be written as a functional of the total density  $n$  and the polarization density  $\xi$ , i.e. as  $\epsilon_{XC}^{\text{LSDA}}[n(\mathbf{r}), \xi(\mathbf{r})]$ , with

$$n(\mathbf{r}) = n^\uparrow(\mathbf{r}) + n^\downarrow(\mathbf{r}) \quad \text{and} \quad \xi(\mathbf{r}) = \frac{n^\uparrow(\mathbf{r}) - n^\downarrow(\mathbf{r})}{n(\mathbf{r})}$$

Accurate, numerically “exact”, data is available on the uniform electron gas for the unpolarized ( $\xi = 0$ ) and fully polarized ( $\xi = 1$ ) case. It can be used to parametrize the functional for these extreme cases. An interpolation is typically used to describe intermediate cases.

## 5.2 Another view on exchange and correlation, the XC-hole

The contribution of the electron-electron repulsion to the energy can be written:

$$E_{e-e} = \frac{e^2}{2} \iint \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' + \frac{e^2}{2} \iint \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \{g(\mathbf{r}, \mathbf{r}') - 1\} d\mathbf{r} d\mathbf{r}'$$

The first term is the Hartree energy, the second the exchange-correlation energy.<sup>12</sup> The function  $g(\mathbf{r}, \mathbf{r}')$  is the electron-electron pair correlation function. For large distance  $|\mathbf{r} - \mathbf{r}'|$  the electrons are un-correlated and  $g(\mathbf{r}, \mathbf{r}') \rightarrow 1$  and the contribution to the XC energy vanishes. For small distances  $g(\mathbf{r}, \mathbf{r}')$  drops below 1, yielding a stabilization in a lowering of the energy. For a fully polarized system ( $\xi = 1$ ) we have  $g = 0$  for  $|\mathbf{r} - \mathbf{r}'| = 0$  (Pauli). In other cases  $g$  can be larger than 0 for  $\mathbf{r} = \mathbf{r}'$ .

Now we’ll define the “exchange-correlation hole”:

$$n_{xc}(\mathbf{r}, \mathbf{r}') = n(\mathbf{r}')\{g(\mathbf{r}, \mathbf{r}') - 1\}$$

<sup>12</sup>Note that the Hartree energy cancels exactly the second part of the exchange-correlation energy, i.e.

$$E_{e-e} = \frac{e^2}{2} \iint \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} g(\mathbf{r}, \mathbf{r}') d\mathbf{r} d\mathbf{r}' .$$

Intuitively, this makes sense:  $g(\mathbf{r}, \mathbf{r}')$  says how likely it is to have an electron at  $\mathbf{r}'$  given there is an electron at  $\mathbf{r}$ . It is normalized by both single-particle densities  $n(\mathbf{r})$  and  $n(\mathbf{r}')$  (this is, admittedly, somewhat confusing). If the electrons are truly not-interacting, i.e. have no exchange and correlation,  $g(\mathbf{r}, \mathbf{r}') = 1$  and the expression is just the Coulomb repulsion between the charge densities, as it should be.

Thus one can re-write the XC part of  $E_{e-e}$  as follows:<sup>13</sup>

$$E_{e-e, \text{XC}} = \frac{e^2}{2} \iint \frac{n(\mathbf{r})}{|\mathbf{r} - \mathbf{r}'|} n_{\text{xc}}(\mathbf{r}, \mathbf{r}') d\mathbf{r} d\mathbf{r}'$$

This “hole”, as several properties. One of the most important (and related to its name) is:

$$\int n_{\text{xc}}(\mathbf{r}, \mathbf{r}') d\mathbf{r}' = -1 \quad (9)$$

I.e., wherever you are ( $\mathbf{r}$ ), integrating over the other coordinate yields exactly  $-1$  (this is because of the “self-exchange”). This *averaged* property of the hole is very important. As the LDA is constructed from the exact uniform electron gas data, this average property is well-obeyed.<sup>14</sup>

Another important point is that  $E_{e-e, \text{XC}}$  depends only the *spherical average* of the hole, i.e. many details are irrelevant. You can see this easily when you write  $\mathbf{r}' - \mathbf{r} = \mathbf{R}$  and do the integration over  $\mathbf{R}$  in spherical shells ( $d\mathbf{r}' = d\mathbf{R} = R^2 dR d\Omega$ ):

$$E_{e-e, \text{XC}} = \frac{e^2}{2} \int d\mathbf{r} n(\mathbf{r}) \int R^2 dR \frac{1}{R} \int d\Omega n_{\text{xc}}(\mathbf{r}, \mathbf{R})$$

The key observation (of Jones & Gunnarsson, see footnote) is that although the LDA exchange-correlation hole differs considerably from the exact exchange-correlation hole, the spherical average of the LDA and real hole are actually very similar.

### 5.3 L(S)D, features

The LSDA in general yields too homogeneous electron densities (here “gradient expansions” can help, see below). As a consequence, it typically “over-binds”, i.e. binding energies are overestimated (HF often behaves just opposite). It does not provide any reasonable bonding for weakly bonded systems. It performs badly for hydrogen-bonds and van der Waals (vdW) systems. The vdW interaction is a manifestation of *non-local*, dynamical correlation. No way such an effect can be described with any reasonable accuracy by the inherently *local* LSDA (That the LSDA nevertheless often exhibits bonding for vdW systems is fortuitous, i.e. it happens but *not for a physically sound reason.*) Hydrogen bonds have small, inhomogeneous densities, which is are too challenging for the LSDA. Consequently, geometries obtained with the LSDA for such systems are not to be trusted. For stronger bonds (covalent, ionic), however, the optimized geometries tend to be quite good. Bond-lengths are typically underestimated by a few percent.

A fundamental drawback is the non-perfect cancellation of the Hartree self-interaction and the self-exchange. This is most acutely felt near the atomic nuclei. Hartree-Fock does a much better job here (the artificial self-interactions cancel completely). Consequently HF performs much better for atoms. Another fundamental issue is the decay of the XC-potential into vacuum. For a finite system it should decay as  $\sim 1/r$ , i.e. inversely proportional to the distance (c.f. the HF exchange). However, in LSDA it decays exponentially, i.e. much faster. So, electrons are insufficiently bound and negatively charged atoms and molecules are often found to be unstable (where experimentally they are known to exist).<sup>15</sup>

A very important issue is the “band gap” problem. All (regular) insulators and semi-conductors have an energy (band) gap separating the occupied valence bands from the unoccupied conduction bands. This size of the band gap, and the position of defect levels within the gap, are very important technological parameters. In traditional LDA (and also in GGA, see below) this gap is severely underestimated. A correct, formal definition of the band gap is the difference between the ionization

<sup>13</sup>We sweep something under the carpet here by implicitly assuming this relation to hold for the DFT exchange-correlation energy. We then overlook the repairs  $E_{\text{XC}}$  has to do for the kinetic energy. There is a solution to this problem, see: R.O. Jones & O. Gunnarsson, Rev. Mod. Phys. **61**, 689 (1989).

<sup>14</sup>Whereas in the LDA Eq. (9) is well-obeyed for the uniform electron gas, that does not necessarily hold for other systems, like atoms and molecules.

<sup>15</sup>See the weird computer exercise on  $\text{Li}^-$  to see that often it isn't that bad, yet...

potential (removing an electron from the top of the valence band) and the electron affinity (putting the electron in the lowest conduction band). In practical applications of DFT this is often approximated by the difference between the LUMO and HOMO eigenvalues (for the system in its ground state). Typically in LDA this  $\epsilon_g^{\text{LDA}}$  is much lower than the experimental gap (of the order of 40 %). Something very deep lurks behind this discrepancy: the real DFT XC functional makes a discontinuous “jump” when the occupation crosses the band gap, however, in crystalline systems the LDA functional does not. Somewhat surprisingly, hybrid functionals tend to give much better values for the gap.<sup>16</sup>

Now, let’s try to formulate the band gap problem a bit more precise.<sup>17</sup> We use that (see werkcollege)

$$\frac{\partial E}{\partial n_i} = \epsilon_i$$

and for the highest occupied orbital<sup>18</sup>

$$\begin{aligned} & \epsilon_N(n_1 = 1, n_2 = 1, \dots, n_{N-1} = 1, n_N = n) \\ & = \epsilon_N(n_1 = 1, n_2 = 1, \dots, n_{N-1} = 1, n_N = 1) \quad \text{if } 0 < n \leq 1. \end{aligned}$$

Note that  $0 \neq n!$  We start with making the definition of the gap explicit:

$$\epsilon_g = IP - EA = [E(N-1) - E(N)] - [E(N) - E(N+1)]$$

Here  $E(N-1)$ ,  $E(N)$  and  $E(N+1)$  are the ground state energies for a system with  $N-1$ ,  $N$  and  $N+1$  electrons, respectively. We use the expressions above to write:

$$\begin{aligned} E(N) - E(N-1) &= \int_0^1 \epsilon_N(N-\delta) dn_N = \epsilon_N(N-\delta) = \epsilon_N(N) \\ E(N+1) - E(N) &= \int_0^1 \epsilon_{N+1}(N+\delta) dn_{N+1} = \epsilon_{N+1}(N+\delta) \neq \epsilon_{N+1}(N) \end{aligned}$$

Here  $0 < \delta \ll 1$ . We return to the gap:

$$\epsilon_g = \epsilon_{N+1}(N+\delta) - \epsilon_N(N) = \overbrace{\epsilon_{N+1}(N+\delta) - \epsilon_{N+1}(N)}^{\Delta} + \overbrace{\epsilon_{N+1}(N) - \epsilon_N(N)}^{\epsilon_g^{\text{DFT}}}$$

$\epsilon_g^{\text{DFT}}$  is the band gap as we usually obtain from a band structure calculation: the KS eigenvalue of the LUMO minus the KS eigenvalue of the HOMO of an  $N$ -electron system. The term “ $\Delta$ ” in general does not vanish, as  $\epsilon_{N+1}(N+\delta)$  makes a discontinuous jump when  $\delta$  is reduced to 0. It is due to the (in)famous discontinuity in the exchange-correction potential, at least, that is a common belief.

## 5.4 Generalized Gradient Expansions

One of the weak points of LDA is its purely local nature. Therefore, one expects best performance of the LDA for slowly varying densities. However, in molecules the densities do not vary slowly. A possible solution might be to search for a better approximation of the  $E^{\text{XC}}$  using gradients of the density, i.e. develop the functional in terms of a *gradient expansion*. Developing a *systematic expansion*, however, fails, because convergence is not uniform. The way-out is to develop functionals that by construction obey a set of exact properties of the true density functional (or the exchange-correlation hole). Such functionals make up the family of the *Generalized Gradient Expansions* (GGAs), where the functional depends not only on the spin densities, but also on the size of their gradients  $|\nabla n^\uparrow|$  and  $|\nabla n^\downarrow|$ :

$$E_{\text{XC}}^{\text{GGA}} = \int \epsilon_{\text{XC}}[n^\uparrow, n^\downarrow, |\nabla n^\uparrow|, |\nabla n^\downarrow|] (n^\uparrow(\mathbf{r}) + n^\downarrow(\mathbf{r})) d\mathbf{r}$$

<sup>16</sup>HF overestimates gaps, so that mixing it with DFT yields an increase of the gap isn’t that much of a surprise. That the improvement tends to be rather systematic, however, is.

<sup>17</sup>This discussion follows that in Jones and Gunnarson.

<sup>18</sup>This comes without proof. See Jones and Gunnarson and references therein.

There is no such thing as a “unique GGAs”. Their actual implementations depend on the properties enforced on them by construction. It is also possible to use the “freedom” in constructing the functional to fit to an (experimental) data set, giving the functional a semi-empirical flavor.

Two important GGAs are: BLYP (1988): Becke exchange, Lee-Yang-Parr correlation and PBE (1996) by Perdew, Burke and Ernzerhof. The latter is *not* semi-empirical, and still widely used in condensed matter materials physics (where “hybrids” are much more expensive in computational cost).

The main advantages of GGAs are the improved bond length (correcting for most of the LDA error, and - occasionally - also yielding too long bonds) and the ability to give a reasonable description of hydrogen bonding.

## 5.5 Hybrid Functionals

These functionals replace part of the DFT exchange, with Hartree-Fock exchange (calculated from the KS orbitals). This makes sense in some heuristic way, as LDA and HF often have opposite “errors” (LDA/HF often over/under-binds, LDA/HF gaps are too small/large). There also exists a more formal justification for doing this. In formula the idea is:

$$E_{\text{XC}}^{\text{hybrid}} = \alpha E_{\text{X}}^{\text{HF}} + (1 - \alpha) E_{\text{X}}^{\text{DFT}} + E_{\text{C}}^{\text{DFT}}$$

Two important hybrids are:

- B3LYP (Becke 1993). Here  $\alpha = 0.2$ . The actual functional is quite complicated. This is the DFT “work-horse” of quantum chemistry. It is widely used (although a DFT specialist will always find a functional that is better for a specific system or property calculation). Often accuracies approaching MP2 are possible. Lewars in chapter 7 provides extensive tables comparing B3LYP, MP2 and others for a range of properties.
- PBE0. It’s by the same PBE, but now mixes in HF exchange as:

$$E_{\text{XC}}^{\text{PBE0}} = \frac{1}{4} E_{\text{X}}^{\text{HF}} + \frac{3}{4} E_{\text{X}}^{\text{PBE}} + E_{\text{C}}^{\text{PBE}}$$

An important recent development are so-called range-separated functions. They use a substantial fraction of HF exchange at short distances, where is it important (cf. the  $g(\mathbf{r}, \mathbf{r}')$  above). At longer distance, they switch to full DFT. As an example look at the HSE (Heyd-Scuseria-Ernzerhof):

$$E_{\text{XC}}^{\text{HSE}} = \frac{1}{4} E_{\text{X}}^{\text{HF,SR}} + \frac{3}{4} E_{\text{X}}^{\text{PBE,SR}} + E_{\text{X}}^{\text{PBE,LR}} + E_{\text{C}}^{\text{PBE}}$$

The switching is done by splitting  $1/r$  into a short and long range part:

$$\frac{1}{r} = \frac{\overbrace{\text{erfc}(\mu r)}^{\text{“close”}}}{r} + \frac{\overbrace{\text{erf}(\mu r)}^{\text{“far”}}}{r}$$

Here  $\mu$  is an inverse length that separates “close” from “far”. Typical values for  $\mu$  are  $0.2 - 0.3 \text{ \AA}^{-1}$ .

## 5.6 Describing van der Waals interactions in DFT

To avoid confusion: “van der Waals” here is used in the strict sense, i.e. it only refers to the London dispersion interaction that has a  $R^{-6}$  behaviour at larger separation. The dispersion interaction is not, or at best only partially, accounted for by standard density functionals. This was, until recently, a serious drawback of DFT. Several methods have been developed to overcome most of the problem.<sup>19</sup> We’ll discriminate between two approaches:

<sup>19</sup>This is still an active area of research. DFT methods with van der Waals extension cannot (yet?) achieve the high accuracy of wave function methods (MP4, CI, CCS(D)T, etc.).

- *Accounting for the missing dispersion with an additional force field.* Here the electronic structure calculation, carried out the DFT level, is not affected by the vdW correction. This correction is added in an *ad hoc* fashion, and (often) has the form of a pair-wise additive potential depending on the nuclear coordinates. This potential has to be constructed such that it accounts well for the missing interactions in as wide a range of (relevant) chemical environments as possible. Many such approaches exist and we will discuss a few, i.e. those that appear to be most important/promising presently: The methods by Grimme and co-workers (called “DFT-D”,<sup>20</sup> “DFT-D2”<sup>21</sup> and “DFT-D3”<sup>22</sup>) and the method of Tkatchenko and Scheffler (called “TS”).<sup>23</sup>
- *Incorporating the missing interaction into the density functional for the correlation energy.* Here the vdW part is incorporated into the self-consistent DFT calculations. Also here we cannot be comprehensive (at all), and restrict to the currently most popular method by Dion *et al.*<sup>24</sup> (called “vdW-DF”) and its flavors.<sup>25</sup>

---

<sup>20</sup>S. Grimme, J. Comput. Chem. **25**, 1463 (2004).

<sup>21</sup>S. Grimme, J. Comput. Chem. **27**, 1787 (2007).

<sup>22</sup>S. Grimme, J. Antony, S. Ehrlich and H. Krieg, J. Chem. Phys. **132**, 154104 (2010).

<sup>23</sup>A. Tkatchenko and M. Scheffler, Phys. Rev. Lett. **102**, 073005 (2009).

<sup>24</sup>M. Dion, H. Rydberg, E. Schröder, D.C. Langreth and B.I. Lundqvist, Phys. Rev. Lett. **92**, 246401 (2004).

<sup>25</sup>A comprehensive review is given by: K. Berland, V.R. Cooper, K. Lee, E. Schröder, T. Thonhauser, P. Hyldgaard and B.I. Lundqvist, Rep. Prog. Phys. **78**, 066501 (2015).