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:

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

Here V_{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:[1]

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

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

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

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[1] 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 degeneraty 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:[2]

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

The ϵ_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 ρ also the charge density ρ_i of particle i itself. So ρ 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 ρ_i.

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

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

Here we first multiplied with 1. Next we recognize an exchange of $\mathbf{r}$ and $\mathbf{r}'$ in the ψ_i and ψ_j in the 4 red ψ's in the numerator. If we "normalize" this with the density of the denominator, we have defined a charge density ρ^X that accounts for the exchange (hence the "X"). We're not there yet. Next we include in ρ^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 ρ_i.

Finally:

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

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 ρ_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.[3]

3 Uniform electron gas

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

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

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.

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[2] This is just the HF equation but now written down for the full spin-ortibals.

[3] 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.

[4] 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 decribes 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 Ω, we assume $\Omega \to \infty$):

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

$\mathbf{k}$ 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 $|\phi_{\mathbf{k}}\rangle$:

$$-e^2 \int \frac{\rho^X_{\mathbf{k}}(\mathbf{r},\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\, d\mathbf{r}' \phi_{\mathbf{k}}(\mathbf{r}) = -e^2 \int \sum_{\mathbf{k}'}^{\text{occ}} \frac{\phi_{\mathbf{k}}(\mathbf{r}')\phi^*_{\mathbf{k}}(\mathbf{r})\phi_{\mathbf{k}'}(\mathbf{r})\phi^*_{\mathbf{k}'}(\mathbf{r}')}{\phi_{\mathbf{k}}(\mathbf{r})\phi^*_{\mathbf{k}}(\mathbf{r})}\, \frac{1}{|\mathbf{r}-\mathbf{r}'|}\, d\mathbf{r}'\, \frac{e^{i\mathbf{k}\cdot\mathbf{r}}}{\sqrt{\Omega}} \overset{\text{a}}{=}$$

$$-e^2 \int d\mathbf{r}' \int \frac{\Omega}{(2\pi)^3}\, d\mathbf{k}'\, \frac{\Omega}{\Omega^2}\, \frac{e^{i(\mathbf{k}\cdot\mathbf{r}'-\mathbf{k}\cdot\mathbf{r}+\mathbf{k}'\cdot\mathbf{r}-\mathbf{k}'\cdot\mathbf{r})}}{e^{i(\mathbf{k}\cdot\mathbf{r}-\mathbf{k}\cdot\mathbf{r})}}\, \frac{1}{(2\pi)^3} \int d\mathbf{q}\, \frac{4\pi}{q^2} e^{i\mathbf{q}\cdot(\mathbf{r}-\mathbf{r}')}\, \frac{e^{i\mathbf{k}\cdot\mathbf{r}}}{\sqrt{\Omega}} \overset{\text{b}}{=}$$

$$-\frac{4\pi e^2}{(2\pi)^3} \int d\mathbf{k}' \int d\mathbf{q}\, \frac{1}{q^2} \left\{ \frac{1}{(2\pi)^3} \int d\mathbf{r}'\, e^{-i(\mathbf{k}-\mathbf{k}')\cdot(\mathbf{r}-\mathbf{r}')+i\mathbf{q}\cdot(\mathbf{r}-\mathbf{r}')} \right\} \frac{e^{i\mathbf{k}\cdot\mathbf{r}}}{\sqrt{\Omega}} \overset{\text{c}}{=}$$

$$-\frac{4\pi e^2}{(2\pi)^3} \int d\mathbf{k}' \left\{ \int d\mathbf{q}\, \frac{1}{q^2}\, \delta(\mathbf{q}-(\mathbf{k}-\mathbf{k}')) \right\} \frac{e^{i\mathbf{k}\cdot\mathbf{r}}}{\sqrt{\Omega}} \overset{\mathbf{d}}{=}$$

$$\left[-\frac{4\pi e^2}{(2\pi)^3} \int d\mathbf{k}'\, \frac{1}{|\mathbf{k}-\mathbf{k}'|^2} \right] \frac{e^{i\mathbf{k}\cdot\mathbf{r}}}{\sqrt{\Omega}}$$

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:

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

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

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

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:

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

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:

$$\frac{E_{\mathrm{HF}}}{N} = \frac{3}{5}\epsilon_{\mathrm{F}} - \frac{3}{4}\frac{e^2 k_{\mathrm{F}}}{\pi}$$

Here we have divided by the total number of (occupied) states N. From the werkcollege you know that $k_{\mathrm{F}}^3/(3\pi^2) = N/\Omega = n$, 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:

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

4 Density Functional Theory, basics

You can construct the electron density from the wave function:[5]

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

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[6] 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.[7] 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 $n(\mathbf{r})$, than the external potential that yields that function is unique.[8]

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:[9]

$$E \overset{\text{RR}}{<} \langle\Psi'|H|\Psi'\rangle = \langle\Psi'|H + \overbrace{V' - V'}^{0}|\Psi'\rangle = \langle\Psi'|H' + V - V'|\Psi'\rangle = E' + \langle\Psi'|V - V'|\Psi'\rangle$$
$$E' \overset{\text{RR}}{<} \langle\Psi|H'|\Psi\rangle = \langle\Psi|H' + \underbrace{V - V}_{0}|\Psi\rangle = \langle\Psi|H + V' - V|\Psi'\rangle = E - \langle\Psi|V - V'|\Psi\rangle$$

We used: $H^{(')} = T + W + V^{(')}$ with T the kinetic energy operator, W the electron-electron repulsion and V and $V^{(')}$ 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_{ext}). This mimumum should be the ground state energy.

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[5] Sloppy about spin again...

[6] and more...

[7] It is unique except for an additive constant: V_{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.

[8] 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.

[9] 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_{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:

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

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:

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

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.[10] The solution, by Kohn & Sham, is to think $n(\mathbf{r})$ to be made from a set of non-interacting orbitals,

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

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:

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

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 $\langle\Phi[n]|W|\Phi[n]\rangle$.

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[10] 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 $E^{\mathrm{XC}}[n(\mathbf{r})]$ 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*:

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

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

Provided a suitable and simple form for the exchange correlation potential v_{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.[11]

Now we want to use the knowledge on the uniform electron gas to devise an approximate expression for the exchange part in $E^{\mathrm{XC}}[n(\mathbf{r})]$. 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^{X} in that volume $d\mathbf{r}$:

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

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

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

Its functional derivative:

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

To complete the LDA we use a similar Ansatz of a local (energy) density $\epsilon_{\mathrm{C}}^{\mathrm{LDA}}$ 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).

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[11] In (7) one fixes $n(\mathbf{r})$ in the Kohn-Sham Hamiltonian (in brackets "[...]"). This is the "input" density $n^{\mathrm{in}}(\mathbf{r})$. After solving, the orbitals $\phi_i(\mathbf{r})$ go into (5) to yield the output density $n^{\mathrm{out}}(\mathbf{r})$. Next $n^{\mathrm{out}}(\mathbf{r})$ should to into (7) again, and the procedure be repeated until self-consistency is reached, i.e. $n^{\mathrm{out}}(\mathbf{r}) = n^{\mathrm{in}}(\mathbf{r})$. 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 α and β densities to get the total). The kinetic-energy is also trivial, the α and β 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:

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

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

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

The first term is the Hartree energy, the second the exchange-correlation energy.[12] 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 $g(\mathbf{r},\mathbf{r}')\to 1$ 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":

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

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[12] Note that the Hartree energy cancels exactly the second part of the exchange-correlation energy, i.e.

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

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 $E_{\mathrm{e-e}}$ as follows:[13]

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

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

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

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.[14]

Another important point is that $E_{\mathrm{e-e,XC}}$ 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 ($d\mathbf{r}' = d\mathbf{R} = R^2\, dR\, d\Omega$):

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

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.

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[13] 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_{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).

[14] 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.