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

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

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

$$\begin{split} \langle \Psi^{HF} | H | \Psi^{HF} \rangle &= \sum_{i} \langle \psi_{i} | - \frac{\hbar^{2}}{2m_{e}} \nabla_{i}^{2} + V_{\text{ext}} | \psi_{i} \rangle + \frac{e^{2}}{2} \sum_{i,j(i \neq j)} \langle \psi_{i}(\mathbf{r})\psi_{j}(\mathbf{r}') | \frac{1}{|\mathbf{r} - \mathbf{r}'|} | \psi_{i}(\mathbf{r})\psi_{j}(\mathbf{r}') \rangle \\ &- \frac{e^{2}}{2} \sum_{i,j(i \neq j)} \langle \psi_{i}(\mathbf{r})\psi_{j}(\mathbf{r}') | \frac{1}{|\mathbf{r} - \mathbf{r}'|} | \psi_{j}(\mathbf{r})\psi_{i}(\mathbf{r}') \rangle \end{split}$$

¹It 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:

1

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

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 $\rho_{\text{ext}} = -\rho(\mathbf{r}') = \text{constant}$. 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.

²This 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.

⁴Here 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 $|\phi_{\mathbf{k}}\rangle$:

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

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 **k**. The integral can be done:

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

The Fermi wave vector $k_{\rm F}$ separates occupied ($|\mathbf{k}| = k < k_{\rm F}$) from unoccupied states ($|\mathbf{k}| = k > k_{\rm F}$). 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:

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

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:

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

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

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