Towards DFT: the plan

With HF we can now calculate energies, orbitals and orbital energies. With some "simple" extensions (e.g., force on the atoms *via* the Hellmann-Feynman theorem) and perturbation theory we have access to structural optimization, vibrational frequencies, reaction enthalpies, transition state barriers, and a host of spectroscopic observables: Raman, IR, NMR shieldings, etc., and - at a simplified level - also, e.g., light absorption.

HF is not very accurate ... It *overestimates* the energy, and often too much ... We need something better ... Two routes:

▶ **Quantum chemical wave function methods**: account for electron correlation explicitly. Many such methods allow for systematic improvements. Improvements often have a substantial computational cost. A route to "ultimate accuracy". A concise discussion in week 7.

▶ **Density functional theory (DFT)**: simpler than HF (in principle), and often more accurate. Very useful, but not the ultimate answer. It approximately calculates exchange and correlation from the electron densities. Relatively affordable, cheaper than HF. We look at foundations and applications in weeks 4–6.

▶ Well... there is also quantum Monte Carlo ... and Machine Learning entering the stage, but we won't talk about those.

Towards DFT: preliminaries

Help slide: One can repeatedly carry out HF ground state energy calculations for fixed positions of the atoms $\mathbf{R}_1$, $\mathbf{R}_2$, $\mathbf{R}_3$, etc. You get a potential energy surface:

$$E = E(\mathbf{R}_1, \mathbf{R}_2, \mathbf{R}_3, \ldots, \mathbf{R}_m)$$

The force on atom ν is minus the gradient:

$$\mathbf{F}_\nu = -\boldsymbol{\nabla}_{\mathbf{R}_\nu} E = - \begin{pmatrix} \partial E/\partial x_\mu \\ \partial E/\partial y_\mu \\ \partial E/\partial z_\mu \end{pmatrix}$$

One can optimize a structure by moving the atoms along the forces until they vanish.

One can calculate the gradient knowing only the *ground state* wavefunction for a specific configuration (of the atoms):

$$\boldsymbol{\nabla}_{\mathbf{R}_\nu} E = \boldsymbol{\nabla}_{\mathbf{R}_\nu} \langle \Psi | H | \Psi \rangle = \langle \Psi | \boldsymbol{\nabla}_{\mathbf{R}_\nu} H | \Psi \rangle$$

Both the (normalized) ground state wavefunction $|\Psi\rangle$ and the Hamiltonian H depend on all atomic positions. So the 2nd equality is not obvious. It holds by virtue of the **Hellmann-Feynman theorem**. In short: $|\Psi\rangle$ minimizes the energy so first order changes in $|\Psi\rangle$ do not affect the energy. Hence only the direct derivative of H matters.

You can even do molecular-dynamics while solving the HF equations on the fly (Car-Parrinello method, DFT).

Towards DFT: preliminaries

To develop DFT:

1. Do Hartree-Fock for the uniform electron gas. That yields an exact result for the exchange energy density as function of the electron density.

2. Develop the theoretical foundations of Density Functional Theory: Remove the wave function from the theory and find that the ground state energy of a system can be calculated *in principle* using only the electron density, as the minimum of the density functional. This electron density is not uniform. This yields the Hohenberg-Kohn theorems and a formal definition of the density functional. It does not yet provide a method we can use to calculate something useful.

3. Turn DFT into a practical scheme: (re-)introduction of orbitals to approximate the kinetic energy. Approximations of the exchange and correlation energy, using, as a starting point the exchange and correlation energies of the uniform electron gas (LDA). This yields the Kohn-Sham equations, the DFT analogon of the HF eigenvalue equations.

4. Climb the "Jacobs ladder" (Perdew) of DFT functionals: gradients of the density, hybrid functionals (mixing with HF), etc.

Recap Hartree-Fock

The Hartree-Fock Ansatz for the wave function (spin-orbitals $|\psi_i\rangle$):

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

The Hamiltonian [for (Hartree) atomic units: $\hbar = 1$, $m_e = 1$, $e = 1$]:

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

$V_{\text{ext}}(\mathbf{r}_i)$ is "external potential" (typically the attraction by the nuclei).
The expectation value of the energy for orthonormal $|\psi_i\rangle$:

$$\langle \Psi^{HF} | H | \Psi^{HF} \rangle = \sum_i \langle \psi_i | - \frac{\hbar^2}{2m_e} \nabla_i^2 + V_{\text{ext}} | \psi_i \rangle$$

$$+ \frac{e^2}{2} \sum_{i,j(i \neq j)} \langle \psi_i(\mathbf{r}) \psi_j(\mathbf{r}') | \frac{1}{|\mathbf{r} - \mathbf{r}'|} | \psi_i(\mathbf{r}) \psi_j(\mathbf{r}') \rangle - \frac{e^2}{2} \sum_{i,j(i \neq j)} \langle \psi_i(\mathbf{r}) \psi_j(\mathbf{r}') | \frac{1}{|\mathbf{r} - \mathbf{r}'|} | \psi_j(\mathbf{r}) \psi_i(\mathbf{r}') \rangle$$

We see the Coulomb J_{ij} and exchange integrals K_{ij} for spin-orbitals.

Recap Hartree-Fock

Minimization yields the HF eigenvalue equation with *spin-orbitals* [c.f. $\hat{f}(1)\phi_k(1) = \epsilon_k \phi_k(1)$ for the orbitals]:

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

$$\text{where} \quad V_i^H = e^2 \int \frac{\rho(\mathbf{r}')-\rho_i(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}' \quad, \quad \rho(\mathbf{r}') = \sum_j \rho_j(\mathbf{r}') = \sum_j \psi_j^*(\mathbf{r}')\psi_j(\mathbf{r}')$$

Note: the action of the "P_{12}" has been made explicit.

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

Note: again the artificial *self-interaction* in Coulomb (Hartree) and exchange "potentials" cancel exactly. We can suppress the $\rho_i(\mathbf{r}')$ corrections, i.e. **not** subtract them in the equations above.

Note: the "displaced charge density" $\rho_i^X(\mathbf{r}, \mathbf{r}')$ is orbital dependent and non-local!

Recap Hartree-Fock

Now we have the complete spin-orbital analogon of the HF eigenvalue equation:

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

Let's compare:

$$\hat{f}(1)\phi_k(1) = \epsilon_k \phi_k(1) \;\; ,$$

$$\hat{f}(1) = \hat{h}(1) + \sum_{m=1}^{N/2}\left(2\hat{J}_m(1) - \hat{K}_m(1)\right) \;\; ,$$

$$\hat{J}_m(1) \equiv \int d\mathbf{r}_2 \frac{\phi_m^*(2)\phi_m(2)}{|\mathbf{r}_1-\mathbf{r}_2|} \;\; , \quad \hat{K}_m(1) \equiv \int d\mathbf{r}_2 \frac{\phi_m^*(2)\hat{P}_{12}\phi_m(2)}{|\mathbf{r}_1-\mathbf{r}_2|}$$

Note: we have spin orbitals $|\psi_i\rangle = |\phi_k\rangle|\alpha\rangle$ or $|\psi_{i'}\rangle = |\phi_k\rangle|\beta\rangle$.

Remember: the exchange integral is non-vanishing only if both orbitals have the same spin.

The uniform electron gas

We have a "Jellium" (English: Jelly, Dutch: gelei): The electrons (nuclei) are uniformly smeared out and have opposite charge densities (the total is neutral):

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

This implies for the eigenvalue equation, i.e. the red part vanishes:

$$\left[-\frac{\hbar^2}{2m_e}\nabla_i^2 + \overbrace{V_{\text{ext}} + e^2 \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}\, d\mathbf{r}'}^{0} - e^2 \int \frac{\rho_i^{\text{X}}(\mathbf{r}, \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}\, d\mathbf{r}' \right]\psi_i(\mathbf{r}) = \epsilon_i\psi_i(\mathbf{r})$$

We can remove the spin function(s) and relabel:

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

We continue on the "black" board. We postpone the exchange part and start with the non-interacting part:

$$-\frac{\hbar^2}{2m_e}\nabla^2\phi_{\mathbf{k}}(\mathbf{r}) = \epsilon_{\mathbf{k}}\phi_{\mathbf{k}}(\mathbf{r})$$

The uniform electron gas

The uniform electron gas

Help slide:

Plane waves, normalized in box $\Omega = L_x L_y L_z$:

$$\phi_{\mathbf{k}}(\mathbf{r}) = \frac{1}{\sqrt{\Omega}} e^{i\mathbf{k}\cdot\mathbf{r}} \qquad -\frac{\hbar^2 \nabla^2}{2m_e} \phi_{\mathbf{k}}(\mathbf{r}) = \frac{\hbar^2 |\mathbf{k}|^2}{2m_e} \phi_{\mathbf{k}}(\mathbf{r}) = \epsilon_{\mathbf{k}} \phi_{\mathbf{k}}(\mathbf{r}) \qquad \epsilon_F = \frac{\hbar^2 k_F^2}{2m_e}$$

P.B.C.: $L_x k_x = 2\pi n_x \rightarrow k_x = (2\pi/L_x) n_x$

Counting:

$$\sum_{k_x} \cdots = \frac{L_x}{2\pi} \int \ldots dk_x \Rightarrow \sum_{\mathbf{k}} = \frac{L_x L_y L_z}{(2\pi)^3} \iiint \ldots d\mathbf{k} \qquad \text{volume per state} = \frac{(2\pi)^3}{\Omega}$$

$$\# \text{ of states} = 2 \sum_{|\mathbf{k}| < k_F} = 2\frac{\Omega}{(2\pi)^3} \int_0^{k_F} d\mathbf{k} = 2\frac{\Omega}{(2\pi)^3} \frac{4}{3}\pi k_F^3 = \frac{\Omega k_F^3}{3\pi^2} \equiv N \qquad \frac{N}{\Omega} = \frac{k_F^3}{3\pi^2}$$

$$E_{tot} = E_{kin} = 2 \sum_{|\mathbf{k}| < k_F} e_{\mathbf{k}} = 2\frac{\Omega}{(2\pi)^3} \iiint_{|\mathbf{k}| < k_F} \frac{\hbar^2 k^2}{2m_e} d\mathbf{k} = \frac{2\Omega \hbar^2}{2m_e (2\pi)^3} \int_0^{k_F} k^2 \, 4\pi k^2 \, dk$$

$$= \frac{\Omega \hbar^2 k_F^5}{10 m_e \pi^2} = \frac{3}{5} \frac{\Omega k_F^3}{3\pi^2} \frac{\hbar^2 k_F^2}{2m_e} = \frac{3}{5} N \epsilon_F$$

The uniform electron gas

Help slide:

Add the interaction, the eigenfunction is unaffected, the eigenvalue lowered.

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

$$-e^2 \int \sum_j \frac{\psi_j^*(\mathbf{r}')\psi_i(\mathbf{r}')\psi_i^*(\mathbf{r})\psi_j(\mathbf{r})}{\psi_i^*(\mathbf{r})\psi_i(\mathbf{r})|\mathbf{r}-\mathbf{r}'|}\,d\mathbf{r}'\psi_i(\mathbf{r}) = -e^2 \int \sum_j \frac{\psi_i(\mathbf{r}')\psi_i^*(\mathbf{r})\psi_j(\mathbf{r})\psi_j^*(\mathbf{r}')}{\psi_i(\mathbf{r})\psi_i^*(\mathbf{r})|\mathbf{r}-\mathbf{r}'|}\,d\mathbf{r}'\psi_i(\mathbf{r})$$

$$\rightarrow -e^2 \int \sum_{\mathbf{k}'} \frac{\psi_{\mathbf{k}}(\mathbf{r}')\psi_{\mathbf{k}}^*(\mathbf{r})\psi_{\mathbf{k}'}(\mathbf{r})\psi_{\mathbf{k}'}^*(\mathbf{r}')}{\psi_{\mathbf{k}}(\mathbf{r})\psi_{\mathbf{k}}^*(\mathbf{r})|\mathbf{r}-\mathbf{r}'|}\,d\mathbf{r}' \frac{1}{\sqrt{\Omega}}e^{i\mathbf{k}\cdot\mathbf{r}}$$

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

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

The magenta part is a Dirac delta function: $\delta(\mathbf{q}-(\mathbf{k}-\mathbf{k}'))$, continuing:

$$-e^2 \int \frac{d\mathbf{k}'}{(2\pi)^3}\int d\mathbf{q}\frac{4\pi}{q^2}\delta(\mathbf{q}-(\mathbf{k}-\mathbf{k}'))\frac{e^{i\mathbf{k}\cdot\mathbf{r}}}{\sqrt{\Omega}} = -4\pi e^2 \int_{|\mathbf{k}'|<k_{\mathsf{F}}}\frac{d\mathbf{k}'}{(2\pi)^3}\frac{1}{|\mathbf{k}-\mathbf{k}'|^2}\frac{e^{i\mathbf{k}\cdot\mathbf{r}}}{\sqrt{\Omega}} = -\frac{e^2}{\pi}k_{\mathsf{F}}F(k/k_{\mathsf{F}})\frac{e^{i\mathbf{k}\cdot\mathbf{r}}}{\sqrt{\Omega}}$$

The uniform electron gas

Help slide:
$$\frac{1}{|\mathbf{r}-\mathbf{r}'|} = \frac{1}{(2\pi)^3}\int d\mathbf{q}\frac{4\pi}{q^2}e^{i\mathbf{q}\cdot(\mathbf{r}-\mathbf{r}')} \quad \text{(Fourier transform of Coulomb potential)}$$

$$\frac{1}{(2\pi)^3}\int e^{i(\mathbf{k}\cdot\mathbf{r}'-\mathbf{k}\cdot\mathbf{r}+\mathbf{k}'\cdot\mathbf{r}-\mathbf{k}'\cdot\mathbf{r}')}e^{i\mathbf{q}\cdot(\mathbf{r}-\mathbf{r}')}d\mathbf{r}' = \frac{1}{(2\pi)^3}\int e^{i(\mathbf{q}-(\mathbf{k}-\mathbf{k}'))\cdot(\mathbf{r}-\mathbf{r}')}d\mathbf{r}'$$

$$= \frac{1}{(2\pi)^3}\int e^{i((\mathbf{k}-\mathbf{k}')-\mathbf{q})\cdot(\mathbf{r}'-\mathbf{r})}d\mathbf{r}' = \frac{1}{(2\pi)^3}\int e^{i((\mathbf{k}-\mathbf{k}')-\mathbf{q})\cdot\mathbf{r}''}d\mathbf{r}'' = \delta((\mathbf{k}-\mathbf{k}')-\mathbf{q}) = \delta(\mathbf{q}-(\mathbf{k}-\mathbf{k}'))$$

We used $\mathbf{r}'' = \mathbf{r}'-\mathbf{r}$ and integrated over whole space. Thus the $\mathbf{r}$ dependence disappears and our $\phi_{\mathbf{k}}(\mathbf{r})$ is indeed an eigenstate.

Further we used $\delta(\mathbf{x}) = \delta(-\mathbf{x})$.

A Dirac delta function is a zero everywhere, except where its argument is 0. There it is "infinite" in such a way that its integral is 1. You can imagine it as an infinitely narrow peak with area 0 located at the position where its argument is 0. E.g., in one dimension:

$$\delta(x) = 0 \text{ if } x \neq 0, \int_{-a}^{a}\delta(x)\,dx = 1 \text{ for any } a > 0.$$

In combination with a (smooth) function $g(x)$:

$$\int_{-a}^{a}g(x)\delta(x)\,dx = g(0) \text{ and } \int_{-\infty}^{\infty}g(x)\delta(x-a)\,dx = g(a)$$

The uniform electron gas

$$\epsilon_{\mathbf{k}} = \frac{\hbar^2 k^2}{2m_e} - \frac{e^2}{\pi} k_{\mathsf{F}} F(k/k_{\mathsf{F}}) \quad \text{with} \quad F(x) = 1 + \frac{1-x^2}{2x} \ln \left| \frac{1+x}{1-x} \right|$$

To get the energy we sum over occupied states and account for double counting (red factors 2 for spin, blue factor 2 for double counting):

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

The integral is non-trivial, but can be done:

$$\frac{E_{\mathsf{HF}}}{N} = \overset{\text{kin}}{\frac{3}{5} \epsilon_{\mathsf{F}}} - \overset{\text{exchange}}{\frac{3}{4} \frac{e^2 k_{\mathsf{F}}}{\pi}}$$
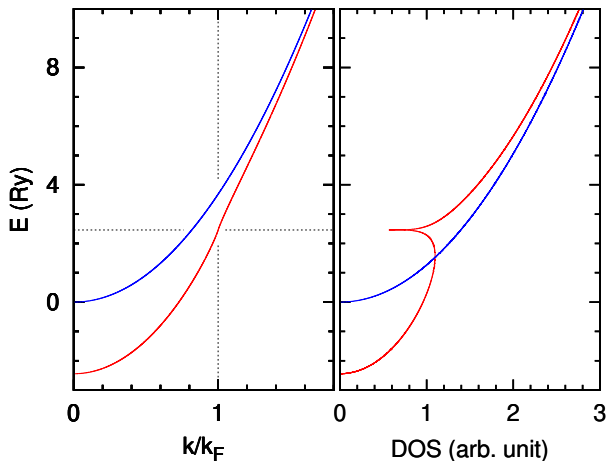
We want to express the exchange as function of the density $\rho = n$,

$$n = \frac{N}{\Omega} = \frac{k_{\mathsf{F}}^3}{3\pi^2} \Rightarrow k_{\mathsf{F}} = \sqrt[3]{3\pi^2 n}$$

hence, for the exchange energy per particle,

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

The uniform electron gas

Blue: free electrons, red: HF electrons (pathological behaviour at E_F).
1 Ry = $\frac{1}{2}$ Hartree = 13.6 eV. RWS= 1 Bohr.