CHEM6085: Density Functional Theory

Lecture 6

Kohn-Sham DFT

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Replacing one problem with another

Shortcomings of orbital-free DFT

- Pure (or "orbital-free") DFT attempts to compute the energy of interacting electrons, as a functional of the density

- While this brute force approach is in principle correct, in practice it is not very accurate

- This is due to the lack of accurate approximations for the **kinetic energy functional**

The Kohn-Sham suggestion

- Kohn and Sham proposed an alternative approach in order to overcome this problem

    [W. Kohn and L. J. Sham. "Self-consistent equations including exchange and correlation effects", *Phys. Rev.* **140**, A1133 (1965)]

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Replacing one problem with another

The Kohn-Sham suggestion

- Proposed to work instead with a system of non-interacting electrons

- In general, the wavefunction of the non-interacting electrons is different from that of the interacting ones and so is the density

- However in the Kohn-Sham approach, a fictitious non-interacting system is constructed, **in such a way, that its density is the same as that of the interacting electrons**

- The challenge is then shifted from finding the universal H-K functional to finding the fictitious system of non-interacting electrons which has the same density as the "real" one with the interacting electrons

- This allows to set up more accurate DFT calculations as the expression for the kinetic energy of non-interacting electrons is known (so no need for approximate kinetic energy functionals of the density)

- In order to see how it works we first need to examine the Schrödinger equation for non-interacting electrons

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Interacting electrons

Exact
Hamiltonian
operator for all
electrons
together
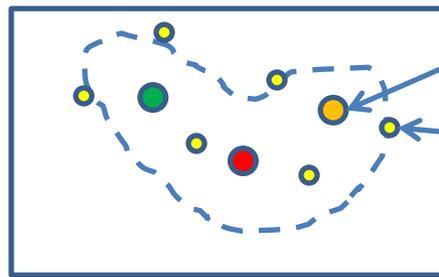
nucleus of real molecule

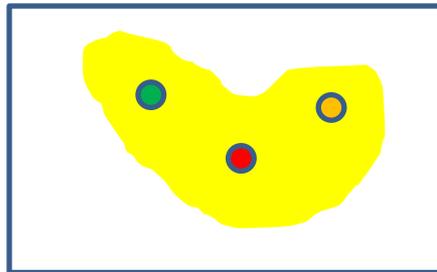electron

Construct and solve Schrödinger equation to
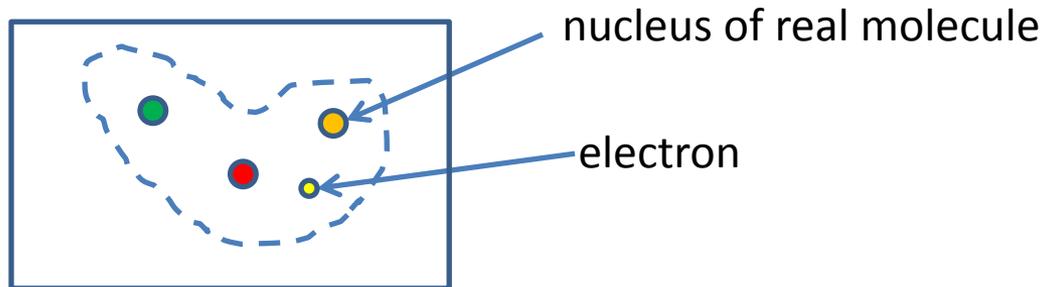obtain **exact** wavefunction for interacting electrons
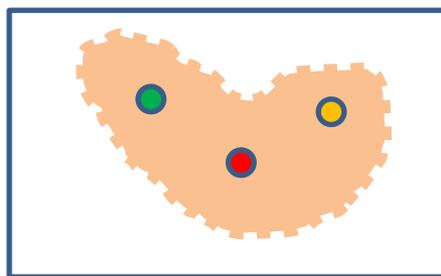
Exact electron
density

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Non-interacting electrons

Hamiltonian operator for one electron moving in an "average" potential caused by the rest of the electrons

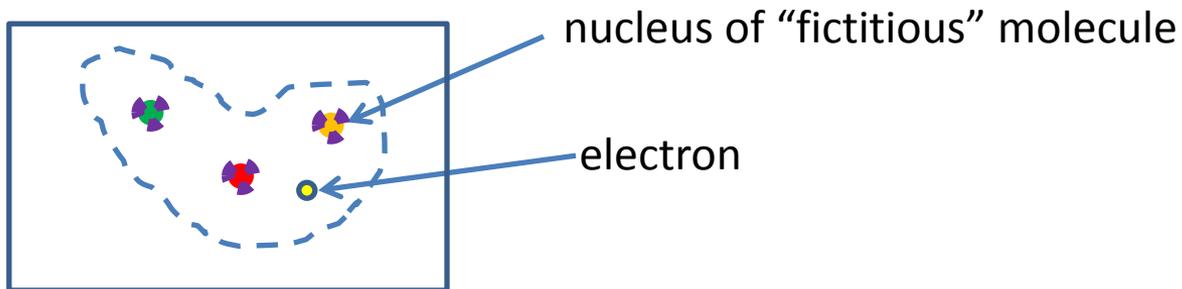nucleus of real molecule

electron

Construct and solve Schrödinger equation for one electron. Combine many one-electron wavefunctions (molecular orbitals) to obtain **approximate** wavefunction for all electrons
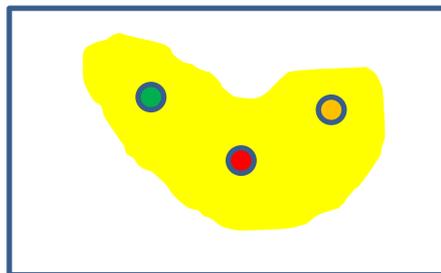
Approximate electron density

Kohn-Sham non-interacting electrons

Hamiltonian operator for one electron moving in an "average" potential caused by a special **fictitious** system of electrons



nucleus of "fictitious" molecule

electron

Construct and solve Schrödinger equation for one electron. Combine one-electron wavefunctions (molecular orbitals) to obtain **approximate wavefunction** for all electrons

Exact electron density

These are not any non-interacting electrons... These are Kohn-Sham electrons!

- Interacting electrons
- Exact Hamiltonian for real molecule
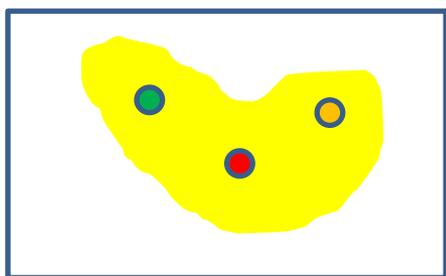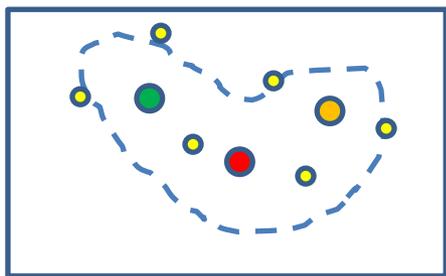
- Non-Interacting electrons
- Approximate Hamiltonian for real molecule

- Kohn-Sham non-interacting electrons
- Approximate Hamiltonian for fictitious molecule

Density of interacting electrons (=exact density)
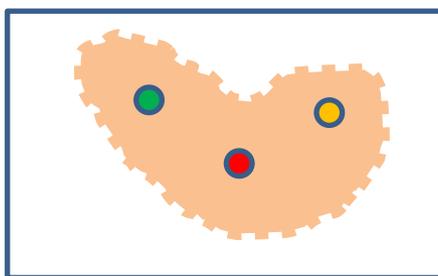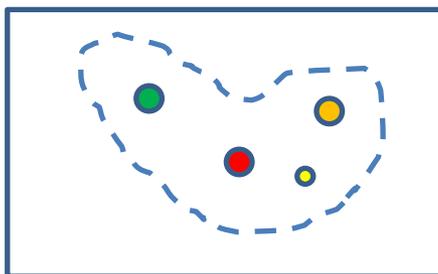
Density of non-interacting electrons (=approximate density)
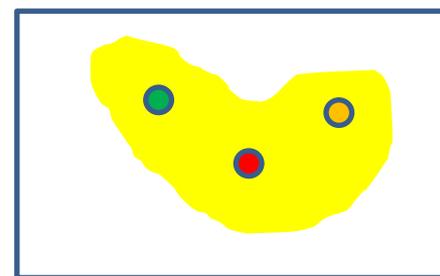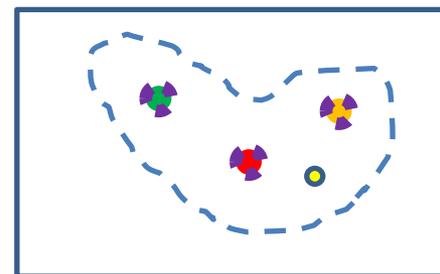
Density of fictitious system of non-interacting electrons (= exact density of interacting electrons)

Interacting and non-interacting electrons

- We have seen that the exact electronic Hamiltonian is

$$\hat{H}_{\rm el} = \sum_{i=1}^{N_{\rm el}} -\frac{1}{2}\nabla_i^2 + \sum_{i=1}^{N_{\rm el}} \left(\sum_{A=1}^{N_{at}} \frac{-Z_A}{|\mathbf{r}_i - \mathbf{R}_A|} \right) + \sum_{i=1}^{N_{\rm el}} \sum_{j=i+1}^{N_{\rm el}} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}$$

$$= \sum_{i=1}^{N_{\rm el}} -\frac{1}{2}\nabla_i^2 + \sum_{i=1}^{N_{\rm el}} V_{\rm ext}(\mathbf{r}_i) + \sum_{i=1}^{N_{\rm el}} \sum_{j=i+1}^{N_{\rm el}} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}$$

- This describes a system of **_interacting electrons_** (as the $1/|r_i\text{-}r_j|$ can not be broken into a sum of terms containing only r_i and only r_j)

- A much simpler problem is that of *non-interacting electrons*: This involves replacing the direct interaction by some one-electron operator (potential) $V_{\rm av}$ that describes the "average" effect of the interaction

$$\hat{H}_{\rm eff} = \sum_{i=1}^{N_{\rm el}} -\frac{1}{2}\nabla_i^2 + \sum_{i=1}^{N_{\rm el}} V_{\rm ext}(\mathbf{r}_i) + \sum_{i=1}^{N_{\rm el}} V_{\rm av}(\mathbf{r}_i)$$

Why $V_{\rm av}$ can be no better than an "average" interaction?

Hamiltonian for non-interacting electrons

- In the case of the non-interacting electrons the Hamiltonian operator is simply a sum of one-electron operators

$$
\begin{aligned}
\hat{H}_{\text{eff}} &= \sum_{i=1}^{N_{\text{el}}} -\frac{1}{2}\nabla_i^2 + \sum_{i=1}^{N_{\text{el}}} V_{\text{ext}}(\mathbf{r}_i) + \sum_{i=1}^{N_{\text{el}}} V_{\text{av}}(\mathbf{r}_i) \\
&= \sum_{i=1}^{N_{\text{el}}} -\frac{1}{2}\nabla_i^2 + \sum_{i=1}^{N_{\text{el}}} \{V_{\text{ext}}(\mathbf{r}_i) + V_{\text{av}}(\mathbf{r}_i)\} \\
&= \sum_{i=1}^{N_{\text{el}}} -\frac{1}{2}\nabla_i^2 + \sum_{i=1}^{N_{\text{el}}} V_{\text{eff}}(\mathbf{r}_i) \\
&= \sum_{i=1}^{N_{\text{el}}} \left\{ -\frac{1}{2}\nabla_i^2 + V_{\text{eff}}(\mathbf{r}_i) \right\} \\
&= \sum_{i=1}^{N_{\text{el}}} \hat{h}(\mathbf{r}_i)
\end{aligned}
$$

- So the entire Hamiltonian is just a sum of one-electron Hamiltonians: one for each electron

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Wavefunction for non-interacting electrons

• The Hamiltonian is a sum of one-electron Hamiltonians

$$\hat{H}_{\text{eff}} = \sum_{i=1}^{N_{\text{el}}} \hat{h}(\mathbf{r}_i)$$

• We can write (and solve) a Schrödinger equation for each one-electron Hamiltonian separately

$$\hat{h}(\mathbf{r}_i)\psi_a(\mathbf{r}_i) = \varepsilon_a \psi_a(\mathbf{r}_i)$$
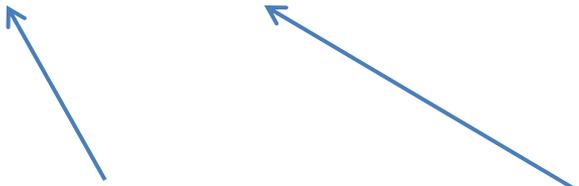
• From this we obtain **molecular orbitals** and their **energies**

Molecular orbitals

- A **wavefunction for a single electron** is called a molecular orbital (MO)

- MO with spatial and spin coordinates are called **spin orbitals** and are products of a spatial orbital and a spin function, e.g.

$$\chi^{\uparrow}(\mathbf{x}) = \psi(\mathbf{r})\alpha(\omega)$$

Spin orbital   **Spatial orbital**   **Spin function**
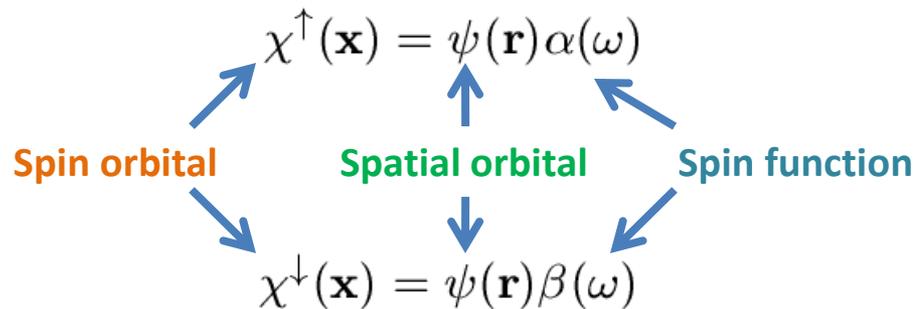
$$\chi^{\downarrow}(\mathbf{x}) = \psi(\mathbf{r})\beta(\omega)$$

- As our one-electron Hamiltonians depend only on spatial coordinates, the spin orbitals are also acceptable eigenfunctions

$$\hat{h}(\mathbf{r}_i)\psi_a(\mathbf{r}_i) = \varepsilon_a\psi_a(\mathbf{r}_i)$$

$$\hat{h}(\mathbf{r}_i)\chi_a(\mathbf{x}_i) = \varepsilon_a\chi_a(\mathbf{x}_i)$$

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Wavefunction for (many) non-interacting electrons

- Let's see what happens for two non-interacting electrons

$$\hat{h}(\mathbf{r}_1)\chi_a(\mathbf{x}_1) = \varepsilon_a\chi_a(\mathbf{x}_1) \qquad\qquad \hat{h}(\mathbf{r}_2)\chi_b(\mathbf{x}_2) = \varepsilon_b\chi_b(\mathbf{x}_2)$$

$$\left[\hat{h}(\mathbf{r}_1) + \hat{h}(\mathbf{r}_2)\right]\chi_a(\mathbf{x}_1)\chi_b(\mathbf{x}_2) = (\varepsilon_a + \varepsilon_b)\chi_a(\mathbf{x}_1)\chi_b(\mathbf{x}_2)$$

- In a similar way, we can show that the (exact) solution to the Schrödinger equation for N_{el} non-interacting electrons is

$$\left[\sum_{i=1}^{N_{el}}\hat{h}(\mathbf{r}_i)\right]\chi_a(\mathbf{x}_1)\chi_b(\mathbf{x}_2)\cdots\chi_z(\mathbf{x}_{N_{el}}) = (\varepsilon_a+\varepsilon_b+\ldots+\varepsilon_z)\chi_a(\mathbf{x}_1)\chi_b(\mathbf{x}_2)\cdots\chi_z(\mathbf{x}_{N_{el}})$$

- The total energy eigenvalue is simply the sum of the spin orbital energies

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Hartree products

- So the exact wavefunction of the independent electrons is simply the product the spin-orbital for each electron

$$\Psi_{\text{eff}}(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_{N_{\text{el}}}) = \chi_a(\mathbf{x}_1)\chi_b(\mathbf{x}_2)\cdots\chi_z(\mathbf{x}_{N_{\text{el}}})$$

- Such a wavefunction is called a **Hartree product**

- A Hartree product is a mathematically acceptable solution to the Schrödinger equation for independent electrons

- However it is not physically acceptable because it does not satisfy some of the conditions we have set for wavefunctions (which ones?)

Slater determinants

You can verify that the following wavefunction for two electrons is antisymmetric:

$$\Psi(\mathbf{x}_1, \mathbf{x}_2) = \chi_1(\mathbf{x}_1)\chi_2(\mathbf{x}_2) - \chi_2(\mathbf{x}_1)\chi_1(\mathbf{x}_2)$$

It can also be written as a determinant:

$$\Psi(\mathbf{x}_1, \mathbf{x}_2) = \begin{vmatrix} \chi_1(\mathbf{x}_1) & \chi_2(\mathbf{x}_1) \\ \chi_1(\mathbf{x}_2) & \chi_2(\mathbf{x}_2) \end{vmatrix}$$

- This can be generalised to any number of electrons

- A wavefunction of this form is called a **Slater determinant**

- It obeys antisymmetry by construction (determinants change sign when two rows or columns are interchanged)

- It also respects the indistinguishability of the electrons

Slater determinants

Slater determinant for N electrons:

$$\Psi_{SD}(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \chi_1(\mathbf{x}_1) & \chi_2(\mathbf{x}_1) & \cdots & \chi_N(\mathbf{x}_1) \\ \chi_1(\mathbf{x}_2) & \chi_2(\mathbf{x}_2) & \cdots & \chi_N(\mathbf{x}_2) \\ \vdots & \vdots & & \vdots \\ \chi_1(\mathbf{x}_N) & \chi_2(\mathbf{x}_N) & \cdots & \chi_N(\mathbf{x}_N) \end{vmatrix}$$

Normalisation
constant

Shorthand representation, as a ket:

$$\Psi_{SD}(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_N) = |\chi_1(\mathbf{x}_1)\chi_2(\mathbf{x}_2)\ldots\chi_N(\mathbf{x}_N)\rangle$$

Spin orbitals in Slater determinants are always orthonormal, i.e.

$$\langle \chi_i | \chi_j \rangle = \delta_{ij}$$

The Pauli principle

- A determinant is zero if two or more of its rows or columns are identical

- Therefore, a given spin orbital can be included only once in a Slater determinant, as otherwise the determinant would become zero everywhere in space and such a wavefunction is not acceptable

Allowed cases
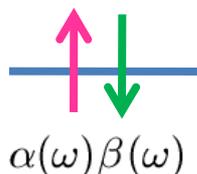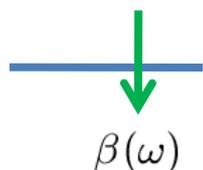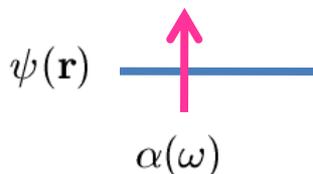
Examples of not allowed cases

$\psi(\mathbf{r})$

$\alpha(\omega)$ $\beta(\omega)$ $\alpha(\omega)\beta(\omega)$ $\beta(\omega)\,\beta(\omega)$ $\alpha(\omega)\alpha(\omega)\beta(\omega)$
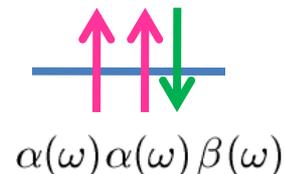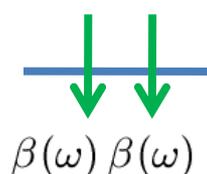
- The Pauli principle follows naturally as a spatial orbital can result in at most two spin orbitals (one with up and one with down spin functions)

- In other words, a spatial orbital can be occupied by no more than two electrons of opposite spins

Electronic density of a Slater determinant

- We have seen that the electronic density of any wavefunction is defined by the following expression

$$n(\mathbf{r}) = N_{\text{el}} \int \cdots \int \Psi^*(\mathbf{r}, \omega_1, \mathbf{r}_2, \omega_2, \ldots, \mathbf{r}_{N_{\text{el}}}, \omega_{N_{\text{el}}}) \Psi(\mathbf{r}, \omega_1, \mathbf{r}_2, \omega_2, \ldots, \mathbf{r}_{N_{\text{el}}}, \omega_{N_{\text{el}}}) d\omega_1 \, d\mathbf{r}_2 d\omega_2 \ldots d\mathbf{r}_{N_{\text{el}}} d\omega_{N_{\text{el}}}$$

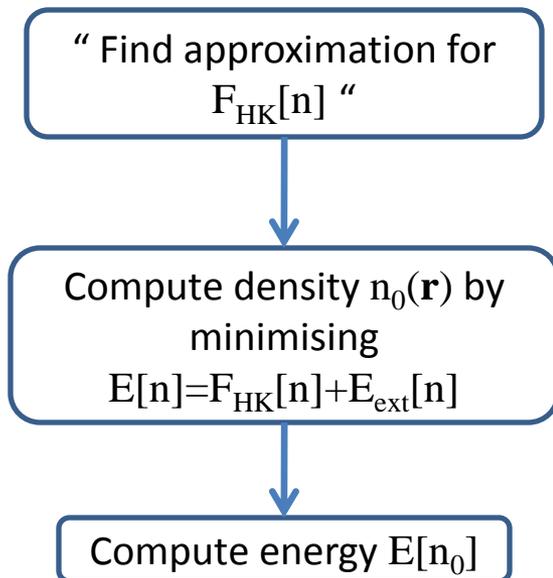- When the wavefunction is a Slater determinant, the above expression simplifies to (assuming an even number of electrons, doubly occupying the spatial orbitals)

$$n(\mathbf{r}) = 2 \sum_{i=1}^{N_{\text{el}}/2} |\psi_i(\mathbf{r})|^2$$

- Therefore, the electronic density of a Slater determinant wavefunction is simply equal to the sum of the squares of the occupied orbitals

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Orbital-free vs Kohn-Sham DFT

Orbital-free approach

" Find approximation for $F_{HK}[n]$ "

$\downarrow$

Compute density $n_0(\mathbf{r})$ by minimising $E[n]=F_{HK}[n]+E_{ext}[n]$

$\downarrow$

Compute energy $E[n_0]$

Kohn-Sham approach

" Find a $V_{eff}(\mathbf{r})=V_{KS}(\mathbf{r})$ such that $n_{KS}(\mathbf{r}) = n_0(\mathbf{r})$ "

$\downarrow$

Solve for the wavefunction (Slater determinant) of the non-interacting electrons (i.e. find the molecular orbitals)

$\downarrow$

Build the density $n_0(\mathbf{r})$ from the molecular orbitals

$\downarrow$

Compute energy $E[n_0]$

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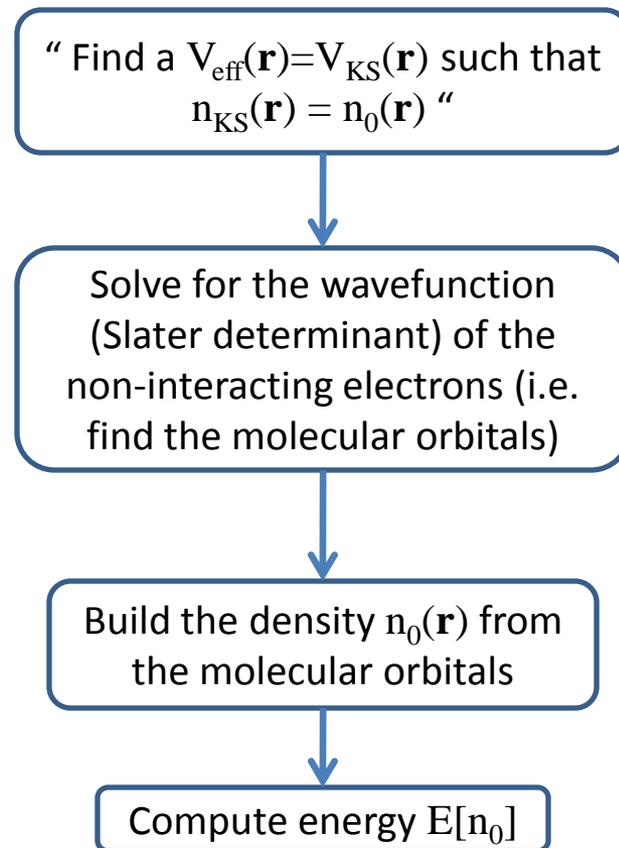
The Kohn-Sham trick

- In pure (orbital-free) DFT the energy is given by the functional

$$E[n] = E_{\text{kin}}[n] + E_{\text{Coul}}[n] + E_{\text{xc}}[n] + E_{\text{ext}}[n]$$

and the biggest obstacle is the lack of an accurate expressions for the kinetic energy functional

- With the Kohn-Sham DFT approach we can re-write the energy as

$$E[n] = E_{\text{kin,KS}}[n] + (E_{\text{kin}}[n] - E_{\text{kin,KS}}[n]) + E_{\text{Coul}}[n] + E_{\text{xc}}[n] + E_{\text{ext}}[n]$$

- Where $E_{\text{kin,KS}}[n]$ is the energy of the (non-interacting) Kohn-Sham electrons
- We have an exact expression for $E_{\text{kin,KS}}[n]$, albeit **in terms of molecular orbitals, rather than the density**
- The difference $(E_{\text{kin}}[n]-E_{\text{kin,KS}}[n])$ is smaller than the errors in the approximations for $E_{\text{kin}}[n]$ in pure (orbital-free) DFT

Kohn-Sham energy expression

- The total energy functional is now written as the sum of a functional of the molecular orbitals for the kinetic energy part and functionals of the density for the rest of the energy components

$$E[n] = E_{\text{kin,KS}}[n] + E_{\text{Coul}}[n] + E_{\text{ext}}[n] + (E_{\text{kin}}[n] - E_{\text{kin,KS}}[n]) + E_{\text{xc}}[n]$$

$$= 2\sum_{i=1}^{N_{\text{el}}/2} \int \psi_i^*(\mathbf{r})\left(-\frac{1}{2}\nabla^2\right)\psi_i(\mathbf{r})d\mathbf{r} + E_{\text{Coul}}[n] + E_{\text{ext}}[n] + (E_{\text{kin}}[n] - E_{\text{kin,KS}}[n]) + E_{\text{xc}}[n]$$

$$= 2\sum_{i=1}^{N_{\text{el}}/2} \int \psi_i^*(\mathbf{r})\left(-\frac{1}{2}\nabla^2\right)\psi_i(\mathbf{r})d\mathbf{r} + E_{\text{Coul}}[n] + E_{\text{ext}}[n] + \{E_{\text{kin}}[n] - E_{\text{kin,KS}}[n] + E_{\text{xc}}[n]\}$$

$$= 2\sum_{i=1}^{N_{\text{el}}/2} \int \psi_i^*(\mathbf{r})\left(-\frac{1}{2}\nabla^2\right)\psi_i(\mathbf{r})d\mathbf{r} + E_{\text{Coul}}[n] + E_{\text{ext}}[n] + E_{\text{xc}}'[n]$$

- Approximations are sought for $E'_{\text{xc}}[n]$, which even though it now contains also contributions from the kinetic energy, it is still just called "Exchange-correlation functional" and from now on we will be writing it as $E_{\text{xc}}[n]$

Homework

1) Write down an expression for the energy of a system of non-interacting electrons (e.g. in the Kohn-Sham approach) in terms of molecular orbitals

2) Compare the above expression with the Kohn-Sham expression for the energy of the interacting system. In what do they differ? Can you write the one in terms of the other?

3) Write down an explicit (i.e. one you can use for computations) approximate expression for the energy of interacting electrons in the Kohn-Sham approach, using the Thomas-Fermi-Dirac orbital-free DFT model for inspiration. In actual DFT calculations this approach is called exchange-only LDA (local density approximation).

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5-minute quiz

Name :

Date :

Surname:

1) Which operator prevents the full electronic Hamiltonian from being an "non-interacting electron" Hamiltonian?

2) What is special about the system of non-interacting electrons in the Kohn-Sham DFT approach as compared to any other collection of non-interacting electrons?

3) Write down the expression used for the kinetic energy in Kohn-Sham calculations. How is this different from the exact kinetic energy functional in orbital-free DFT?

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