CHEM6085: Density Functional Theory

Lecture 5

Orbital-free (or "pure") DFT

C.-K. Skylaris

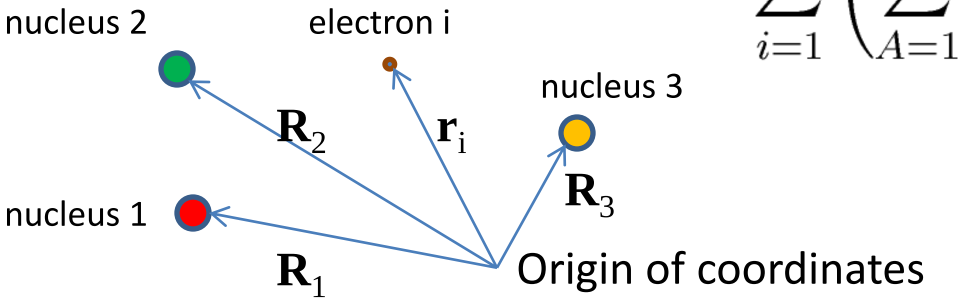
UNIVERSITY OF Southampton
School of Chemistry

The electronic Hamiltonian operator

- Consists of three terms
  - Electronic kinetic energy operator
  - Electron-Electron repulsion operator
  - Electron-nucleus attraction operator, called “**external potential**” in DFT terminology

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

$$\sum_{i=1}^{N_{\mathrm{el}}} \left(\sum_{A=1}^{N_{\mathrm{at}}} \frac{-Z_A}{|\mathbf{r}_i - \mathbf{R}_A|} \right) = \sum_{i=1}^{N_{\mathrm{el}}} V_{\mathrm{ext}}(\mathbf{r}_i)$$



The electronic energy

Conventional quantum theory

$$E_{\mathrm{el}} = \underbrace{\int \Psi^* \left(\sum_{i=1}^{N_{\mathrm{el}}} \frac{-1}{2} \nabla_i^2 \right) \Psi \, d\mathbf{X} + \int \Psi^* \left(\sum_{i=1}^{N_{\mathrm{el}}} \sum_{j=i+1}^{N_{\mathrm{el}}} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \right) \Psi \, d\mathbf{X}} + \underbrace{\int \Psi^* \left(\sum_{i=1}^{N_{\mathrm{el}}} V_{\mathrm{ext}}(\mathbf{r}_i) \right) \Psi \, d\mathbf{X}}$$

$$= \boxed{F_{HK}[n]} + \boxed{\int V_{\mathrm{ext}}(\mathbf{r}) n(\mathbf{r}) \, d\mathbf{r}} = E_{\mathrm{el}}[n]$$

Hohenberg and Kohn contribution

The electronic energy

- It is known from conventional quantum theory that the electronic energy can be (rigorously) separated to the following contributions

$$E_{\text{el}} = \int \Psi^* \left(\sum_{i=1}^{N_{\text{el}}} \frac{-1}{2} \nabla_i^2 \right) \Psi \, d\mathbf{X} + \int \Psi^* \left(\sum_{i=1}^{N_{\text{el}}} \sum_{j=i+1}^{N_{\text{el}}} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \right) \Psi \, d\mathbf{X} + \int \Psi^* \left(\sum_{i=1}^{N_{\text{el}}} V_{\text{ext}}(\mathbf{r}_i) \right) \Psi \, d\mathbf{X}$$

$$E_{\text{el}} = E_{\text{kin}} + E_{\text{Coul}} + E_{\text{x}} + E_{\text{c}} + E_{\text{ext}}$$

$$\frac{1}{2} \int \int \frac{n(\mathbf{r})\, n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \, d\mathbf{r} d\mathbf{r}'$$

$$\int V_{\text{ext}}(\mathbf{r}) n(\mathbf{r}) d\mathbf{r}$$

Where:

- kin: kinetic energy
- Coul: Coulomb energy
- x: exchange energy
- c: correlation energy
- ext: external potential energy

The electronic energy

$$E_{\mathrm{el}} = E_{\mathrm{kin}} + E_{\mathrm{Coul}} + E_{\mathrm{x}} + E_{\mathrm{c}} + E_{\mathrm{ext}}$$

$$\frac{1}{2}\int\int \frac{n(\mathbf{r})\,n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\,d\mathbf{r}\,d\mathbf{r}'$$

$$\int V_{\mathrm{ext}}(\mathbf{r})\,n(\mathbf{r})\,d\mathbf{r}$$

Where:

- kin: kinetic energy
- Coul: Coulomb energy
- x: exchange energy
- c: correlation energy
- ext: external potential energy

- The separation of the electronic energy into these components in conventional quantum theory has influenced the development of approximations for $F_{HK}[n]$ in DFT
- Therefore , it is assumed that the Hohenberg and Kohn functional can be split into a sum of functionals

$$F_{\mathrm{HK}}[n] = E_{\mathrm{kin}}[n] + E_{\mathrm{Coul}}[n] + E_{\mathrm{x}}[n] + E_{\mathrm{c}}[n]$$

Early DFT attempts: The Thomas-Fermi model

- The Hohenberg-Kohn proof for the existence of a universal functional was presented in 1964

$$E_{\mathrm{el}}[n] = F_{\mathrm{HK}}[n] + \int V_{\mathrm{ext}}(\mathbf{r})n(\mathbf{r})d\mathbf{r}$$

- However, already from 1927 Thomas and Fermi proposed the following approximate functional for the electronic energy

$$E_{\mathrm{TF}}[n] = C_1 \int n(\mathbf{r})^{\frac{5}{3}} d\mathbf{r} + \frac{1}{2}\int\int \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}d\mathbf{r}' + \int V_{\mathrm{ext}}(\mathbf{r})n(\mathbf{r})d\mathbf{r}$$

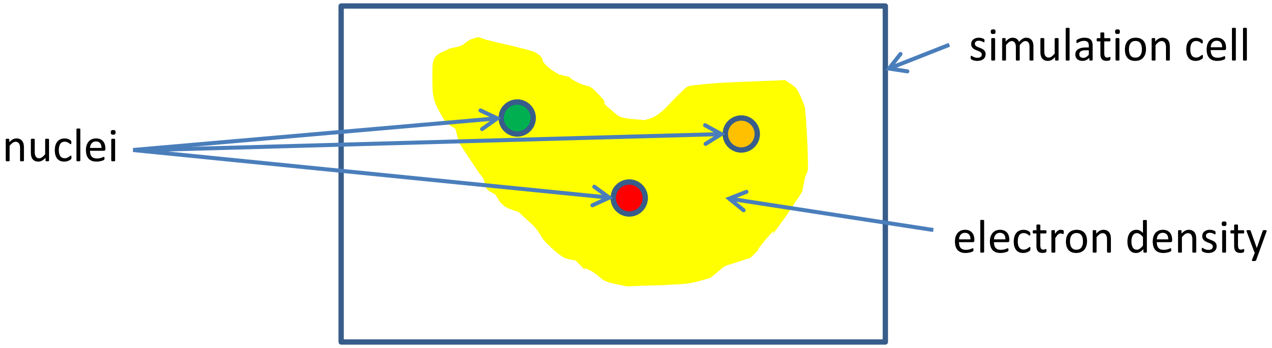
Kinetic energy of a system of non-interacting electrons with uniform density

Electrostatic energy of n(r). Also called “Coulomb” or “Hartree” energy

$$C_1 = \frac{3}{10}(3\pi^2)^{\frac{2}{3}}$$

The Uniform electron gas (or jellium) model

- A molecule (under the BO approximation) consists of nuclei (i.e. positive point charges) fixed at positions in space, and electrons that move as described by quantum theory



- The jelium model replaces the nuclei by a uniform background of positive charge. The electrons are still treated as quantum particles, moving in this medium, and hence forming a Uniform Electron Gas (UEG)

The local density approximation (LDA)

- The Thomas-Fermi model approximates the kinetic energy functional using the UEG as a model
- In the UEG there is a very large number N of electrons in a large volume V, so that the electronic density n(**r**)=N/V **is a constant**
- It turns out that the kinetic energy of the electrons in this system is proportional to $n(\mathbf{r})^{5/3}\,V$
- In the local density approximation we exploit this result, by assuming that in a real molecule, the contribution to the electronic kinetic energy from an infinitesimal volume element dV is proportional to $n(\mathbf{r})^{5/3}\,dV$
- Therefore the total electronic kinetic energy will be obtained by summing (i.e. integrating) these contributions from volume elements over all space, hence we obtain the following result

$$C_1 \int n(\mathbf{r})^{\frac{5}{3}} d\mathbf{r}$$

- This is called the Local Density Approximation and it has been also used to approximate E_X and E_c

The Thomas-Fermi-Dirac model

- A subsequent improvement was the addition of a functional for the exchange energy by Dirac (1930)

- This is the Thomas-Fermi-Dirac model

$$E_{\mathrm{TFD}}[n] = E_{\mathrm{TF}}[n] + C_2 \int n(\mathbf{r})^{\frac{4}{3}} d\mathbf{r}$$

$$E_{\mathrm{TFD}}[n] = C_1 \int n(\mathbf{r})^{\frac{5}{3}} d\mathbf{r} + \frac{1}{2} \int \int \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}d\mathbf{r}' + C_2 \int n(\mathbf{r})^{\frac{4}{3}} d\mathbf{r} + \int V_{\mathrm{ext}}(\mathbf{r}) n(\mathbf{r}) d\mathbf{r}$$

Exchange energy of uniform electron gas

$$C_2 = -\frac{3}{4}\left(\frac{3}{\pi}\right)^{\frac{1}{3}}$$

Energy terms in the DFT functional

- The DFT energy functional is usually broken up into a sum of functionals

$$E_{\text{el}}[n] = E_{\text{kin}}[n] + \underset{\underset{\displaystyle \frac{1}{2}\int\int\frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}d\mathbf{r}'}{\downarrow}}{E_{\text{Coul}}[n]} + E_x[n] + E_c[n] + \underset{\underset{\displaystyle \int V_{\text{ext}}(\mathbf{r})n(\mathbf{r})d\mathbf{r}}{\downarrow}}{E_{\text{ext}}[n]}$$

- These functionals represent well-defined types of energy that are known from wavefunction-based methods (which historically predate DFT)

- Approximations are sought for the unknown functionals:
  1. Kinetic energy $E_{\text{kin}}[n]$
  2. Exchange energy $E_x[n]$
  3. Correlation energy $E_c[n]$

How to do a DFT calculation

- Having chosen a form for our DFT energy (e.g. the Thomas-Fermi) we can perform a DFT calculation by taking advantage of the variational principle
- This involves finding the density that minimises our energy functional
- Subject to conserving the number of electrons $\int n(\mathbf{r})d\mathbf{r} = N_{el}$
- To achieve this, we need minimise with respect to the density the following expression

$$\Omega_{\mathrm{el}}[n] = E_{\mathrm{el}}[n] - \mu\left(\int n(\mathbf{r})d\mathbf{r} - N_{\mathrm{el}}\right)$$

This is called the
"Lagrangian" functional

- The minimum is reached when the **functional derivative** becomes zero

$$\frac{\delta\Omega_{\mathrm{el}}[n]}{\delta n(\mathbf{r})} = 0$$

Functional derivatives

- Let's begin with an analogy with functions of many variables, e.g.

$$F(g_1, g_2, \ldots, g_N)$$

- Assume a change in the variables

$$g_1 \longrightarrow g_1 + h_1 \qquad g_2 \longrightarrow g_2 + h_2 \qquad \cdots \qquad g_N \longrightarrow g_N + h_N$$

- The corresponding change in the function is

$$\Delta F = F(g_1 + h_1, g_2 + h_2, \ldots, h_N + g_N) - F(g_1, g_2, \ldots, g_N)$$

- You can approximate this change by using first derivatives

$$\Delta F \simeq \frac{\partial F}{\partial g_1} h_1 + \frac{\partial F}{\partial g_2} h_2 + \cdots + \frac{\partial F}{\partial g_N} h_N$$

- Consider a functional as a function of an infinite number of continuous variables.
- Use this analogy to understand functional derivatives

Function of N variables (maps N variables into a number)		Functional (maps a function into a number)
$F(g_1, g_2, \ldots, g_N)$		$F[g(x)]$
g_x	"variables"	$g(x)$
$\dfrac{\partial F}{\partial g_x}$	Derivative	$\dfrac{\delta F}{\delta g(x)}$

Change

$$\Delta F \simeq \frac{\partial F}{\partial g_1} h_1 + \frac{\partial F}{\partial g_2} h_2 + \cdots + \frac{\partial F}{\partial g_N} h_N$$

$$\Delta F \simeq \int \frac{\delta F}{\delta g(x)} h(x)\, dx$$

Formal definition of functional derivatives

- Consider the following change in the functional

$$\Delta F = F[g(x) + \epsilon\, h(x)] - F[g(x)]$$

- The functional derivative is defined by

$$\lim_{\epsilon \to 0} \frac{\Delta F}{\epsilon} = \int \frac{\delta F}{\delta g(x)} h(x)\, dx$$

- The functional derivative $\frac{\delta F}{\delta g(x)}$ exists if the above limit is defined for **any** well-behaved function *h(x)*

Simplest case

- The simplest kind of **functional**, has the form:

$$F[g] = \int f(g(x))dx$$

where ***f*** is just an ordinary **function.** We often work with such functionals.

- The formula for the functional derivative gives:

$$\Delta F = F[g(x) + \epsilon\, h(x)] - F[g(x)] = \int f(g(x) + \epsilon h(x))dx - \int f(g(x))dx$$

$$= \int \{f(g(x) + \epsilon h(x)) - f(g(x))\}\, dx$$

$$\lim_{\epsilon \to 0} \frac{\Delta F}{\epsilon} = \int \lim_{\epsilon \to 0} \frac{f(g(x) + \epsilon h(x)) - f(g(x))}{\epsilon h(x)} h(x)dx = \int \frac{d\, f(g(x))}{d\, g(x))} h(x)dx$$

- So, the functional derivative in this case turns out to be the derivative of function ***f*** with respect to function ***g*** (treated as a variable of ***f***)

$$\frac{\delta F[g]}{\delta g(x)} = \frac{d\, f(g(x))}{d\, g(x)}$$

How to do a DFT calculation (continued)

- Minimise with respect to the density the "Lagrangian" (energy plus the constraint for the number of electrons)

$$\Omega_{\mathrm{el}}[n] = E_{\mathrm{el}}[n] - \mu\left(\int n(\mathbf{r})d\mathbf{r} - N_{\mathrm{el}}\right)$$

- This happens when the functional derivative is zero

$$\frac{\delta\Omega_{\mathrm{el}}[n]}{\delta n(\mathbf{r})} = 0$$

- So the following equation needs to be solved for the density

$$\frac{\delta E_{\mathrm{el}}}{\delta n(\mathbf{r})} - \mu = 0$$

Calculations with the TF model

- The Lagrangian functional is

$$\Omega_{\mathrm{TF}}[n] = C_1 \int n(\mathbf{r})^{\frac{5}{3}} d\mathbf{r} + \frac{1}{2} \int \int \frac{n(\mathbf{r}) n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' + \int V_{\mathrm{ext}}(\mathbf{r}) n(\mathbf{r}) d\mathbf{r} - \mu \left(\int n(\mathbf{r}) d\mathbf{r} - N_{\mathrm{el}} \right)$$

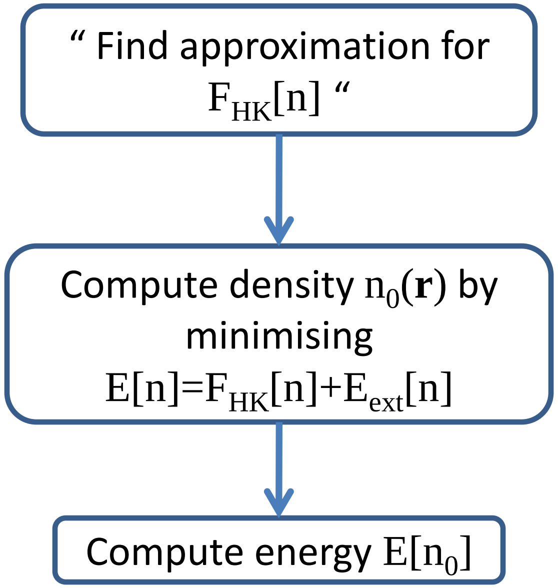
- Which leads to the following equation for the density

$$C_1 \frac{5}{3} n(\mathbf{r})^{2/3} + \int \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + V_{\mathrm{ext}}(\mathbf{r}) - \mu = 0$$

- Notice that the above equation contains a functional of the density, so it needs to be solved in an iterative way (how?)

How to do a DFT calculation (continued)

(Orbital-free approach)



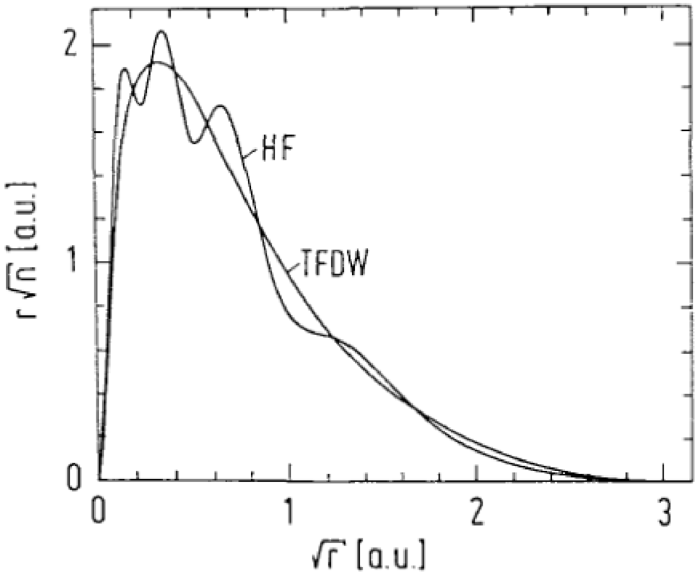
“ Find approximation for $F_{HK}[n]$ “

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

Compute energy $E[n_0]$

Is orbital-free DFT useful for molecular calculations?

- TFD predicts that atoms always repel each other, so all molecules are unstable and prefer to dissociate
- Even for isolated atoms, the shell structure is missing



Hartree-Fock and TFDW density of the Kr atom(from W. Stich, E.K.U. Gross and R. M. Dreizler. *Z. Phys. A – Atoms and Nuclei* **309**, 5-11 (1982)) .

Progress in orbital-free DFT

- Improvements in the TFD model included a modified version of the kinetic energy functional which includes the gradient of the density (von Weizsacker correction)
- Orbital-free DFT is currently an active area of research (for example, see *Chem. Phys. Lett.* **473** (2009) 263, and references therein)
- Its great advantage is its simplicity
- However its accuracy is still too low for most kinds of chemistry and materials simulation
- This is mainly due to the lack of sufficiently accurate approximations for the kinetic energy functional
- The breakthrough that allows us to do DFT calculations today with high accuracy is called Kohn-Sham DFT
- Kohn-Sham DFT involves the use of molecular orbitals, so it does not have the simplicity of orbital-free DFT
- The rest of this course will focus on Kohn-Sham DFT

Homework

1) Use the definition of functional derivatives to obtain an expression for the functional derivative of the Coulomb energy. Does this represent any electrostatic property of the charge density?

2) Compare the dimensions of the kinetic energy in terms of wavefunctions with the kinetic energy functional $\int n(\mathbf{r})^{\frac{5}{3}} d\mathbf{r}$ and show that for these two expressions to be compatible the density in the functional can only appear raised to the power of 5/3 and no other power.

3) Write down the equations for the calculation on the density with the TFD model (similar to the equations for the TF model on slide 11).

5-minute quiz

Name :
Surname:

Date :

1) Name the types of energy that are usually represented as individual DFT functionals in orbital-free DFT

2) Match these energies with the energies in which the electronic Hamiltonian operator is divided

3) What are the dimensions (e.g. L^{-1}, where L is length) of the density and of the wavefunction?

UNIVERSITY OF Southampton
School of Chemistry