

CHEM6085: Density Functional Theory

Lecture 4

Density instead of the wavefunction

The Hohenberg-Kohn justification

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Functions and functionals

- A **function** takes a number as input and outputs a number.

Examples:

$$f(x) = x^2$$

$$g(x, y) = \cos(x) + e^{-3\sqrt{x^2+y^2}}$$

- A **functional** takes an entire function as input and outputs a number.

Examples:

$$F[f] = \int_{-\infty}^{\infty} f^3(x) dx$$

$$H[g] = \int_2^3 \int_{-10}^4 \left(\frac{\partial^2 g(x, y)}{\partial x^2} - 2.3 g(x, y) \right) dx dy$$

Can you suggest other examples of functionals?

Can we express the energy directly in terms of the density?

Not really... The Hamiltonian operator for the electrons is:

$$\begin{aligned}\hat{H}_{\text{el}} &= \sum_{i=1}^{N_{\text{el}}} -\frac{1}{2}\nabla_i^2 + \sum_{i=1}^{N_{\text{el}}} \sum_{j=i+1}^{N_{\text{el}}} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} + \sum_{i=1}^{N_{\text{el}}} \sum_{A=1}^{N_{\text{at}}} \frac{-Z_A}{|\mathbf{r}_i - \mathbf{R}_A|} \\ &= \sum_{i=1}^{N_{\text{el}}} -\frac{1}{2}\nabla_i^2 + \sum_{i=1}^{N_{\text{el}}} \sum_{j=i+1}^{N_{\text{el}}} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} + \sum_{i=1}^{N_{\text{el}}} V_{\text{ext}}(\mathbf{r}_i)\end{aligned}$$

The electronic energy is the expectation (average) value of the operator:

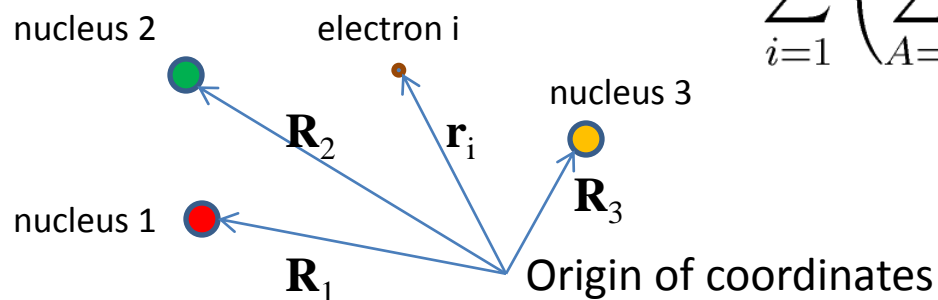
$$E_{\text{el}} = \int \cdots \int \Psi^* \hat{H}_{\text{el}} \Psi d\mathbf{x}_1 \cdots d\mathbf{x}_{N_{\text{el}}}$$

The external potential

- The nuclear attraction energy part of the electronic Hamiltonian operator is called “external potential” in DFT
- “External” because due to the BO approximation we are doing a quantum calculation only on the electrons so the nuclei are “external” fixed objects which exert their Coulomb potential to the electrons

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

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



Electronic energy components

$$E_{\text{el}} = \int \cdots \int \Psi^* \hat{H}_{\text{el}} \Psi d\mathbf{x}_1 \cdots d\mathbf{x}_{N_{\text{el}}}$$
$$= \int \cdots \int \Psi^* \left(\sum_{i=1}^{N_{\text{el}}} -\frac{1}{2} \nabla_i^2 \right) \Psi d\mathbf{x}_1 \cdots d\mathbf{x}_{N_{\text{el}}} + \int \cdots \int \Psi^* \left(\sum_{i=1}^{N_{\text{el}}} \sum_{j=i+1}^{N_{\text{el}}} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \right) d\mathbf{x}_1 \cdots d\mathbf{x}_{N_{\text{el}}}$$
$$+ \int \cdots \int \Psi^* \left(\sum_{i=1}^{N_{\text{el}}} V_{\text{ext}}(\mathbf{r}_i) \right) \Psi d\mathbf{x}_1 \cdots d\mathbf{x}_{N_{\text{el}}}$$

only this can be written as an explicit functional of the density

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

Show this!

The variational principle of Quantum Theory

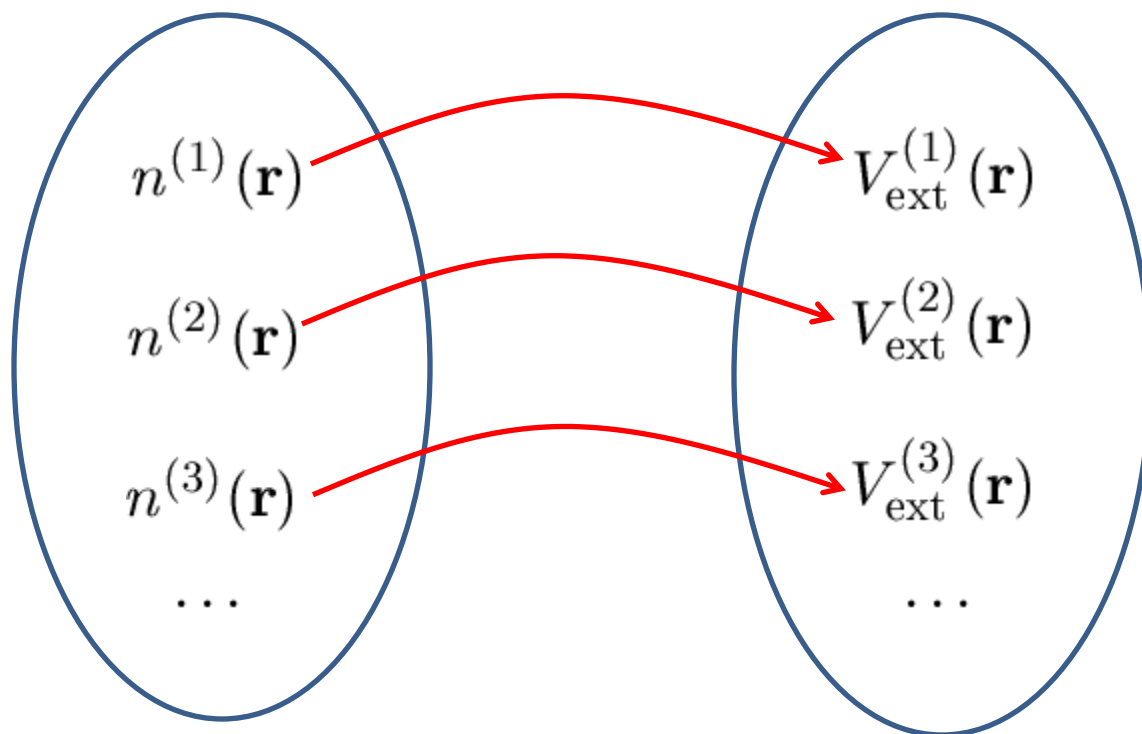
- The Hamiltonian operator is Hermitian
- Using the properties of Hermitian operators you can show that the energy calculated with any **approximate** wavefunction will be **larger than or equal to** the **exact ground state energy**

$$E_{\text{exact}} = \frac{\int \Psi_{\text{exact}}^* \hat{H} \Psi_{\text{exact}} dx}{\int \Psi_{\text{exact}}^* \Psi_{\text{exact}} dx} \leq \frac{\int \Psi_{\text{approx}}^* \hat{H} \Psi_{\text{approx}} dx}{\int \Psi_{\text{approx}}^* \Psi_{\text{approx}} dx} = E_{\text{approx}}$$

- The equality above holds only when $\Psi_{\text{approx}} = \Psi_{\text{exact}}$
- All the computational techniques we will study in this course make use of the variational principle: the lower the energy, the better the approximation

Relation between electronic density and external potential

- For a given number of electrons, different densities correspond to different nuclear positions and/or atomic numbers and hence to different external potentials and electronic Hamiltonians



- To be able to have a quantum theory based on the density, the opposite must also be true but this is not obvious

Hohenberg -Kohn Density Functional Theory

P. Hohenberg and W. Kohn, *Phys. Rev.* **136**, B864 (1964)

- A quantum theory where the density replaces the wavefunction as the central quantity
- Based on an “existence proof”: such a “Density Functional Theory” exists, but the actual expressions for the computation of the density, energy, etc, are unknown (This is the first H-K theorem)
- In this form it is not practically useful, but it does provide the first step for deriving the computational techniques on which DFT is based
- These techniques make use of a variational principle for DFT, which is known as the second H-K theorem
- These theorems are considered to be amongst the greatest developments in quantum theory since the Schrödinger equation in 1926

Hohenberg -Kohn Density Functional Theory

- Start with two external potentials that differ by more than a constant, so that their full electronic Hamiltonians are:

$$\hat{H}_{\text{el}}^{(1)} = \hat{T}_{\text{el}} + \hat{V}_{ee} + \sum_{i=1}^{N_{\text{el}}} V_{\text{ext}}^{(1)}(\mathbf{r}_i) \quad \hat{H}_{\text{el}}^{(2)} = \hat{T}_{\text{el}} + \hat{V}_{ee} + \sum_{i=1}^{N_{\text{el}}} V_{\text{ext}}^{(2)}(\mathbf{r}_i)$$

- The difference between the Hamiltonian operators is:

$$\hat{H}_{\text{el}}^{(1)} - \hat{H}_{\text{el}}^{(2)} = \sum_{i=1}^{N_{\text{el}}} [V_{\text{ext}}^{(1)}(\mathbf{r}_i) - V_{\text{ext}}^{(2)}(\mathbf{r}_i)]$$

Hohenberg -Kohn Density Functional Theory

- Since the two electronic Hamiltonians differ by more than a constant, the solutions of their Schrödinger equations will lead to different wavefunctions and energies:

$$\hat{H}_{\text{el}}^{(1)} \Psi^{(1)} = E_{\text{el}}^{(1)} \Psi^{(1)} \quad \hat{H}_{\text{el}}^{(2)} \Psi^{(2)} = E_{\text{el}}^{(2)} \Psi^{(2)}$$

- Nevertheless, let's assume that their corresponding **different** ground-state wavefunctions produce the **same** density

$$n(\mathbf{r}) = N_{\text{el}} \int \cdots \int \Psi^{(1)*} \Psi^{(1)} d\omega_1 d\mathbf{x}_2 \cdots d\mathbf{x}_{N_{\text{el}}} = N_{\text{el}} \int \cdots \int \Psi^{(2)*} \Psi^{(2)} d\omega_1 d\mathbf{x}_2 \cdots d\mathbf{x}_{N_{\text{el}}}$$

- Apply the variational theorem treating $\Psi^{(2)}$ as an approximate wavefunction for Hamiltonian $H^{(1)}$:

$$E_{\text{el}}^{(1)} = \int \Psi^{(1)*} \hat{H}_{\text{el}}^{(1)} \Psi^{(1)} d\mathbf{X} < \int \Psi^{(2)*} \hat{H}_{\text{el}}^{(1)} \Psi^{(2)} d\mathbf{X}$$

$$\begin{aligned} \int \Psi^{(2)*} \hat{H}_{\text{el}}^{(1)} \Psi^{(2)} d\mathbf{X} &= \int \Psi^{(2)*} \hat{H}_{\text{el}}^{(2)} \Psi^{(2)} d\mathbf{X} + \int \Psi^{(2)*} \left(\hat{H}_{\text{el}}^{(1)} - \hat{H}_{\text{el}}^{(2)} \right) \Psi^{(2)} d\mathbf{X} \\ &= E_{\text{el}}^{(2)} + \int \left[V_{\text{ext}}^{(1)}(\mathbf{r}) - V_{\text{ext}}^{(2)}(\mathbf{r}) \right] n(\mathbf{r}) d\mathbf{r} \end{aligned}$$

- We showed that:

$$E_{\text{el}}^{(1)} < E_{\text{el}}^{(2)} + \int \left[V_{\text{ext}}^{(1)}(\mathbf{r}) - V_{\text{ext}}^{(2)}(\mathbf{r}) \right] n(\mathbf{r}) d\mathbf{r}$$

- We showed that

$$E_{\text{el}}^{(1)} < E_{\text{el}}^{(2)} + \int \left[V_{\text{ext}}^{(1)}(\mathbf{r}) - V_{\text{ext}}^{(2)}(\mathbf{r}) \right] n(\mathbf{r}) d\mathbf{r}$$

- In exactly the same way, by treating $\Psi^{(1)}$ as an approximate wavefunction for Hamiltonian $H^{(2)}$ we can also show

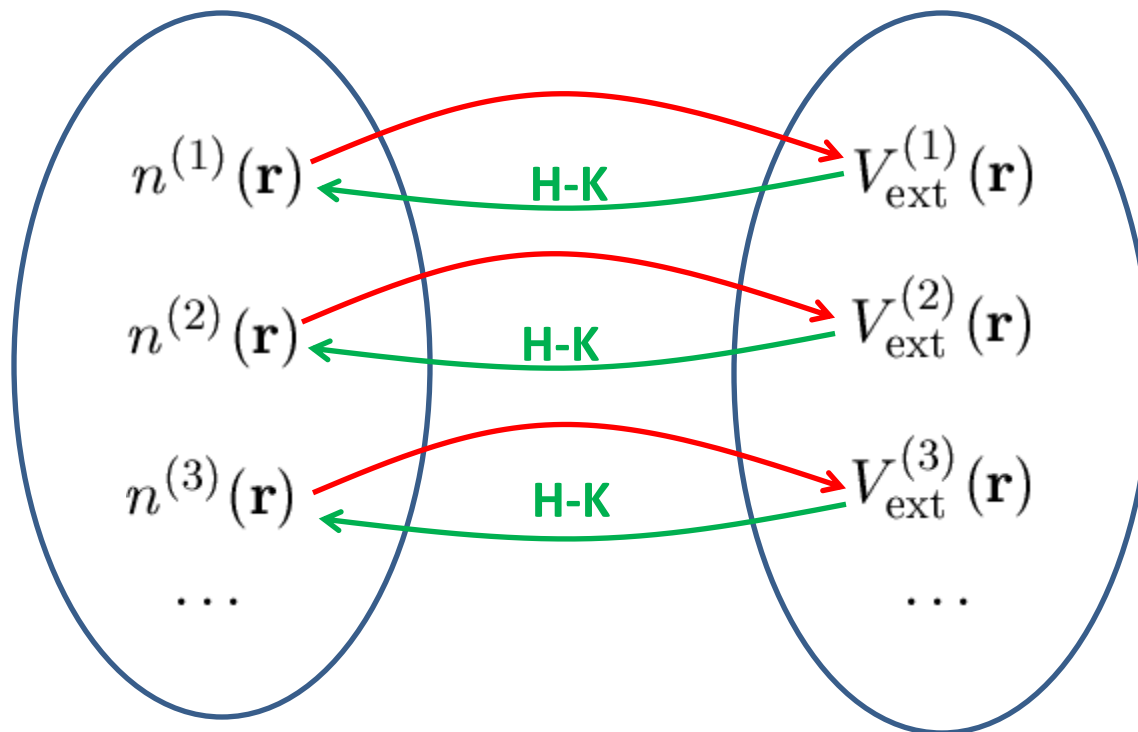
$$E_{\text{el}}^{(2)} < E_{\text{el}}^{(1)} + \int \left[V_{\text{ext}}^{(2)}(\mathbf{r}) - V_{\text{ext}}^{(1)}(\mathbf{r}) \right] n(\mathbf{r}) d\mathbf{r}$$

- By adding the above two equations we obtain

$$E_{\text{el}}^{(1)} + E_{\text{el}}^{(2)} < E_{\text{el}}^{(1)} + E_{\text{el}}^{(2)}$$

which is obviously **not possible** (proof by contradiction).

- Therefore, different external potentials will always produce different densities
- We have just shown that **there is a one-to-one correspondence between densities and external potentials** (this is the first H-K theorem)



It should therefore be possible to write the electronic energy entirely as a functional of the density

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

The diagram shows three red brackets under the three terms of the energy equation. The first two brackets are connected by a horizontal line that then splits into two arrows pointing to the $F_{\text{HK}}[n]$ box in the simplified equation below. The third bracket is connected by a horizontal line that then splits into one arrow pointing to the $\int V_{\text{ext}}(\mathbf{r})n(\mathbf{r}) d\mathbf{r}$ box in the simplified equation below.

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

- Therefore Hohenberg and Kohn showed that a **universal functional** (does not depend on external potential) $F_{\text{HK}}[n]$ exists
- Unfortunately, no explicit formula is known for this functional

Variational principle for the density

- A variational theorem for the density follows directly from the variational theorem for the wavefunctions

$$\int \Psi^{(1)*} \hat{H}_{\text{el}}^{(1)} \Psi^{(1)} d\mathbf{X} \leq \int \Psi^* \hat{H}_{\text{el}}^{(1)} \Psi d\mathbf{X}$$

$$E_{\text{el}}^{(1)}[n^{(1)}] \leq E_{\text{el}}^{(1)}[n]$$

- Only the ground state density $n^{(1)}$ of $H_{\text{el}}^{(1)}$ minimises the value of its ground state energy functional (this is the second H-K theorem)

DFT calculations with the Hohenberg-Kohn approach

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

- We need an expression for the functional $F_{\text{HK}}[n]$ (even an approximate expression)
- Based on the variational principle for the density we can then calculate the electronic energy by searching for the density that minimises $E_{\text{el}}[n]$
- This is the simplest way to do DFT calculations (often called “pure DFT”)
- We will examine it, with examples, in the next lecture

Homework

- 1) If you knew the exact form of $F_{\text{HK}}[n]$ can you suggest practical ways in which you could vary $n(\mathbf{r})$ in order to minimise $E_{\text{el}}[n]$ according to the variation theorem? Would you need to impose any constraints to $n(\mathbf{r})$ during this minimisation procedure?
- 2) In addition to the external potential operator, can you suggest other quantum theory operators whose expectation values can be explicitly written as functionals of the density?
- 3) First read and then repeat on paper (so that you understand all steps) the derivation of the variational principle from one of the textbooks

5-minute quiz

Name :
Surname:

Date :

- 1) Why it is preferable to work with the density rather than the electronic wavefunction?
- 2) If you were to write down $F_{HK}[n]$ as a sum of functionals, what type of energy would you represent with each functional in the sum?
- 3) Do either of $F_{HK}[n]$ or $\int V_{\text{ext}}(\mathbf{r}) n(\mathbf{r}) d\mathbf{r}$ depend on the positions of the nuclei? If yes, write their explicit form for the case of a He atom whose nucleus is centred at point \mathbf{R}