

Density Functional Theory

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Outline

- Start with Hatree-Fock
- Introduce Hohenberg-Kohn theorems
- Derive the DFT equations

HF in language of second quantization

Define Hamiltonian

$$H = \int d^3 r \frac{\hbar^2}{2m} \nabla \psi^\dagger(\mathbf{r}) \cdot \nabla \psi(\mathbf{r}) + \frac{1}{2} \int d^3 r \int d^3 r' \frac{e^2}{|\mathbf{r} - \mathbf{r}'|} \psi^\dagger(\mathbf{r}) \psi^\dagger(\mathbf{r}') \psi(\mathbf{r}') \psi(\mathbf{r}) + \int d^3 r V_{ext}(\mathbf{r}) \psi^\dagger(\mathbf{r}) \psi(\mathbf{r})$$

$$|N\rangle = \prod_a^N c_a^\dagger |0\rangle - \text{Slater Determinant}, \quad \psi^\dagger(\mathbf{r}') = \sum_a c_a^\dagger \phi_a^*(\mathbf{r}'), \quad \psi(\mathbf{r}') = \sum_a \phi_a(\mathbf{r}') c_a$$

Next, calculate $\langle N|H|N\rangle$

$$\begin{aligned} \langle N|H|N\rangle &= \sum_a^N \frac{\hbar^2}{2m} \int d^3 r \nabla \phi_a^*(\mathbf{r}) \cdot \nabla \phi_a(\mathbf{r}) + \frac{1}{2} \int d^3 r \int d^3 r' \frac{e^2}{|\mathbf{r} - \mathbf{r}'|} n(\mathbf{r}) n(\mathbf{r}') - \\ &\quad - \sum_{a < b}^N \left[\int d^3 r \int d^3 r' \frac{e^2}{|\mathbf{r} - \mathbf{r}'|} \phi_a^*(\mathbf{r}) \phi_a(\mathbf{r}') \phi_b^*(\mathbf{r}') \phi_b(\mathbf{r}) \right] + \int d^3 r V_{ext}(\mathbf{r}) n(\mathbf{r}) \end{aligned}$$

Minimize w.r.t. $\phi(\mathbf{r})$ under constraint $\int d^3 r \phi_a^*(\mathbf{r}) \phi_a(\mathbf{r}) = 1$

$$\begin{aligned} & - \frac{\hbar^2}{2m} \nabla^2 \phi_a(\mathbf{r}) + \int d^3 r' \frac{e^2}{|\mathbf{r} - \mathbf{r}'|} n(\mathbf{r}') \phi_a(\mathbf{r}) - \sum_b \int d^3 r' \frac{e^2}{|\mathbf{r} - \mathbf{r}'|} \phi_a(\mathbf{r}') \phi_b^*(\mathbf{r}') \phi_b(\mathbf{r}) + \\ & + V_{ext}(\mathbf{r}) \phi_a(\mathbf{r}) = \epsilon_\alpha \phi_a(\mathbf{r}) \end{aligned}$$

Hartree-Fock Theory

- Write the Hamiltonian as a sum of Fock operators

$$\hat{H} = \sum_i f_i \quad f_i = -\frac{1}{2} \nabla_i^2 - \sum_{A=1}^M \frac{Z_A}{r_{iA}} + v_i^{\text{HF}}$$

where the Hartree-Fock potential is defined in terms of coulomb and exchange operators

$$v_i^{\text{HF}} = \sum_b [J_b(i) - K_b(i)]$$

$$\langle \chi_a(1) | J_b(1) | \chi_a(1) \rangle = \int dx_1 dx_2 \chi_a^*(1) \chi_a(1) r_{12}^{-1} \chi_b^*(2) \chi_b(2) \quad \text{Coulomb integral}$$

$$\langle \chi_a(1) | K_b(1) | \chi_a(1) \rangle = \int dx_1 dx_2 \chi_a^*(1) \chi_b(1) r_{12}^{-1} \chi_b^*(2) \chi_a(2) \quad \text{Exchange integral}$$

- Use the variational and langrangian methods to arrive at

$$f_i \sum_{v=1}^K |\varphi_v\rangle C_v^i = \varepsilon \sum_{v=1}^K |\varphi_v\rangle C_v^i \quad |\chi(x_i)\rangle = \begin{cases} |\psi_i(\underline{r})\rangle \alpha(\omega) \\ |\psi_i(\underline{r})\rangle \beta(\omega) \end{cases} \quad \mathbf{F}'\mathbf{C}' = \mathbf{C}'\mathbf{E}$$



Douglas Rayner Hartree
English
1897-1958



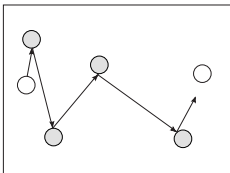
Vladimir Aleksandrovich Fock
Russian 1898-1974

The Hartree-Fock Equations

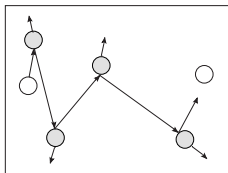
$$-\frac{\hbar^2}{2m}\nabla^2\phi_a(\mathbf{r}) + \int d^3r' \frac{e^2}{|\mathbf{r}-\mathbf{r}'|} n(\mathbf{r}')\phi_a(\mathbf{r}) - \sum_b \int d^3r' \frac{e^2}{|\mathbf{r}-\mathbf{r}'|} \phi_a(\mathbf{r}')\phi_b^*(\mathbf{r}')\phi_b(\mathbf{r}) + V_{ext}(\mathbf{r})\phi_a(\mathbf{r}) = \epsilon_\alpha\phi_a(\mathbf{r}), \quad \epsilon_\alpha - \text{total energy of system}$$

$\phi_a(\mathbf{r})$ – single particle wave functions, $n(\mathbf{r}) = \sum_a^N \phi_a^*(\mathbf{r})\phi_a(\mathbf{r})$ – density

- Variational principle applied to expectation value of the Hamiltonian - $\langle N|H|N\rangle$
- $|N\rangle \rightarrow$ allows all wave functions that can be represented by a Slater determinant \Rightarrow **No Correlation**



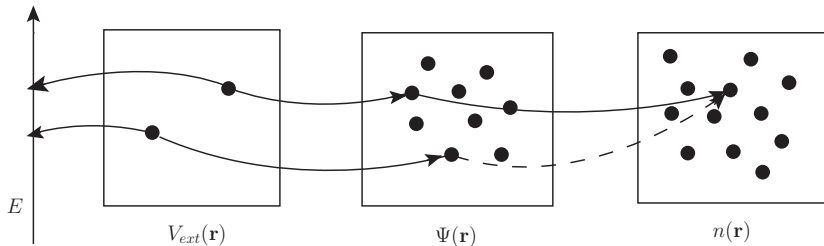
No Correlation



Correlation

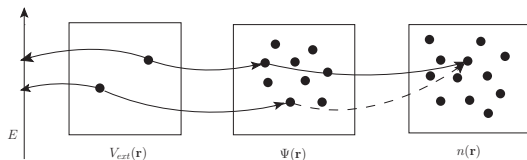
Hohenberg-Kohn Theorem 1

The ground state density $n(\mathbf{r})$ of a many-electron system uniquely determines the many-body wave function $\Psi(\mathbf{r})$ and the potential $V_{ext}(\mathbf{r})$



- **Unique density** for each external potential $V_{ext}(\mathbf{r})$.
Dashed mapping is impossible if another mapping exists.

Hohenberg-Kohn Theorem 1 - Proof



$$H = H_0 + V_{ext}:$$

H_0 - electron kinetic energy + electron-electron interaction ($T + V_{ee}$)

V_{ext} - interaction with external field

Ψ - ground state wave function

$E = \langle \Psi | H_0 + V_{ext} | \Psi \rangle$ - ground state energy

$n(\mathbf{r}) = \langle \Psi | \psi^\dagger(\mathbf{r})\psi(\mathbf{r}) | \Psi \rangle$ - ground state density

Could another Hamiltonian, differing only in V_{ext} ($H = H_0 + V'_{ext}$), have the same ground state density?

Hohenberg-Kohn Theorem 1 - Proof

Suppose V'_{ext} and Ψ' exist such that $n'(\mathbf{r}) = n(\mathbf{r})$ with ground state energy $E' = \langle \Psi' | H_0 + V'_{ext} | \Psi' \rangle$,

$$\Rightarrow \langle \Psi | H_0 + V'_{ext} | \Psi \rangle > E'$$

$$\Rightarrow \langle \Psi | H_0 + V'_{ext} + V_{ext} - V_{ext} | \Psi \rangle > E'$$

$$\Rightarrow \langle \Psi | H_0 + V_{ext} | \Psi \rangle + \langle \Psi | V'_{ext} - V_{ext} | \Psi \rangle > E'$$

$$\Rightarrow E + \langle \Psi | V'_{ext} - V_{ext} | \Psi \rangle > E'$$

now let's start with $E = \langle \Psi | H_0 + V_{ext} | \Psi \rangle$

$$\Rightarrow \langle \Psi' | H_0 + V_{ext} | \Psi' \rangle > E$$

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$$\Rightarrow E' + \langle \Psi' | V_{ext} - V'_{ext} | \Psi' \rangle > E$$

but we assumed $n'(\mathbf{r}) = n(\mathbf{r}) \Rightarrow \langle \Psi' | \hat{O}(\mathbf{r}) | \Psi' \rangle = \langle \Psi | \hat{O}(\mathbf{r}) | \Psi \rangle = \int n(\mathbf{r}) \hat{O}(\mathbf{r})$
therefore we have so far deduced:

$$\underline{E > E' - \int n(\mathbf{r}) \hat{O}(\mathbf{r})} \text{ and } \underline{E < E' - \int n(\mathbf{r}) \hat{O}(\mathbf{r})} - \text{contradiction}$$

Hohenberg-Kohn Theorem 2

The ground state energy can be obtained variationally: the density that minimizes the total energy is the exact ground state density.

Proof:

The ground state energy E can be obtained by the ground state density $n(\mathbf{r})$,

but since there is a unique mapping between $n(\mathbf{r})$, V_{ext} and Ψ ,

$$E = \langle \Psi[n(\mathbf{r})] | H_0 + V_{ext} | \Psi[n(\mathbf{r})] \rangle < \langle \Psi'[n'(\mathbf{r})] | H_0 + V_{ext} | \Psi'[n'(\mathbf{r})] \rangle = E'$$

and since $n(\mathbf{r})$ determines V_{ext} and Ψ , and therefore E ,

the density which minimizes $E[n(\mathbf{r})]$ is the exact ground state density \Rightarrow

\Rightarrow one can apply the variational principle to obtain exact ground state density and energy.

Hohenberg-Kohn Theorem 3

The kinetic and electron-electron interaction energies ($H_0[n] = T[n] + V_{ee}[n]$) are described by a universal functional.

$H_0[n] = T[n] + V_{ee}[n]$ is independent of $V_{ext}(\mathbf{r})$

$V_{ext}(\mathbf{r})$ is system dependent and $V_{ext}[n(\mathbf{r})] = \int d^3r n(\mathbf{r}) V_{ext}(\mathbf{r})$

DFT from the Hohenberg-Kohn Theorems

- Express the expectation value of your Hamiltonian - $\langle \Psi | H_0 + V_{ext} | \Psi \rangle$ in terms of the density $n(\mathbf{r})$
- Apply the variational principle and minimize the Energy as a functional of the density w.r.t. the density under the constraint that you have a fixed number of particles

$$N = \int n(\mathbf{r}) d^3(\mathbf{r}), \quad \left[\frac{\delta E[n(\mathbf{r})]}{\delta n(\mathbf{r})} - \mu = 0 \right]$$

- Obtain equations (Kohn-Sham eqs.) that are exact for the ground state energy and density *regardless of your initial ansatz for Ψ*
- You can now account for **correlation** effects even with Slater determinant ansatz, provided that you find the appropriate energy functional $E[n(\mathbf{r})]$

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Going back to HF

Define Hamiltonian

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Not functionals of the density!

First attempt at DFT - Thomas-Fermi theory

- Rewrite kinetic term $\left(T[\phi(\mathbf{r})] = \sum_a^N \frac{\hbar^2}{2m} \int d^3r \frac{\hbar^2}{2m} \nabla \phi_a^*(\mathbf{r}) \cdot \nabla \phi_a(\mathbf{r}) \right)$ in terms of density. Consider free electron gas and integrate single electron kinetic energy over Fermi sphere.

$$\text{Result is } T[n(\mathbf{r})] = \int d^3r \frac{3}{10} \frac{\hbar^2 (3\pi^2)^{2/3}}{m} n^{5/3}(\mathbf{r})$$

- Neglect exchange term

$$E_x[\phi(\mathbf{r})] = \sum_{a < b}^N \left[\int d^3r \int d^3r' \frac{e^2}{|\mathbf{r} - \mathbf{r}'|} \phi_a^*(\mathbf{r}) \phi_a(\mathbf{r}') \phi_b^*(\mathbf{r}') \phi_b(\mathbf{r}) \right]$$

- Obtain energy functional that only depends on density

$$E[n(\mathbf{r})] = \int d^3r \left[\frac{3}{10} \frac{\hbar^2 (3\pi^2)^{2/3}}{m} n^{5/3}(\mathbf{r}) + \frac{1}{2} \int d^3r' \frac{e^2}{|\mathbf{r} - \mathbf{r}'|} n(\mathbf{r}) n(\mathbf{r}') + V_{ext}(\mathbf{r}) n(\mathbf{r}) \right]$$

→ Minimize w.r.t. density under constraint $N = \int n(\mathbf{r}) d^3(\mathbf{r})$

→ Thomas-Fermi theory

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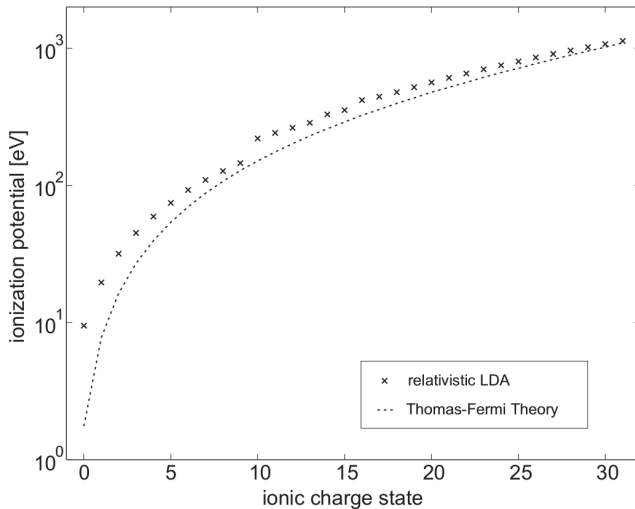
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platinum atomic ionization potential



Improving on Thomas-Fermi

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Improving on Thomas-Fermi theory

- Assume we have been able to write the kinetic energy functional in terms of density - $T[n(\mathbf{r})]$.
- Assume we have been able to write the exchange term $\sum_{a < b}^N \left[\int d^3 r \int d^3 r' \frac{e^2}{r-r'} \phi_a^*(\mathbf{r}) \phi_a(\mathbf{r}') \phi_b^*(\mathbf{r}') \phi_b(\mathbf{r}) \right]$ in terms of density - $E_{exc}[n(\mathbf{r})]$.
- Assume we have been able to come up with a term that accounts for correlations which we can also express in terms of the density - $E_{corr}[n(\mathbf{r})]$
- These are both *ad hoc* terms so in practice one introduces a term that accounts for both - $E_{xc}[n(\mathbf{r})]$
- $E[n(\mathbf{r})] = T[n(\mathbf{r})] + \frac{1}{2} \int d^3 r \int d^3 r' \frac{e^2}{r-r'} n(\mathbf{r}) n(\mathbf{r}') + E_{xc}[n(\mathbf{r})] + \int d^3 r V_{ext}(\mathbf{r}) n(\mathbf{r})$

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- Assume we have been able to write the exchange term $\sum_{a < b}^N \left[\int d^3 r \int d^3 r' \frac{e^2}{|\mathbf{r} - \mathbf{r}'|} \phi_a^*(\mathbf{r}) \phi_a(\mathbf{r}') \phi_b^*(\mathbf{r}') \phi_b(\mathbf{r}) \right]$ in terms of density - $E_{exc}[n(\mathbf{r})]$.
- Assume we have been able to come up with a term that accounts for correlations which we can also express in terms of the density - $E_{corr}[n(\mathbf{r})]$
- These are both *ad hoc* terms so in practice one introduces a term that accounts for both - $E_{xc}[n(\mathbf{r})]$
- $E[n(\mathbf{r})] = T[n(\mathbf{r})] + \frac{1}{2} \int d^3 r \int d^3 r' \frac{e^2}{|\mathbf{r} - \mathbf{r}'|} n(\mathbf{r}) n(\mathbf{r}') + E_{xc}[n(\mathbf{r})] + \int d^3 r V_{ext}(\mathbf{r}) n(\mathbf{r})$

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$$\left[\frac{\delta E[n(\mathbf{r})]}{\delta n(\mathbf{r})} - \mu = 0 \right]$$

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