Density Functional Theory

-an introduction-

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Introduction

QM System with N electrons is described by the Schrödinger equation:

$$\left(\hat{T} + \hat{V}_{e-e} + \hat{V}_{e-n}\right)|\Psi_N\rangle = E|\Psi_N\rangle \tag{1}$$

- $\hat{T}$, $\hat{V}_{e-e}$: kinetic engery, electron-electron-interaction.
- $\hat{V}_{e-n}$: external potential.
- $\hat{V}_{e-n} \Rightarrow \hat{H} \Rightarrow |\Psi_N\rangle \Rightarrow$ **Observables** (E,...).
- problem: size limitation, complexity
- **Hartree-Fock-Theory:** Map N-particle problem to one-particle problem by a special Ansatz for $|\Psi_N\rangle$.
- **Density Functional Theory:** the density uniquely determines the energy of the ground state and ist the primary variable.

Hartree-Fock Theory

- Hartree-Fock-Equations: similiar to Kohn-Sham-Equations (DFT).
- Ritz variational principle: absolute minimum of energy-function for ground-state.
- Ansatz: $|\psi\rangle = \frac{1}{\sqrt{N!}} \det(\phi_i(x_j))$ with single-particle wave functions.
- $\Rightarrow$ find the states that minimize $E = \frac{\langle\psi|H|\psi\rangle}{\langle\Psi|\Psi\rangle}$.
- equations for ϕ_i: $\left[-\frac{\hbar^2}{2m}\nabla^2 + \hat{V}_{HF}\right] \phi_i(\vec{r}) = \epsilon_i \phi_i(\vec{r})$.
- with $\hat{V}_{HF} = \hat{V}_{ext} + \hat{V}_{coul} + \hat{V}_{Fock}$.
- N coupled differential equations for the optimal single-particle wave functions.
- Hartree-Term $\hat{V}_{coul}$: potential energy in the field of the electrons $\Rightarrow$ selfconsistency.
- Fock-Term: (nonloacal) correlation engergy of the electrons (same spin).

Hohenberg-Kohn-Theorems

1. **Correspondance of density and external potenial**

   For a non-degenerate ground-state, the external potential $V(\vec{r})$ is determined (within a trivial additive constant) by the electron density $\rho(\vec{r})$.
   Since $\rho(\vec{r})$ determines N, $\rho(\vec{r})$ determines $|\Psi_N\rangle$.

2. **Variational principle**

   For a trial density $\tilde{\rho}(\vec{r})$ with $\tilde{\rho}(\vec{r}) \geq 0$ and $\int \tilde{\rho}(\vec{r}) dr = N$ it holds

   $$E[\rho_0] \leq E[\tilde{\rho}] \tag{2}$$

   or: variational principle: $\delta \left[E[\rho] - E\{\int dr \rho(\vec{r}) - N\} \right] = 0$.

Problem: How can the energy be expressed by the density, so that the HK-Theorems can be applied.

Hohenberg-Kohn Theorem: Proofs I

Remember: *For a non-degenerate ground-state, the external potential* $V(\vec{r})$ *is determined (within a trivial additive constant) by the electron density* $\rho(\vec{r})$*. Since* $\rho(\vec{r})$ *determines* N*,* $\rho(\vec{r})$ *determines* $|\Psi_N\rangle$*.*

Proof:

Consider an N electron system. Suppose two external potentials $\hat{V}(\vec{r})$ and $\hat{V}'(\vec{r})$ are yielded from the same electron density $\rho(\vec{r})$.

Ground state energies:

- $E_0 = \langle\Psi|\hat{H}|\Psi\rangle$ with $\hat{H} = \hat{T} + \hat{V}$.
- $E_0' = \langle\Psi'|\hat{H}'|\Psi'\rangle$ with $\hat{H}' = \hat{T} + \hat{V}'$.

with the ground state wave functions Ψ and Ψ'. As Ψ can be seen as a trial wave function to $\hat{H}'$ (analoguous for Ψ' and $\hat{H}$), the variational priciple tells us:

$$E_0 < \langle\Psi'|\hat{H}|\Psi'\rangle \tag{3}$$

$$E_0' < \langle\Psi|\hat{H}'|\Psi\rangle. \tag{4}$$

Hohenberg-Kohn Theorem: Proofs II

We can write:

$$\hat{H} = \hat{H} + \hat{H}' - \hat{H}' = \underbrace{\hat{T} + \hat{V}'}_{\hat{H}'} + \hat{V} - \hat{V}' \quad (5)$$

$$\hat{H}' = \hat{H} + \hat{V}' - \hat{V}. \quad (6)$$

So we find:

$$E_0 = E_0' + \int dr \underbrace{|\Psi'|^2}_{\rho(\vec{r})} (\hat{V} - \hat{V}') \quad (7)$$

$$E_0' = E_0 - \int dr \underbrace{|\Psi|^2}_{\rho(\vec{r})} (\hat{V} - \hat{V}') \quad (8)$$

Hohenberg-Kohn Theorem: Proofs III

Adding (7) and (8) ....

$$E_0 + E'_0 < E'_0 + E_0 \tag{9}$$

This is a contradiction and the basic asumption (two potentials connected to one density) can not be true.

Remember: *For a trial density* $\tilde{\rho}(\vec{r})$ *with* $\tilde{\rho}(\vec{r}) \geq 0$ *and* $\int \tilde{\rho}(\vec{r})dr = N$ *it holds*

$$E[\rho_0] \leq E[\tilde{\rho}] \tag{10}$$

or*: variational principle:* $\delta \left[E[\rho] - E\{\int dr\,\rho(\vec{r}) - N\} \right] = 0$.

Hohenberg-Kohn Theorem: Proofs IV

The total energy can be written as a function of the density:

$$E[\rho] = \underbrace{T[\rho] + V_{e-e}[\rho]}_{F_{HK}[\rho]} + \underbrace{V_{e-n}[\rho]}_{=\int dr\rho(\vec{r})\hat{V}_{e-n}(\vec{r})} \quad . \tag{11}$$

Suppose a trial density $\tilde{\rho}(\vec{r})$ with the corresponding trial wavefunction $\tilde{\Psi}(\vec{r})$.
The ground state (described by ρ_0, Ψ_0) energy E_0 and the energy belonging to the trial density $\tilde{E}$ can be written as:

$$E_0[\rho_0] = \langle\Psi_0|\hat{H}|\Psi_0\rangle = F_{HK}[\rho_0] + \int dr\rho_0(\vec{r})\hat{V}(\vec{r}) \tag{12}$$

$$\tilde{E}[\tilde{\rho}] = \langle\tilde{\Psi}|\hat{H}|\tilde{\Psi}\rangle = F_{HK}[\tilde{\rho}] + \int dr\tilde{\rho}(\vec{r})\hat{V}(\vec{r}). \tag{13}$$

Variational Principle:

$$\langle\Psi_0|\hat{H}|\Psi_0\rangle \leq \langle\tilde{\Psi}|\hat{H}|\tilde{\Psi}\rangle \;\Rightarrow\; E_0[\rho_0] \leq \tilde{E}[\tilde{\rho}]. \tag{14}$$

Kohn-Sham-Formalism I

AIM: Use the Hohenberg-Kohn theorems to find the ground-state energy.

IDEA: Use (single particle) orbitals to construct a wave function to gain a trial density.

- Start with a fictous non-interacting N-particle system (described by the wave function $|\Psi_N\rangle$) with an electron density identical to the density of the interacting system.
- $\Rightarrow |\Psi_N\rangle$: Slater-Det. $|\Psi_N\rangle = \frac{1}{\sqrt{N!}} \det \phi_i(\vec{r}_j)$.
- HK-Theorem: denstiy $\rho(\vec{r}) = \sum_i^N |\phi_i(\vec{r})|$ defines the ground-state-energy.

Now: describe interacting electrons: Construct a Hamiltonian $\hat{H}_{KS} = \hat{T}_{KS} + \hat{V}_{eff}$

- $\hat{T}_{KS} = \sum_i^N \frac{\hbar^2}{2m} \nabla_i^2$: kinetic energy operator for N electrons
- $\hat{V}_{eff}$: effective potential, undefined so far.
- $\hat{H}_{KS}$ applied to the wave-function $|\Psi_N\rangle$ (non-interacting system): exact energy of the interacting system (HK).

Kohn-Sham-Formalism II

From $E[\rho] = T[\rho] + V_{e-n}[\rho] + V_{e-e}[\rho]$ we get with $V_{e-e}[\rho] = E_{coul}[\rho] + E_{QM}[\rho]$:

$$E[\rho] = T_{KS}[\rho] + V_{e-n}[\rho] + E_{coul}[\rho] + \underbrace{T[\rho] - T_{KS}[\rho] + E_{QM}[\rho]}_{E_{xc}[\rho]} \tag{15}$$

- $T_{KS}[\rho]$, $V_{e-n}[\rho]$: kinetic and potential energy of a non-interacting N-electron system.
- $T[\rho]$: kinetic energy of the interacting system.
- $E_{coul}[\rho]$: coulomb-part of the electron-electron interaction.
- E_{QM}: QM correlation term.
- $\Rightarrow E_{xc}$: contains exchange-correlation effects from the electron-electron interaction and in the kinetic energy.

TO DO: Find an equation for the ϕ_i!

Kohn-Sham-Formalism III

$$
\begin{aligned}
E[\rho] &= T_{KS} + V_{e-n}[\rho] + E_{coul}[\rho] + E_{xc}[\rho] = && (16)\\
&= -\frac{\hbar^2}{2m}\sum_{i=1}^{N}\int dr\phi_i^*(\vec{r})\nabla^2\phi_i(\vec{r}) + \int dr\hat{V}_{e-n}(\vec{r})\rho(\vec{r}) + && (17)\\
&\quad +\frac{1}{2}\int dr'\int dr\frac{\rho(\vec{r})\rho(\vec{r}')}{|\vec{r}-\vec{r}'|} + E_{xc}[\rho]. && (18)
\end{aligned}
$$

Find the minimum of $E[\rho]$ under the condition $\int dr|\phi_i(\vec{r})|^2 = 1$:

$$
\frac{\delta}{\delta\phi_i^*}\left\{E[\rho] - \sum_{j=1}^{N}\epsilon_j\left(\int dr|\phi_i(\vec{r})|^2 - 1\right)\right\} = 0 \tag{19}
$$

Remember the rules $\frac{\delta F[\rho]}{\delta\phi_i(\vec{r})} = \frac{\delta F[\rho]}{\delta(\rho(\vec{r}))}\phi_i(\vec{r})$ *and*

$$
F[f(\vec{r})] = \int drg(f(\vec{r})) \Rightarrow \frac{\delta F}{\delta f(\vec{r})} = \frac{\delta g(f(\vec{r}))}{\delta f(\vec{r})} \tag{20}
$$

Kohn-Sham-Formalism IV

Finally the Kohn-Sham-Equations:

$$\left\{ -\frac{\hbar^2}{2m}\nabla^2 + \underbrace{\hat{V}_{e-n}(\vec{r}) + \int dr' \, \frac{\rho(\vec{r})}{|\vec{r}-\vec{r}'|} + \frac{\delta E_{xc}[\rho]}{\delta \rho}}_{\hat{V}_{eff}(\vec{r})} \right\} \phi_i(\vec{r}) = \epsilon_i \phi_i(\vec{r}). \tag{21}$$

CONCLUSION

- solve KS-equations selfconsistent.
- N-particle problem $\Rightarrow$ single-particle problems.
- EXACT theory (when $E_{xc}[\rho]$ is known), no approximations (so far).
- single-particle wave functions $\phi_i(\vec{r})$ and -energies ϵ_i: no direct physical meaning.
- DFT: NO knowledge of GS wave function $|\Psi_N\rangle$.
- single-particle potential is local in space (unlike HF).
- BUT: We do not know $E_{xc}[\rho] \Rightarrow$ challenge now: find $E_{xc}[\rho]$

LDA and beyond

PROBLEM: No knowledge of the exchange-correlation energy $E_{xc}[\rho]$.

First approximation: **Local Density Approximation**: electron system with slowly varying density

$\Rightarrow$ can be described by the behaviour of a homogeneous electron gas

$$\Rightarrow E_{xc}[\rho] = \int dr \rho(\vec{r}) \epsilon_{xc}(\rho(\vec{r})) \tag{22}$$

$\epsilon_{xc}(\rho)$: exchange-correlation-energy of a homogeneous electron gas

- LDA gives surprisingly good results for inhomogeneous systems
- Gradient corrections: $E_{xc}[\rho, \nabla\rho]$
- Generalized Gradient Approximation: $E_{xc} = \int dr \rho(\vec{r}) \epsilon_{xc}[\rho, \nabla\rho]$.
- size limitations: HF: $N \simeq 30$, DFT: $N \simeq 200$.
- **DFTB.**