Density functional theory

Kohn-Sham idea

exact mapping between non-interacting and interacting electronic systems

$$\Psi^{\text{real}} \longleftarrow V^{\text{eff}}[\rho(\mathbf{r})] \longrightarrow \Psi^{\text{non-int.}}$$

effective potential exists, so that densities are the same (ground-state only!!)

$$H^{\text{non-int.}} = \sum_i^N (-\frac{1}{2}\nabla^2 + V^{\text{eff}})$$

one-electron wavefunctions: Kohn-Sham orbitals

$$(-\frac{1}{2}\nabla^2 + V^{\text{eff}})\phi_i(\mathbf{r}) = \epsilon_i \phi_i(\mathbf{r})$$

density of both systems

$$\rho(\mathbf{r}) = \sum_i^n |\phi_i(\mathbf{r})|^2$$

with exact effective potential

$$\rho(\mathbf{r}) = \rho^{\text{real}}(\mathbf{r})$$

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exact mapping between non-interacting and interacting electronic systems

$$\Psi^{\text{real}} \longleftarrow V^{\text{eff}}[\rho(\mathbf{r})] \longrightarrow \Psi^{\text{non-int.}}$$

ground-state only

energy functional

$$E[\rho(\mathbf{r})] = T[\rho(\mathbf{r})] + E_{ee}[\rho(\mathbf{r})] + E_{ne}[\rho(\mathbf{r})]$$

$$E[\rho(\mathbf{r})] = T[\rho(\mathbf{r})] + E_{ee}[\rho(\mathbf{r})] + \int \rho[(\mathbf{r})] \sum_A \frac{Z_A}{|\mathbf{r} - \mathbf{R}_A|} d\mathbf{r}$$

$$E[\rho(\mathbf{r})] = T[\rho(\mathbf{r})] + E_{ee}[\rho(\mathbf{r})] + \int \rho[(\mathbf{r})] V_{ne}(\mathbf{r}) d\mathbf{r}$$

variational principle

$$E[\rho(\mathbf{r})] = \min_{\Psi \to \rho} \langle \Psi | \hat{H} | \Psi \rangle \geq E_0$$

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Kohn-Sham idea

exact mapping between non-interacting and interacting electronic systems

$$\Psi^{\text{real}} \longleftarrow V^{\text{eff}}[\rho(\mathbf{r})] \longrightarrow \Psi^{\text{non-int.}}$$

ground-state only

energy functional for interacting system

$$E[\rho(\mathbf{r})] = T[\rho(\mathbf{r})] + E_{ee}[\rho(\mathbf{r})] + \int \rho[(\mathbf{r})] V_{ne}(\mathbf{r}) d\mathbf{r}$$

add and subtract energy functionals for a non interacting systems

$$E[\rho(\mathbf{r})] = T_S[\rho(\mathbf{r})] + E^H_{ee}[\rho(\mathbf{r})] + \int \rho[(\mathbf{r})] V_{ne}(\mathbf{r}) d\mathbf{r} + E_{XC}[\rho(\mathbf{r})]$$

dump all that we don't want to compute in the exchange-correlation functional

$$E_{XC}[\rho(\mathbf{r})] = (T[\rho(\mathbf{r})] - T_S[\rho(\mathbf{r})]) + (E_{ee}[\rho(\mathbf{r})] - E^H_{ee}[\rho(\mathbf{r})])$$

variational principle

$$E[\rho(\mathbf{r})] = \min_{\Psi \to \rho} \langle \Psi | \hat{H} | \Psi \rangle \geq E_0$$

Density functional theory

energy functional

$$E[\rho(\mathbf{r})] = T_S[\rho(\mathbf{r})] + E_{ee}^H[\rho(\mathbf{r})] + E_{ne}[\rho(\mathbf{r})] + E_{XC}[\rho(\mathbf{r})]$$

electron-electron repulsion: Hartree potential

$$E_{ee}^H[\rho(\mathbf{r})] = \frac{1}{2}\int\int \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}d\mathbf{r}'$$

electron-nuclei attraction: external potential

$$E_{en}[\rho] = \int \sum_A^N \frac{Z_A}{|\mathbf{R}_A - \mathbf{r}|}\rho(\mathbf{r})d\mathbf{r} = \int V_{en}(\mathbf{r})\rho(\mathbf{r})d\mathbf{r}$$

exchange-correlation energy (e.g. uniform electron gas)

$$E_{XC}^{\mathrm{LDA}}[\rho] = \int \epsilon_{XC}(\rho(\mathbf{r}))\rho(\mathbf{r})d\mathbf{r}$$

kinetic energy of non-interacting systems

$$T_S[\rho(\mathbf{r})] = \min_{\psi\to\rho}\langle\Psi|\hat{T}_S|\Psi\rangle$$

Density functional theory

minimize functional with respect to density

$$\partial E = \int \left(\frac{\partial}{\partial \rho} T_S + V_{ee}^H + E_{ne} + V_{XC} \right) \partial \rho d\mathbf{r} = 0$$

electron-electron repulsion (Hartree potential)

$$V_{ee}^H([\rho], r) = \frac{1}{2} \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}|} d\mathbf{r}'$$

electron-nuclei attraction: external potential

$$V_{en}([\rho], \mathbf{r}) = \sum_A \frac{Z_A}{|\mathbf{R}_A - \mathbf{r}|}$$

exchange-correlation energy (e.g., uniform electron gas)

$$V_{XC}^{\mathrm{LDA}}([\rho], \mathbf{r}) = \frac{\partial}{\partial \rho} E_{XC}^{\mathrm{LDA}} = \rho(\mathbf{r}) \frac{\partial \epsilon_{XC}(\rho(\mathbf{r}))}{\partial \rho} \Big|_{\rho=\rho(r)} + \epsilon_{XC}(\rho(\mathbf{r}))$$

Density functional theory

energy functional of non-interacting system

$$E^{\text{non-int.}}[\rho] = T_S[\rho] + \int V^{\text{eff.}}(\mathbf{r})\rho(\mathbf{r})d\mathbf{r}$$

minimize functional of non-interacting system

$$\delta E^{\text{non-int.}}[\rho] = \int \left(\frac{\partial}{\partial \rho} T_S[\rho] + V^{\text{eff.}}(\mathbf{r}) \right) \delta\rho(\mathbf{r})d\mathbf{r} = 0$$

kinetic energy functional

$$\frac{\partial}{\partial \rho} T_S[\rho] = -V^{\text{eff.}}(\mathbf{r})$$

effective potential function of true potentials

$$V^{\text{eff.}}(\mathbf{r}) = V_{en}(\mathbf{r}) + V_{ee}^{H}([\rho], \mathbf{r}) + V_{XC}([\rho], \mathbf{r})$$

Density functional theory

Practical Kohn-Sham DFT scheme

Step 1: guess density $\rho(\mathbf{r})$

Step 2: construct effective potential with chosen exchange-correlation potential

$$V^{\text{eff.}}(\mathbf{r}) = V_{en}(\mathbf{r}) + V_{ee}^{H}([\rho], \mathbf{r}) + V_{XC}([\rho], \mathbf{r})$$

Step 3a: solve the Schrödinger equation for non-interacting electrons

$$(-\frac{1}{2}\nabla^2 + V^{\text{eff}})\phi_i(\mathbf{r}) = \epsilon_i \phi_i(\mathbf{r})$$

Step 3b: compute new density & kinetic energy

$$\rho(\mathbf{r}) = \sum_i^n |\phi_i(\mathbf{r})|^2$$

$$T_S[\rho] = \sum_i^n \langle \phi_i | -\frac{1}{2}\nabla^2 | \phi_i \rangle = \sum_i^n \epsilon_i - \int V^{\text{eff.}}(\mathbf{r})\rho(\mathbf{r})d\mathbf{r}$$

Step 4: goto step 2, until convergence is reached

final energy:

$$E[\rho_0] = \sum_i^n \epsilon_i - \int V^{\text{eff.}}(\mathbf{r})\rho_0(\mathbf{r})d\mathbf{r} + E_{en}[\rho_0] + E_{ee}^{H}[\rho_0] + E_{XC}[\rho_0]$$

Density functional theory

Exchange-correlation functionals ("Jacob's ladder")

Local Density Approximation

$$E_{XC}^{\mathrm{LDA}}[\rho(\mathbf{r})] = \int f[\rho(\mathbf{r})]d\mathbf{r}$$

VWN

Generalized Gradient Approximation (GGA)

$$E_{XC}^{\mathrm{GGA}}[\rho(\mathbf{r})] = \int f[\rho(\mathbf{r}), \nabla\rho(\mathbf{r})]d\mathbf{r}$$

PW91, PBE, BLYP

Meta-GGA

$$E_{XC}^{\text{Meta-GGA}}[\rho(\mathbf{r})] = \int f[\rho(\mathbf{r}), \nabla\rho(\mathbf{r}), \nabla^2\rho(\mathbf{r})]d\mathbf{r}$$

M06-L

Hybrid (with fraction of Hartree Fock exchange)

$$E_{XC}^{\mathrm{Hybrid}}[\rho(\mathbf{r})] = \int f[\rho(\mathbf{r}), \nabla\rho(\mathbf{r})]d\mathbf{r} + \alpha E_X^{\mathrm{HF}}$$

PBE0, B3LYP

Range-separated (fraction of HF exchange depends on distance)

CAM-B3LYP, LC-ωPBE