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

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

Density functional theory

Kohn-Sham idea

exact mapping between non-interacting and interacting electronic systems

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

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

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

Density functional theory

Kohn-Sham idea

exact mapping between non-interacting and interacting electronic systems

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

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

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

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

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

variational principle

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

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 energy

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

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

$$\partial E = \int \left(\frac{\partial}{\partial \rho} T_S + V_{ee}^H + V_{en} + V_{XC} \right) \delta \rho \underset{\cdot}{\mathbf{r}} = 0$$

constraint

$$\int \rho(\mathbf{r}) d\mathbf{r} = N$$

Lagrangian

$$L = T_S[\rho] + E_{ee}^H + E_e n[\rho] + E_{XC} - \lambda \left(\int \rho(\mathbf{r}) d\mathbf{r} - N \right)$$

minimize Lagrangian with respect to density

$$\partial L = \int \left(\frac{\partial}{\partial \rho} T_S + V_{ee}^H + V_{en} + V_{XC} - \lambda \right) \delta \rho d\mathbf{r} = 0$$

Density functional theory

minimize Lagrangian with respect to density

$$\partial L = \int \left(\frac{\partial}{\partial \rho} T_S + V_{ee}^{H} + V_{en} + V_{XC} - \lambda \right) \delta \rho d\mathbf{r} = 0$$

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 a non-interacting system

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

constraint

$$\int \rho(\mathbf{r})d\mathbf{r} = N$$

Lagrangian

$$L^{\text{non-int.}}[\rho] = T_S[\rho] + \int V^{\text{eff}}(\mathbf{r})\rho(\mathbf{r})d\mathbf{r} - \lambda\left(\int \rho(\mathbf{r})d\mathbf{r} - N\right)$$

minimize Lagrangian of non-interacting electron system

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

Density functional theory

minimize Lagrangian of non-interacting electron system

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

kinetic energy potential of non-interacting electrons

$$\frac{\partial}{\partial \rho} T_S = -V^{\text{eff}} + \lambda$$

substitute in Lagrangian for the interacting system

$$\partial L = \int \left(\frac{\partial}{\partial \rho} T_S + V_{ee}^{H} + V_{en} + V_{XC} - \lambda \right) \delta\rho d\mathbf{r} = 0$$

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

minimize Lagrangian of non-interacting electron system

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

kinetic energy potential of non-interacting electrons

$$\frac{\partial}{\partial \rho} T_S = -V^{\text{eff}} + \lambda$$

substitute in Lagrangian for the interacting system

$$\partial L = \int \left(\frac{\partial}{\partial \rho} T_S + V_{ee}^{H} + V_{en} + V_{XC} - \lambda \right) \delta\rho d\mathbf{r} = 0$$

to arrive at expression for the Kohn-Sham “effective” potential

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

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

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

VWN

Generalized Gradient Approximation (GGA)

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

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)

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

PBE0, B3LYP

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

CAM-B3LYP, LC-ωPBE

Quantum Monte Carlo

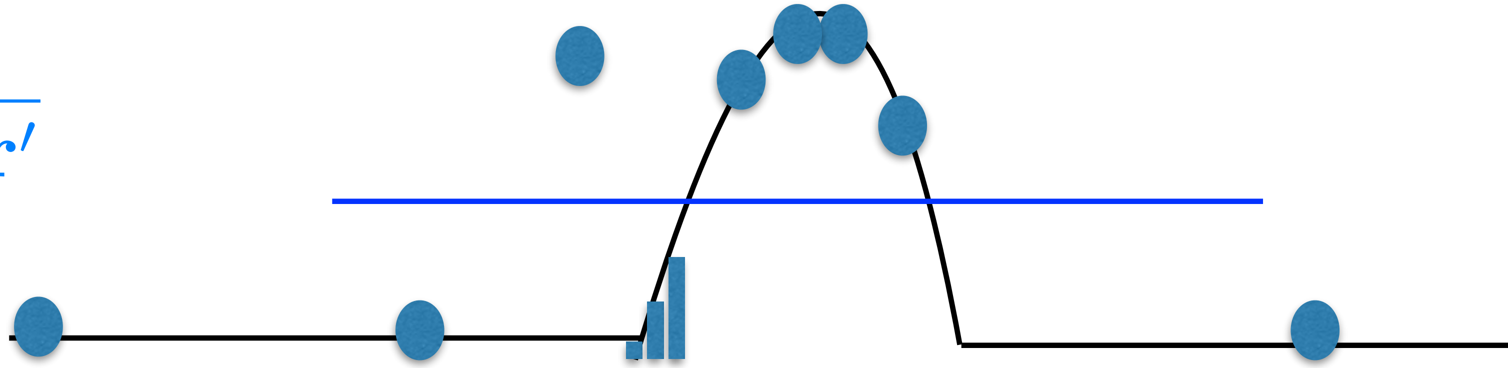
Variational Monte Carlo

expectation value of energy

$$\frac{\int \Psi_T^*(\mathbf{r},\{\alpha\})\hat{H}\Psi_T(\mathbf{r},\{\alpha\})d\mathbf{r}}{\int \Psi_T^*(\mathbf{r},\{\alpha\})\Psi_T(\mathbf{r},\{\alpha\})d\mathbf{r}} = E(\{\alpha\}) \geq E_0$$

importance sampling (Monte Carlo)

$$p(\mathbf{r}) = \frac{|\Psi(\mathbf{r})|}{\int |\Psi(\mathbf{r}')|d\mathbf{r}'}$$



local energy

$$E_L(\mathbf{r}) = \frac{\hat{H}\Psi_T(\mathbf{r})}{\Psi_T(\mathbf{r})}$$

Sampling of energy, optimise coefficients in wave function

$$\langle \hat{H} \rangle = \int p(\mathbf{r})E_L(\mathbf{r})d\mathbf{r}$$

$$\langle \hat{H} \rangle = \frac{1}{M}\sum_{i=1}^{M} E_L(\mathbf{r}_i) = \frac{1}{M}\sum_{i=1}^{M} \frac{\hat{H}\Psi_T(\mathbf{r})}{\Psi_T(\mathbf{r})}$$

Quantum Monte Carlo

Variational Monte Carlo

wave function

$$\Psi_T(\mathbf{x}) = \exp[J(\mathbf{x})] \sum_i c_i D_i(\mathbf{x})$$

determinant (antisymmetric) of molecular orbitals (again!)

$$D_i(\mathbf{x}) = \begin{vmatrix} \varphi_1(\mathbf{x}_1) & \varphi_1(\mathbf{x}_2) & \dots & \varphi_1(\mathbf{x}_n) \\ \varphi_2(\mathbf{x}_1) & \varphi_2(\mathbf{x}_2) & \dots & \varphi_2(\mathbf{x}_n) \\ \dots & \dots & & \dots \\ \varphi_n(\mathbf{x}_1) & \varphi_n(\mathbf{x}_2) & \dots & \varphi_n(\mathbf{x}_n) \end{vmatrix}$$

Jastrow factor (electron-electron, eln-nuc, eln-eln-nuc, …)

$$J(\mathbf{r}) = \sum_{i>j}^{N} u(r_{ij}) + \sum_{i=1}^{N} \sum_{I=1}^{N_I} \chi_I(r_{iI}) + \sum_{i>j}^{N} \sum_{I=1}^{N_I} f_I(r_{ij}, r_{iI}, r_{jI})$$

Quantum Monte Carlo

Diffusion Monte Carlo

propagate Schrödinger equation in *imaginary* time

$$i\frac{\partial\Psi(\mathbf{r},t)}{\partial t} = -\frac{1}{2}\nabla^2\Psi(\mathbf{r},t) + V(\mathbf{r},t)\Psi(\mathbf{r},t)$$

$$\tau = it$$

diffusion equation of electronic positions and rate equation)

$$-\frac{\partial\Psi^{\mathrm{DMC}}(\mathbf{R},t)}{\partial\tau} = -\frac{1}{2}\nabla^2\Psi(\mathbf{r},\tau) + (V(\mathbf{r}) - E_T)\Psi(\mathbf{r},t)$$

project out ground state

Quantum Monte Carlo

Diffusion Monte Carlo

propagate Schrödinger equation in imaginary time

$$-\frac{\partial \Psi^{\mathrm{DMC}}(\mathbf{R}, t)}{\partial \tau} = -\frac{1}{2}\nabla^2 \Psi(\mathbf{r}, \tau) + (V(\mathbf{r}) - E_T)\Psi(\mathbf{r}, t)$$

expansion in (unknown) eigenstates

$$\Psi(\mathbf{r}, t) = \sum_{n=0}^{\infty} c_n \psi_n(\mathbf{r}) e^{-i(E_n - E_t)t}$$

$$\Psi(\mathbf{r}, \tau) = \sum_{n=0}^{\infty} c_n \psi_n(\mathbf{r}) e^{-(E_n - E_t)\tau}$$

with $E_T = E_0$ we can single out ground state in diffusion process

$$\Psi(\mathbf{r}, \tau) = c_0 \psi_0(\mathbf{r}) + \sum_{n=1}^{\infty} c_n \psi_n(\mathbf{r}) e^{-(E_n - E_0)\tau}$$

Some practical guidelines

Basissets

- STO-3G too small
- 6-31G* & 6-31G** reasonable results
  - DFT often less sensitive to basisset
  - often better than cc-pVDZ
- higher accuracy with cc-pVTZ, better than 6-311G**, etc.
- diffuse functions (aug- or +)
  - anions
  - excited states
  - dispersion bound complexes

Some practical guidelines

Methods

- prefer DFT over HF
- HF < DFT ~ MP2 < CCSD < CCSD(T)
- MPn may not converge with n
  - beyond MP2, use CC
- CASSCF/CASPT2
  - bond breaking, diradicals, excited states, transition metals
  - DFT can be dangerous
- HF, semi-empirical and DFT fail for VDW complexes
  - MP2, CC, dispersion corrected DFT

Some practical guidelines

Always do!

- check if SCF converged!
  - check for multiconfigurational character (MPn/CC:T2)
- check if geometry converged
  - NMA analysis
  - minimum: all positive frequencies
  - transition state: one negative frequency.
  - non-covalent complexes: flat surface, difficult, go by hand
- think of symmetry
  - optimization cannot break symmetry
- know what to expect: think first
  - never trust the computer
- CASSCF/CASPT2
  - check final natural orbital density matrix
  - check for large orbital rotations

Gradients

Analytical derivatives

$$\frac{\partial E}{\partial X_A} = \frac{\partial \tilde{E}}{\partial X_A} + \sum_{\mu a} \frac{\partial E}{\partial C_{\mu a}} \frac{\partial C_{\mu a}}{\partial X_A}$$

Hartree Fock solution

$$\frac{\partial E}{\partial X_A} = \frac{\partial \tilde{E}}{\partial X_A}$$

Hartree-Fock energy

$$E = \sum_{\mu\nu} P_{\mu\nu} H_{\mu\nu}^{\text{core}} + \frac{1}{2} \sum_{\mu\nu\lambda\sigma} P_{\mu\nu} P_{\lambda\sigma} \langle \mu\nu | \frac{1 - \frac{1}{2}\hat{p}_{12}}{r_{12}} | \lambda\sigma \rangle + V_{NN}$$

$$P_{\mu\nu} = 2 \sum_{a}^{n/2} C_{\mu a}^{*} C_{\nu a}$$

Gradients

Analytical derivatives

Hartree Fock energy

$$E = \sum_{\mu\nu} P_{\mu\nu} H^{\mathrm{core}}_{\mu\nu} + \frac{1}{2} \sum_{\mu\nu\lambda\sigma} P_{\mu\nu} P_{\lambda\sigma} \langle \mu\nu | \frac{1 - \frac{1}{2}\hat{p}_{12}}{r_{12}} | \lambda\sigma \rangle + V_{NN}$$

gradient

$$\begin{aligned} \frac{\partial E}{\partial X_A} \quad = \quad & \textstyle\sum_{\mu\nu} P_{\mu\nu} \frac{\partial H^{\mathrm{core}}_{\mu\nu}}{\partial X_A} \\ & + \tfrac{1}{2} \textstyle\sum_{\mu\nu\lambda\sigma} P_{\mu\nu} P_{\lambda\sigma} \frac{\partial}{\partial X_A} \langle \mu\nu | \frac{1 - \frac{1}{2}\hat{p}_{12}}{r_{12}} | \lambda\sigma \rangle + \frac{V_{NN}}{\partial X_A} \\ & + \textstyle\sum_{\mu\nu} \frac{\partial P_{\mu\nu}}{\partial X_A} H^{\mathrm{core}}_{\mu\nu} + \textstyle\sum_{\mu\nu\lambda\sigma} \frac{\partial P_{\mu\nu}}{\partial X_A} P_{\lambda\sigma} \langle \mu\nu | \frac{1 - \frac{1}{2}\hat{p}_{12}}{r_{12}} | \lambda\sigma \rangle \end{aligned}$$

Gradients

Analytical derivatives

orthogonality of RHF molecular orbitals

$$\sum_{\mu\nu} C_{\mu a} S_{\mu\nu} C_{\nu b} = \delta_{ab}$$

$$2 \sum_{\mu\nu} \frac{\partial C_{\mu a}}{\partial X_A} S_{\mu\nu} \quad = - \sum_{\mu\nu} C_{\mu a} C_{\nu a} \frac{\partial S_{\mu\nu}}{\partial X_A}$$

gradient

$$\frac{\partial E}{\partial X_A} \quad = \quad \textstyle\sum_{\mu\nu} P_{\mu\nu} \frac{\partial H^{\mathrm{core}}_{\mu\nu}}{\partial X_A}$$

$$+ \frac{1}{2} \textstyle\sum_{\mu\nu\lambda\sigma} P_{\mu\nu} P_{\lambda\sigma} \frac{\partial}{\partial X_A} \langle \mu\nu | \frac{1 - \frac{1}{2}\hat{p}_{12}}{r_{12}} | \lambda\sigma \rangle + \frac{V_{NN}}{\partial X_A}$$

$$- \textstyle\sum_{\mu\nu} Q_{\mu\nu} \frac{\partial S_{\mu\nu}}{\partial X_A}$$

with

$$Q_{\mu\nu} = 2 \sum_{a}^{n/2} \epsilon_a C_{\mu a} C_{\nu a}$$

Gradients

Analytical derivatives

Configuration interaction

$$|\Psi\rangle = \sum_I c_I |\psi_I\rangle$$

general gradient

$$\frac{\partial E}{\partial X_A} = \frac{\partial \tilde{E}}{\partial X_A} + \sum_{\mu a} \frac{\partial E}{\partial C_{\mu i}} \frac{\partial C_{\mu i}}{\partial X_A} + \sum \frac{\partial E}{\partial c_I} \frac{\partial c_I}{\partial X_A}$$

MCSCF gradient

$$\frac{\partial E}{\partial X_A} = \frac{\partial \tilde{E}}{\partial X_A}$$

CI gradient

$$\frac{\partial E}{\partial X_A} = \frac{\partial \tilde{E}}{\partial X_A} + \sum_{\mu a} \frac{\partial E}{\partial C_{\mu i}} \frac{\partial C_{\mu i}}{\partial X_A}$$