Kohn-Sham DFT

$$E_0 = \inf_{\substack{\Psi \in A_N \\ \langle \Psi | \Psi \rangle = 1}} \langle \Psi | H | \Psi \rangle$$

$$= \inf_{\rho \in \mathcal{J}_N} \left(\inf_{\substack{\Psi \in A_N \\ \Psi \mapsto \rho}} \langle \Psi | H | \Psi \rangle \right)$$

$$\mathcal{J}_N = \left\{ \rho \geq 0 \,\middle|\, \int \rho \, d\vec{r} = N, \ \sqrt{\rho} \in H^1(\mathbb{R}^3) \right\}$$

$$\nabla \sqrt{\rho} = \frac{1}{2\sqrt{\rho}} \nabla \rho .$$

$$\int |\nabla \sqrt{\rho}|^2 = \frac{1}{4} \int \frac{1}{\rho} |\nabla \rho|^2$$

$$\leq \int \frac{N^2}{\rho} \left(\sum_{\sigma} \int |\nabla \psi((\vec{r},\sigma),\hat{x})|^2 d\hat{x} \right) \left(\sum_{\sigma} \int |\psi((\vec{r},\sigma),\hat{x}|^2 d\hat{x} \right)$$

$$= 2 \langle \psi | \hat{T} | \psi \rangle .$$

necessary cond. to bound KE.

[Lieb 83]. $\rho \in J_N$. At least one $\psi \in \mathcal{A}_N^0$, $\psi \mapsto \rho$.

w. finite KE.

add one orbital w. high KE.

Think: why $T(\psi) \leq \|\sqrt{\rho}\|_{H^1}$ not possible in general?

In particular.

$$T(\psi) \leq 8\pi^2 N^2 \int |\nabla \sqrt{\rho}|^2 dr.$$

N-representability.

$\rho \in \mathcal{J}_N$, $\{\psi \in \mathcal{A}_N \mid \psi \mapsto \rho\} \neq \phi$? Yes.

bounding $\langle \psi | V_{ee} | \psi \rangle$:

$$\int \frac{|\psi(r_1, \cdots, r_N)|^2}{|r_1 - r_2|} dr_1 \cdots dr_N$$

$$f(t) = \psi(r_2 + t(r_1 - r_2), r_2, r_3, \cdots, r_N).$$

$$\psi(r_1, r_2, \cdots, r_N) = f(1) = \int_0^1 \nabla_{r_1}\psi(r_2 + t(r_1 - r_2), r_2, \cdots, r_N) \cdot (r_1 - r_2)\, dt$$

$$|\psi|^2 \le \int_0^1 |\nabla_{r_1}\psi(r_2 + t(r_1 - r_2), \cdots r_N)|^2 dt \cdot |r_1 - r_2|^2.$$

$$\mathbb{R}^3 = B(r_2, R) \cup (\mathbb{R}^3 \setminus B(r_2, R)).$$

$$\langle\psi| V_{ee} |\psi\rangle \le \int_{\mathbb{R}^{3(N-1)}} dr_2 \cdots dr_N \int_{B(r_2, R)} dr_1 \frac{|\psi|^2}{|r_1 - r_2|}$$

$$+ \int_{\mathbb{R}^{3(N-1)}} dr_2 \cdots dr_N \frac{|\psi|^2}{R}$$

$$\le \int_0^1 dt \int_{\mathbb{R}^{3N}} |\nabla_{r_1}\psi|^2 \cdot |r_1 - r_2| + \frac{1}{R}$$

$$\le \frac{R}{N} \int |\nabla_{r_1}\psi|^2 + \frac{1}{R}.$$ Hence e-e repulsion is bounded by $\|\psi\|_{H^1}$

Constrained minimization.

$$E = \inf_{\rho \in \mathcal{J}_N} \left(\inf_{\substack{\psi \in \mathcal{A}_N \\ \psi \mapsto \rho}} \langle \psi | T + V_{ee} | \psi \rangle + \int \rho V_{ext} \right) + E_{II}.$$

$$:= \inf_{\rho \in \mathcal{J}_N} \left(F_{LL}[\rho] + \int \rho V_{ext} \right) + E_{II}.$$

Orbital free DFT.

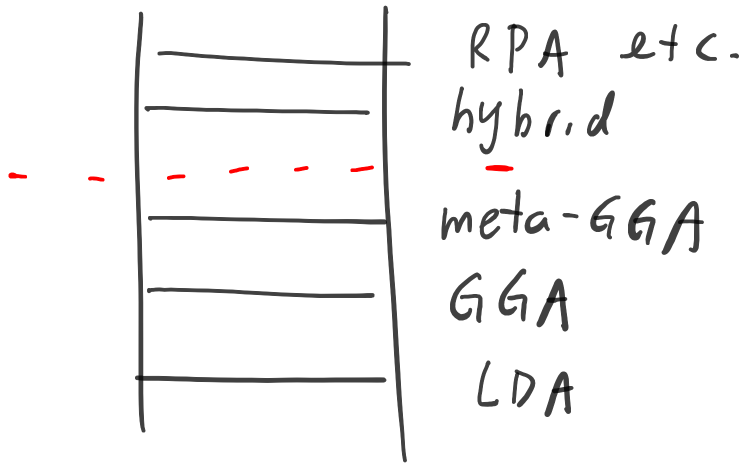
Kohn-Sham DFT.

$$F_{LL}[\rho] = \inf_{\substack{\psi \in \mathcal{A}_N^0 \\ \psi \mapsto \rho}} \langle \Psi | T | \Psi \rangle + \frac{1}{2} \int \frac{\rho(\vec{r})\rho(\vec{r}')}{|\vec{r}-\vec{r}'|} d\vec{r} d\vec{r}' + E_{xc}[\rho]$$

$$E^{KS} = \inf_{\psi \in \mathcal{A}_N^0} \Big(\langle \Psi | T | \Psi \rangle + \int \rho V_{ext} + \frac{1}{2} \int \frac{\rho(\vec{r})\rho(\vec{r}')}{|\vec{r}-\vec{r}'|} d\vec{r} d\vec{r}' + E_{xc}[\rho] \Big\} + E_{II}$$

$$\underline{\Psi} \Leftarrow \psi_1(\vec{x}), \cdots, \psi_N(\vec{x}).$$

$$\langle \Psi | T | \Psi \rangle = \frac{1}{2} \sum_{i=1}^{N} \int |\nabla_i \psi_i(\vec{x})|^2 d\vec{x}$$



LDA

$$E_{xc}[\rho] = \int \tilde{\varepsilon}_{xc}(\rho(\vec{r}))\,\rho(\vec{r})\,d\vec{r} := \int \epsilon_{xc}(\rho(\vec{r}))\,d\vec{r}.$$

Ceperley-Alder. 81.

Uniform electron gas. $\rho_a(\vec{r}) = -\rho(\vec{r}) \equiv \rho$

(jellium)

$$H = \sum_{i=1}^{N} \frac{1}{2} \Delta_{\vec{r}_i} + \sum_{i<j} V_c(\vec{r}_i, \vec{r}_j) - \frac{1}{2} \iint \rho_a(\vec{r}) \rho_a(\vec{r}') V_c(\vec{r}, \vec{r}')$$

$$\Psi((\vec{r}_1 + L, \sigma), \vec{x}_2, \cdots, \vec{x}_N) = \Psi((\vec{r}_1, \sigma), \vec{x}_2, \cdots, \vec{x}_N)$$

$$|\Omega| = L^3.$$

$$\rho = \frac{N}{|\Omega|}.$$

Wigner-Seitz radius

$$\frac{4}{3}\pi r_s^3 = \frac{|\Omega|}{N} = \frac{1}{\rho} \Rightarrow r_s = \left(\frac{3}{4\pi\rho}\right)^{\frac{1}{3}}$$

r_s large: low density.

small: high density.

QMC: $E_0[\rho]$

KS-DFT (exer)

$$E_0[\rho] = \inf_{\substack{\Psi \in A_N^0 \\ \Psi \mapsto \rho}} \langle \Psi | T | \Psi \rangle + E_{xc}[\rho].$$

KS-eq.

$$-\frac{1}{2}\Delta \varphi_i = \epsilon_i \varphi_i . \longrightarrow \text{Fourier}$$

$$T_s = \sum_{i=1}^{N} \epsilon_i$$

$$E_{xc}[\rho] = E_0[\rho] - T_s[\rho] = \int \epsilon_{xc}(\rho) \, d\vec{r} = |\Omega| \epsilon_{xc}(\rho)$$

Kohn-Sham eq.

Restricted spin. $(N = 2N_{occ})$.

$$\psi_i(\vec{x}) = \varphi_i(\vec{r})\langle\sigma|\uparrow\rangle. \quad i = 1, \cdots, N_{occ}$$

$$\psi_{i+N_{occ}}(\vec{x}) = \varphi_i(\vec{r})\langle\sigma|\downarrow\rangle.$$

$$\frac{1}{2}\frac{\delta \mathcal{E}^{KS}}{\delta \varphi_i^*(r)} = \left(-\frac{1}{2}\Delta_{\vec{r}} + V_{ext}(\vec{r}) + \int \frac{\rho(\vec{r}')}{|\vec{r}-\vec{r}'|} + V_{xc}[\rho](\vec{r})\right)\varphi_i = \varepsilon_i \varphi_i$$

$$V_{xc}[\rho](\vec{r}) = \frac{\delta E_{xc}[\rho]}{\delta \rho(\vec{r})}$$

$$\rho(\vec{r}) = 2\sum_{i=1}^{N_{occ}} |\varphi_i(\vec{r})|^2,$$

$$\delta\rho(\vec{r}) = 2\sum_{i=1}^{N_{occ}}\left[\delta\varphi_i^*(\vec{r})\ \varphi_i(\vec{r}) + \varphi_i^*(\vec{r})\,\delta\varphi_i(\vec{r})\right]$$

LDA

$$\delta E_{xc} = \int \frac{\partial \epsilon_{xc}(\rho)}{\partial \rho}(\rho(\vec{r}))\ \delta\rho(\vec{r})\,d\vec{r}$$

$$\Rightarrow\ V_{xc}[\rho](\vec{r}) = \frac{\partial \epsilon_{xc}(\rho)}{\partial \rho}(\rho(\vec{r}))$$

GGA.

$$E_{xc} = \int \epsilon_{xc}(\rho(\vec{r}), \sigma(\vec{r}))\,d\vec{r}$$

$$\sigma(\vec{r}) = |\nabla\rho(\vec{r})|^2$$

$$\delta E_{xc} = \int \left(\frac{\partial \epsilon_{xc}}{\partial \rho} \delta \rho + \frac{\partial \epsilon_{xc}}{\partial \sigma} \delta \sigma \right)$$

$$= \int \frac{\partial \epsilon_{xc}}{\partial \rho} \delta \rho + \int \frac{\partial \epsilon_{xc}}{\partial \sigma} 2 \nabla \rho \cdot \nabla \delta \rho$$

$$= \int \frac{\partial \epsilon_{xc}}{\partial \rho} \delta \rho - 2 \int \nabla \cdot \left(\frac{\partial \epsilon_{xc}}{\partial \sigma} \nabla \rho \right)$$

$$\Rightarrow V_{xc}[\rho](\vec{r}) = \frac{\partial \epsilon_{xc}}{\partial \rho}\left(\rho(\vec{r}), \sigma(\vec{r})\right) - 2 \nabla \cdot \left(\frac{\partial \epsilon_{xc}}{\partial \rho}\left(\rho(\vec{r}), \sigma(\vec{r})\right) \nabla \rho(\vec{r}) \right)$$

Meta-GGA.

$$E_{xc} = \int \epsilon_{xc}(\rho, \sigma, \tau)$$

$$\tau(\vec{r}) = \frac{1}{2}\sum_{i=1}^{N} |\nabla \psi_i(\vec{r})|^2 .$$ orbital dependent!

$$\int \frac{\partial \epsilon_{xc}}{\partial \tau} \delta\tau = +\frac{1}{2}\sum_{i=1}^{N} \int \nabla \delta \psi_i^* \cdot \left(\frac{\partial \epsilon_{xc}}{\partial \tau} \nabla \psi_i \right)$$

$$+ \frac{1}{2}\sum_{i=1}^{N} \int \nabla \psi_i^* \left(\frac{\partial \epsilon_{xc}}{\partial \tau} \nabla \delta \psi_i \right)$$

$$= -\frac{1}{2}\sum_{i=1}^{N} \int \delta \psi_i^* \nabla \cdot \left(\frac{\partial \epsilon_{xc}}{\partial \tau} \nabla \psi_i \right)$$

$$- \frac{1}{2}\sum_{i=1}^{N} \int \psi_i^* \nabla \cdot \left(\frac{\partial \epsilon_{xc}}{\partial \tau} \nabla \delta \psi_i \right)$$

KS-eq.

$$\underbrace{-\frac{1}{2}\nabla\cdot\left(\frac{\partial E_{xc}}{\partial \tau}\nabla\right)}_{}\psi_i$$

semi-local term. "V_{xc}".

Hybrid.

$$E_{xc} = (1-\alpha)E_x[\rho] + \alpha E_{xx}[P] + E_c[\rho].$$

$$E_{xx}[P] = -\frac{1}{2}\int |P(\vec{r},\vec{r}')|^2 K(\vec{r},\vec{r}')\, d\vec{r}\, d\vec{r}'$$

$$V_{xx}[P]\psi_i(\vec{r}) = \int P(\vec{r},\vec{r}')K(\vec{r},\vec{r}')\psi_i(\vec{r}')$$

HF-like eq.

Total energy (LDA. GGA)

$$E = 2\sum_{i=1}^{N_{occ}} \epsilon_i - \frac{1}{2}\int \frac{\rho(\vec{r})\,\rho(\vec{r}\,')}{|\vec{r}-\vec{r}\,'|}\,d\vec{r}\,d\vec{r}\,' + E_{xc}[\rho]$$

$$- \int V_{xc}[\rho]\,\rho(\vec{r})\,d\vec{r} + E_{II}.$$

Iterative method for solving eigenvalue problems.

$$A v_i = \lambda_i v_i, \quad \lambda_1 \le \cdots \le \lambda_N. \quad A \in \mathbb{C}^{d\times d}$$

$V = [v_1, \cdots, v_N]$.

Davidson.

$S_0 \in \mathbb{C}^{d\times N}$. $S_0^* S_0 = I$.

$S_0^* A S_0 \, C = \quad C \Lambda_0$ Rayleigh-Ritz

$V_0 = S_0 C,$ Residual.

$R_0 = A V_0 - V_0 \Lambda_0$.

$k=1$

while $\|R_0\|_F > \tau$.

$W_{k-1} = T R_{k-1}$ preconditioned residual.

$$\tilde{S}_k = [S_{k-1} \; W_{k-1}]$$

$$S_{k1} = \mathrm{svd}(\tilde{S}_k, \epsilon).$$ (or cheaper orthogonalization procedure)

$$S_k^* A S_k C = C \Lambda_k$$

$$V_k = S_k C$$

$$R_k = A V_k - V_k \Lambda_k.$$

$$k \leftarrow k+1$$

end.

Limited memory version

$$\tilde{S}_k = [V_k, W_k, V_{k-1}, \cdots, V_{k-l}]. \quad S_k = \mathrm{svd}(\tilde{S}_k, \tau)$$

Steepest descent

$$\tilde{S}_k = [V_k, W_k].$$

Locally optimal block conjugate gradient.

$$\tilde{S}_k = [V_k, W_k, V_{k-1}]$$

(conceptual). [Knyazev '01]

eigs: ARPACK.

SCF. LDA/GGA.

potential mixing

$$V_* = V_{eff}[F_{KS}[V_*]]$$

Fixed pt iteration

$$V_{k+1} = V_{eff}[F_{KS}[V_k]]$$

Simple mixing

$$V_{k+1} = \alpha V_{eff}[F_{KS}[V_k]] + (1-\alpha) V_k$$
$$=: V_k - \alpha r_k.$$

Newton

$$J_k = I - \frac{\partial V_{eff}}{\partial \rho} \frac{\partial F_{KS}}{\partial V}(V_k)$$

$$V_{k+1} = V_k - J_k^{-1} r_k$$

Anderson / Pulay

$$V_{k+1} = V_k - C_k r_k . \qquad C_k \approx J_k^{-1}$$

$$r = V - V_{eff}[F_{KS}[V]]$$

$$\Rightarrow \delta r = J_k \, \delta V \quad \text{or} \quad \delta V = J_k^{-1} \delta r$$

$$S_k = (s_{k-l}, \cdots, s_k) \qquad Y_k = (y_{k-l}, \cdots, y_k)$$

$$s_j = V_j - V_{j-1}, \quad y_j = r_j - r_{j-1}$$

$$\min_{C} \ \frac{1}{2} \| C - C_0 \|_F^2$$

$$\text{s.t.} \quad S_k = C \, Y_k .$$

$$C = C_0 + (S_k - C_0 Y_k) Y_k^{\dagger},$$

$$V_{k+1} = V_k - C_0 (I - Y_k Y_k^{\dagger}) r_k - S_k Y_k^{\dagger} r_k$$

$C_0 = \alpha I.$ Anderson's method / Pulay