Lean Divide-&-Conquer Density Functional Theory (LDC-DFT)

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— Divide-&-conquer density functional theory (DC-DFT)

⊙ Key approximation: $\hat{H} \to \hat{H}^\alpha$

⊙ Interpretation

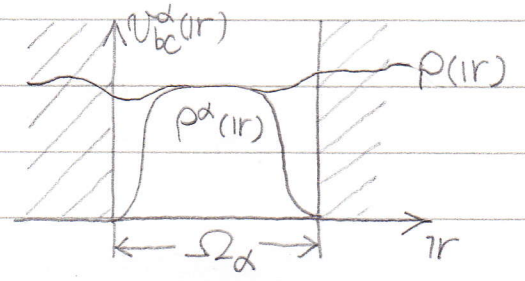
① Projection

$$\hat{H}^\alpha = \sum_{m,n \in \Omega_\alpha} |m\rangle\langle m|\hat{H}|n\rangle\langle n| \qquad (1)$$

② Boundary potential $v_{bc}^\alpha(\mathbf{r})$

e.g. Dirichlet (hard wall) boundary condition

$$v_{bc}^\alpha(\mathbf{r}) = \begin{cases} 0 & (\mathbf{r} \in \Omega_\alpha) \\ \infty & (\text{else}) \end{cases} \qquad (2)$$



— Improved boundary potential: Minimize $|\rho^\alpha(\mathbf{r}) - \rho(\mathbf{r})|$!

⊙ According to the Hohenberg-Kohn theorem, $\rho^\alpha(\mathbf{r})$ corresponds to a unique external potential $v(\mathbf{r})$, which is distinct from the actual potential coresponding to the total $\rho(\mathbf{r})$.

⊙ To reduce $|\rho^\alpha(\mathbf{r}) - \rho(\mathbf{r})|$, we use perturbation

$$v_{bc}^\alpha(\mathbf{r}) = \int d\mathbf{r}' \frac{\delta v(\mathbf{r})}{\delta \rho(\mathbf{r}')} [\rho^\alpha(\mathbf{r}') - \rho(\mathbf{r})] \qquad (3)$$

≃ Purification for FMO (Tsuneyuki, CPL 476, 104 ('09)), but we want material/geometry-indipendent recipes!

– Local approximation (cf. PRB 39, 4930 ('89))

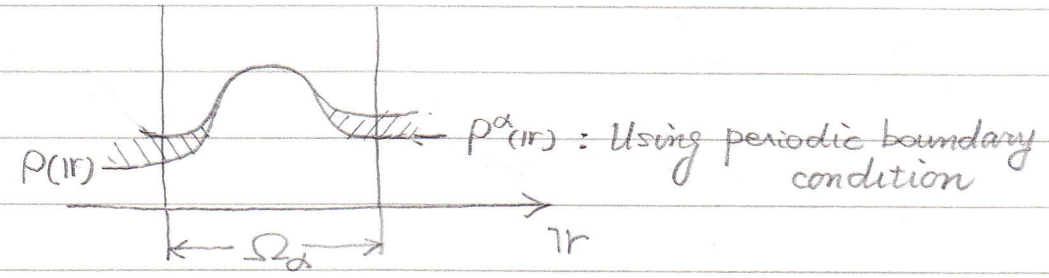
$$\frac{\delta v(\mathbf{r})}{\delta \rho(\mathbf{r}')} \simeq \frac{\delta(\mathbf{r}-\mathbf{r}')}{\alpha} \qquad (4)$$

◦ Justification = quantum nearsightedness as formulated by Prodan & Kohn (PNAS 102, 11635 ('05)) to be the short range of the influence of $v(\mathbf{r})$ on $\rho(\mathbf{r}')$ at nearby points $\mathbf{r}'$.

◦ Substituting Eq. (4) in (3),

$$v_{bc}^{\alpha}(\mathbf{r}) \simeq \frac{\rho^{\alpha}(\mathbf{r}) - \rho(\mathbf{r})}{\alpha} \qquad (5)$$

$\begin{cases} \rho^{\alpha}(\mathbf{r}) > \rho(\mathbf{r}) : \text{Positive } v_{bc}^{\alpha}(\mathbf{r}) \text{ reduces } \rho^{\alpha}(\mathbf{r}) \\ \quad < \qquad\quad \text{Negative} \qquad\quad \text{increases} \end{cases}$



– Perturbation

$$(\hat{H}+\lambda\hat{V})(|0\rangle+\lambda|1\rangle+\cdots) = (\epsilon_0+\lambda\epsilon_1+\cdots)(|0\rangle+\lambda|1\rangle+\cdots) \quad (6)$$

$$\begin{aligned} \hat{H}|0\rangle &= \epsilon_0|0\rangle \\ +\lambda(\hat{H}|1\rangle+\hat{V}|0\rangle) &\quad +\lambda(\epsilon_0|1\rangle+\epsilon_1|0\rangle) \\ +\cdots &\quad +\cdots \end{aligned}$$

Equating the linear terms of λ in the l.h.s. & r.h.s.,

$$\hat{H}|1\rangle + \hat{V}|0\rangle = \epsilon_0|1\rangle + \epsilon_1|0\rangle \quad (7)$$

$\langle 0| \times$ Eq. (6)

$$\underbrace{\langle 0|\hat{H}|1\rangle}_{\epsilon_0\langle 0|1\rangle} + \langle 0|\hat{V}|0\rangle = \epsilon_0\langle 0|1\rangle + \epsilon_1\underbrace{\langle 0|0\rangle}_{1}$$

$$\therefore \quad \epsilon_1 = \langle 0|\hat{V}|0\rangle \quad (8)$$

Substituting Eq. (8) in (7),

$$(\hat{H}-\epsilon_0)|1\rangle = -(\hat{V}-\langle 0|\hat{V}|0\rangle)|0\rangle \quad (9)$$

Each local Kohn-Sham orbital $\psi_n^\alpha(\mathbf{r})$ with energy ϵ_n^α will be corrected as

$$|\psi_n^\alpha\rangle \leftarrow |\psi_n^\alpha\rangle - \frac{\hat{V}_{bc}^\alpha - \langle\psi_n^\alpha|\hat{V}_{bc}^\alpha|\psi_n^\alpha\rangle}{\hat{H}_\alpha - \epsilon_n^\alpha}|\psi_n^\alpha\rangle \quad (10)$$

— LDC algorithm

1. Obtain $\{\psi_n^\alpha(\mathbf{r}), \epsilon_n^\alpha\}$ using periodic boundary condition
2. for $\forall n$

$$|\psi_n^\alpha\rangle \leftarrow |\psi_n^\alpha\rangle - \frac{\hat{V}_{bc}^\alpha - \langle\psi_n^\alpha|\hat{V}_{bc}^\alpha|\psi_n^\alpha\rangle}{\hat{H}_\alpha - \epsilon_n^\alpha}|\psi_n^\alpha\rangle \tag{10}$$

(Gram-Schmidt orthogonalization)

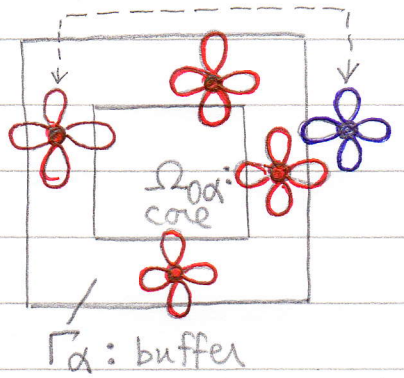
$$|\psi_n^\alpha\rangle \leftarrow |\psi_n^\alpha\rangle - \sum_{m=1}^{n-1}|\psi_m^\alpha\rangle\langle\psi_m^\alpha|\psi_n^\alpha\rangle \tag{11}$$

$$|\psi_n^\alpha\rangle \leftarrow \frac{|\psi_n^\alpha\rangle}{\sqrt{\langle\psi_n^\alpha|\psi_n^\alpha\rangle}} \tag{12}$$

3. (Subspace diagonalization)
   Diagonalize $\langle\psi_m^\alpha|\hat{H}_\alpha|\psi_n^\alpha\rangle$ to obtain new $\{\psi_n^\alpha(\mathbf{r}), \epsilon_n^\alpha\}$

– Implementation : Projection augmentation with orthogonalized pseudo-atomic orbitals (PAOPAO) (Perturbative) (?)

◦ Represent the perturbative wave function as a linear combination of boundary atomic orbitals (LCBAO).



Note : We need periodic images of this w.r.t. Ω_α
↑
Source of PBC error

$$|\delta\psi_n^\alpha\rangle = -\frac{\hat{V}_{bc}^\alpha - \langle\psi_n^\alpha|\hat{V}_{bc}^\alpha|\psi_n^\alpha\rangle}{\hat{H}_\alpha - \epsilon_n^\alpha}|\psi_n^\alpha\rangle$$

$$= \sum_{\nu\in\Gamma_\alpha} C_{n\nu}^\alpha |\nu\rangle \qquad (13)$$

$|\nu\rangle$ ↳ pseudo atomic orbital

$\nu\in\Gamma_\alpha$ ↳ only within the buffer layer

Substituting Eq. (13) in (9) (N_{bao} ↑ # of boundary atomic orbitals)

$$(\hat{H}_\alpha - \epsilon_n^\alpha)\sum_{\nu=1}^{N_{bao}} C_{n\nu}^\alpha |\nu\rangle = -(\hat{V}_{bc}^\alpha - \langle\psi_n^\alpha|\hat{V}_{bc}^\alpha|\psi_n^\alpha\rangle)|\psi_n^\alpha\rangle \qquad (14)$$

$\langle\mu|\times$ Eq. (14)

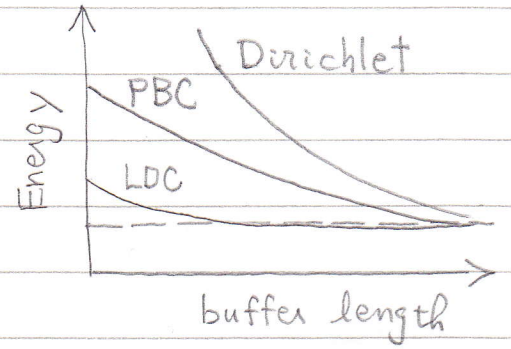
$$\sum_{\nu=1}^{N_{bao}} \langle\mu|(\hat{H}_\alpha - \epsilon_n^\alpha)|\nu\rangle C_{n\nu}^\alpha = -\langle\mu|(\hat{V}_{bc}^\alpha - \langle\psi_n^\alpha|\hat{V}_{bc}^\alpha|\psi_n^\alpha\rangle)|\psi_n^\alpha\rangle$$

or

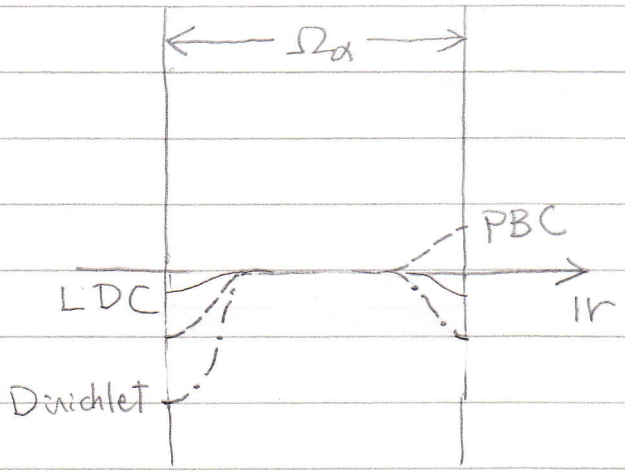
$$\underset{N_{bao}\times N_{bao}}{\left[\langle\mu|(\hat{H}_\alpha - \epsilon_n^\alpha)|\nu\rangle\right]} \underset{N_{bao}\times 1}{\begin{bmatrix} C_{n1}^\alpha \\ \vdots \\ C_{nN_\alpha}^\alpha \end{bmatrix}} = \underset{N_{bao}\times 1}{\left[-\langle\mu|(\hat{V}_{bc}^\alpha - \langle\psi_n^\alpha|\hat{V}_{bc}^\alpha|\psi_n^\alpha\rangle)|\psi_n^\alpha\rangle\right]} \qquad (15)\ (16)$$

- Expected results : Amorphous CdSe ?

  ◦ Rapid energy convergence w.r.t. buffer length



  ◦ Explanation = reduced $\rho^{\alpha}(\mathbf{r}) - \rho(\mathbf{r})$



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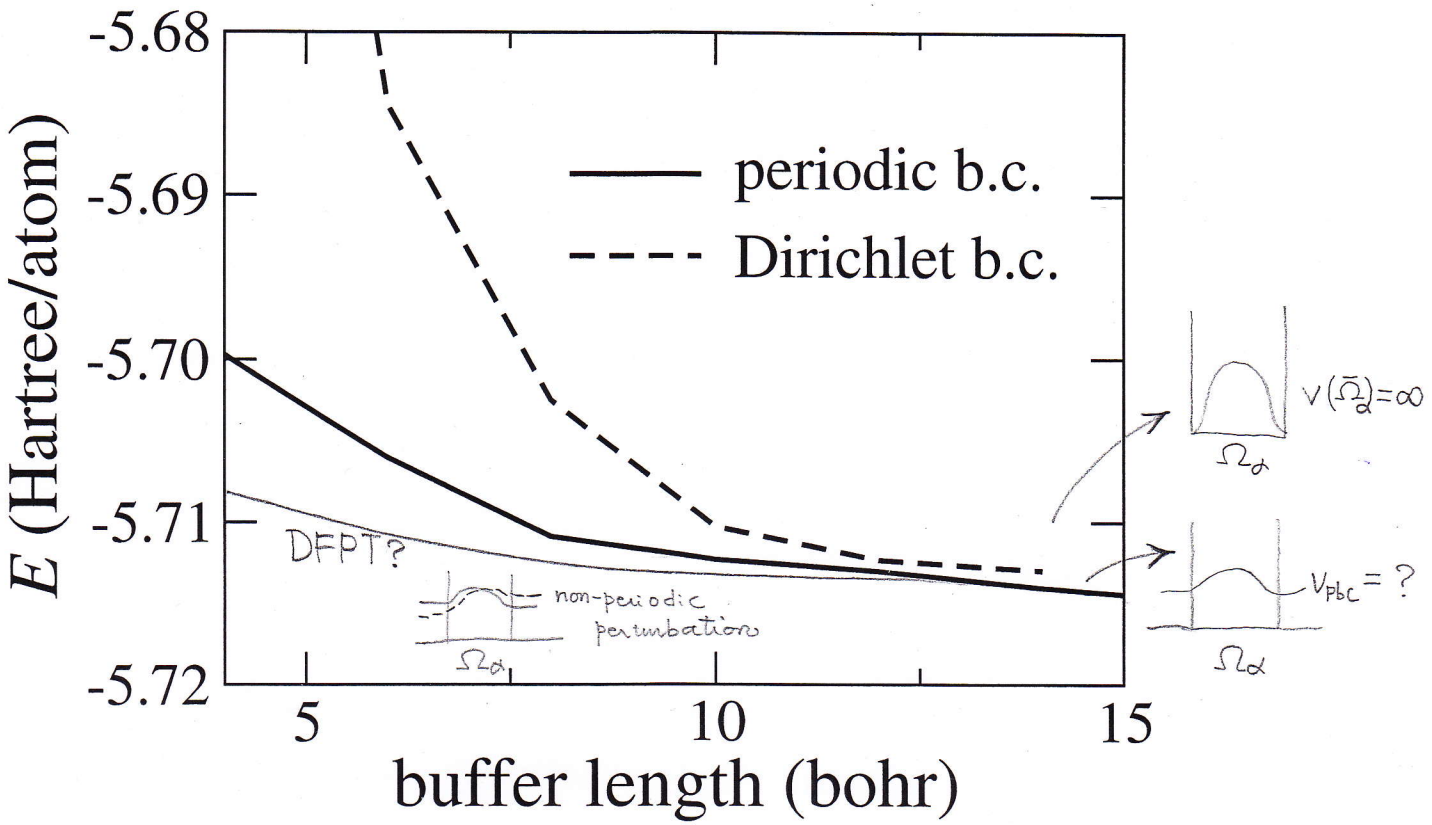

DF perturbation theory ?

$$\delta v_{bc}(\mathbf{r}) = \int d\mathbf{r}' \chi_{KS}^{-1}(\mathbf{r},\mathbf{r}') \underbrace{\delta\rho(\mathbf{r}')}_{\rho_\alpha(\mathbf{r}') - \rho_{global}(\mathbf{r}')}$$

$\Downarrow$

Solve KS-eq again

$O(N) - O(N^3)$ Crossover

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L: Cubic box length

l: Cubic domain length

b: Buffer length

$O(N)$ DFT computation time $\quad$ $O(N^3)$ DFT $\quad$ DFT complexity

$$\left(\frac{L}{l}\right)^3 \times (l+2b)^{3\nu} = L^{3\nu} \qquad \begin{pmatrix} \nu=2 & N<10^3 \\ \nu=3 & N>10^3 \end{pmatrix}$$

$$\left(\frac{L}{l}\right)^3 = \left(\frac{L}{l+2b}\right)^{3\nu}$$

For minimizing computational time, $l = l_* = 2b/(\nu-1)$.

$$\therefore \quad \frac{L}{\frac{2b}{\nu-1}} = \left(\frac{L}{\frac{2b}{\nu-1} + 2b}\right)^{\nu}$$

$$\frac{L}{\frac{2b}{\nu-1}} = \left(\frac{L}{\frac{\nu}{\nu-1} 2b}\right)^{\nu}$$

Assuming L is small enough so that $\nu = 2$ (to be checked),

$$\frac{L}{2b} = \left(\frac{L}{4b}\right)^2$$

$$\frac{L}{2b}\left(1 - \frac{L}{8b}\right) = 0$$

$$\therefore \; L = 8b$$

With LDC-DFT, $b = 3.57$ a.u. to achieve the energy convergence of 5×10^{-3} a.u., then the $O(N^3) - O(N)$ crossover point is

$$L = 8 \times 3.57 = 28.56 \text{ au.}$$

$$N = 512 \times \left(\frac{28.56}{45.664}\right)^3 = 125.26 \text{ atoms.} \quad (< 10^3 \text{ indeed})$$