

Lecture on First-principles Computations (7): The Exchange-Correlation Energy Functional

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The Key Issue in KS-DFT

The exchange-correlation energy functional:

$$E_{xc}[n] = F[n] - T_s[n] - E_H[n]$$

$$E_{xc}[n] = E_x[n] + E_c[n]$$

$$E_x[n] = \langle \Phi_0^{\text{KS}} | \hat{V}_{ee} | \Phi_0^{\text{KS}} \rangle - E_H[n]$$

The exchange-correlation potential:


$$v_{xc}[n](\mathbf{r}) = \frac{\delta E_{xc}[n]}{\delta n(\mathbf{r})} \quad \longleftarrow \text{Local, multiplicative potential}$$

The key in practical KS-DFT calculations is to find useful approximations for $E_{xc}[n]$ and the corresponding $v_{xc}[n](\mathbf{r})$.

The expression of $E_{xc}[n(\mathbf{r})]$

It is convenient to express $E_{xc}[n]$ as

$$E_{xc}[n] = \int d^3 r n(\mathbf{r}) \epsilon_{xc}[n](\mathbf{r})$$

$$v_{xc}[n](\mathbf{r}) = \epsilon_{xc}[n](\mathbf{r}) + n(\mathbf{r}) \frac{\delta \epsilon_{xc}[n](\mathbf{r})}{\delta n(\mathbf{r})}$$


Energy per electron at point \mathbf{r} , in theory depending on the density in the entire space, but usually only on the density in the neighborhood of \mathbf{r} matters.

Some basic quantities to know

- Spin-polarized electron density :

$$n_{\sigma}(\mathbf{r}) = N \sum_{\sigma_2, \dots, \sigma_N} \int d^3 r_2 \cdots d^3 r_N |\Psi(\mathbf{r}, \sigma; \mathbf{r}_2, \sigma_2; \cdots; \mathbf{r}_N, \sigma_N)|^2$$

$$n(\mathbf{r}) = \sum_{\sigma=\uparrow, \downarrow} n_{\sigma}(\mathbf{r})$$

- Spin density:

$$m(\mathbf{r}) = n_{\uparrow}(\mathbf{r}) - n_{\downarrow}(\mathbf{r})$$

- Polarization density

$$\zeta(\mathbf{r}) = \frac{n_{\uparrow}(\mathbf{r}) - n_{\downarrow}(\mathbf{r})}{n(\mathbf{r})}$$

One-particle reduced density matrix

- One-particle density matrix :

$$\rho_{\sigma}(\mathbf{r}, \mathbf{r}') = N \sum_{\sigma_2, \dots, \sigma_N} \int d^3 r_2 \cdots d^3 r_N \times$$
$$[\Psi^*(\mathbf{r}, \sigma; \mathbf{r}_2, \sigma_2; \cdots; \mathbf{r}_N, \sigma_N) * \Psi(\mathbf{r}', \sigma; \mathbf{r}_2, \sigma_2; \cdots; \mathbf{r}_N, \sigma_N)]$$

$$n_{\sigma}(\mathbf{r}) = \rho_{\sigma}(\mathbf{r}, \mathbf{r})$$

For noninteracting systems (Ψ is a single Slater determinant):

$$\rho_{\sigma}(\mathbf{r}, \mathbf{r}') = \sum_l^{occ} \phi_{l\sigma}^*(\mathbf{r}) \phi_{l\sigma}(\mathbf{r}')$$

Two-particle correlation function

- Two-particle spin-integrated density :

$$\gamma(\mathbf{r}, \mathbf{r}') = N(N-1) \sum_{\sigma_1, \sigma_2, \sigma_3, \dots, \sigma_N} \int d^3 r_3 \cdots d^3 r_N |\Psi^*(\mathbf{r}, \sigma_1; \mathbf{r}', \sigma_2; \mathbf{r}_3, \sigma_3; \dots; \mathbf{r}_N, \sigma_N)|^2$$

This is the joint probability of finding one electron at \mathbf{r} and another electron at \mathbf{r}' .

Define the pair-correlation function $g(\mathbf{r}_1, \mathbf{r}_2)$

$$\gamma(\mathbf{r}, \mathbf{r}') = n(\mathbf{r})n(\mathbf{r}')g(\mathbf{r}_1, \mathbf{r}_2)$$

$$\Delta\gamma(\mathbf{r}, \mathbf{r}') = \gamma(\mathbf{r}, \mathbf{r}') - n(\mathbf{r})n(\mathbf{r}')$$

$$g(\mathbf{r}, \mathbf{r}') = \frac{\gamma(\mathbf{r}, \mathbf{r}')}{n(\mathbf{r})n(\mathbf{r}')} = 1 + \frac{\Delta\gamma(\mathbf{r}, \mathbf{r}')}{n(\mathbf{r})n(\mathbf{r}')}$$

Normalized pair distribution function

The exchange-correlation (XC) hole

$$\Delta\gamma(\mathbf{r}, \mathbf{r}') = \gamma(\mathbf{r}, \mathbf{r}') - n(\mathbf{r})n(\mathbf{r}') = n(\mathbf{r})n_{xc}(\mathbf{r}, \mathbf{r}')$$

$$n_{xc}(\mathbf{r}, \mathbf{r}') = \frac{\Delta\gamma(\mathbf{r}, \mathbf{r}')}{n(\mathbf{r})} = \frac{\gamma(\mathbf{r}, \mathbf{r}')}{n(\mathbf{r})} - n(\mathbf{r}') \leftarrow \text{The exchange-correlation hole}$$

The depletion of the electron density at \mathbf{r}' due to the presence of an electron at \mathbf{r} .

The sum rule:

$$\int d^3 r' \Delta\gamma(\mathbf{r}, \mathbf{r}') = -n(\mathbf{r}); \quad \int d^3 r' n_{xc}(\mathbf{r}, \mathbf{r}') = -1$$

Exchange-correlation hole for the non-interacting ground state

$$\gamma(\mathbf{r}, \mathbf{r}') = N(N-1) \sum_{\sigma_1, \sigma_2, \sigma_3, \dots, \sigma_N} \int d^3 r_3 \cdots d^3 r_N |\Psi^*(\mathbf{r}, \sigma_1; \mathbf{r}', \sigma_2; \mathbf{r}_3, \sigma_3; \cdots; \mathbf{r}_N, \sigma_N)|^2$$

If Ψ is a single Slater determinant,

$$\gamma(\mathbf{r}, \mathbf{r}') = n(\mathbf{r})n(\mathbf{r}') - \sum_{\sigma} |\rho_{\sigma}(\mathbf{r}, \mathbf{r}')|^2$$

$$\Delta\gamma(\mathbf{r}, \mathbf{r}') = - \sum_{\sigma} |\rho_{\sigma}(\mathbf{r}, \mathbf{r}')|^2$$

$$n_{xc}(\mathbf{r}, \mathbf{r}') = n_x(\mathbf{r}, \mathbf{r}') = - \frac{\sum_{\sigma} |\rho_{\sigma}(\mathbf{r}, \mathbf{r}')|^2}{n(\mathbf{r})}$$

Property of the XC hole

- $n_{xc}(\mathbf{r}, \mathbf{r}') = n_x(\mathbf{r}, \mathbf{r}') + n_c(\mathbf{r}, \mathbf{r}')$
- $n_x(\mathbf{r}, \mathbf{r}') \leq 0$
- $\int d^3 r' n_x(\mathbf{r}, \mathbf{r}') = -1$
- $\int d^3 r' n_c(\mathbf{r}, \mathbf{r}') = 0$
- $n_x(\mathbf{r}, \mathbf{r}) = -\frac{n_{\uparrow}^2(\mathbf{r}) + n_{\downarrow}^2(\mathbf{r})}{n(\mathbf{r})}$
- $n_c(\mathbf{r}, \mathbf{r}) < 0$

Interaction energy in terms of the XC hole

$$\begin{aligned}\langle \hat{V}_{ee} \rangle &= \frac{1}{2} \sum_{i \neq j} \langle \Psi | \frac{1}{|\hat{\mathbf{r}}_i - \hat{\mathbf{r}}_j|} | \Psi \rangle = \frac{N(N-1)}{2} \langle \Psi | \frac{1}{|\hat{\mathbf{r}}_1 - \hat{\mathbf{r}}_2|} | \Psi \rangle \\ &= \frac{1}{2} \int d^3 r \int d^3 r' \frac{\gamma(\mathbf{r}, \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \\ &= \underbrace{\frac{1}{2} \int d^3 r \int d^3 r' \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}}_{E_H[n(\mathbf{r})]} + \underbrace{\frac{1}{2} \int d^3 r n(\mathbf{r}) \int d^3 r' \frac{n_{xc}(\mathbf{r}, \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}}_{U_{xc}[n(\mathbf{r})]}\end{aligned}$$

Interaction energy in terms of the XC hole

$$\begin{aligned}\langle \hat{V}_{ee} \rangle &= \frac{1}{2} \sum_{i \neq j} \langle \Psi | \frac{1}{|\hat{\mathbf{r}}_i - \hat{\mathbf{r}}_j|} | \Psi \rangle = \frac{N(N-1)}{2} \langle \Psi | \frac{1}{|\hat{\mathbf{r}}_1 - \hat{\mathbf{r}}_2|} | \Psi \rangle \\ &= \frac{1}{2} \int d^3 r \int d^3 r' \frac{\gamma(\mathbf{r}, \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \\ &= \underbrace{\frac{1}{2} \int d^3 r \int d^3 r' \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}}_{E_H[n(\mathbf{r})]} + \underbrace{\frac{1}{2} \int d^3 r n(\mathbf{r}) \int d^3 r' \frac{n_{xc}(\mathbf{r}, \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}}_{U_{xc}[n(\mathbf{r})]}\end{aligned}$$

$$\begin{aligned}E_{xc} &= \langle \hat{T} + \hat{V}_{ee} \rangle - T_s - E_H = \underbrace{T - T_s}_{= T_c?} + U_{xc}\end{aligned}$$

Hellmann-Feynman theorem

Assume the Hamiltonian \hat{H}_λ depends on certain parameter λ , how does its eigenvalue $E_\lambda = \langle \Psi_\lambda | \hat{H}_\lambda | \Psi_\lambda \rangle$ change as a function of λ ?

Assume $|\Psi_\lambda\rangle$ is normalized, $\langle \Psi_\lambda | \Psi_\lambda \rangle = 1$, then

$$\begin{aligned} \frac{dE_\lambda}{d\lambda} &= \frac{d}{d\lambda} \langle \Psi_\lambda | \hat{H}_\lambda | \Psi_\lambda \rangle \\ &= \underbrace{\left\langle \frac{\partial \Psi_\lambda}{\partial \lambda} | \hat{H}_\lambda | \Psi_\lambda \right\rangle + \left\langle \Psi_\lambda | \hat{H}_\lambda | \frac{\partial \Psi_\lambda}{\partial \lambda} \right\rangle}_{= E_\lambda \frac{d}{d\lambda} \langle \Psi_\lambda | \Psi_\lambda \rangle = 0} + \left\langle \Psi_\lambda | \frac{\partial \hat{H}_\lambda}{\partial \lambda} | \Psi_\lambda \right\rangle \end{aligned}$$

Hellmann-Feynman theorem

$$\frac{dE_\lambda}{d\lambda} = \frac{d}{d\lambda} \langle \Psi_\lambda | \hat{H}_\lambda | \Psi_\lambda \rangle = \langle \Psi_\lambda | \frac{\partial \hat{H}_\lambda}{\partial \lambda} | \Psi_\lambda \rangle$$

The amount of energy change by changing λ from λ_1 to λ_2 :

$$\Delta E = \int_{\lambda_1}^{\lambda_2} \left(\frac{dE_\lambda}{d\lambda} \right) d\lambda = \int_{\lambda_1}^{\lambda_2} \langle \Psi_\lambda | \frac{\partial \hat{H}_\lambda}{\partial \lambda} | \Psi_\lambda \rangle d\lambda$$

The adiabatic connection construction for $E_{xc}[n(\mathbf{r})]$

Design a path connecting the KS state and the full many-body state

$$\hat{H}_\lambda = \hat{T} + \lambda \hat{V}_{ee} + \hat{V}_{aux}^\lambda, \quad \hat{V}_{aux}^\lambda = \int d^3 r v_{aux}^\lambda(\mathbf{r}) \hat{n}(\mathbf{r})$$

$v_{aux}^\lambda(\mathbf{r})$ is chosen such that :

$$\hat{H}_{\lambda=0} = \hat{H}_{KS} = \hat{T} + \int d^3 r v_{eff}(\mathbf{r}) \hat{n}(\mathbf{r}) \quad (\text{the KS system})$$

$$\hat{H}_{\lambda=1} = \hat{H} = \hat{T} + \hat{V}_{ee} + \int d^3 r v_{ext}(\mathbf{r}) \hat{n}(\mathbf{r}) \quad (\text{the Interacting system})$$

The electron density is kept fixed at the physical $n(\mathbf{r})$ for $0 < \lambda < 1$.

Adiabatic connection construction for $E_{xc}[n(\mathbf{r})]$

$$E_{\lambda=0} = T_s + \int d^3 r v_{eff}(\mathbf{r}) n(\mathbf{r})$$

$$E_{\lambda=1} = T + V_{ee} + \int d^3 r v_{ext}(\mathbf{r}) n(\mathbf{r})$$

$$E_{\lambda=1} - E_{\lambda=0} = T - T_s + V_{ee} + \int d^3 r (v_{ext}(\mathbf{r}) - v_{eff}(\mathbf{r})) n(\mathbf{r}) \quad (\text{I})$$

The Hellmann-Feynman theorem:


$$\begin{aligned} E_{\lambda=1} - E_{\lambda=0} &= \int_0^1 d\lambda \langle \Psi_0^\lambda | \frac{\partial \hat{H}_\lambda}{\partial \lambda} | \Psi_0^\lambda \rangle = \int_0^1 d\lambda \langle \Psi_0^\lambda | \hat{V}_{ee} + \frac{\partial \hat{V}_{aux}^\lambda}{\partial \lambda} | \Psi_0^\lambda \rangle \\ &= \int_0^1 d\lambda \langle \Psi_0^\lambda | \hat{V}_{ee} | \Psi_0^\lambda \rangle + \int d^3 r (v_{ext}(\mathbf{r}) - v_{eff}(\mathbf{r})) n(\mathbf{r}) \quad (\text{II}) \end{aligned}$$

Adiabatic connection construction for $E_{xc}[n(\mathbf{r})]$

Compare the two equations (I) and (II), one obtains

$$T - T_s + V_{ee} = \int_0^1 d\lambda \langle \Psi_0^\lambda | \hat{V}_{ee} | \Psi_0^\lambda \rangle = \frac{1}{2} \int_0^1 d\lambda \int d^3 r \int d^3 r' \frac{\gamma_\lambda(\mathbf{r}, \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}$$

$$\begin{aligned} E_{xc}[n(\mathbf{r})] &= T - T_s + V_{ee} - E_H \\ &= \frac{1}{2} \int_0^1 d\lambda \int d^3 r n(\mathbf{r}) \int d^3 r' \frac{n_{xc}^\lambda(\mathbf{r}, \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \\ &= \frac{1}{2} \int d^3 r n(\mathbf{r}) \int d^3 r' \frac{\bar{n}_{xc}(\mathbf{r}, \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \end{aligned}$$


$$n_{xc}^\lambda = \frac{\gamma_\lambda(\mathbf{r}, \mathbf{r}')}{n(\mathbf{r})} - n(\mathbf{r}')$$

Adiabatic connection construction for $E_{xc}[n(\mathbf{r})]$

$$E_{xc}[n(\mathbf{r})] = \frac{1}{2} \int d^3 r n(\mathbf{r}) \int d^3 r' \frac{\bar{n}_{xc}(\mathbf{r}, \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}$$

The XC energy can be interpreted as the Coulomb interaction energy between the electron and its XC hole.

$$\epsilon[n](\mathbf{r}) = \frac{1}{2} \int d^3 r' \frac{\bar{n}_{xc}(\mathbf{r}, \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}$$

The energy density per electron $\epsilon[n](\mathbf{r})$ at a given spatial point \mathbf{r} is fully specified via the average XC hole $\bar{n}_{xc}(\mathbf{r}, \mathbf{r}')$.

The exchange-correlation hole

$$\begin{aligned}\epsilon[n](\mathbf{r}) &= \frac{1}{2} \int d^3 r' \frac{\bar{n}_{xc}(\mathbf{r}, \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} = \frac{1}{2} \int d^3 u \frac{\bar{n}_{xc}(\mathbf{r}, \mathbf{r} + \mathbf{u})}{|\mathbf{u}|} \\ &= \frac{1}{2} \int du \left(\frac{u^2}{u} \right) \int d\Omega_{\mathbf{u}} \bar{n}_{xc}(\mathbf{r}, \mathbf{r} + \mathbf{u}) \\ &= \frac{1}{2} \int du u \langle \bar{n}_{xc}(\mathbf{r}, \mathbf{r} + \mathbf{u}) \rangle_{\Omega_{\mathbf{u}}}\end{aligned}$$

Angular-integrated exchange-correlation hole

$$\langle \bar{n}_{xc}(\mathbf{r}, \mathbf{r} + \mathbf{u}) \rangle_{\Omega_{\mathbf{u}}} = \int d\theta_{\mathbf{u}} d\varphi_{\mathbf{u}} \bar{n}_{xc}(\mathbf{r}, \mathbf{r} + \mathbf{u})$$

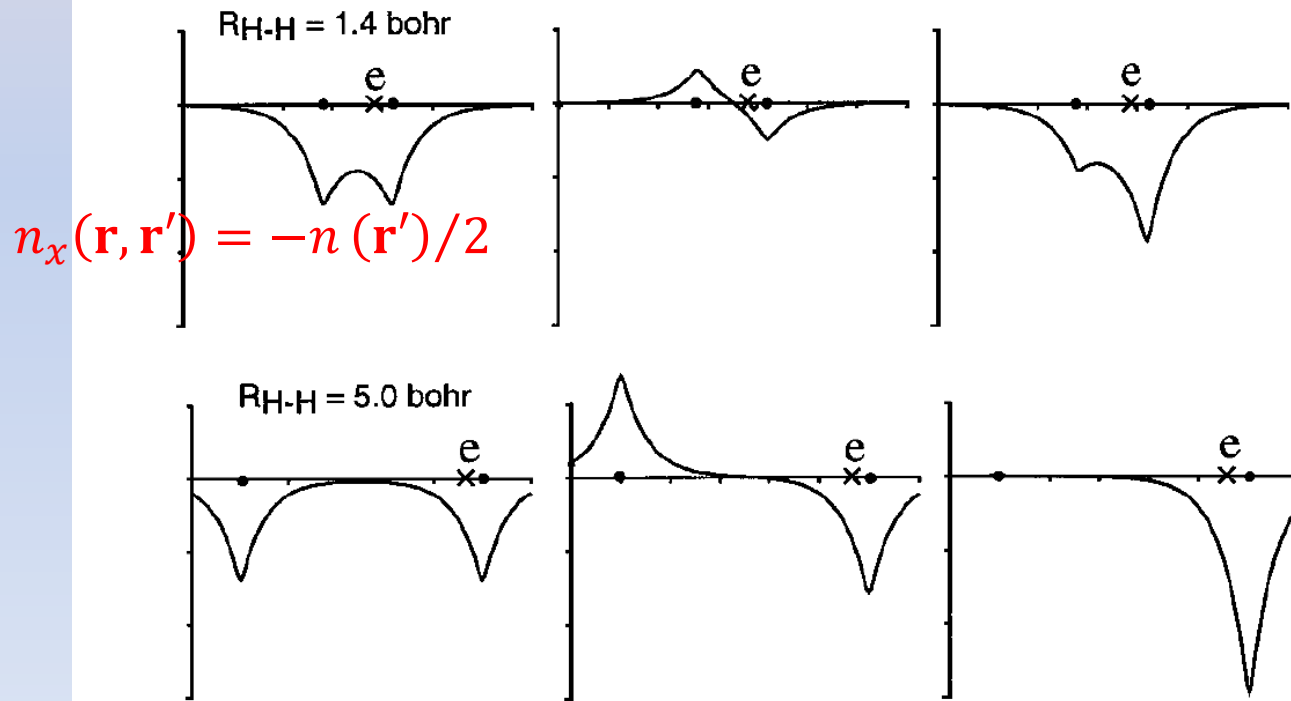
The detailed angular-dependence of the XC hole is irrelevant, only the angular-integrated value matters.

Exchange-correlation hole for H₂

Exact-exchange
hole

Correlation
hole

Fermi hole + Coulomb hole = total hole



The spin scaling relation

For exchange energy:

$$E_x[n_\uparrow, n_\downarrow] = E_x[n_\uparrow, 0] + E_x[0, n_\downarrow]$$

For spin-degenerate system: $n_\uparrow = n_\downarrow = n/2$

$$E_x[n] = E_x[n/2, n/2] = E_x[n/2, 0] + E_x[0, n/2] = 2E_x[n/2, 0]$$

Therefore,

$$E_x[n_\uparrow, n_\downarrow] = \frac{1}{2} (E_x[2n_\uparrow] + E_x[2n_\downarrow])$$

Popular functionals

- Local Density Approximation (LDA)
 - Vosko, Wilk, Nusair (VWN), 1980;
 - Perdew & Wang (PW), 1992;
 - Perdew & Zunger (PZ), 1981;
- Generalized Gradient Approximation (GGA)
 - Lee, Yang, Parr (LYP), 1988;
 - Becke (B88, B97, BLYP), 1988, 1997;
 - Perdew, Burke, Ernzerhof (PBE), 1996
- Meta-GGA
 - Tao, Perdew, Staroverov, Scuseria (TPSS), 2003
 - Strongly Constrained and Appropriately Normed functional (SCAN) (Sun, Ruzsinszky, Perdew), 2015
- Hybrid density functionals
 - B3LYP, 1993; PBE0, 1996;
 - Heyd, Scuseria, Ernzerhof (HSE), 2003

Jacob's ladder in DFT (John Perdew, 2001)



Hell -- The Hartree world

And Jacob went out from Beersheba, and went toward Haran. And he lighted upon a certain place, and tarried there all night, because the sun was set; and he took of the stones of that place, and put them for his pillows, and lay down in that place to sleep. And he dreamed, and behold a ladder set up on the earth, and the top of it reached to heaven: and behold the angels of God ascending and descending on it.

Genesis, 28.10-12

J. P. Perdew and K. Schmidt, in
“*Jacob's ladder of Density Functional Approximations for the Exchange-Correlation Energy*”,
2001