DFT Functionals

Recent developments in LIBXC — A comprehensive library of functionals for density functional theory

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ABSTRACT

LIBXC is a library of exchange–correlation functionals for density-functional theory. We are concerned with semi-local functionals (or the semi-local part of hybrid functionals), namely local-density approximations, generalized-gradient approximations, and meta-generalized-gradient approximations. Currently we include around 400 functionals for the exchange, correlation, and the kinetic energy, spanning more than 50 years of research. Moreover, LIBXC is by now used by more than 20 codes, not only from the atomic, molecular, and solid-state physics, but also from the quantum chemistry communities.

Local Density Approximation

- Assumes same density everywhere
- Exact for the uniform electron gas "Jellium"
- Used for materials, deprecated
- Strictly local

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

- Popular choice: VWN

- Includes local gradient
- "semi-local" nature: gradient tells a bit about close proximity
- Widely used, both for materials and molecules

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

- Popular choice: PBE

- Next derivative
- Sensitive to numerical integration through Laplacian
- Default settings sometimes not good enough

$$E_{\mathrm{XC}}^{\mathrm{GGA}} = \int d\mathbf{r}\rho(\mathbf{r})\epsilon_{\mathrm{XC}}^{\mathrm{GGA}}[\rho(\mathbf{r}), \nabla\rho(\mathbf{r}), \nabla^2\rho(\mathbf{r}), \tau]$$

$$\tau \equiv \sum_i^{\mathrm{occ}} |\nabla\psi_i(\mathbf{r})|^2$$

- Popular choices: SCAN (built on constraints!), M06, TPSS

- Commonly improved band gaps and relative energies between spin states
- Popular choices: B3LYP, PBE0

$$E_{\mathrm{XC}}^{\mathrm{hyb}} = aE_{\mathrm{X}}^{\mathrm{HF}} + (1 - a)E_{\mathrm{X}}^{\mathrm{DFT}} + E_{\mathrm{C}}^{\mathrm{DFT}}$$

$$E_{\mathrm{x}}^{\mathrm{HF}} = -\frac{1}{2}\sum_{i,j}\iint \psi_i^*(\mathbf{r}_1)\psi_j^*(\mathbf{r}_2)\frac{1}{r_{12}}\psi_j(\mathbf{r}_1)\psi_i(\mathbf{r}_2)\, d\mathbf{r}_1\, d\mathbf{r}_2$$

- Computationally more efficient
- Popular choice: HSE06

$$\frac{1}{r_{12}} = \underbrace{\frac{1 - [\alpha + \beta(1 - \omega_{\mathrm{RSF}}(\gamma, r_{12}))]}{r_{12}}}_{\mathrm{SR,\ DFT}} + \underbrace{\frac{\alpha + \beta(1 - \omega_{\mathrm{RSF}}(\gamma, r_{12}))}{r_{12}}}_{\mathrm{LR,\ HF}}$$

- Can be tuned in many cases to specific system based on Koopman's condition

$$-\varepsilon_{\mathrm{HOMO}}(N_e) = \mathrm{IE}(N_e) \equiv E(N_e - 1) - E(N_e)$$