DFT Functionals

XC 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

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

- Popular choice: VWN

Generalized-Gradient Approximation

- 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

Meta-GGA

- 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

Hybrid Functional

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

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

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

Range-separated hybrid

- 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

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

Post-HF methods

Post-HF method

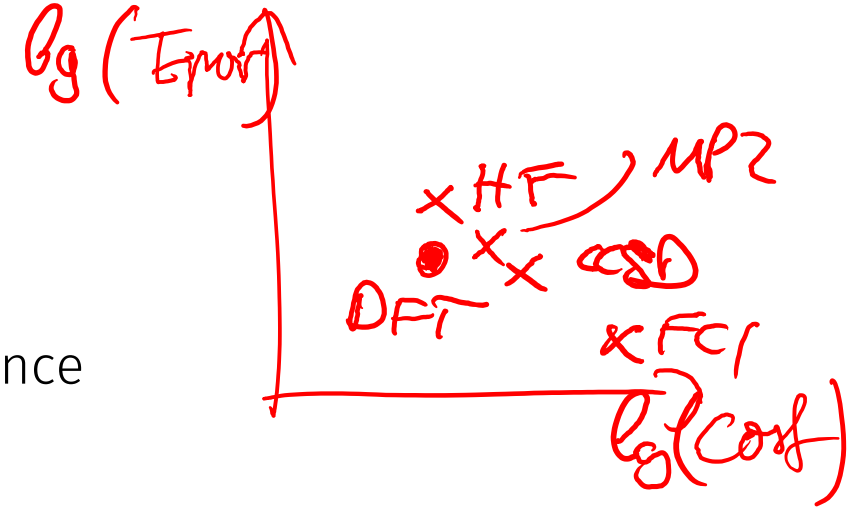
- HF only has mean-field limit and only one determinant
- Correlation important for relative energy differences, driving chemistry
    - Reaction energies
    - Barrier heights
- Correlation: “How does having a single electron here impact all other electrons?”
    - Often understood as expansion in excitations
- Different approaches
    - Full Configuration Interaction (FCI)
    - Perturbative: Moller-Plesset (MPn)
    - Truncated: Coupled Cluster (e.g. CCSD)
    - Multi-reference Methods

Full Configuration Interaction

$$\Psi_{\text{FCI}} = c_0\psi + \sum_{a}^{\text{occ}}\sum_{r}^{\text{virt}} c_a^r \psi_a^r + \sum_{a<b}^{\text{occ}}\sum_{r<s}^{\text{virt}} c_{ab}^{rs}\psi_{ab}^{rs} + \sum_{a<b<c}^{\text{occ}}\sum_{r<s<t}^{\text{virt}} c_{abc}^{rst}\psi_{abc}^{rst} + \dots$$

- Expansion in excited determinants of the HF solution
- Find coefficients c* by minimizing energy subject to normalization
- Exact iff all orders are included and we have a complete basis set, otherwise upper limit
  - Unoccupied orbitals need to be represented well
- Inefficient: number of determinants quickly becomes too large
- Split into two regimes:
  - “Dynamic/weak correlation”: c_0 dominates, i.e. HF is a good approximation
  - “Static/strong correlation”: otherwise, requires multi-reference methods
- Yields energies, new wave function, variational

$$\psi \equiv \Psi_{\text{HF}}$$



Configuration Interaction

$$\Psi_{\text{CISD}} = c_0\psi + \sum_{a}^{\text{occ}}\sum_{r}^{\text{virt}} c_a^r \psi_a^r + \sum_{a<b}^{\text{occ}}\sum_{r<s}^{\text{virt}} c_{ab}^{rs}\psi_{ab}^{rs}$$

- Finite truncation after first orders
  - Here “Configuration Interaction Singles Doubles”
- No size consistency
  - E(A+B at infinite separation) != E(A) + E(B)
- Yields energies, new wave functions, variational

Møller-Plesset Perturbation Theory

$$E_{\mathrm{MP2,c}} = -\frac{1}{4}\sum_{a<b}^{\mathrm{occ}}\sum_{r<s}^{\mathrm{virt}} \frac{|\langle ab||rs\rangle|^2}{\varepsilon_r + \varepsilon_s - \varepsilon_a - \varepsilon_b}$$

- Include correlation as perturbation up to order n
  - Zeroth order is Hartree-Fock
- Does not necessarily converge (or behave well)
- Comparably simple method, common for weak correlation
- Higher orders possible, yet much more expensive and not quite better
- Yields energies, no new wave functions, not variational, size-consistent