

Lecture 20: Density Functional Theory

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Basics

- Hohenberg-Kohn theorem (refined by Levy and Lieb)
 1. The ground-state energy of a many-electron system is a unique functional of the electron density ρ
 2. One-to-one mapping between ground state densities ρ and local multiplicative one-electron potentials
- Kohn-Sham (KS) Scheme: Use Slater determinant (KS determinant) to determine the exact ground state density from KS orbitals $\{\phi_i\}$,

$$\rho_{\sigma}(\mathbf{r}) = \sum_i |\phi_{i\sigma}(\mathbf{r})|^2$$

Density constraint determines the local KS potential

$$v_{s\sigma}(\mathbf{r}) = v_{\text{ne}}(\mathbf{r}) + v^{\text{H}}(\mathbf{r}) + \frac{\delta E^{\text{XC}}[\rho]}{\delta \rho_{\sigma}(\mathbf{r})},$$

where $E^{\text{XC}}[\rho]$ is the exchange-correlation (XC) energy functional

- Warning: $E^{\text{XC}}[\rho]$ is extremely complicated and notoriously hard to approximate reliably

Hybrid KS Energy Functional

$$E[\{\phi_i\}] = \sum_i \langle \phi_i | \hat{h}_{\text{core}} | \phi_i \rangle + E^{\text{H}}[\{\phi_i\}] + c^{\text{X}} E^{\text{XX}}[\{\phi_i\}] + E^{\text{XC, hybrid}}[\{\phi_i\}]$$

- E^{XC} depends on MOs coefficients through ρ and other “semilocal” quantities
- c^{X} : “HF/exact/hybrid exchange mixing parameter”
- “Generalized” KS: Variationally minimize E with respect to the orbitals, not just ρ (proper KS)

Generalized KS Equations

- Canonical GKS equations:

$$\mathbf{F}^{\text{GKS}}[\{\phi_i\}] |\phi_k\rangle = \epsilon_k |\phi_k\rangle$$

- GKS effective one-electron Hamiltonian

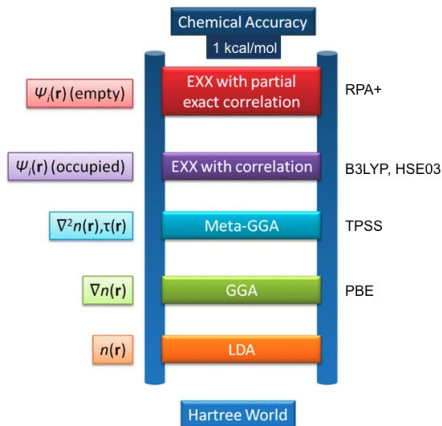
$$\mathbf{F}^{\text{GKS}}[\{\phi_i\}] = \hat{h}_{\text{core}} + \hat{J}[\{\phi_i\}] + c^{\text{X}} \hat{K}[\{\phi_i\}] + \hat{K}^{\text{XC}}[\{\phi_i\}]$$

- XC potential matrix (nonlocal in GKS)

$$K^{\text{XC}}[\{\phi_i\}](x, x') = \frac{\delta E^{\text{XC}}}{\delta \gamma(x, x')}$$

- Solved “selfconsistently”

Jacob's Ladder



Schmidt, Perdew; Tao

- The higher the rung, the more “ingredients”, but also the more constraints
- Computational complexity also increases
- No guarantee for convergence

Local Spin Density Approximation

$$E^{\text{XC, LSDA}}[\rho_\alpha, \rho_\beta] = \int d^3r \epsilon^{\text{XC}}(\rho_\alpha(\mathbf{r}), \rho_\beta(\mathbf{r})) \rho(\mathbf{r})$$

- ϵ^{XC} : XC energy per particle (energy density) of a uniform electron gas with constant electron density $n_\sigma = \rho_\sigma$
- Example: Slater-Dirac exchange,

$$E^{\text{X, LSDA}}[\rho_\alpha, \rho_\beta] = -\frac{1}{8\pi^3} \sum_\sigma \int d^3r (6\pi^2 \rho_\sigma(\mathbf{r}))^{4/3}.$$

- Common LSDA correlation functionals: Vosko, Wilk, Nusair (VWN), Perdew and Wang (PW, 1992)
- LSDA becomes exact in the uniform limit $\rho_\sigma \rightarrow n_\sigma$ and in thermodynamic limit $N \rightarrow \infty$

(Meta-)Generalized Gradient Approximation

$$\epsilon^{\text{XC, MGGA}} = \epsilon^{\text{XC, MGGA}}(\rho_\alpha(\mathbf{r}), \rho_\beta(\mathbf{r}), \nabla\rho_\alpha(\mathbf{r}), \nabla\rho_\beta(\mathbf{r}), \tau_\alpha(\mathbf{r}), \tau_\beta(\mathbf{r}))$$

- In addition to ρ_σ , $\nabla\rho_\sigma$ (GGA), MGGA functionals depend locally on KS kinetic energy density

$$\tau_\sigma(\mathbf{r}) = \frac{1}{2} \sum_i |\nabla\phi_i(\mathbf{r})|^2$$

- Popular GGA functionals: Becke-Perdew 86 (BP86, Becke 1988 GGA for exchange plus Perdew 1986 GGA for correlation), Perdew-Burke-Ernzerhof (PBE), Lee-Yang-Parr (LYP), Becke 1997 GGA (B97).
- Common MGGA functionals: Tao-Perdew-Staroverov-Scuseria (TPSS), strongly constrained and normed (SCAN, Perdew and co-workers), r^2 SCAN, many Minnesota functionals
- Often “hybridized” semi-empirically with HF exchange
- Many more (empirical) functionals, see, e.g., Mardirossian and Head-Gordon 2017, libxc

Uses of HF and Semilocal DFT

	HF	Semilocal DFT
Covalent bond energies (kcal/mol)	> 50 – 100	3 – 5
Barrier heights (kcal/mol)	5 – 10	> 20
Covalent bond distances (pm)	~ 1	> 3
Harmonic vibrational frequencies (cm^{-1})	100	200 – 500

Typical errors (coarse estimates) in HF and DFT calculations

- HF: Mostly for HF-based correlated wavefunction methods
- LSDA: (Metallic) solids only
- Workhorse for chemistry: GGAs and MGGA's for fast screening, preoptimization; metal clusters
- Hybrid functionals (e.g. TPSSH): all-around
- DFT results can be strongly functional-dependent, especially for empirically “optimized” functionals

Limitations

- HF and HF-based methods qualitatively wrong for “multi-reference” ground states and poor even for weakly correlated systems: Stretched and multiple bonds, open-shell transition and *f*-metal compounds)
- Semilocal DFAs may fail for
 - ▶ noncovalent interactions. Dispersion corrections needed.
 - ▶ quasi-one-electron systems, e.g. radicals, odd-electron bonds; negative ions: Self-interaction error
 - ▶ strongly correlated systems, especially magnetic/spin properties
 - ▶ charge-transfer and Rydberg excitations in time-dependent DFT
- Highly parameterized functionals may fail for systems/properties different from the ones used to fit them
- Calibration should be used where possible