

Recap: Density functionals

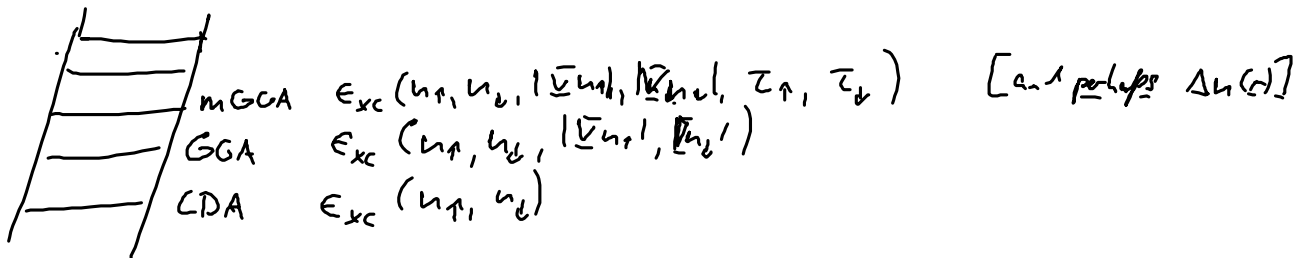
$$E[n] = T_S[n] + \int d^3r v^{nuc}(\mathbf{r}) n(\mathbf{r}) + \int d^3r d^3r' \frac{n(\mathbf{r}) n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + E_{xc}[n]$$

Approximations to $E_{xc}[n]$:

- Local-density approximation $E_{xc}^{LDA}[n] = \int d^3r n(\mathbf{r}) \epsilon_{xc}^{HEG}(n(\mathbf{r}))$
 - surprisingly successful for "well-behaved" systems, esp. solids
 - well-understood limitations
 - "first principles"
- Generalized gradient approximation GGA: $E_{xc}^{GGA}[n] = \int d^3r n(\mathbf{r}) \epsilon_{xc}^{GGA}(n(\mathbf{r}), |\nabla n(\mathbf{r})|)$
 - widest-used "production" method today
 - corrects several LDA failures (overbinding, H-banded systems, atomization energies)
 - still, well-understood limitations
 - incomplete "self-interaction" cancellation
 - no "van der Waals" bound systems

5.6 "meta"-Generalized Gradient Approximations

"Jacob's ladder" of DFT (Perdew)



$\tau_{\uparrow, \downarrow}$: "positive kinetic energy density" [of the KS orbitals]

$$\tau_s = \frac{1}{2} \sum_{k=1}^{N_s} |\nabla \phi_{ok}|^2$$

NB: kinetic energy $-\int d^3r \sum_k \phi_{ok}^*(\mathbf{r}) \frac{\nabla^2}{2} \phi_{ok}(\mathbf{r}) = -\int d^3r \sum_k (\nabla \phi_{ok}^*(\mathbf{r})) \cdot (\nabla \phi_{ok}(\mathbf{r}))$

$$\Rightarrow E_{xc}^{mGGA} = \int d^3r n(r) \epsilon_{xc} (n_r(r), n_b(r), |\nabla n_r(r)|, |\nabla n_b(r)|, \tau_r(r), \tau_b(r))$$

→ Various parametrizations exist

→ either fitted to databases or parameters derived from fundamental constraints

→ Presence of $\nabla \phi_{oh}(r)$ can be used to cancel self-interaction almost exactly for 1 electron systems

Result: - clearly improved structure prediction (comp to LDA/GGA)

- clearly improved atomization energies, cohesive energies

However: - some self-interactions related do not go away for ME systems

- van der Waals still not captured

- "strong correlation" (ME wave functions with complicated SD structure)

5.7 "Hybrid functionals"

Molecules, solids: Self-interaction is still problem.

Becke 1993: Heuristic fix by mixing fraction of "exact exchange"

$$E_{xc}^{hyb}[n] = \alpha \cdot E_x^{exact}[n] + (1-\alpha) E_x^{(m)GGA}[n] + E_c^{(m)GGA}[n]$$

$$E_x^{exact}[n] = - \sum_{k=1}^N \sum_{k'=1}^{N'} \delta_{S_k S_{k'}} \int d^3r d^3r' \frac{\phi_{oh S_{k'}}^*(r) \phi_{oh S_k}^*(r') \phi_{oh S_k}(r) \phi_{oh S_{k'}}(r')}{|r - r'|}$$

almost (but not quite) Hartree-Fock (not evaluated for optimum HF Slater determinant but for DFT instead)

α typically $\sim 0.25, 0.33$

Note: $\rho_{\text{ou}} \equiv \rho_{\text{ou}}[n] \Rightarrow E_{xc}^{\text{hyb}}[n]$ still implicitly a density functional

BUT $V_{xc} \equiv V_{xc}(r, r')$ non-local!

not "Kohn-Sham" but "generalized Kohn-Sham"

Parameterized forms - somewhat "ad hoc":

- "B3LYP" (Becke 1993) widely used in molecular quantum chemistry
almost synonymous with DFT for many chemists

- Semi-rigorous justification: Perdew et al. 1996 "PBEh"
 $\alpha = 0.25$, (h)GGA \equiv PBE

- Most general form: 4th rung of Jacob's ladder



but: - still difficult for special cases
(metal cohesive energy do not like Hartree-Fock)

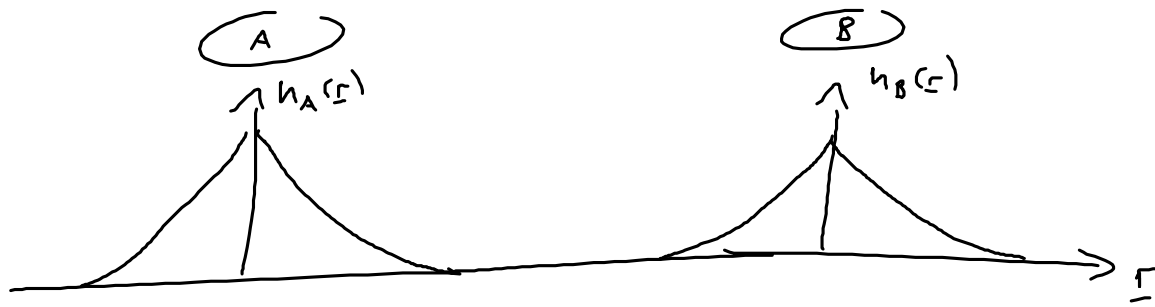
- still no van der Waals

- "strong correlation..." (what if you really "map" a complicated Slater Determinant combination)

Also: Computationally, Exact exchange is still " $\mathcal{O}(N^4)$ " (naively)

5.7 Repairing van der Waals

Fundamental problem: "No-bonded" systems



$$n(r) \approx n_A(r) + n_B(r)$$

Trivially, DFT up to mGGA:

$$E_{xc}[n] = E_{xc}[n_A] + E_{xc}[n_B]$$

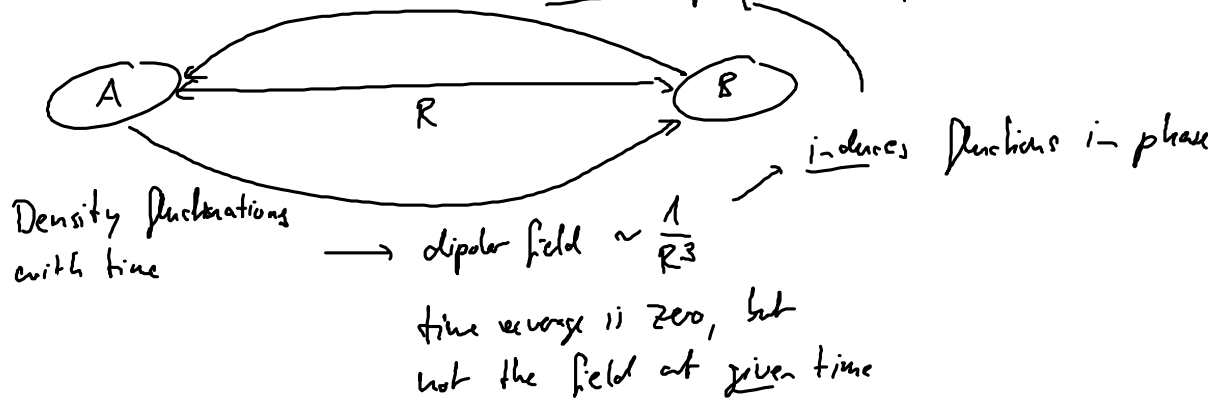
unless there are electrostatic terms:

$$E[A+B] - E[A] - E[B] = 0$$

no bonding through XC

Reality: Coulomb interaction $\frac{1}{|r-r'|}$ is non-local.

For more than one SD, can couple separate systems
induced dipolar field $\sim \frac{1}{R^3}$

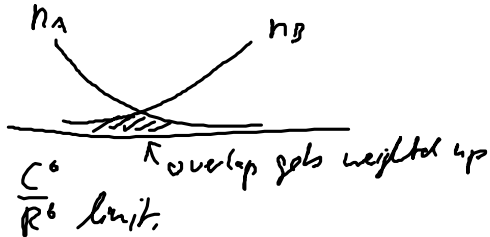


Net interaction: $E_{\text{fluct}} \sim \frac{1}{R^3} \cdot \frac{1}{R^3} = \frac{C_6}{R_6}$

- C_6 approaches constant for large distances
- First term of a series
- depends only on intrinsic response of A or B for $R \rightarrow \infty$

DFT in practice:

- LDA: Always attractive, $\sim n^{1/3}$
→ spurious binding, but certainly not $\frac{C_6}{R^6}$ limit.
- GGA, n -GGA, hybrids: Fix LDA for small densities with gradients
→ no binding
- Expensive benchmark methods ("coupled cluster") get it, but not simple post-HF perturbation (MP2) - overestimates C_6



DFT solutions to van der Waals:

1) Formal path: Need non-local interactions
⇒ create them.

"Langreth-Lundquist" - $E_{xc}[n] = E_x^{(GGA)}[n] + E_c^{(LDA)}[n] + E_c^{nl}[n]$

$$E_c^{nl}[n] = \int d^3r d^3r' n(r) K(r, r') n(r')$$

"kernel" $K(r, r')$: - design to recover $E_c^{nl}[n = \text{const}] = 0$ for HEG

$$- K = K(n(r), n(r'), |r - r'|)$$

and parameterized to approximate density-density response of separated "fragment" densities

Advantage: - density-only, non-empirical DFT
- reasonable binding energies for many vdW bound systems

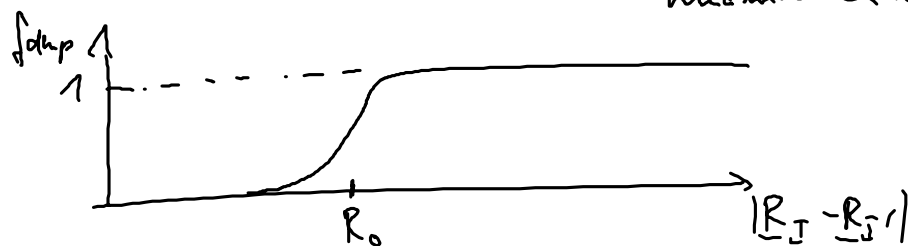
- Disadvantages: - local GGA corrections to LDA E_c are not in
- depends strongly on choice E_x [(w)GGA or HF]
 - binding distance and binding energy together hard to get "exact"

2) Fix: If $\frac{C_6}{R^6}$ is missing, just add it.

$$E[\psi] = T_S[\psi] + \int d^3r v^{nuc}(\mathbf{r}) \psi(\mathbf{r}) + \frac{1}{2} \int d^3r d^3r' \frac{\psi(\mathbf{r})\psi(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} + E_{xc}^{(mGGA)}[\psi]$$

$$+ \sum_{\substack{I, I' \\ I \neq I'}}^{M, M} \frac{C_{6, I, I'}}{|\mathbf{R}_I - \mathbf{R}_{I'}|^6} \cdot \int d\text{amp} (|\mathbf{R}_I - \mathbf{R}_{I'}|)$$

for well separated isolated atoms: $C_{6, I, I'}$ can be calculated or measured exactly.



also, C_6 themselves should depend on structure if not isolated atoms

[e.g. Carbon in C_6H_6 is not isolated]

6. Practical DFT ("and beyond")

6.1 Outline of the problem

$$\underbrace{\left[-\frac{\nabla^2}{2} + v^{nuc}(\mathbf{r}) + v_e^{ex}(\mathbf{r}) + v_{xc}(\mathbf{r}) \right]}_{\hat{h}_{KS}} \psi_{0k}(\mathbf{r}) = \epsilon_{0k} \psi_{0k}(\mathbf{r})$$

V_{xc} local - Kohn-Sham

V_{xc} non-local \rightarrow Hartree-Fock, "generalized Kohn-Sham"

$$E_{g.s} = E[n], \text{ could be } E[\{\phi_{0k}[n]\}, n]$$

Self-consistent problem:

$$V_{es}^e(r), V_{xc}(r) \text{ depend on } \underline{\text{solutions}} \quad \{\phi_{0k}(r)\}$$

First step to solution: "Basis set" $\{\phi_i(r); i=1, \dots, S > N\}$
(could even be $\delta(r, r_i)$)

$$\text{and discretize: } \phi_{0k}(r) = \sum_j c_{kj} \phi_j(r)$$

$$\Rightarrow \sum_j h_{ij} c_{kj} = E_{0k} \sum_j s_{ij} c_{kj}$$

Matrix equation
(generalized eigenvalue problem)

for each orbital k

$$h_{ij} = \int d^3r \phi_i^*(r) \hat{h}_{KS} \phi_j(r)$$

$$s_{ij} = \int d^3r \phi_i^*(r) \phi_j(r)$$

could be δ_{ij} for
orthonormal basis

and seek eigenvalue/eigenvector pairs $\{E_{0k}, \underline{c}_k; k=1, \dots, S\}$

(1) $V^{nuc}(r) \rightarrow$ Geometry $\{\underline{R}_I\}$

(2) Decide on basis set $\{\phi_i(r)\}$ - which factor?

(3) starting guess, e.g. $n_0(r)$

