

# Recap: Density functionals

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

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

- Local-density approximation  $E_{xc}^{LDA}[n] = \int d^3r n(r) \epsilon_{xc}^{HEG}(n(r))$

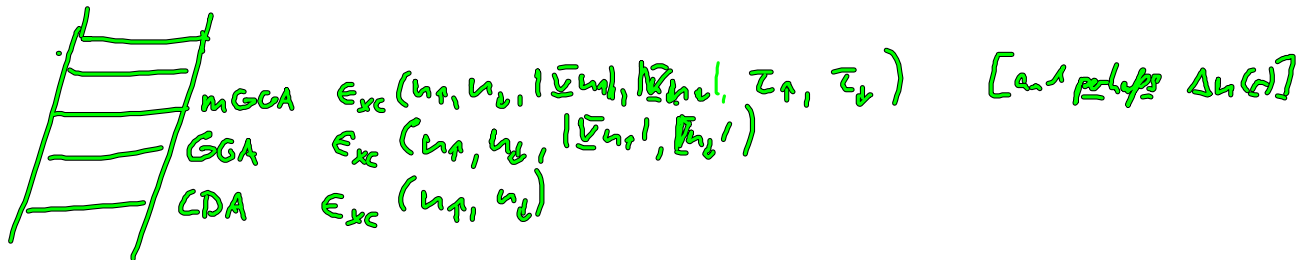
- surprisingly successful for "well-behaved" systems, esp. solids
- well-understood limitations
- "first principles"

- Generalized gradient approximation GGA:  $E_{xc}^{GGA}[n] = \int d^3r n(r) \epsilon_{xc}^{GGA}(n(r), |\nabla n(r)|)$

- widest-used "production" method today
- corrects several LDA failures (overbinding, H-bonded 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  $-\int d^3r \sum_k \phi_{ok}^*(r) \frac{\nabla^2}{2} \phi_{ok}(r) = -\int d^3r \sum_k (\nabla \phi_{ok}^*(r)) \cdot (\nabla \phi_{ok}(r))$

$$\Rightarrow E_{xc}^{mGGA} = \int d^3r n(r) \epsilon_{xc}(n(r), \nabla n(r), |\nabla^2 n(r)|, \tau(r), \tau_2(r))$$

→ Various parametrizations exist

→ either fitted to databases or parameters derived from fundamental constraints

→ Presence of  $\nabla^2 \rho_{0k}(r)$  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 detail do not go away for ME systems

- van der Waals still not captured

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

## 5.7 "Hybrid functionals"

Molecules, solids: Self-interaction is still problem.

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

$$E_{xc}^{hyb}[n] = \alpha \cdot E_x^{exact}[\rho_{0\uparrow\downarrow}] + (1-\alpha) E_x^{(m)GGA}[n] + E_c^{(m)GGA}[n]$$

$$E_x^{exact}[\rho_{0\uparrow\downarrow}] = - \sum_{k=1}^N \sum_{k'=1}^{N'} \delta_{S_k S_{k'}} \int d^3r d^3r' \frac{\rho_{0\uparrow\downarrow}^*(r) \rho_{0\uparrow\downarrow}^*(r') \rho_{0\uparrow\downarrow}(r) \rho_{0\uparrow\downarrow}(r')}{|r-r'|}$$

almost (but not quite) Hartree-Fock

(not evaluated for optimum HF Slater determinant but for DFT instead)

$\alpha$  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!

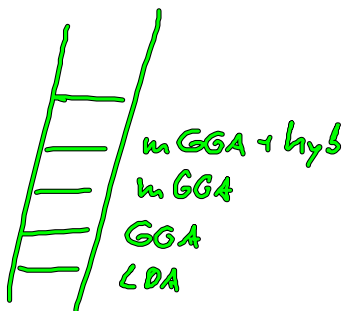
not "Kohn-Sham" but "generalized Kohn-Sham"

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 does not like Hartree-Fock)

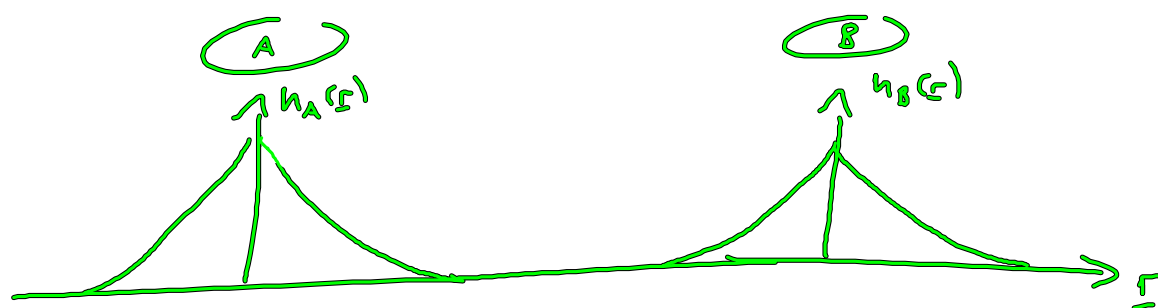
- still no van der Waals

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

Also: Computationally, exact exchange is still " $O(N^4)$ " (varies)

5.7 Repairing van der Waals

Fundamental problem: "No. bonded" systems



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

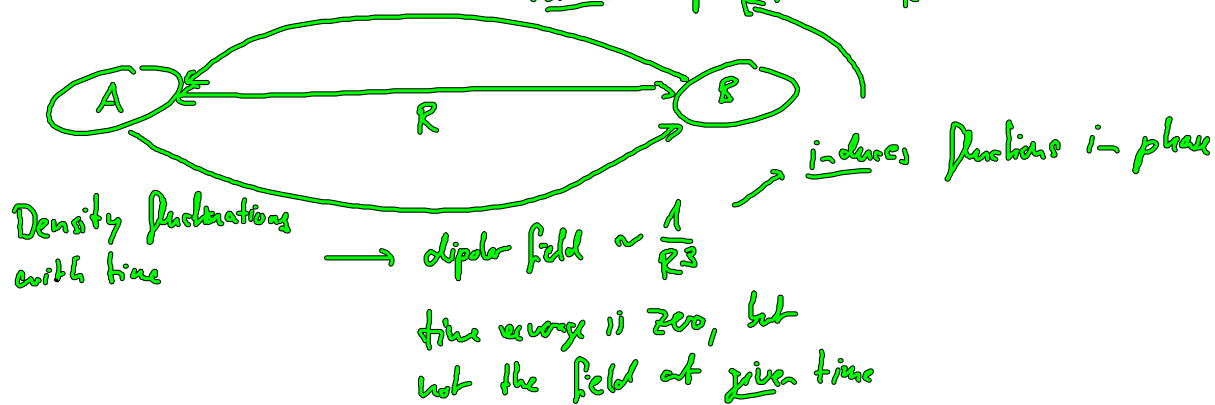
Trivially, DFT up to m GGA:

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

unless there are electrostatic terms:  $E[A+B] - E[A] - E[B] = 0$   
no bad by through XC

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

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



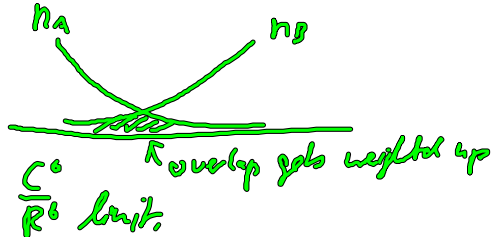
Net interaction:  $E_{\text{just}} \sim \frac{1}{R^3} \cdot \frac{1}{R^3} = \frac{C_6}{R_6}$

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

DFT is practice:

- LDA: Always attractive,  $\sim n^{1/3}$

→ spurious binding, but certainly not



- 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" -  $E_{xc}[n] = E_x^{HF} [n] + E_c^{GGA} [n] + E_c^{nl} [n]$

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

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

$$- K = K(n(\mathbf{r}), n(\mathbf{r}'), |\mathbf{r} - \mathbf{r}'|)$$

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

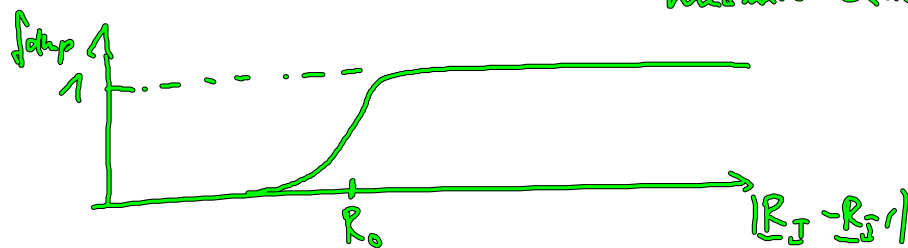
- Disadvantages: - local GGA corrections to LDA  $E_c$  are not  $\hbar$
- depends strongly on choice  $E_x$  [wGGA or HF]
  - binding distance and binding energy together hard to get "exact"

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

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

$$+ \sum_{\substack{I, I' \\ I \neq I'}}^{M, M} \frac{C_{6, I, I'}}{|R_I - R_{I'}|^6} \cdot f_{damp}(|R_I - R_{I'}|)$$

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

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

$V_{xc}$  local - Kohn-Sham

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

$$E_{g.s} = E[n], \text{ could be } E[\{\varphi_{\alpha_k}[n]\}, n]$$

Self-consistent problem:

$$V_{el}^e(r), V_{xc}(r) \text{ depend on } \underline{\text{solutions}} \{ \varphi_{\alpha_k}(r) \}$$

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

$$\text{and discretize: } \varphi_{\alpha_k}(r) = \sum_j c_{kj} \varphi_j(r)$$

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

Matrix equation  
(generalized eigenvalue problem)  
for each orbital  $k$

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

$$s_{ij} = \int d^3r \varphi_i^*(r) \varphi_j(r) \quad \text{could be } \delta_{ij} \text{ for } \underline{\text{orthonormal}} \text{ basis}$$

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

(1)  $V_{nuc}(r) \rightarrow$  Geometry  $\{ \underline{R}_i \}$

(2) Decide on basis set  $\{ \varphi_i(r) \}$  - which form?

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

