

Hybrid DFT

$$E_{xc}[\rho] = C_x E_x^{GGA}[\rho] + E_c^{GGA}[\rho] + (1 - C_x) E_K^{HF}$$

| Property                | HF      | Hybrid      | MP2          | CCSD(T)             |
|-------------------------|---------|-------------|--------------|---------------------|
| IPs and EAs             | ±0.5 eV | ±0.2 eV     | ±0.2 eV      | ±0.05 eV            |
| Bond Lengths            | -1%     | ±1 pm       | ±1 pm        | ±0.5 pm             |
| Vibrational Frequencies | +10%    | +3%         | +3%          | ±5 cm <sup>-1</sup> |
| Barrier Heights         | +30-50% | -25%        | +10%         | ±2 kcal/mol         |
| Bond Energies           | -50%    | ±3 kcal/mol | ±10 kcal/mol | ±1 kcal/mol         |

20%K ← B3LYP PBE0 → 25%K

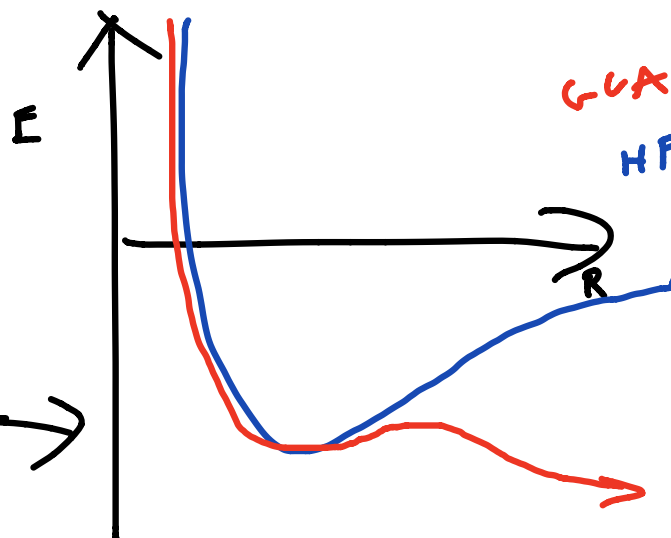
Why does this work so well?

H

Dissociation  
of H<sub>2</sub><sup>+</sup>

H . . . . H

SIE →

Self-Interaction Error

HF Interaction Energy for H<sub>2</sub><sup>+</sup>

$$\sum_{ij}^N \langle ij | ij \rangle - \langle ij | ji \rangle = \langle || | i \rangle - \langle || | i \rangle = 0$$

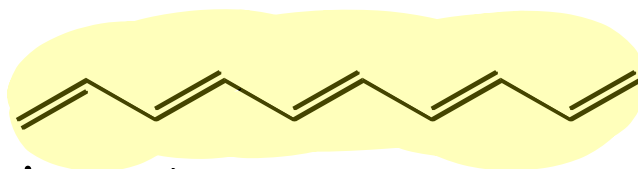
GGA Interaction Energy for H<sub>2</sub><sup>+</sup>

$$\langle || | i \rangle + E_{xc}[\rho] \neq 0 (> 0 \text{ typically})$$

# Manifestations of SIE in Chemistry

Polaron  
Formation

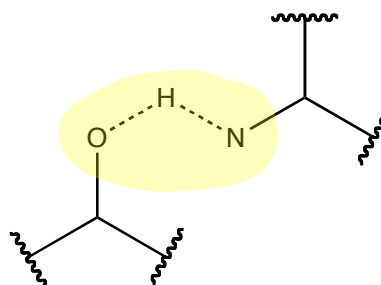
delocalization length too big!



⊕

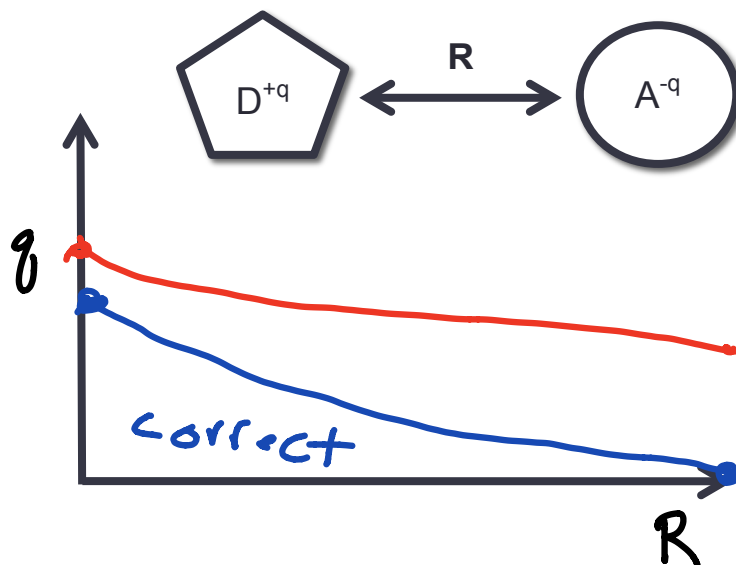
Transition  
States

$\rho$  delocalized  $\rightarrow E_{TS} \downarrow$   
Barriers too Low



Intermolecular  
Charge Transfer

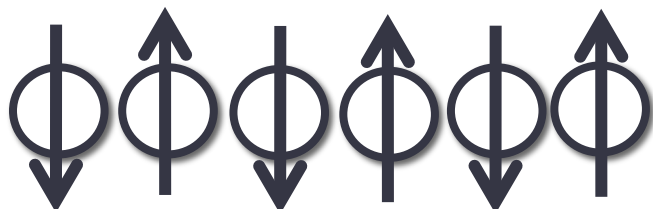
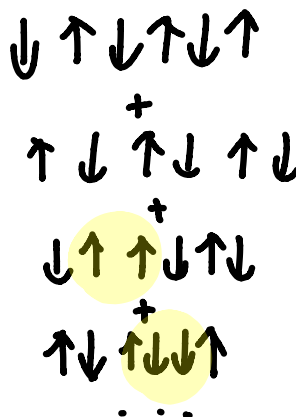
DFT favors  
fractional charges!



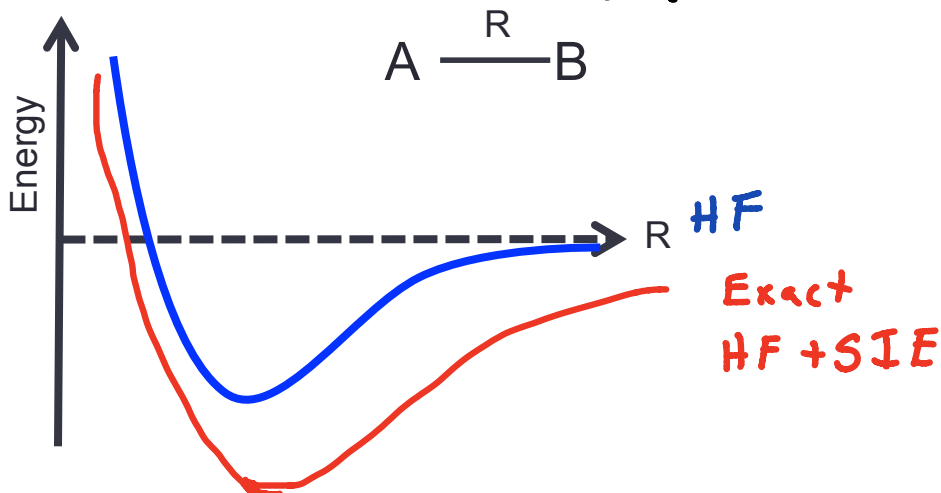
So then we should include 100% HF exchange, right?

100%K + GGAc  $\rightarrow$  HF-like

## Example 1: Antiferromagnetism

mean field  $\rightarrow$  localized!correlation  
 $\downarrow$   
de-localization

## Example 2: Bond Energy



## Theoretical Justification: Adiabatic Connection

In DFT,  $E_{xc}$  contains more than just e-e interaction terms

$$E[\rho] = \int \sum_i^N |\nabla \phi_i(\mathbf{r})|^2 d\mathbf{r} + \dots$$

Non-interacting KE

$$E_{xc}[\rho] = V_{ee}[\rho] + (T_{\text{exact}} - T_{\text{NI}})$$

How do we get these extra kinetic energy terms?

Idea: Adiabatic Connection

$$\hat{H}_\lambda = -\frac{1}{2} \sum_i \nabla_i^2 + v_\lambda(\mathbf{r}) + \sum_{i<j} \frac{\lambda}{r_{ij}}$$

$\lambda=0$  Non-interacting (KS)  
 $\lambda=1$  exact

$V_\lambda$  forces  $\rho_\lambda = \rho_{\text{exact}}$  @ all  $\lambda$

Adiabatic Connection Theorem:

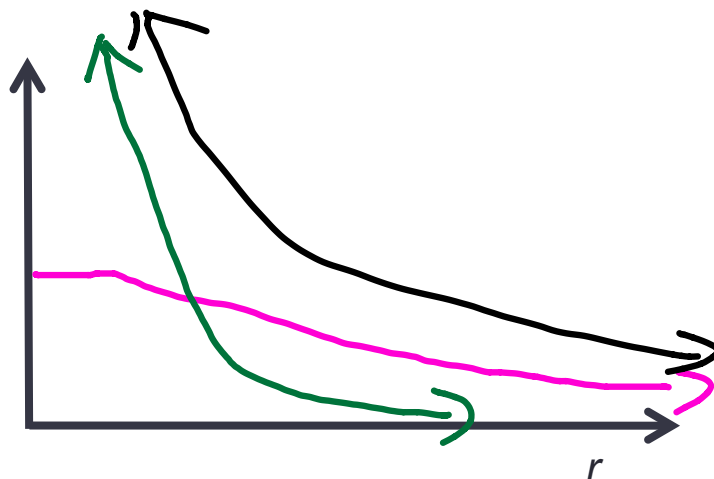
$$E_{xc}[\rho] = \int_0^1 V_{ee}^\lambda[\rho] d\lambda \approx \left( V_{ee}^{\lambda=0} + V_{ee}^{\lambda=1} \right) \frac{1}{2}$$

$\nwarrow$   $ee$  interaction @ coupling  $\lambda$   
 $\downarrow$   $E_K^{HF}$        $\downarrow$   $E_{xc}^{GGA}$

accounts for K.E. terms.

Range Separated Hybrids

$$\frac{1}{r} = \underbrace{\frac{\text{erf}(\omega r)}{r}}_{LR} + \underbrace{\frac{1 - \text{erf}(\omega r)}{r}}_{SR}$$



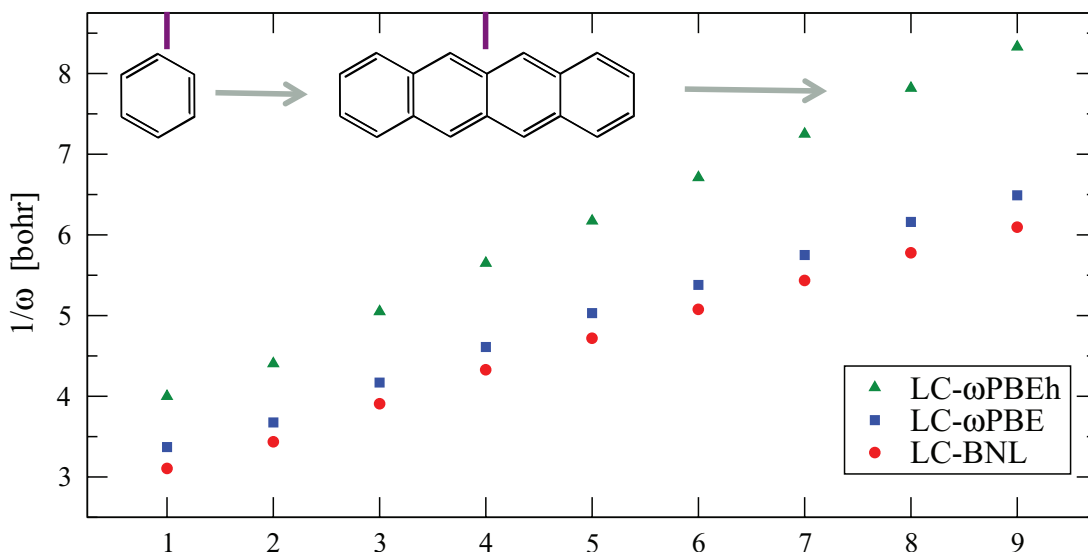
Original Idea: Treat LR with HF, short range with DFT

$$E_{xc} = E_x^{LR-HF} + E_x^{SR-GGA} \quad 1 \text{ param } (\omega)$$

LC- $\omega$ PBE, CAM-B3LYP, BNLC, ...

$\omega$  is extensive!?

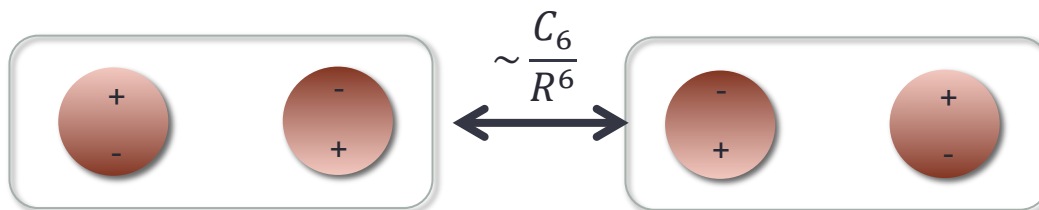
HSE  $\rightarrow$  LR-GGA, SR-HF.



Korzdorfer, Sears, Sutton, Bredas *JCP* **135** 204107 (2011).

### Dispersion Interactions

Weak, Long Range Correlation Effect:



Three (Good) Ideas:

Double Hybrid DFT

$$E_{xc}[\rho] = C_x E_x^{GGA}[\rho] + C_c E_c^{GGA}[\rho] + (1 - C_x) E_K^{HF} + (1 - C_c) E_c^{MP2}$$

✓ Exploits good properties of  $\Psi$  theory

✗ Cost of MP2

Atomic Partitioning of Density

$$\rho \rightarrow \rho_A + \rho_B + \rho_C + \dots$$

$$C_6^{IJ} = F[\rho_I, \rho_J]$$

✓ Cheap, Density Based

✗ What about  $C_8$ ? Or Three Body Dispersion?

Nonlocal Functionals

$$E_c[\rho] = \int \rho(\mathbf{r}_1) \phi(\mathbf{r}_1, \mathbf{r}_2, \rho) \rho(\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2$$

✓ Builds new physics into correlation functional

✗ Difficult to derive new functionals

Suggested Further Reading:

Cohen, Mori-Sanchez, Yang, "Challenges for DFT", *Chem Rev* **112**, pp289-320 (2012).

Burke, "Perspective on DFT" *J Chem Phys* **136**, 150901 (2012).

Klimes and Michaelides, "Advances and challenges in treating vdW dispersion forces in DFT," *J Chem Phys* **137** 120901 (2012).