

# Exchange-Correlation Functionals II

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ASESMA 2021

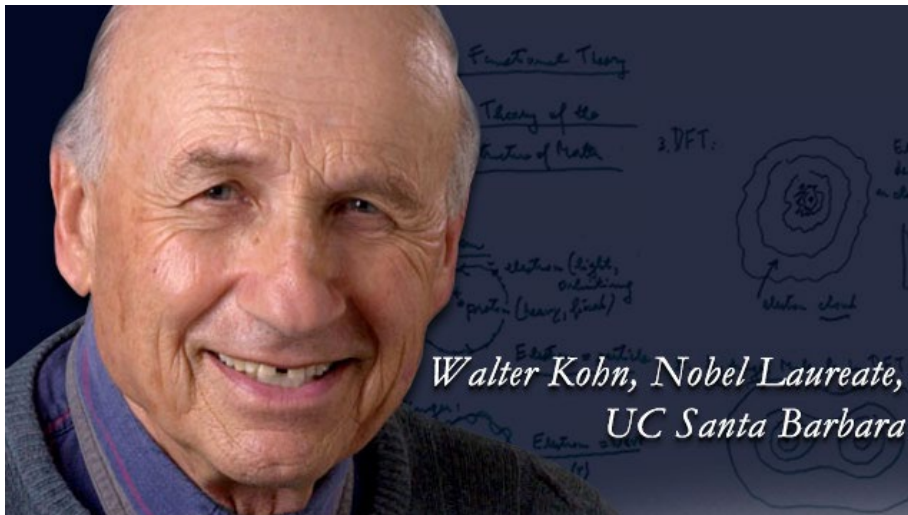


- **Brief recap of Kohn-Sham DFT**
- **Strategies for approximating XC functionals**
- **GGAs and meta-GGAs**
- **hybrid functionals and beyond**

You can formulate a complete many-body theory entirely in terms of the probability density!

Wave function: N coordinates  $\Psi(\mathbf{r}_1, \dots, \mathbf{r}_N)$

Density: only one coordinate  $n(\mathbf{r})$  **much simpler!!**



Walter Kohn  
(1923-2016)  
Nobel Prize 1998

The Kohn-Sham many-body wave function is a single Slater determinant, whose single-particle orbitals follow from the following **self-consistent** equation:

$$\left[ -\frac{\nabla^2}{2} + V(\mathbf{r}) + V_H(\mathbf{r}) + V_{xc}[n](\mathbf{r}) \right] \varphi_j(\mathbf{r}) = \varepsilon_j \varphi_j(\mathbf{r})$$

where  $n_0(\mathbf{r}) = \sum_{j=1}^N |\varphi_j(\mathbf{r})|^2$  is the **exact** ground-state density.

Exchange-correlation (xc) potential: 
$$V_{xc}[n](\mathbf{r}) = \frac{\delta E_{xc}[n]}{\delta n(\mathbf{r})}$$

The total ground-state energy can be written as

$$E_0[n] = \sum_{j=1}^N \varepsilon_j - \frac{1}{2} \int d\mathbf{r} \int d\mathbf{r}' \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + \int d\mathbf{r} n(\mathbf{r})V_{xc}(\mathbf{r}) + E_{xc}[n]$$



For any given  $n(\mathbf{r})$ , you can go and look up exact  $E_{xc}$

Unfortunately, the library is locked!  
 We don't have access to the exact xc functional.



- ▶ Exact xc functional would require solving the many-body problem.  
This can only be done for extremely simple toy models.
- ▶ Need to find approximations for  $E_{xc}[n]$

**Empirical**

**VS**

**Nonempirical**

(uses fitting parameters)

(uses exact constraints and conditions)

**Both philosophies have been very successful.**

- ▶ **Slowly varying densities:** must reduce to homogeneous electron gas limit
- ▶ **Asymptotic behavior:** for finite systems (atoms, molecules)

$$V_{xc}^{exact}(\mathbf{r}) \rightarrow -\frac{1}{r} \quad \text{for } r \rightarrow \infty$$

- ▶ The exact xc functional must be **self-interaction free.**

For  $N = 1$ :

$$V_{xc}^{exact}(\mathbf{r}) = -\int \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}'$$

- ▶ **Other constraints.** Gradient expansions, scaling,...



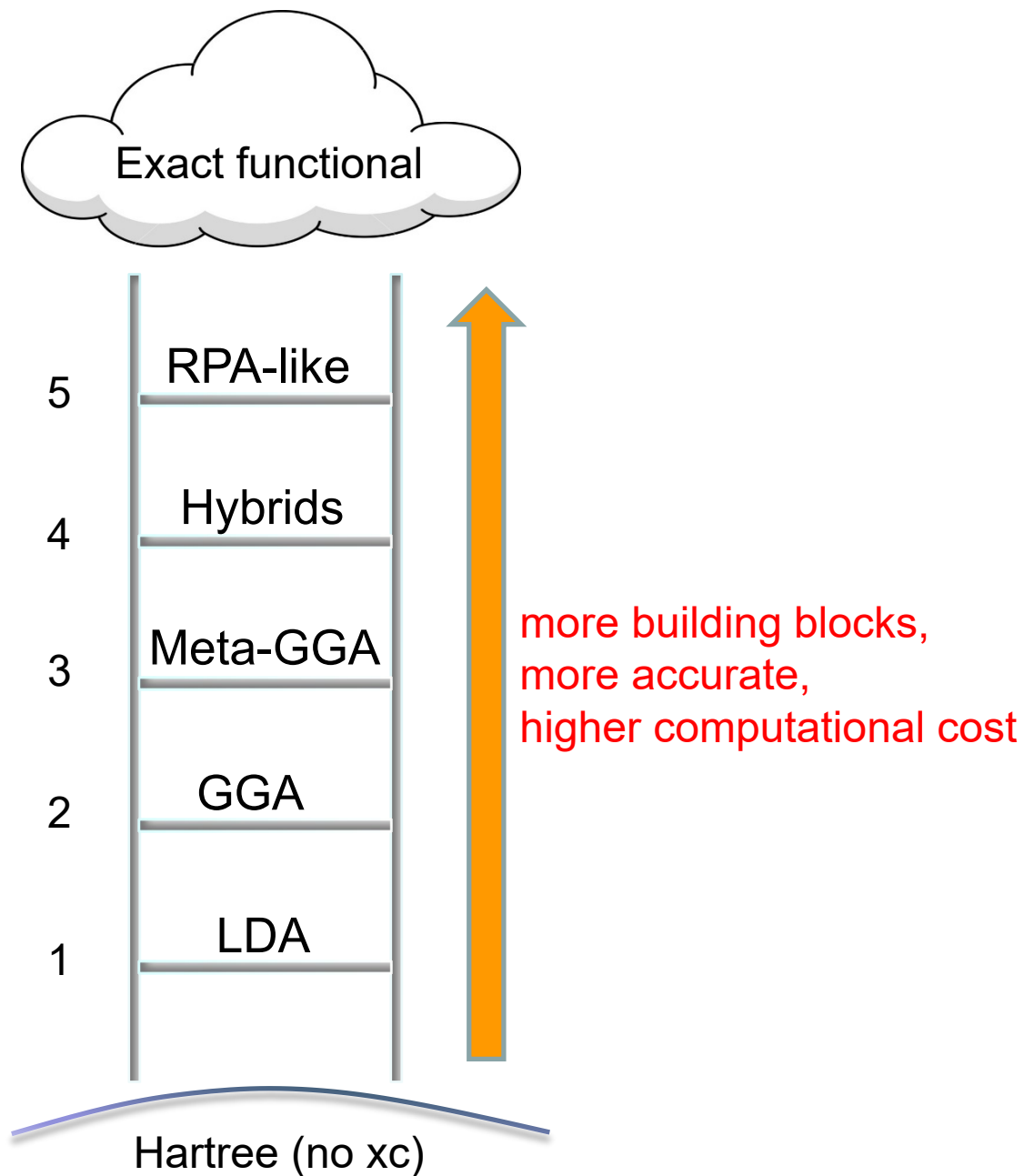


Heaven: exact xc functional

In between: better and better approximations

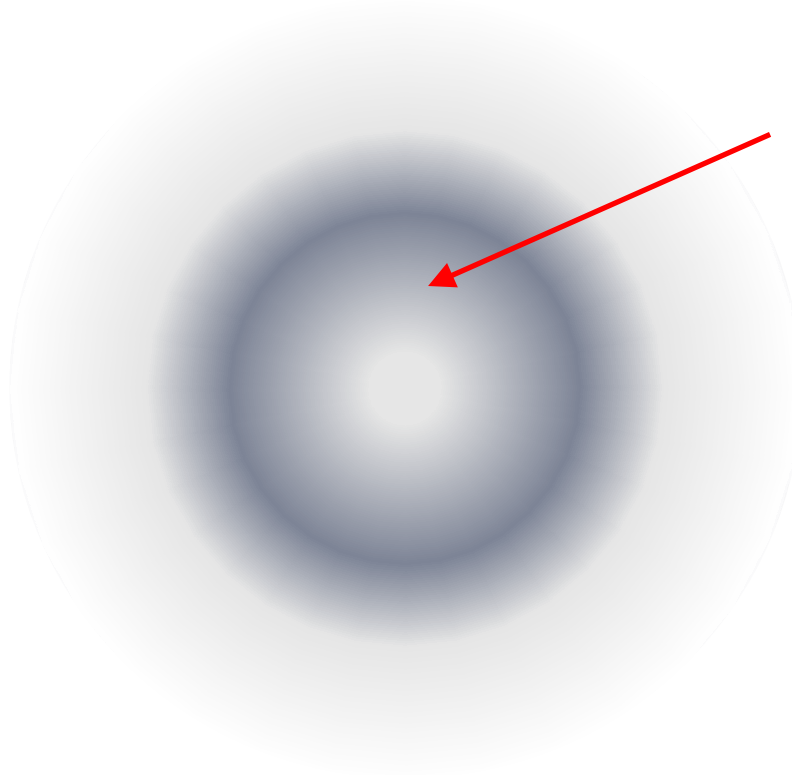
Earth: no xc (Hartree only)

[https://commons.wikimedia.org/wiki/File:Figures\\_Jacobs\\_Ladder.jpg](https://commons.wikimedia.org/wiki/File:Figures_Jacobs_Ladder.jpg)



XC energy:

$$E_{xc} = \int d\mathbf{r} e_{xc}(\mathbf{r})$$

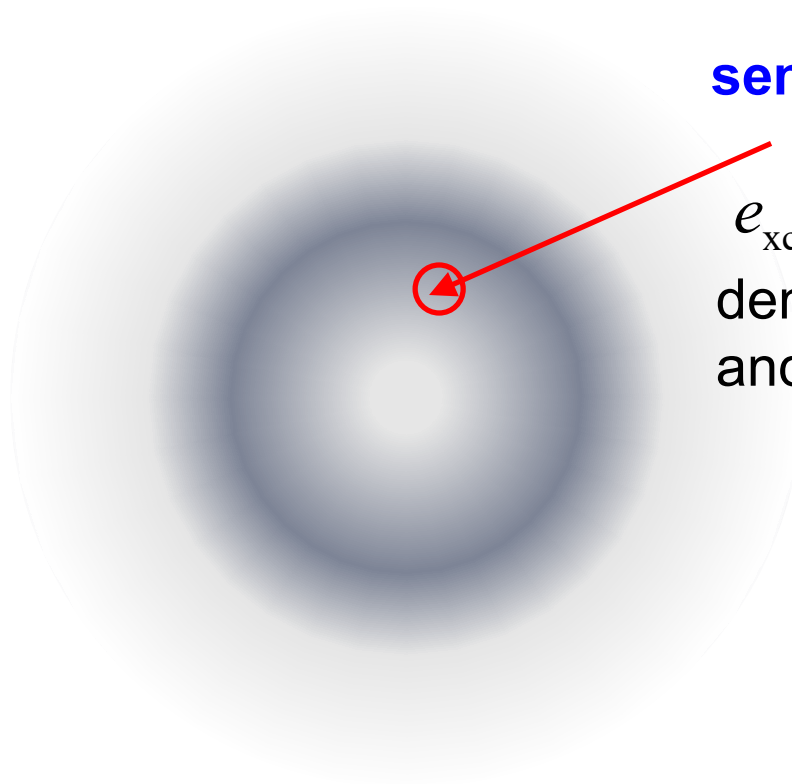


**local functional:**

$e_{xc}(\mathbf{r})$  depends  
only on density at  
the **same** point  $\mathbf{r}$

XC energy:

$$E_{xc} = \int d\mathbf{r} e_{xc}(\mathbf{r})$$

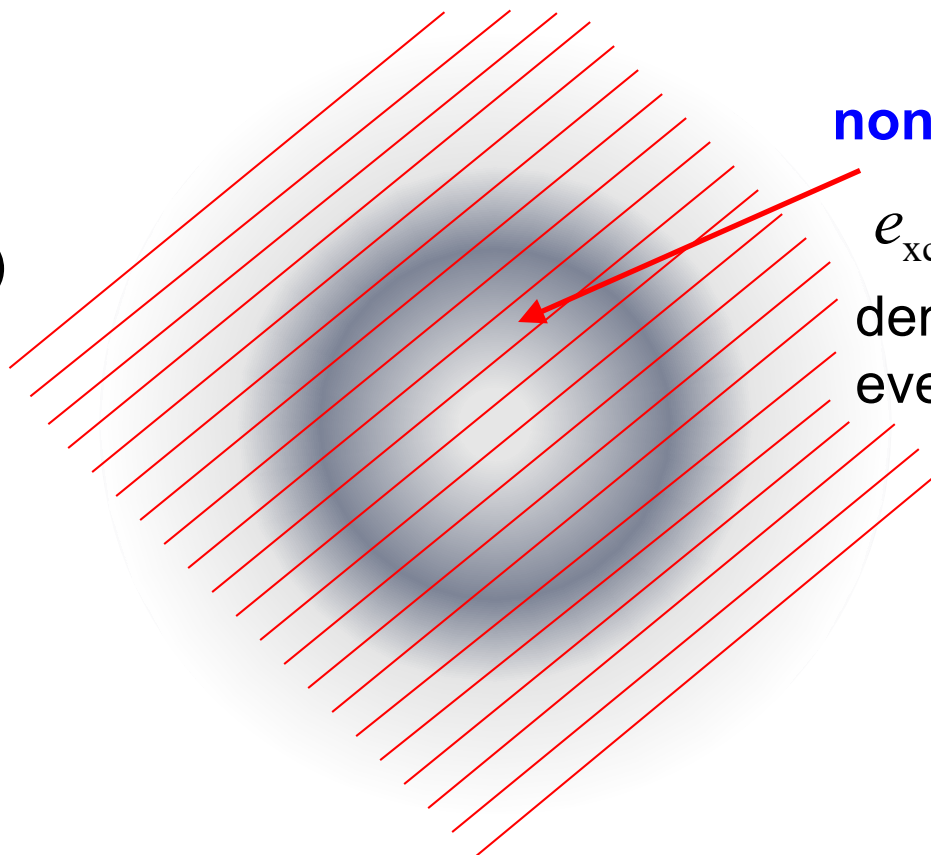


**semilocal functional:**

$e_{xc}(\mathbf{r})$  depends on density and/or orbitals and their **gradients** at  $\mathbf{r}$

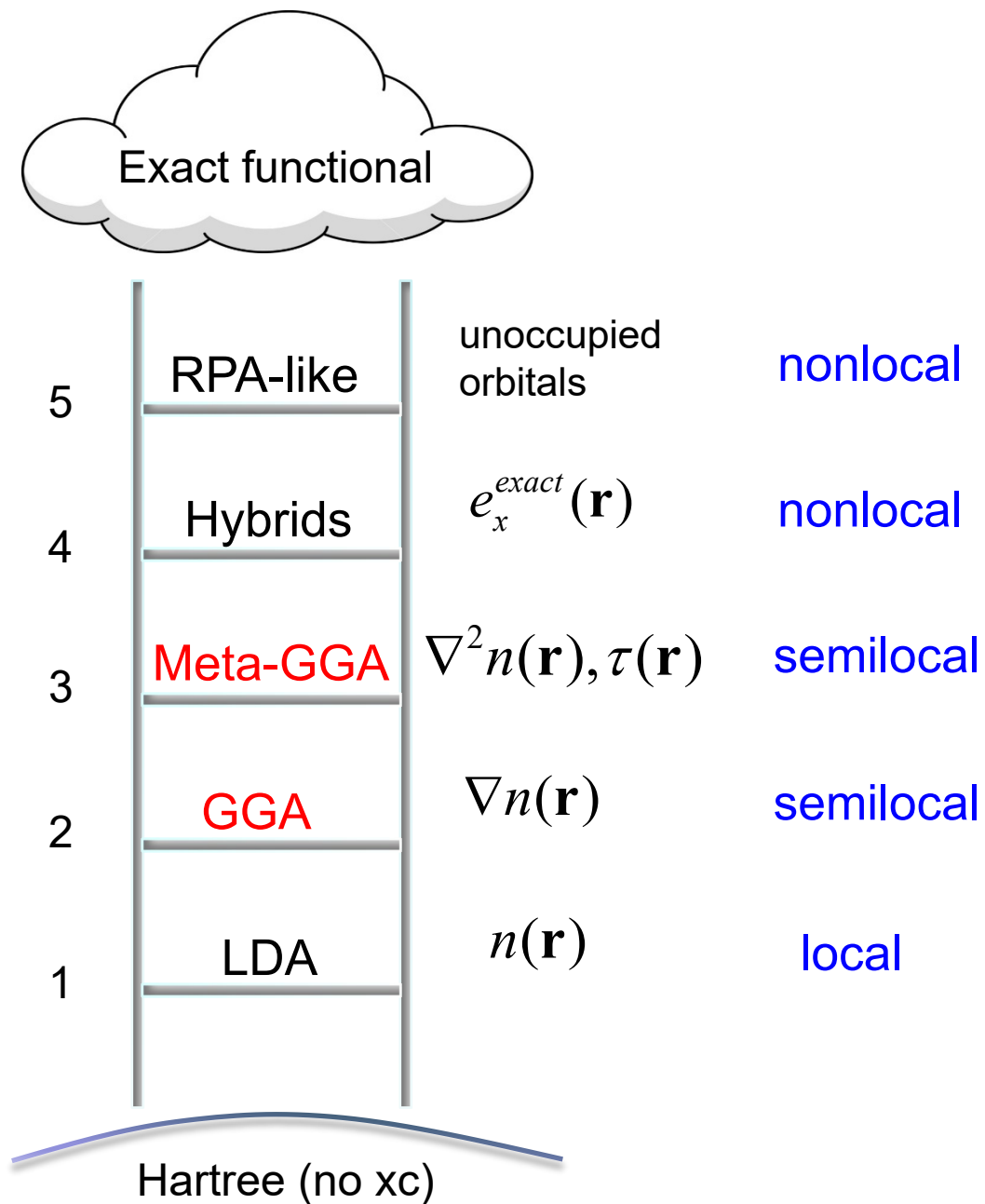
XC energy:

$$E_{\text{xc}} = \int d\mathbf{r} e_{\text{xc}}(\mathbf{r})$$



**nonlocal functional:**

$e_{\text{xc}}(\mathbf{r})$  depends on  
density and/or orbitals  
everywhere



Formally, one can write Taylor expansion:

$$e_{xc}(\mathbf{r}) = e_{xc}^{(0)}(\mathbf{r}) + e_{xc}^{(1)}(\mathbf{r}) + e_{xc}^{(2)}(\mathbf{r}) + \dots$$

No gradients  
(LDA)

First-order  
gradients

$$\nabla n$$

Second-order  
gradients

$$\nabla^2 n, (\nabla n)^2$$

**Systematic gradient expansion very difficult,  
does not improve LDA, often makes things worse!**  
(Asymptotic series, does not converge)



$$E_{\text{xc}}^{\text{GGA}}[n^{\sigma}] = \int d\mathbf{r} e_{\text{xc}}^{\text{GGA}}(n_{\uparrow}, n_{\downarrow}, \nabla n_{\uparrow}, \nabla n_{\downarrow})$$

Find a functional form which satisfies known constraints, and which may contain empirical parameters.

There are many empirical and nonempirical GGAs.



## Exchange: Becke 1988 functional

$$E_x^{B88}[n_\sigma] = E_x^{LSDA}[n_\sigma] - \beta \sum_\sigma \int d\mathbf{r} n_\sigma^{4/3} \frac{x_\sigma^2}{1 + 6\beta \sinh^{-1}(x_\sigma)}$$

where  $\beta = 0.0042$  (empirical parameter)

$$x_\sigma = \frac{|\nabla n_\sigma|}{n_\sigma^{4/3}}$$

## Correlation: Lee-Yang-Parr 1988 functional

$$E_c^{LYP}[n] = -a \int \frac{d\mathbf{r}}{1+dn} \left\{ n + bn^{-1/3} \left[ C_F n^{5/3} - 2t_W + \frac{1}{9} \left( t_W + \frac{\nabla^2}{2} n \right) e^{-cn^{-1/3}} \right] \right\}$$

where

$$t_W = \frac{1}{8} \left( \frac{|\nabla n|^2}{n} - \nabla^2 n \right) \quad C_F = \frac{3}{10} (3\pi^2)^{2/3}$$

$$a = 0.049, b = 0.132, c = 0.2533, d = 0.399$$

(fitting parameters)

Perdew-Burke-Ernzerhof 1996

most widely used functional:  
>130,000 citations!

$$E_x^{PBE}[n] = \int d\mathbf{r} e_x^h(n) \left[ 1 + \kappa - \frac{\kappa}{1 + \beta\pi^2 s^2 / 3\kappa} \right]$$

where

$$s(\mathbf{r}) = \frac{|\nabla n(\mathbf{r})|}{2n(\mathbf{r})k_F(\mathbf{r})}$$

$$\kappa = 0.804$$

$$\beta = 0.066725$$

Oliver-Perdew spin scaling:

$$E_x[n_\uparrow, n_\downarrow] = \frac{1}{2} E_x[2n_\uparrow] + \frac{1}{2} E_x[2n_\downarrow]$$

Perdew-Burke-Ernzerhof 1996

most widely used functional:  
>130,000 citations!


$$E_c^{PBE}[n, \zeta] = \int d\mathbf{r} \left[ e_c^h(n, \zeta) + nc_0 \phi^3 \ln \left\{ 1 + \frac{(1 + At^2) \beta t^2 / c_0}{1 + At^2 + A^2 t^4} \right\} \right]$$

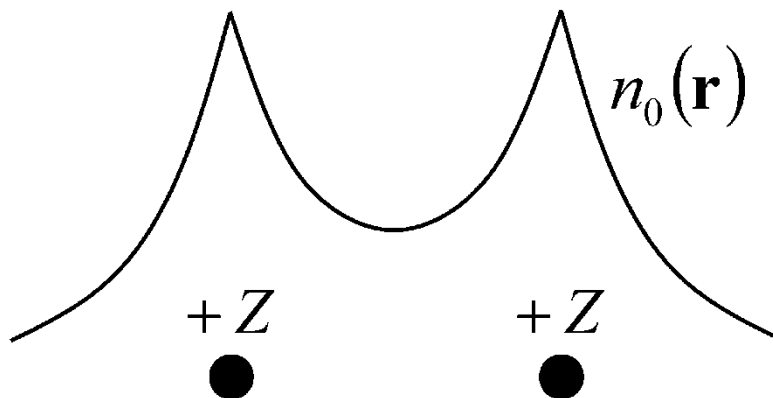
where

$$t = \frac{|\nabla n|}{2k_s n} \quad k_s = \sqrt{4k_F / \pi}$$

$$\phi = \frac{1}{2} \left[ (1 + \zeta)^{2/3} + (1 - \zeta)^{2/3} \right] \quad c_0 = 0.031091$$

$$E_{xc}^{\text{MGGA}}[n_{\sigma}] = \int d\mathbf{r} f(n_{\sigma}, \nabla n_{\sigma}, \nabla^2 n_{\sigma}, \tau_{\sigma})$$


 Laplacian of the density



Laplacian of density  
 diverges at cusp:  
 numerical problems!

$$E_{\text{xc}}^{\text{MGGA}}[n_{\sigma}] = \int d\mathbf{r} f(n_{\sigma}, \nabla n_{\sigma}, \nabla^2 n_{\sigma}, \tau_{\sigma})$$

kinetic energy densities



$$\tau_{\sigma}(\mathbf{r}) = \frac{1}{2} \sum_j^{\text{occ}} |\nabla \varphi_{j\sigma}(\mathbf{r})|^2$$

$$\tau(\mathbf{r}) = \frac{1}{2} \sum_j^{\text{occ}} |\nabla \varphi_j(\mathbf{r})|^2$$

- ▶  $\tau(\mathbf{r})$  is sensitive to the degree of localization of electrons
- ▶ helps to distinguish covalent single bonds and metallic bonds
- ▶ incorporates exact constraints of one- and two-electron densities

$$E_{\text{xc}}^{\text{MGGA}}[n_{\sigma}] = \int d\mathbf{r} f(n_{\sigma}, \nabla n_{\sigma}, \tau_{\sigma})$$

Examples:

- **TPSS** (Tao-Perdew-Staroverov-Scuseria 2003)
- **SCAN** (Sun-Ruzsinszky-Perdew 2016)  
“Strongly Constrained Appropriately Normed”

**SCAN satisfies all 17 known exact conditions that a meta-GGA can satisfy.**

**SCAN is a nonempirical functional.**

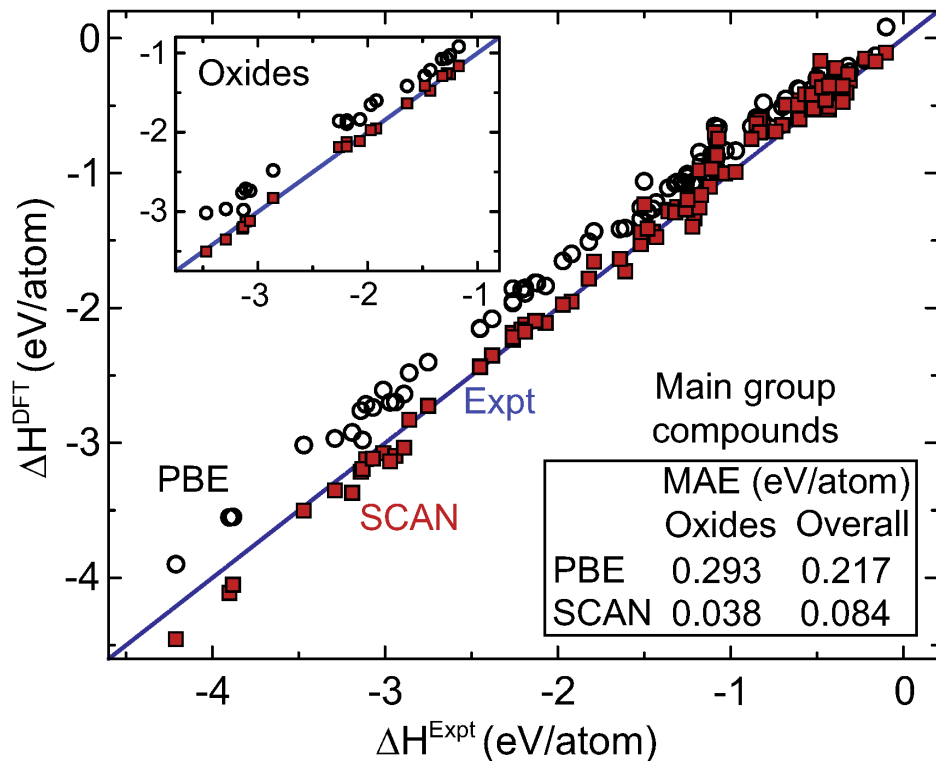




	hydrocarbons				barrier heights		weakly bonded complexes		lattice constants of solids	
	G 3 <sup>HC</sup> (kcal/mol)		G3 (kcal/mol)		BH76 (kcal/mol)		S22 (kcal/mol)		LC20(Å)	
	ME	MAE	ME	MAE	ME	MAE	ME	MAE	ME	MAE
LSDA	-5.6	13.0	-83.7	83.7	-15.2	15.4	2.3	2.3	-0.081	0.081
BLYP	1.8	6.2	3.8	9.5	-7.9	7.9	-8.7	8.8		
PBEsol	-4.1	6.5	-58.7	58.8	-11.5	11.5	-1.3	1.8	-0.012	0.036
PBE	-2.1	6.6	-21.7	22.2	-9.1	9.2	-2.8	2.8	0.051	0.059
TPSS	1.9	3.8	-5.2	5.8	-8.6	8.7	-3.7	3.7	0.035	0.043
M06 L	-0.2	4.6	-1.6	5.2	-3.9	4.1	-0.9	0.9	0.015	0.069
SCAN	-0.8	2.7	-4.6	5.7	-7.7	7.7	-0.7	0.9	0.007	0.016

Uses “molecular test sets” such as the G3 data base

J. Sun et al., Phys. Rev. Lett. **115**, 036402 (2015)

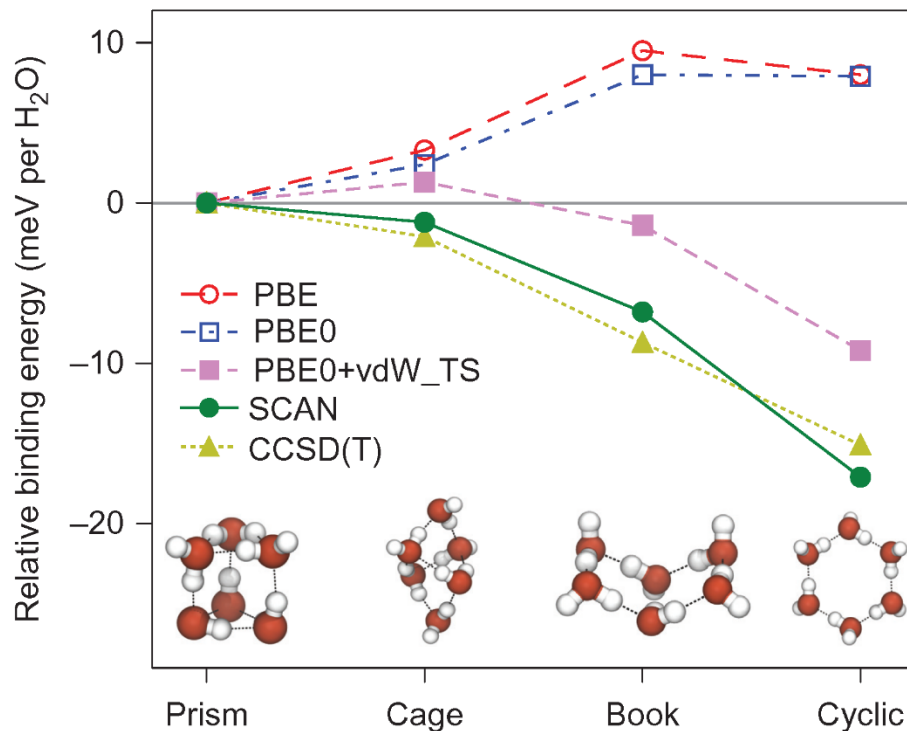


Formation enthalpy of solids (main group binary compounds)

► Mean absolute error (MAE) close to chemical accuracy (0.04 eV per atom)

► Less accurate for transition metal compounds (but still good)

Y. Zhang et al., NPJ Comput. Mater. **4**, 9 (2018)



► Correct ordering of water hexamer structures

► SCAN can describe medium range van der Waals interactions

J. Sun et al., Nature Chem. **8**, 831 (2016)

▶ **Nonempirical xc functionals:**

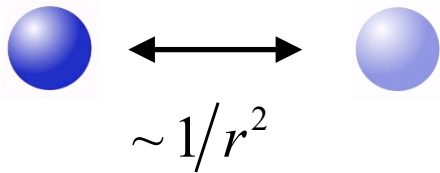
constructed so as to satisfy known exact constraints

▶ **GGAs and Meta-GGAs:**

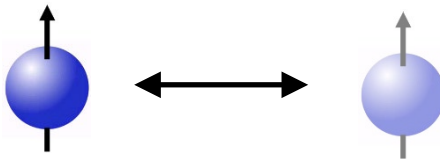
reliable accuracy, can predict materials properties efficiently

▶ **When are semilocal functionals OK?**

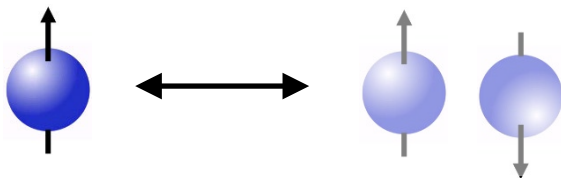
Electrons avoid each other in three ways:



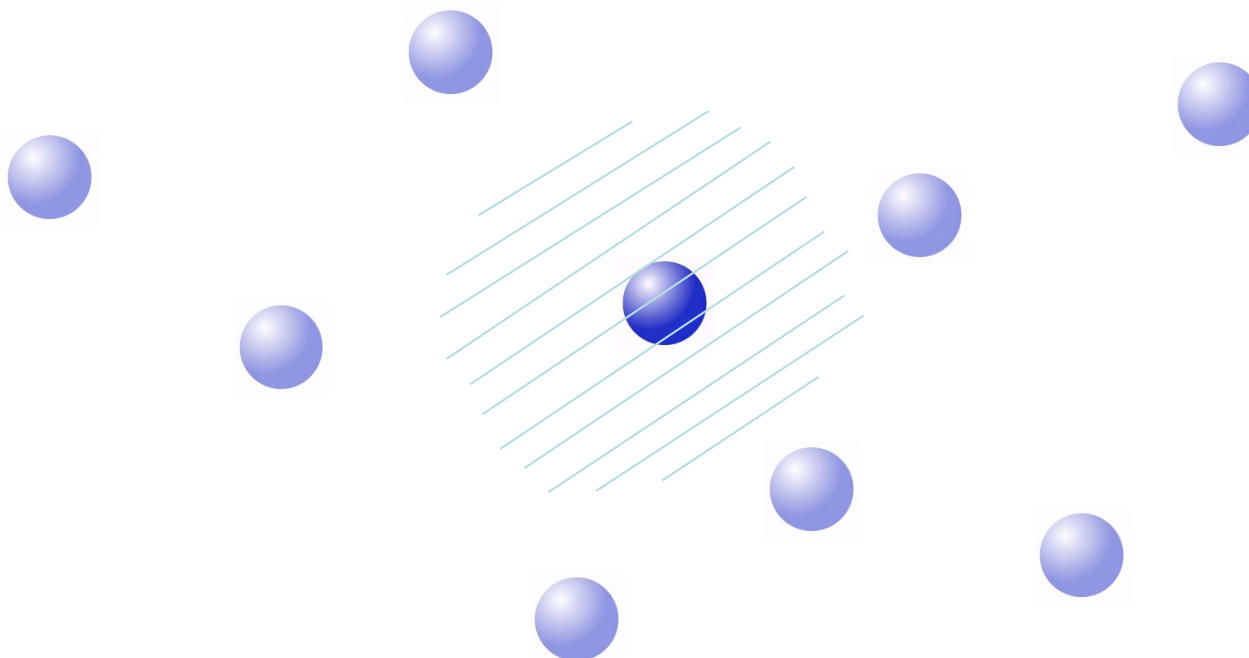
1. through classical Coulomb interaction (negative charges repel each other)



2. through the Pauli principle (exchange interaction between parallel spins)



3. through correlation (both parallel and antiparallel spin)



- ▶ **Region around an electron where it is less likely to find another electron, due to xc effects: electrons practice social distancing!**
- ▶ **The xc hole is often confined to a small region around the reference electrons, but sometimes it can reach quite far**

▶ **Nonempirical xc functionals:**

constructed so as to satisfy known exact constraints

▶ **GGA and Meta-GGA:**

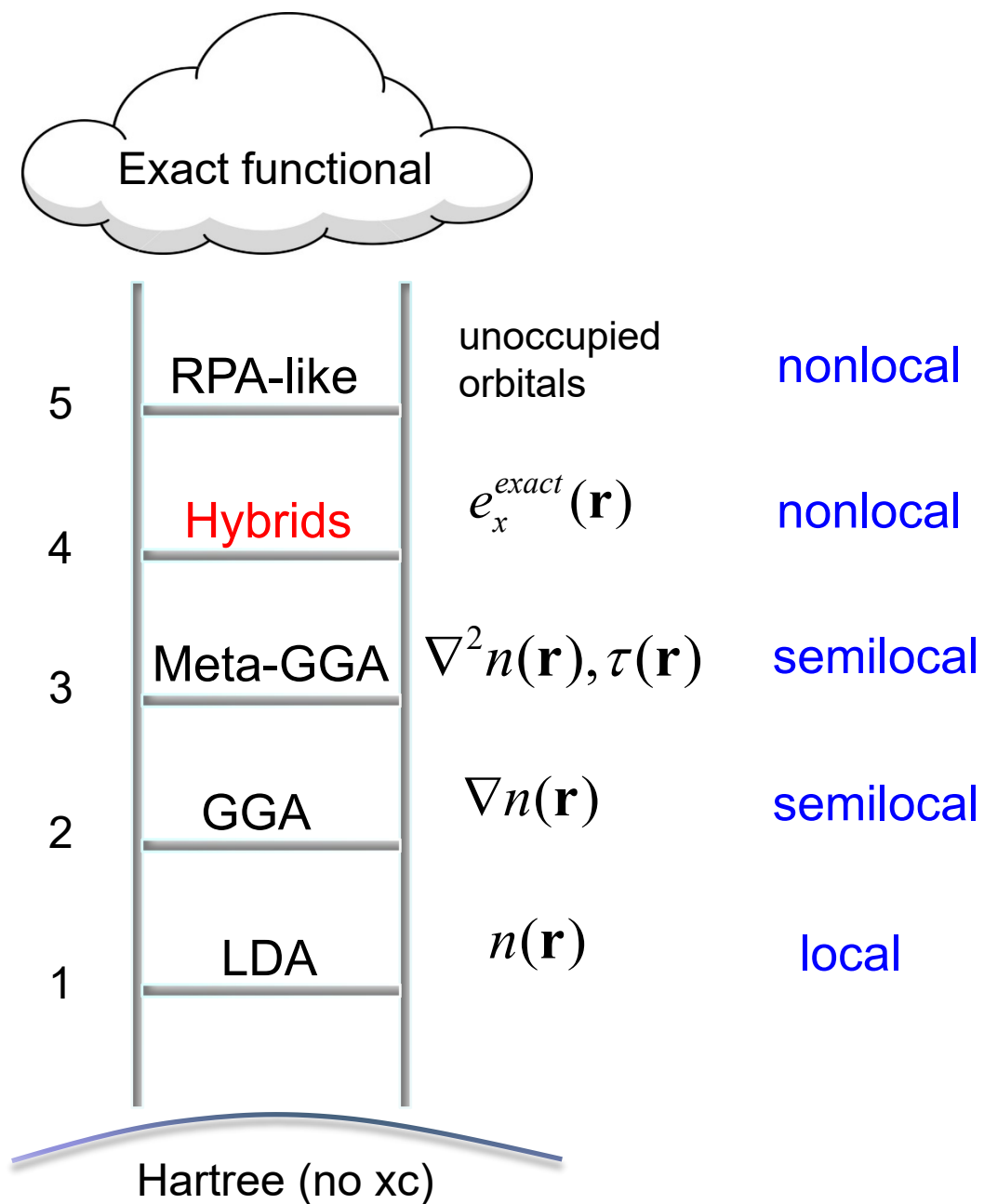
reliable accuracy, can predict materials properties efficiently

▶ **When are semilocal functionals OK?**

Whenever the xc hole is sufficiently localized.

▶ **Where do they fail?**

- Weakly bonded systems
- Strongly correlated systems
- Band gap calculation





$$E_x^{\text{exact}} = -\frac{1}{2} \sum_{\sigma=\uparrow\downarrow} \sum_{ij}^{\text{occ}} \int d\mathbf{r} \int d\mathbf{r}' \frac{\varphi_{i\sigma}^*(\mathbf{r})\varphi_{i\sigma}(\mathbf{r}')\varphi_{j\sigma}(\mathbf{r})\varphi_{j\sigma}^*(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}$$

- ▶ Hartree-Fock exchange energy, but with Kohn-Sham orbitals
- ▶ Self-interaction free
- ▶ Has correct asymptotic form (-1/r) for large r

First guess:

$$E_{xc}^{\text{hybrid}} \stackrel{?}{=} E_x^{\text{exact}} + E_c^{\text{LDA/GGA}}$$

**Very bad! Why?**

**Error cancellation in LDA/GGA:  $E_x^{\text{LDA}}$  and  $E_c^{\text{LDA}}$  have errors of opposite sign, which (mostly) cancel out!**

**$E_c^{\text{LDA}}$  by itself has large errors, not compensated by  $E_x^{\text{exact}}$**

$$E_{xc}^{\text{hybrid}} = aE_x^{\text{exact}} + (1 - a)E_x^{\text{GGA}} + E_c^{\text{GGA}}$$

mixing parameter:  $0 < a < 1$  (optimized by fits to data sets, or based on XC hole arguments)

## Compromise:

- ▶ Still benefit from error cancellation
- ▶ Take advantage of nice properties of exact exchange

**PBE0** (1999):

$$E_{\text{xc}}^{\text{PBE0}} = \frac{1}{4} E_{\text{x}}^{\text{exact}} + \frac{3}{4} E_{\text{x}}^{\text{PBE}} + E_{\text{c}}^{\text{PBE}}$$

**B3LYP** (1994):

$$E_{\text{xc}}^{\text{B3LYP}} = (1 - a) E_{\text{x}}^{\text{LDA}} + a E_{\text{x}}^{\text{exact}} + b E_{\text{x}}^{\text{B88}} + c E_{\text{c}}^{\text{LYP}} + (1 - c) E_{\text{c}}^{\text{LDA}}$$

$$a = 0.20$$

$$b = 0.72$$

$$c = 0.81$$

} fitted to a molecular  
data set



	Formation enthalpy (kcal/mol)	Ionization potential	Equilibrium bond length (Å)	Vibrational frequency	
	HF	211.54	1.028	0.0249	136.2
	LSDA	121.85	0.232	0.0131	48.9
GGA	BLYP	9.49	0.286	0.0223	55.2
	PBE	22.22	0.235	0.0159	42.0
MGGA	TPSS	5.81	0.242	0.0142	30.4
hybrid	PBE0	6.66	0.199	0.0097	43.6
	B3LYP	4.93	0.184	0.0104	33.5

		Cohesive energy (eV/atom)	lattice constant (Å)
GGA	LDA	0.77	0.071
	BLYP	0.69	0.120
	PBE	0.19	0.061
MGGA	TPSS	0.20	0.054
	SCAN	0.19	0.030
hybrid	PBE0	0.46	0.038
	B3LYP	0.84	0.084

PBE and B3LYP are the most widely used functionals in DFT.

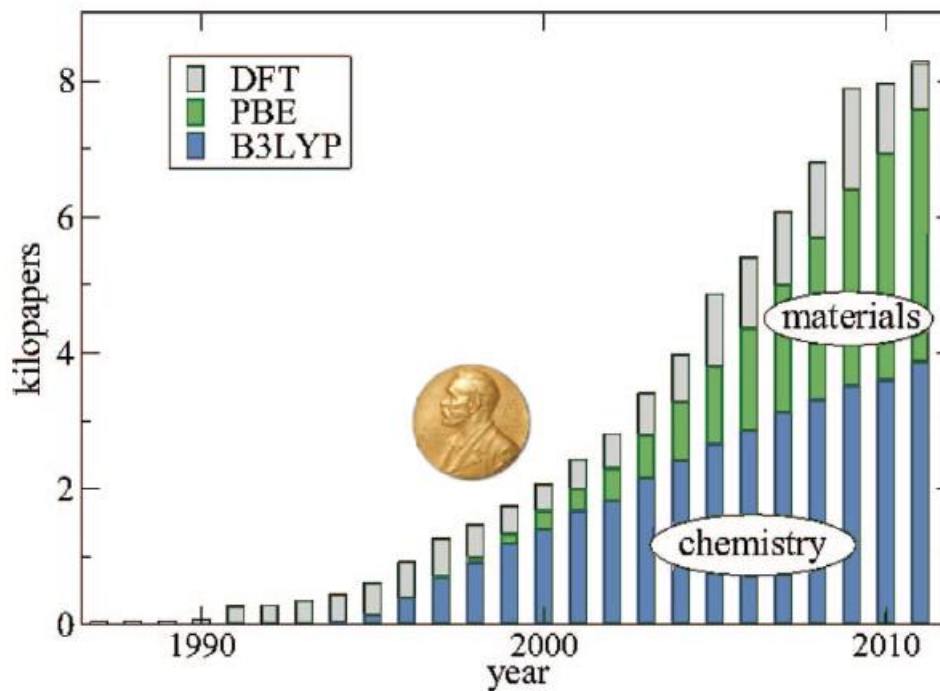


FIG. 1. Numbers of papers when DFT is searched as a topic in Web of Knowledge (grey), B3LYP citations (blue), and PBE citations (green, on top of blue).

K. Burke, J. Chem. Phys. **136**, 150901 (2012)

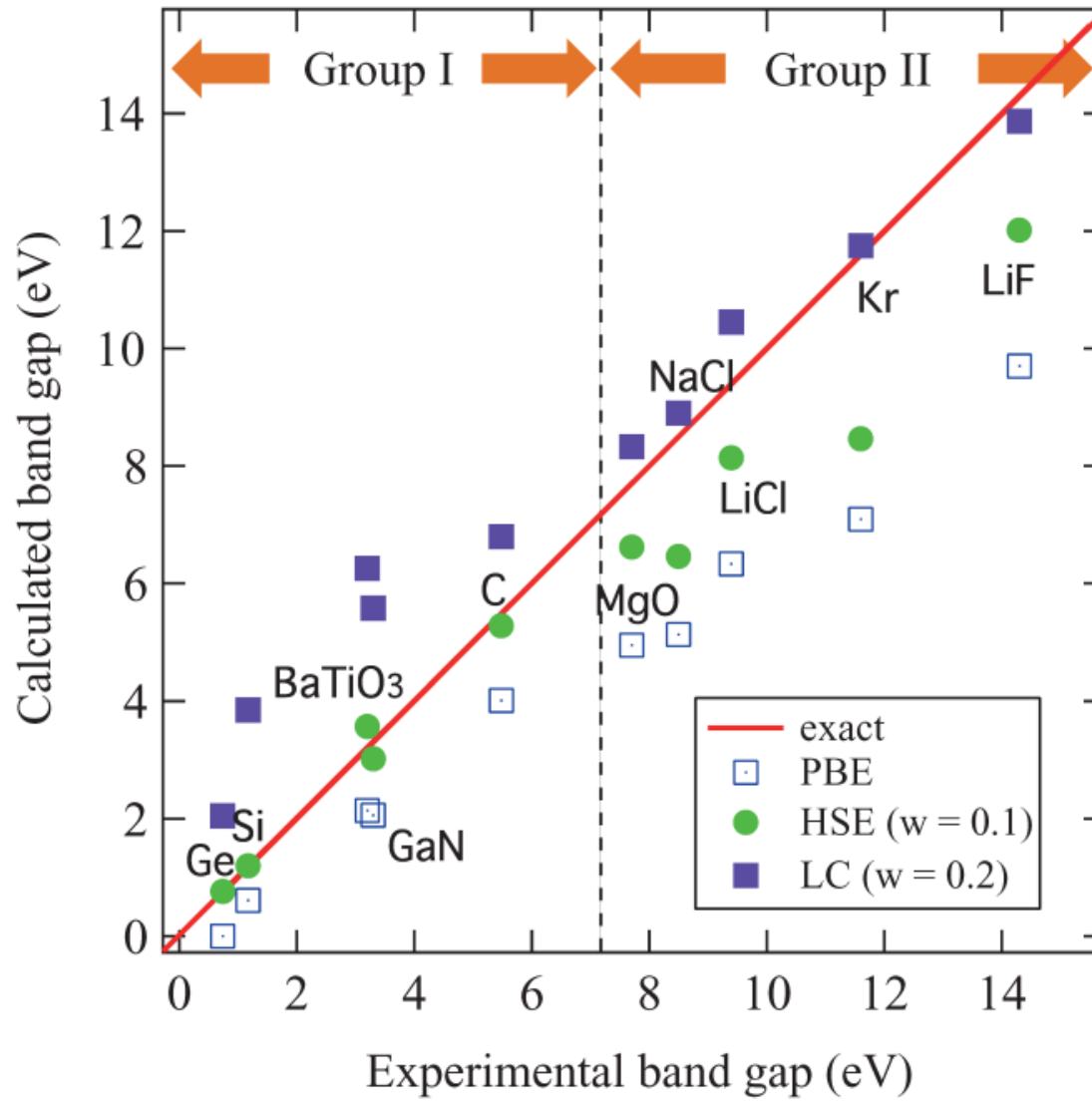
## ► Hybrid xc functionals contain a fraction of Hartree-Fock exchange

- The mixing parameters can be determined empirically (B3LYP) or semi-empirically (PBE0)
- Hybrids are nonlocal orbital functionals
- Generalized Kohn-Sham scheme:  
nonlocal xc potential (similar to HF equations)
- Alternatively: solve Kohn-Sham with LDA or GGA and plug the orbitals into the meta-GGA or hybrid functionals

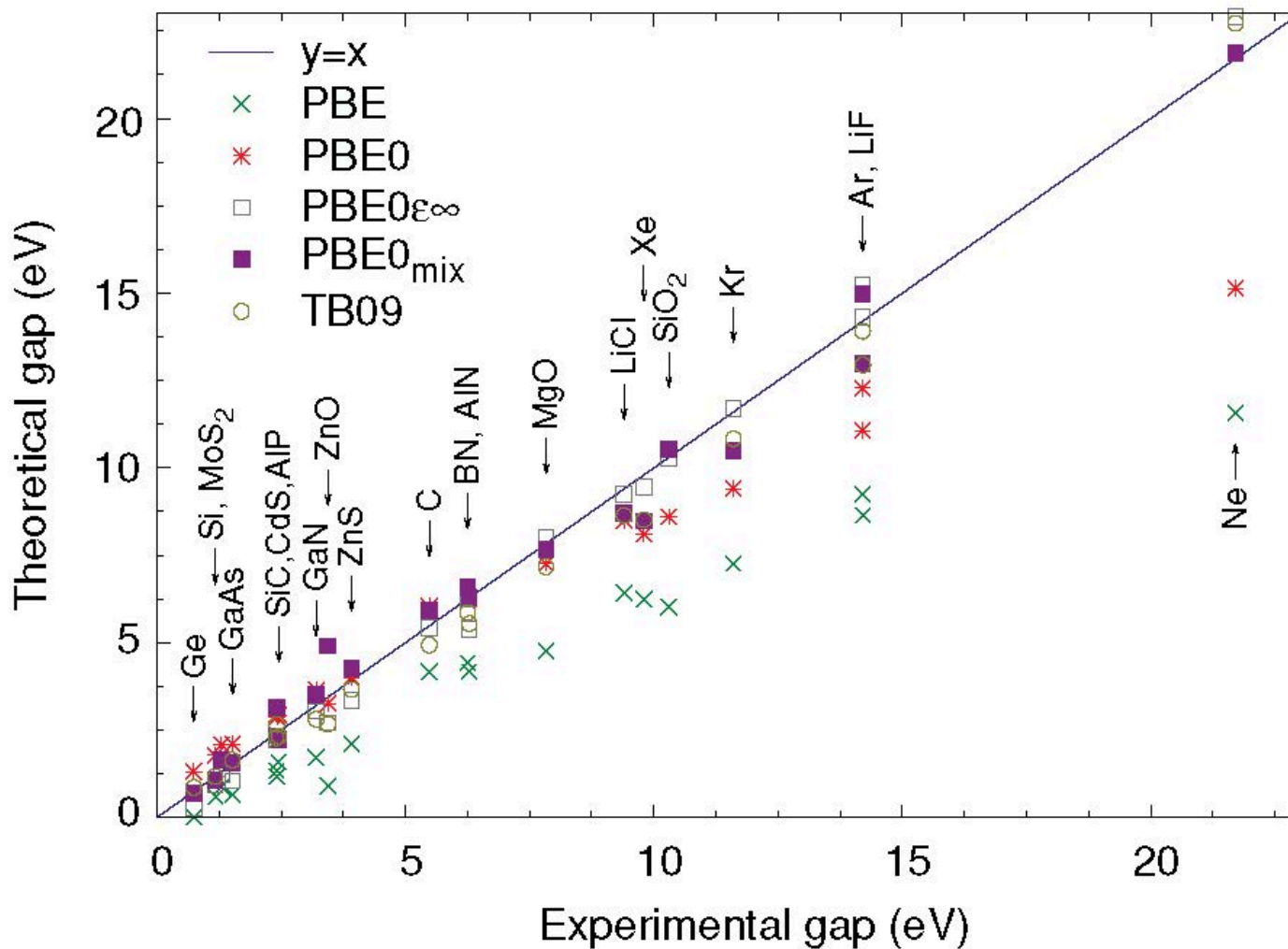




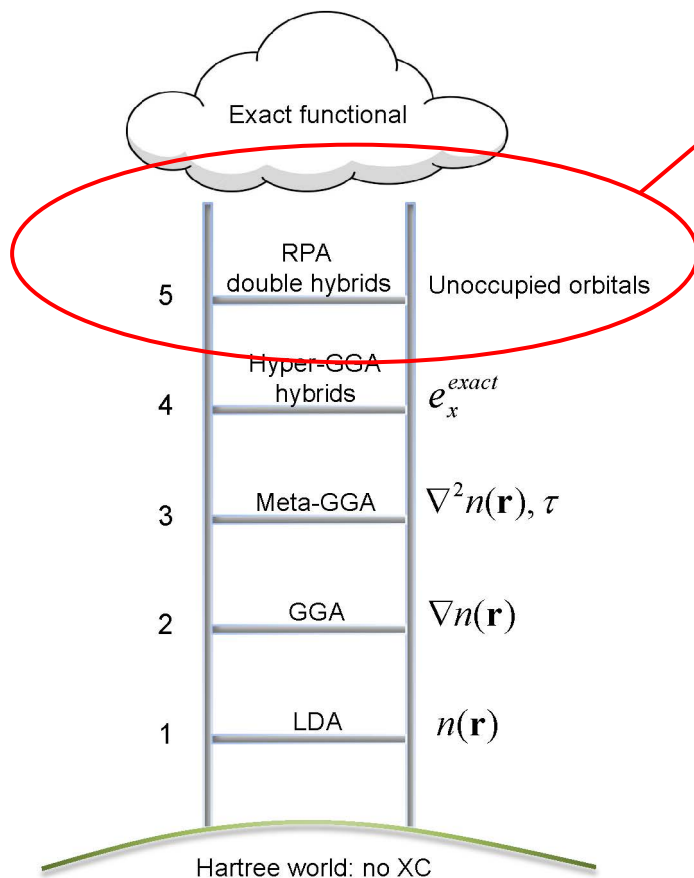
- Very good: energetics of molecules
- Good geometries/lattice constants, but GGA/MGGA often better
- HF exchange can be expensive for solids (depending on method)
- Good band gaps



Matsushita, Nakamura and Oshiyama, PRB **84**, 075205 (2011)



Marques et al., PRB **83**, 035119 (2011)

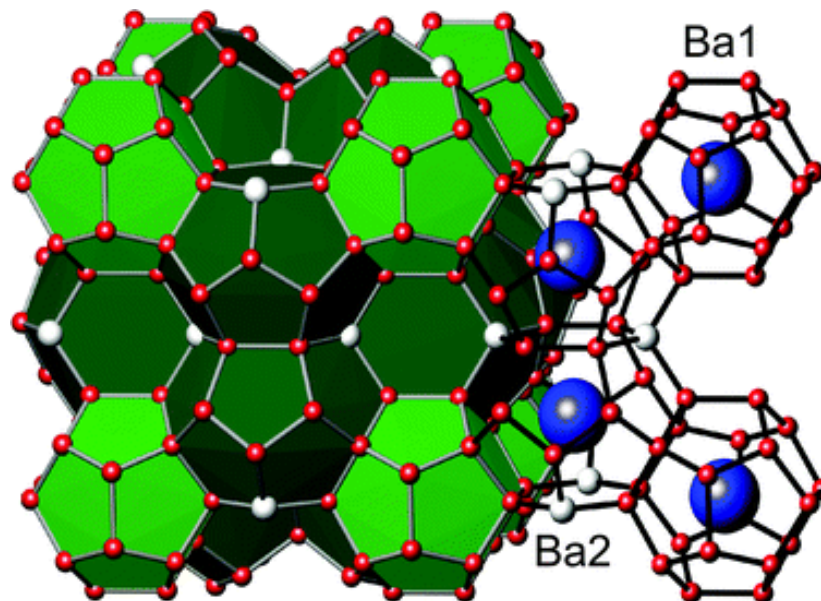
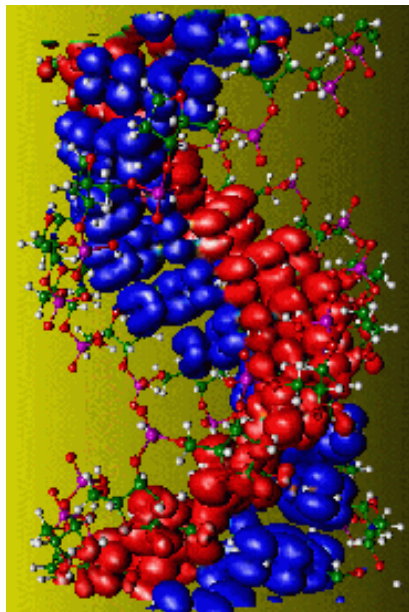


RPA-type functionals,  
depending on unoccupied orbitals

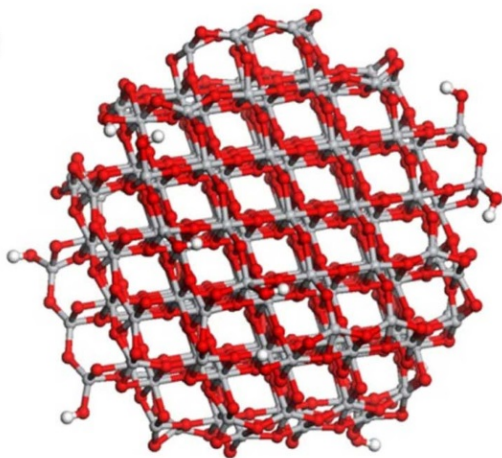
- ▶ Better description of correlation, screening, dissociation, dispersion interactions
- ▶ But: rather expensive! Rarely used for materials.

## Alternatives:

- ▶ Dispersive corrections for van der Waals interactions
- ▶ LDA+U (to shift band gap)
- ▶ Quasiparticle-based theories such as GW (expensive!)



a



b

