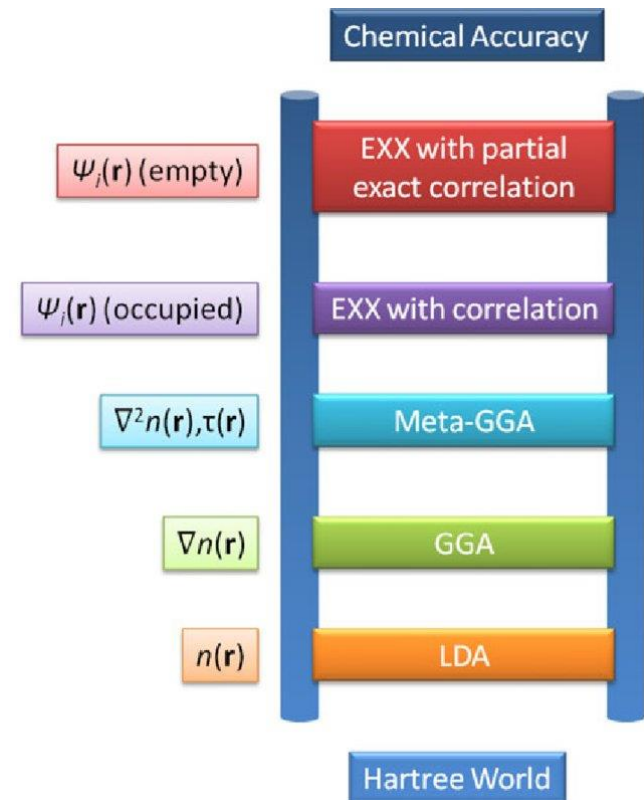


# Density functional theory in solid state physics

## Lecture 5

# Summary

- Exchange-correlation functionals are the central approximation of Kohn-Sham DFT
- Exchange-correlation functionals often designed by modeling the exchange-correlation hole.
- Many (order 200-300) such functionals with different degrees of simplicity and accuracy available:  
„Jacob’s ladder“ of exchange-correlation functionals:
- Simple model for solids: Homogeneous electron gas (HEG). Exchange expression known analytically, correlation parametrized based on Monte Carlo and experimental data



<https://www.sas.upenn.edu/~jianmint/Research/>

- First rung of Jacob's Ladder: Local density approximation (LDA).  
Approximate XC interaction at point  $\vec{r}$  with that of HEG of density  $n(\vec{r})$ .

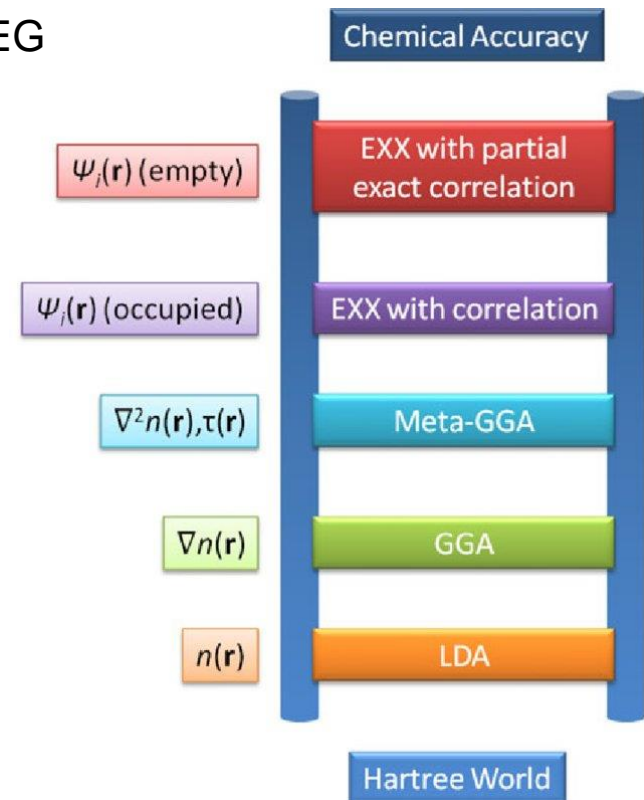
$$E_{xc}^{LDA} = \int n(\vec{r}) \epsilon_{xc}^{HEG}(n^\uparrow, n^\downarrow) dr$$

Simple and local approximation that is exact for the HEG  
Surprisingly good results, esp. for structures, but  
„overbinding“.  
Bad electronic band gaps

- Second rung: Generalized gradient approximation (GGA)  
(Semi-)local improvement on LDA through inclusion of the density gradient.

$$E_{xc}^{GGA} = \int n(\vec{r}) \epsilon_{xc}^{GGA}(n^\uparrow, n^\downarrow, \nabla n^\uparrow, \nabla n^\downarrow) dr$$

Typically structural and energetic properties of similar or better accuracy than LDA, but often „underbinding“  
Bad electronic band gaps due to lack of derivative discontinuity



<https://www.sas.upenn.edu/~jianmint/Research/>

- Third rung: metaGGAs. More generalized form of GGAs with additional degrees-of-freedom
- Observation: Taylor expansion of the exchange hole  $n_x$  for small  $|\vec{r} - \vec{r}'|$  depends on  $n^\sigma, \nabla n^\sigma, \nabla^2 n^\sigma$ , but also on the *kinetic energy density*

$$\tau^\sigma(\vec{r}) = \frac{1}{2} \sum_{\alpha} f_{F-D}^{\alpha} |\nabla \varphi_{\alpha}^{\sigma}|^2$$

- metaGGA functional form:

$$E_{xc}^{metaGGA} = \int n(\vec{r}) \varepsilon_{xc}^{metaGGA}(n^{\uparrow}, n^{\downarrow}, \nabla n^{\uparrow}, \nabla n^{\downarrow}, \nabla^2 n^{\uparrow}, \nabla^2 n^{\downarrow}, \tau^{\uparrow}, \tau^{\downarrow}) dr$$

- Additional degrees-of-freedom allows for the satisfaction of additional exact constraints that go beyond the capabilities of pure GGAs
- Example: One-electron regions can be recognized by the condition

$$\tau^\sigma(\vec{r}) = \frac{|\nabla n^\sigma|^2}{8n^\sigma}$$

and the correlation part of can be set to zero in these regions.

- Popular metaGGAs:
  - Tao-Perdew-Staroverov-Scuseria (TPSS): based on PBE, but can respect both the paradigms of slowly-varying densities and one- and two-electron ground states.

*Phys. Rev. Lett. 91, 146401 (2003)*

Great improvement of atomization energies, surface energies of metals and lattice constants of solids compared to LDA or GGAs, such as PBE

TABLE I. Statistical summary of the errors of five density functionals for various properties of molecules, solids, and surfaces. 1 kcal/mol = 0.0434 eV = 0.00159 hartree. For jellium,  $r_s = (3/4\pi n)^{1/3}$  characterizes bulk density.

Property (units)	Test set	Mean value of property	Mean absolute errors					Mean error of TPSS
			LSD	PBE	PBE0	PKZB	TPSS	
Atomization energy $\Sigma D_0$ (kcal/mol)	G2 (148 mols.)	478	83.8	17.1	5.1	4.4	6.2	5.4
Ionization potential (eV)	G2 (86 species)	10.9	0.22	0.22	0.20	0.29	0.23	-0.11
Electron affinity (eV)	G2 (58 species)	1.4	0.26	0.12	0.17	0.14	0.14	-0.01
Bond length $r_e$ (Å)	96 molecules	1.56	0.013	0.016	0.010	0.027	0.014	0.014
Harmonic frequency $\omega_e$ (cm <sup>-1</sup> )	82 diatomics	1430	48.9	42.0	43.6	51.7	30.4	-18.7
H-bond dissoc. energy $D_0$ (kcal/mol)	10 complexes	13.4	5.8	1.0	0.7	2.9	0.6	0.2
H-bond lengths $r_e$ (Å)	11 H-bonds	2.06	0.147	0.043	0.032	0.179	0.021	0.021
H-bond angles (deg)	13 angles	111	4.0	2.6	1.8	3.5	2.0	2.0
Lattice constant (Å)	18 solids	4.47	0.069	0.057	...	0.078	0.040	0.039
Bulk modulus (GPa)	18 solids	116	15.1	7.6	...	7.8	8.2	-0.5
XC surface energy (erg/cm <sup>2</sup> )	$r_s = 2, 4, 6$	1245	22	55	39	5	13	-10

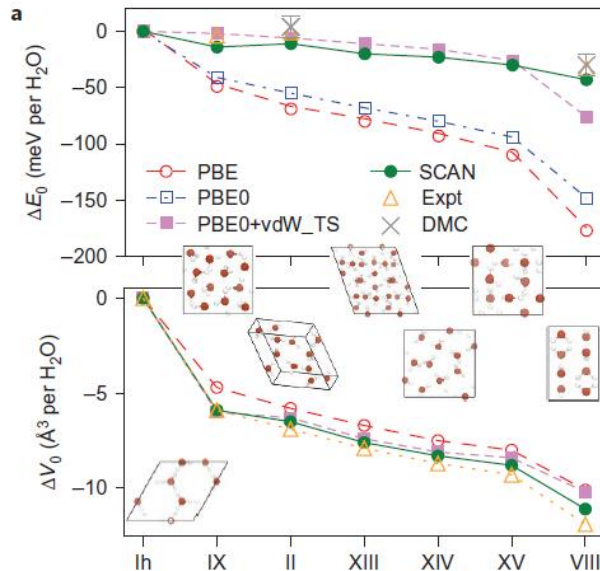
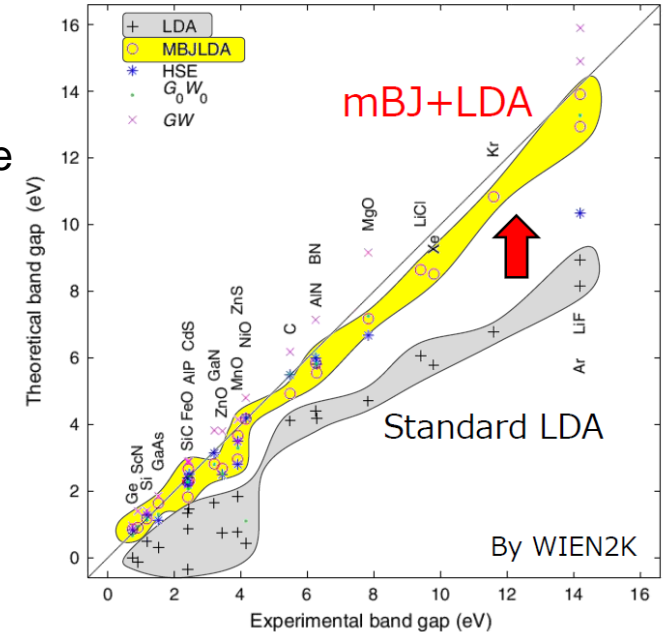
TABLE I. Errors in equilibrium lattice constants (in Å × 10<sup>-2</sup>) on our data set of 18 solids, relative to experiment with estimates of the zero-point anharmonic expansion removed [28].

Class	LSDA	PBE	TPSS	PBEsol
Mean error				
4 simple metals	-9.0	2.9	5.3	-0.3
5 semiconductors	-1.1	7.9	6.2	3.0
5 ionic solids	-8.4	8.5	6.8	2.0
4 transition metals	-4.0	6.4	2.5	0.0
Total	-5.5	6.6	5.4	1.3
Mean absolute error				
4 simple metals	9.0	3.4	5.3	2.3
5 semiconductors	1.3	7.9	6.2	3.0
5 ionic solids	8.4	8.5	6.8	2.7
4 transition metals	4.0	6.4	2.7	1.9
Total	5.6	6.7	5.4	2.5

- Tran-Blaha modified Becke-Johnson (TB-mBJ):

exchange potential with distinct derivative discontinuity. Two parameters fitted to reproduce experimental band gaps at low computational cost. Correlation effects can be accounted for by adding  $v_c^{LDA}$

*Phys. Rev. Lett. 102, 226401 (2009)*



- SCAN: fulfills all exact constraints possible for a meta-GGA. Probably superior to any other metaGGA for structural and energetic properties.

*Phys. Rev. Lett. 115, 036402 (2015)*

# Hybrid functionals

- Beyond local approximations: Hybrid functionals mixing Hartree-Fock exchange and GGA. Fourth rung
- Motivation: adiabatic connection

$$E_{xc} = \int_0^1 E_{xc}^\lambda d\lambda = \int_0^1 (\langle \Psi_\lambda | V^{e-e} | \Psi_\lambda \rangle - E_{Hartree}) d\lambda$$

Fully-interacting electrons
Groundstate wavefunction for  $\lambda$

Non-interacting electrons

- $E_{xc,\lambda=0}$  is Hartree-Fock exchange  $E_x^{HF}$ ,  $E_{xc,\lambda=1}$  limit is approximated by an LDA or GGA
- Idea: approximate the adiabatic-connection integral by

$$E_{xc}^{hyb} = E_x^{HF} + \underbrace{(1-a)(E_x^{DFT} - E_x^{HF})}_{\text{static correlation}} + \underbrace{E_c^{DFT}}_{\text{dynamic correlation}}$$

- $E_{xc}^{hyb}[\{\varphi[n]\}]$  depends implicitly on electron density

# Hybrid functionals

- Further refinement: „Range-separated“ hybrid functionals
- Short-range hybrid:

$$E_{xc}^{sr-hyb} = a(E_x^{HF,SR} - E_x^{DFT,SR}) + E_{xc}^{DFT}$$

- „Screening“ of Hartree-Fock contribution, useful form for solids due to slow decay of the bare HF-type exchange component

- Long-range hybrid:

$$E_{xc}^{lr-hyb} = a(E_x^{HF,LR} - E_x^{DFT,LR}) + E_{xc}^{DFT}$$

- Useful form for molecular systems, asymptotic decay of exchange potential in long-range is restored

- „Middle-range“ hybrids:  $E_{xc}^{mr-hyb} = E_x^{DFT,SR} + aE_x^{HF,MR} + (1 - a)E_x^{DFT,MR} + E_x^{DFT,LR} + E_c^{DFT}$



- Important hybrid functionals:

- B3LYP:  $E_{xc}^{B3LYP} = 0.2(E_x^{HF} - E_x^{LDA}) + 0.72(E_x^{B88} - E_x^{LDA}) + E_c^{VWN} + 0.81(E_c^{LYP} - E_c^{VWN})$

(„fudge“ factors chosen empirically)

*J. Chem. Phys.* 98, 5648(1993)

- PBE0:  $E_{xc}^{PBE0} = 0.25E_x^{HF} + 0.75E_x^{PBE} + E_c^{PBE}$

*J. Chem. Phys.* 110, 6158 (1999)

( $a=0.25$  obtained from perturbation theory)

# Hybrid functionals

- Heyd-Scuseria-Ernzerhof (HSE):  $E_{xc}^{HSE} = 0.25(E_x^{HF,SR} - E_x^{PBE,SR}) + E_{xc}^{PBE}$

Short range HF:  $E_x^{HF,SR} = -\frac{1}{2} \sum_{i,j} \iint \frac{\text{erfc}(\omega|\vec{r}-\vec{r}'|)}{|\vec{r}-\vec{r}'|} \varphi_i^*(\vec{r}) \varphi_j^*(\vec{r}') \varphi_i(\vec{r}') \varphi_j(\vec{r}) d\vec{r} d\vec{r}'$

Occupied orbitals

*J. Chem. Phys.* 118, 8207 (2004)

*J. Chem. Phys.* 125, 224106 (2006)

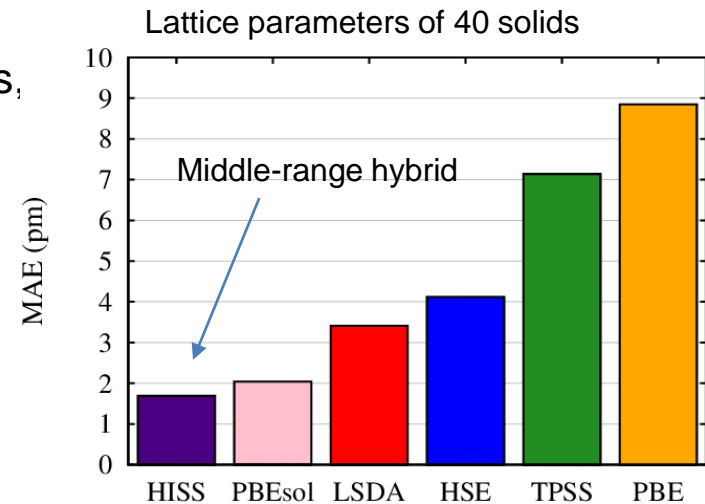
- „screened exchange“ (sX-LDA):  $E_{xc}^{sX-LDA} = (E_x^{HF,SR} - E_x^{LDA,SR}) + E_{xc}^{LDA}$

Short range HF:  $E_x^{HF,SR} = -\frac{1}{2} \sum_{i,j} \iint \frac{\exp(-k_{TF}|\vec{r}-\vec{r}'|)}{|\vec{r}-\vec{r}'|} \varphi_i^*(\vec{r}) \varphi_j^*(\vec{r}') \varphi_i(\vec{r}') \varphi_j(\vec{r}) d\vec{r} d\vec{r}'$

Thomas-Fermi-type screening  
of exchange interaction

*Phys. Rev. B* 53, 3764 (1996)

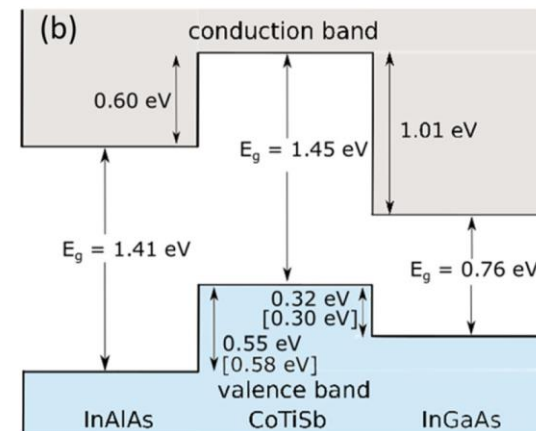
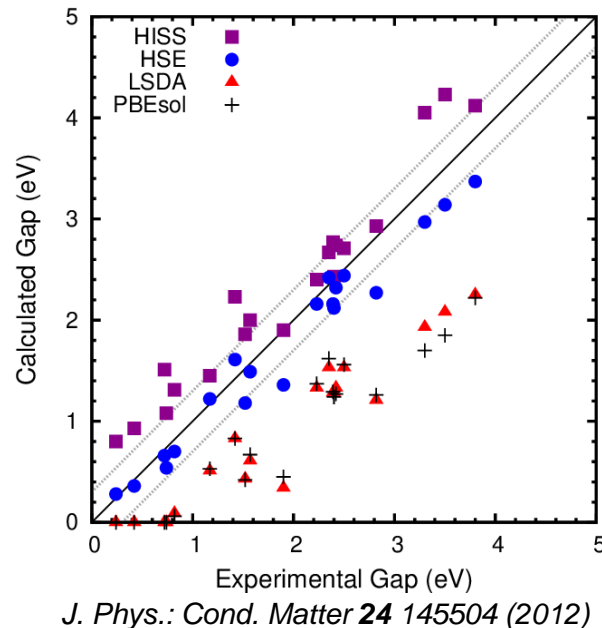
- Hybrid-functionals based on meta-GGAs also possible (and have been proposed)
- Hybrid functionals only satisfy exact constraints that their underlying DFT components satisfy
- Typically good structural and energetic properties, (for solids) but not always better than GGAs or metaGGAs
- Widely used for properties of molecules
- HF contribution aids canceling self-interaction errors
- But: computationally much more expensive than pure density-based functionals



*J. Phys.: Cond. Matter* **24** 145504 (2012)

# Hybrid functionals

- Superior description of electronic properties (band gaps, magnetism) in solids compared to GGA or metaGGAs
- Improved band gaps originate in a partial incorporation of the derivative discontinuity
- (Pseudo-)single-particle energies are usually in good agreement with exp. band edges

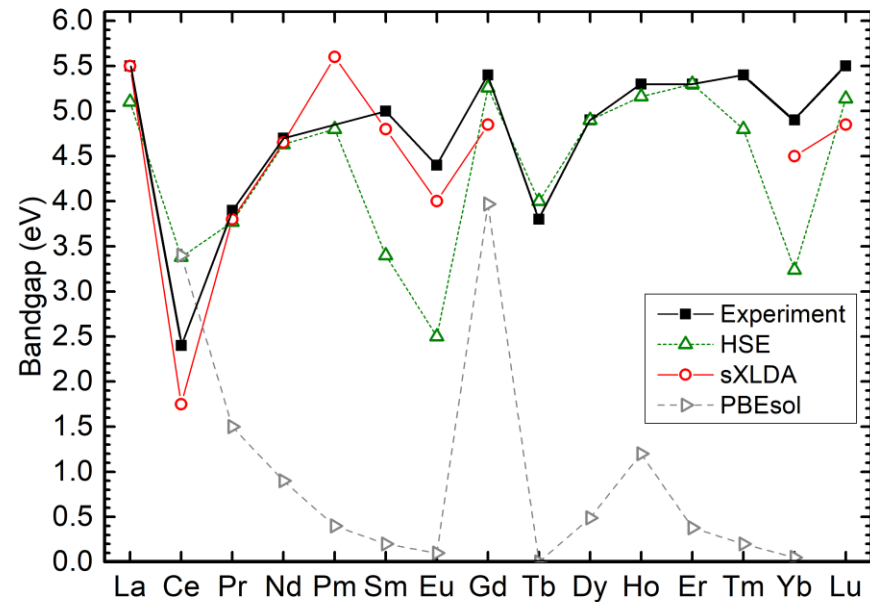
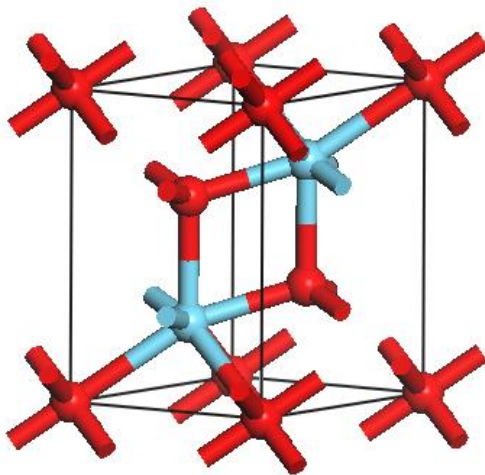


*Appl. Phys. Lett.* 111, 061605 (2017)

- Can be used to treat „pathological“ materials where LDAs or GGAs fail

## Example: Strongly-correlated oxides

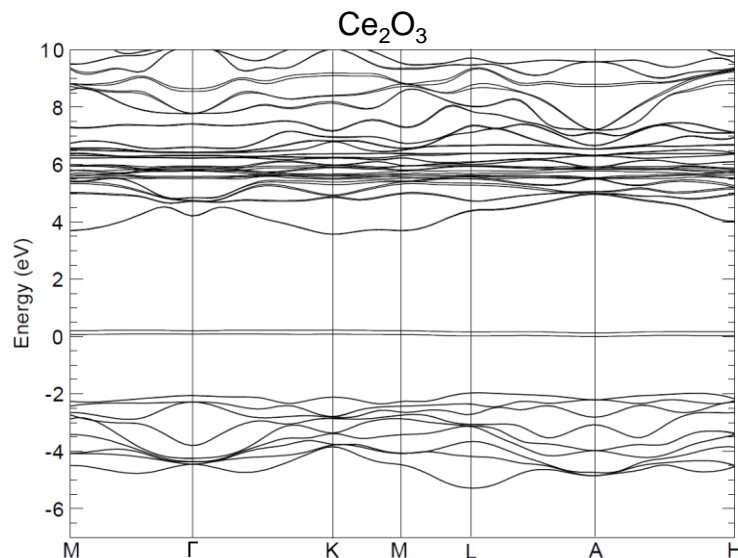
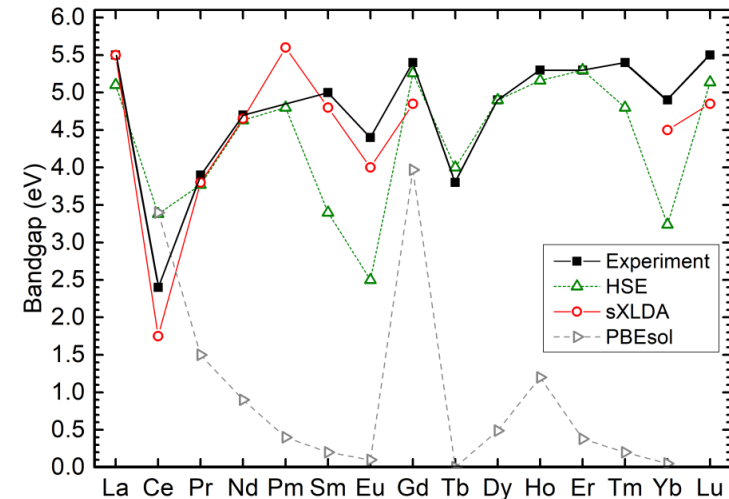
- Example: antiferromagnetic lanthanide sesquioxides
- Experiments: Periodic behaviour of electronic band gaps
- Hybrid functionals reproduce the behaviour, but PBEsol fails



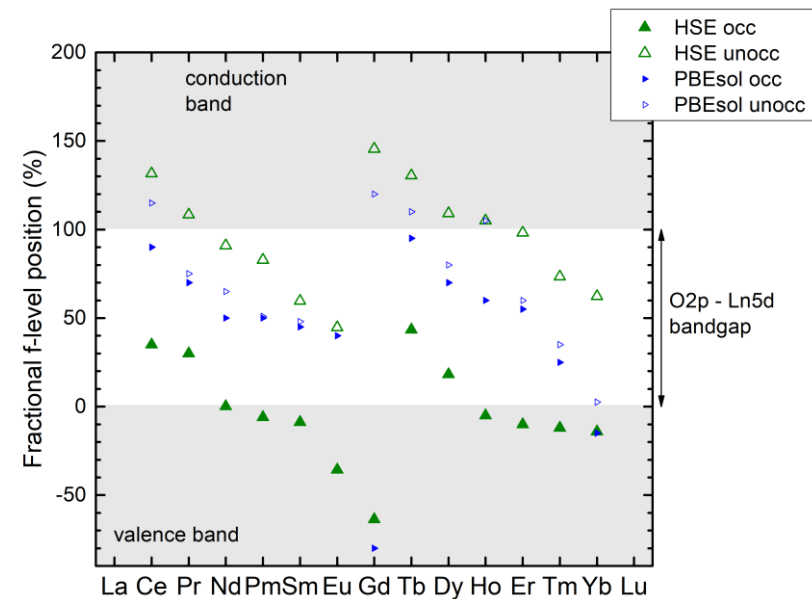
*Phys. Rev. B 87, 125116 (2013)*

# Example: Strongly-correlated oxides

- Hybrid functionals: Band gap evolution originates in 4f levels being occupied and traveling through the band gap
- Local XC functionals strongly underestimate the splitting between occupied and unoccupied 4f states



Phys. Rev. B 87, 125116 (2013)



# The fifth rung: Make everything non-local

- So far: Correlation component was treated locally
- The fifth rung: combine Hartree-Fock exchange (sometimes called „exact exchange“ (EXX) when evaluated with KS orbitals) with non-local correlation

$$E_{xc} = E_x^{HF} + E_c^{non-loc}$$

- Example: ACFD-RPA correlation
- Adiabatic connection:

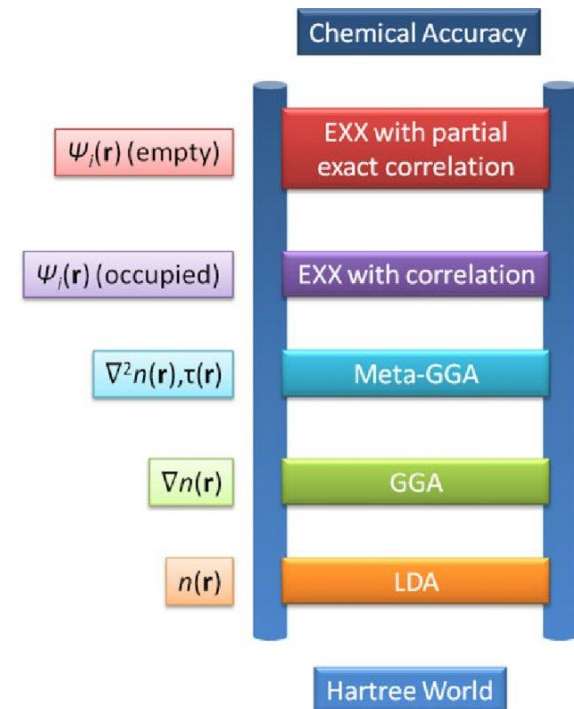
$$E_c = \int_0^1 E_c^\lambda d\lambda$$

- Fluctuation-dissipation theorem:

$$E_c^\lambda = -\frac{1}{2} \int Tr[(\chi_\lambda - \chi_0) * v] \frac{d\omega}{\pi}$$

Non-interacting response function

External/electrostatic potential



<https://www.sas.upenn.edu/~jianmint/Research/>

# The fifth rung: Make everything non-local

- Non-interacting response function from KS-DFT:

$$\chi_0(\vec{r}, \vec{r}', \omega) = 2Re \left\{ \sum_{ij} (f_i - f_j) \frac{\varphi_i^*(\vec{r}) \varphi_i(\vec{r}') \varphi_j^*(\vec{r}') \varphi_j(\vec{r})}{\varepsilon_i - \varepsilon_j + i\omega} \right\}$$

Occupied and unoccupied orbitals

- Dyson equation for  $\chi_\lambda$ :  $\chi_\lambda = \chi_0 + \chi_0 * (v + f_{xc}^\lambda) * \chi_\lambda$

Random phase approximation:  $f_{xc}^\lambda = 0$

- EXX-cRPA exchange-correlation functional:  $E_{xc} = E_x^{HF} + E_c^{RPA}$
- This approach only gives total energies, i.e. there is no exchange-correlation *potential*
- Much higher computational complexity than the lower four rungs, should in principle be more accurate than the other four rungs.
- On-going development of new algorithms and approaches to solve existing problems



- The good:
  - Exact treatment of exchange (usually with GGA or hybrid functional orbitals)
  - Van-der-Waals interactions are automatically included, e.g. correct decay of the interaction between metal surfaces and adsorbate molecules *Phys. Rev. Lett.* 101, 266106 (2008)
  - Screening effects are taken into account in a non-empirical way
  - Better results for ‚pathological‘ systems, such as strongly-correlated materials, where LDA, GGA and maybe even hybrid functionals fail
- The not so good:
  - No error cancellation between exchange and correlation terms in EXX-cRPA, in contrast to LDA or GGAs
  - EXX-cRPA results are not always better than hybrid functionals

- The fourth and fifth rungs of Jacob's Ladder are not explicit density functionals anymore.
- Does the Kohn-Sham ansatz still work in this case, i.e. does it yield the ground-state density?

- Define energy functionals  $\Xi[\{\varphi_i\}]$  and  $F^\Xi[n] = \min_{\{\varphi_i\} \rightarrow n(\vec{r})} \Xi[\{\varphi_i\}]$ , and  

$$F^{HK}[n] = F^\Xi[n] + R^\Xi[n]$$

- Generalized Kohn-Sham Equations ( Phys. Rev. B 53, 3764 (1996) ):

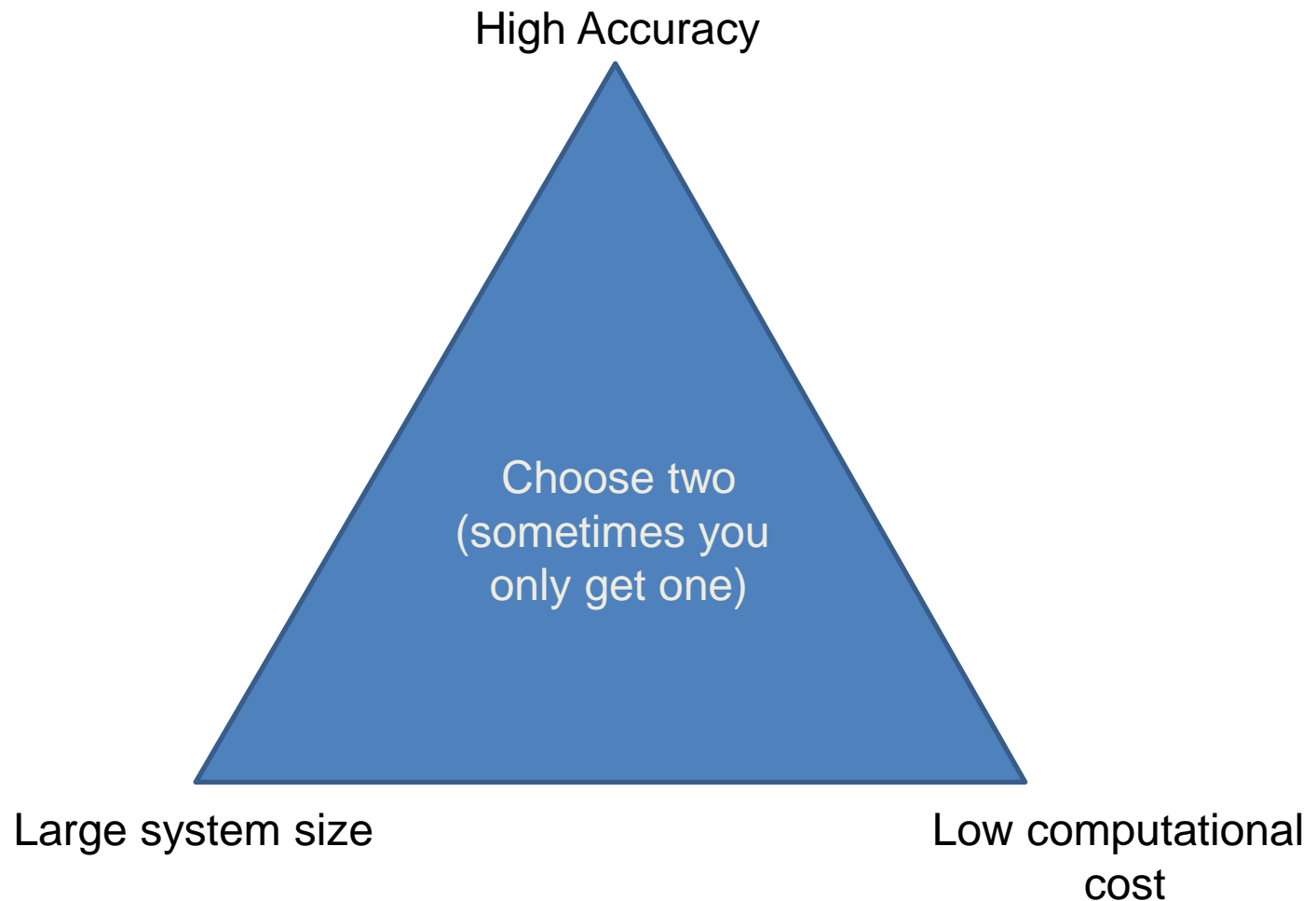
$$\hat{O}^\Xi[\{\varphi_i\}]\varphi_j + v[n]\varphi_j + \hat{v}_R[n]\varphi_j = \varepsilon_j\varphi_j$$

$$\hat{v}_R = \frac{dR^\Xi}{dn}$$

- Standard Kohn-Sham equations:  $\hat{O}^\Xi = \hat{T}^S$ ,  $\hat{v}_R = \hat{v}_H[n] + \hat{v}_{XC}[n]$
- Hybrid functionals:  $\hat{O}^\Xi = \hat{T}^S + a\hat{v}_{x,j}^{HF}[\{\varphi_i\}]$ ,  $\hat{v}_R = \hat{v}_H[n] + (1-a)\hat{v}_x[n] + \hat{v}_c[n]$

# How to choose?

- Which XC functional to choose?



- Kohn-Sham DFT is based on Hartree-(Fock) theory
- one disadvantage of KS-DFT: we still have to deal with  $3N$  coordinates, but weakly coupled, computation time scales with  $N^3$
- Goal: A density functional theory that is independent of (pseudo-) single electron orbitals

„orbital-free density functional theory“ (OF-DFT)

$$E^{DFT}[n] = T^{DFT}[n] + U^{DFT}[n] + \int v(\vec{r})n(\vec{r})dr (+E_{n-n})$$

- As it is orbital-free, this approach should scale much better with  $N$  (linear) compared to KS-DFT
- Idea: DFT based on Thomas-Fermi theory

$$E^{TF}[n] = \underbrace{T^{S,HEG}[n]}_{T^{TF}} + \int v^{eff}(\vec{r})n(\vec{r})dr (+E_{n-n})$$

- Problems of TF theory & DFT:
  - TF: Realistic systems are not homogeneous electron gases,  $T^{S,HEG}$  is too simplistic
  - DFT: We do not know an exact density functional expression for the kinetic energy  $T^{DFT}$  and for the electron-electron interaction  $U^{DFT}$
- Kohn-Sham DFT gives an idea, how we can approximate  $U[n]$ :

$$T^{DFT}[n] = T^S[n]$$

$$U^{DFT}[n] = \frac{1}{2} \int \frac{n(\vec{r})n(\vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r}d\vec{r}' + E_{xc}[n]$$

This includes all exchange correlation effects missing in the other terms

$$\rightarrow E^{DFT}[n] = T^S[n] + \int v(\vec{r})n(\vec{r})d\vec{r} + \frac{1}{2} \int \frac{n(\vec{r})n(\vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r}d\vec{r}' + E_{xc}[n] (+E_{n-n})$$

- We can use the same wealth of exchange-correlation functionals as derived for KS-DFT

# Approximations to $T^S$

- Task now: what is  $T^S[n]$ ? Need a high-accuracy expression
- $T^S[n] \approx T^{TF}[n] = \frac{3h^2}{10m} \left(\frac{3}{8\pi}\right)^{\frac{2}{3}} \int [n(\vec{r})]^{\frac{5}{3}} d\vec{r}$  is not good enough
- Go the GEA way and improve  $T^{S,HEG}[n]$  by adding a correction based on the density gradient

von-Weizsäcker approximation: 
$$T^S[n] \approx T^{TF}[n] + \underbrace{\lambda \frac{1}{8} \int \frac{|\nabla n(\vec{r})|^2}{n(\vec{r})} d\vec{r}}_{T^{vW}[n]}$$
  
(exact for one-orbital system)

- Generalized gradient approximation:

Conjointness conjecture: 
$$E_x[n] = \int \varepsilon_x^{HEG}[n] F_x[n, \nabla n] d\vec{r} \leftrightarrow T^S[n] = \int \tau_s^{HEG}[n] F_s[n, \nabla n] d\vec{r}$$

See, e.g. Phys. Rev. Lett. 106, 186406 (2011)

- Recently: non-local KEDF

$$T^S[n] = T^{TF}[n] + T^{vW}[n] + \langle n^\alpha | w^{\alpha,\beta}(\vec{r}, \vec{r}') | n^\beta \rangle$$

Nonlocal kernel with parameters  $\alpha$  and  $\beta$

Several NL-KEDF have been proposed recently, see, e.g., Phys. Rev B 100, 205132 (2019)

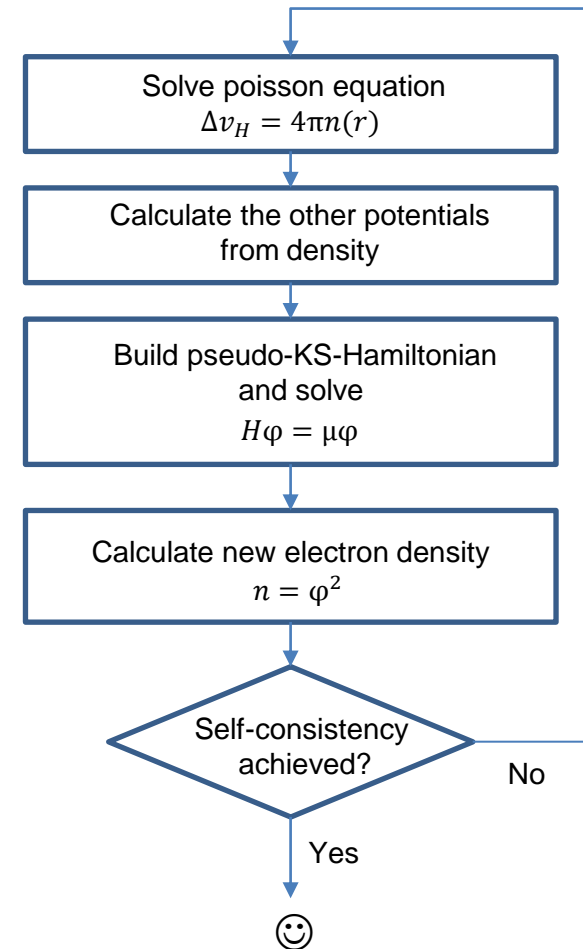
# Obtaining the electron density in OF-DFT

- How to find the groundstate density  $n(\vec{r})$ ?
- Euler Eq. for non-interacting electrons:  $\frac{dE^{DFT}}{dn} = \mu$   
↗  
Chemical potential
- Often used: Transform to pseudo-KS Eq.

$$\left( -\frac{\nabla^2}{2} + v + v_H + v_{xc} + \frac{dT^S}{dn} - \frac{dT^B}{dn} \right) \varphi = \mu \varphi$$

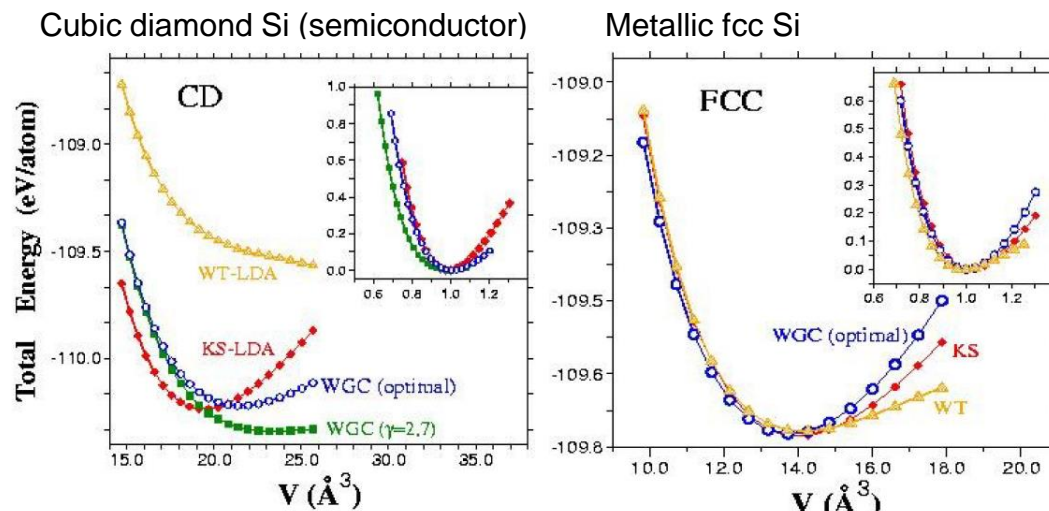
$$\text{With } \varphi = \sqrt{n} \text{ and } T^B = -\frac{1}{2} \int \sqrt{n} \nabla^2 \sqrt{n} dr, \rightarrow \frac{dT^B}{dn} = -\frac{\nabla^2 \varphi}{2\varphi}$$

- Quasi-one particle equation for a fictitious boson, solve with SCF method
- Gives access to groundstate energy and density



# Why (and why not) OF-DFT?

- Only few free implementations of OF-DFT available, for example in GPAW (<https://wiki.fysik.dtu.dk/gpaw/>) or PROFESS (Comput. Phys. Commun 190, 228 (2015))
- Systems of about 10000 atoms can be simulated on one CPU
- Orbital-free DFT works quite well for metallic systems with relatively homogeneous electron density
- Not as good for systems with covalent bonding (i.e. large density gradients)
- Contrast to KS-DFT: Approximation of  $T^S$  introduces significant errors



*J. Chem. Phys.* 122, 044103 (2005)