



DFT functionals in WIEN2k



$$E = T_o[\rho] + \int V_{ext} \rho(\vec{r}) d\vec{r} + \frac{1}{2} \int \frac{\rho(\vec{r}) \rho(\vec{r}')}{|\vec{r}' - \vec{r}|} d\vec{r} d\vec{r}' + E_{xc}[\rho]$$

vary ρ
 $dE/d\rho=0$

1-electron equations (Kohn Sham)

$$\left\{ -\frac{1}{2} \nabla^2 + V_{ext}(\vec{r}) + V_C(\rho(\vec{r})) + V_{xc}(\rho(\vec{r})) \right\} \Phi_i(\vec{r}) = \varepsilon_i \Phi_i(\vec{r})$$

$$-Z/r$$

$$\int \frac{\rho(\vec{r}')}{|\vec{r}' - \vec{r}|} d\vec{r}'$$

$$\frac{\partial E_{xc}(\rho)}{\partial \rho}$$

$$\rho(\vec{r}) = \sum_{\varepsilon_i \leq E_F} |\Phi_i|^2$$

- $E_{xc} = E_x + E_c$: exchange-correlation energy
- $V_{xc} = \frac{\partial E_{xc}(\rho)}{\partial \rho}$: exchange–correlation potential
- Both, E_{xc} and V_{xc} are unknown and must be **approximated**



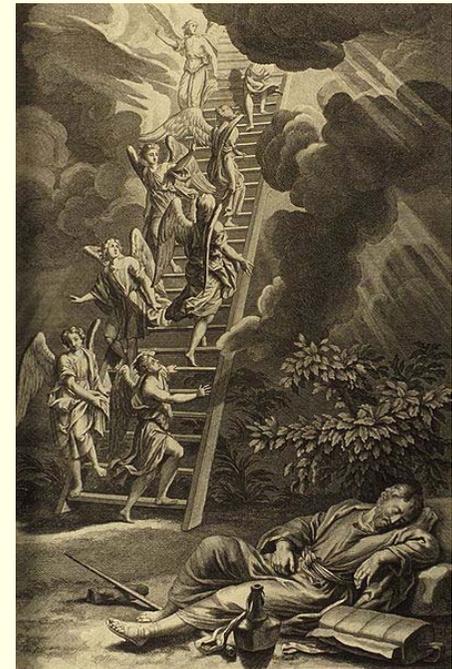
Approximations for E_{xc} (Jacob's ladder ¹)



$$E_{xc} = \int \epsilon_{xc}(\mathbf{r}) d^3r$$

- 1. Local density approximation (LDA): $\epsilon_{xc} = f(\rho)$
- 2. Generalized gradient approximation (GGA): $\epsilon_{xc} = f(\rho, \nabla\rho)$
- 3. Meta-GGA: $\epsilon_{xc} = f(\rho, \nabla\rho, \nabla^2\rho, \tau)$, $\tau = (1/2) \sum_{i=1}^{N_\sigma} \nabla\psi_{i,\sigma}^* \cdot \nabla\psi_{i,\sigma}$
- 4. use of **occupied orbitals** (e.g., Hartree-Fock)
 - *hybrid-DFT (PBE0, HSE, YS-PBE0)*
- 5. use of **unoccupied orbitals** (e.g., RPA)

- ¹J. P. Perdew *et al.*, J. Chem. Phys. **123**, 062201 (2005)





GGA functionals



- A huge number of GGA functionals have been proposed:

$$\epsilon_{XC}^{GGA}(\rho, \nabla\rho) = \epsilon_{XC}^{LDA}(\rho) F_{XC}(r_s, \mathbf{s})$$

$$r_s \propto \frac{1}{\rho^{1/3}}$$

$$\mathbf{s} \propto \frac{|\nabla\rho|}{\rho^{4/3}}$$

- where F_{XC} is the **enhancement factor**

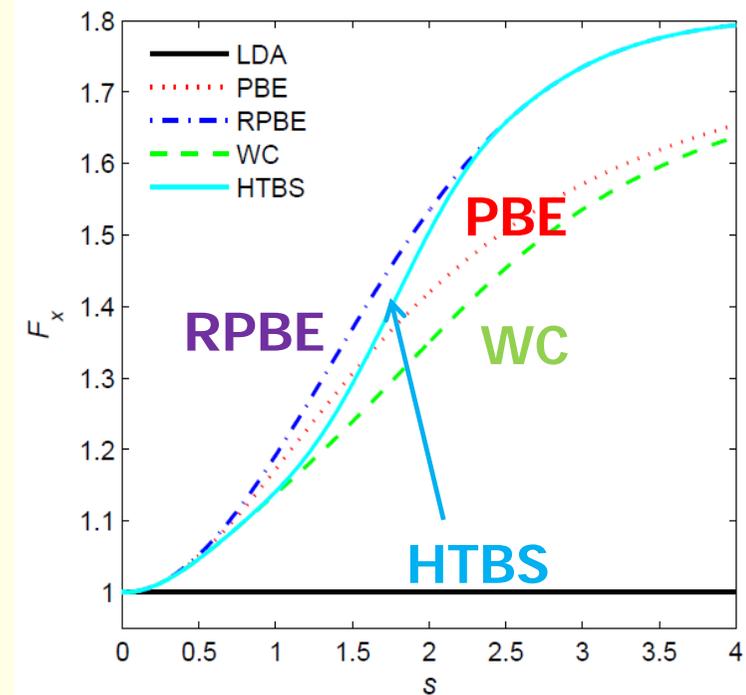
- specialized GGAs (WC, PBESOL) give much better lattice parameters than PBE
these GGAs are „**soft**“

- „**hard**“ GGAs (RPBE) are much better for atomization energies of molecules

- PBE is a good compromise for both quantities

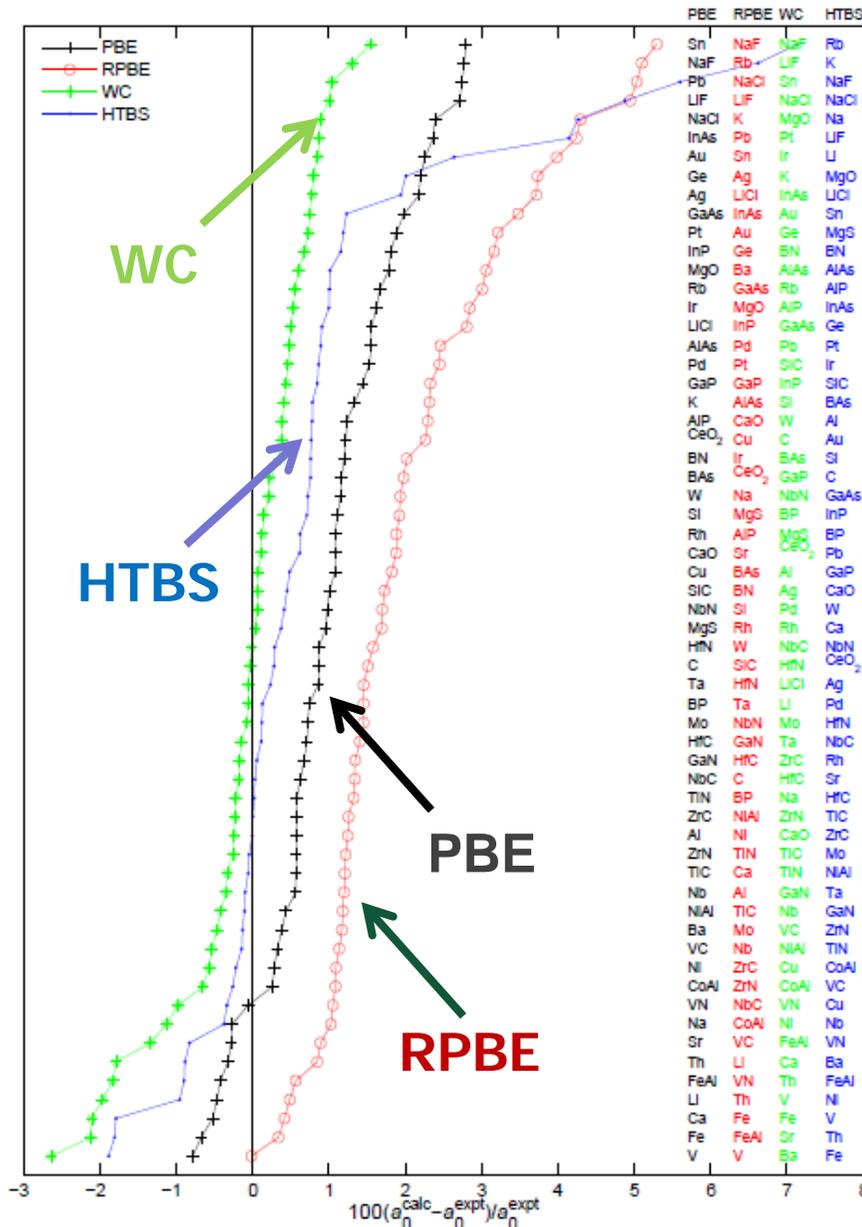
- HTBS might be better (except alkali atoms)

- *Haas, Tran, Blaha, Schwarz, Phys.Rev. B83, 205117 (2011)*





Performance of GGAs in solids and molecules



PBE	RPBE	WC	HTBS
Sn	NaF	NaF	Rb
NaF	Rb	LiF	K
Pb	NaCl	Sn	NaF
LiF	LiF	NaCl	NaCl
NaCl	K	MgO	Na
InAs	Pb	Pt	LiF
Au	Sn	Ir	Li
Ge	Ag	K	MgO
Ag	LiCl	InAs	LiCl
GaAs	InAs	Au	Sn
Pt	Au	Ge	MgS
InP	Ge	BN	BN
MgO	Ba	AlAs	AlAs
Rb	GaAs	Rb	AlP
Ir	MgO	AlP	InAs
LiCl	InP	GaAs	Ge
AlAs	Pd	Pb	Pt
Pd	Pt	SiC	Ir
GaP	GaP	InP	SiC
K	AlAs	Si	Bas
AlP	CaO	W	Al
CeO ₂	Cu	C	Au
BN	Ir	Bas	Si
Bas	Na	NbN	GaAs
W	MgS	BP	InP
Si	Rh	MgS	BP
Rh	AlP	MgS	BP
CaO	Sr	Pb	Pb
Cu	Bas	Al	GaP
SiC	BN	Ag	CaO
NbN	Si	Pd	W
MgS	Rh	Rh	Ca
HfN	W	NbC	NbN
C	SiC	HfN	CeO ₂
Ta	HfN	LiCl	Ag
BP	Ta	Li	Pd
Mo	NbN	Mo	HfN
HfC	GaN	Ta	NbC
GaN	HfC	ZrC	Rh
NbC	C	HfC	Sr
TiN	BP	Na	HfC
ZrC	NiAl	ZrN	TiC
Al	Ni	CaO	ZrC
ZrN	TiN	TiC	Mo
TiC	TiC	TiN	NiAl
Nb	Al	GaN	Ta
NiAl	TiC	Nb	GaN
Ba	Mo	VC	ZrN
VC	Nb	NiAl	TiN
Ni	ZrC	Cu	CoAl
CoAl	ZrN	CoAl	VC
VN	NbC	VN	Cu
Na	CoAl	Ni	Nb
Sr	VC	FeAl	VN
Th	Li	Ca	Ba
FeAl	VN	Th	FeAl
Li	Th	V	Ni
Ca	Fe	Fe	V
Fe	FeAl	Sr	Th
V	V	Ba	Fe

TABLE III: Atomization energy (in kcal/mol) for the molecules of the AE6 test set. See Table I for the definition of me, mae, mre, and mare.

Molecule	RPBE	PBE	WC	AM05	PBEsol	HTBS	Expt.
SiH ₄	308.3	313.0	316.9	329.7	323.4	312.1	322.4
SiO	186.1	195.6	202.1	205.1	204.6	190.5	192.1
S ₂	107.7	114.7	121.1	122.8	123.2	114.4	101.7
C ₃ H ₄	694.8	720.0	735.4	751.1	748.3	701.5	704.8
C ₂ H ₂ O ₂	633.0	663.3	682.9	697.0	695.5	643.9	633.4
C ₄ H ₈	1128.1	1168.5	1195.8	1224.1	1218.9	1144.7	1149.0
me	-7.5	12.0	25.1	37.7	35.1	0.6	
mae	9.6	15.1	27.0	37.7	35.1	7.1	
mre	-0.8	3.4	6.5	8.8	8.3	1.6	
mare	2.8	4.4	7.0	8.8	8.3	3.2	



Trends of GGAs:



■ Structural properties

- *on average GGAs are better than LDA, but*
 - LDA still best for 5d-series (Pt, Au). PBE too large !
 - PBE best for 3d series (Fe, Ni, ..). LDA too small !
 - WC, PBEsol, HTBS best **compromise** for all elements
 - van der Waals: LDA overbinds, GGAs underbind (sometimes non-bonding !)

■ Cohesive properties:

- *(hard) GGAs much better than LDA*

■ Electronic structure:

- *LDA and GGAs very similar*
- *band gaps underestimated by 50 % (→ TB-mBJ)*

■ Strongly correlated electrons (3d, 4f)

- *often LDA and GGA give **qualitatively wrong** results: **metal** instead of **insulator**, too small magnetic moments or even **non-magnetic** instead of AFM cuprates, no (too small) structural distortions, **orbital order**,*



meta-GGAs



- Perdew, Kurth, Zupan, Blaha (1999):

$$E_{xc}^{m-GGA} \propto \int \rho(r) F[\rho(r), \nabla \rho(r), \nabla^2 \rho(r), \tau(r)] dr$$

- use ***laplacian*** of ρ , or ***kinetic energy density*** $\tau(r) = \frac{1}{2} \sum_i |\nabla \psi_i(r)|^2$
- *analytic form for V_{xc} not possible ($V_{xc} = dE_{xc}/d\rho$), SCF very difficult*
- best meta-GGAs today describe structural parameters like WC or PBEsol, but have better atomization energies:
 - ***revTPSS*** by Perdew et al. (2009)



Band gaps by a semi-local potential



- Becke-Johnson potential (J. Chem. Phys. 124, 221101 (2006))
 - *local* potential designed to reproduce *non-local* OEP potentials in *atoms*
- modified Becke-Johnson potential

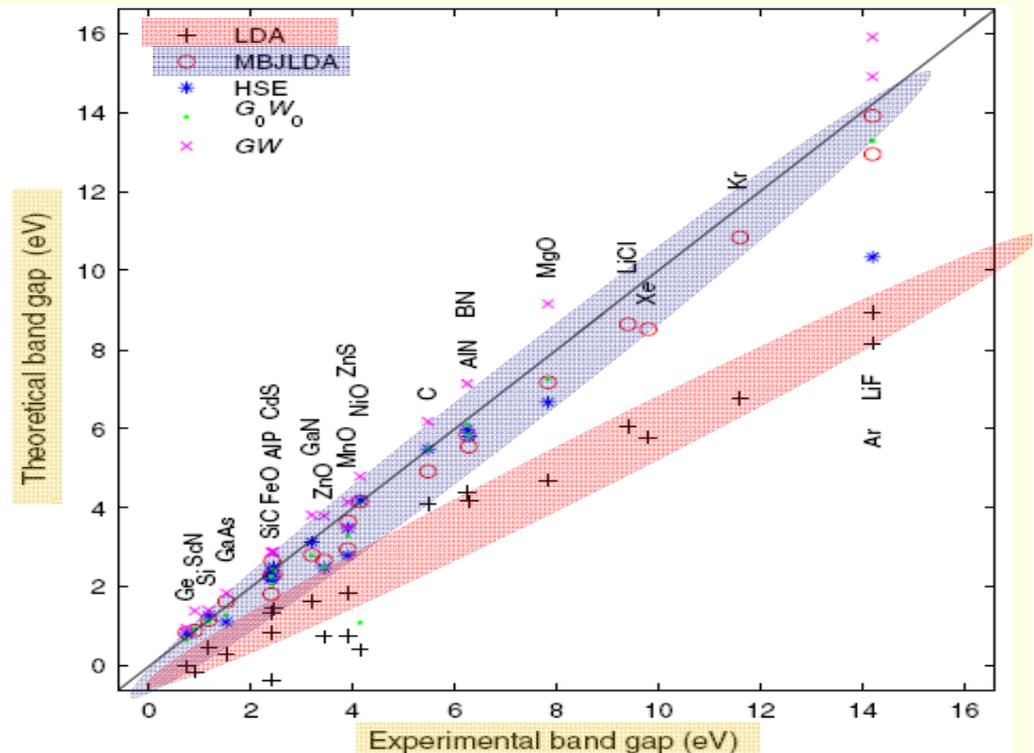
$$v_{x,\sigma}^{\text{MBJ}}(\mathbf{r}) = c v_{x,\sigma}^{\text{BR}}(\mathbf{r}) + (3c - 2) \frac{1}{\pi} \sqrt{\frac{5}{12}} \sqrt{\frac{2t_{\sigma}(\mathbf{r})}{\rho_{\sigma}(\mathbf{r})}},$$

F. Tran P. Blaha
PRL **102**, 226401 (2009)

$$c = \alpha + \beta \left(\frac{1}{V_{\text{cell}}} \int_{\text{cell}} \frac{|\nabla \rho(\mathbf{r}')|}{\rho(\mathbf{r}')} d^3 r' \right)^{1/2}$$

c depends on the density properties of a material

- + gaps of „GW“ quality
- + good for correlated TM-oxides
- NO energy (only V)





How to run a calculation with the MBJ potential?



1. Prepare the input files for an usual PBE (or LDA) calculation
2. run scf cycle (+ structure optimization,)
3. `save_lapw case_pbe`
3. `init_mbj_lapw` (phase 1, creates `case.inm_vresp`, sets R2V in `case.in0`)
4. `run(sp)_lapw -i 1` (Run one PBE cycle to create `case.vresp` and `case.r2v`)
5. `rm *.broyd*`
6. `init_mbj_lapw` (phase 2)
 - sets `indxc=28` (MBJ) in `case.in0` and generates `case.in0_grr` with `indxc=50`;
 - select mBJ-parameters, see Koller et al. PRB 85, 155109 (2012)
7. `run(sp)_lapw -i 80` (mBJ calculations need more cycles than PBE)



semilocal functionals available in WIEN2k



Functional	Authors	Year	indxc (case.in0)
LDA	Dirac, Slater, etc.	1930 - ...	5
GGA:			
PBE	Perdew et al	1996	13
WC	Wu, Cohen	2005	11
PBEsol	Perdew et al.	2007	19
HTBS	Haas et al.	2011	46
TB-mBJ*	Tran, Blaha	2009	28, 50
meta-GGA:			
revTPSS**	Perdew et al.	2009	29

* only a potential ($E_{xc} = \text{LDA}$)

** only E_{xc} ($V_{xc} = \text{PBE}$)



more “non-local” functionals (“beyond DFT”)



- Self-Interaction correction (Perdew, Zunger 1981; Svane+ Temmermann)
 - *vanishes for Bloch-states, select “localized states” by hand*
- **LDA+U** \longrightarrow DMFT (dynamical mean field theory)
 - *approximate HF for selected “highly-correlated” electrons (3d, 4f, 5f)*
 - *empirical parameter U*
- Optimized Exact exchange (OEP, similar to HF, but with a **local** DFT based potential, expensive, numerically problematic, correlation ??)
- Hartree-Fock
 - *neglects correlation, which for most solids is essential*
- **Hybrid functionals** (mixing of DFT+ HF)
- GW method: calculate the quasiparticle self energy Σ

$$\Sigma(r, r', \omega) = \frac{i}{2\pi} \int d\omega' G(r, r', \omega - \omega') W(r, r', \omega)$$
$$\epsilon_{nk}^{QP} = \epsilon_{nk}^{LDA} - \langle nk | \Sigma(\epsilon_{nk}^{QP}) - V_{xc}^{LDA} | nk \rangle$$

available for WIEN2k
M. Scheffler et al.
(very expensive)



Hartree-Fock



$$E_{HF} = \int \phi_i^*(\mathbf{r}) \left(-\frac{1}{2} \sum_i^N \nabla_i^2 + V_{ext} \right) \phi_i(\mathbf{r}) d\mathbf{r} \\ + \frac{1}{2} \sum_{i,j}^N \int \frac{\phi_i^*(\mathbf{r}_1) \phi_i(\mathbf{r}_1) \phi_j^*(\mathbf{r}_2) \phi_j(\mathbf{r}_2)}{|\mathbf{r}_i - \mathbf{r}_j|} d\mathbf{r}_1 d\mathbf{r}_2 \\ - \frac{1}{2} \sum_{i,j}^N \int \frac{\phi_i^*(\mathbf{r}_1) \phi_j(\mathbf{r}_1) \phi_i(\mathbf{r}_2) \phi_j^*(\mathbf{r}_2)}{|\mathbf{r}_i - \mathbf{r}_j|} d\mathbf{r}_1 d\mathbf{r}_2$$

kinetic E + external V

classic Coulomb energy
of electrons

exchange energy

- This leads to a „**non-local**“ (orbital dependent) potential.
- It treats „**exchange**“ (e⁻-e⁻ interaction between e⁻ of same spin, Pauli-principle, Slater det.) **exactly**, but neglects „**correlation**“ completely.
- Correlation can be treated by perturbation methods (MP2), „coupled cluster“ (CCSD), or CI methods, using „many“ Slater determinants.



Hybrid functionals



General strategy: **Mixing exact-exchange (i.e. Hartree-Fock) and local-density energies**, as suggested by the adiabatic connection formula

$$E^{xc}[n] = \int_0^1 U_\lambda^{xc}[n] d\lambda \sim \frac{1}{2} U_0^{xc}[n] + \frac{1}{2} U_1^{xc}[n] \quad (41)$$

$U_0^{xc}[n]$... nonlocal exchange energy of Kohn-Sham orbitals

$U_1^{xc}[n]$... potential energy for exchange and correlation

Example: B3LYP functional

$$E^{xc}[n] = (1 - a)E_{LSDA}^x + aE_{exact}^x + bE_{B88}^x + cE_{LYP}^c + (1 - c)E_{VWN}^c \quad (42)$$

where E_{B88}^x stand for the exchange part of the Becke88 GGA functional, E_{LYP}^c for the correlation part of the Lee-Young-Parr local and GGA functional, and E_{VWN}^c for the local Vosko-Wilk-Nusair correlation functional. a , b , and c are adjustable parameters.

$$\text{PBE0: } E_{xc}^{\text{PBE0}}[\rho] = E_{xc}^{\text{PBE}}[\rho] + \alpha (E_x^{\text{HF}}[\Phi] - E_x^{\text{PBE}}[\rho]) \quad \alpha=0.25$$



screened full-hybrid functionals

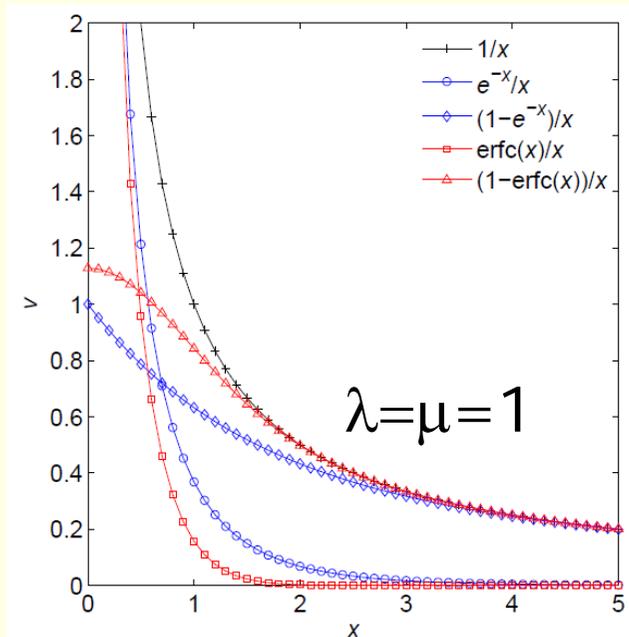


$$E_{xc} = E_{xc}^{SL} + \alpha_x (E_x^{SR-HF} - E_x^{SR-SL})$$

- $1/r$ is decomposed into a short-range and long-range component using an **exponential** (or the error function)

$$\frac{1}{|\mathbf{r} - \mathbf{r}'|} = \underbrace{\frac{e^{-\lambda|\mathbf{r}-\mathbf{r}'|}}{|\mathbf{r} - \mathbf{r}'|}}_{\text{SR}} + \underbrace{\frac{1 - e^{-\lambda|\mathbf{r}-\mathbf{r}'|}}{|\mathbf{r} - \mathbf{r}'|}}_{\text{LR}}$$

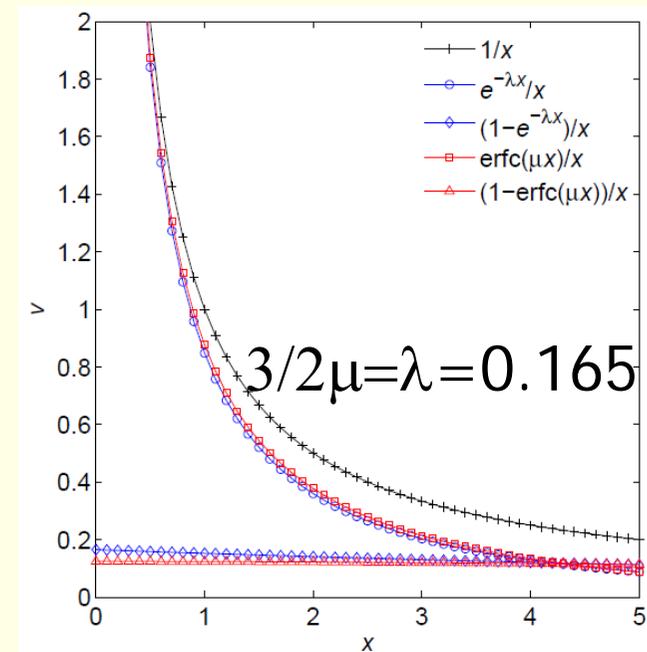
$$(1 - \text{erfc}(\mu x)) / x$$



HSE06 functional:
 $\mu = 0.11 \text{ bohr}^{-1}$

exponential with
 $\lambda = 3/2 \mu$ is very
 similar

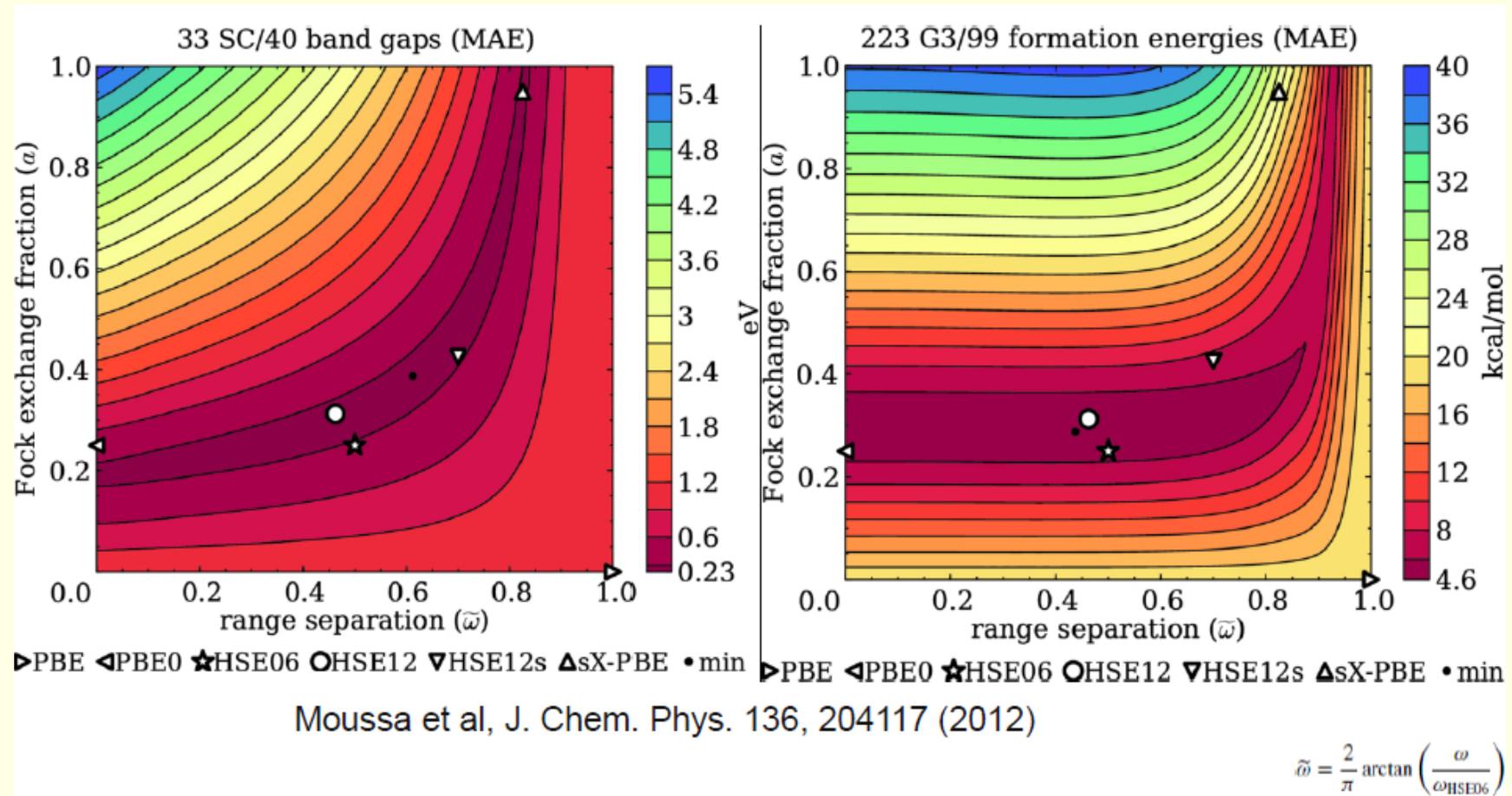
YS-PBE0: Tran, Blaha,
 PRB **83**, 235118 (2011)



screened functionals improve k-mesh convergence dramatically



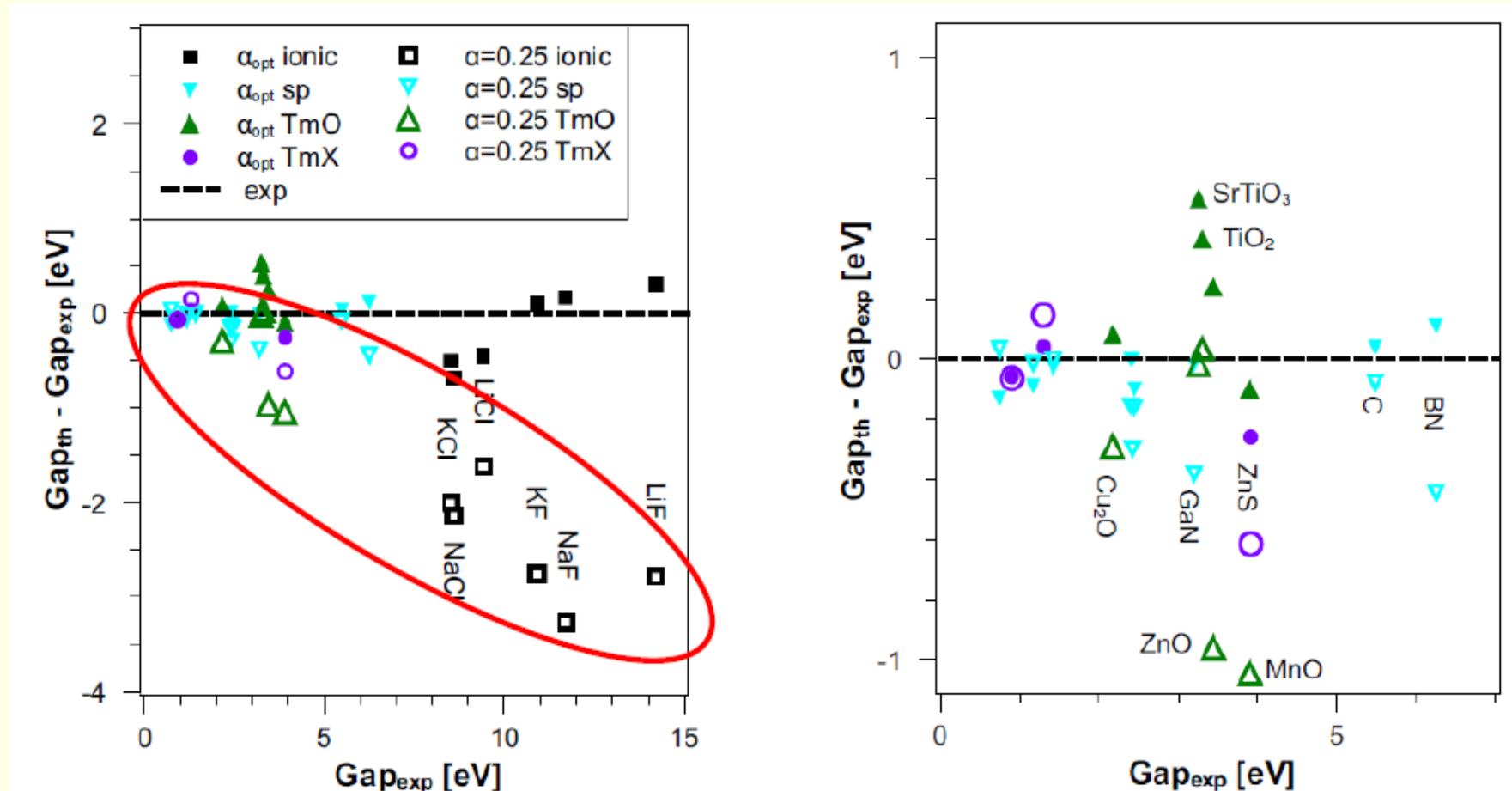
2 parameters: mixing α and screening ω



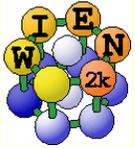
- gaps: strong correlation between α and ω
- formation energies: $\omega < 0.7$ has little influence



band gaps of YS-PBE0 with $\alpha=0.25$



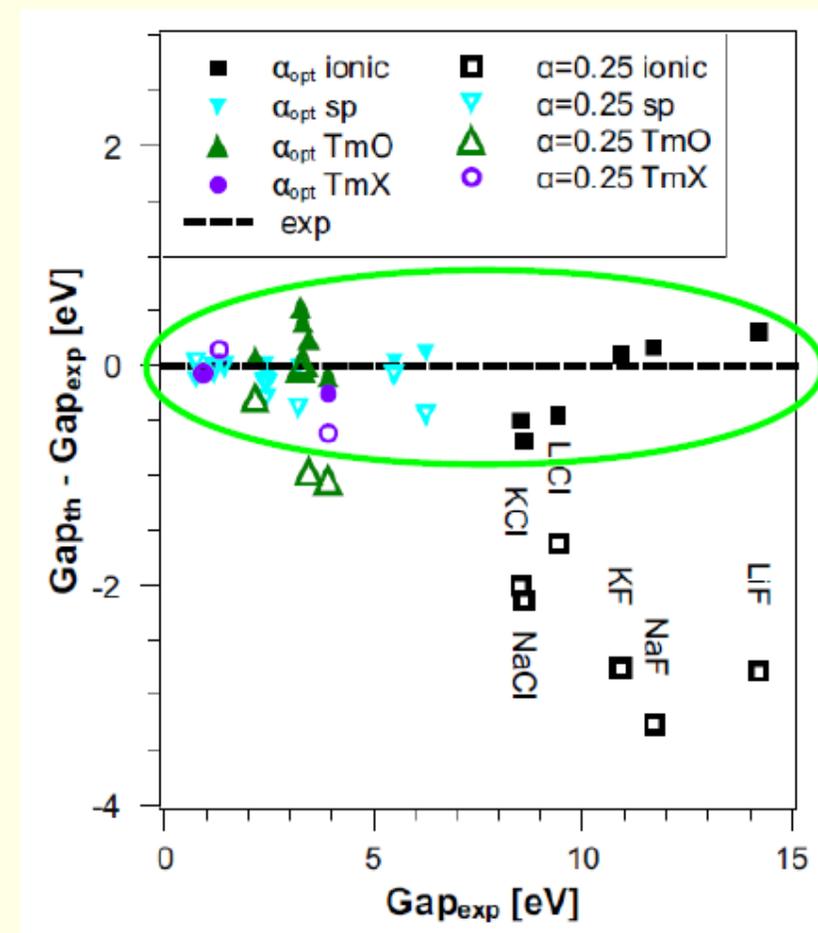
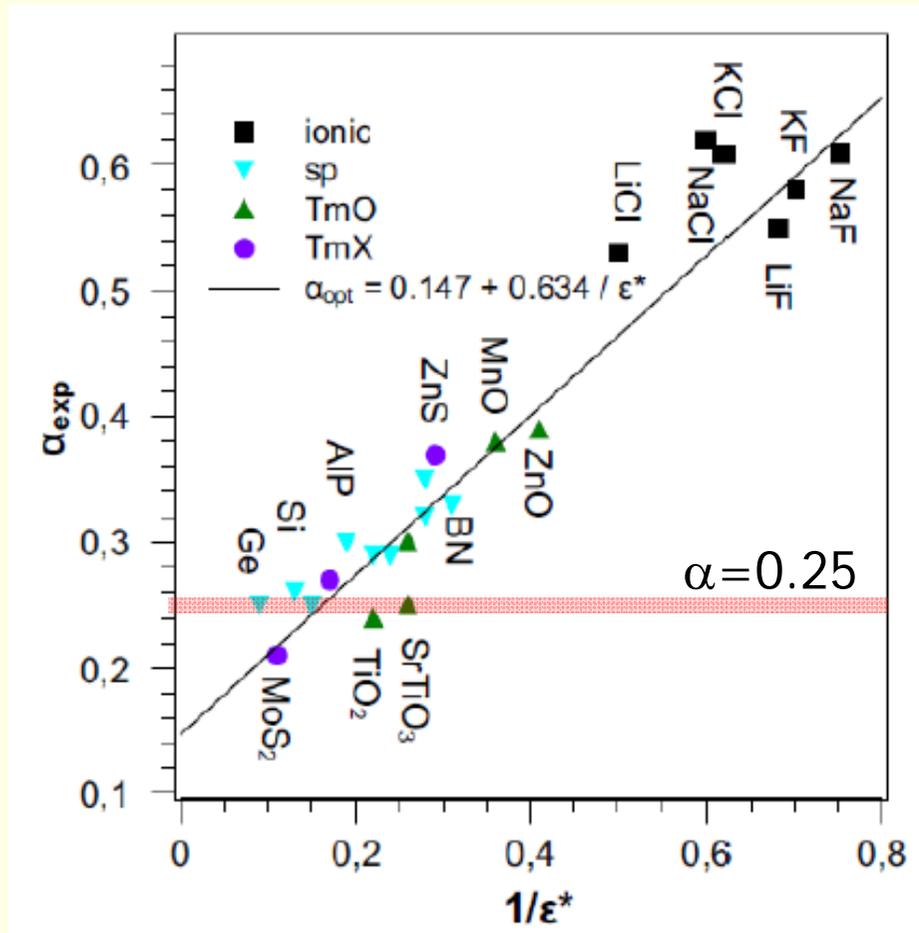
- strong improvement over PBE, but
- gaps of “insulators” still strongly underestimated



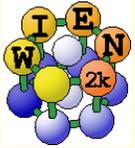
adapt α for each individual system



- optimal α found by fit to exp. as function of $1/\epsilon_0$ (dielectric constant)



yields much better gaps



speed-up by “diagonal-only” approximation



- › Hybrid DFT calculations are done in 2 parts
- › the eigenfunctions of the semilocal potential are used as basis functions for the operator $\alpha (\hat{v}_{x\sigma}^{\text{SR-HF}} - v_{x\sigma}^{\text{SR-SL}})$
- › the non-diagonal matrix elements of this operator are much smaller than the diagonal ones, in the diagonal approximation they are put to 0
- › this saves the trouble of evaluating the non-diagonal matrix elements
- › furthermore the eigenfunctions don't change so that selfconsistence is reached after one iteration

eigenfunctions of the semilocal potential $\varphi_1(\mathbf{r}), \dots, \varphi_N(\mathbf{r})$

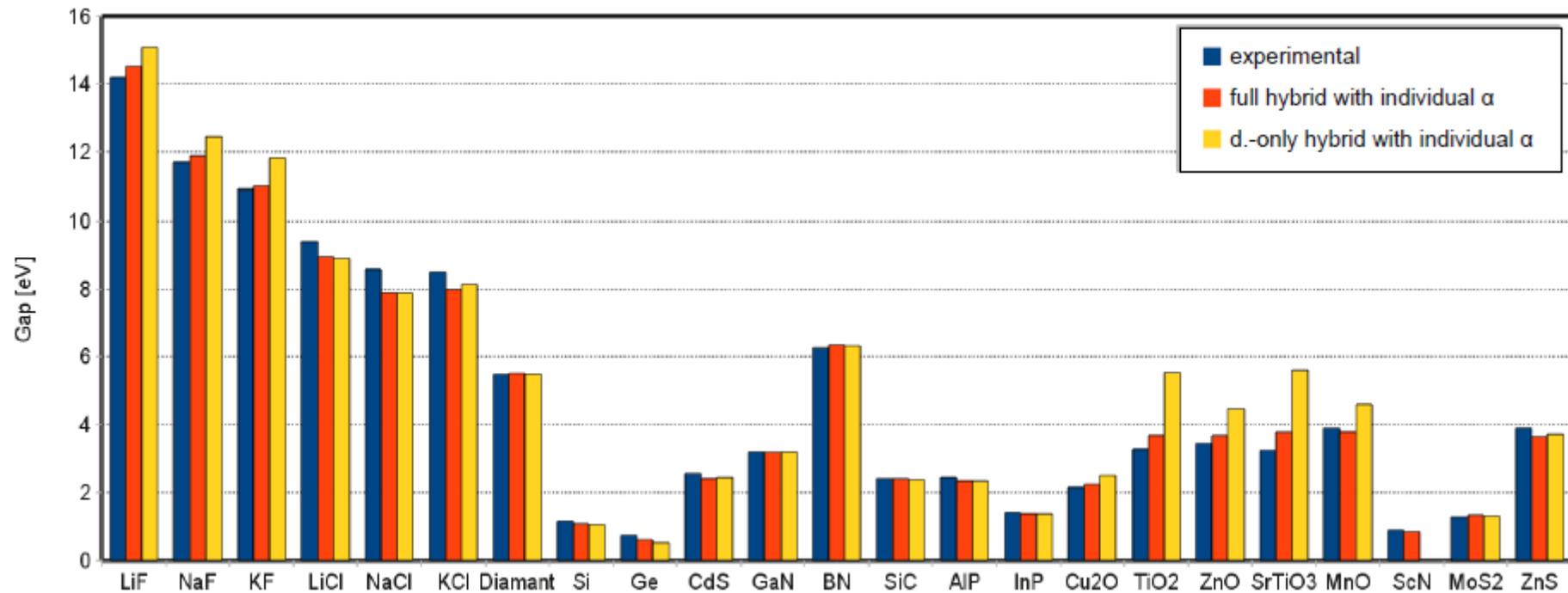
$$\hat{O} = \alpha (\hat{v}_{x\sigma}^{\text{SR-HF}} - v_{x\sigma}^{\text{SR-SL}})$$

$$\begin{pmatrix} \langle \varphi_1 | \hat{O} | \varphi_1 \rangle & \langle \varphi_1 | \hat{O} | \varphi_2 \rangle & \dots & \langle \varphi_1 | \hat{O} | \varphi_N \rangle \\ \langle \varphi_2 | \hat{O} | \varphi_1 \rangle & \langle \varphi_2 | \hat{O} | \varphi_2 \rangle & \dots & \langle \varphi_2 | \hat{O} | \varphi_N \rangle \\ \vdots & \vdots & \ddots & \vdots \\ \langle \varphi_N | \hat{O} | \varphi_1 \rangle & \langle \varphi_N | \hat{O} | \varphi_2 \rangle & \dots & \langle \varphi_N | \hat{O} | \varphi_N \rangle \end{pmatrix}$$

0



band gap comparison



- standard full hybrids (fixed α) work well for semiconductors
- $\alpha(1/\epsilon_0)$ improves the results significantly
- “diagonal-only” approximation works in most cases (speed-up)



hybrid functionals in WIEN2k



- expensive (10-100 times more than LDA)
- k-point and mpi-version (useful already for medium sized cases)
- for bigger cases use a „reduced“ k-mesh for the potential (must be compatible with full mesh (like 4x4x4 and 2x2x2))
- consider non-scf calculations (for DOS, bands) or even the „diagonal“ approximation $PBE0_0$ (Tran, Physics Letters A 376 (2012) 879)
- for **setup** follow the UG 4.5.8; `run_lapw -hf`
- works well for semiconductors and TM-oxides
 - *mixing parameter α (like the U in LDA+U)*
 - α should be bigger for large gap insulators
 - α should be VERY small for (magn.) metals
 - hybrids localize TM-d **and** O-p states
- structural parameters depend mainly on the underlying GGA, but are always a bit smaller than plain GGA.

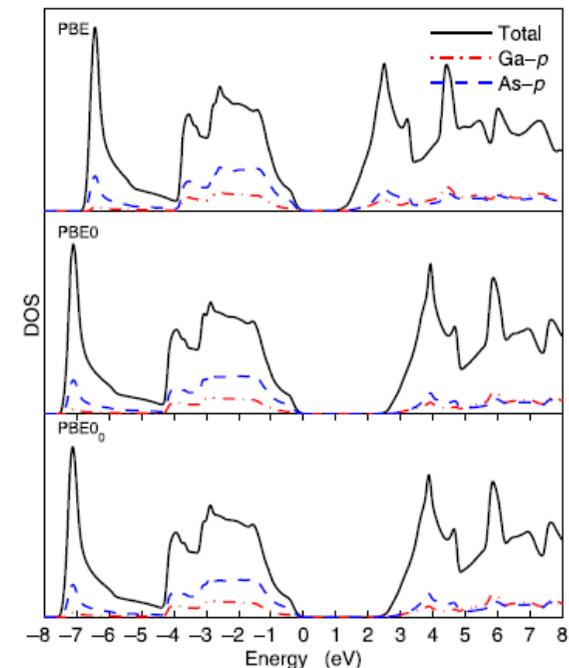


Fig. 1. (Color online.) Density of states of GaAs calculated with the PBE, PBE0, and PBE0₀ methods. The Fermi energy is set at zero.



onsite-hybrid-DFT for “correlated electrons”



- select certain electrons within an atomic sphere
 - mainly 3d or 4f states, since only those valence electrons are sufficiently localized (and require stronger exchange potentials)
 - same spirit and speed as LDA+U (with parameter α instead of U)

$$E_{xc}^{\text{PBE0}}[\rho] = E_{xc}^{\text{PBE}}[\rho] + \alpha (E_x^{\text{HF}}[\Phi_{\text{sel}}] - E_x^{\text{PBE}}[\rho_{\text{sel}}])$$

- `cp $WIENROOT/SRC_templates/template.ineece case.ineece`

```
-9.0 2      emin natom
 1 1 2      iatom nlorb lorb
 2 1 2      iatom nlorb lorb
HYBR       HYBR / EECE mode
0.25      amount of exact exchange
```

- `runsp -eece`

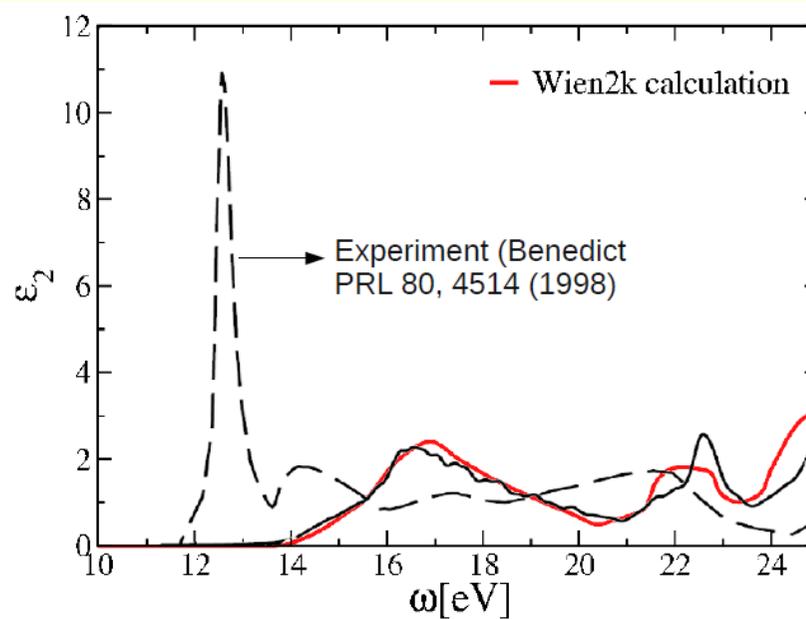
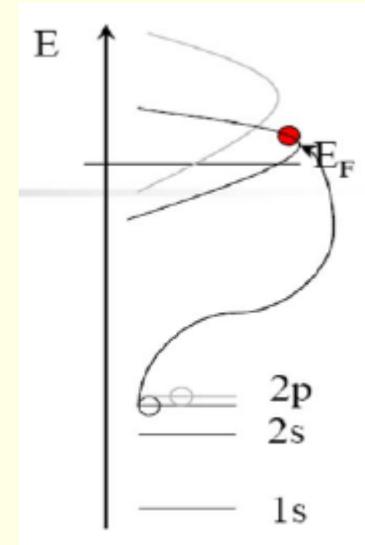
(Tran et al. PRB 74, 155108 (2006))



Failure of the independent particle approximation



- expect large **excitonic** effects when (localized) electrons are excited into the conduction bands (optics, XAS, EELS)
- the remaining hole and the excited electron may interact strongly with each other



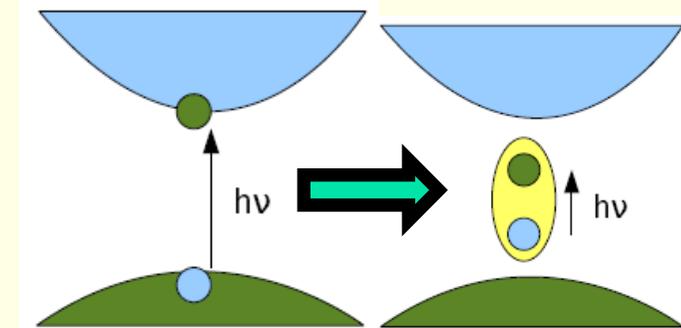
LiF absorption spectra



fully relativistic electron-hole interaction (BSE)



- *Bethe-Salpeter-equation: $L(12;1'2')$*
- *solving a 2-particle ($e^- - h$) equation of large dimension ($N_v N_c N_k \sim 100000$)*



$$\sum_{v'c'k'} (H_{v'c'k',vck}^{eh}) A_{v'c'k'}^\lambda = E^\lambda A_{vck}^\lambda$$

$$H^{eh} = H^{diag} + H^{dir} + 2H^x$$

$$H^{diag} = (E_{v,k} - E_{c,k}) \delta_{cc'} \delta_{vv'} \delta_{kk'}$$

eigenvalue difference between hole (c) and electron(v) state

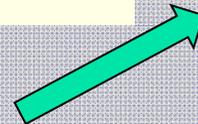
$$H_{vckv'c'k'}^{dir} = - \int d^3r d^3r' \Psi_{vk}(r) \Psi_{ck'}^*(r') W(r,r') \Psi_{v'k'}^*(r) \Psi_{c'k'}(r')$$

attractive screened static Coulomb interaction W ; $W \sim \epsilon^{-1}$

$$H_{vckv'c'k'}^x = \int d^3r d^3r' \Psi_{vk}(r) \Psi_{ck'}^*(r) \bar{v}(r,r') \Psi_{v'k'}^*(r') \Psi_{c'k'}(r')$$

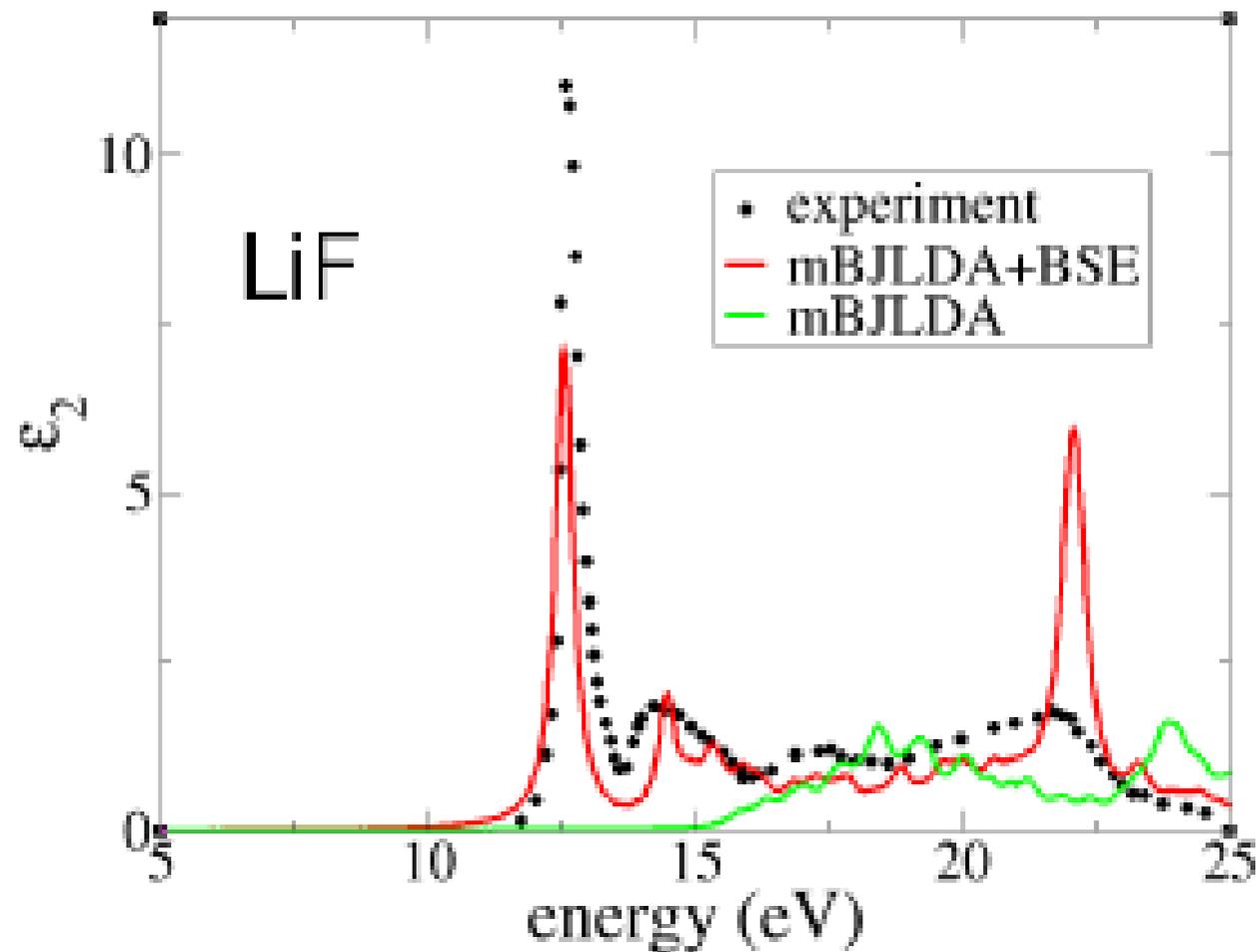
e-h exchange with bare Coulomb potential v

single particle APW (WIEN2k)





Excitons in LiF



- BSE calculations are very expensive
 - *(code available on request, needs hundreds of cores ... + memory)*
R. Laskowski, P. Blaha, Phys. Rev. B, 81, 075418 (2010)



Ca-L₂₃ edge in CaF₂ (Ca-2p → Ca-3d)



■ experiment



■ "ground-state" DOS

