When Many-Body Matters: The CO Adsorption Puzzle and Optical Properties of Color Centers

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KITP: From Basic Concepts to Real Materials

Deutsche
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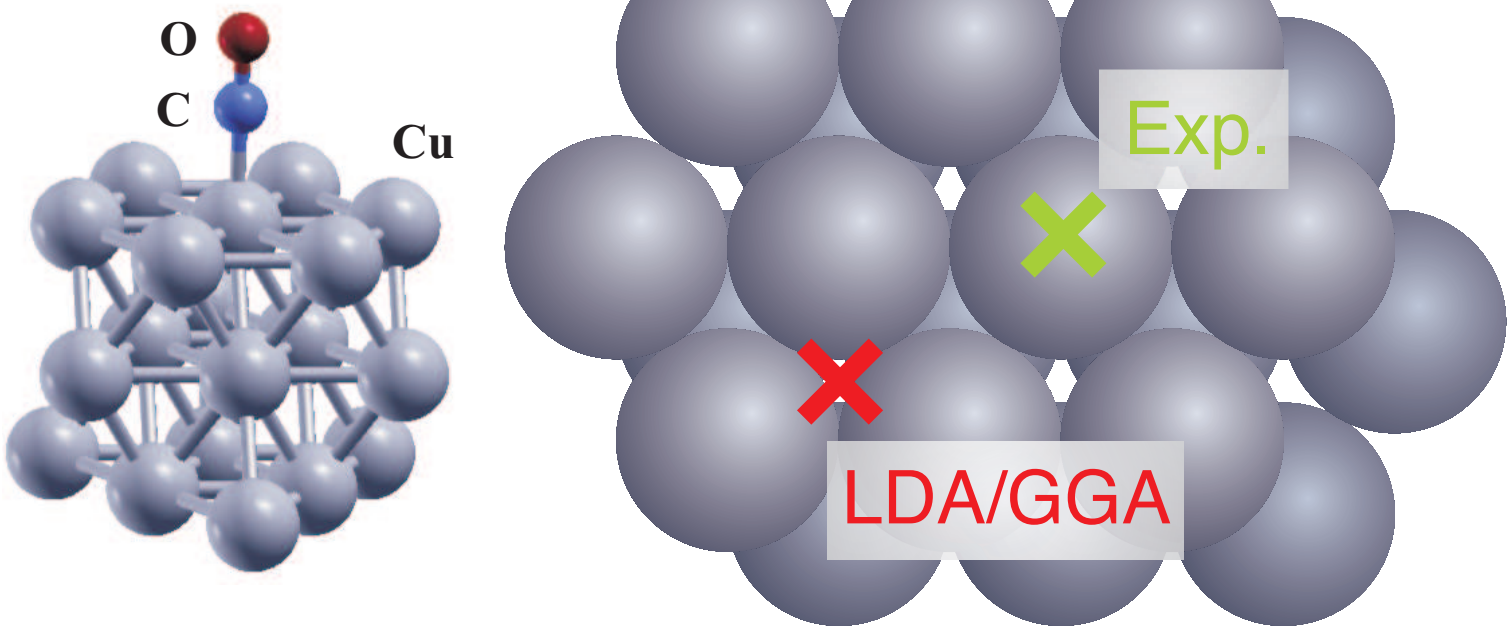
CO adsorption puzzle



- LDA/GGA predict wrong adsorption site for CO on Cu(111), Rh(111), Pt(111)
- error as large as 0.5 eV for CO on Cu(111)

e.g. Feibelman *et al.* J. Phys. Chem. B **105**, 4018 (2001)

F center – Oxygen vacancy in MgO

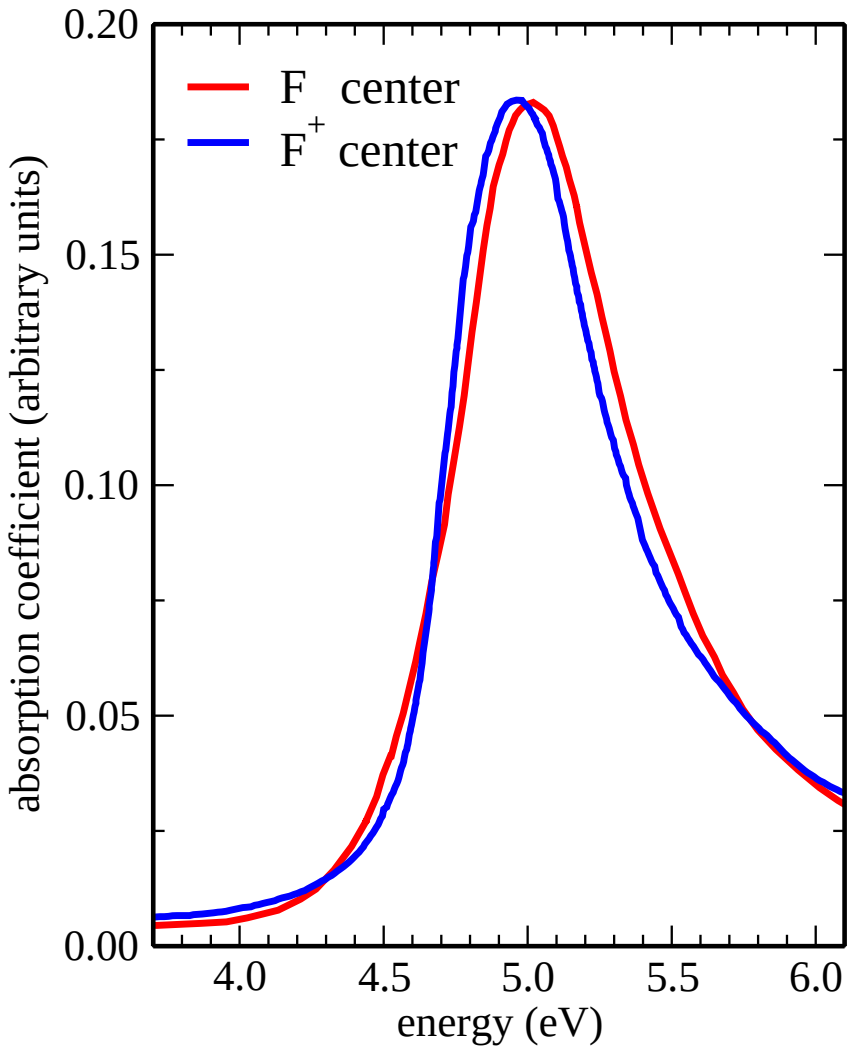
Oxygen vacancy in MgO:

- also called F or color center
- probably *the* classic F center

F and F^+ absorption:

- studied for more than 5 decades
- nearly identical
- not reproduced by theory yet
- not even multi reference CI

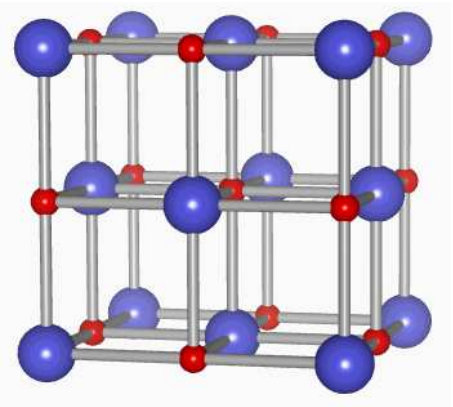
  (Illas & Pacchioni JCP **108**, 7835 (1998))



Kappers *et al.* PRB 1, 4151 (1970)

MgO – why we like it

- features
  - wide band gap insulator
  - simple crystal structure (rocksalt)
  - light elements
  - but: electron-phonon coupling is strong
- applications
  - medical
    - ★ relief for heartburn and sore stomach
    - ★ antacid and magnesium supplement
    - ★ short-term laxative
  - libraries
    - ★ book preservation (moisture reduction)
  - building construction
    - ★ principal ingredient for fireproofing



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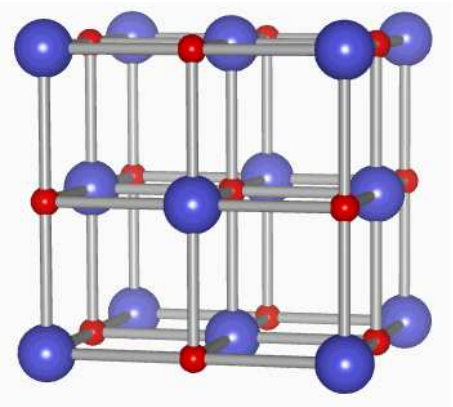
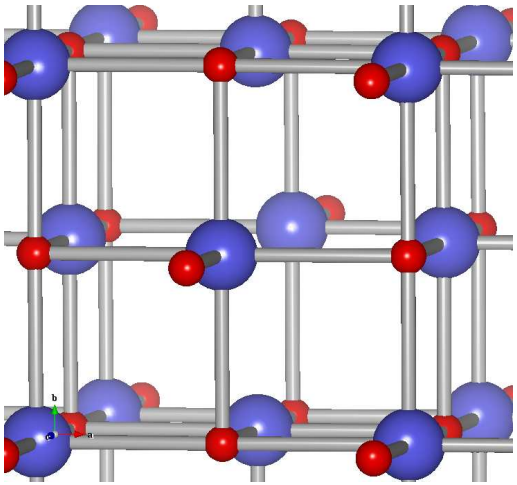
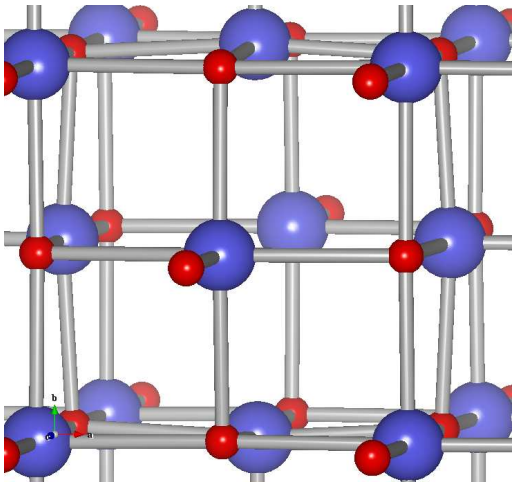


- applications
  - catalysis
    - ★ substrate for catalytically active metal clusters
    - ★ catalyst when Li doped?
  - electronics and microelectronics
    - ★ insulator in electrical cables
    - ★ alloy component in (Mg,Zn,Cd)O
  - spintronics
    - ★ tunnel barrier
- let the many-body machinery loose

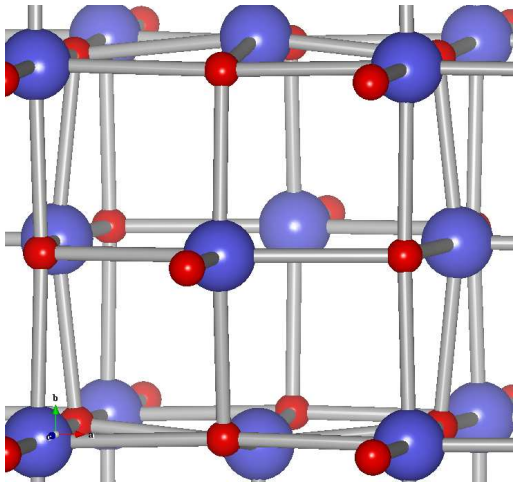
The Oxygen Vacancy in MgO – Nomenclature



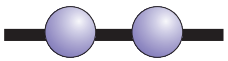
F-center



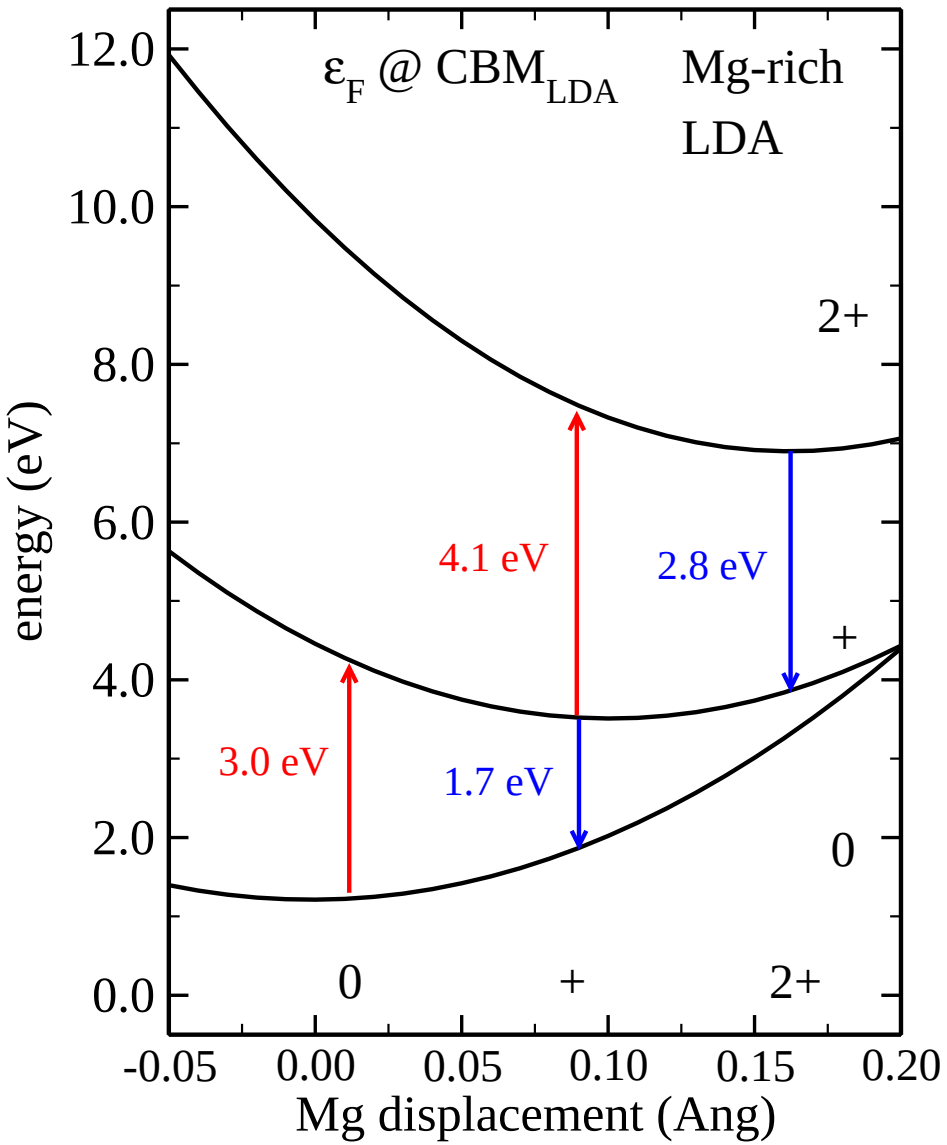
F^{+}-center

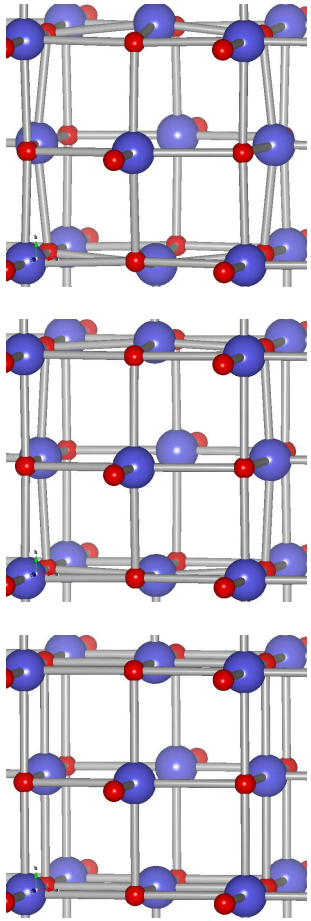


F^{2+}-center



The Oxygen Vacancy – LDA Configuration Diagram





Absorption:

Experiment

(PRB **42**, 1410 (1990))

F : 5.00

F^+ : 4.95

DFT-LDA

F : 3.00

F^+ : 4.10

DFT-HSE (α=0.35)

F : 4.82

F^+ : 5.71

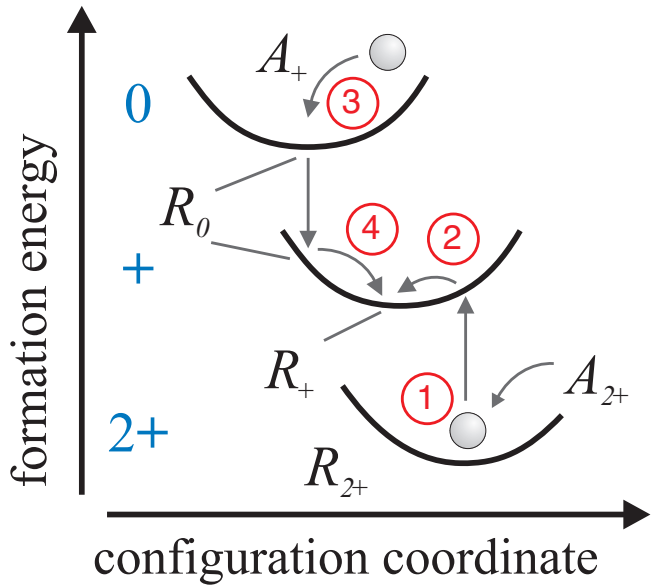
G_0W_0 correction – formation energy decomposition

positive configuration:

$$
\begin{aligned}
E_D^f(+,\epsilon_F) =& E(+,\mathbf{R}_+^D) - E_{ref} + \epsilon_F \\
=& E(+,\mathbf{R}_+^D) - E(+,\mathbf{R}_{2+}^{\text{tet}}) + E(+,\mathbf{R}_{2+}^{\text{tet}}) - E(2+,\mathbf{R}_{2+}^{\text{tet}}) + E(2+,\mathbf{R}_{2+}^{\text{tet}}) - E_{ref} + \epsilon_F \\
=& \underbrace{E(+,\mathbf{R}_+^D) - E(+,\mathbf{R}_{2+}^{\text{tet}})}_{\Delta_{2+}^+} + \underbrace{E(+,\mathbf{R}_{2+}^{\text{tet}}) - E(2+,\mathbf{R}_{2+}^{\text{tet}})}_{A_{2+}} + \underbrace{E(2+,\mathbf{R}_{2+}^{\text{tet}}) - E_{ref}}_{E_{\text{tet}}^f(2+)} + \epsilon_F \\
=& \underbrace{\Delta_{2+}^+}_{LDA} + \underbrace{A_{2+}}_{G_0W_0} + \underbrace{E_{\text{tet}}^f(2+,\epsilon_F=0)}_{LDA} + \epsilon_F
\end{aligned}
$$

neutral configuration:

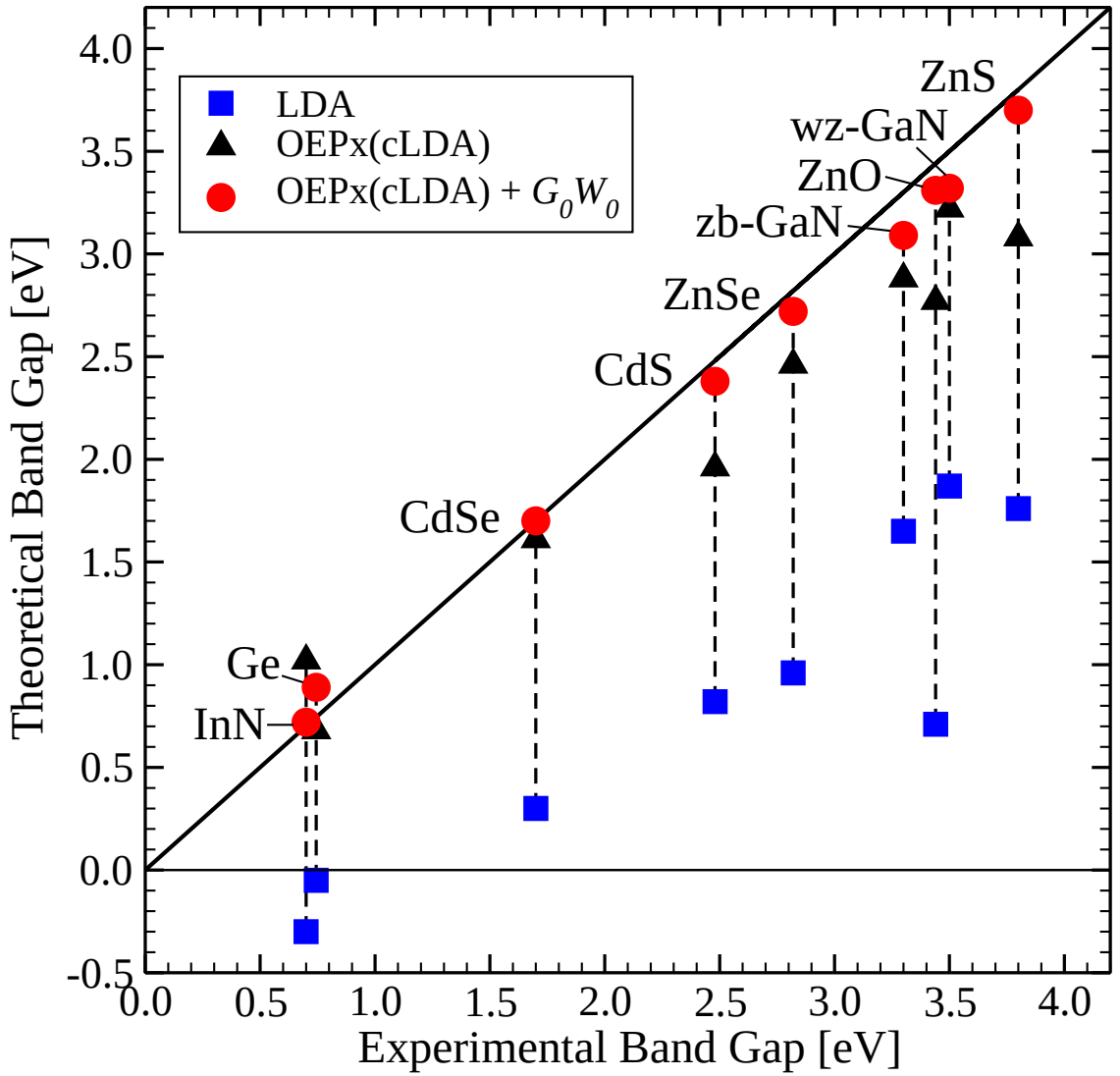
$$
E_D^f(0,\epsilon_F) = \underbrace{\Delta_+^0 + \Delta_{2+}^+}_{LDA} + \underbrace{A_+ + A_{2+}}_{G_0W_0} + \underbrace{E_{\text{tet}}^f(2+,\epsilon_F=0)}_{LDA}
$$



Hedström *et al* PRL **97**, 226401 (2006)

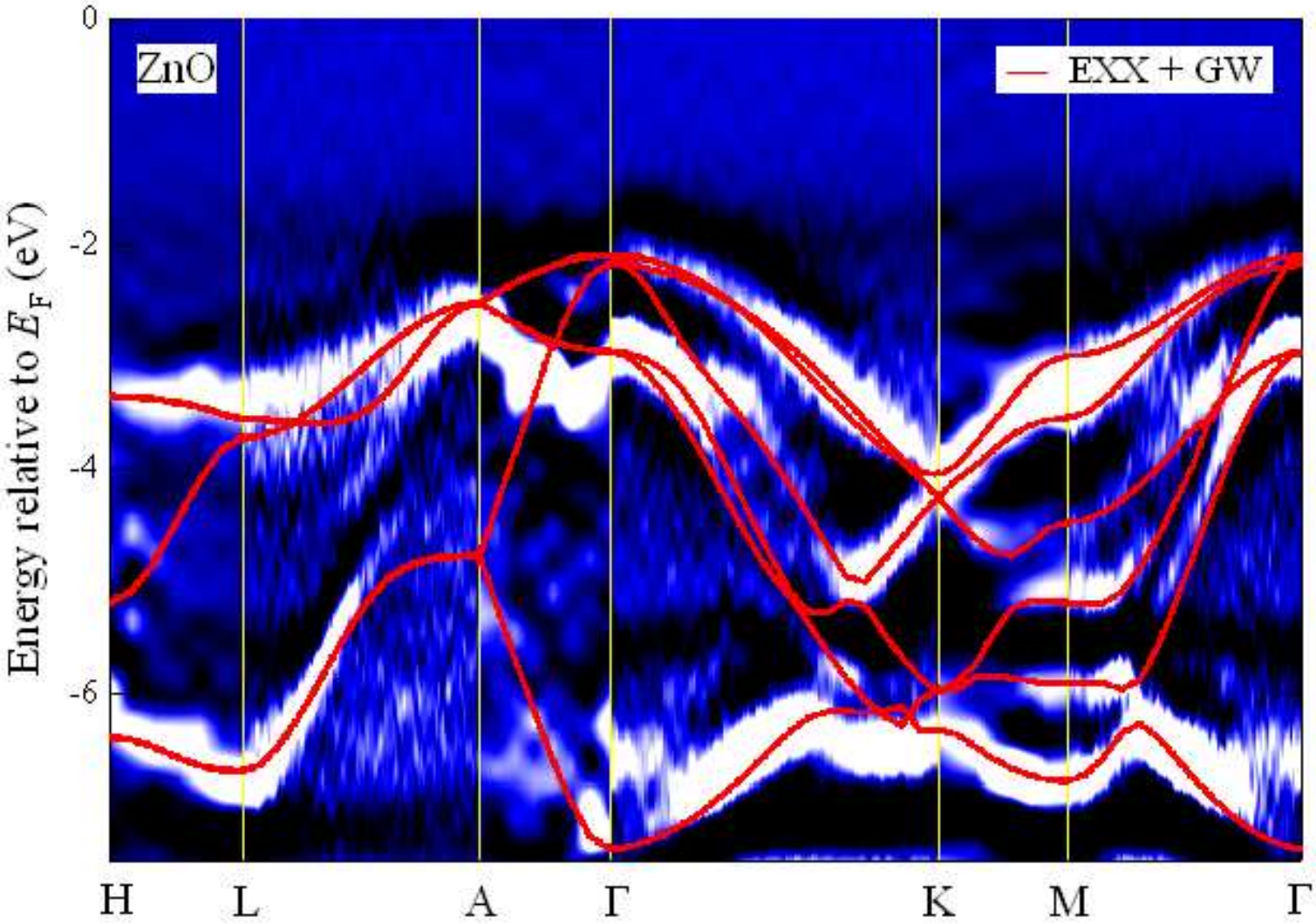
Rinke *et al* PRL **102**, 026402 (2009)

G_0W_0 Band Gaps



Rinke *et al. New J. Phys.* **7**, 126 (2005), phys. stat. sol. (b) **245**, 929 (2008)

ARPES – GW: wurtzite ZnO



ARPES data courtesy of Masaki Kobayashi, PhD dissertation

Band gap of MgO

What is the band gap of MgO?

Band gap of MgO

What is the band gap of MgO?

7.8 eV

(Whited and Walker, PRL **22**, 1428 (1969))

But what about electron-phonon coupling?

Band gap of MgO

electron-phonon self-energy in Migdal approximation:

(Park *et al.* PRL **99**, 086804 (2007), Hedin and Lundqvist, Solid State Physics **23**, 1 (1969))

$$\Sigma_{n\mathbf{k}}(E,T) = \sum_{m,\nu} \int \frac{d\mathbf{q}}{\Omega_{\mathrm{BZ}}} |g_{mn,\nu}(\mathbf{k},\mathbf{q})|^2 \times \left[\frac{n_{\mathbf{q}\nu} + 1 - f_{m\mathbf{k}+\mathbf{q}}}{E - \epsilon_{m\mathbf{k}+\mathbf{q}} - \hbar\omega_{\mathbf{q}\nu} - i\delta} + \frac{n_{\mathbf{q}\nu} + f_{m\mathbf{k}+\mathbf{q}}}{E - \epsilon_{m\mathbf{k}+\mathbf{q}} + \hbar\omega_{\mathbf{q}\nu} - i\delta} \right]$$

$n_{\mathbf{q}\nu}$	:	electron/hole occupation factors
$\epsilon_{m\mathbf{k}+\mathbf{q}}$	:	band structure energies
$f_{m\mathbf{k}+\mathbf{q}}$	:	phonon occupation factors
$\hbar\omega_{\mathbf{q}\nu}$	:	phonon energies
$g_{mn,\nu}$	:	electron-phonon coupling matrix elements

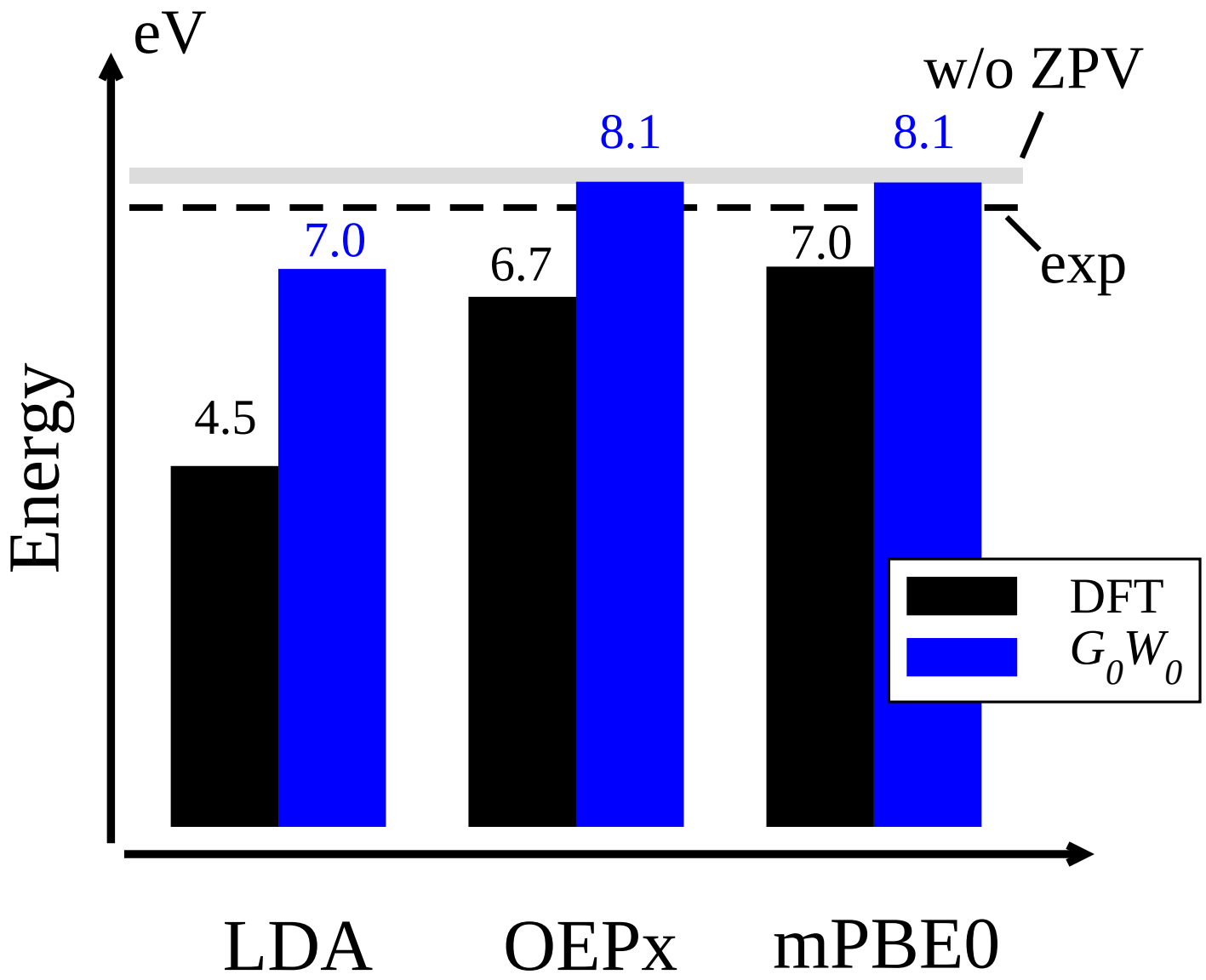
Band gap of MgO

- phonon and electron-phonon calculations:
  - in LDA using Quantum Espresso Code
- band structure:
  - *GW* space-time code: `gwst`
    (Steinbeck, Godby *et al.* CPC **117** (1999), CPC **125** (2000))

band gap renormalization: 0.3 eV !!!

(at 0 K due to zero-point vibrations)

Band gap of MgO



Details of defect calculations

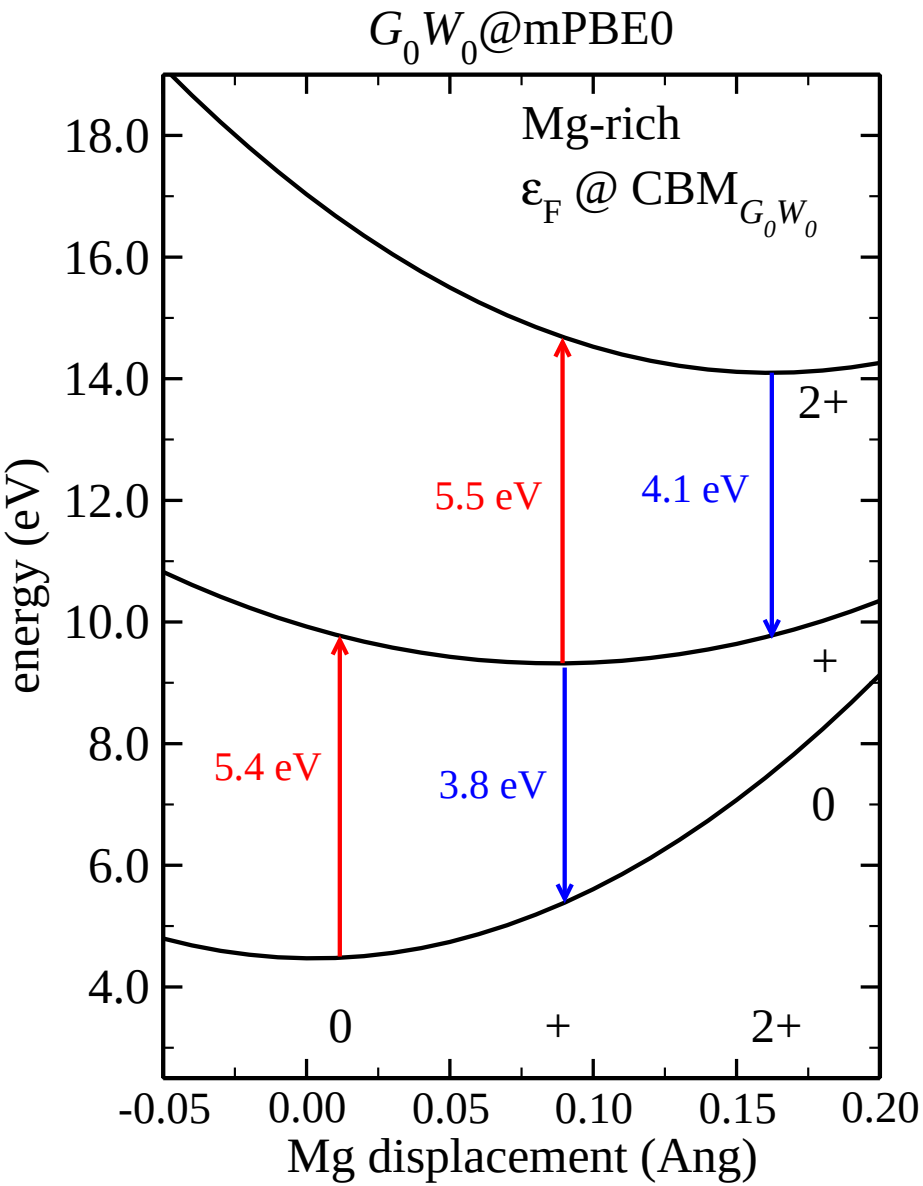
plane-wave DFT program: S/PHI/nX (http://www.sphinxlib.de)

- pseudopotentials
- 64 atom supercells
- 2×2×2 off-center k-point sampling
- for charged supercells:
  - new scheme by Freysoldt *et al.* PRL **102**, 016402 (2009)

GW space-time code: gwst (CPC **117** (1999), CPC **125** (2000), CPC **176** (2007))

- 64 atom cells
- 3×3×3 Γ-point centered k-mesh
- plane wave cutoff: 66 Ry for exchange and 28 Ry for correlation part
- time/frequency cutoff 12 Ry with 18 points per axis
- mPBE0: $0.25 \times \Sigma_x + 0.75 \times v_{xc}^{\mathrm{LDA}}$ (applied perturbatively to LDA)

G_0W_0 corrected configuration coordinate diagram



recall:

Experiment

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DFT-LDA

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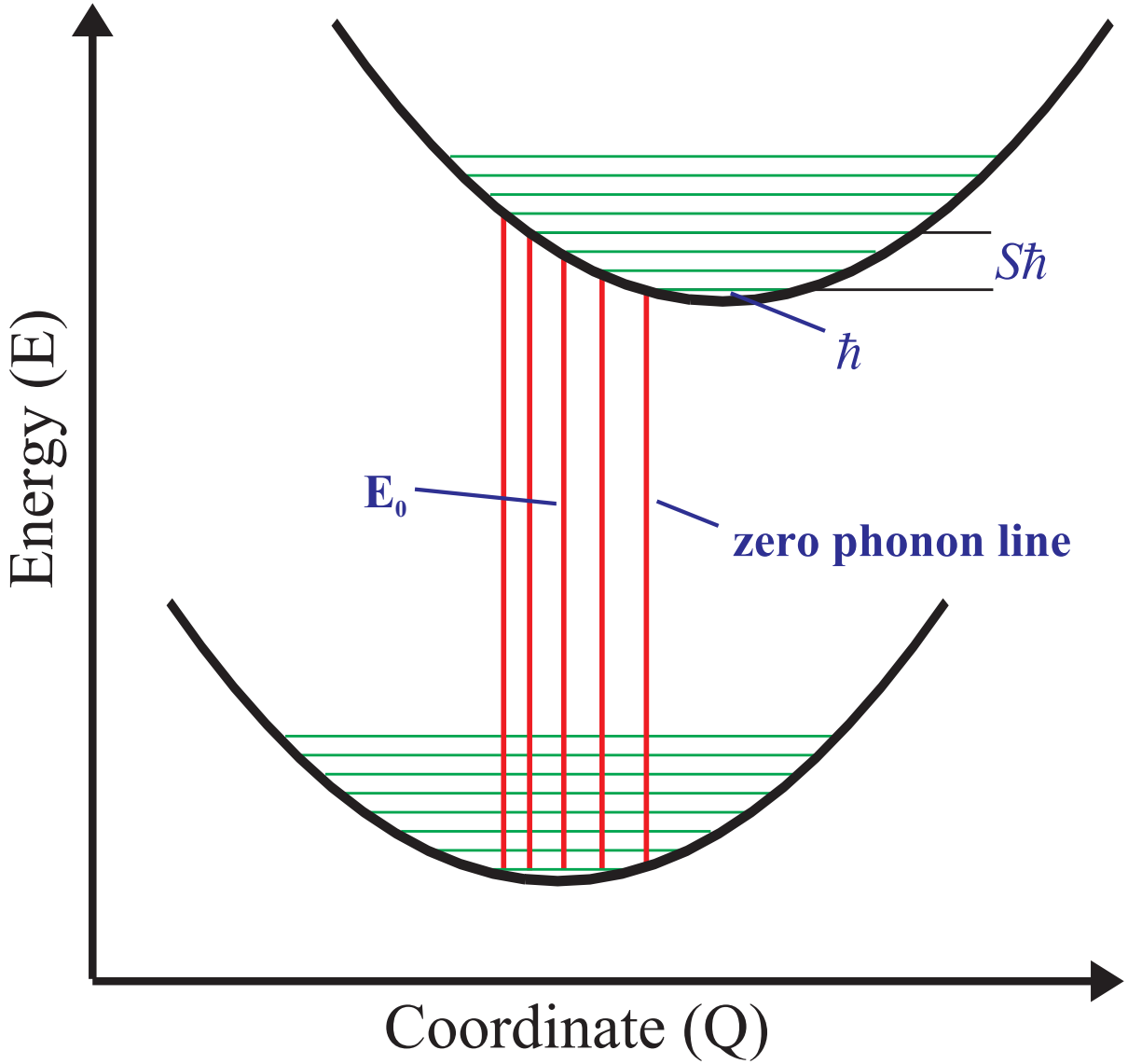
Exciton binding energies for F-center in MgO

Bethe-Salpeter (BSE) calculations: vasp

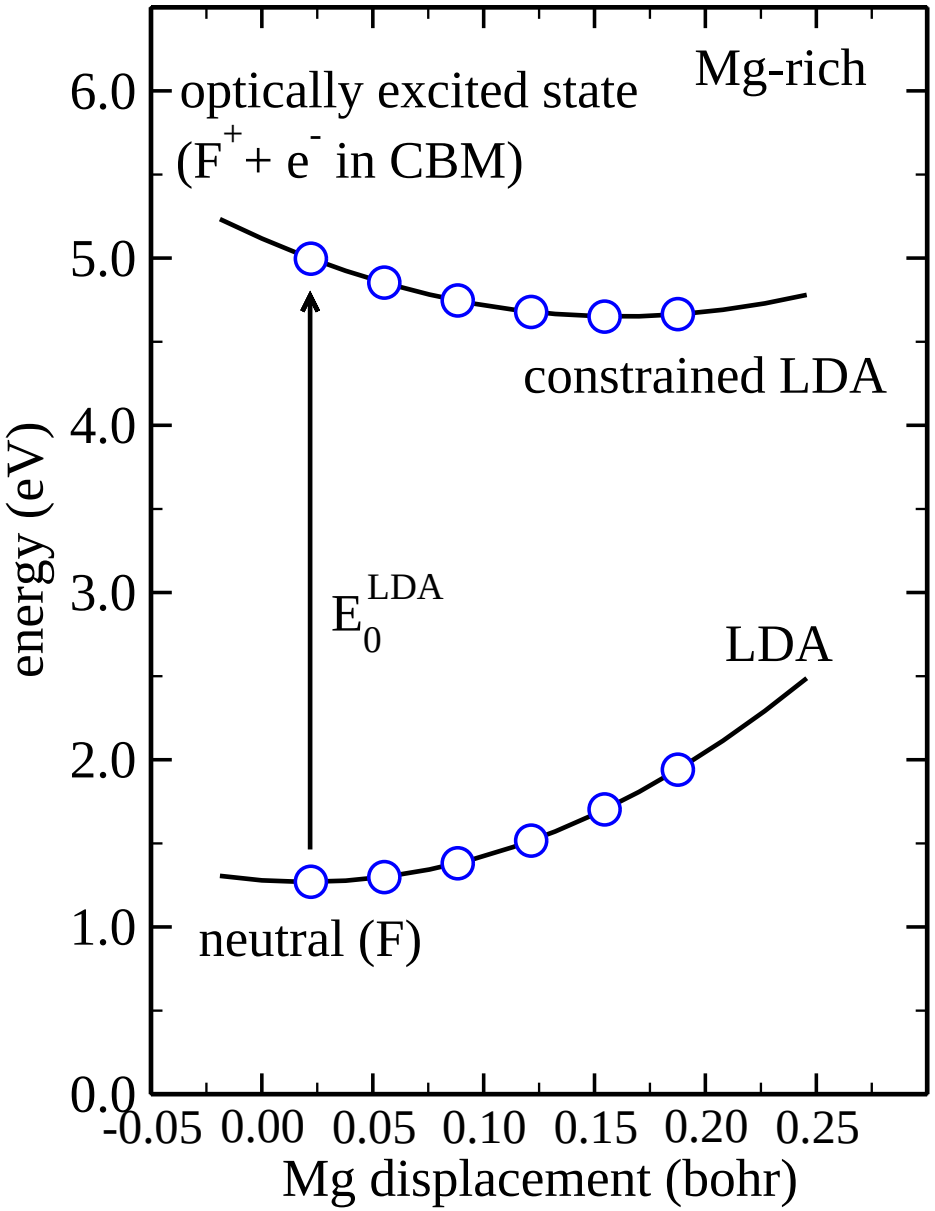
- 64 atom supercells
- model dielectric function
- exciton binding energies:
  - hybrid k-point meshes and extrapolation scheme
    (Fuchs *et al.* PRB **78**, 085103 (2008))

Absorption/eV	F	F^+
G_0W_0 corrected transition	5.40	5.48
BSE exciton binding energy	0.48	0.69
G_0W_0 - BSE	4.92	4.79
Experiment	5.00	4.95

Optical Spectrum – Vibrational Contributions



Contrained LDA calculations

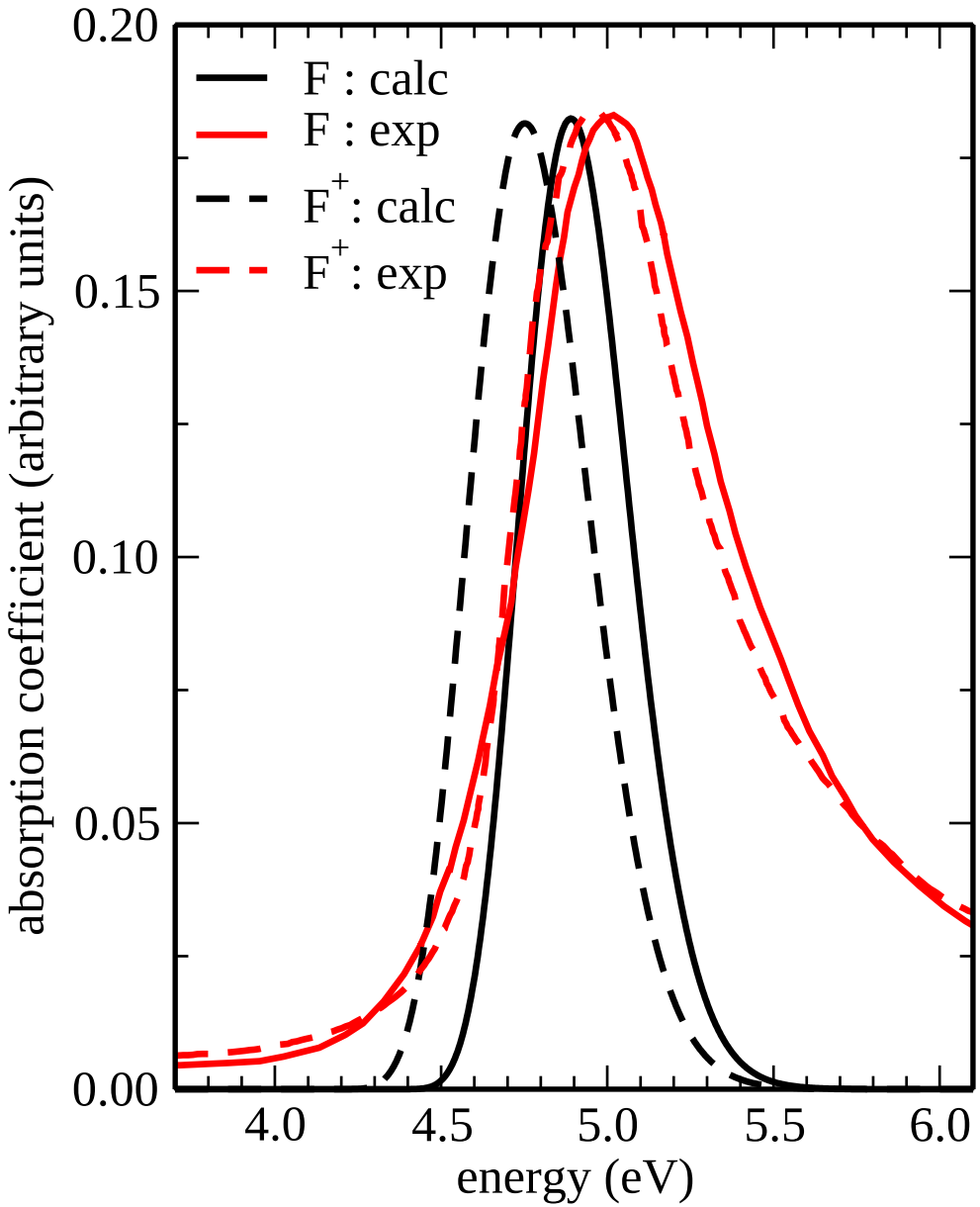


$\hbar\omega$/meV	F	F^+
constr. LDA	70.1	77.5
Experiment	91.0	57.9

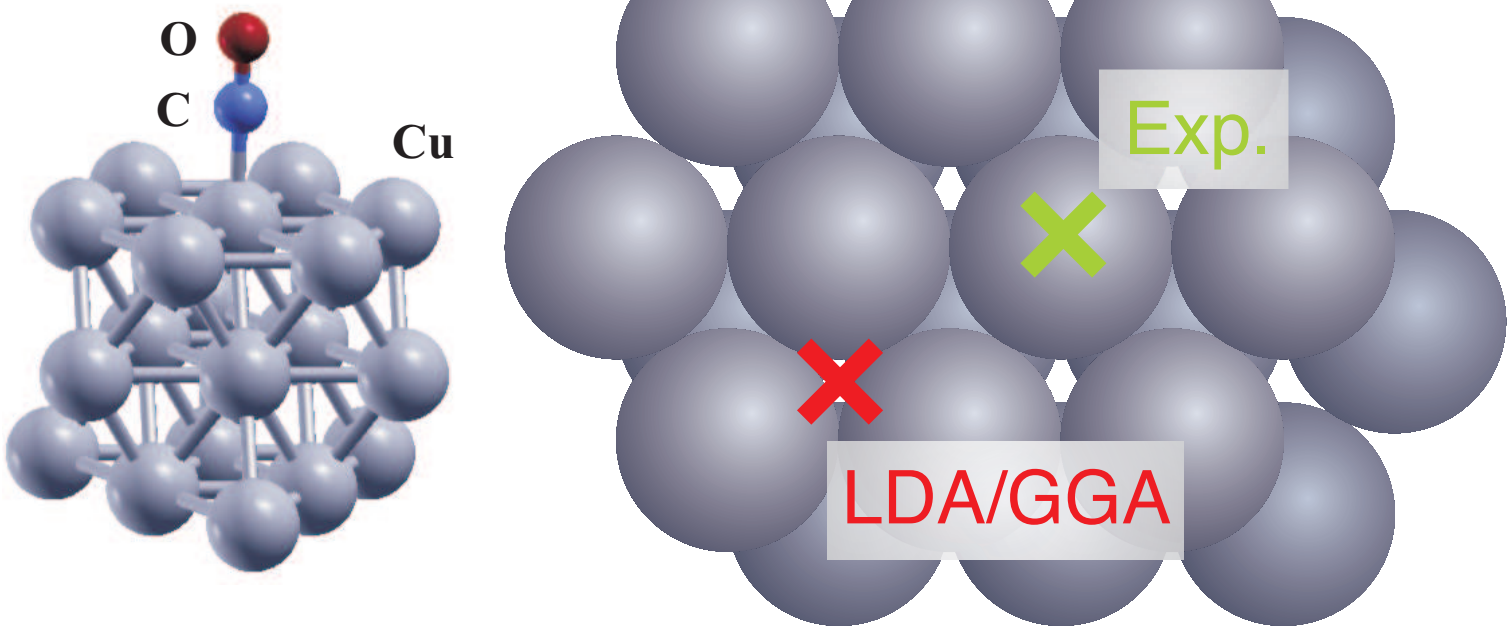
S	F	F^+
constr. LDA	4.95	5.02
Experiment	13.0	29.00

Exp: PRB **42**, 1410 (1990)

F and F^+ center – optical spectrum



CO adsorption puzzle



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- error as large as 0.5 eV for CO on Cu(111)

e.g. Feibelman *et al.* J. Phys. Chem. B **105**, 4018 (2001)

RPA in a Nutshell

- Adiabatic connection:

$$E_{\mathrm{XC}}^{\mathrm{exact}} = \int_0^1 \frac{d\lambda}{\lambda} U_{\mathrm{XC}}^{\lambda}$$

- Fluctuation-dissipation theorem

$$U_{\mathrm{XC}}^{\lambda} = -\frac{1}{2}\int d\mathbf{r}\int d\mathbf{r}' v(\mathbf{r}-\mathbf{r}')\left[-\frac{1}{\pi}\int_0^{\infty} d\omega \mathrm{Im}\chi_{\lambda}(\mathbf{r},\mathbf{r}',\omega) - n(\mathbf{r})\delta(\mathbf{r}-\mathbf{r}')\right]$$

- Dyson equation for χ_λ (χ_0: non-interacting response function)

$$\chi_\lambda = \chi_0 + \chi_0(\lambda v + f_{\mathrm{xc}}^{\lambda})\chi_\lambda$$

- Random phase approximation (RPA): $f_{\mathrm{xc}} = 0$

$$\begin{aligned} E_{\mathrm{xc}}^{\mathrm{RPA}} &= E_{\mathrm{x}}^{\mathrm{exact}} + E_{\mathrm{c}}^{\mathrm{RPA}} \\ E_{\mathrm{c}}^{\mathrm{RPA}} &= \frac{1}{2\pi}\int_0^{\infty} d\omega \mathrm{Tr}\left[\ln(1-\chi_0(i\omega)v) + \chi_0(i\omega)v\right] \end{aligned}$$

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- Fluctuation-dissipation theorem

$U_{\mathrm{XC}}^{\lambda}$ $\left.\right]$

Implemented in FHI-aims:

- all-electron numeric atom centered orbital code
- V. Blum *et al.* Comp. Phys. Comm. **180**, 2175 (2009)
- X. Ren *et al.* Phys. Rev. B **80**, 045402 (2009)

- D

$$\chi_\lambda = \chi_0 + \chi_0(\lambda v + f_{\mathrm{xc}}^{\lambda})\chi_\lambda$$

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Attractive features of the RPA

$$E_{\text{tot}}^{\text{RPA}} = T_{\text{s}} + E_{\text{ext}} + E_{\text{H}} + E_{\text{x}}^{\text{exact}} + E_{\text{c}}^{\text{RPA}}$$

- "Exact exchange" (with Kohn-Sham orbitals)
  - self-interaction error considerably reduced
- vdW interactions included automatically and seamlessly
- Screening taken into account
  - applicable to metals/small gap systems (in contrast to MP2)

Critical assessment of the RPA is emerging.

CO in FHI-aims

CO	E_b eV	R_e Å	ν cm^{-1}	ϵ_{HOMO} eV	ϵ_{LUMO} eV
LDA	12.97	1.127	2179	-9.12	-2.25
PBE	11.67	1.135	2128	-9.04	-2.00
PBE0	11.09	1.123	2235	-10.75	-0.75
RPA/G_0W_0@LDA	10.40	1.138	2117	-13.31	1.74
RPA/G_0W_0@PBE	10.45	1.137	2115	-13.17	1.84
RPA/G_0W_0@PBE0	10.60	1.130	2173	-13.76	2.02
experiment*	11.11	1.128	2170	-14.00	1.80

- different DFT functionals describe different properties well
- G_0W_0@PBE0 gives overall best performance

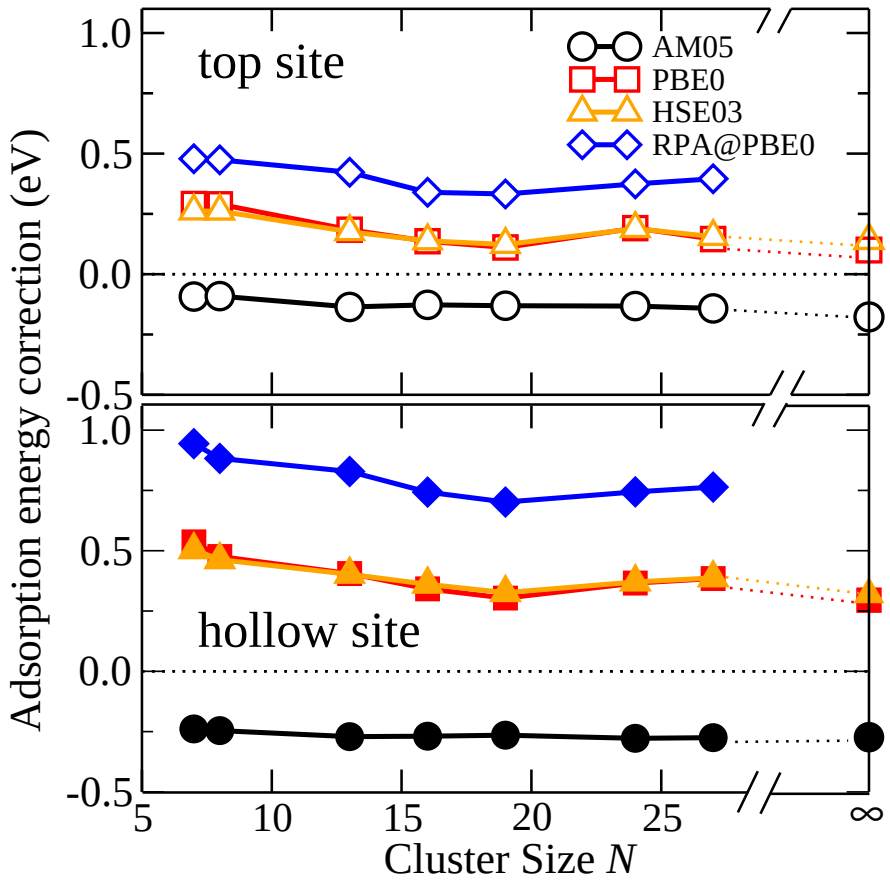
  X. Ren, P. Rinke, and M. Scheffler, PRB **80**, 045402 (2009)

** Constants of Diatomic Molecules* (1979), PRL **22**, 1034 (1969)

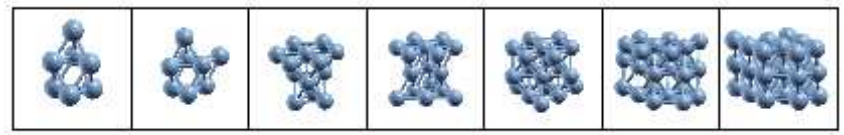
RPA adsorption energies for CO@Cu(111)

Local *xc*-correction approach: Hu, Reuter, Scheffler, PRL **98**, 176103 (2007)

$$\Delta E_{\text{ads}} = \lim_{\text{cluster}\to\infty} E_{\text{ads}}^{\text{cluster}}(\text{XC}) - E_{\text{ads}}^{\text{cluster}}(\text{PBE})$$



$$XC = \begin{cases} AM05, \\ PBE0, HSE03 \\ RPA \end{cases}$$



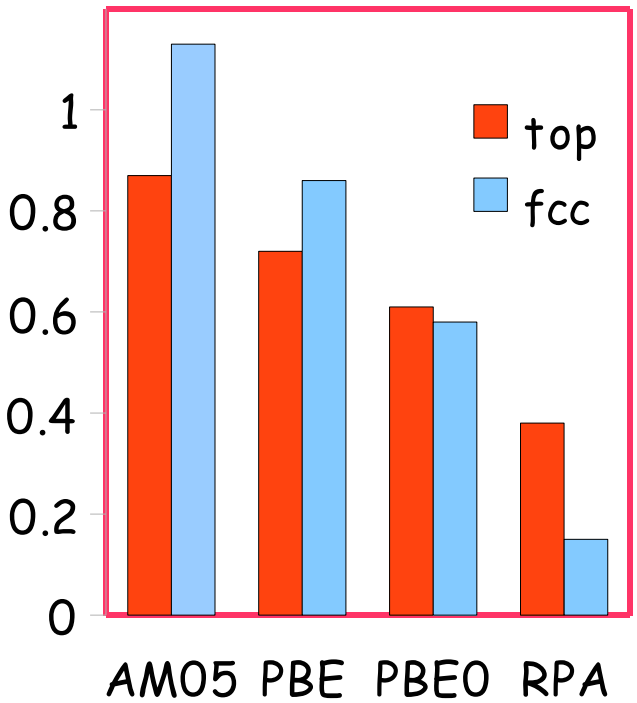
X. Ren, P. Rinke, and M. Scheffler

Phys. Rev. B **80**, 045402 (2009)

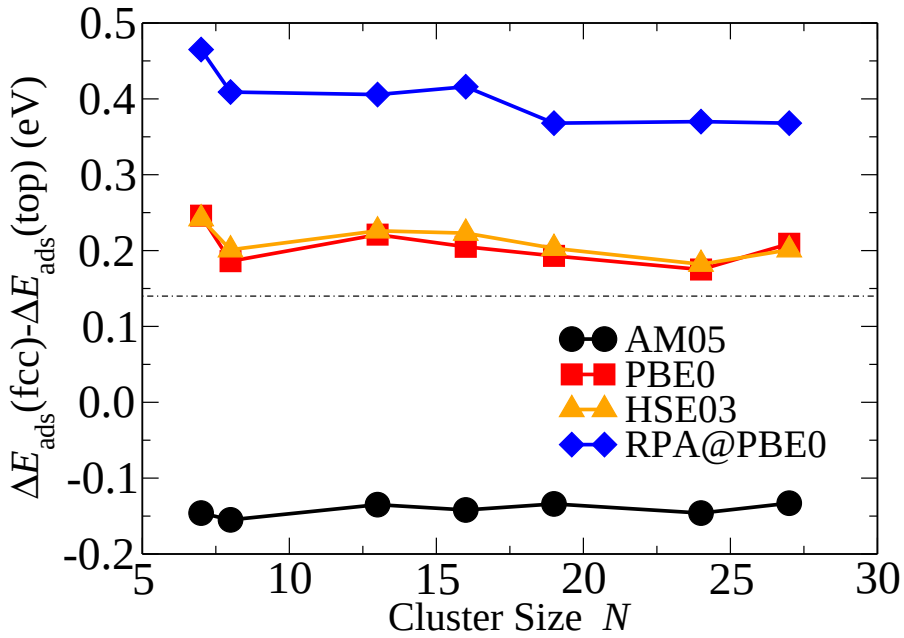
RPA adsorption energy for CO@Cu(111)

$$E_{\mathrm{ads}}(\mathrm{XC}) = E_{\mathrm{ads}}(\mathrm{PBE}) + \Delta E_{\mathrm{ads}}(\mathrm{XC})$$

Adsorption energy for different functionals



Convergence of $\Delta E_{\mathrm{ads}}(\mathrm{XC})$ difference



RPA adsorption energy for CO@Cu(111)

	top	fcc	ΔE_{ads}
E_{ads}(PBE)[a]	-0.71	-0.87	0.16
E_{ads}(PBE0)[a]	-0.61	-0.58	-0.03
E_{ads}(CASPT2)[b]	-0.49	> 0	< -0.49
E_{ads}(EXP)	-0.46[c], -0.49[d]		
	this work		
E_{ads}(PBE)	-0.72	-0.86	0.14
E_{ads}(PBE0)	-0.58 ± 0.04	-0.54 ± 0.03	-0.04 ± 0.01
E_{ads}(RPA@PBE)	-0.35 ± 0.02	-0.17 ± 0.02	0.18 ± 0.01
E_{ads}(RPA@PBE0)	-0.37 ± 0.02	-0.15 ± 0.02	-0.22 ± 0.01

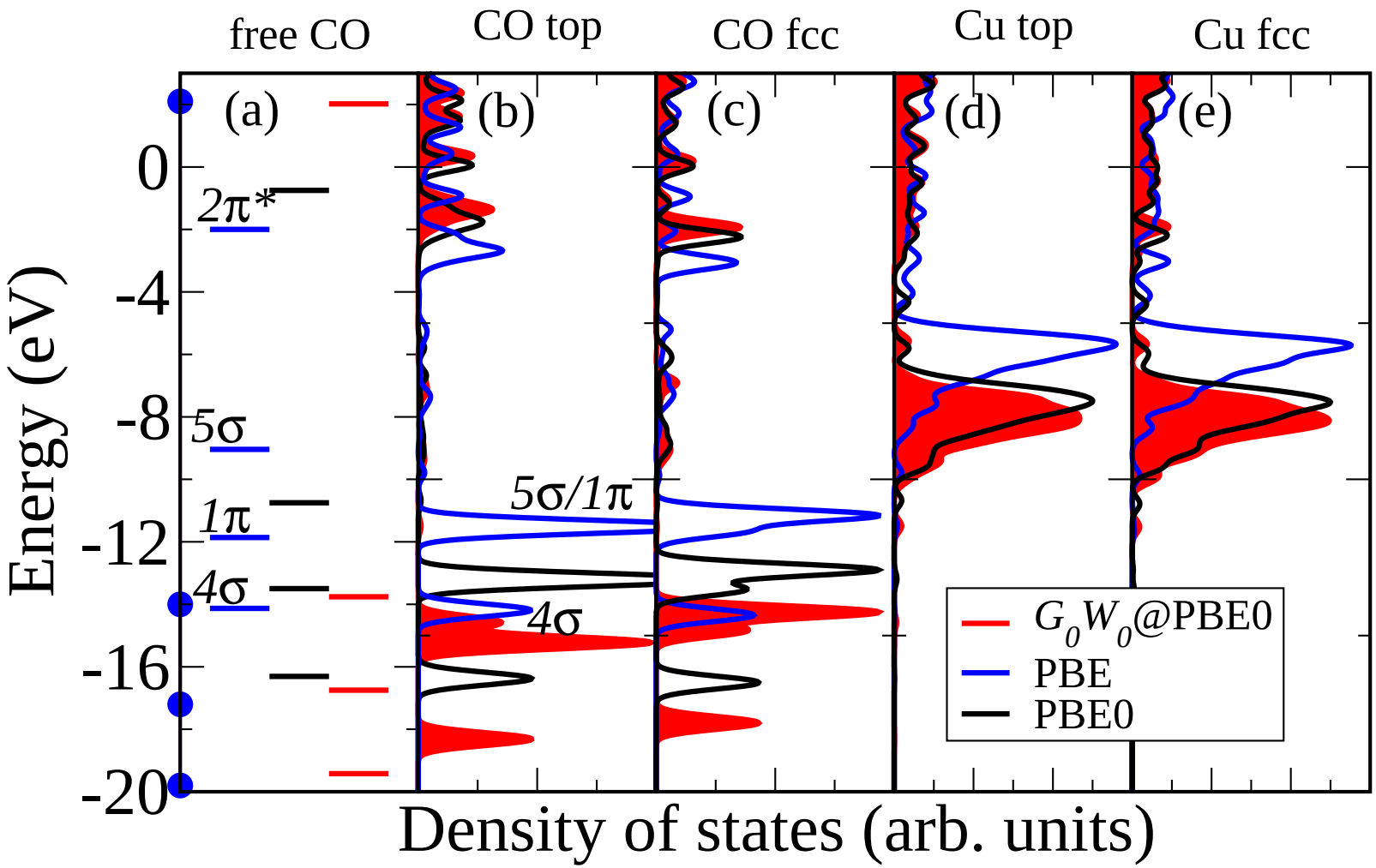
[a] A. Stroppa and G. Kresse, New J. Phys, **10**, 063030 (2008)

[b] S. Sharifzadeh, P. Huang, and E. Carter, J. Phys. Chem. C **112**, 4649 (2008)

[c] J. Kessler and F. Thieme, Surf. Sci. **67**, 405 (1977)

[d] S. Vollmer, G. Witte, and C. Woell, Catal. Lett. **77**, 97 (2001)

CO@Cu(111) Spectra (for Cu_{16} cluster)



X. Ren, P. Rinke, and M. Scheffler PRB **80**, 045402 (2009)

(see also C. Freysoldt *et al.* PRL **103**, 056803 (2009) for CO@NaCl/Ge)

Outlook

- RPA for defect formation energies . . .
- self-consistency in RPA . . .
- beyond RPA?
- consistent framework for electron-hole excitations and electron-phonon coupling. . .
- etc.

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Defects

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Christoph Freysoldt

More information

New J. Phys. **7**, 126 (2005)
phys. stat. sol. (b) **245**, 929 (2008)
Phys. Rev. Lett. **102**, 026402 (2009)
Phys. Rev. B **80**, 045402 (2009)
Phys. Rev. Lett. **103**, 056803 (2009)

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RPA

Xinguo Ren
Matthias Scheffler
Volker Blum
FHI-aims developer team

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