# Towards a unified description of ground and excited state properties: RPA *vs* *GW*

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Towards Reality in Nanoscale Materials V

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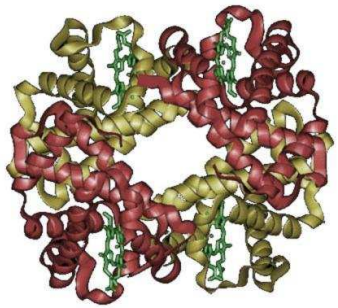
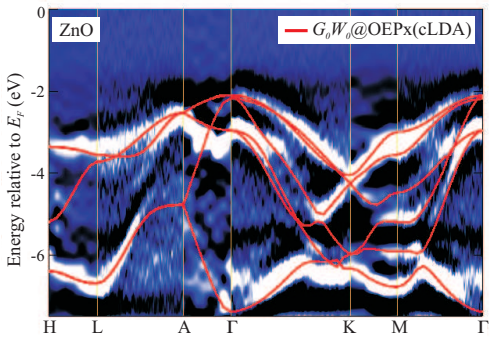
# Wish list for "optimum" electronic structure approach

$d/f$-electrons
(e.g. Cerium)



(bio)molecules




## applicable across dimensionalities:

- molecules/clusters
- wires/tubes
- surfaces/films
- solids, extended systems

## applicable across periodic table:

- from light to heavy elements
- including $d/f$ electron physics/chemistry

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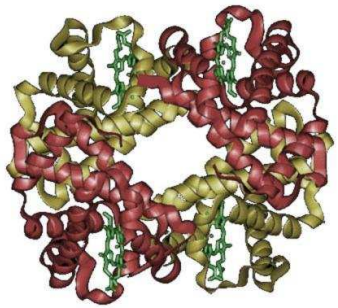

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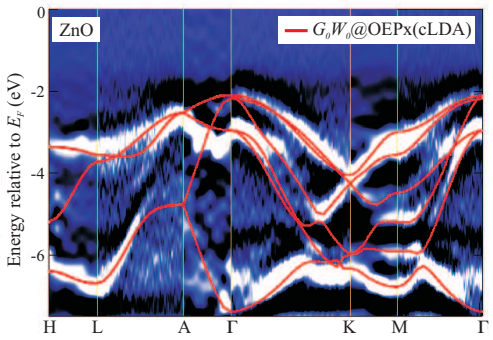


## ground/excited state:

- consistent description
- parameter free
- free from pathologies e.g.:
  - self-interaction error
  - absence of van der Waals
  - band-gap problem
- computationally efficient
- gradients $\Rightarrow$ structure relaxation
- ...

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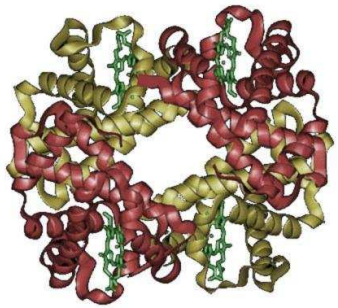

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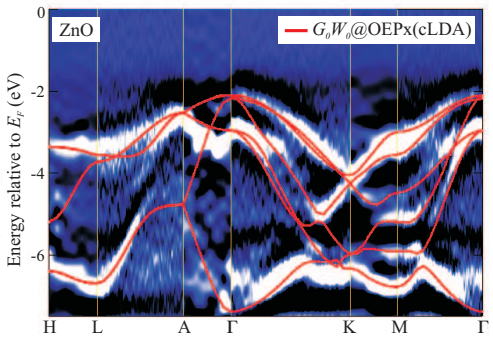


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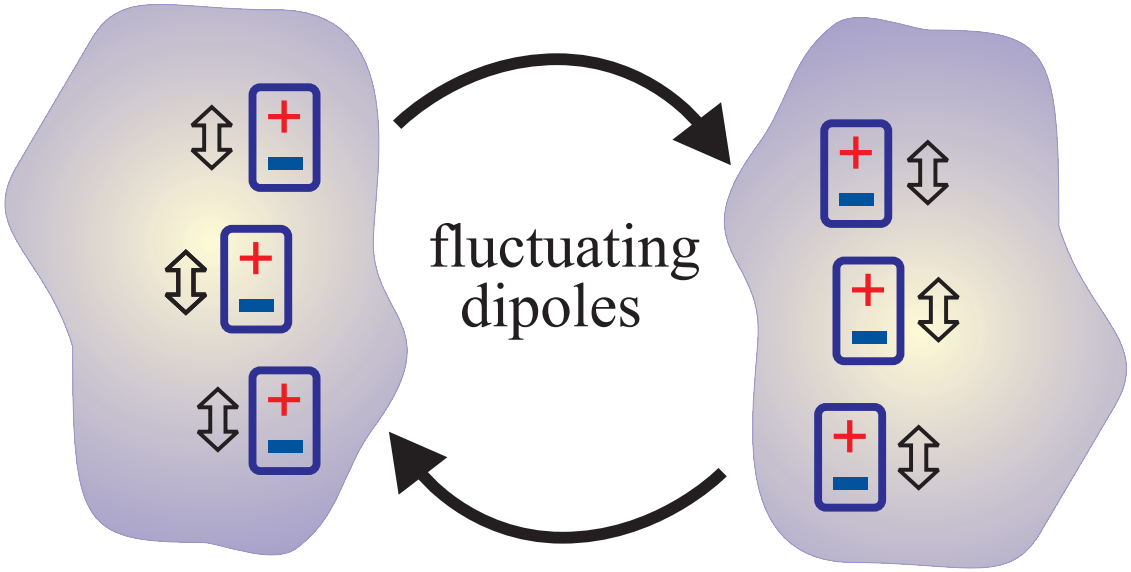
# Treating van der Waals interactions




- difficult, because they require non-local treatment
- fluctuating dipoles described by dielectric function $\varepsilon(\mathbf{r}, \mathbf{r}', \omega)$
- correlation energy in random-phase approximation (RPA):

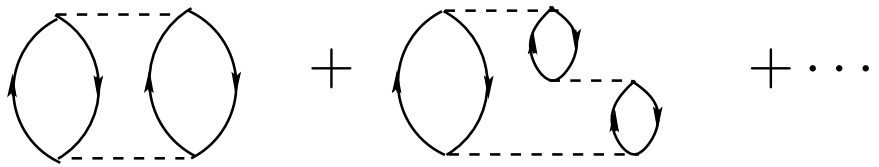
$$E_c^{\mathrm{RPA}} = \frac{1}{2\pi} \int_0^\infty d\omega \mathrm{Tr} \left[ \ln \left( \varepsilon(i\omega) \right) + \left( 1 - \varepsilon(i\omega) \right) \right]$$

# Attractive features of the RPA

exact exchange + random phase approximation: (EX+cRPA)@reference

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

$$E_{\text{c}}^{\text{RPA}} =$$



- "Exact exchange" (with Kohn-Sham orbitals): OEPx
  - 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)

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$$E_{\text{c}}^{\text{RPA}} =$$  $$+ \cdots$$

For an overview of RPA, see

- our recent review article:
  Ren, Joas, Rinke, Scheffler, arXiv:1203.5536v1

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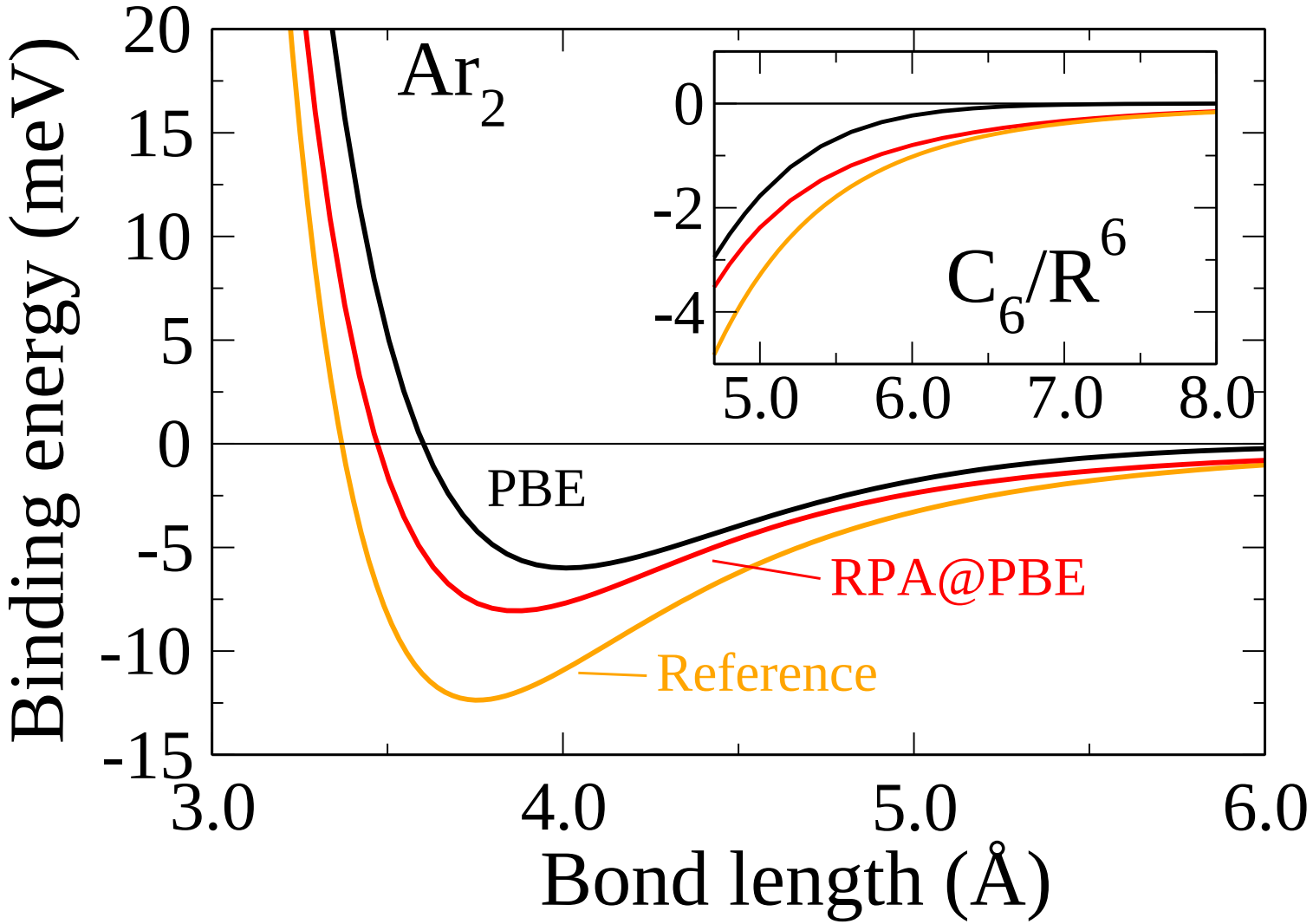
# van der Waals bonding



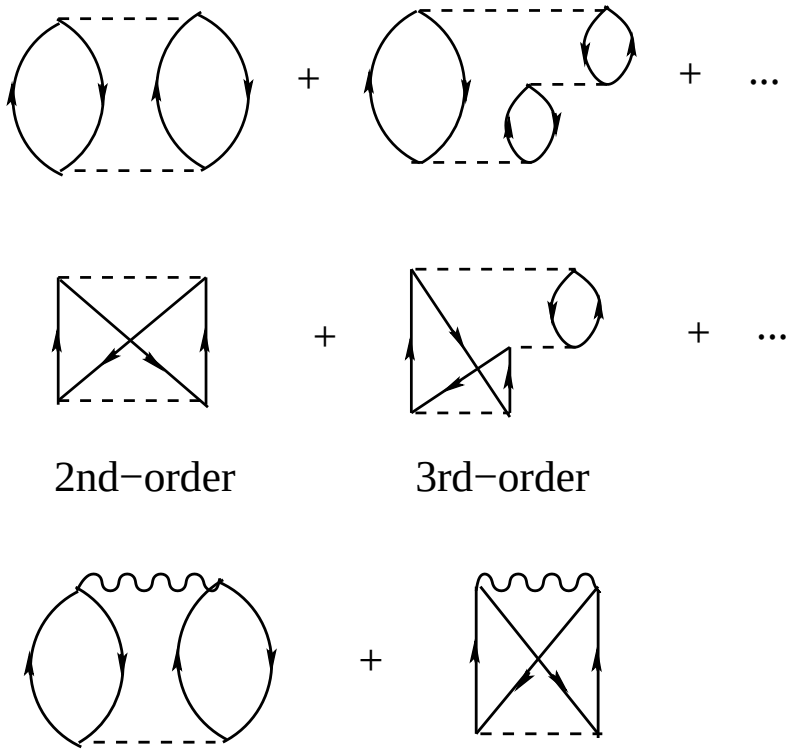

✔ Correct asymptotic behavior ⇒ crucial for large molecules

✘ Underbinding around the equilibrium distance

# The SOSEX correction to RPA

Digrammatic representation (motivated in coupled cluster context)

$E_c^{\text{RPA+SOSEX}} =$




- Arising from the anti-symmetric nature of the many-body wave function
- RPA+SOSEX is one-electron self-correlation free

D. L. Freeman, Phys. Rev. B **15**, 5512 (1977). A. Grüneis *et al.*, J. Chem. Phys. **131**, 154115 (2009). J. Paier *et al.*, J. Chem. Phys. **132**, 094103 (2010); Erratum: **133**, 179902 (2010).

# The concept of single excitation (SE) corrections

Rayleigh-Schrödinger perturbation theory:

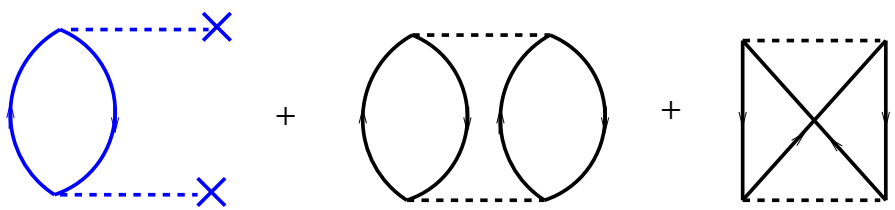
$$\hat{H} = \hat{H}^0 + \hat{H}'$$

Ground-state energy: $E_0 = E_0^{(0)} + E_0^{(1)} + E_0^{(2)} + \cdots$

- zeroth-order: $E_0^{(0)} = \langle \Phi_0 | \hat{H}^0 | \Phi_0 \rangle$
- 1st order: $E_0^{(1)} = \langle \Phi_0 | \hat{H}' | \Phi_0 \rangle$
- 2nd order:

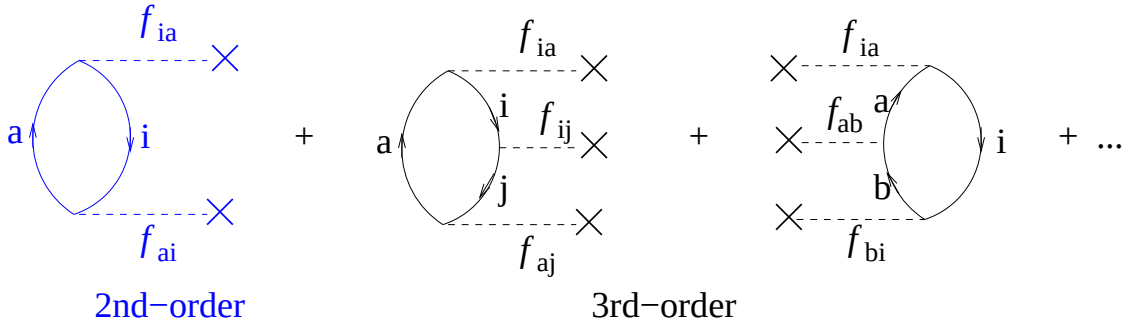
$$E_0^{(2)} = \sum_{n \neq 0} \frac{|\langle \Phi_0 | \hat{H}' | \Phi_n \rangle|^2}{E_0^{(0)} - E_n^{(0)}} = \underbrace{\sum_{i,a} \frac{|\langle \Phi_0 | \hat{H}' | \Phi_{i,a} \rangle|^2}{E_0^{(0)} - E_{i,a}^{(0)}}}_{\text{Single excitations} = E_c^{\text{SE}}} + \underbrace{\sum_{ij,ab} \frac{|\langle \Phi_0 | \hat{H}' | \Phi_{ij,ab} \rangle|^2}{E_0^{(0)} - E_{ij,ab}^{(0)}}}_{\text{Double excitations MP2}}$$

SE accounts for orbital relaxations



# Renormalized single excitations (rSE)

$E_c^{\text{rSE}} =$




$f_{pq} = \langle p|\hat{f}|q\rangle$ : Hartree-Fock operator evaluated within Kohn-Sham orbitals

- $E_c^{\text{SE}} = \sum_i^{\text{occ}} \sum_a^{\text{unocc}} \frac{|f_{ia}|^2}{\epsilon_i - \epsilon_a}$ ($\epsilon_i, \epsilon_a$ : Kohn-Sham orbital energies)

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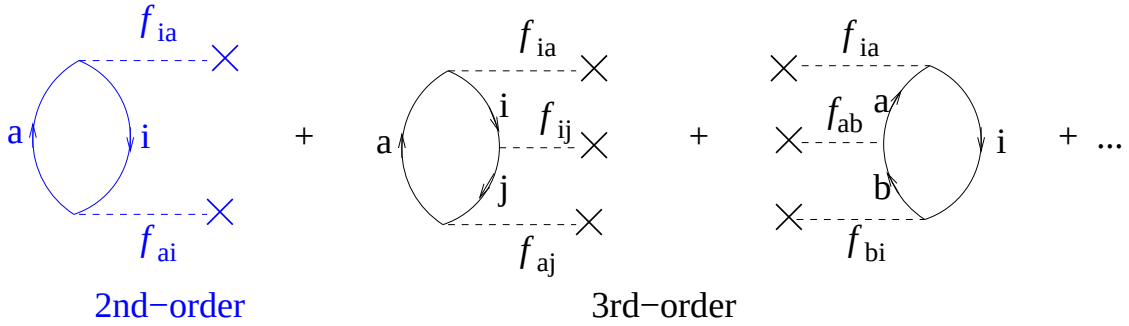


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- "Diagonal rSE " : including only terms with $i = j = \cdots$ and $a = b = \cdots$

  $E_c^{\text{rSE-diag}} = \sum_i^{\text{occ}} \sum_a^{\text{unocc}} \frac{|f_{ia}|^2}{f_{ii} - f_{aa}}$ Problematic for weak interactions

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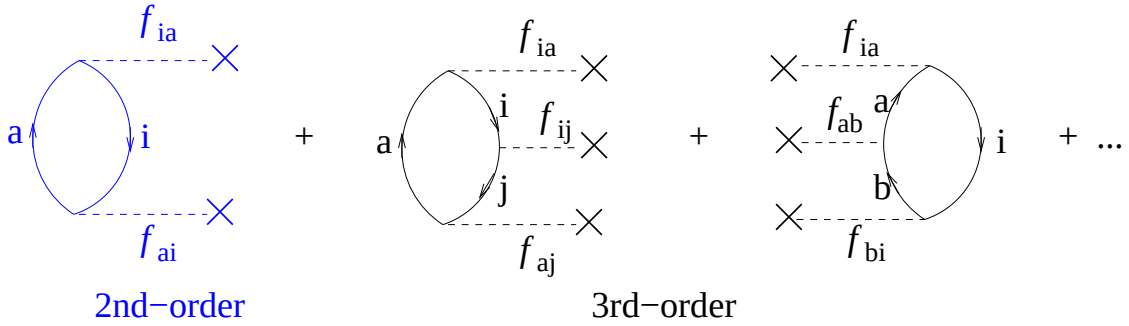


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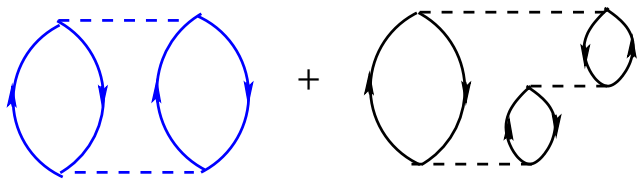
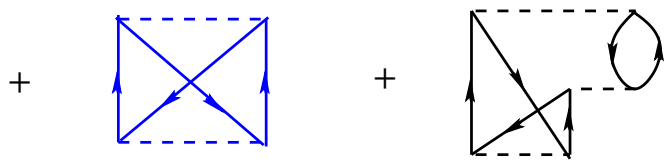
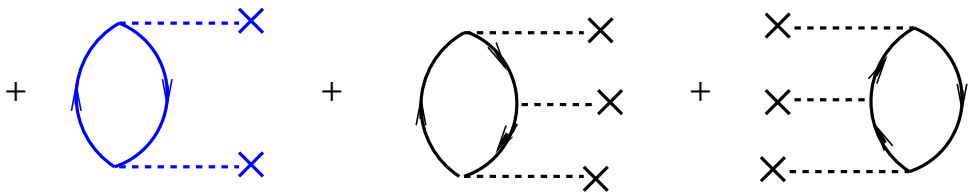
- "full rSE " : $E_c^{\text{rSE-full}} = \sum_i^{\text{occ}} \sum_a^{\text{unocc}} \frac{\left|\tilde{f}_{ia}\right|^2}{\tilde{f}_i - \tilde{f}_a}$

  Diagonalize $f_{ij}$ and $f_{ab}$ blocks separately $\rightarrow \tilde{f}_i$, $\tilde{f}_a$, and transform $f_{ia} \rightarrow \tilde{f}_{ia}$

# Renormalized 2nd-order Perturbation Theory (r2PT)

$E_c^{\text{RPA+SOSEX+rSE}} =$  $+ \ldots$ $(= \text{RPA})$

 $+ \ldots$ $(= \text{SOSEX})$

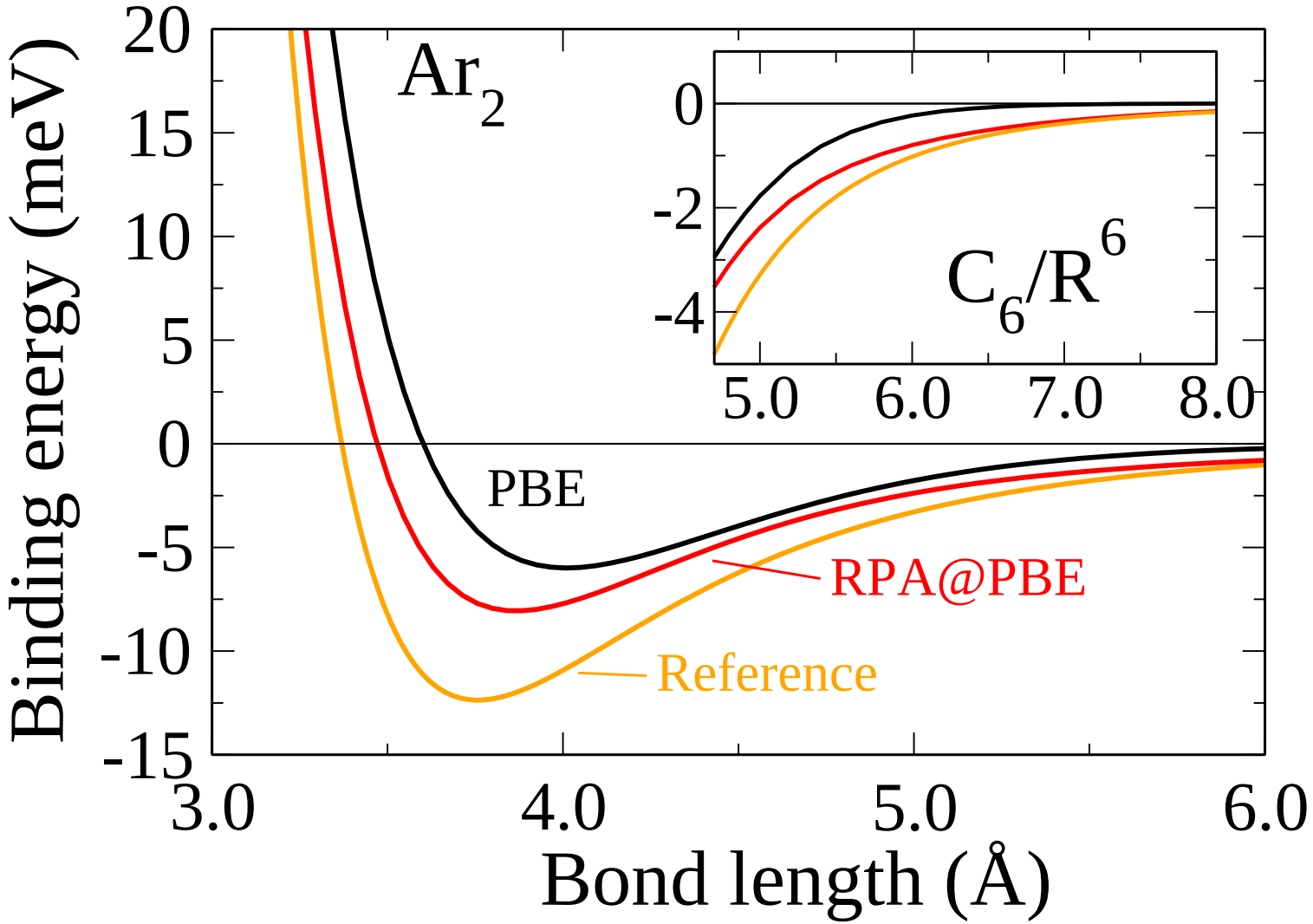



$+ \ldots$ $(= \text{rSE})$

$(= \text{2PT})$

"r2PT" = "RPA+SOSEX+rSE"

# van der Waals bonding

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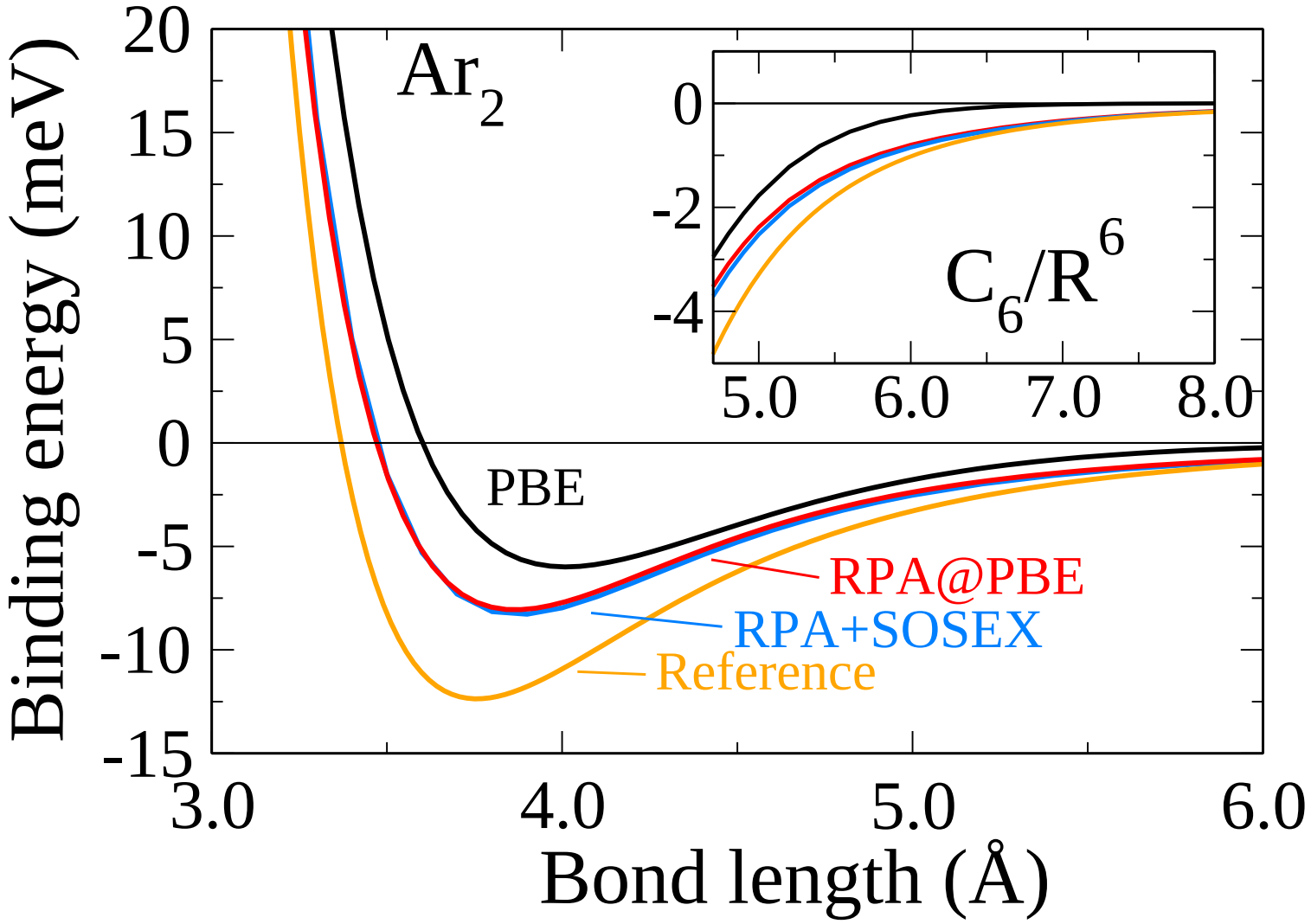


- SOSEX has almost no effect

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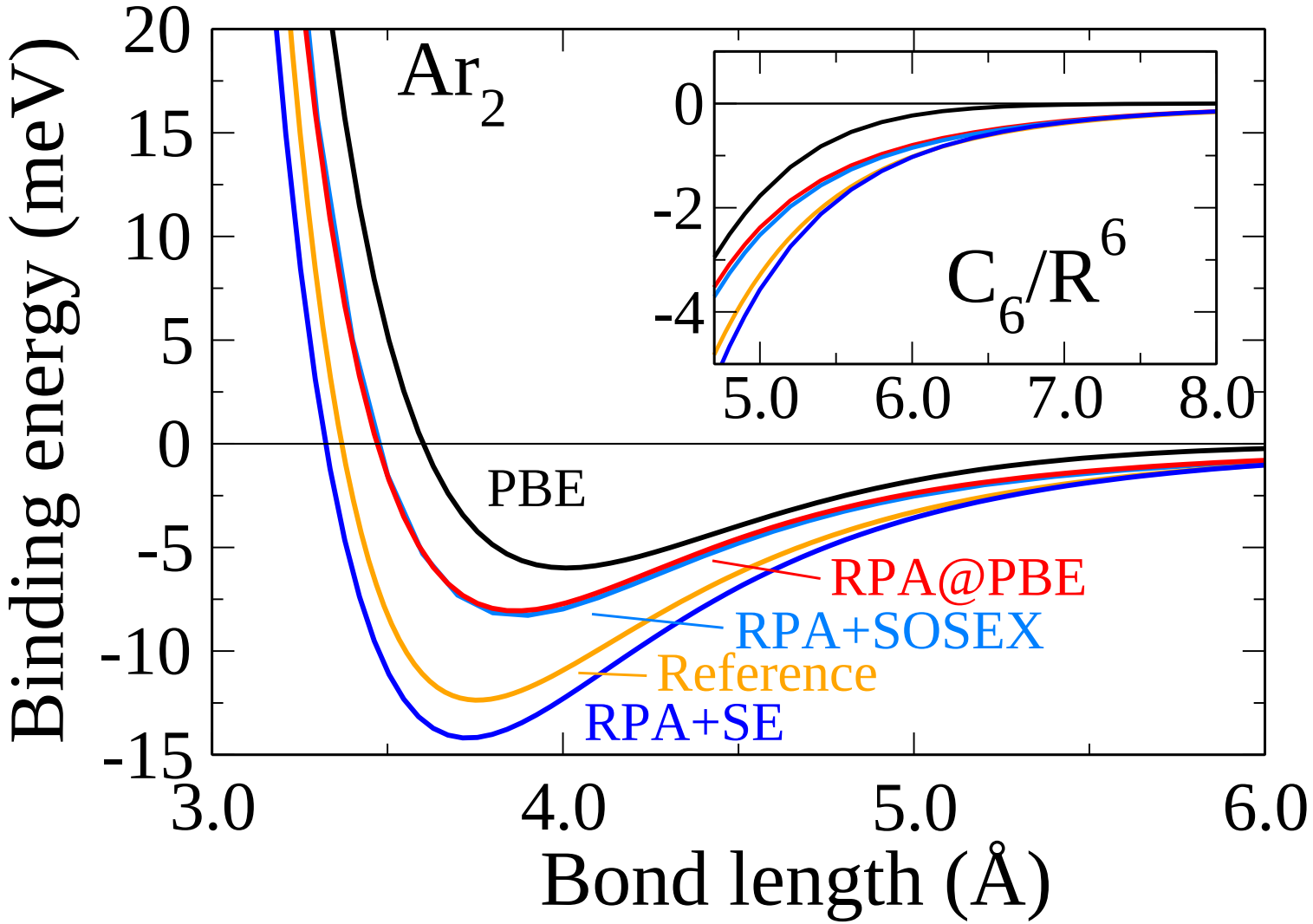
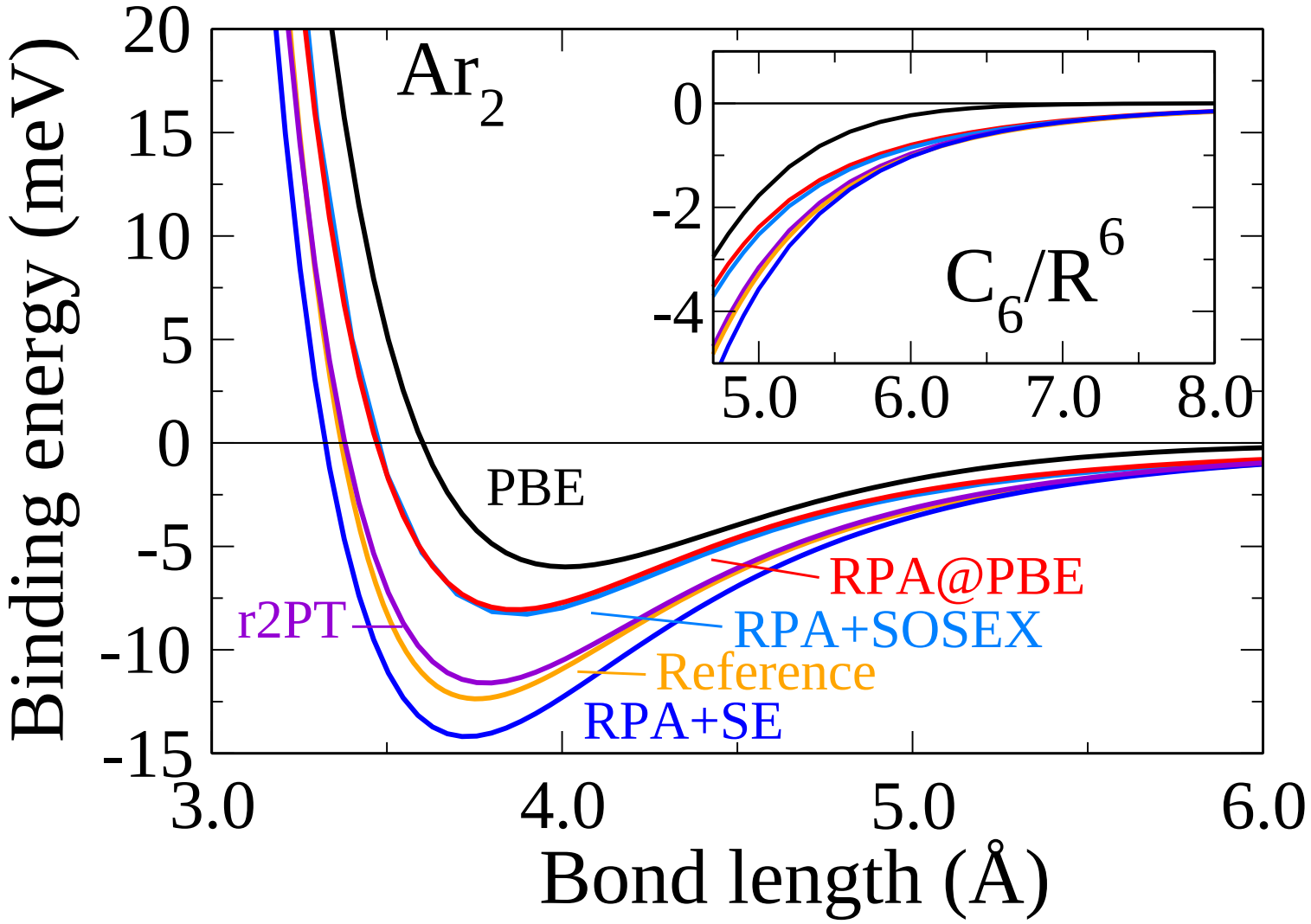



- much improved binding and asymptotics

Ren, Tkatchenko, Rinke, and Scheffler, Phys. Rev. Lett. **106**, 153003 (2011)

# van der Waals bonding

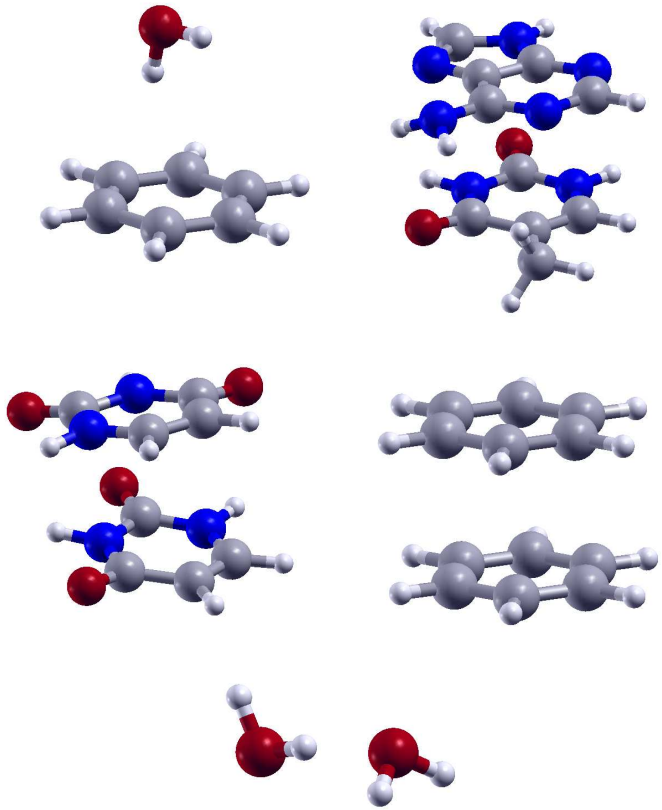



- best overall performance

# Van der Waals interactions - the S22 benchmark set

S22 set of binding energies

- 22 representative dimers:
  - 7 hydrogen bonded
  - 8 dispersion bonded
  - 7 mixed character
- CCSD(T) ("gold standard") reference values



Jurečka *et al.*, PCCP **8**,1985 (2006)

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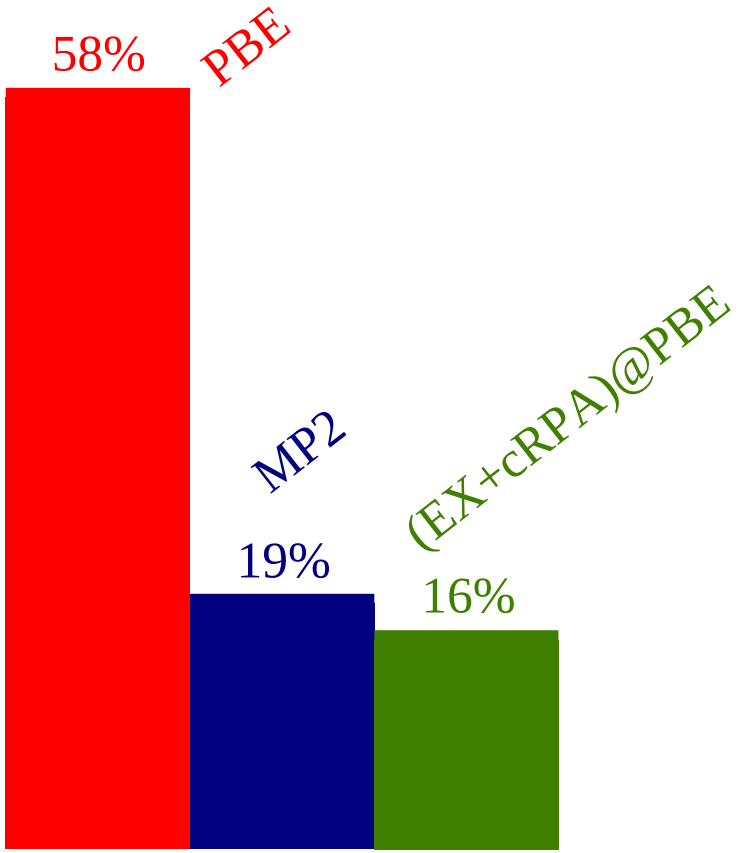
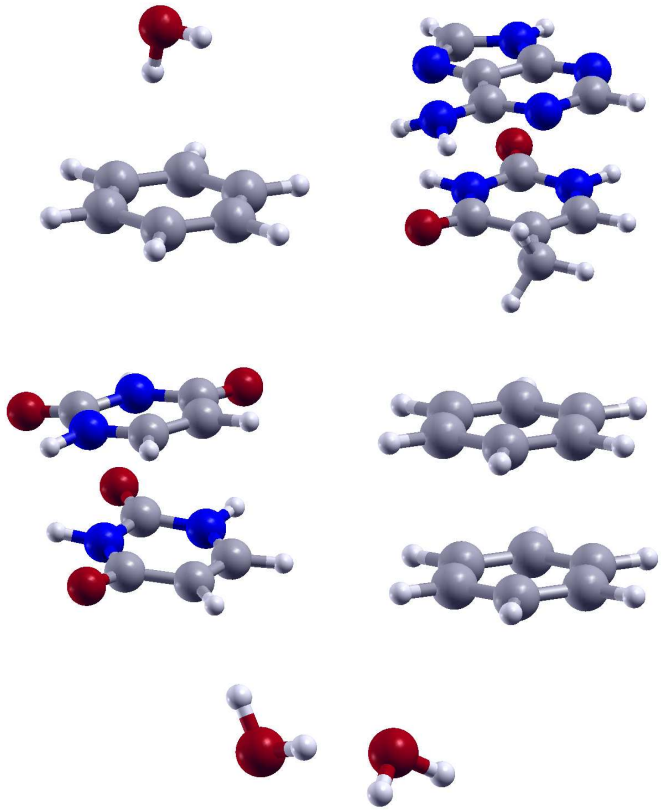



mean absolute percentage error



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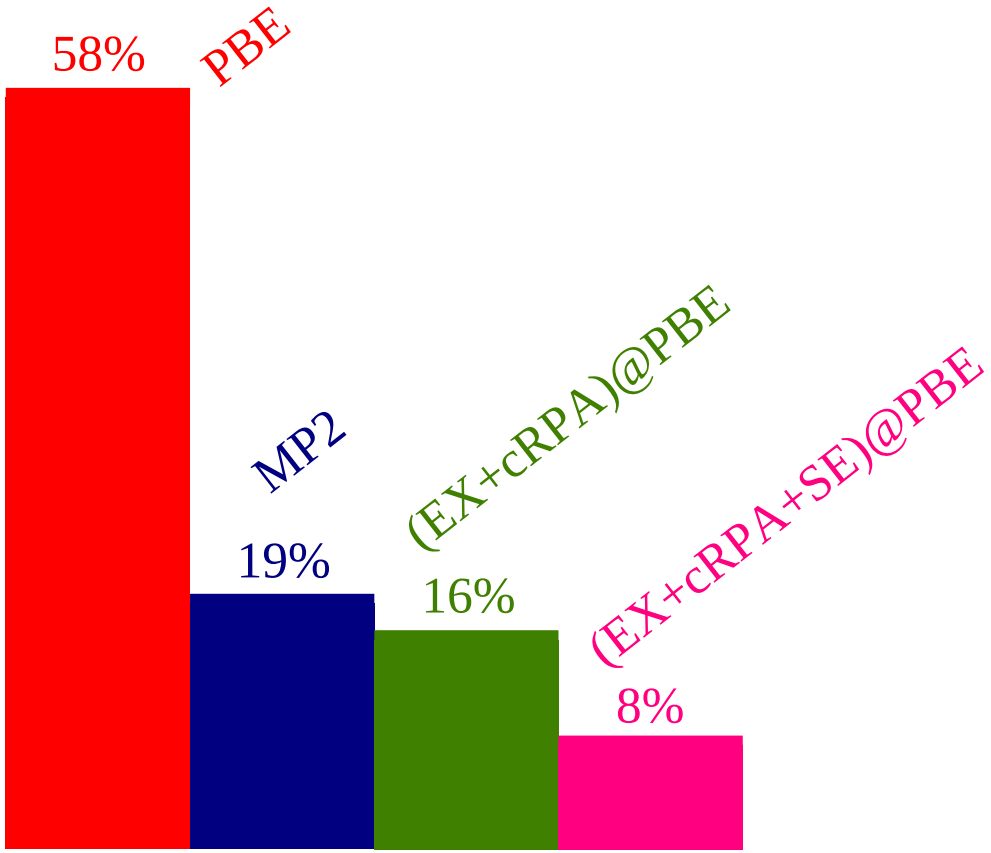


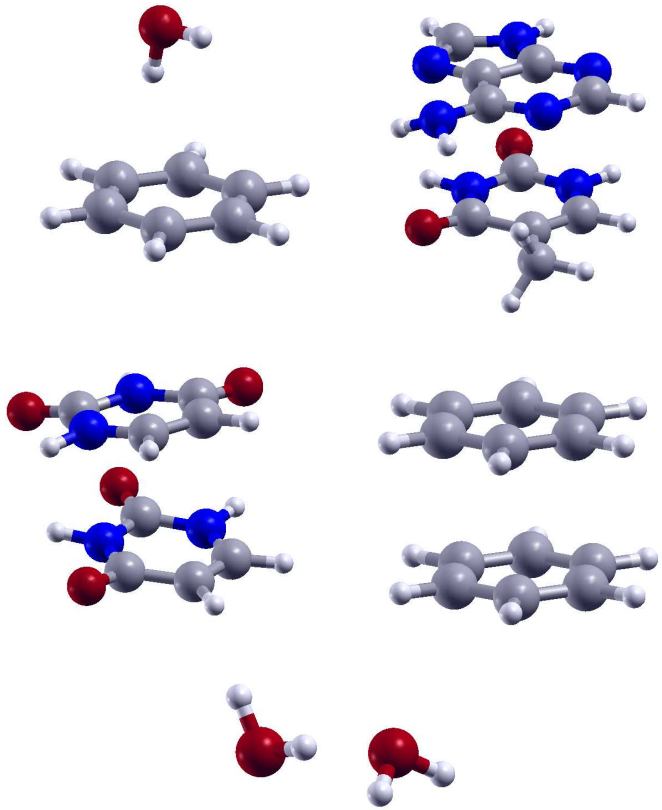

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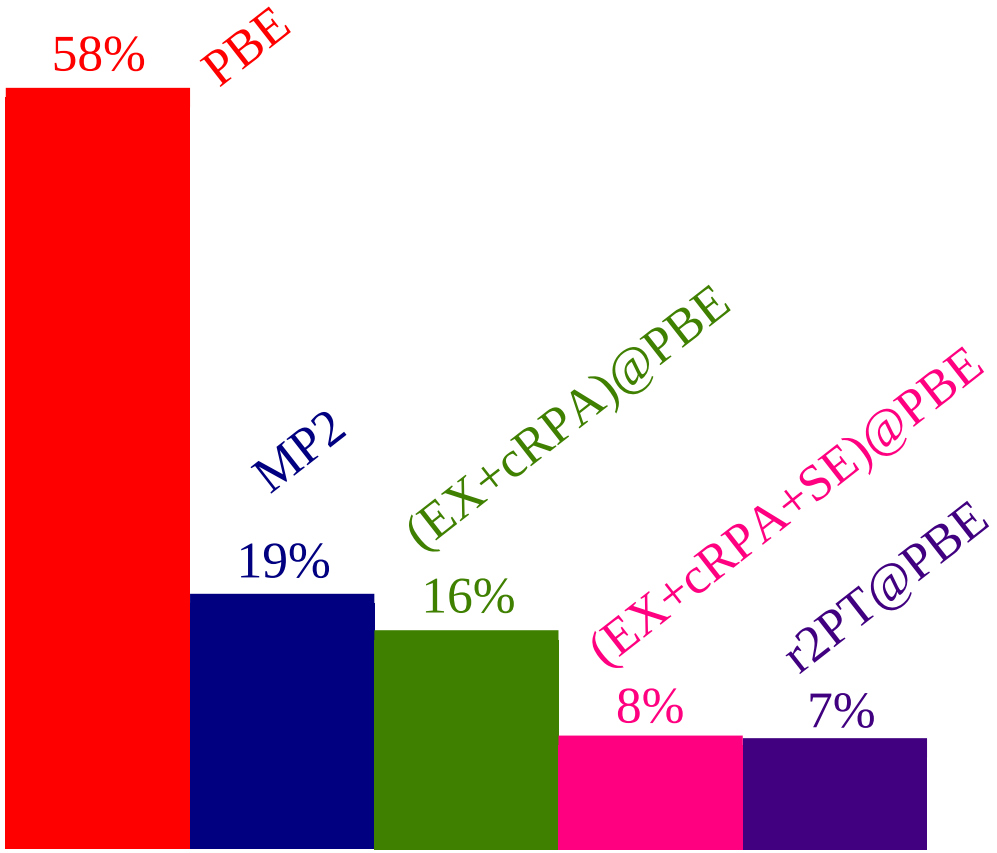


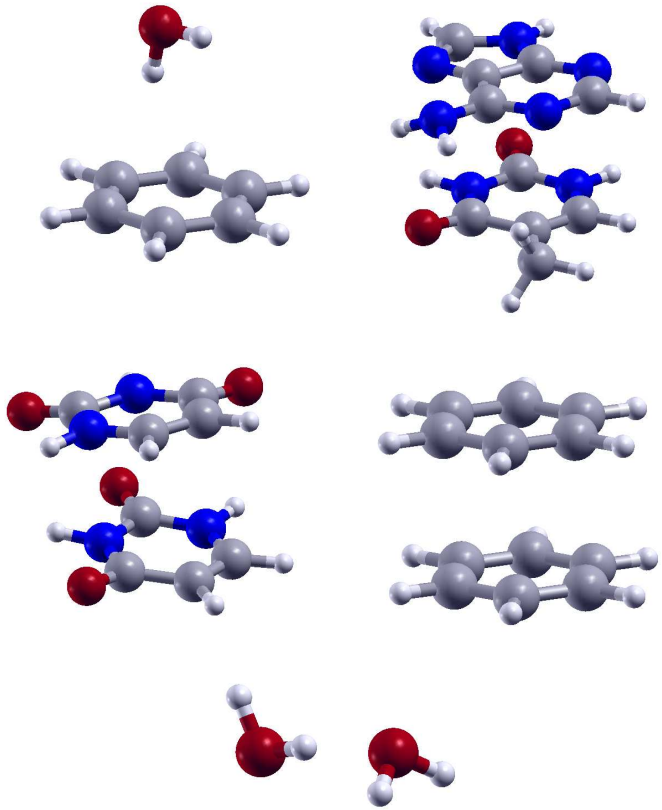

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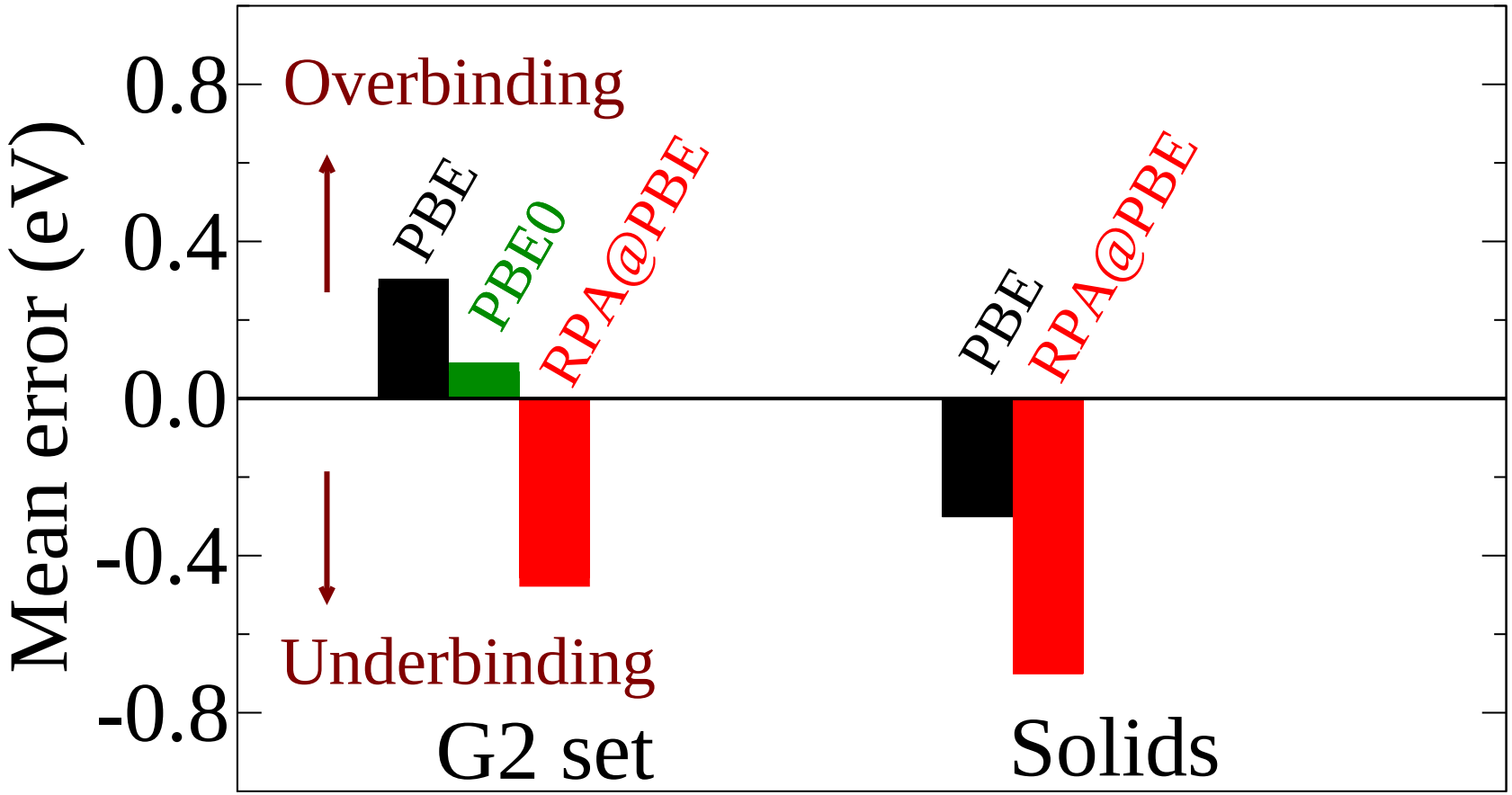
# Atomization energies




- RPA underestimates bond strengths

Paier *et al.*, J. Chem. Phys. **132**, 094103 (2010); **133**, 179902 (2010)
Harl, Schimka, and Kresse, Phys. Rev. B **81**, 115126 (2010)

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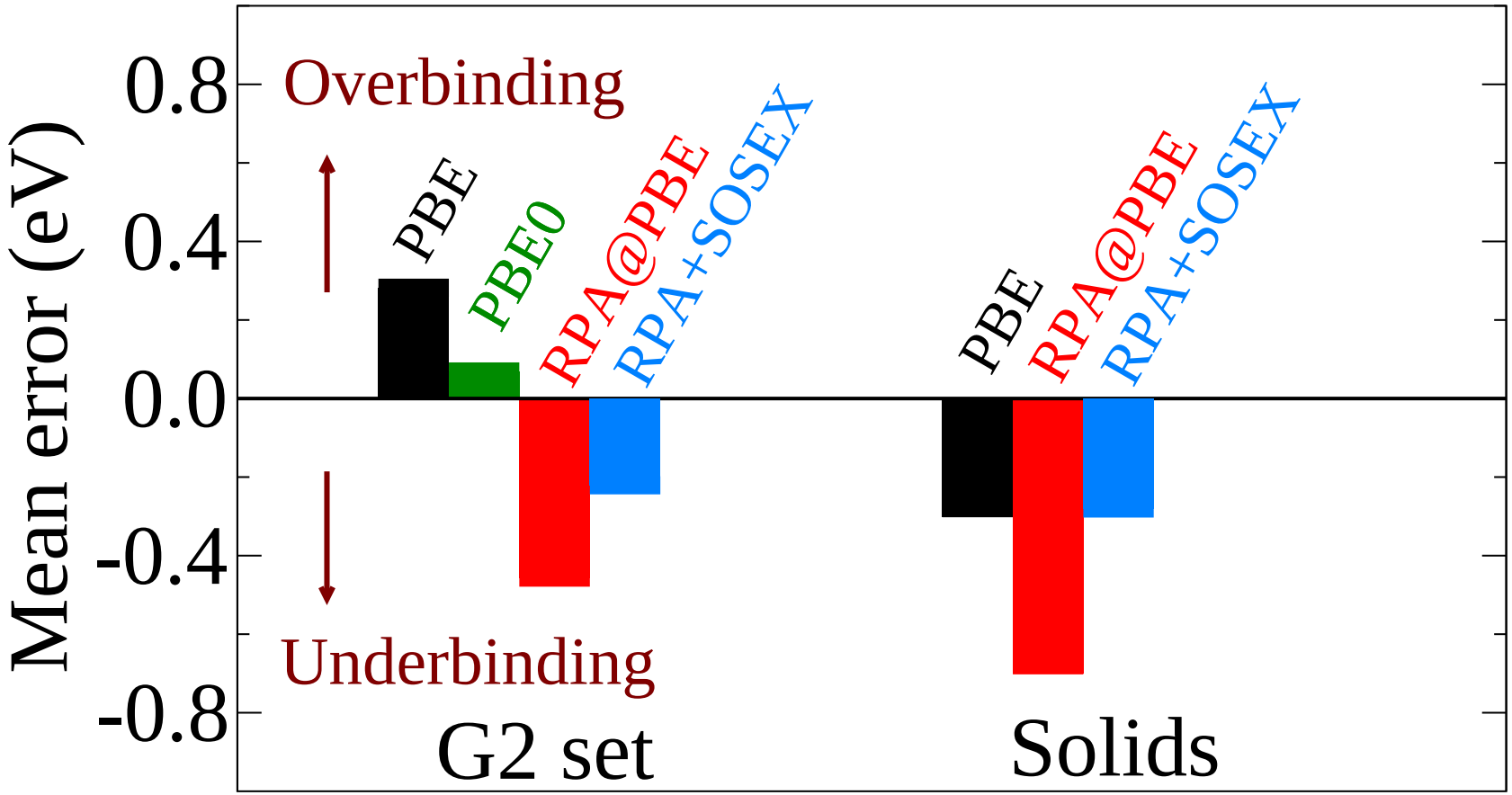


- SOSEX alleviates the underbinding problem


Paier *et al.*, J. Chem. Phys. **132**, 094103 (2010); **133**, 179902 (2010)
Harl, Schimka, and Kresse, Phys. Rev. B **81**, 115126 (2010)
Paier *et al.*, arXiv:1111.0173

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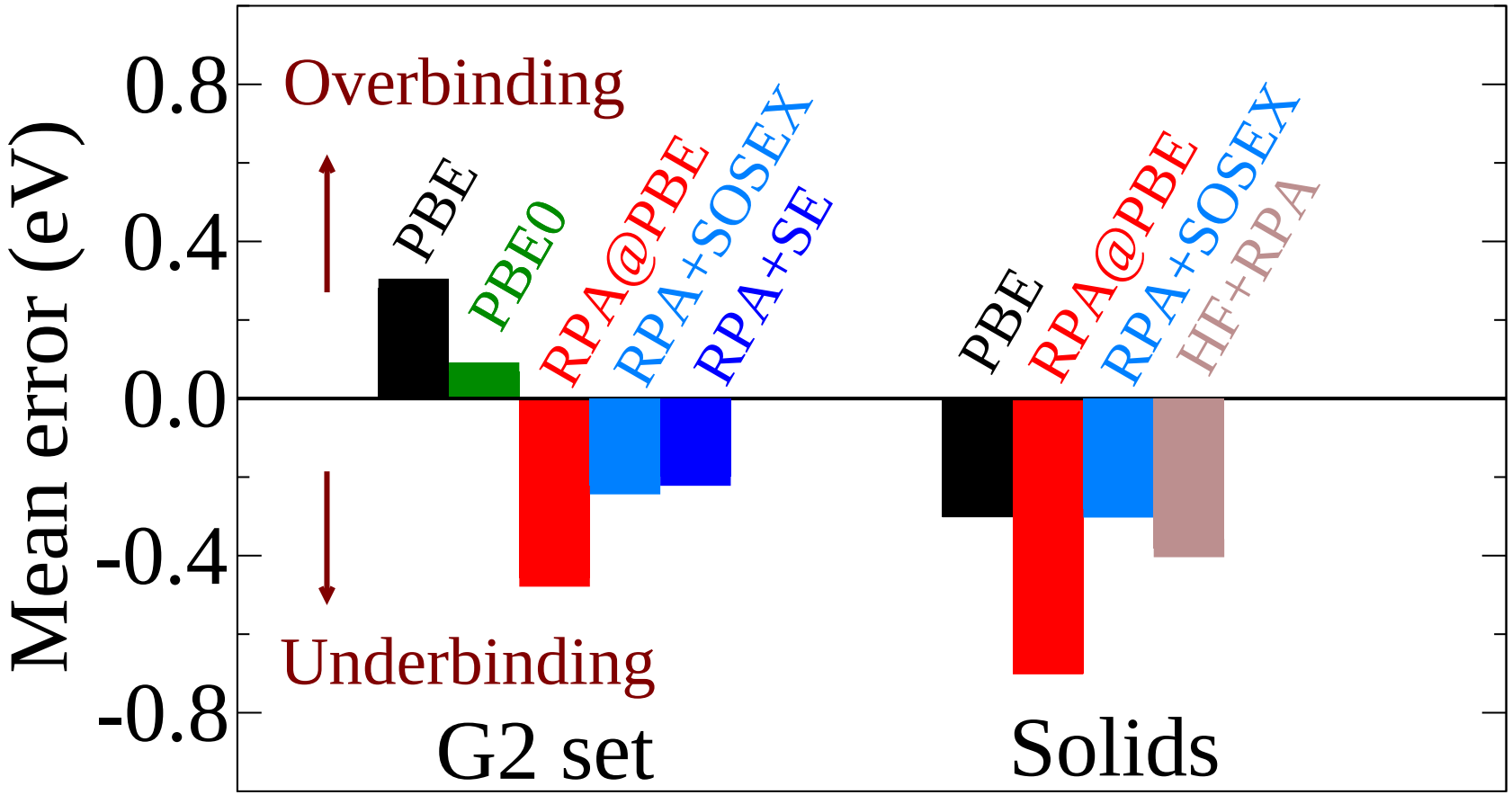


- "HF+RPA": EX@HF + RPA@PBE similar to
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Paier, Ren, Rinke, Scuseria, Grüneis, Kresse, and Scheffler, NJP **14**, 043002 (2012)
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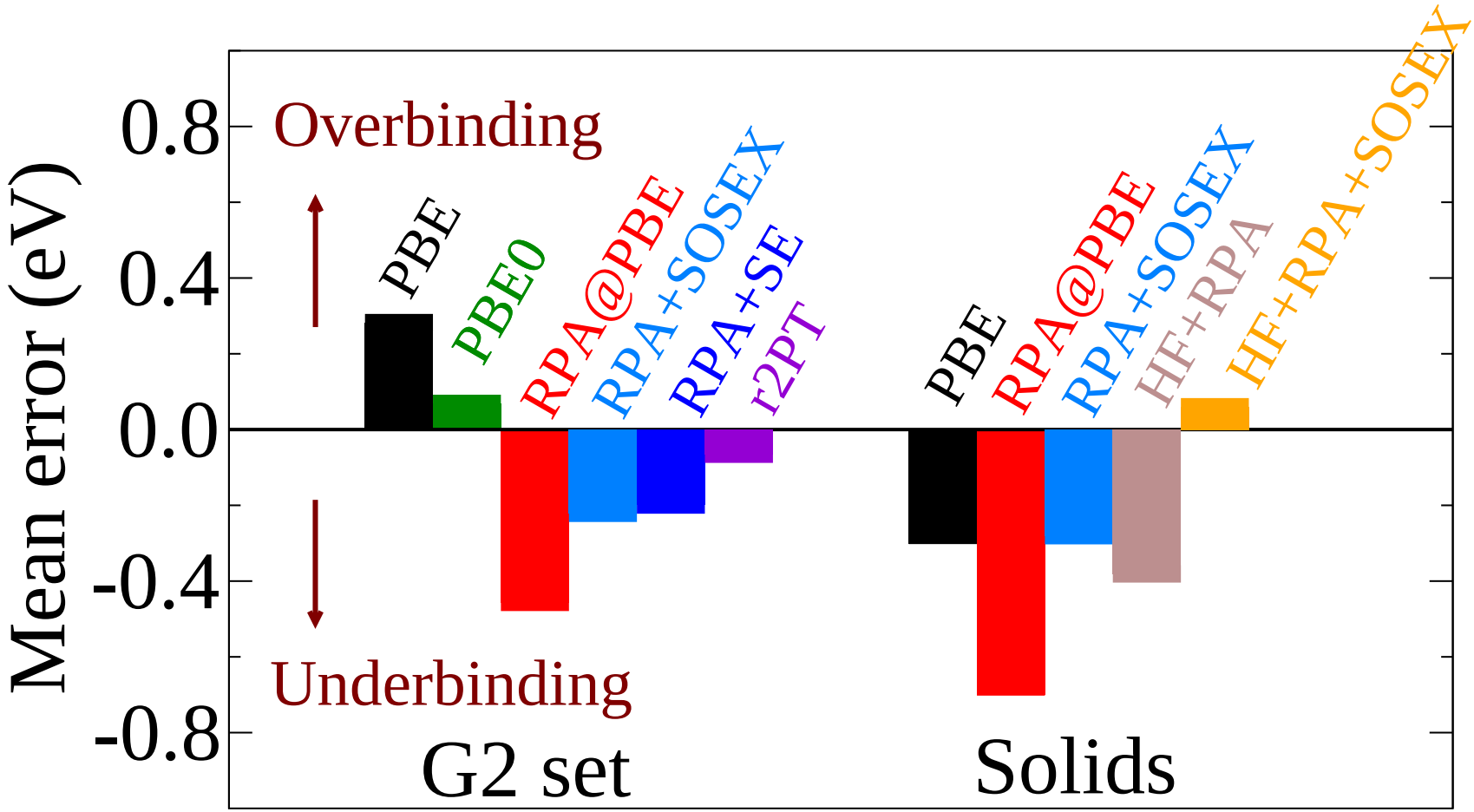


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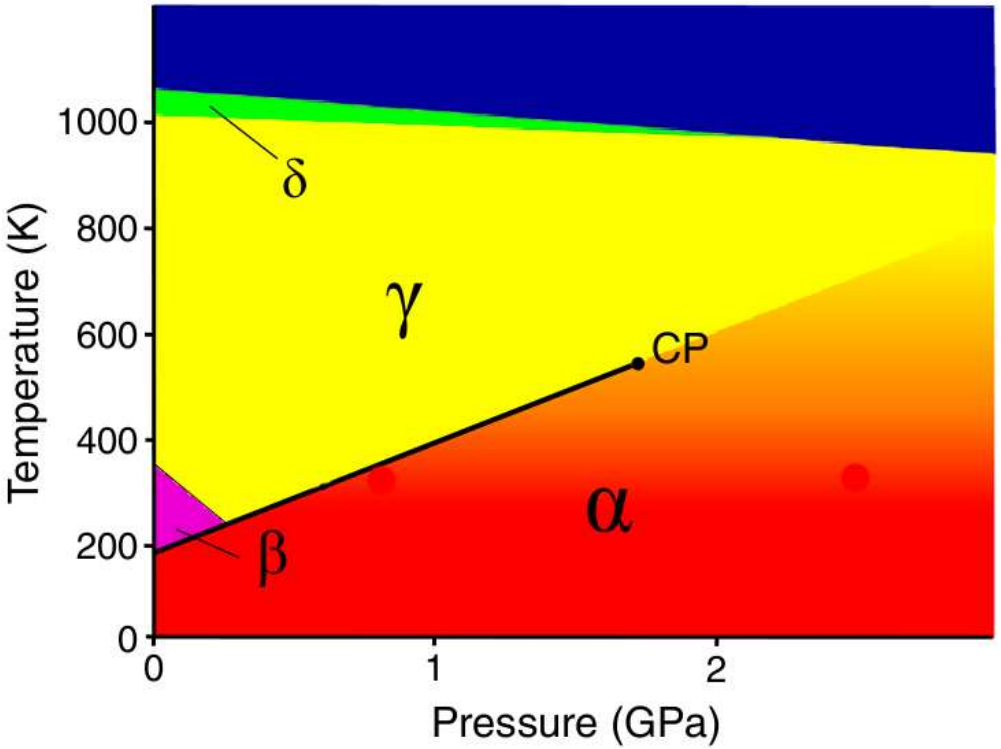
# The $f$-electron system Cerium

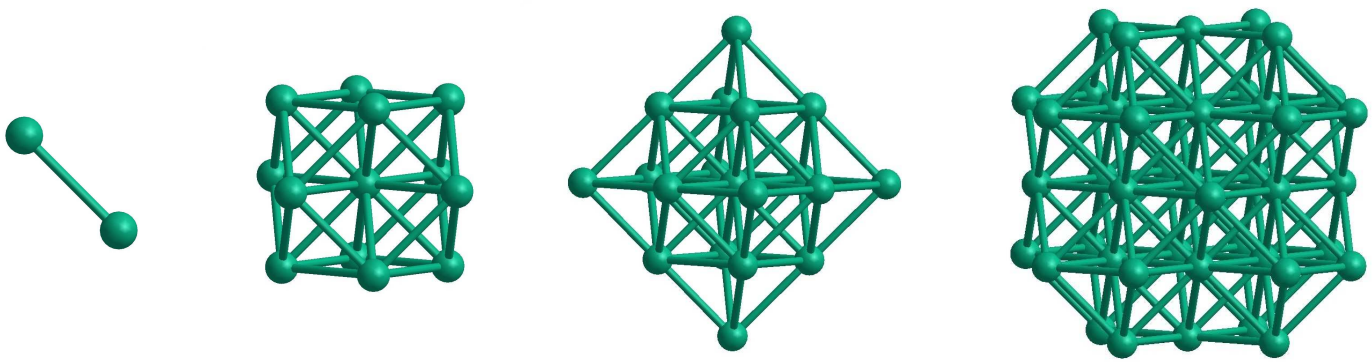



- iso-structural (fcc-fcc) $\alpha$-$\gamma$ phase transition
- accompanied by large (15%-17%) volume collapse

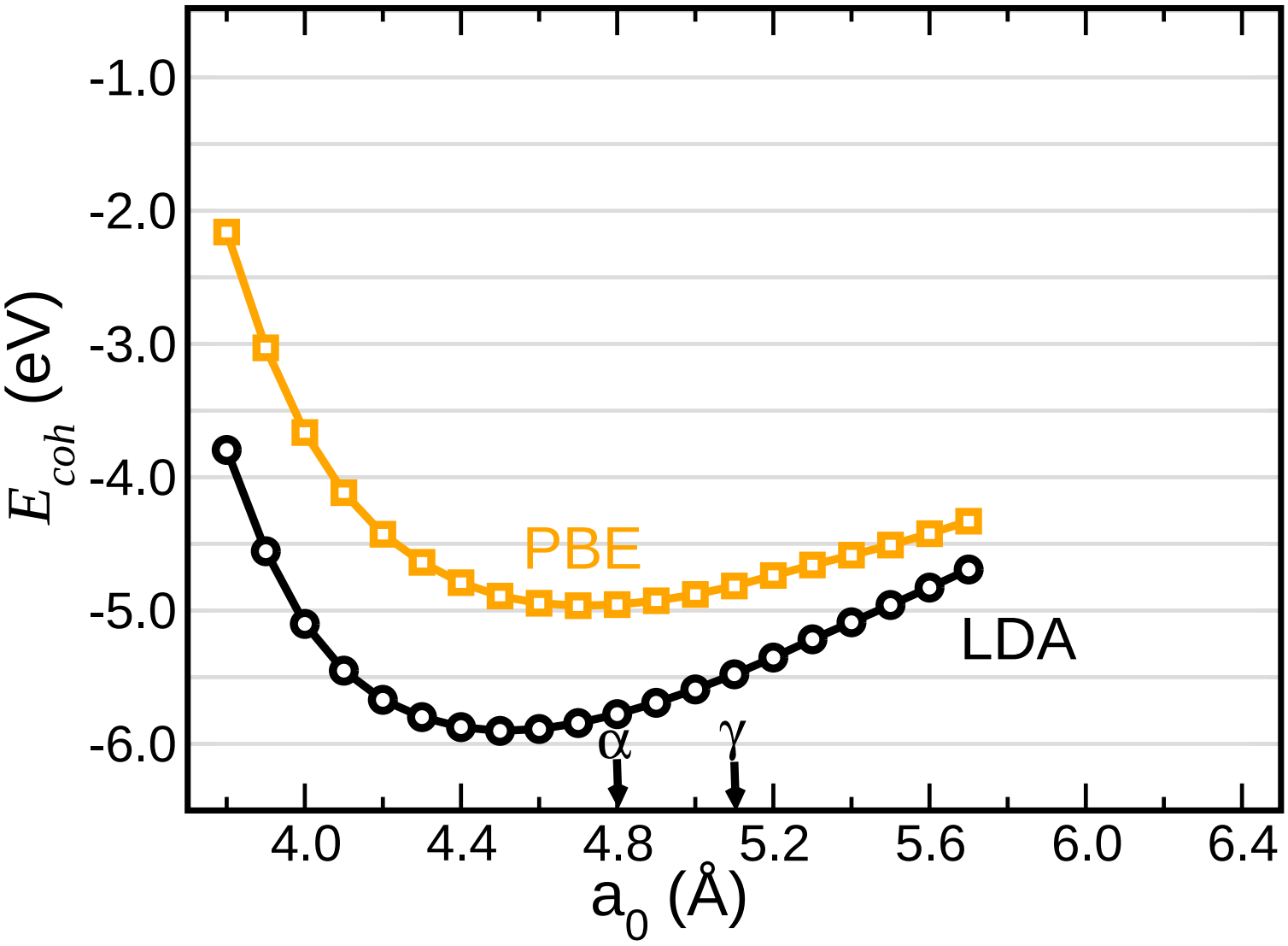
- LDA/GGA capture only low-volume ($\alpha$) phase
- LDA+$U$/SIC-LDA capture only high-volume ($\gamma$) phase
- LDA+DMFT so far restricted to high temperature

# Cerium from first principles

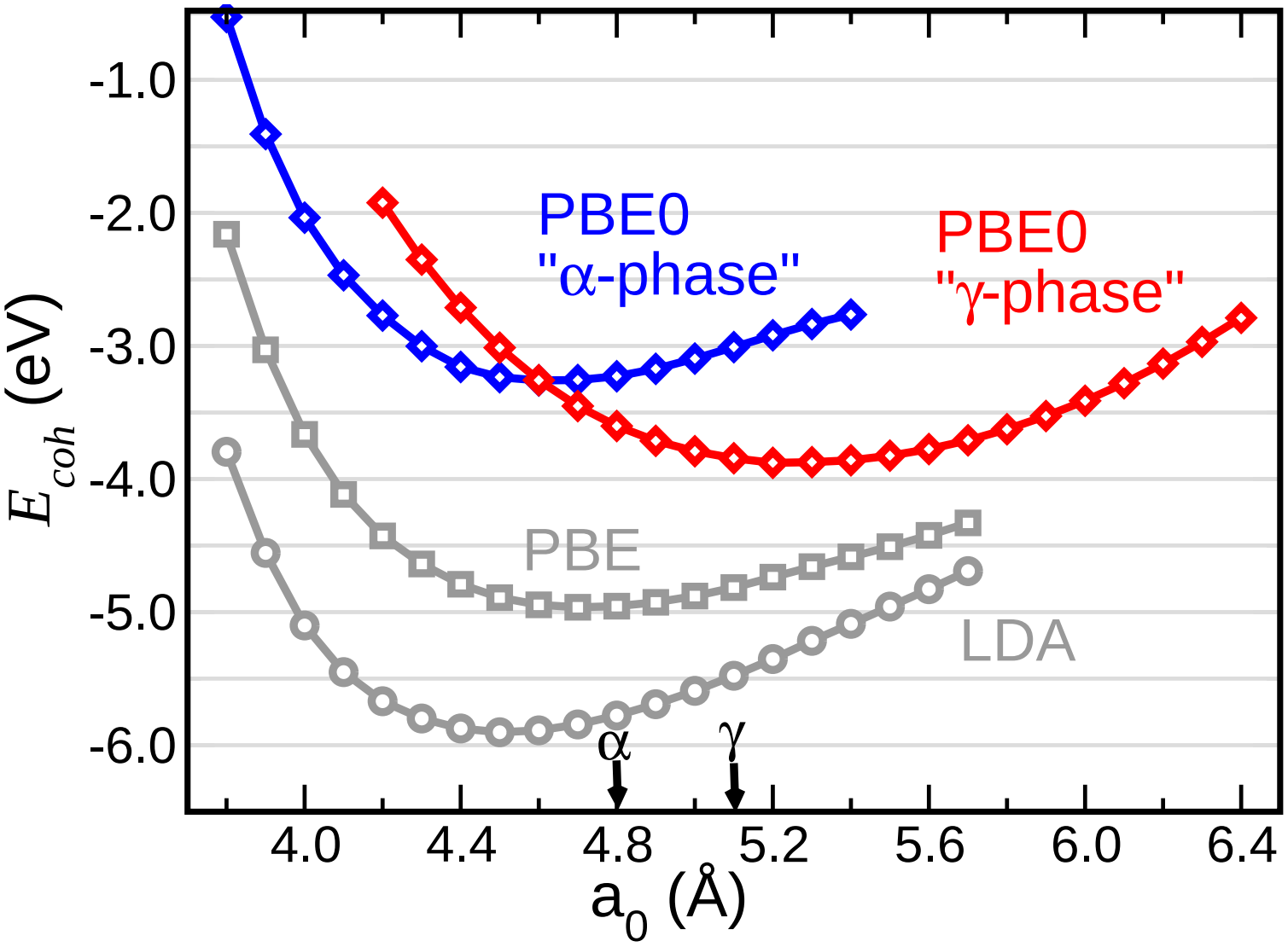
- All electrons are treated on the same quantum mechanical level
- hybrid functional PBE0
  - 25% exact exchange
  - reduces self-interaction error
- (EX+cRPA)@PBE0
  - physically meaningful screening
  - compatible with $GW$ approach
  - cluster extrapolation approach



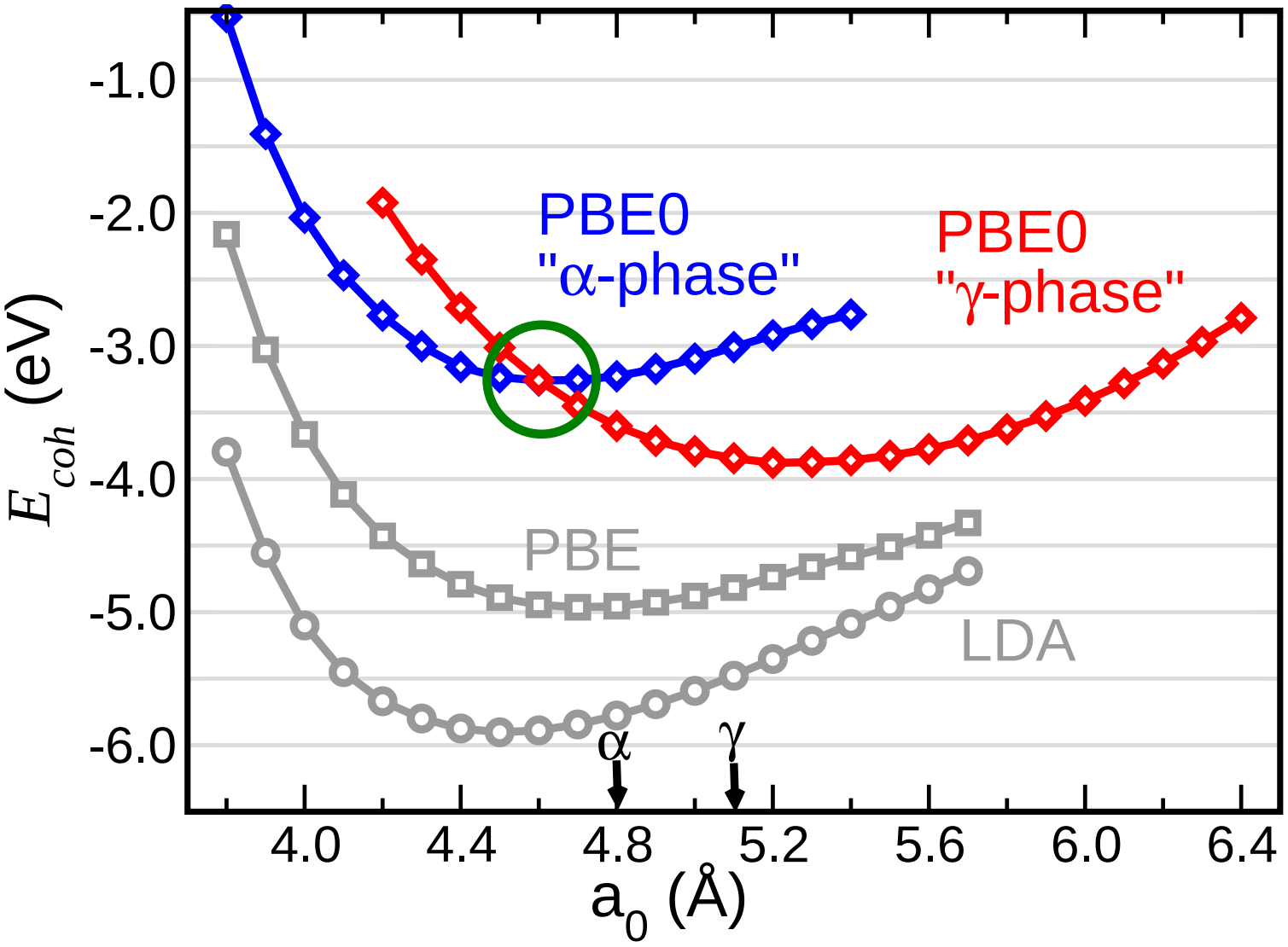
# Cerium - cohesive energy



# Cerium - cohesive energy

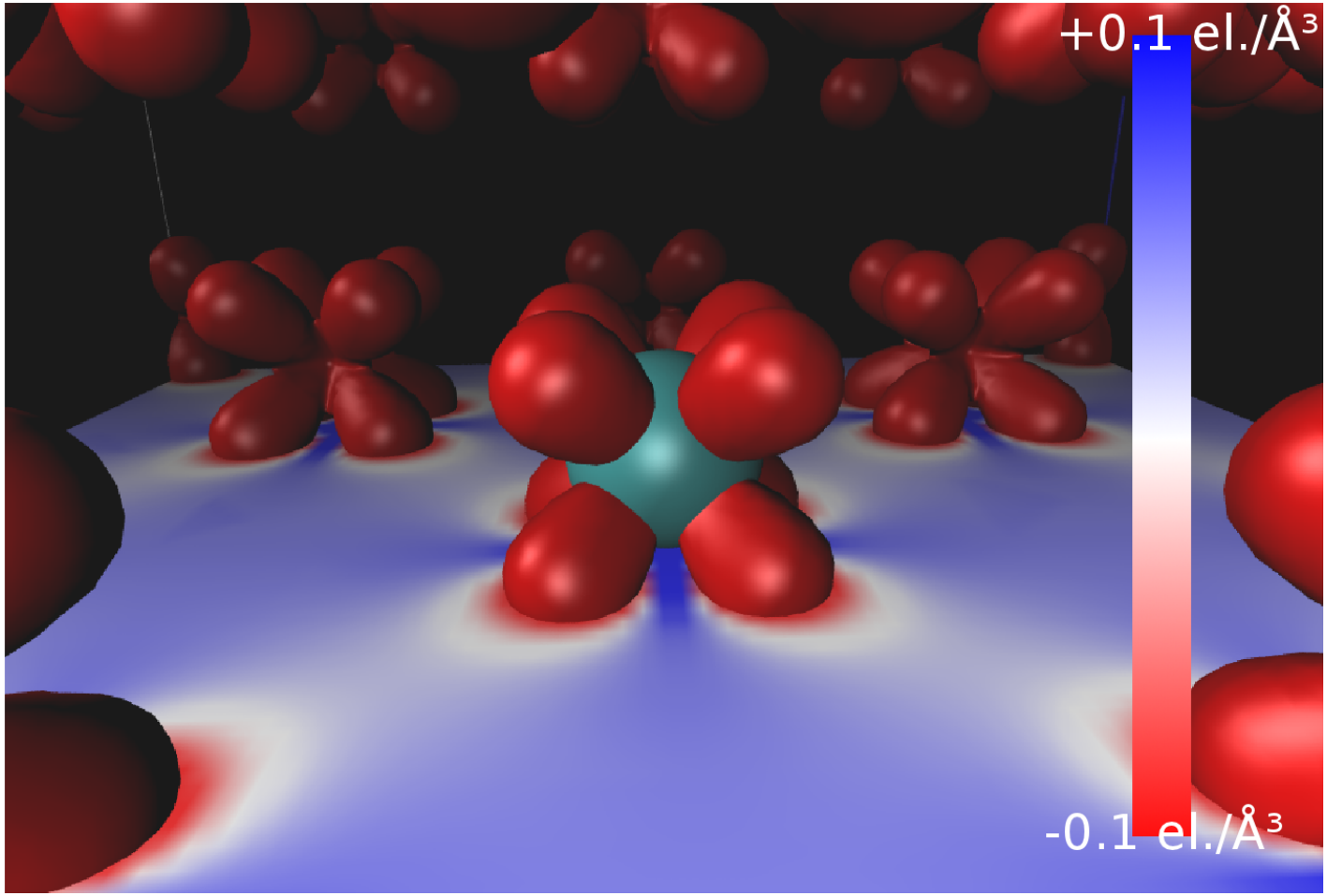


# Cerium - cohesive energy



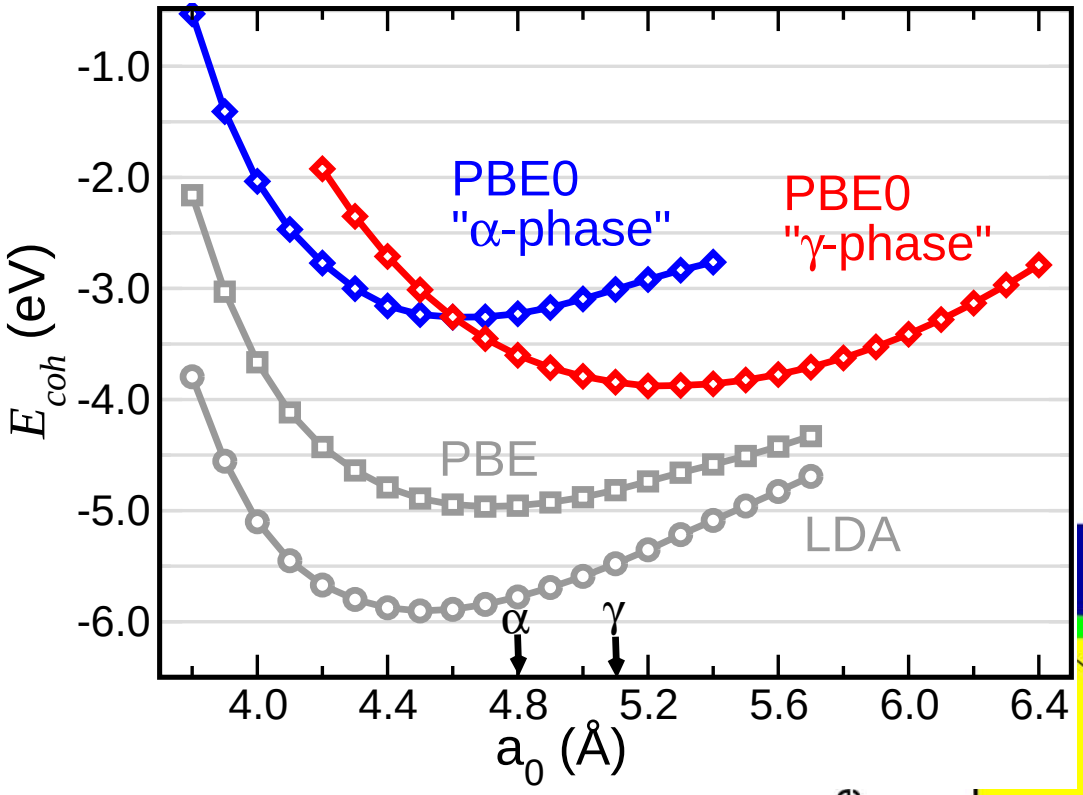
# Cerium - electronic structure

$n(\alpha) - n(\gamma)$ at a=4.6Å

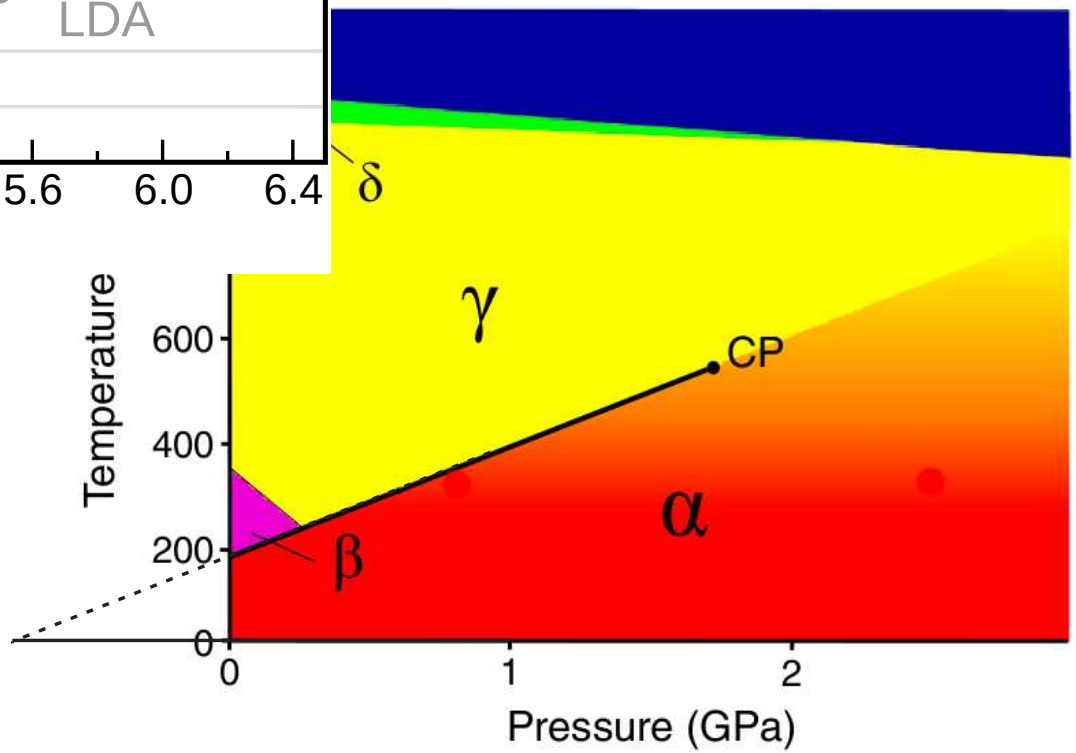



- $f$-electrons more localized in $\gamma$-phase

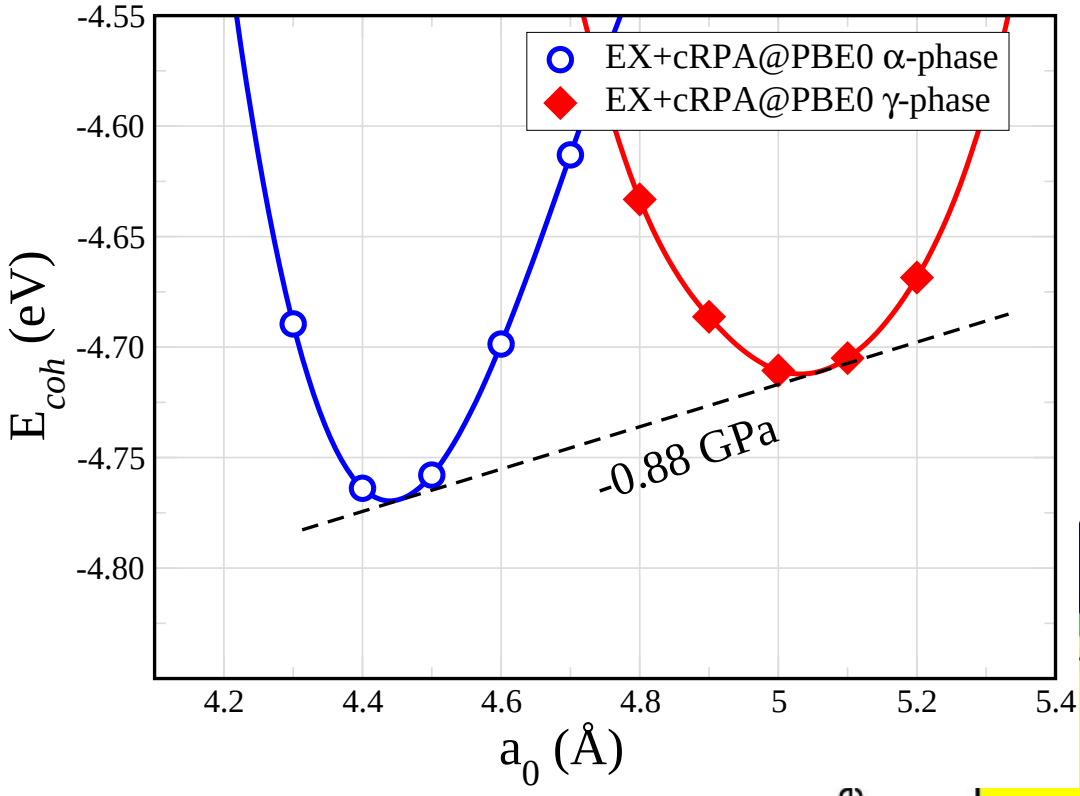
# Cerium - cohesive energy



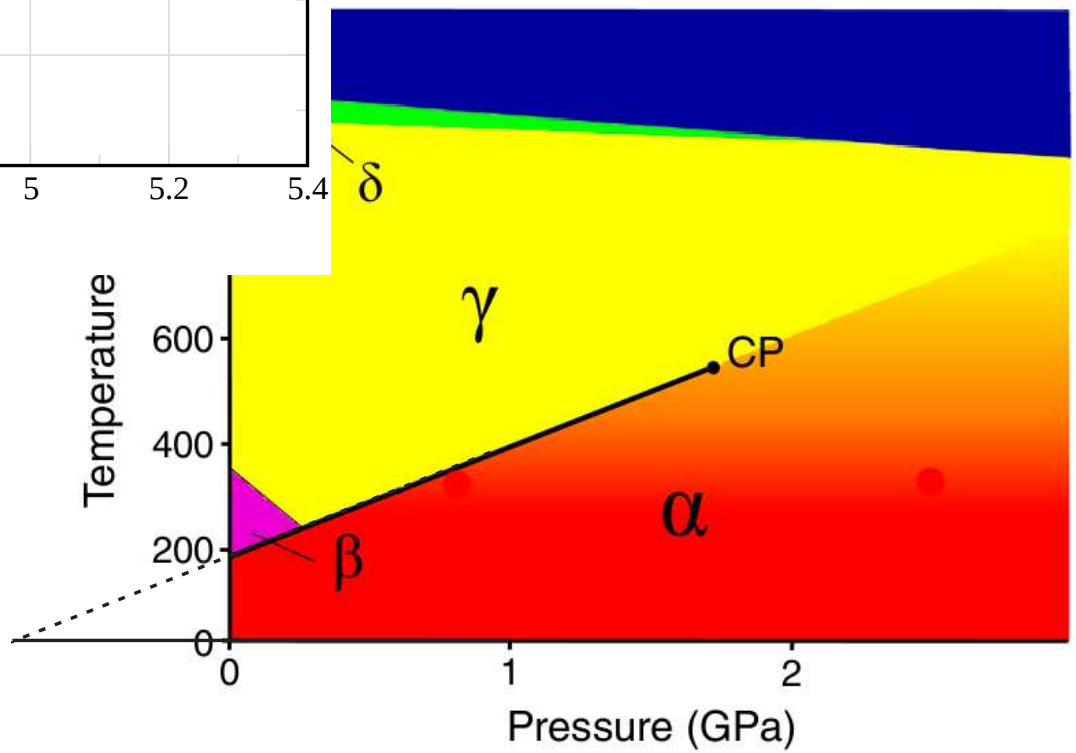

- wrong phase ordering



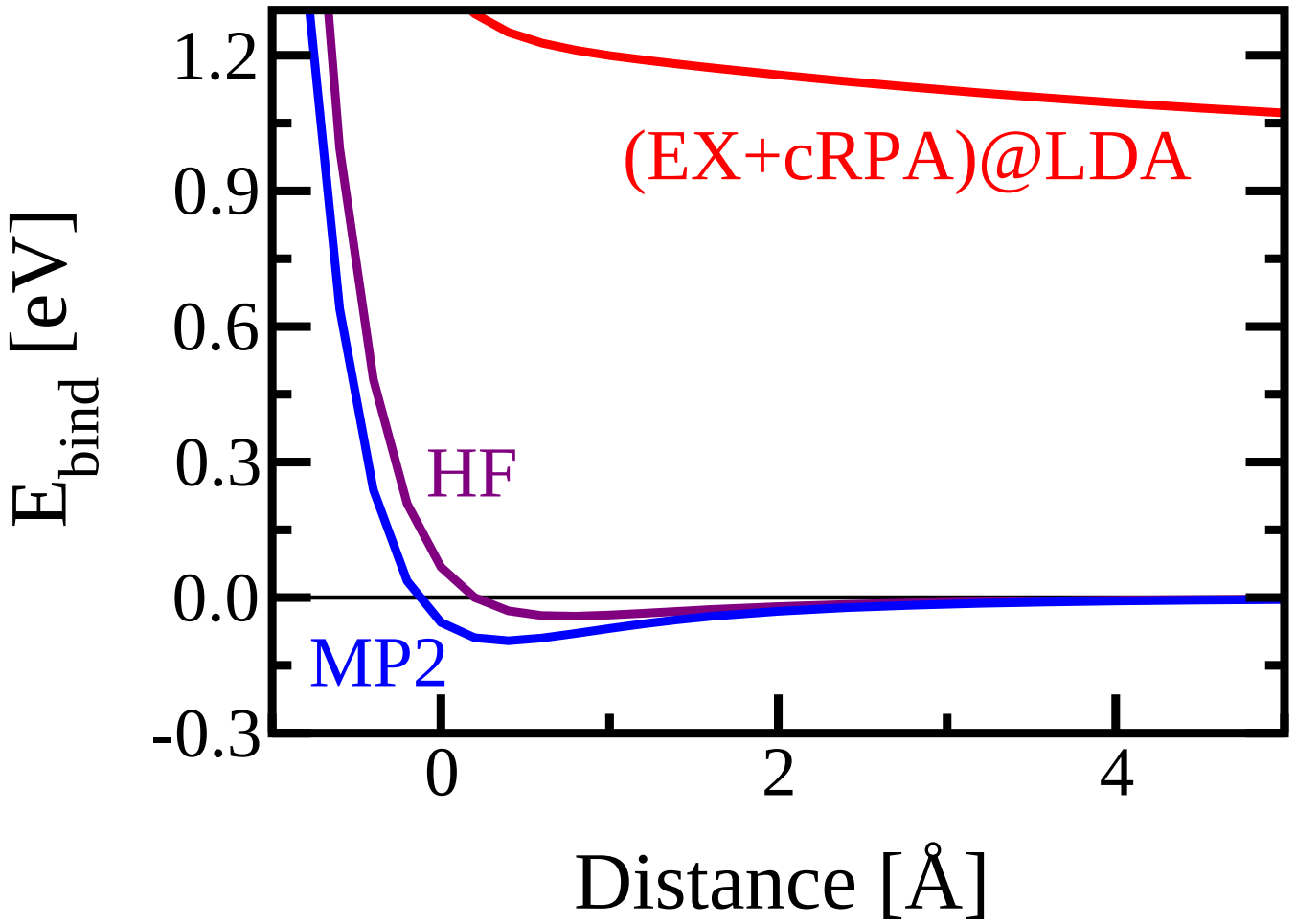
# Cerium - cohesive energy

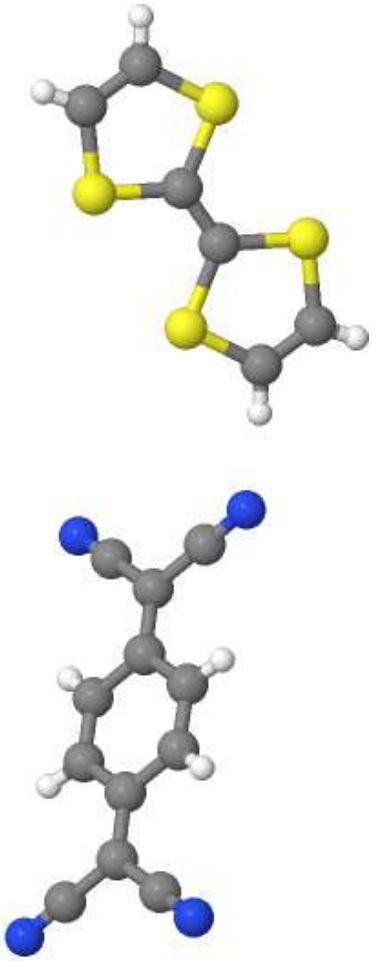



- correct phase ordering
- results for a $Ce_{19}$ cluster



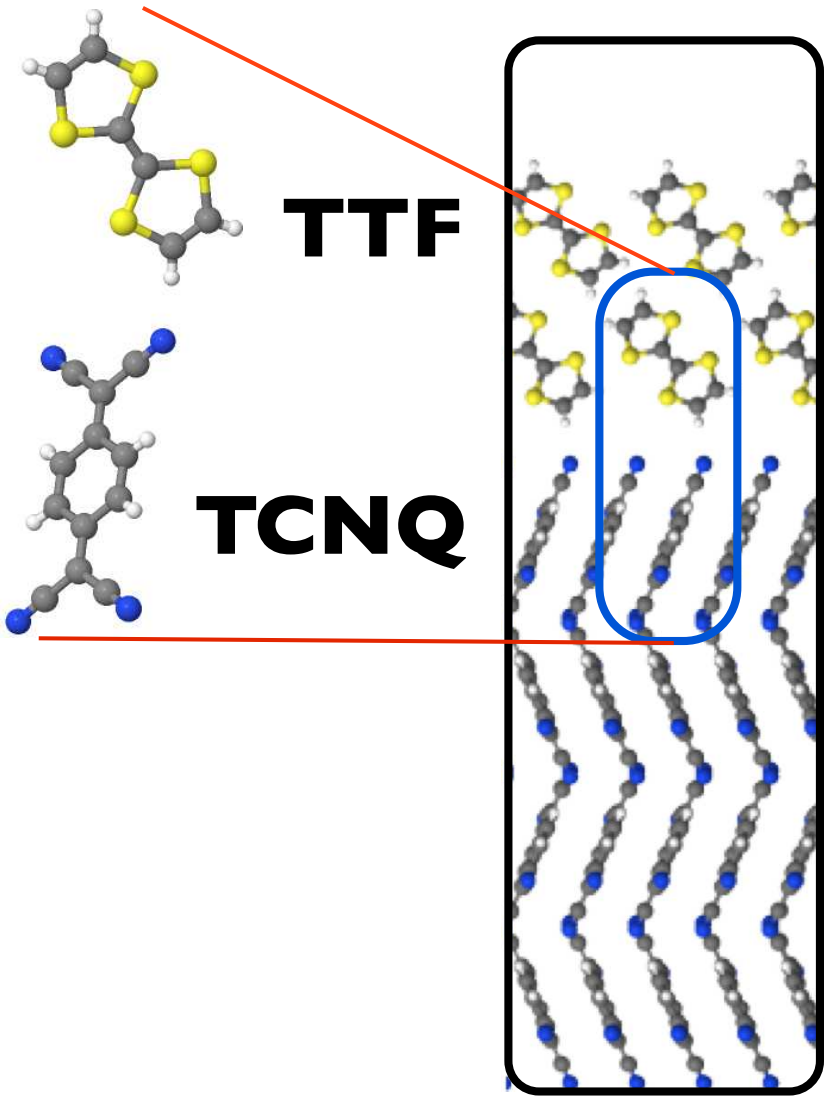
# TTF/TCNQ dimer at infinite separation



# Electron gas at TTF/TCNQ interface

- TTF and TCNQ crystals have large band gap
- but 2 dimensional electron gas observed at interface

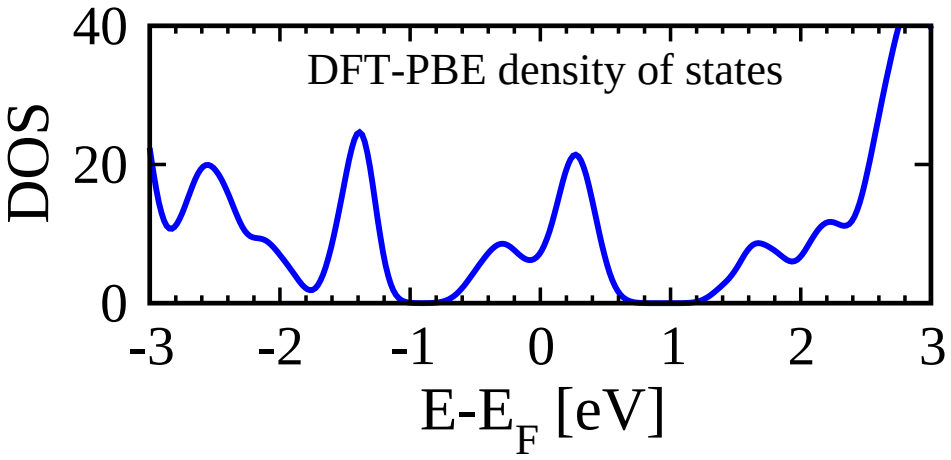


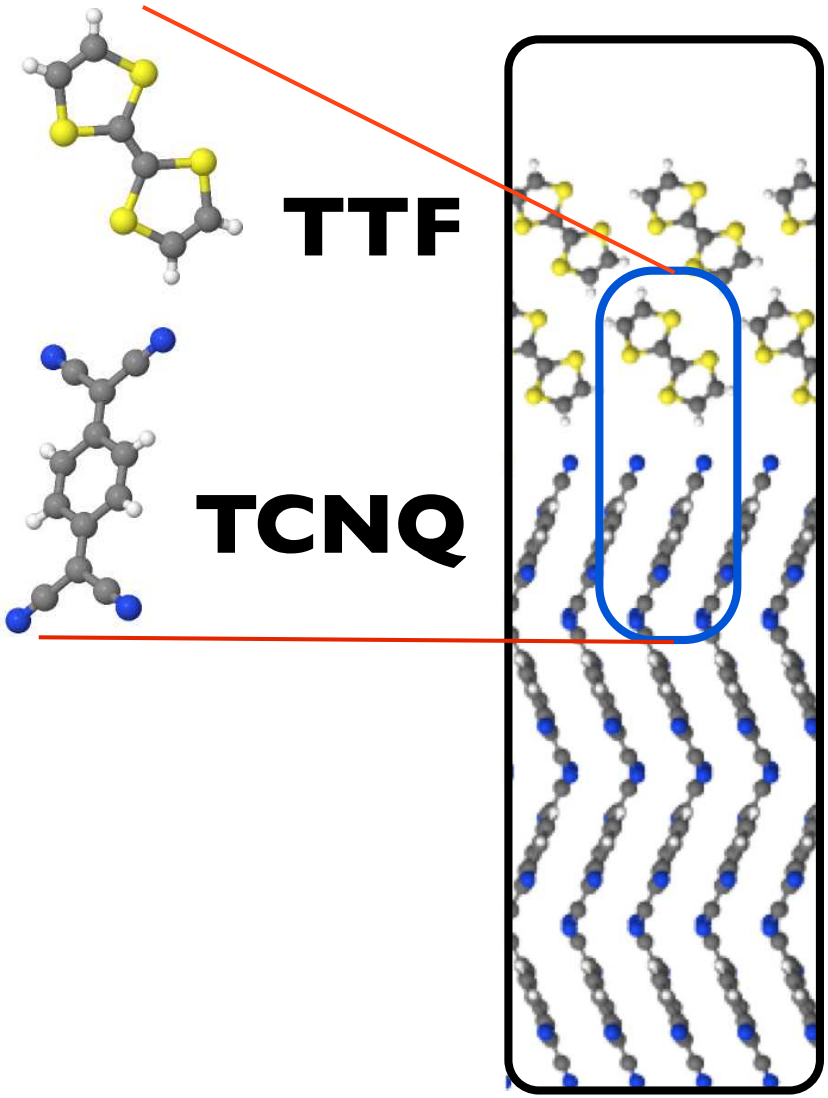

Metallic conduction at organic charge-transfer interfaces

HELENA ALVES, ANNA S. MOLINARI, HANGXING XIE AND ALBERTO F. MORPURGO
Kavli Institute of Nanoscience, Delft University of Technology, Lorentzweg 1, 2628 CJ Delft, The Netherlands
Nat. Mat. 7, 574 (2008)

What is the origin?

# Electron gas at TTF/TCNQ interface

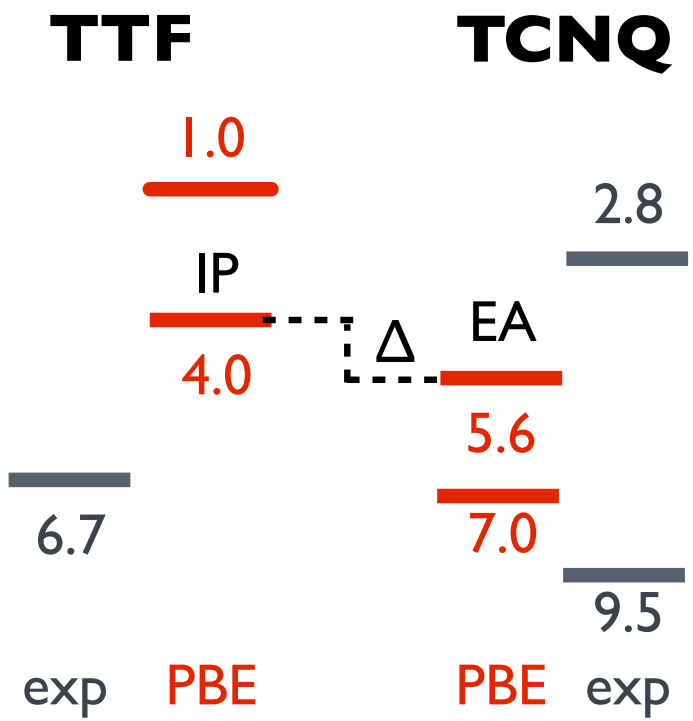


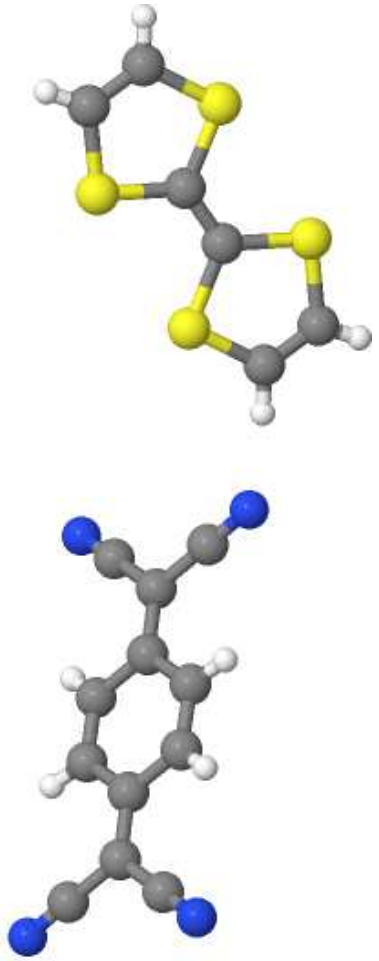




DFT-PBE:

- predicts metallic interface
- 0.12 e/molecule charge transfer to TCNQ
- in seeming agreement with experiment

# TTF/TCNQ dimer at infinite separation



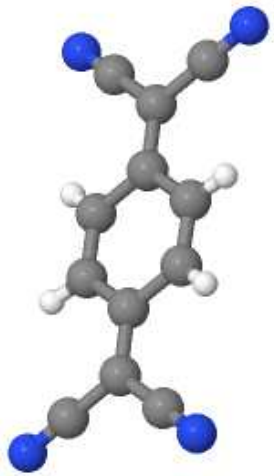
- IP(TTF) $>$ EA(TCNQ)
- erroneous charge transfer

# TTF/TCNQ dimer at infinite separation

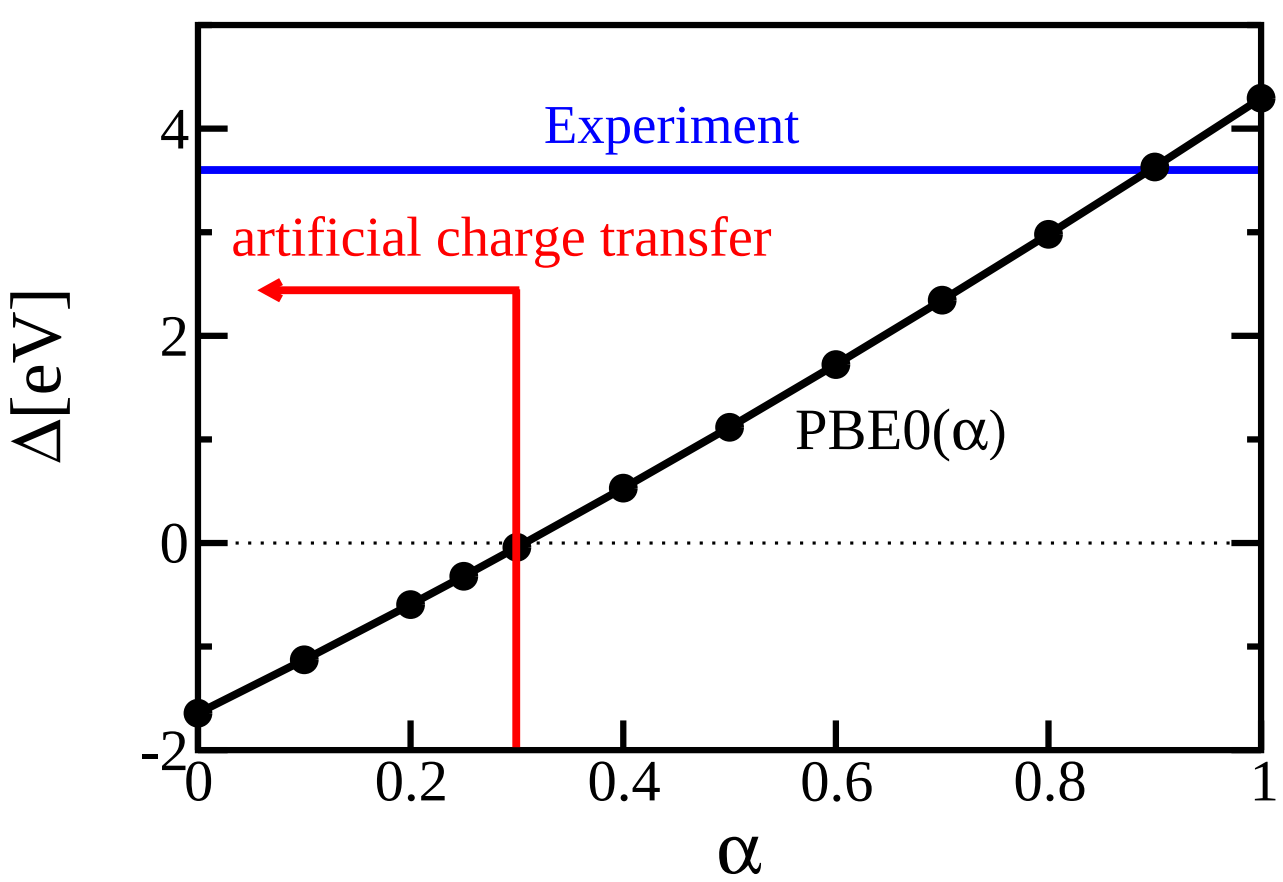
- culprit: self-interaction error in PBE
- add Hartree-Fock (HF) exchange to remove self-interaction

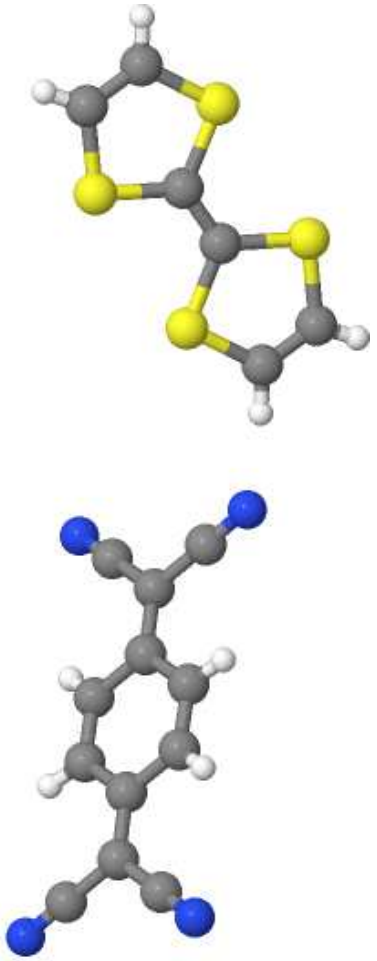
$\Rightarrow$ PBE0-like hybrid functional:

$$E_{xc}(\alpha) = \alpha(E_x^{\mathrm{HF}} - E_x^{\mathrm{PBE}}) + E_c^{\mathrm{PBE}}$$



# TTF/TCNQ dimer at infinite separation

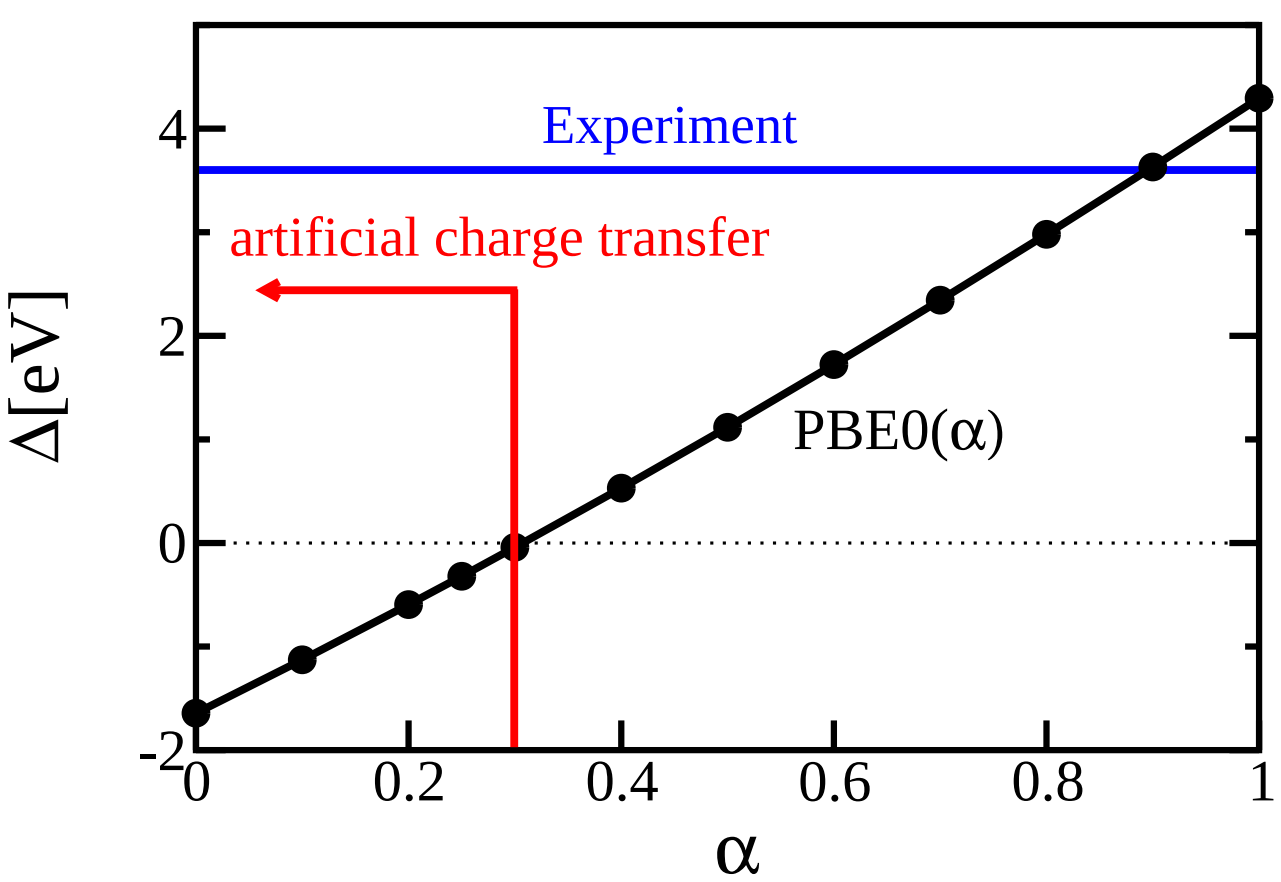


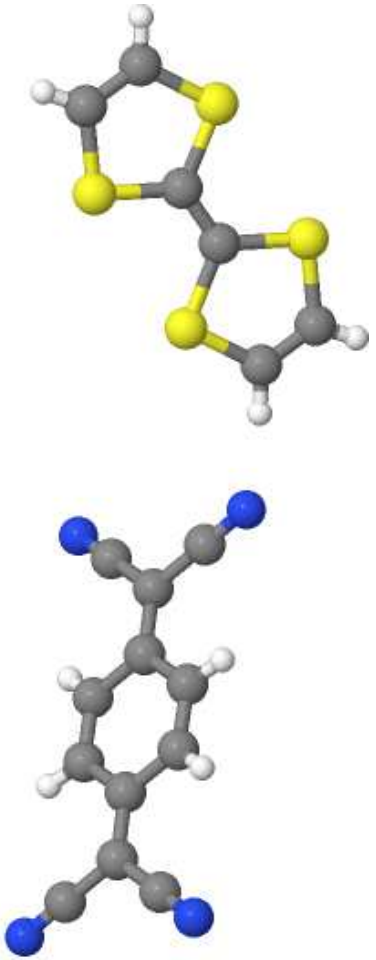



- PBE0-like hybrid functional:

$$E_{xc}(\alpha) = \alpha(E_x^{\mathrm{HF}} - E_x^{\mathrm{PBE}}) + E_c^{\mathrm{PBE}}$$

# TTF/TCNQ dimer at infinite separation

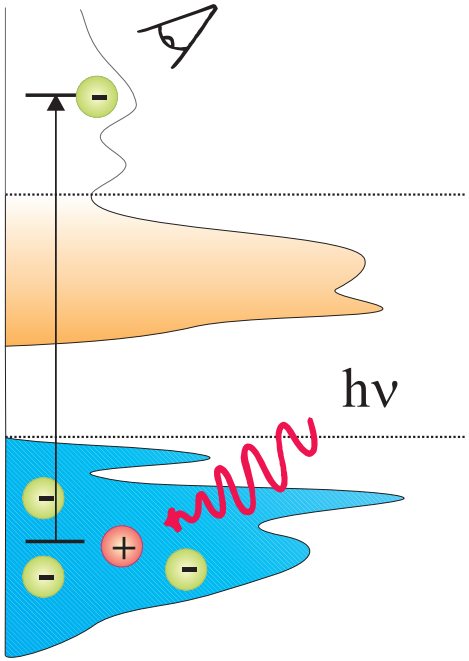


How to choose $\alpha$?

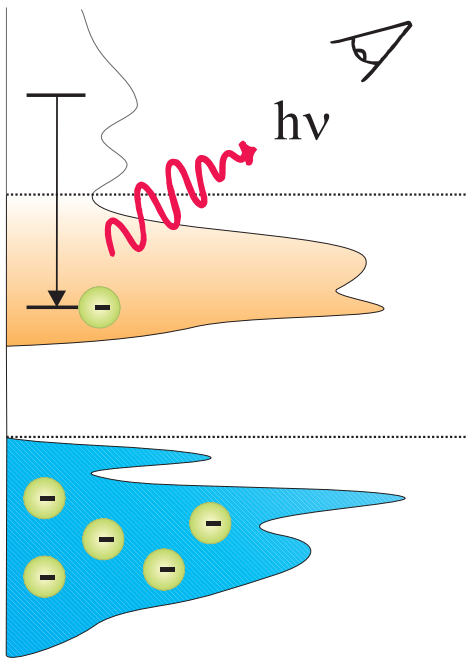
# Band structures: photo-electron spectroscopy

Photoemission



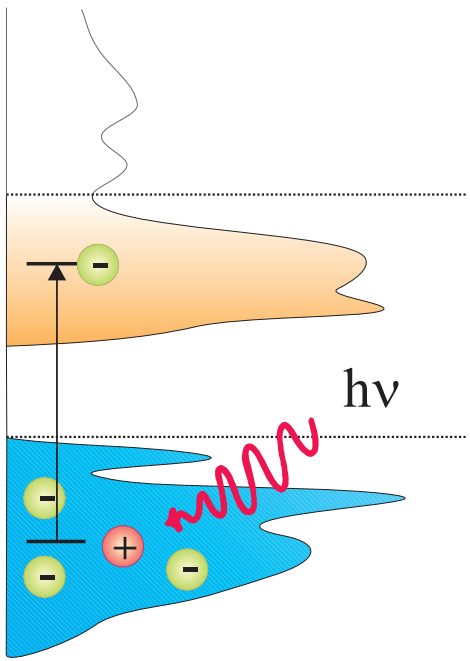

*GW*

Inverse Photoemission



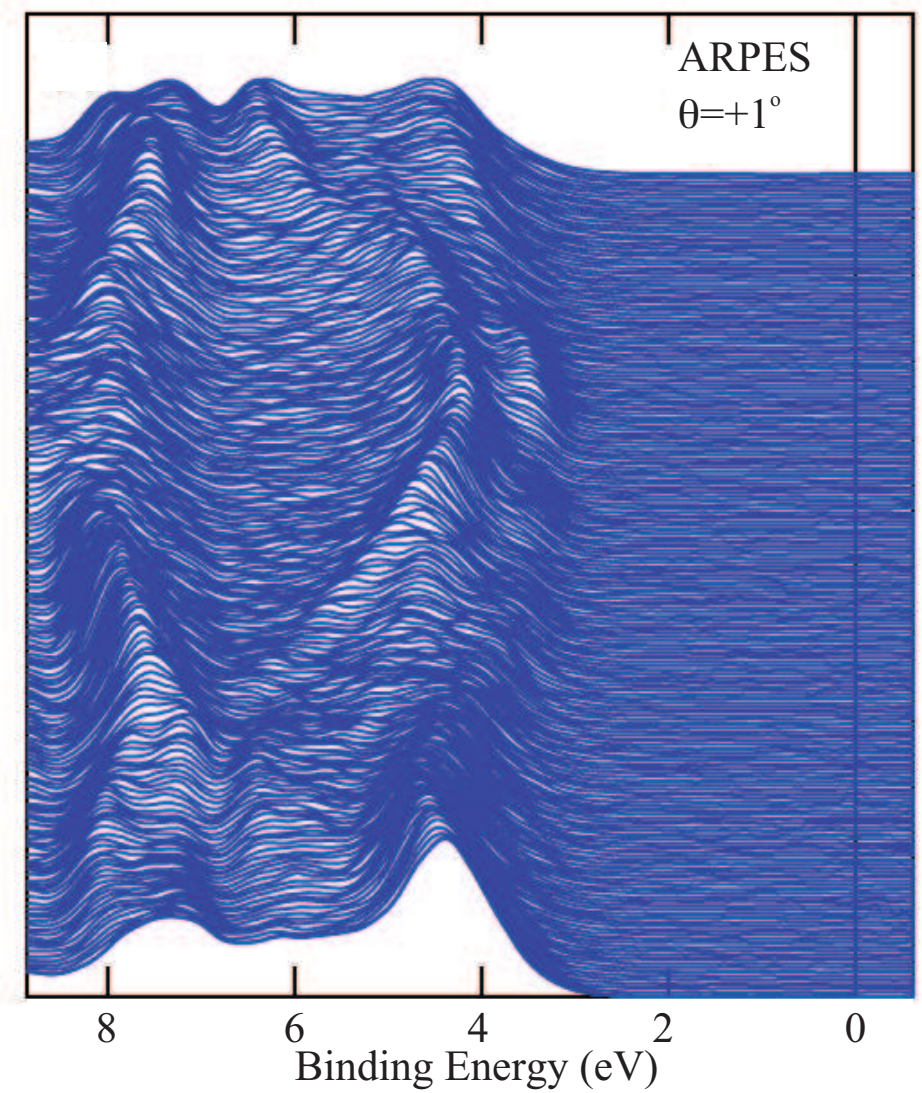

*GW*

Absorption



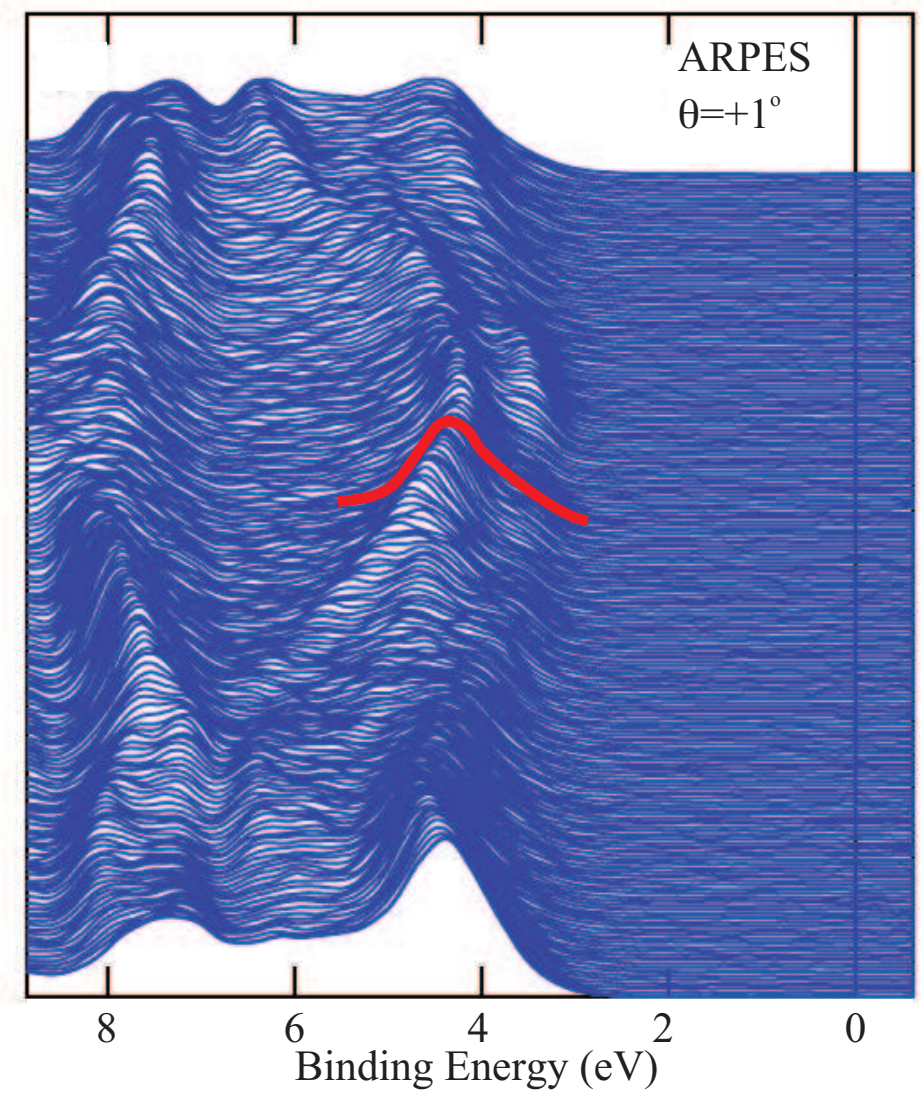

BSE
TDDFT

# Experimental: angle-resolved photoemission spectroscopy




Masaki Kobayashi, PhD dissertation

# Experimental: angle-resolved photoemission spectroscopy

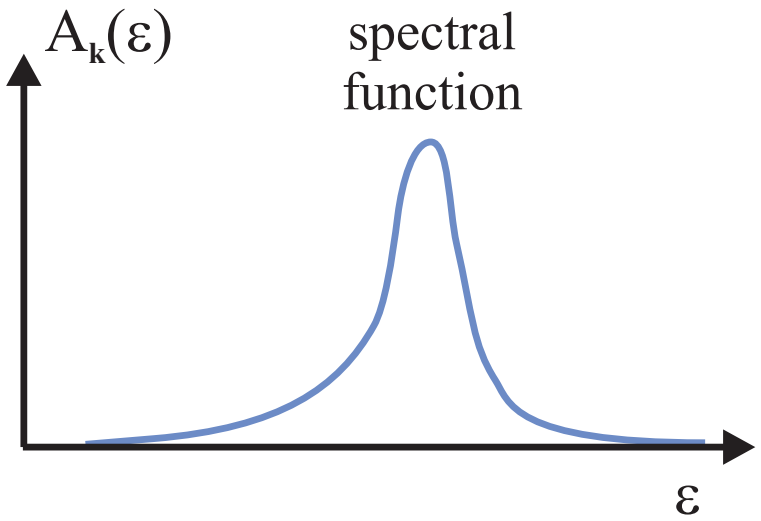



Masaki Kobayashi, PhD dissertation

# ARPES vs $GW$: the quasiparticle concept

**Quasiparticle:**

- single-particle like excitation

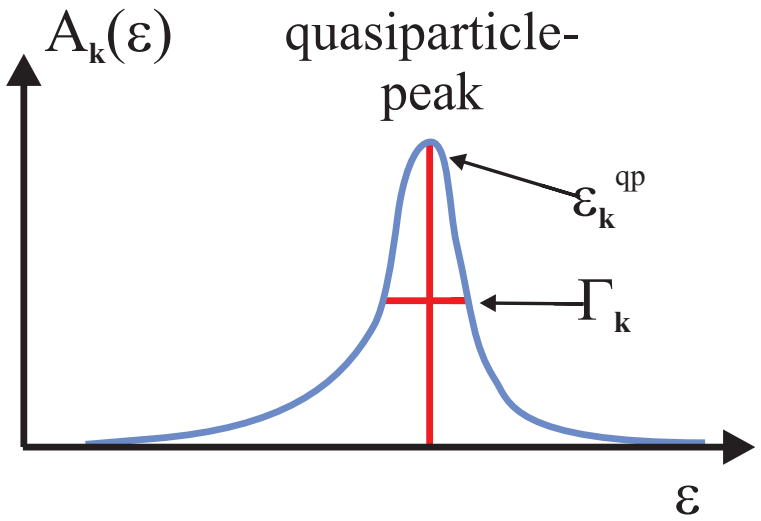


# ARPES vs $GW$: the quasiparticle concept

## Quasiparticle:

- single-particle like excitation
- $A_{\mathbf{k}}(\epsilon) = ImG_{\mathbf{k}}(\epsilon) \approx \dfrac{Z_{\mathbf{k}}}{\epsilon - (\epsilon_{\mathbf{k}} + i\Gamma_{\mathbf{k}})}$

$\epsilon_{\mathbf{k}}$ : excitation energy
$\Gamma_{\mathbf{k}}$ : lifetime
$Z_{\mathbf{k}}$ : renormalisation



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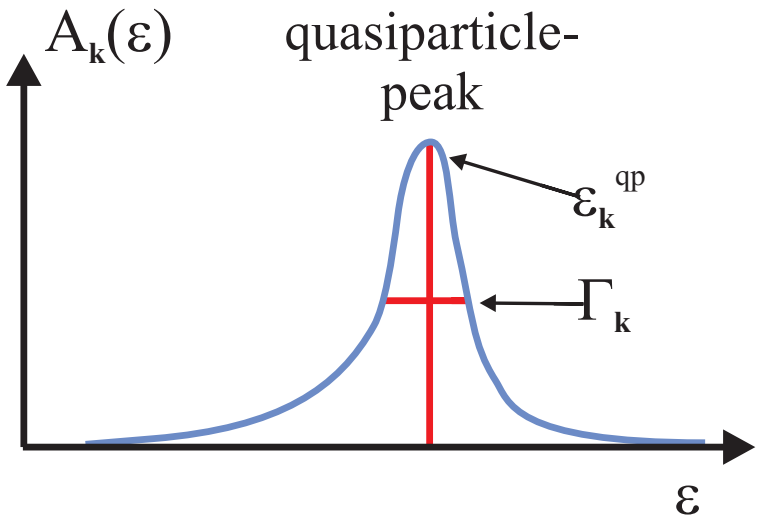


- Density-Functional Theory: $G_0$
- $GW$: $\chi_0 = iG_0G_0 \rightarrow W_0 = v/(1-\chi_0 v) \rightarrow \Sigma_0 = iG_0W_0$

$$G^{-1} = G_0^{-1} - \Sigma_0$$

# The screened Coulomb interaction $W$

## Work with screened coulomb interaction:

$$W(\mathbf{r},\mathbf{r}',t) = \int d\mathbf{r}'' \frac{\varepsilon^{-1}(\mathbf{r},\mathbf{r}'',t)}{|\mathbf{r}''-\mathbf{r}'|}$$

$\varepsilon(\mathbf{r},\mathbf{r}'',t)$: dielectric function

The challenge is to calculate $W(\mathbf{r},\mathbf{r}'',t)$ from first principles!

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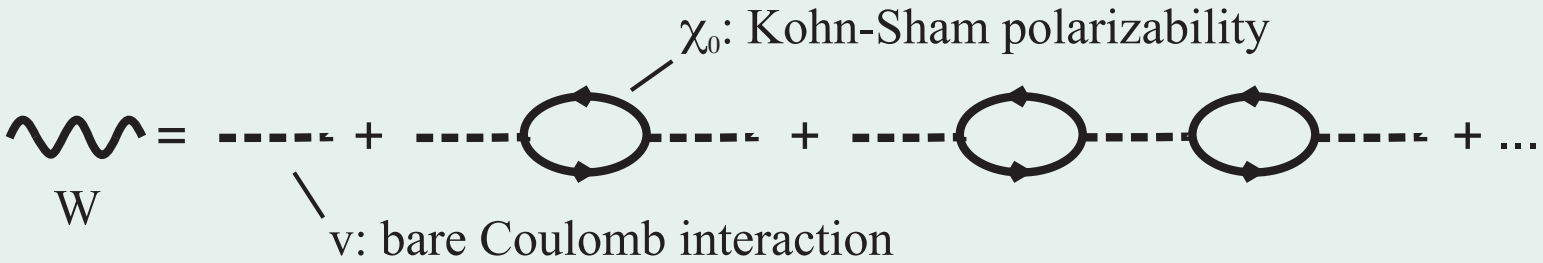
$\varepsilon(\mathbf{r},\mathbf{r}'',t)$: dielectric function

The challenge is to calculate $W(\mathbf{r},\mathbf{r}'',t)$ from first principles!

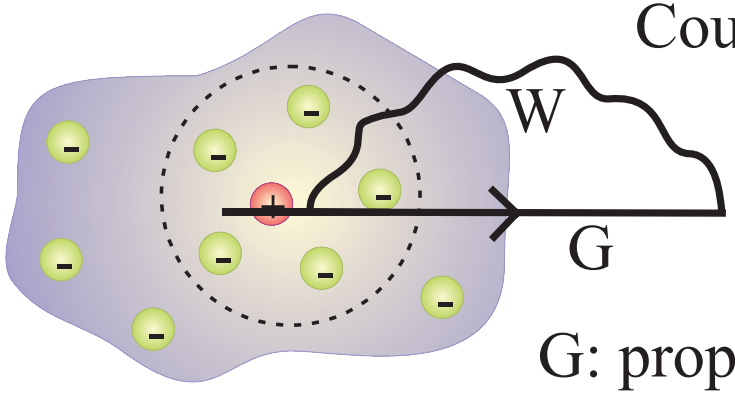
- we use random-phase approximation (RPA) for $W$:




- formally scales with (system size)$^4$

# From screening to quasiparticle energies

$\Sigma$=GW :




W: screened Coulomb

G: propagator

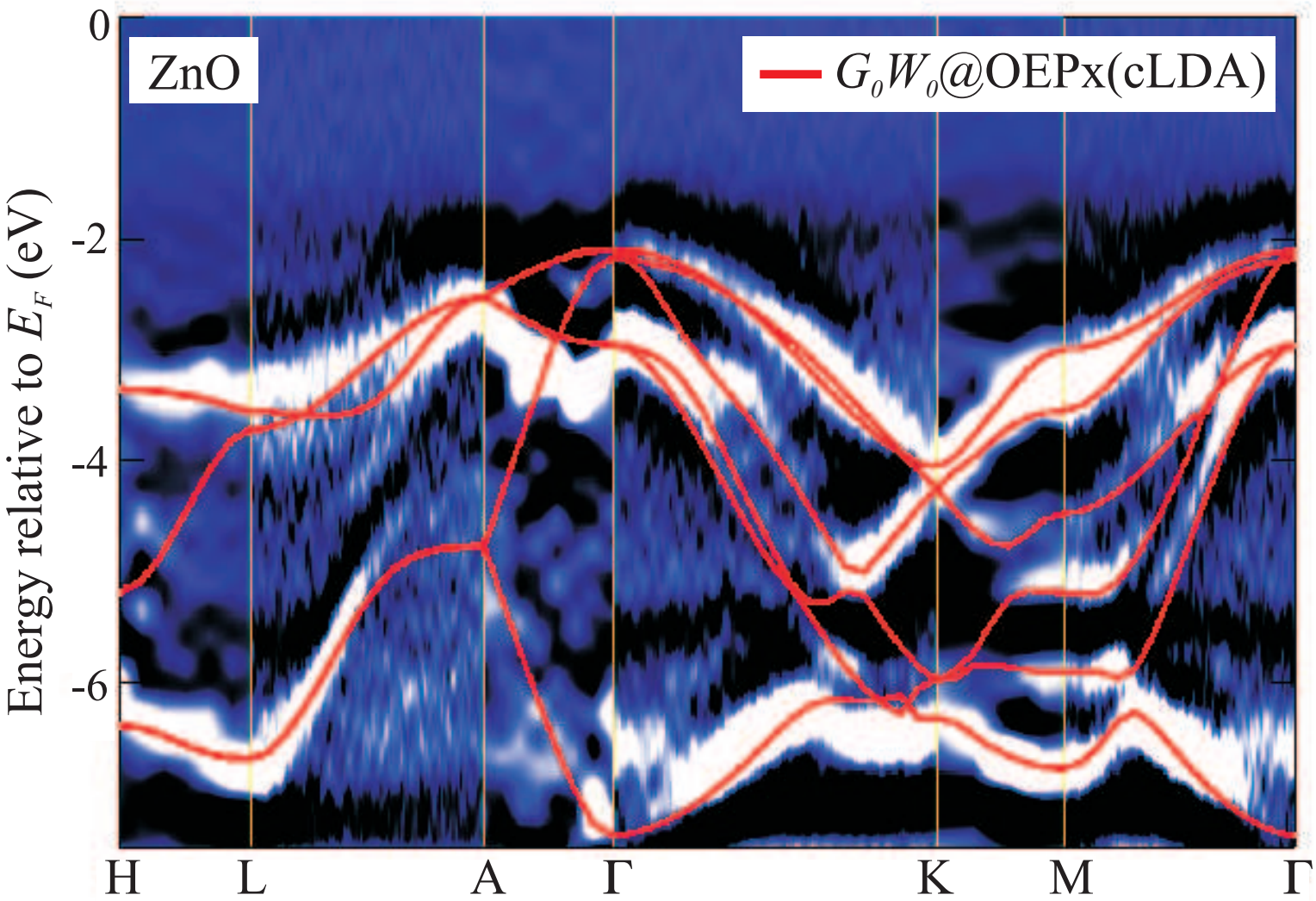
## Quasiparticle energies: $G_0W_0$ scheme

- electron addition and removal energies
- correction to DFT eigenvalues $\epsilon^{\mathrm{DFT}}_{n\mathbf{k}}$:

$$\epsilon^{qp}_{n\mathbf{k}} = \epsilon^{\mathrm{DFT}}_{n\mathbf{k}} + \Sigma^{G_0W_0}_{n\mathbf{k}}(\epsilon^{qp}_{n\mathbf{k}}) - v^{xc}_{n\mathbf{k}}$$

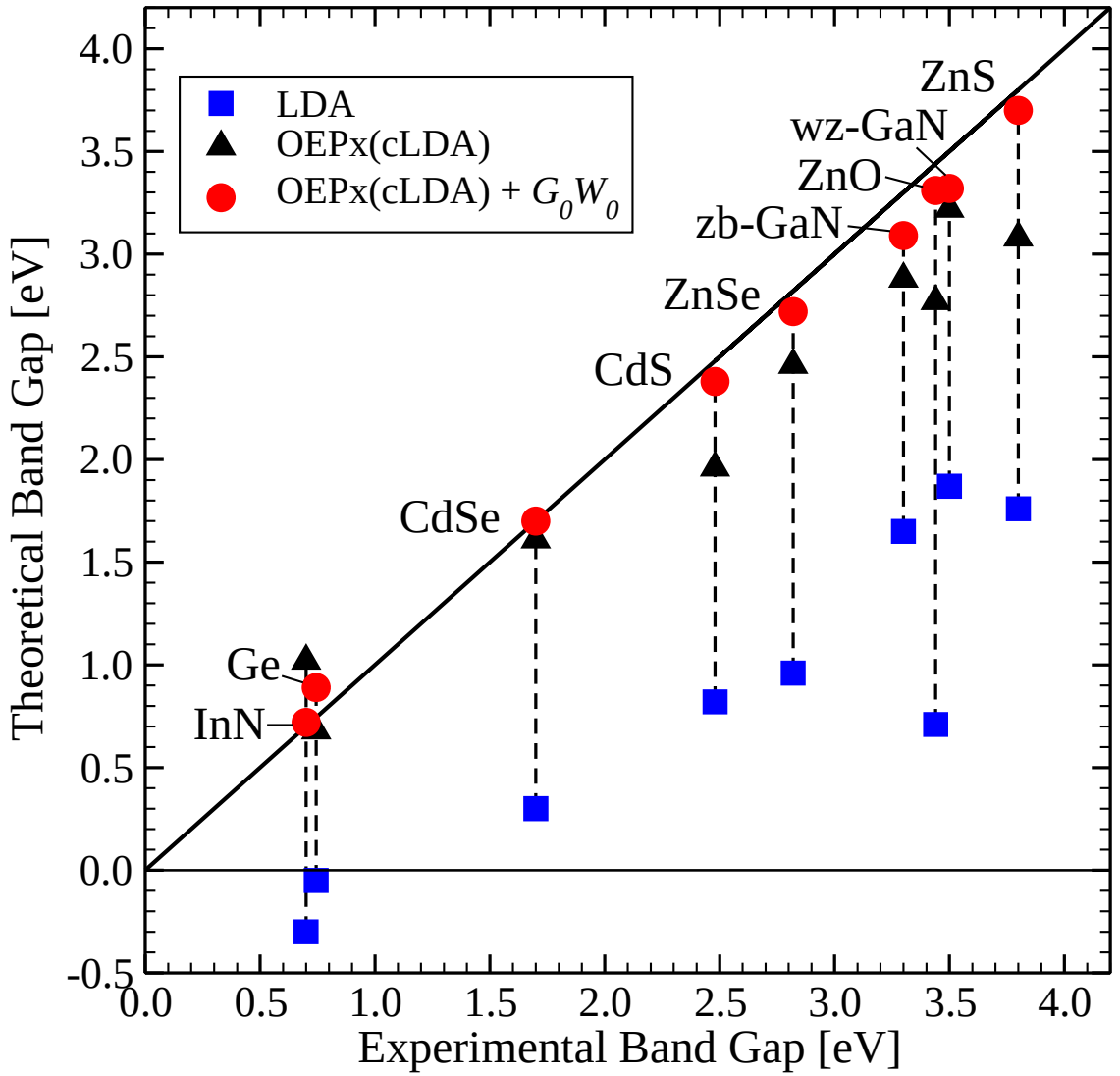
- includes image effect

# ARPES – GW: wurtzite ZnO



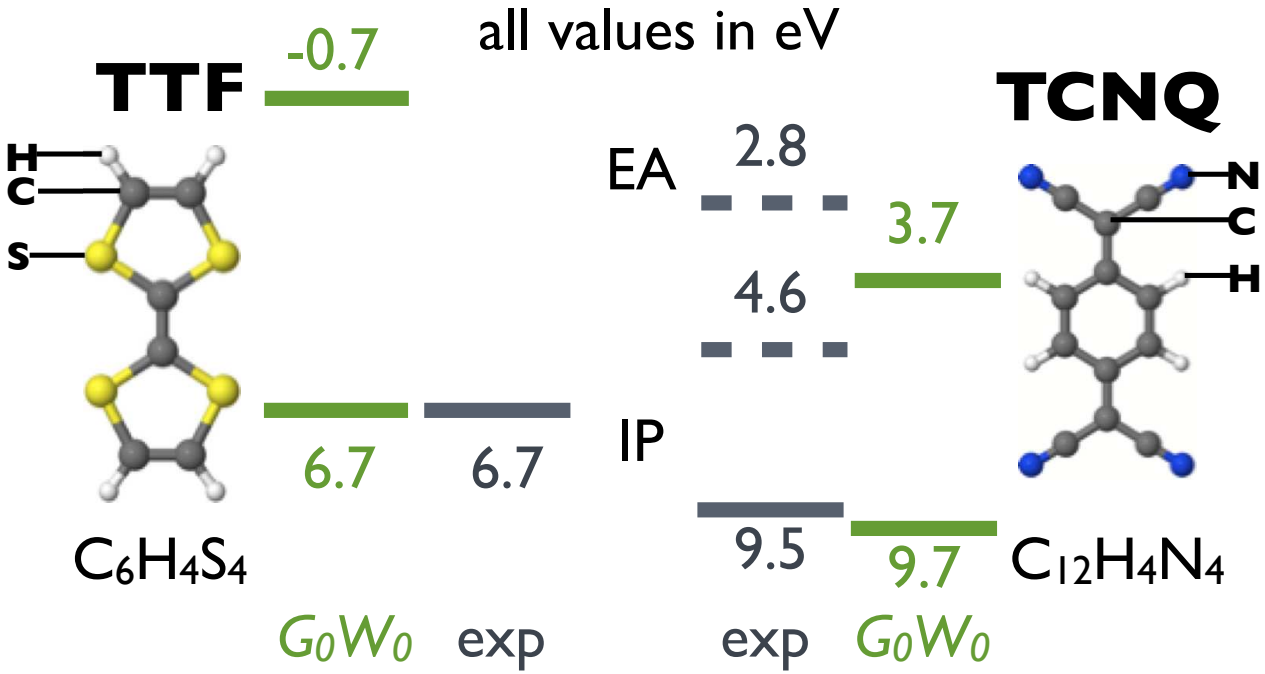

Yan, Rinke, Winkelnkemper, Qteish, Bimberg, Scheffler, Van de Walle, Semicond. Sci. Technol. **26**, 014037 (2011)

# $G_0W_0$ Band Gaps



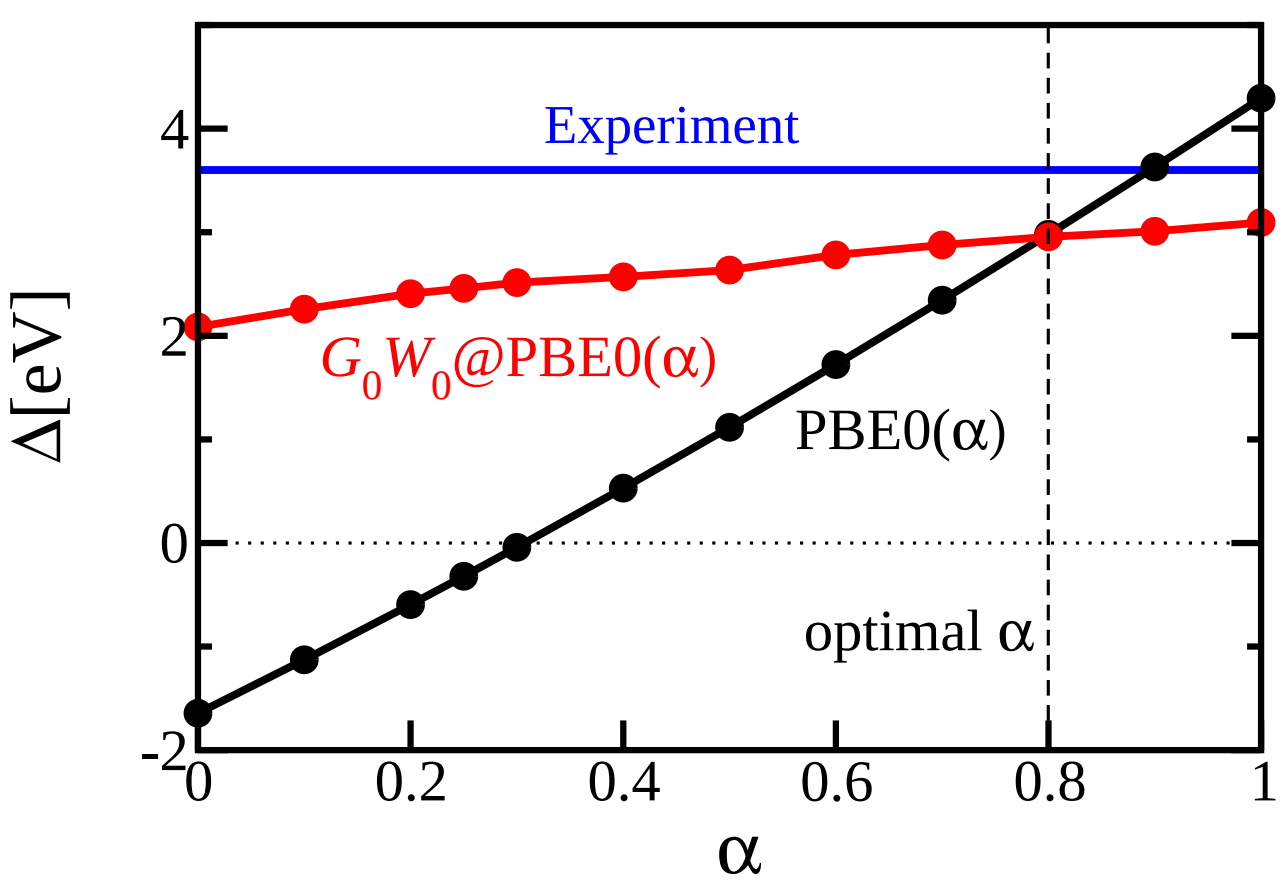

Rinke *et al. New J. Phys.* **7**, 126 (2005), phys. stat. sol. (b) **245**, 929 (2008)

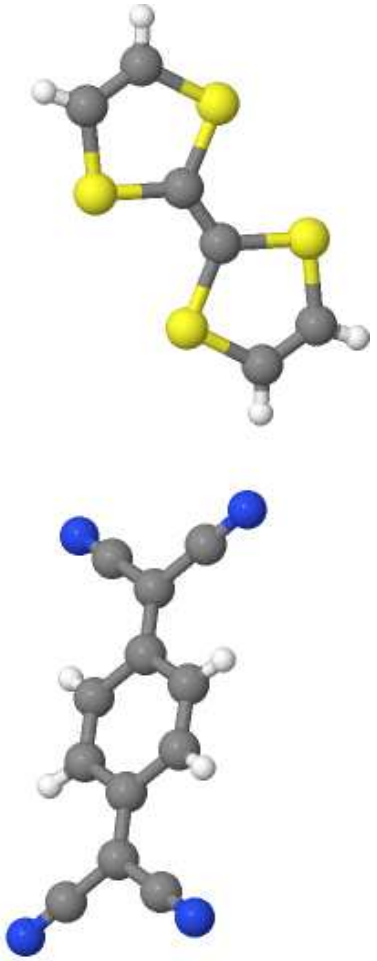
# Performance of $G_0W_0$




Exp.: JACS **112**, 3302 (1990), J. Chem. Phys. **60**, 1177 (1974),
Adv. Mat. **21**,1450 (2009),
Mol. Cryst. Liquid Cryst. Inc. Nonlin. Opt. **171**, 255 (1989)

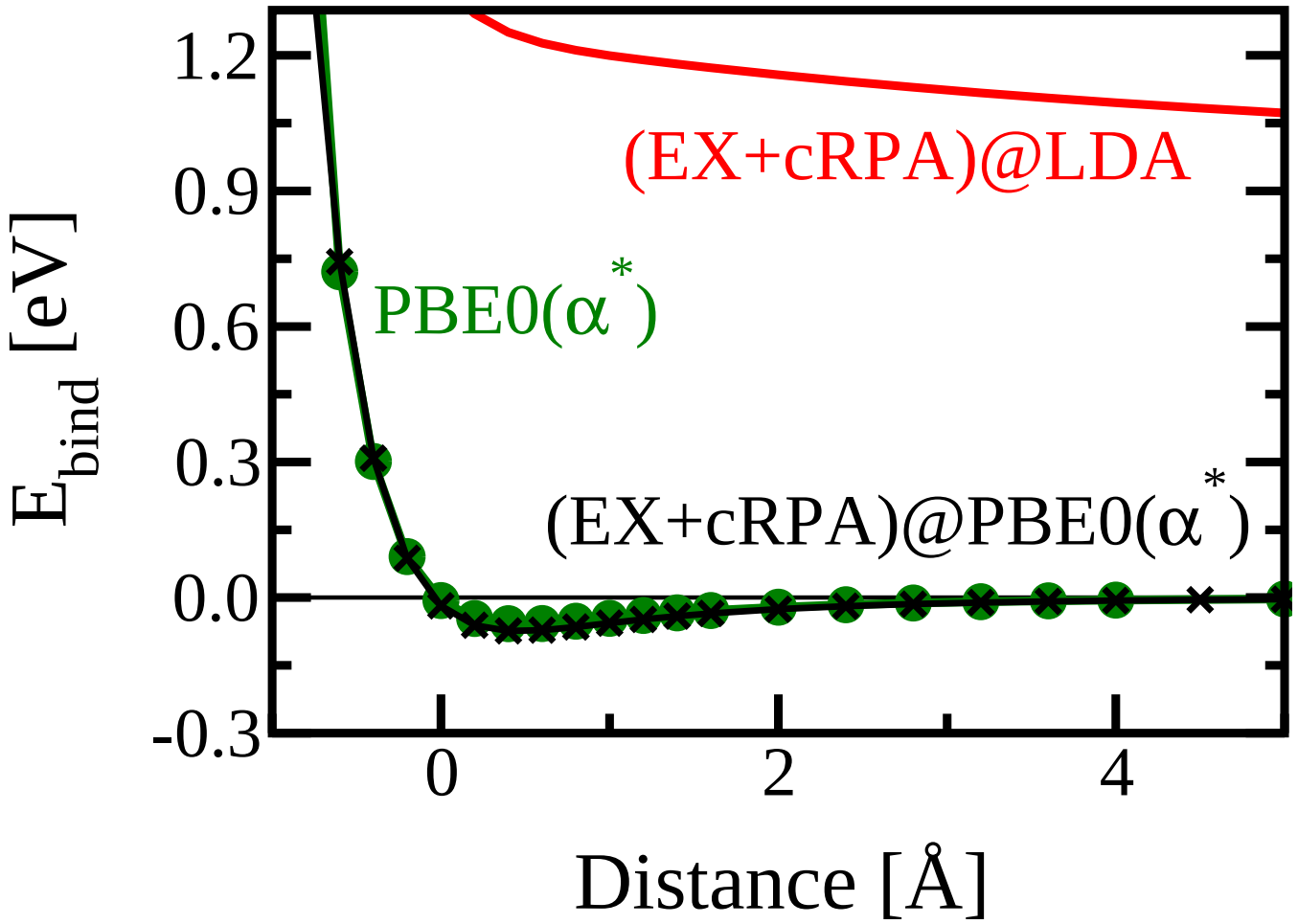
# TTF/TCNQ dimer at infinite separation

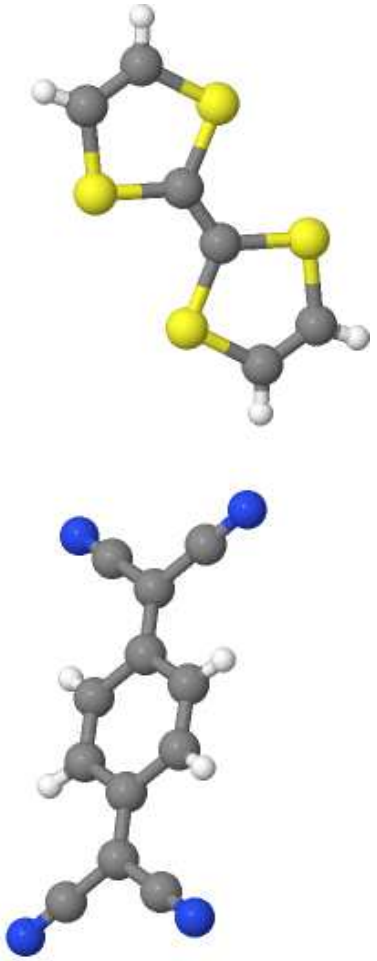


- choose $\alpha$ to match $G_0W_0$

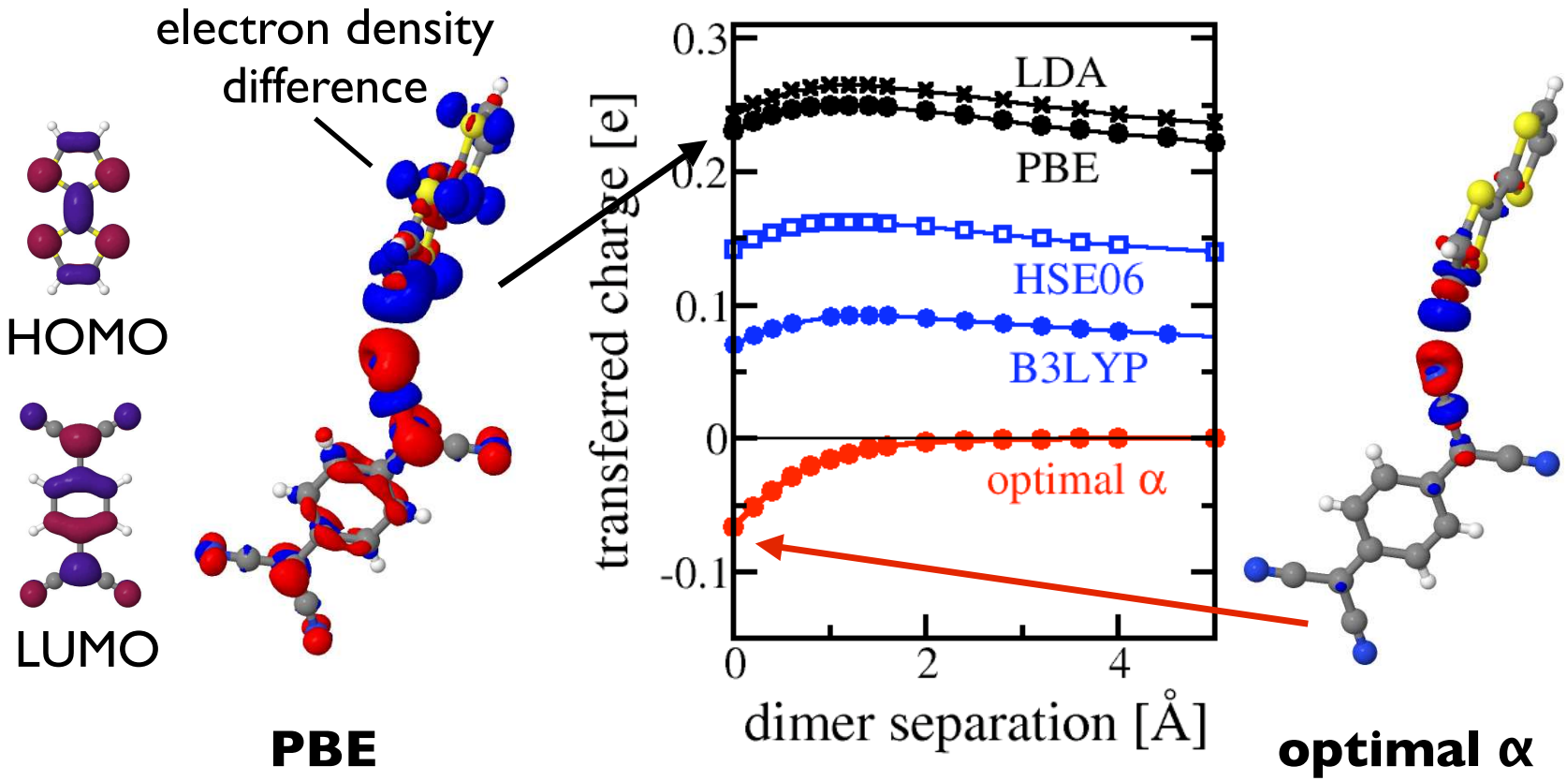
# TTF/TCNQ dimer – RPA binding curve



# TTF/TCNQ dimer – implications for interface

- no charge transfer, but small charge rearrangement
- 2D electron gas not due to charge transfer




- *optimal-*$\alpha$ calculations for interface in progress

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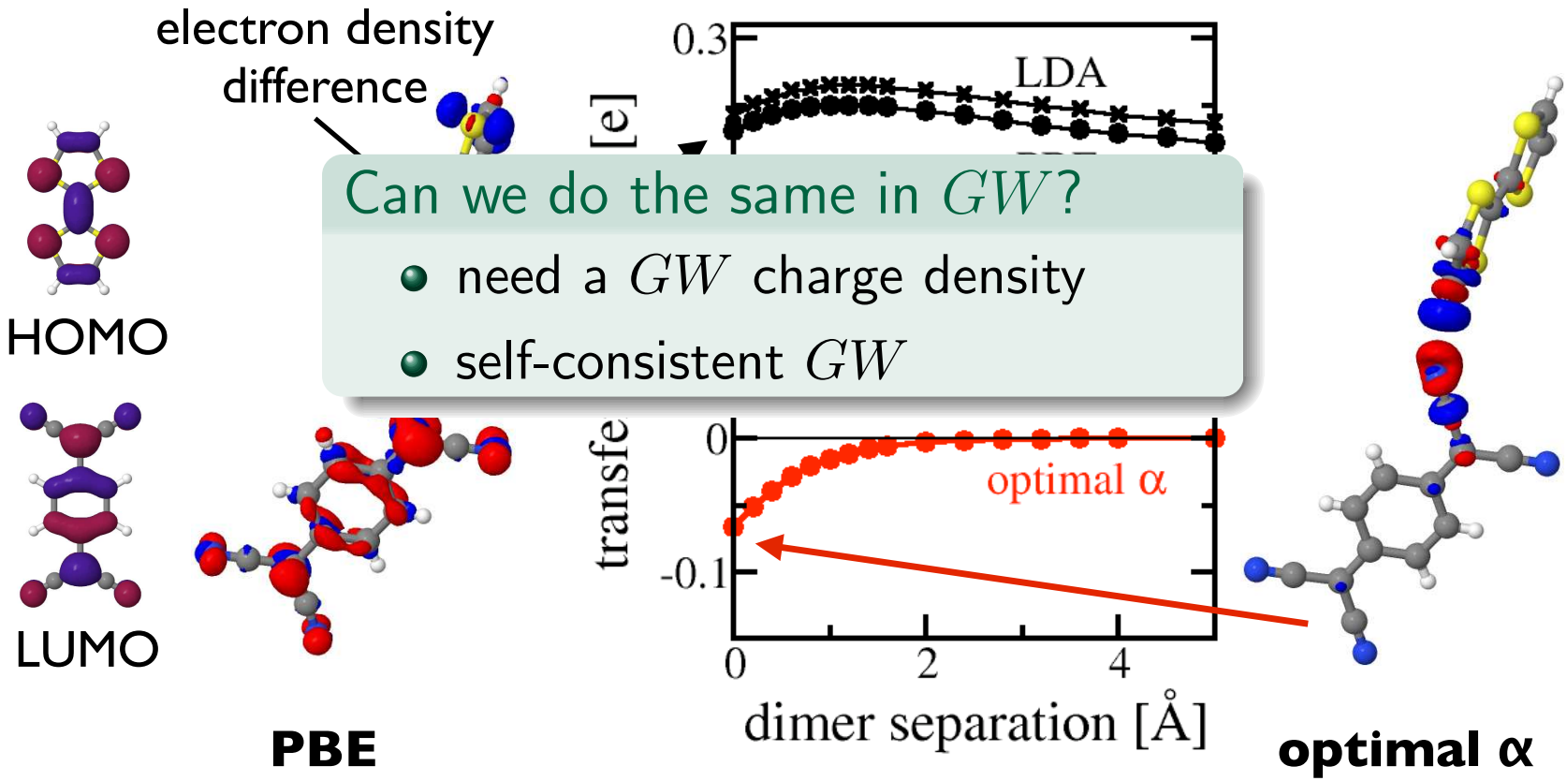
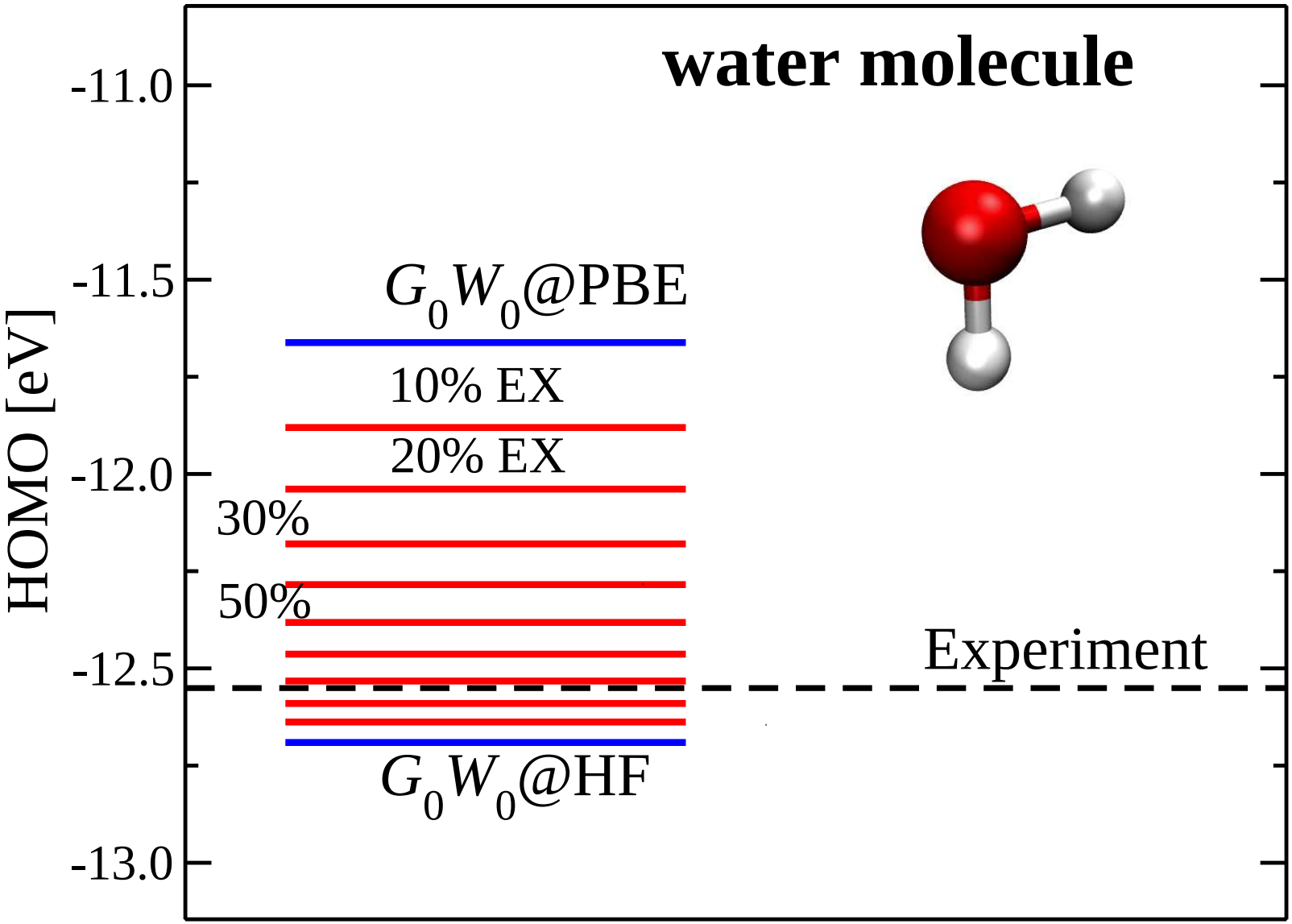



**Can we do the same in $GW$?**

- need a $GW$ charge density
- self-consistent $GW$

- *optimal-*$\alpha$ calculations for interface in progress

# $G_0W_0$ for water



# $GW$ – The Issue of Self-Consistency

Hedin's $GW$ equations:

$$
\begin{aligned}
G(1,2) &= G_0(1,2) \\
\Gamma(1,2,3) &= \delta(1,2)\delta(1,3) \\
P(1,2) &= -iG(1,2)G(2,1^+) \\
W(1,2) &= v(1,2) + \int v(1,3)P(3,4)W(4,2)d(3,4) \\
\Sigma(1,2) &= iG(1,2)W(2,1)
\end{aligned}
$$

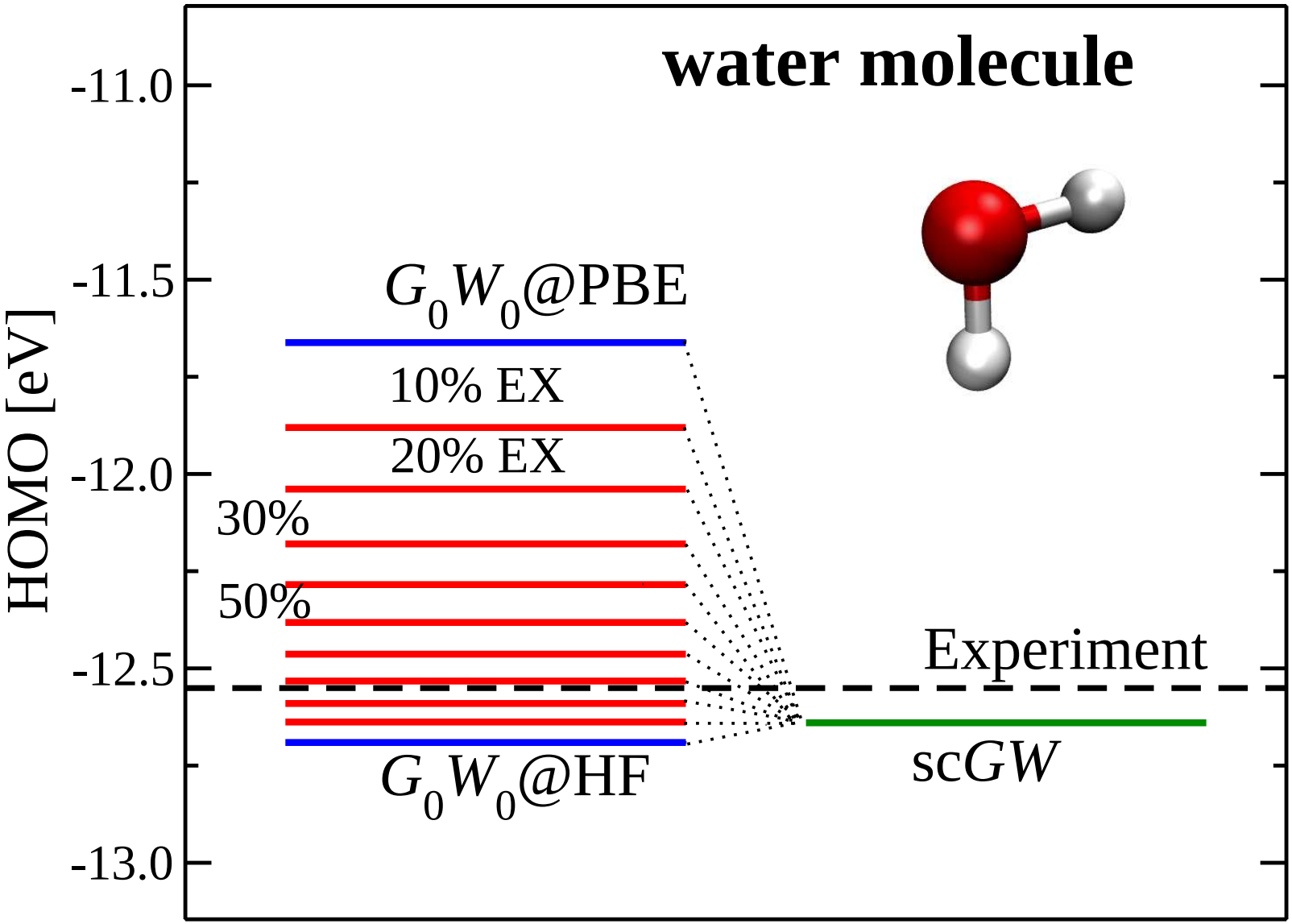
self-consistency

self-consistency

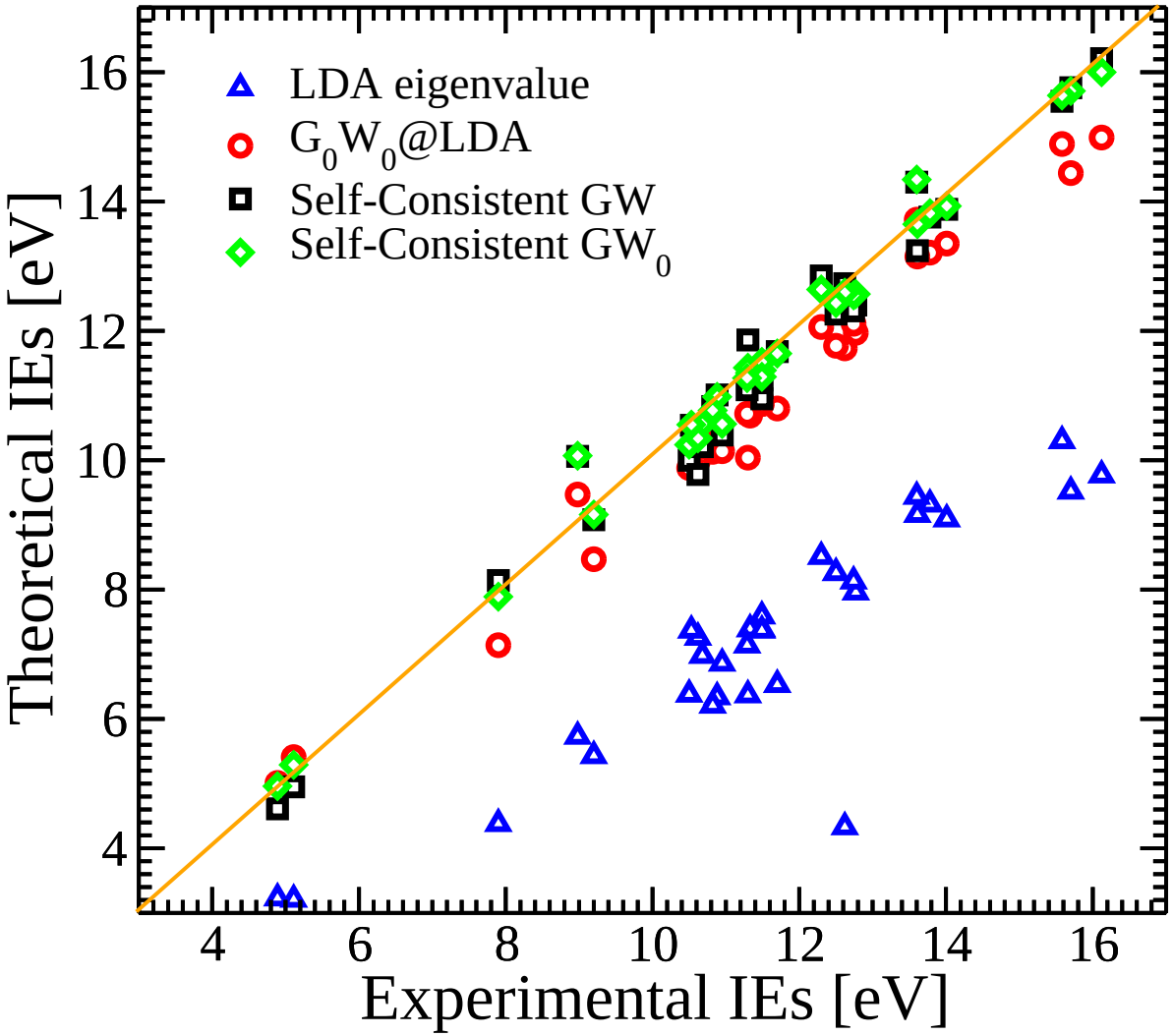
Dyson's equation:

$$G^{-1}(1,2) = G_0^{-1}(1,2) - \Sigma(1,2)$$

# sc$GW$ for water



# scGW and ionization potentials

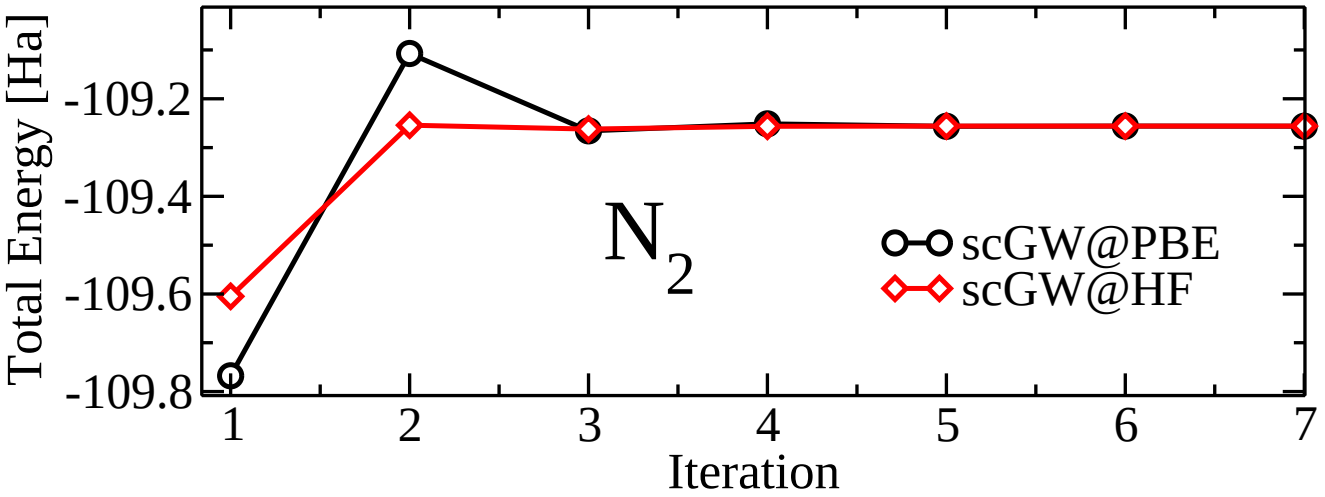


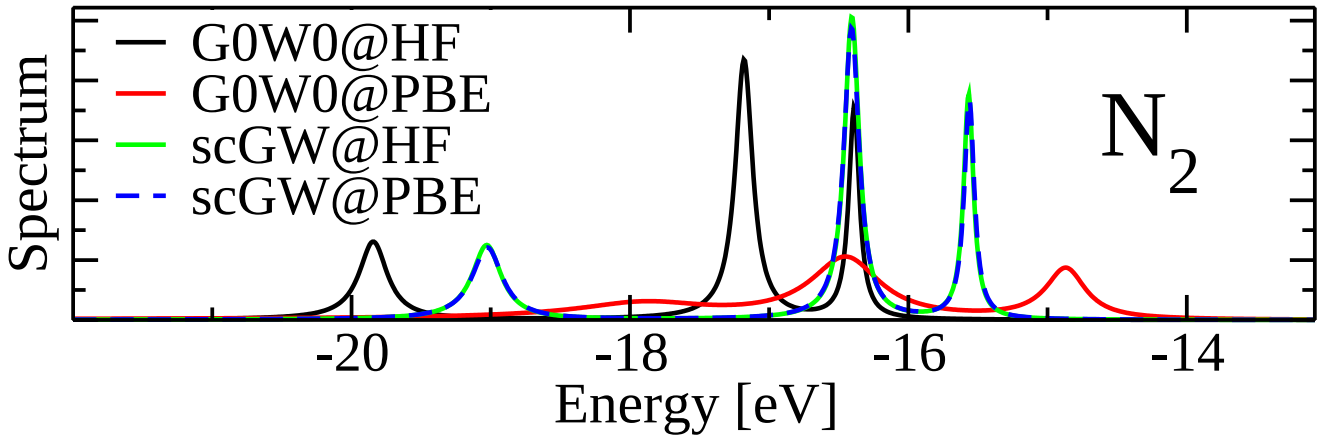

| deviation from exp. | |
|---|---|
| LDA | 40.0% |
| $G_0W_0$@LDA | 5.6% |
| scGW | 2.9% |
| $GW_0$@LDA | 1.5% |

set taken from Rostgaard, Jacobsen, and Thygesen, PRB **81**, 085103, (2010)

# Dependence on the starting point: $N_2$

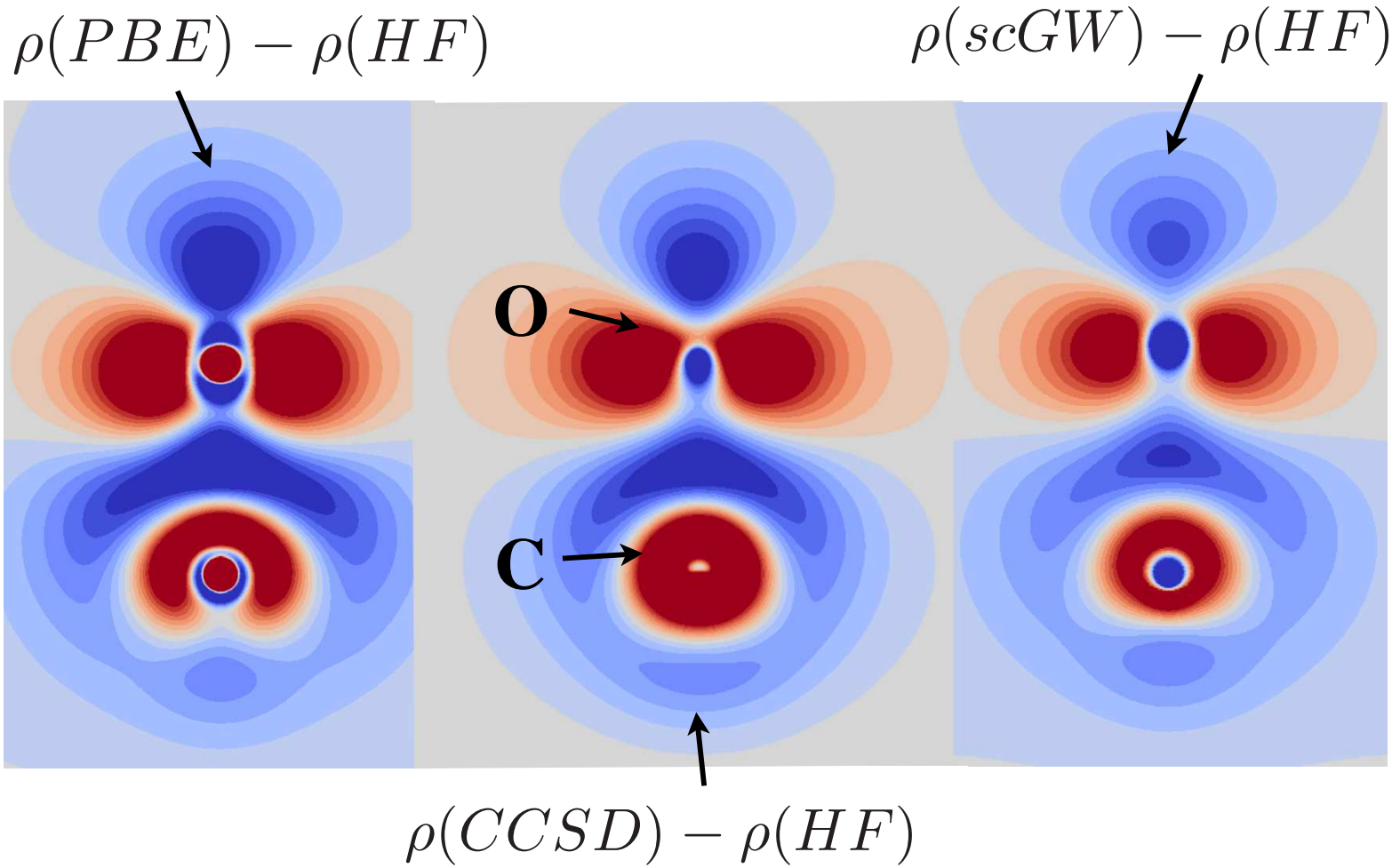
Galitskii-Migdal formula: $E_{\text{tot}} = -\frac{i}{2}\int Tr\left[(\omega + h_0)G(\omega)\right]\frac{d\omega}{2\pi}$




At self-consistency no dependence on input Green's function!

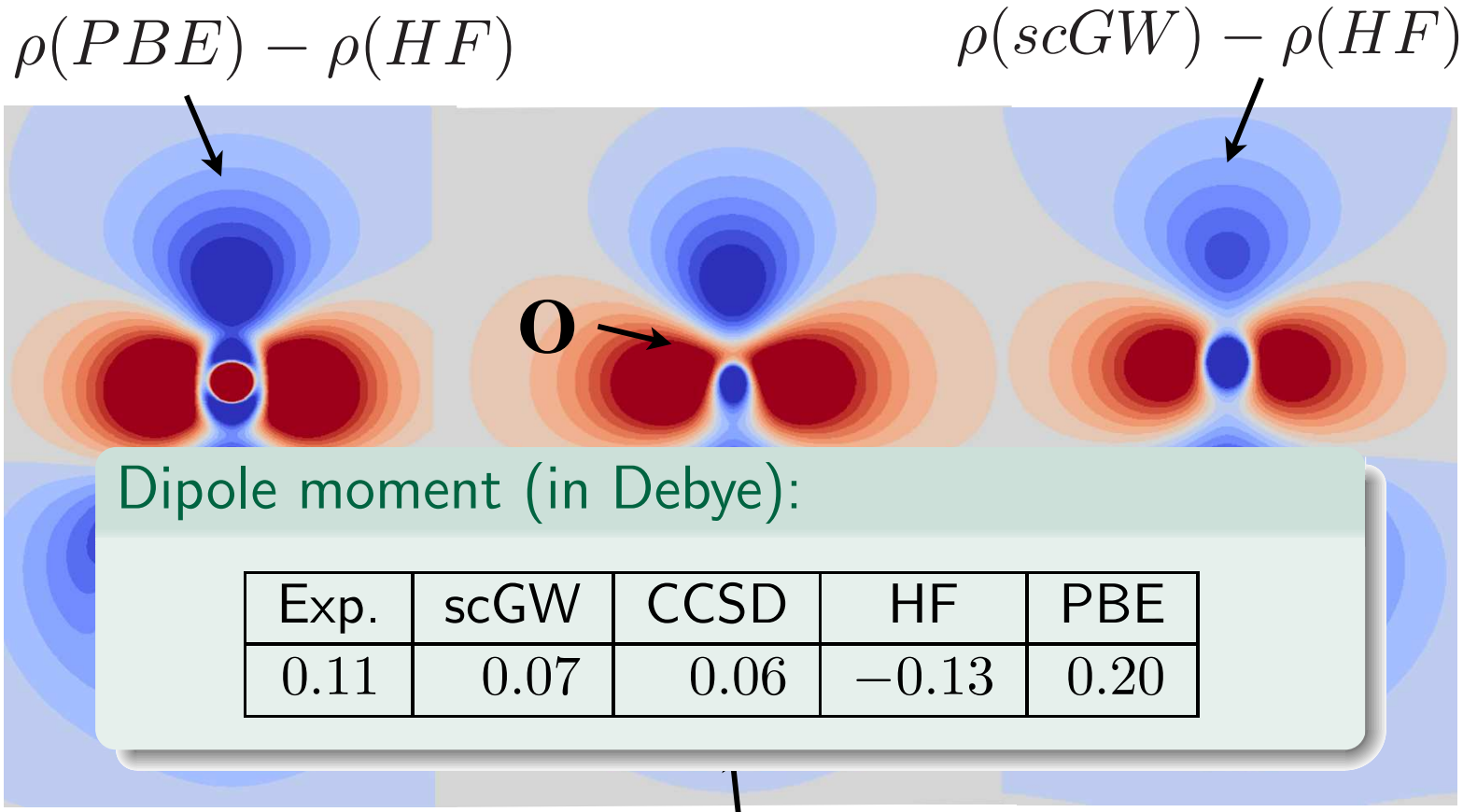
# The sc$GW$ density




- density from Green's function: $\rho(\mathbf{r}) = -i \sum_\sigma G_{\sigma\sigma}(\mathbf{r}, \mathbf{r}, \tau = 0^+)$

Caruso, Ren, Rinke, Rubio, Scheffler: arXiv:1202.3547v1

# The sc$GW$ density




Dipole moment (in Debye):

| Exp. | scGW | CCSD | HF | PBE |
|---|---|---|---|---|
| 0.11 | 0.07 | 0.06 | −0.13 | 0.20 |

- density from Green's function: $\rho(\mathbf{r}) = -i \sum_\sigma G_{\sigma\sigma}(\mathbf{r}, \mathbf{r}, \tau = 0^+)$

Caruso, Ren, Rinke, Rubio, Scheffler: arXiv:1202.3547v1

# CO – ground state properties

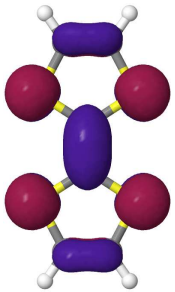
| CO | $d$ | $\nu_{\mathrm{vib}}$ | $\mu$ | $E_{\mathrm{b}}$ |
|---|---|---|---|---|
| Exp. (NIST database) | 1.128 | 2169 | 0.11 | 11.11 |
| sc-$GW$ | 1.118 | 2322 | 0.07 | 10.19 |
| $G_0W_0$@HF | 1.119 | 2647 | – | 11.88 |
| $G_0W_0$@PBE | 1.143 | 2322 | – | 12.16 |
| (EX+cRPA)@HF | 1.116 | 2321 | – | 10.19 |
| (EX+cRPA)@PBE | 1.135 | 2115 | – | 10.45 |
| PBE | 1.137 | 2128 | 0.20 | 11.67 |
| HF | 1.102 | 2448 | -0.13 | 7.63 |

- Galitskii-Migdal formula:

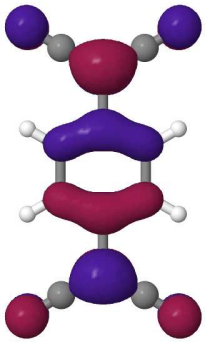
$$E_{\mathrm{GM}} = -i \int \frac{d\omega}{2\pi} Tr \left\{ \left[ \omega + h_0 \right] G(\omega) \right\} + E_{\mathrm{ion}}$$

Caruso, Ren, Rinke, Rubio, Scheffler: arXiv:1202.3547v1

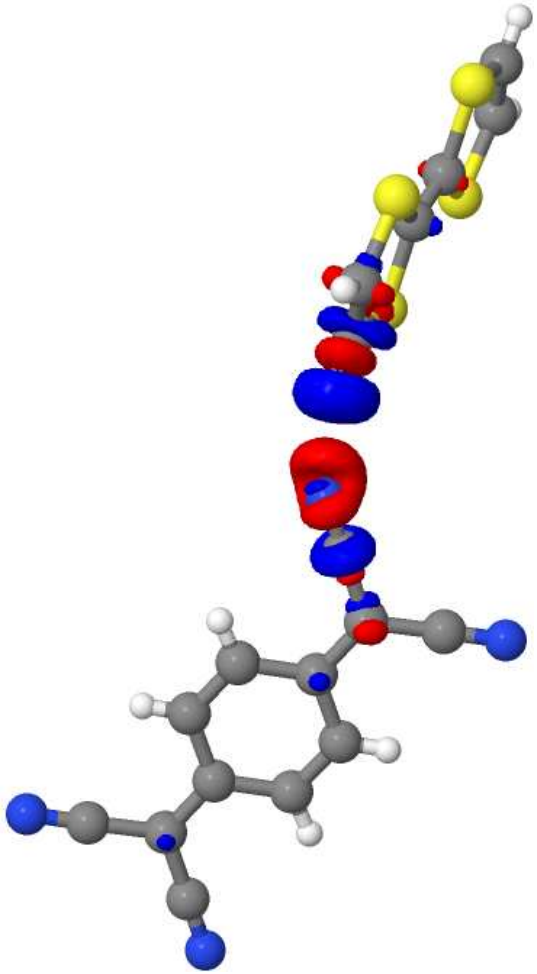
# TTF/TCNQ dimer revisited



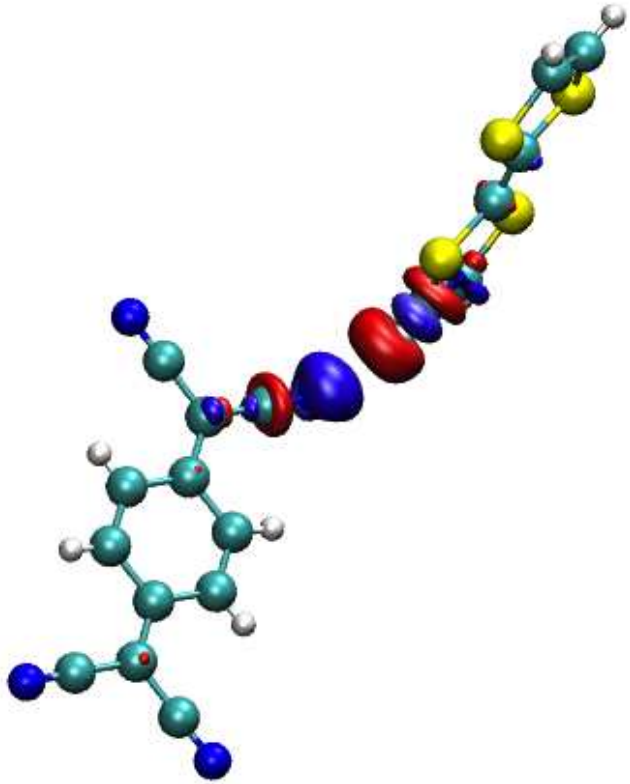
HOMO



LUMO

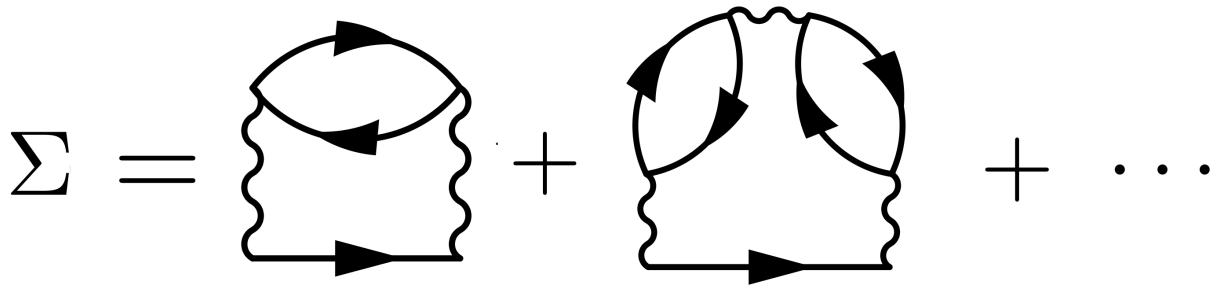


**opt α**



**scGW**

# RPA and $GW$ – a consistent pair



**GW**
**many-body perturbation theory**

**Dyson's equation:**

$$G^{-1} = G_0^{-1} - \Sigma[G]$$

**total energy:**

$$E = E[G]$$

e.g. Galitskii-Migdal

**RPA**
**density-functional theory**

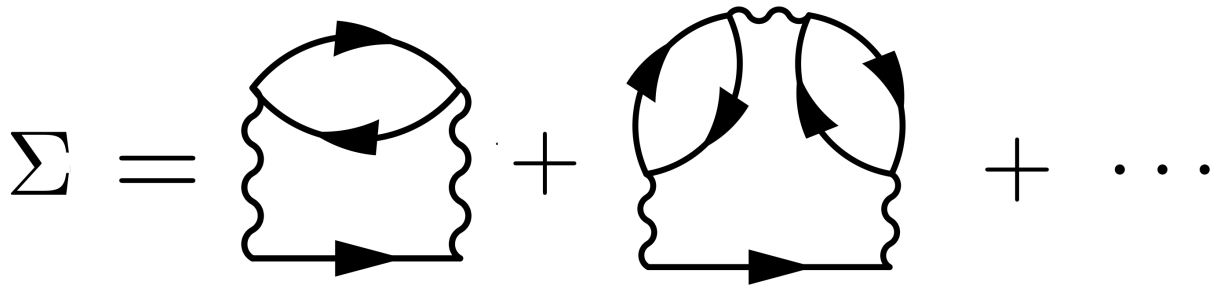
**optimized effective potential:**

$$G_0 \left[\Sigma - v_{xc}^{\mathrm{OEP}}\right] G_0 = 0$$

**Adiabatic connection fluctuation dissipation theorem (ACFDT):**

$$E_{xc} = E_{xc}[\chi_0] = E_{xc}[-iG_0G_0]$$

# RPA and $GW$ – a consistent pair




**GW** **RPA**

**man**

**l:**

scGW versus scRPA:

- RPA also iterated to self-consistency (scRPA)

**Do MBPT and DFT differ for the same diagrams?**

**total energy:**

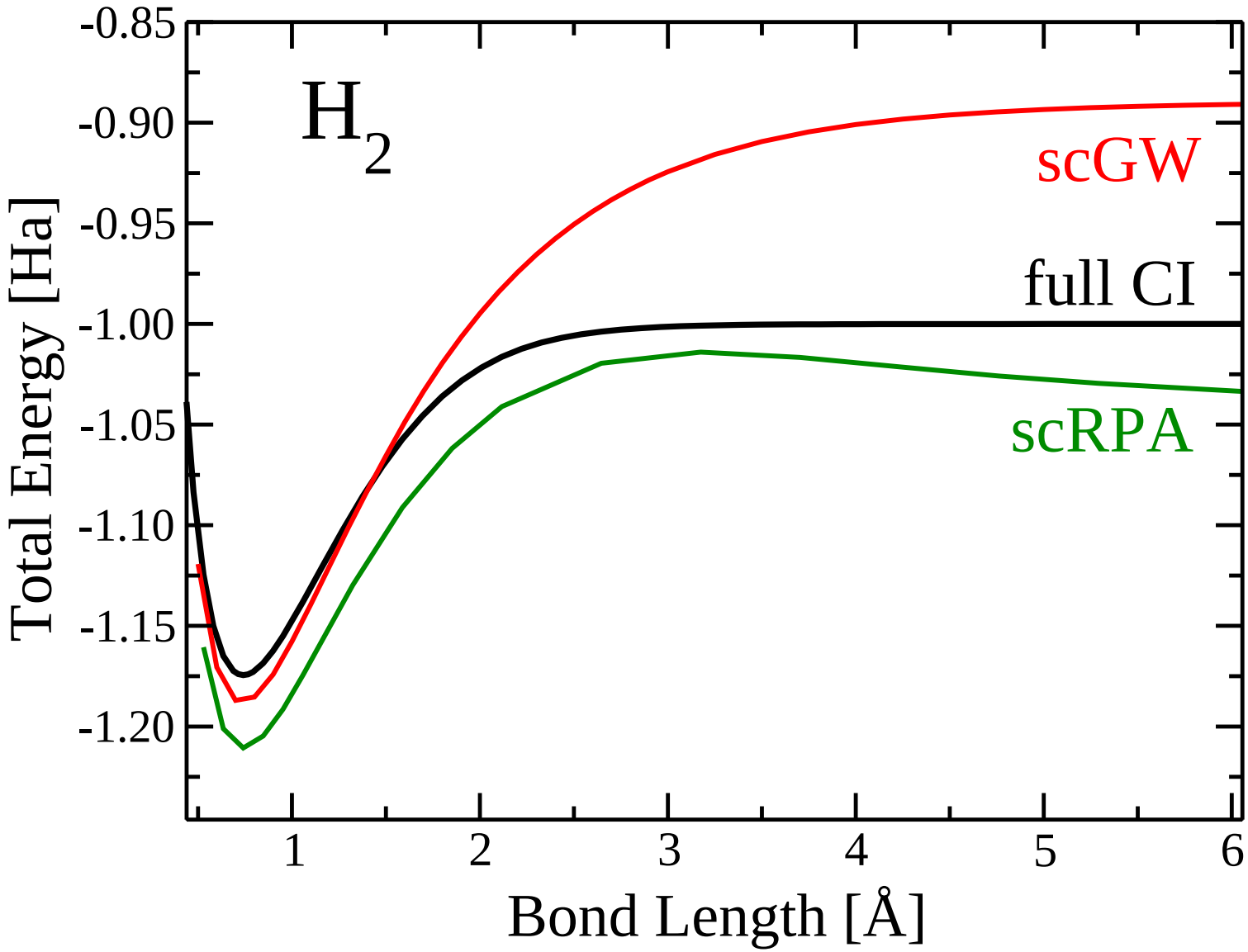
$$E = E[G]$$

e.g. Galitskii-Migdal

**Adiabatic connection fluctuation dissipation theorem (ACFDT):**

$$E_{xc} = E_{xc}[\chi_0] = E_{xc}[-iG_0G_0]$$

# The most strongly correlated system




full CI: L. Wolniewicz, J. Chem. Phys. **99**, 1851 (1993)

# Kinetic energy

- correlation energy in $G_0W_0$:

$$E_{\rm c}^{G_0W_0} = -\int_0^\infty \frac{d\omega}{2\pi} \mathrm{Tr}\left[\sum_{n=2}^{\infty} \left(\chi_0(i\omega)v\right)^n\right]$$

- correlation energy in RPA:

$$E_{\rm c}^{\rm RPA} = -\int_0^\infty \frac{d\omega}{2\pi} \mathrm{Tr}\left[\sum_{n=2}^{\infty} \boxed{\frac{1}{n}} \left(\chi_0(i\omega)v\right)^n\right]$$

- adiabatic connection recovers kinetic energy

# Kinetic and correlation energy

- RPA kinetic energy contribution:

$$T_{\mathrm{c}}^{\mathrm{RPA}} = E_{\mathrm{c}}^{\mathrm{RPA}} - E_{\mathrm{c}}^{G_0W_0}$$

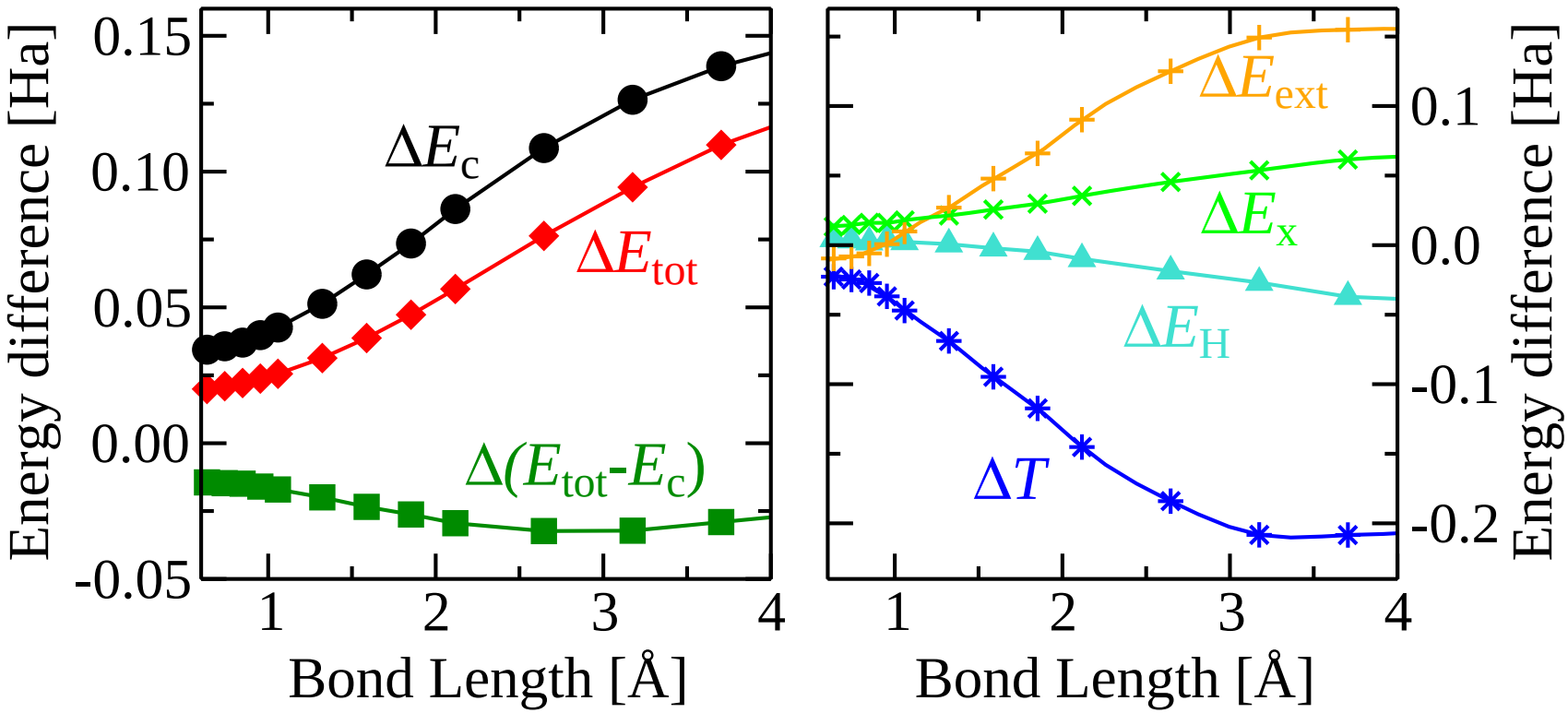
- RPA kinetic energy:

$$T^{\mathrm{RPA}} = T_0 + T_{\mathrm{c}}^{\mathrm{RPA}}$$

- RPA Coulomb correlation:

$$U_{\mathrm{c}}^{\mathrm{RPA}} = E_{\mathrm{c}}^{\mathrm{RPA}} - T_{\mathrm{c}}^{\mathrm{RPA}}$$

# $H_2$ – energy contributions




- Coulomb correlation energy makes the difference

# Acknowledgements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Mina Yoon

## scRPA

Daniel Rohr
Maria Hellgren

## scGW/Cerium

Fabio Caruso/Marco Casadei
Xinguo Ren
Angel Rubio

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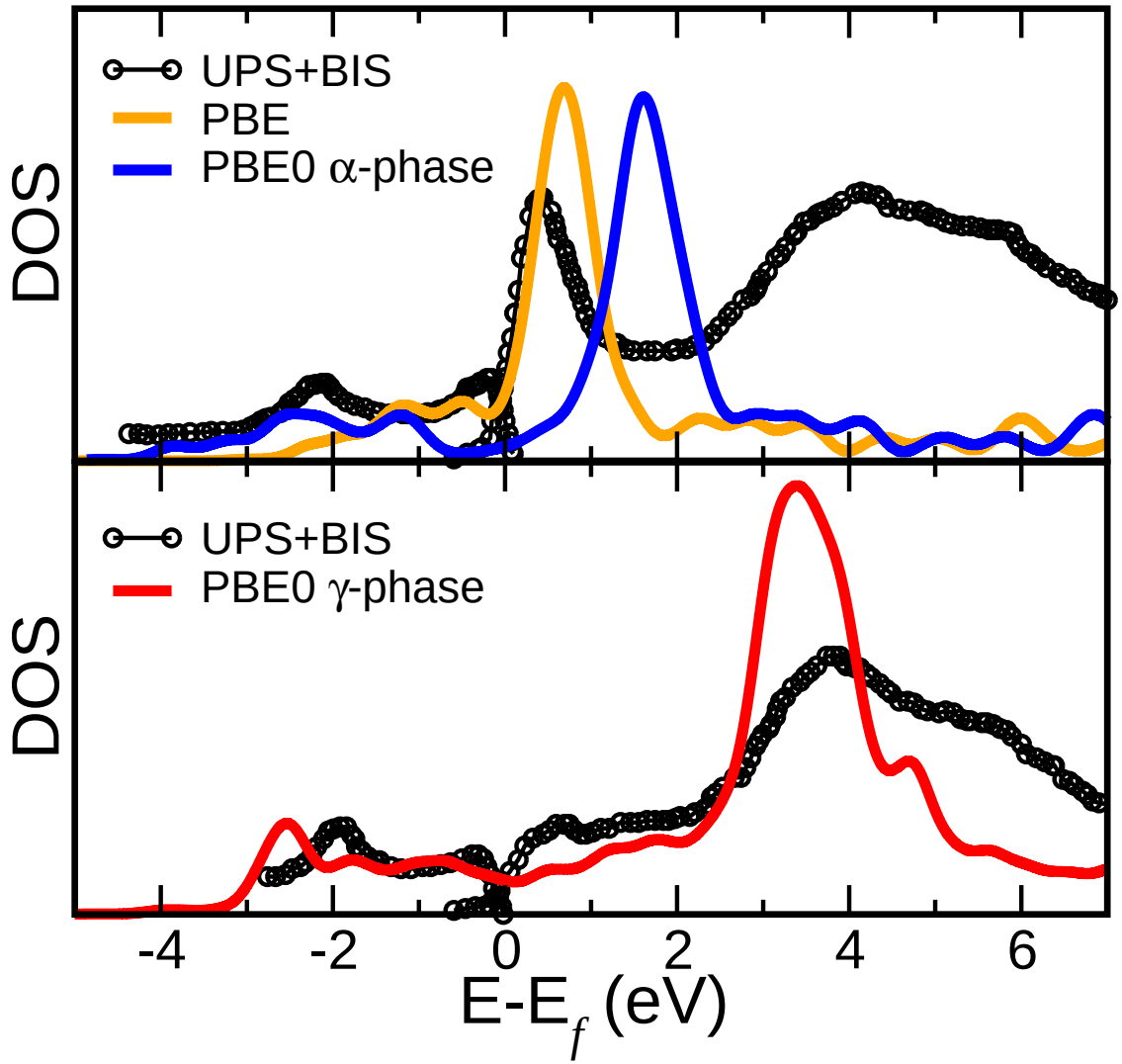
Matthias Scheffler

## FHI-*aims* code

Volker Blum
the whole FHI-*aims* developer team


# Cerium - spectroscopy




- description of $\gamma$-phase ok – $\alpha$-phase problematic

UPS: Wieliczka *et al.* PRB 29, 3028 (1984) – BIS: Wuilloud *et al.* PRB