The Abdus Salam International Centre for Theoretical Physics

2440-2

16th International Workshop on Computational Physics and Materials Science: Total Energy and Force Methods

10 - 12 January 2013

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

Patrick Rinke

Fritz-Haber-Institut der Max-Planck-Gesellschaft
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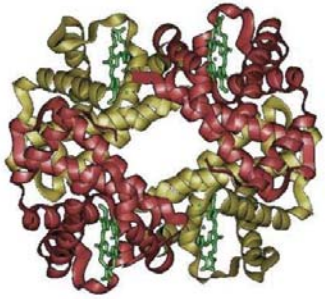
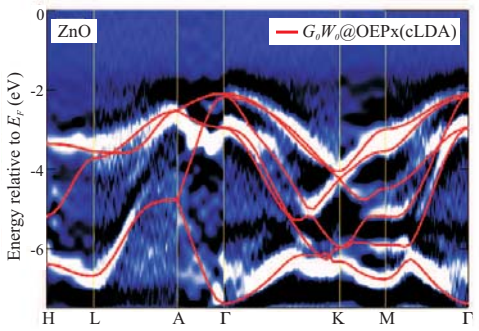
Wish list for "optimum" electronic structure approach

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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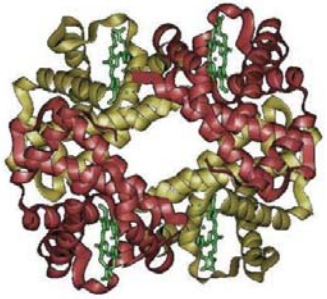

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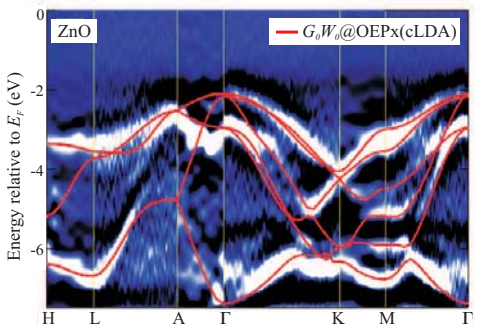
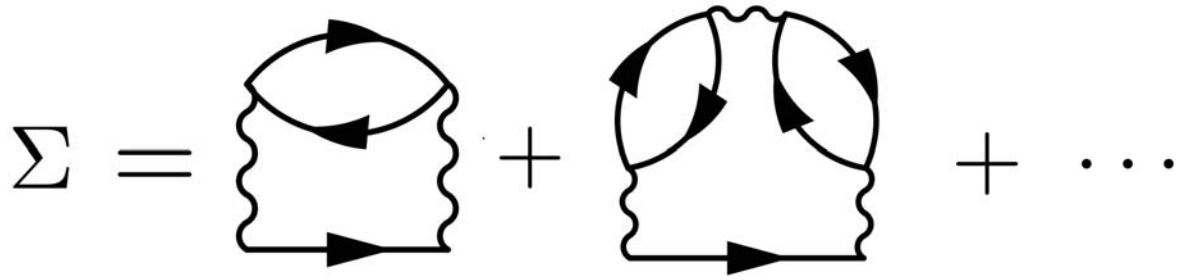


ground/excited state:

- 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
- ...

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):

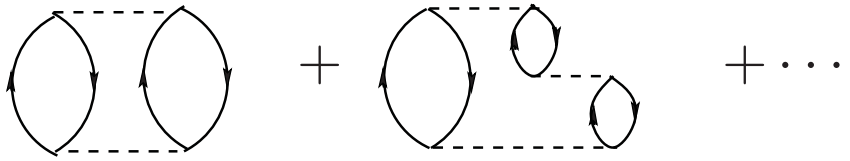
$$E_{xc} = E_{xc}[\chi_0] = E_{xc}[-iG_0G_0]$$

Attractive features of the RPA

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

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

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



$$+ \cdots$$

- "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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For an overview of RPA, see our recent review article:

- Ren, Joas, Rinke, Scheffler, J. Mat. Sci. **47**, 7447 (2012)

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Attractive features of the RPA

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FHI-aims code:

- all-electron electronic structure code
- numeric atom centred basis functions
- beyond LDA/GGA functionality:
  hybrids, MP2, GW, RPA, SOSEX

V. Blum, *et al.* Comput. Phys. Commun. **180**, 2175 (2009)
X. Ren, *et al.* New J. Phys. **14**, 053020 (2012)

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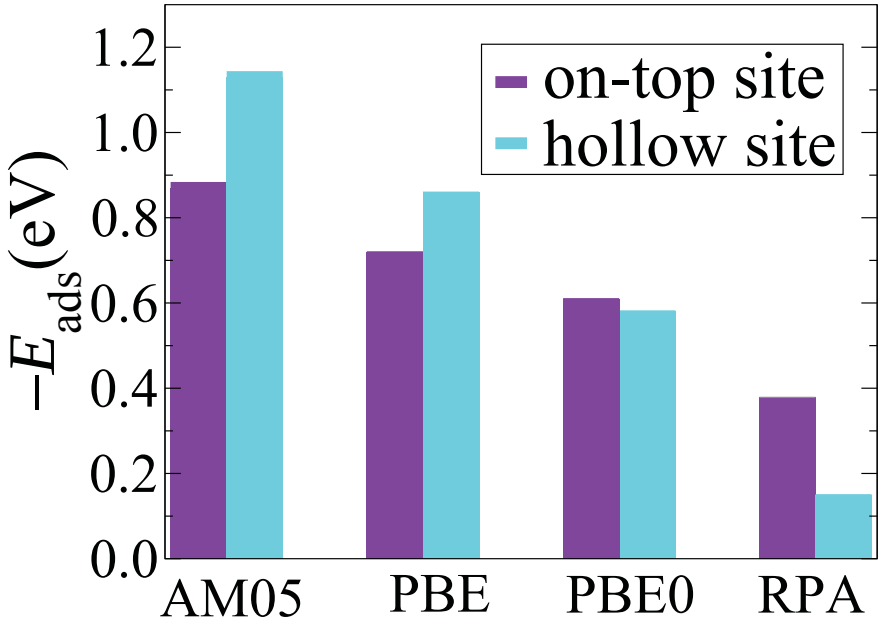
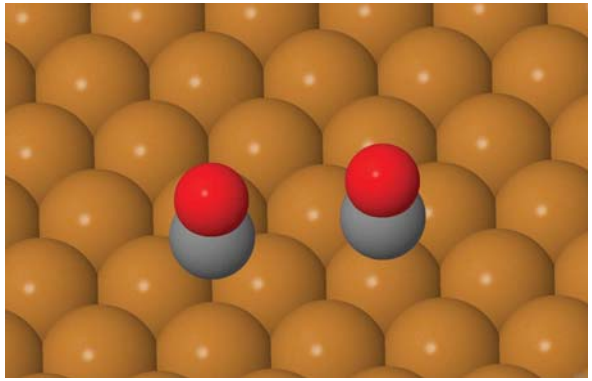
RPA applied to surface adsorption problem

"CO adsorption puzzle"





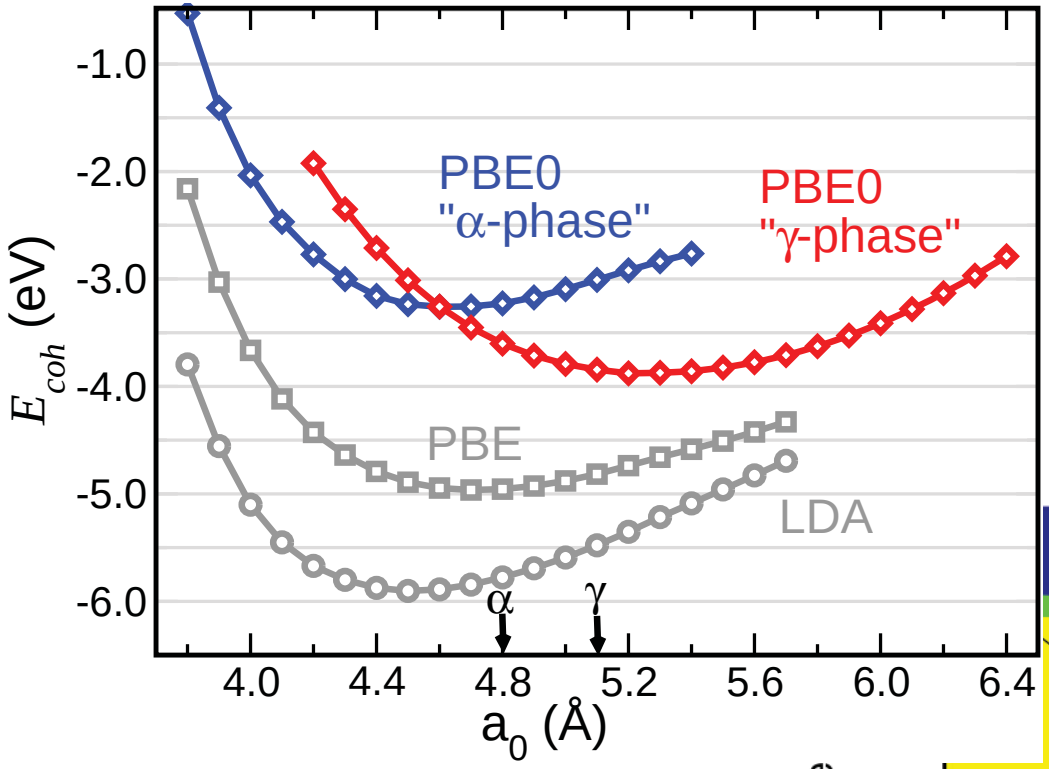
CO@Cu(111)

LDA/GGAs : hollow site

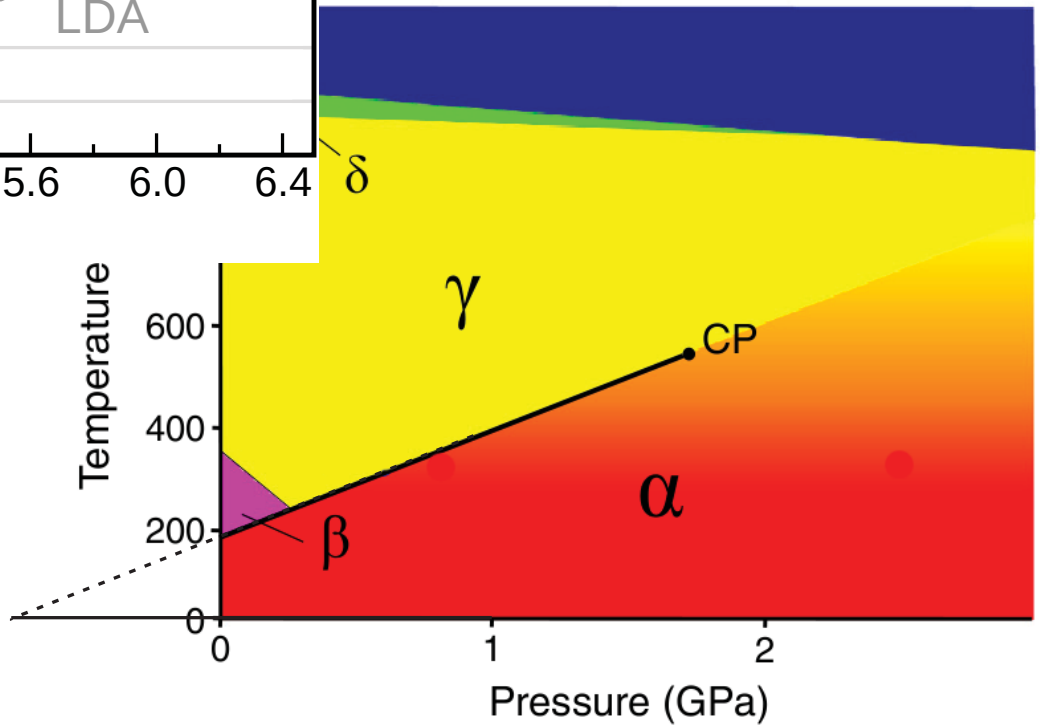
RPA/Exp. : on-top site

X. Ren, P. Rinke, and M. Scheffler, Phys. Rev. B **80**, 045402 (2009).

The f-electron system Cerium



- wrong phase ordering



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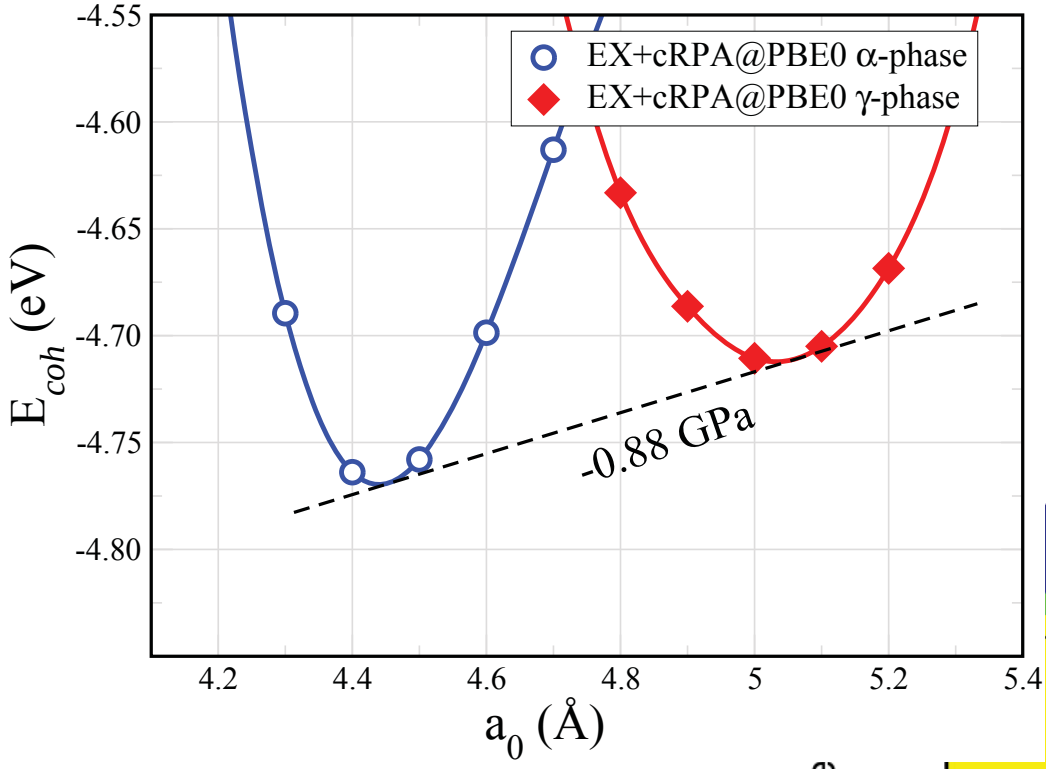
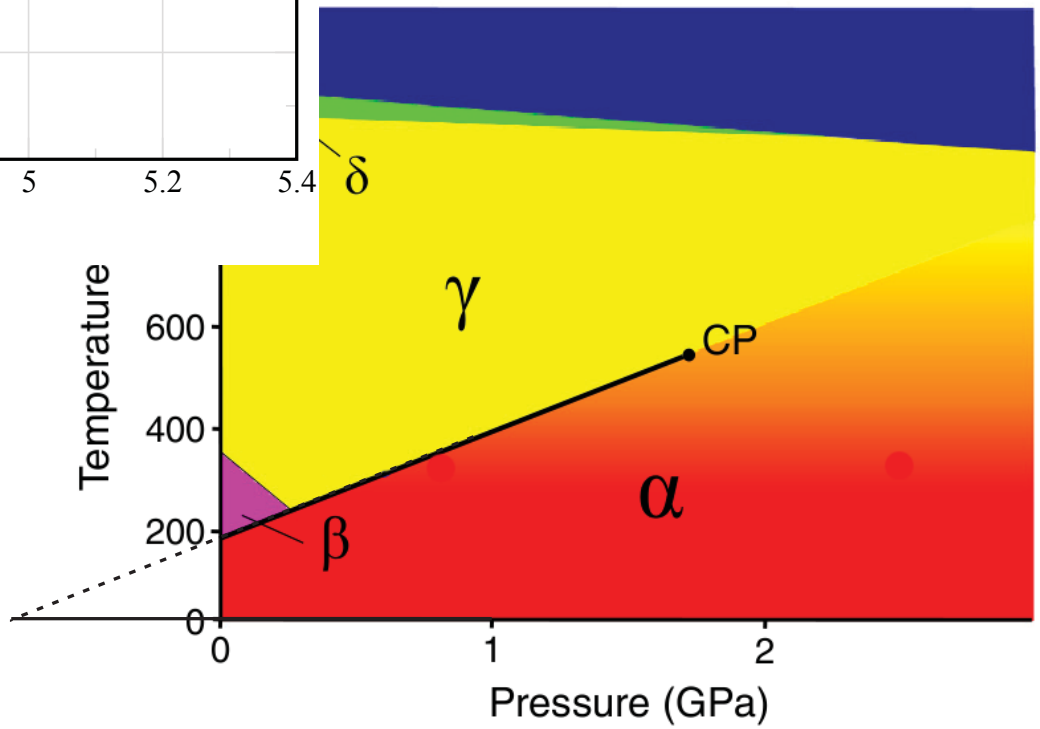
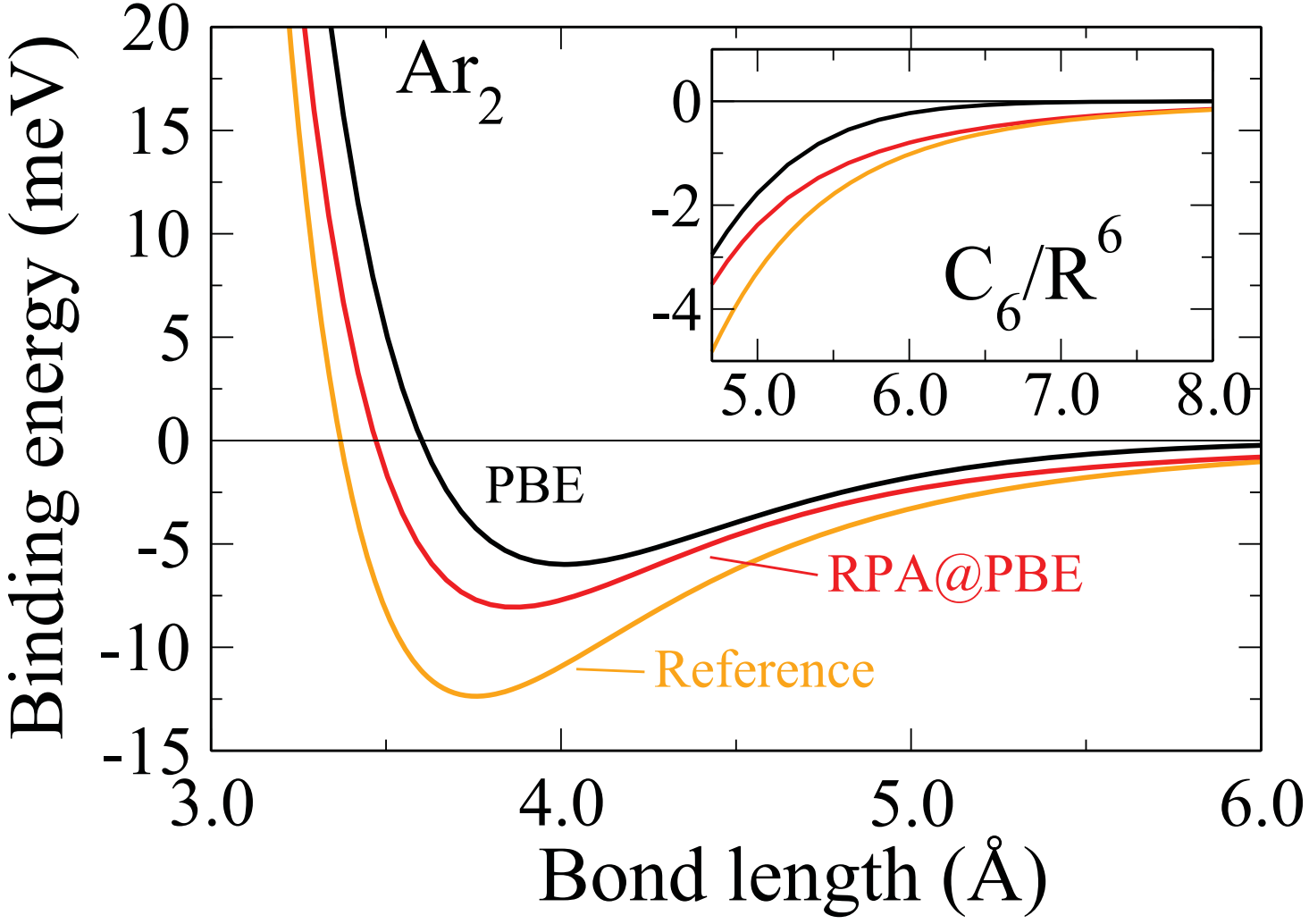


- correct phase ordering
- results for a Ce_{19} cluster

M. Casadei, X. Ren, P. Rinke,
A. Rubio, M. Scheffler,
Phys. Rev. Lett. 109, 146402 (2012)



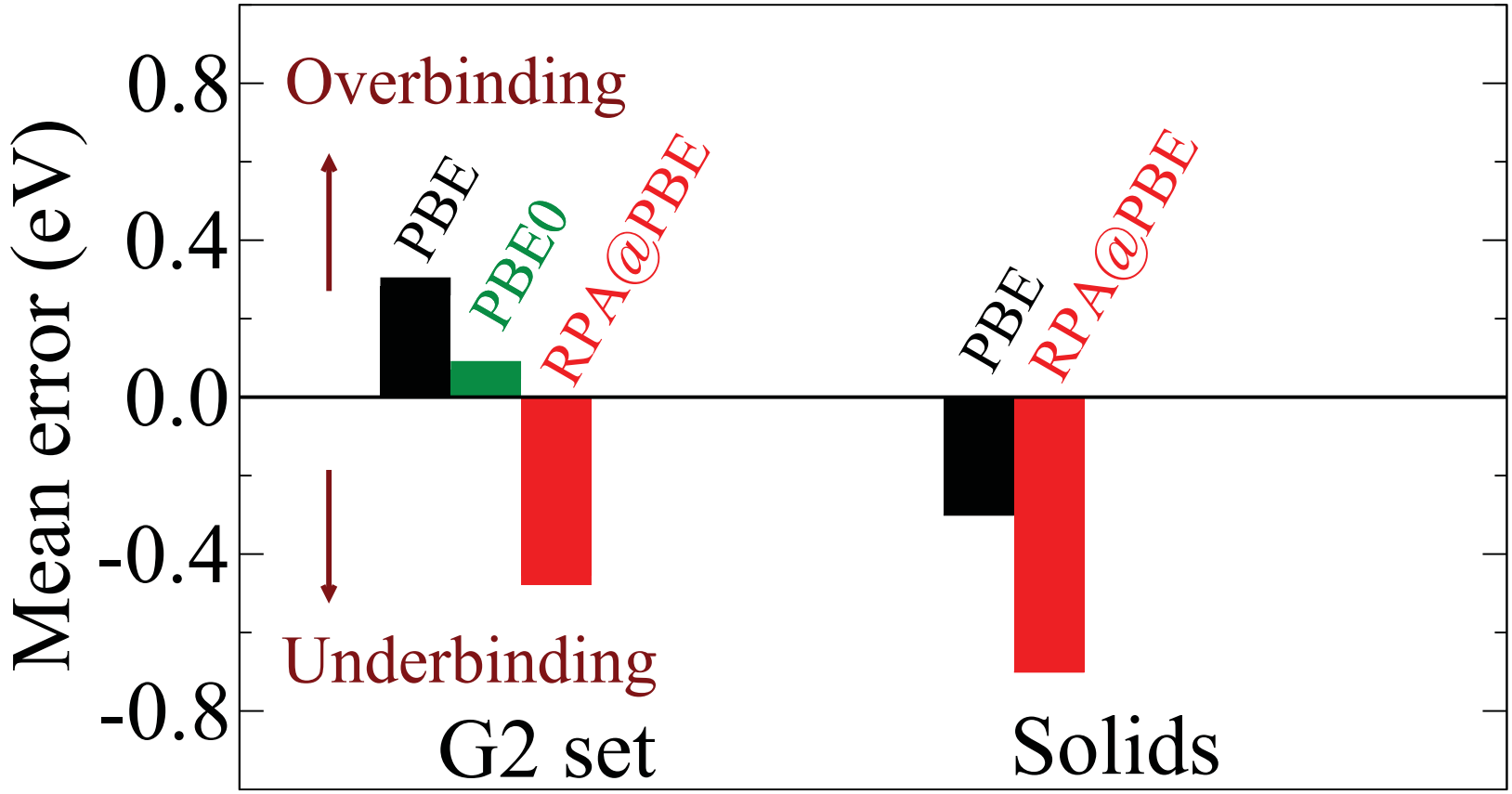
van der Waals bonding



✔ Correct asymptotic behavior ⇒ crucial for large molecules

✘ Underbinding around the equilibrium distance

Atomization energies



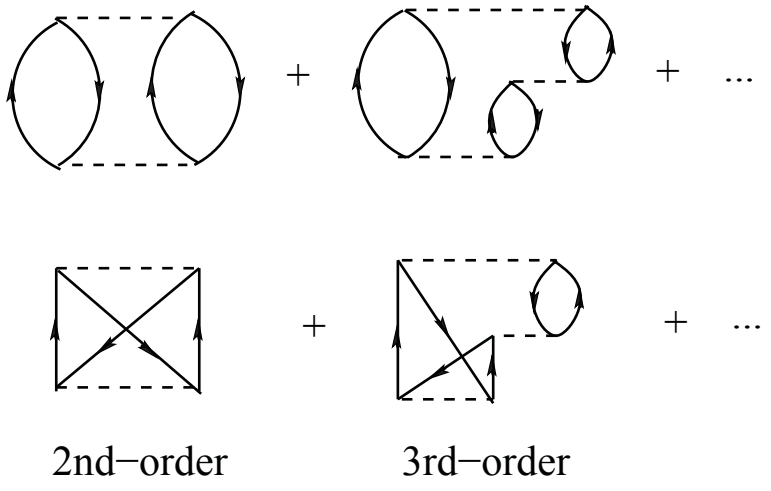
- RPA underestimates bond strengths

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

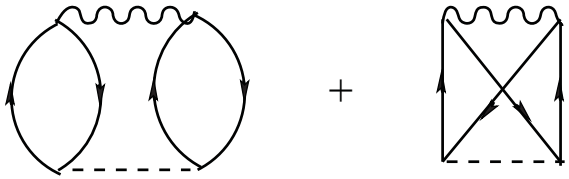
The SOSEX correction to RPA

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:

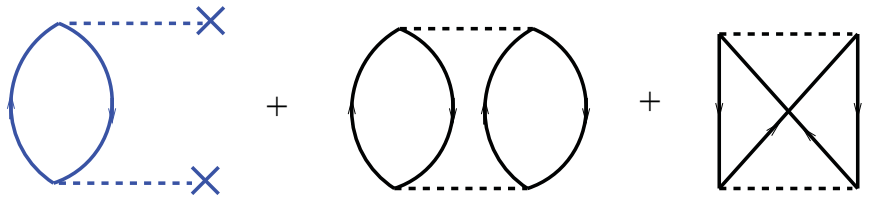
$$\hat{H} = \hat{H}^0 + \hat{H}'$$

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

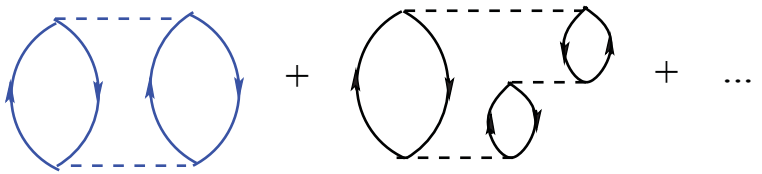
- zeroth-order: $E_0^{(0)} = \langle \Phi_0 | \hat{H}^0 | \Phi_0 \rangle$
- 1st order: $E_0^{(1)} = \langle \Phi_0 | \hat{H}' | \Phi_0 \rangle$
- 2nd order:

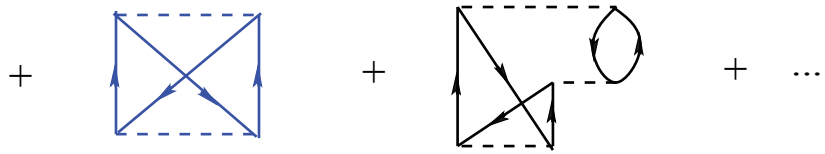
$$E_0^{(2)} = \sum_{n \neq 0} \frac{|\langle \Phi_0 | \hat{H}' | \Phi_n \rangle|^2}{E_0^{(0)} - E_n^{(0)}} = \underbrace{\sum_{i,a} \frac{|\langle \Phi_0 | \hat{H}' | \Phi_{i,a} \rangle|^2}{E_0^{(0)} - E_{i,a}^{(0)}}}_{\text{Single excitations} = E_c^{\text{SE}}} + \underbrace{\sum_{ij,ab} \frac{|\langle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

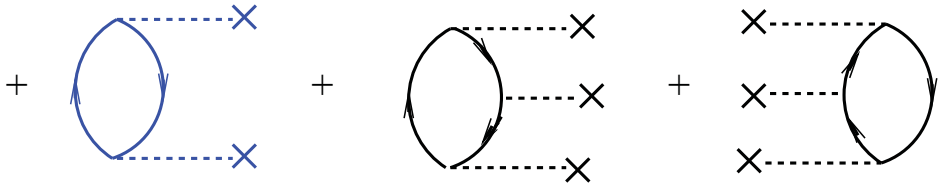
SE accounts for orbital relaxations



Renormalized 2nd-order Perturbation Theory (rPT2)

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

 $(= \text{SOSEX})$

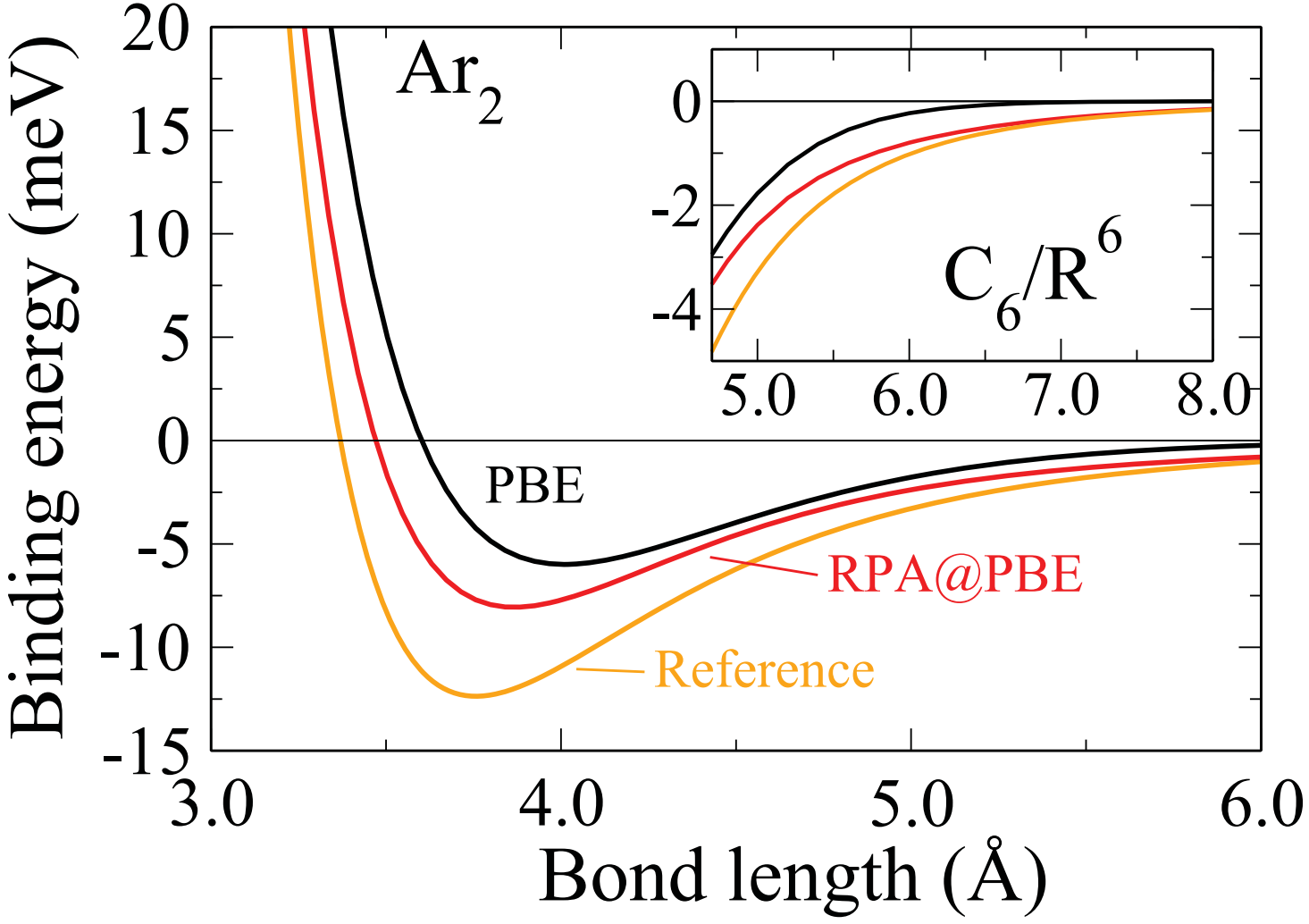


$(= \text{2PT})$

"rPT2" = "RPA+SOSEX+rSE"

X. Ren, P. Rinke, G. Scuseria, and M. Scheffler, arXiv:1212.3674

van der Waals bonding



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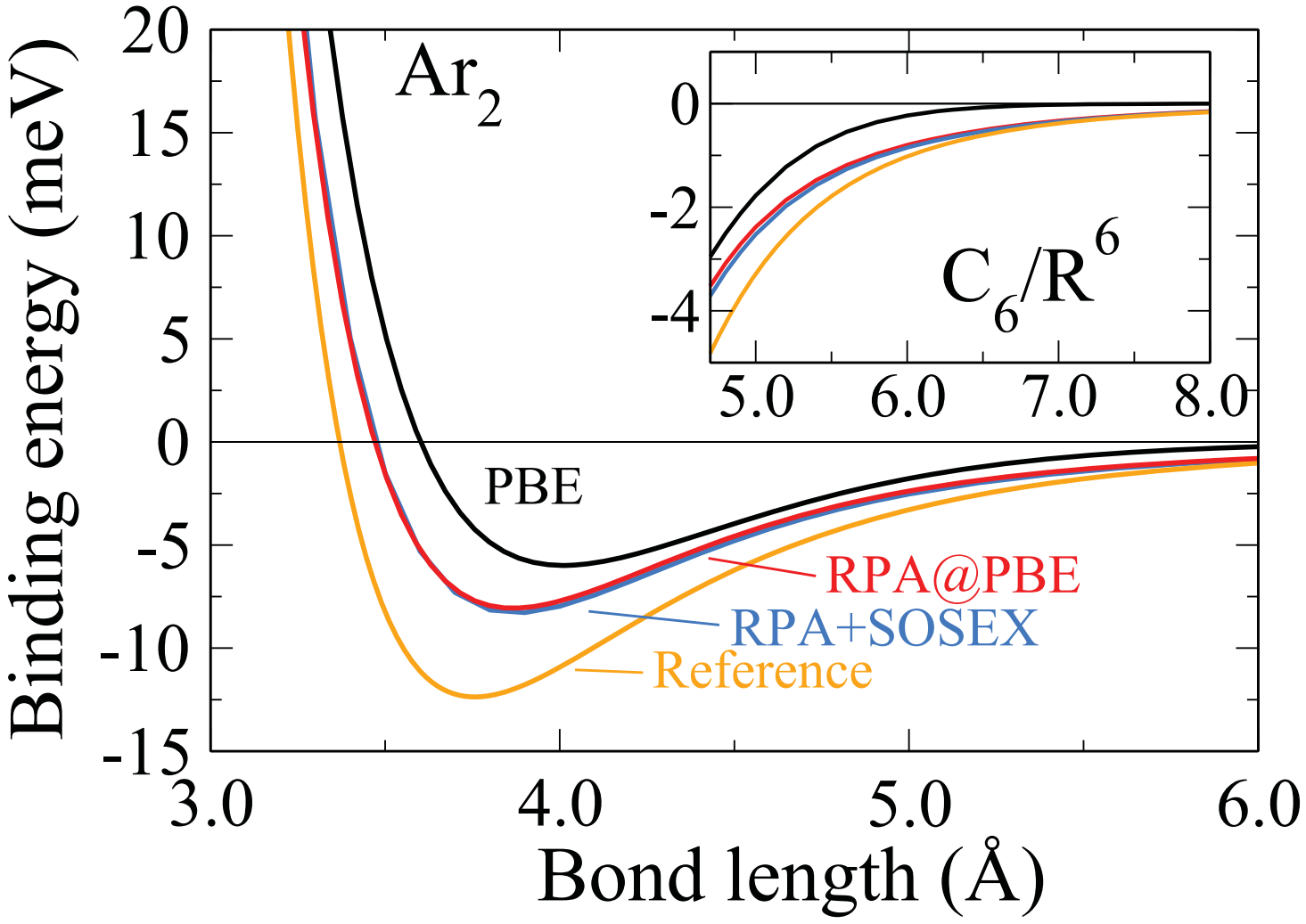
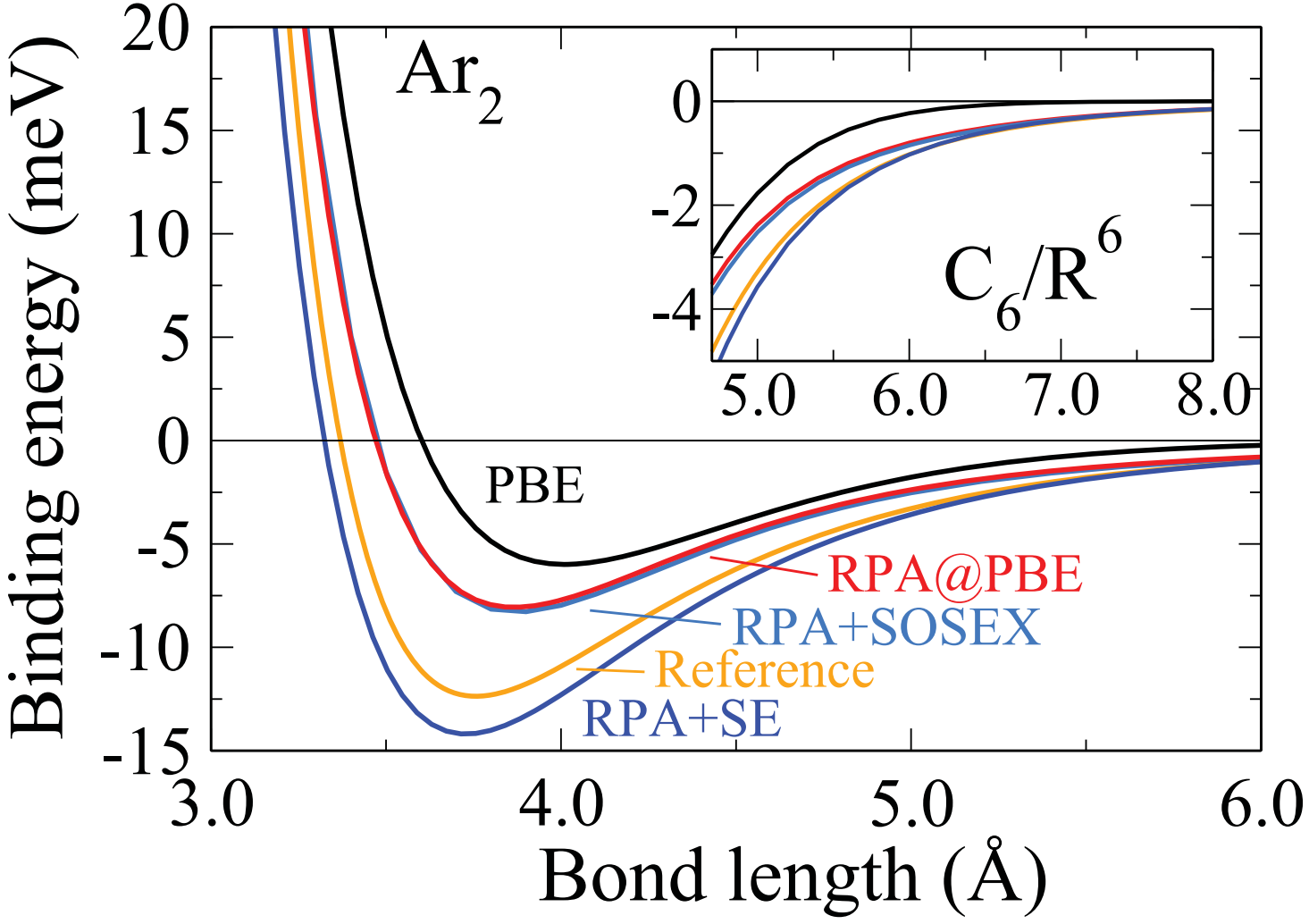


- SOSEX has almost no effect

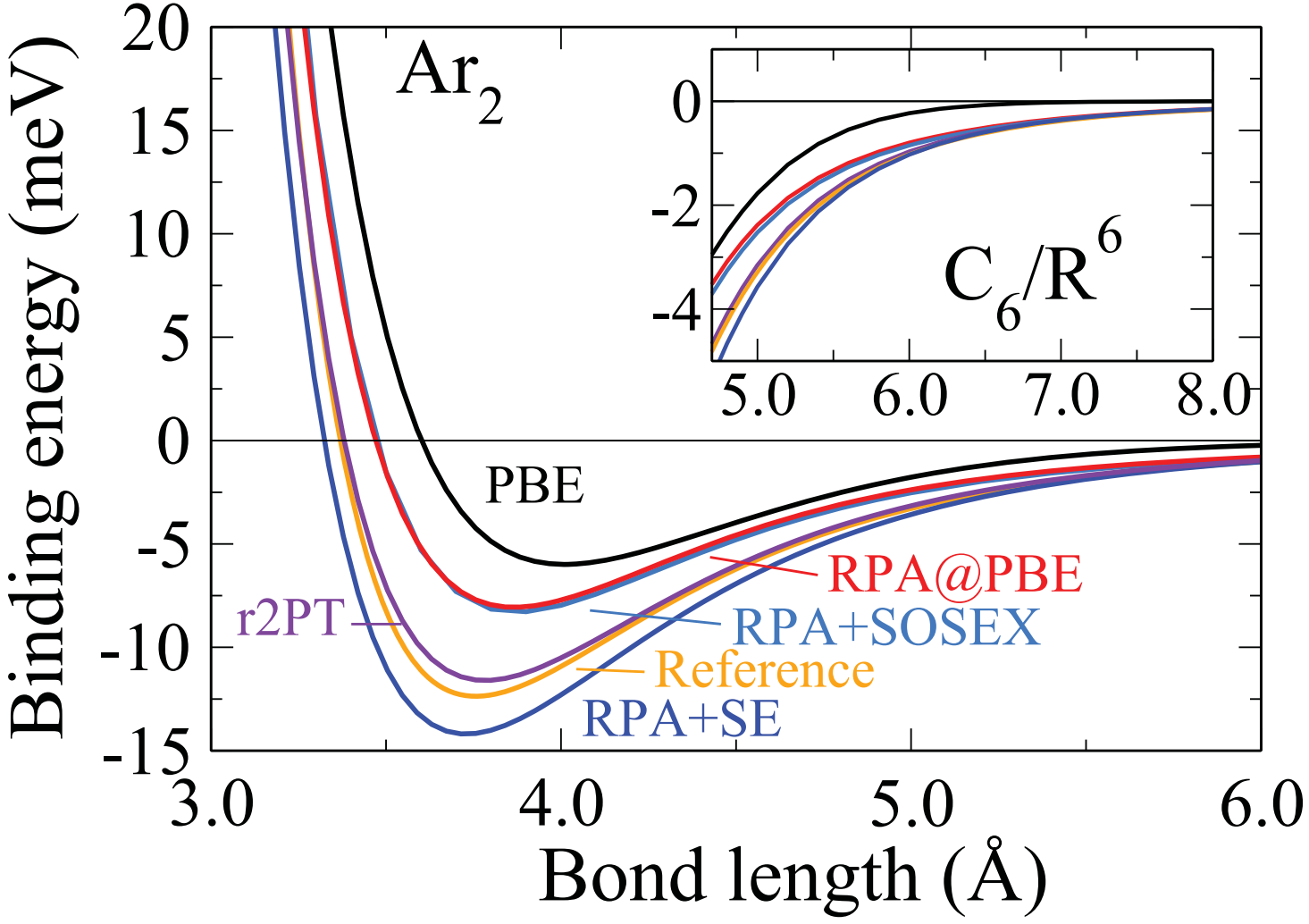
van der Waals bonding



- much improved binding and asymptotics

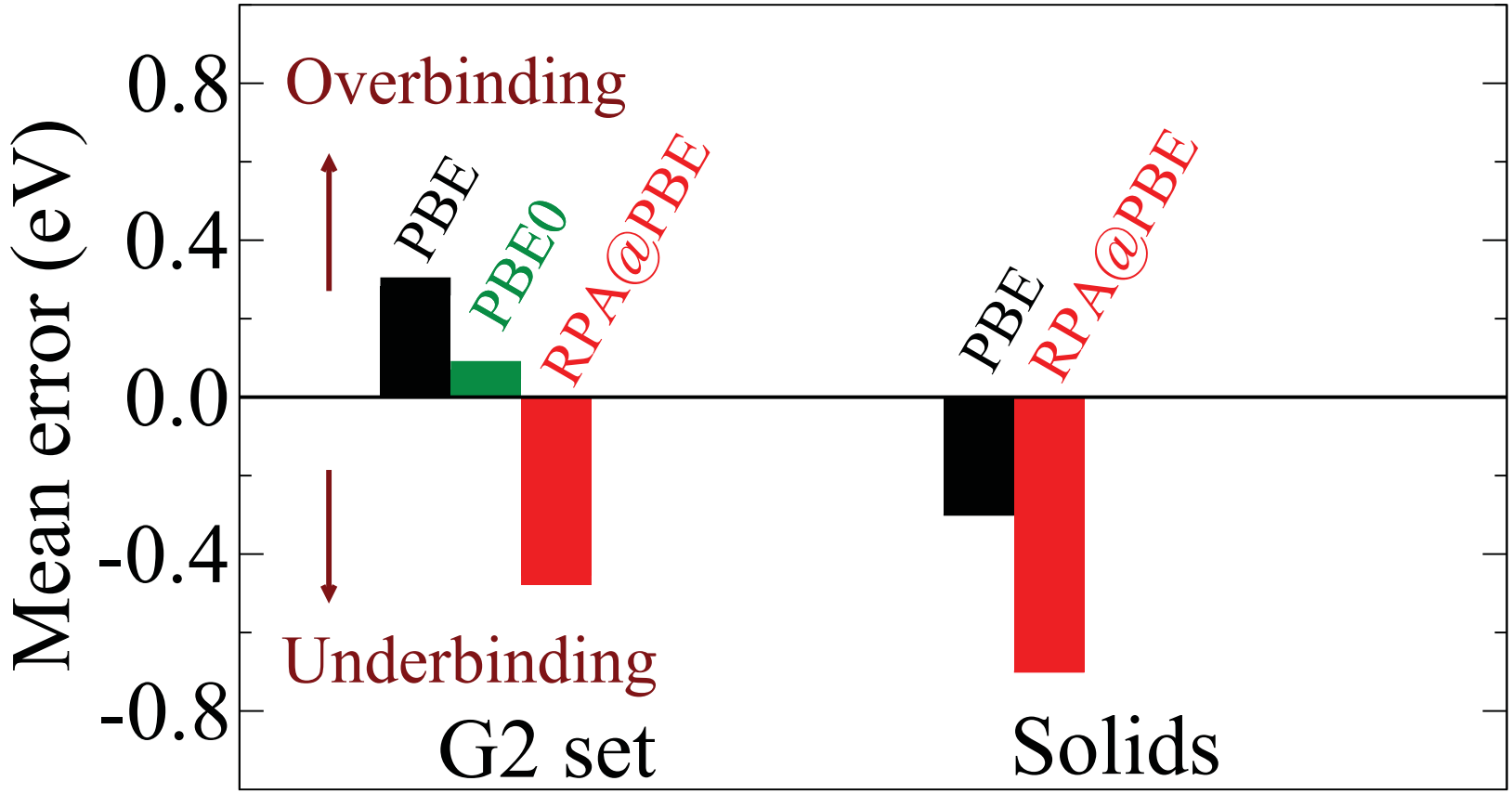
Ren, Tkatchenko, Rinke, and Scheffler, Phys. Rev. Lett. **106**, 153003 (2011)

van der Waals bonding



- best overall performance

Atomization energies



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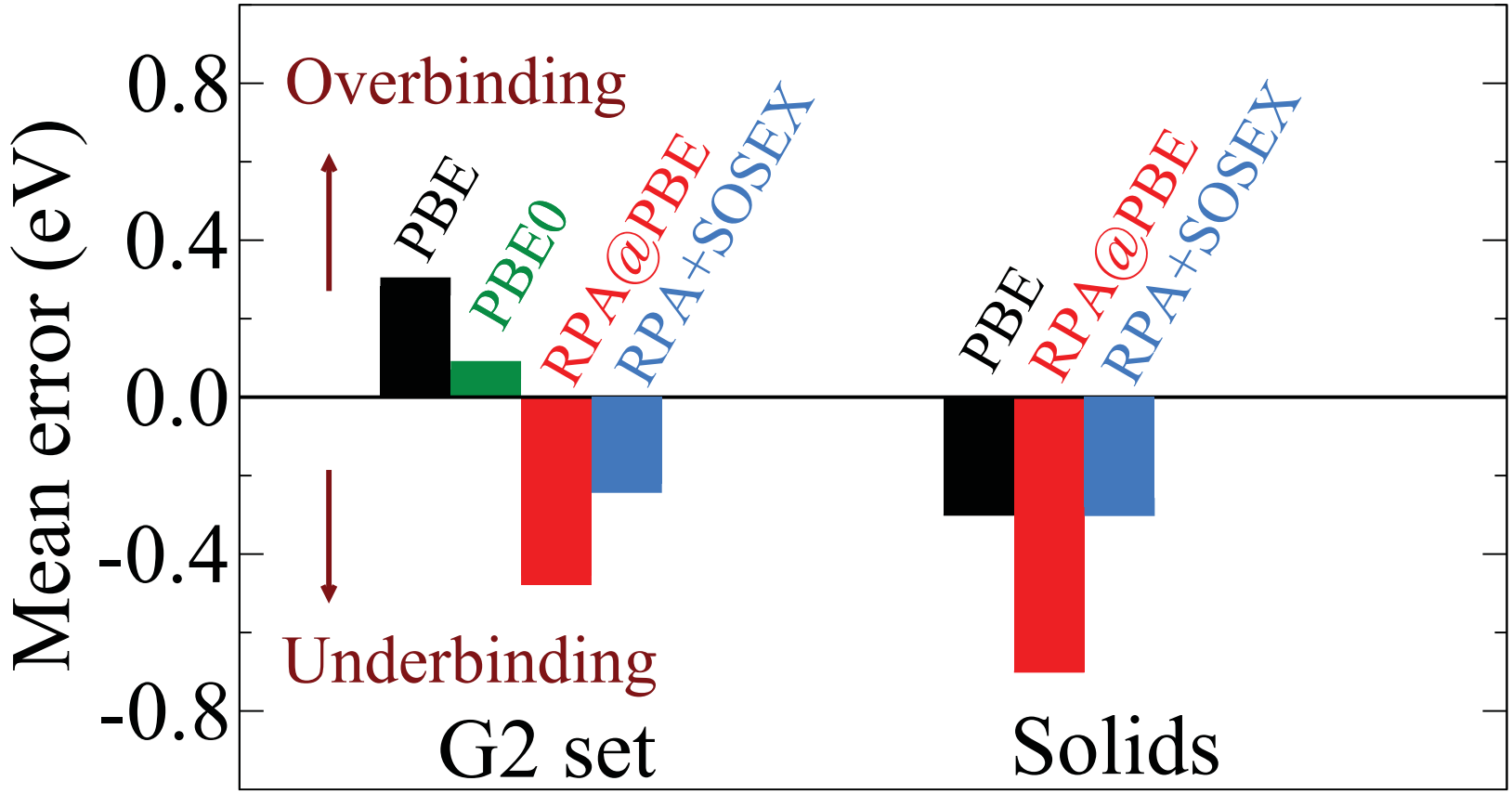

- SOSEX alleviates the underbinding problem

Paier *et al.*, J. Chem. Phys. **132**, 094103 (2010); **133**, 179902 (2010)
Harl, Schimka, and Kresse, Phys. Rev. B **81**, 115126 (2010)
Paier, Ren, Rinke, Scuseria, Grüneis, Kresse, and Scheffler, NJP **14**, 043002 (2012)

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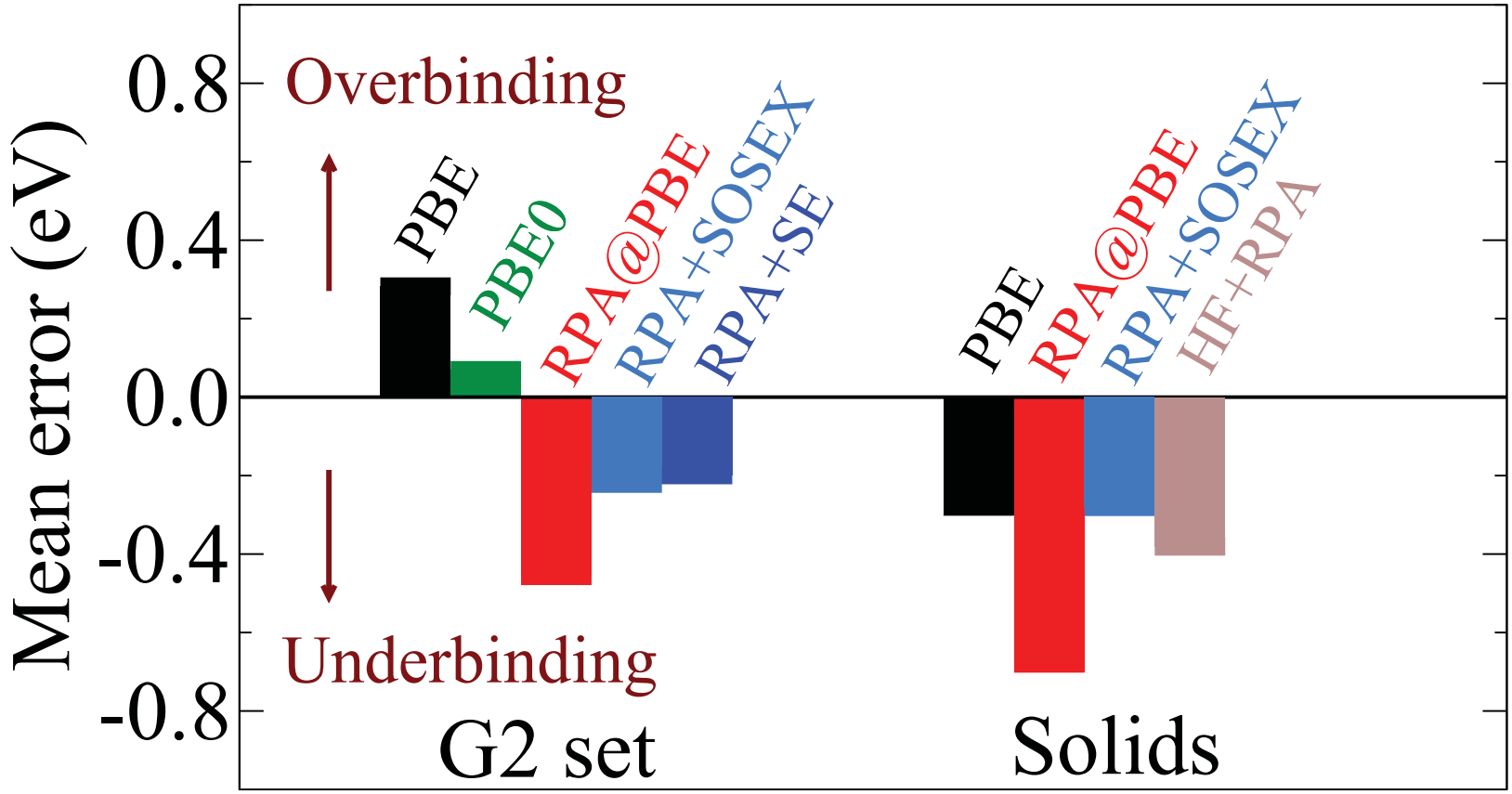

- "HF+RPA": EX@HF + RPA@PBE similar to
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Paier, Ren, Rinke, Scuseria, Grüneis, Kresse, and Scheffler, NJP **14**, 043002 (2012)
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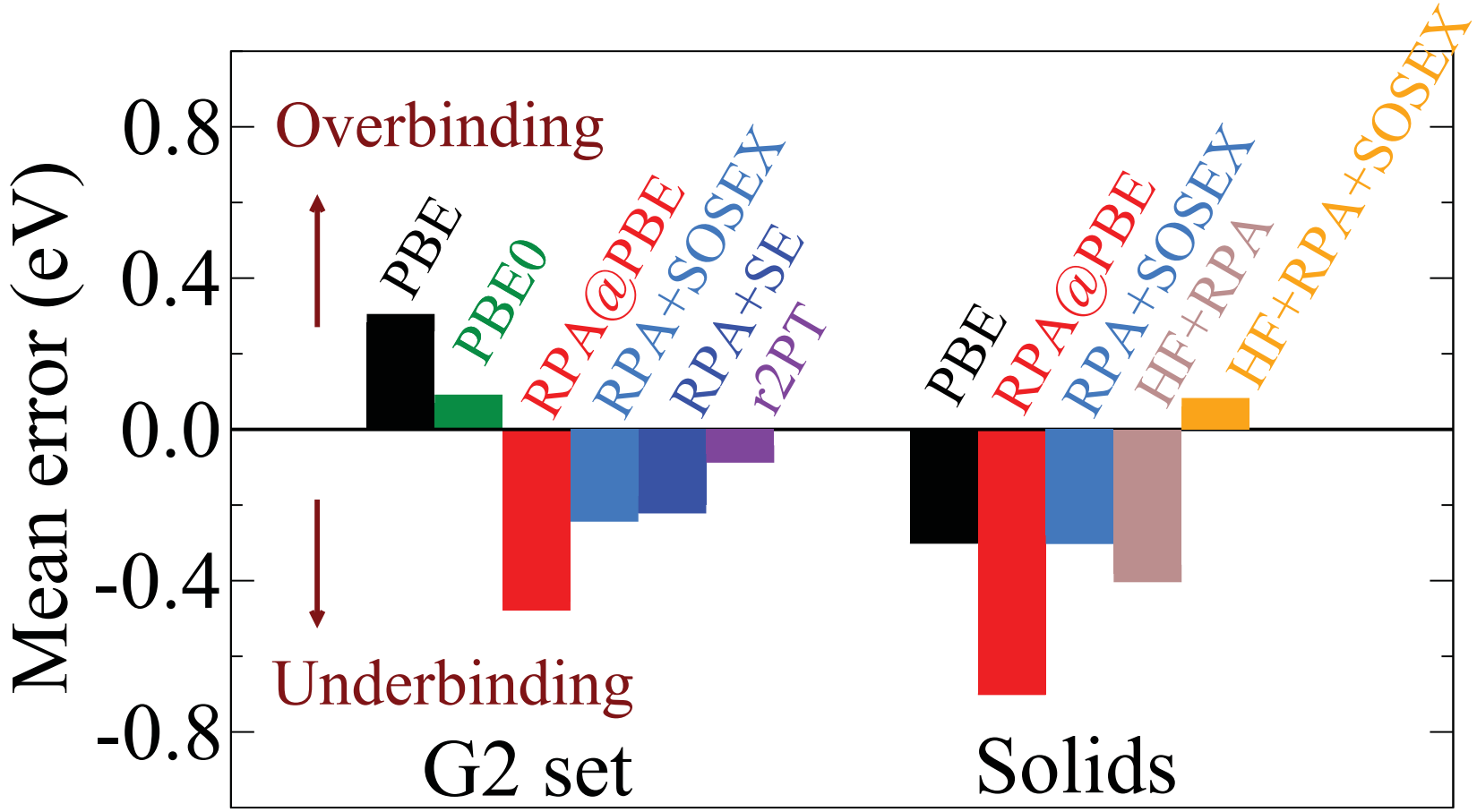

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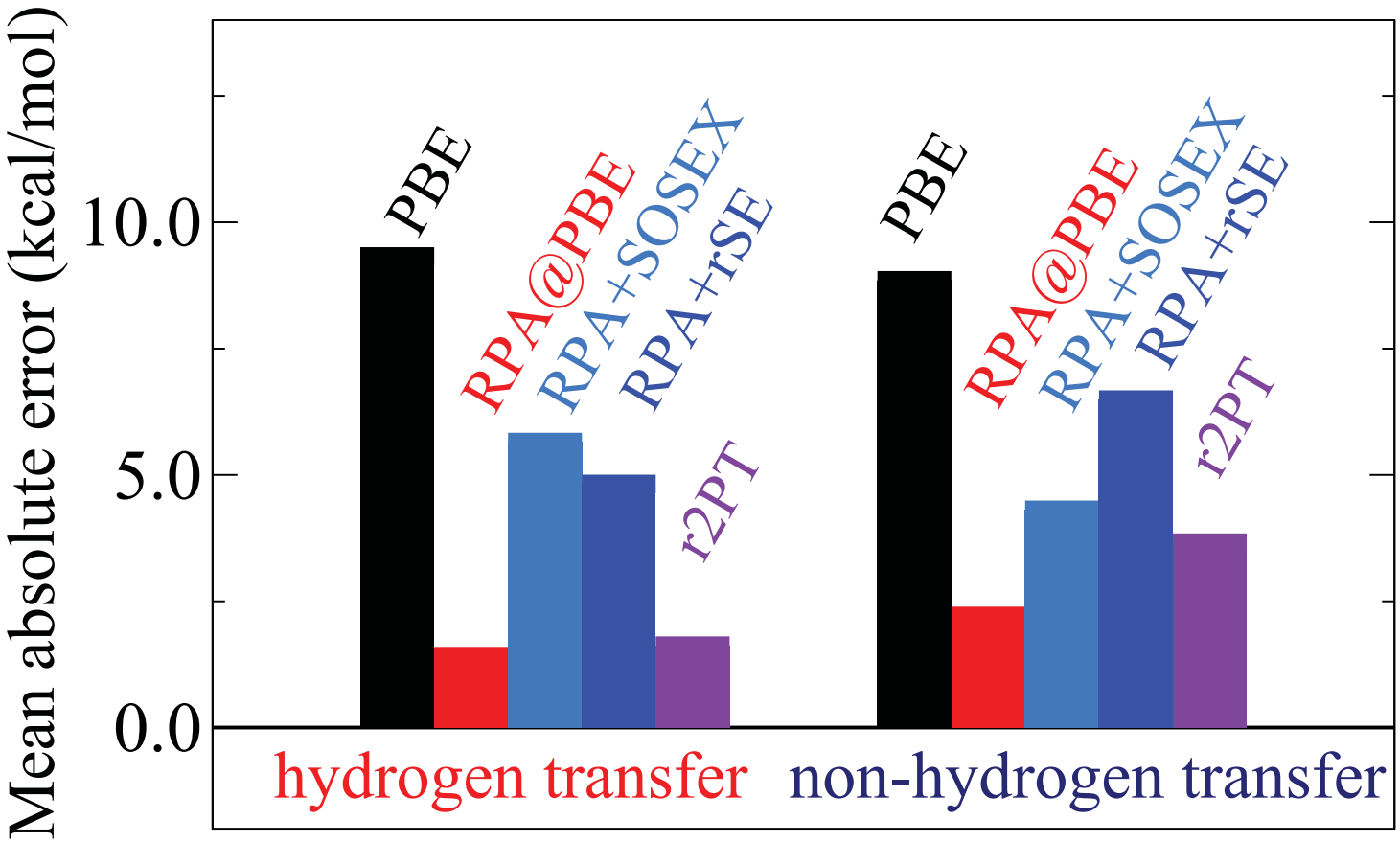
Reaction Barrier Heights

76 barrier heights HTBT-38 and NHTBH-38

(Y. Zhao, N. González-García, and D. G. Truhlar, J. Phys. Chem. A **109**, 2012 (2005)



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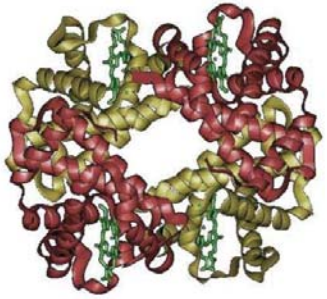

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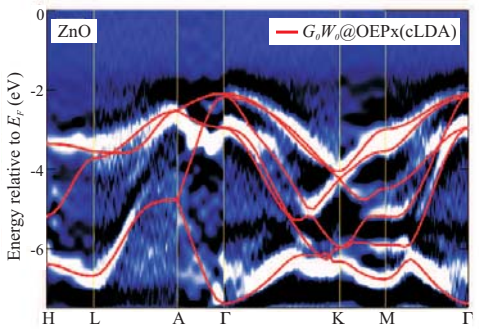
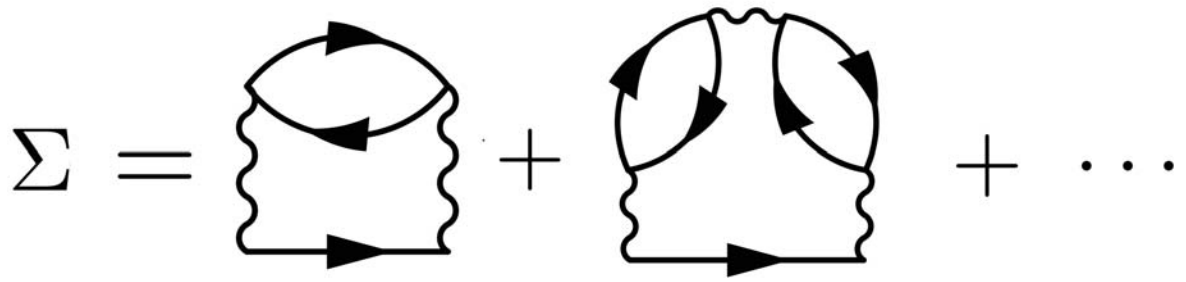


RPA and beyond for ground state:

- ✔ RPA performs well:
  - ✔ across dimensions
  - ✔ across chemical environments
- ✔ rPT2 gives best overall performance
- ✔ more benchmarking required
- ✘ rPT2 scales as N^5...

But what about excited states?

RPA and GW – a consistent pair



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Adiabatic connection fluctuation dissipation theorem (ACFDT):

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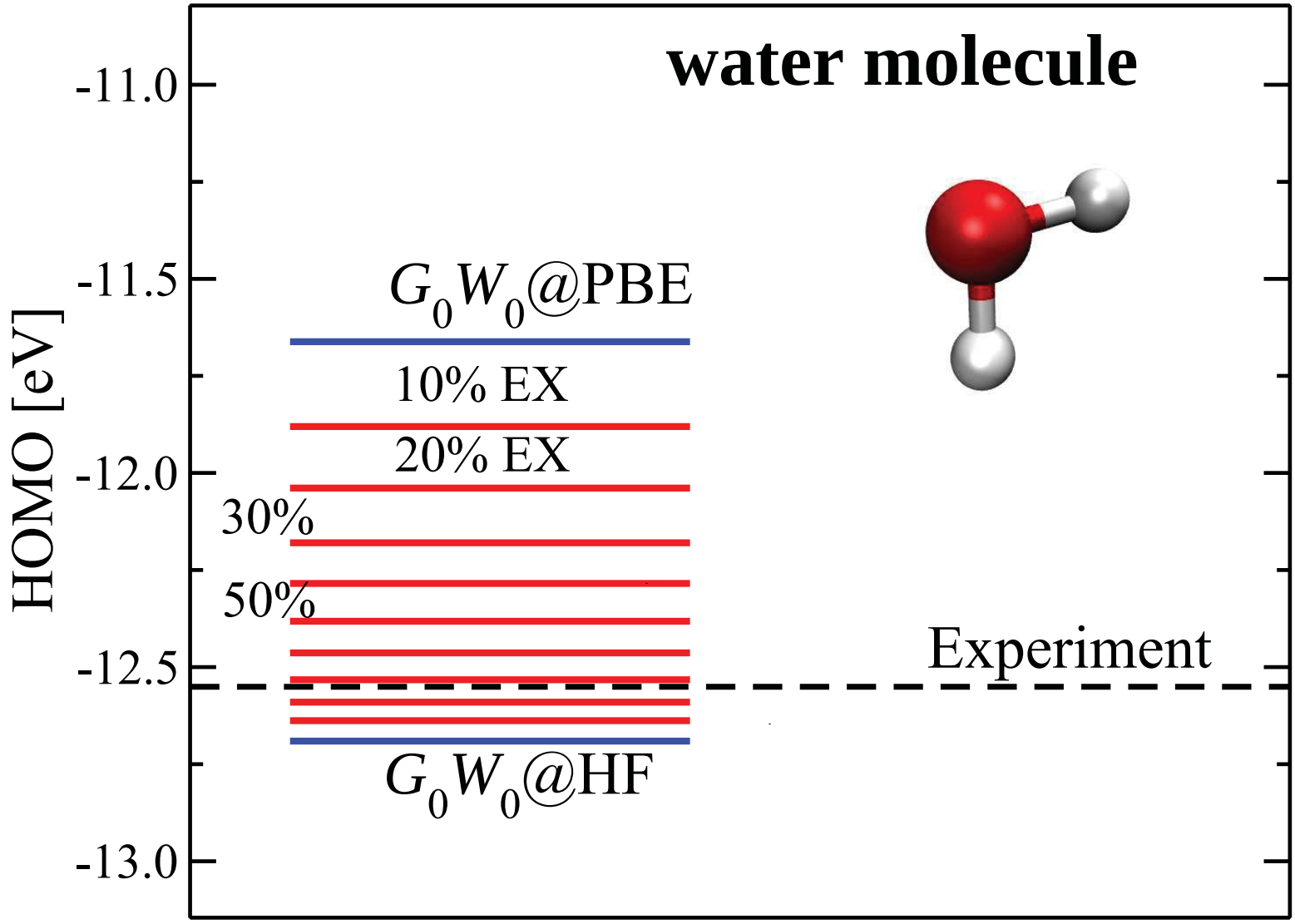
G_0W_0 for water



GW – The Issue of Self-Consistency

Hedin's GW equations:

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

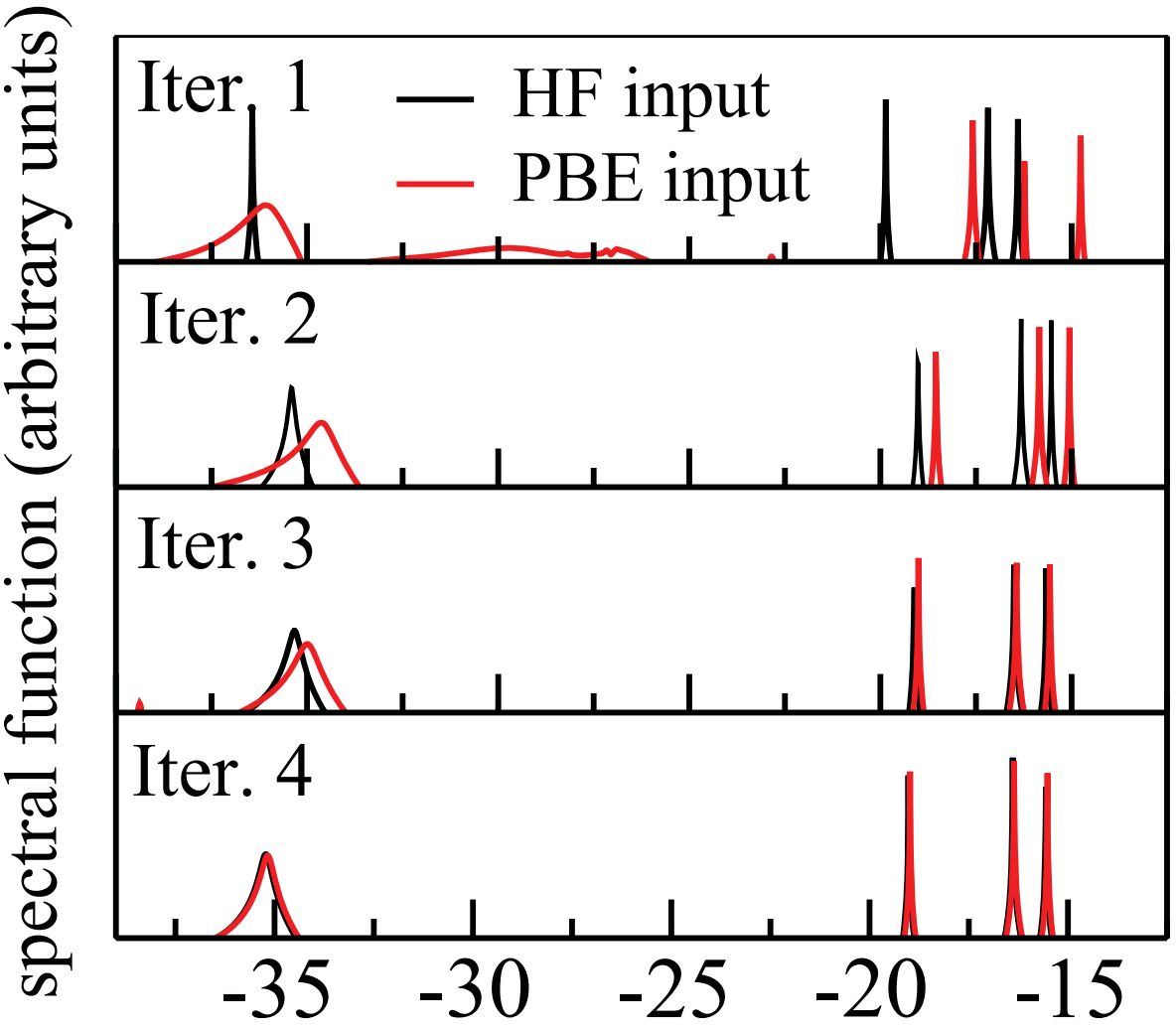
self-consistency

self-consistency

Dyson's equation:

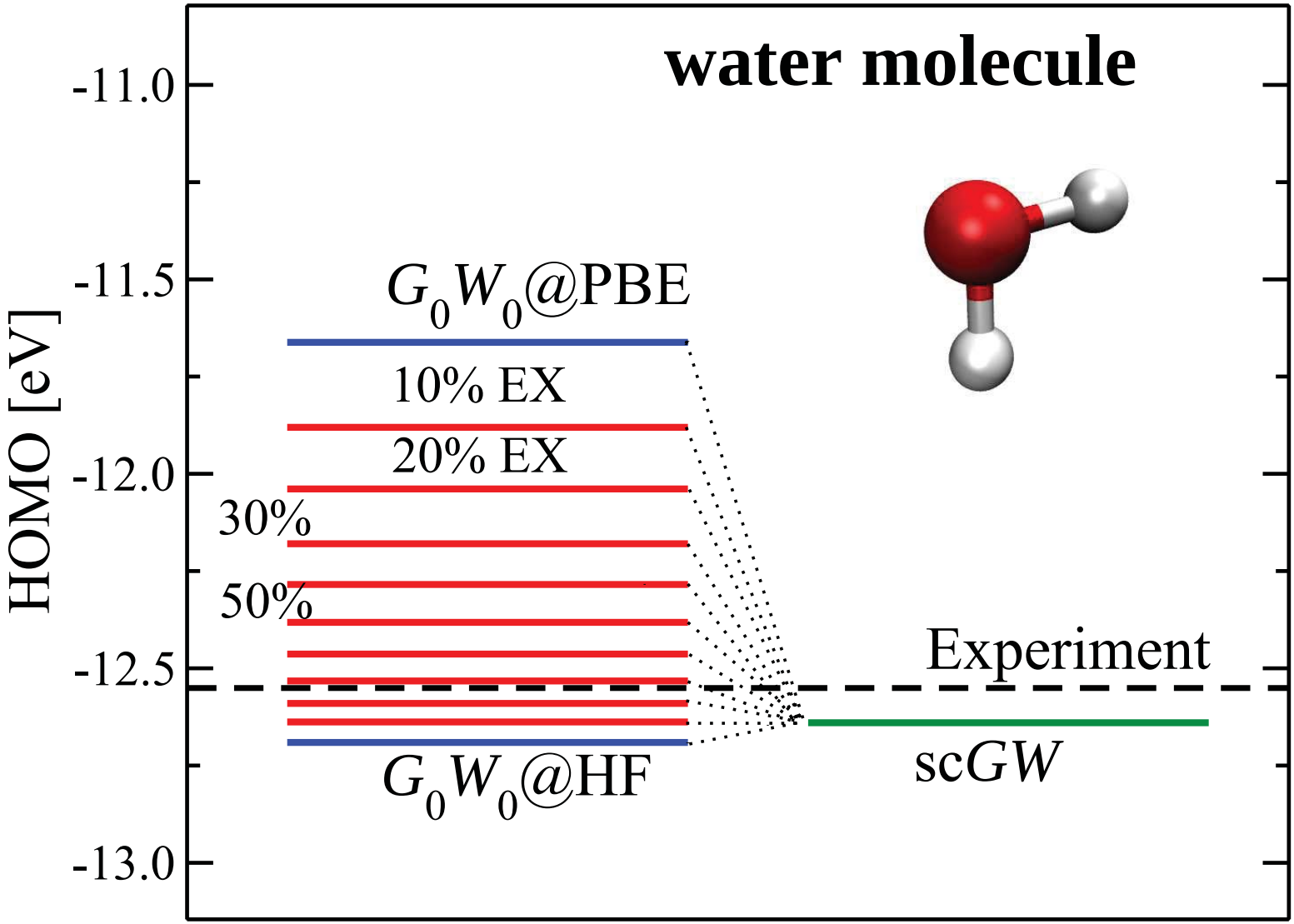
$$G^{-1}(1,2) = G_0^{-1}(1,2) - \Sigma(1,2)$$

Unique solution in self-consistent GW – N_2

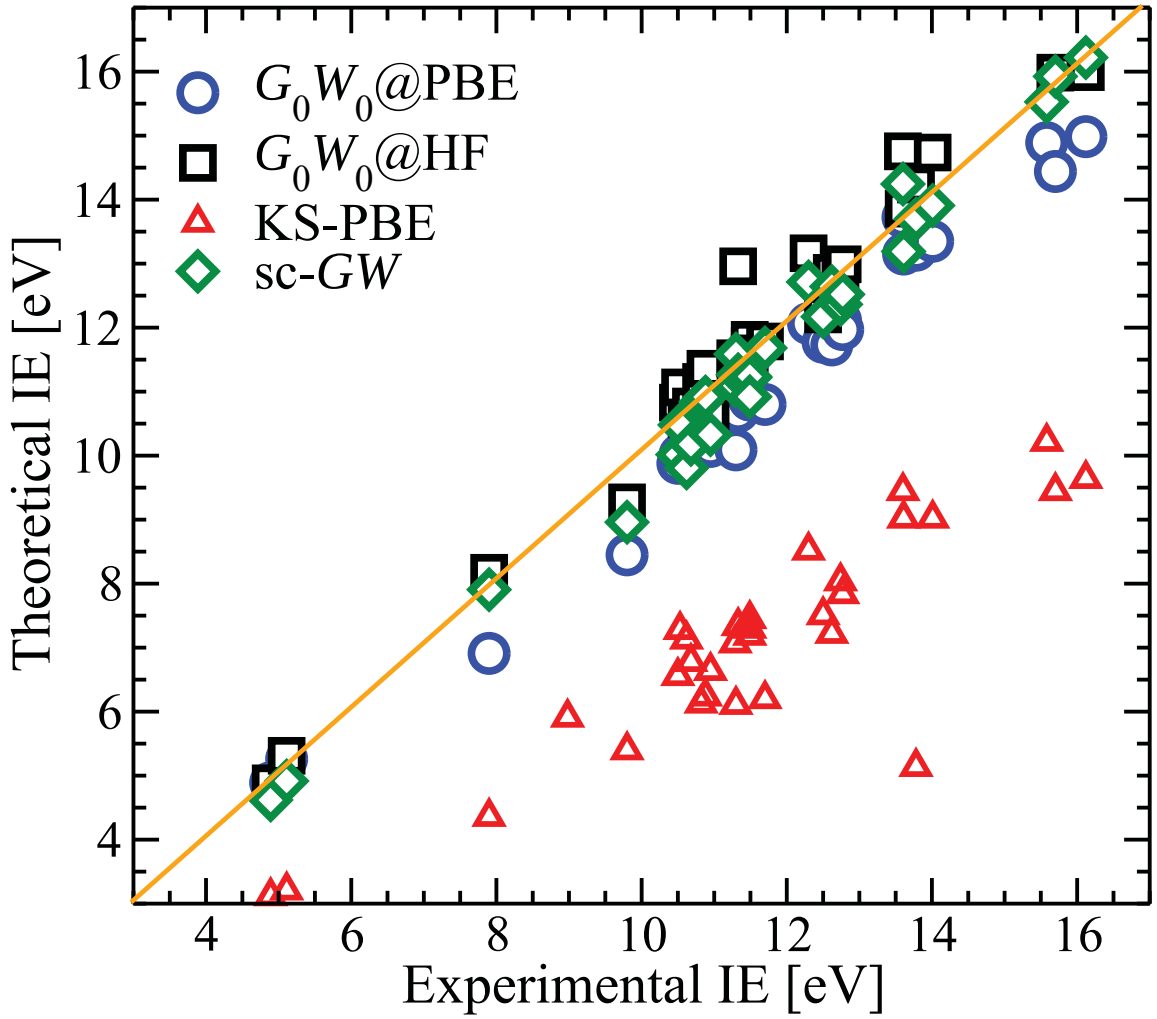


- sc-GW solution is independent of starting point

scGW for water



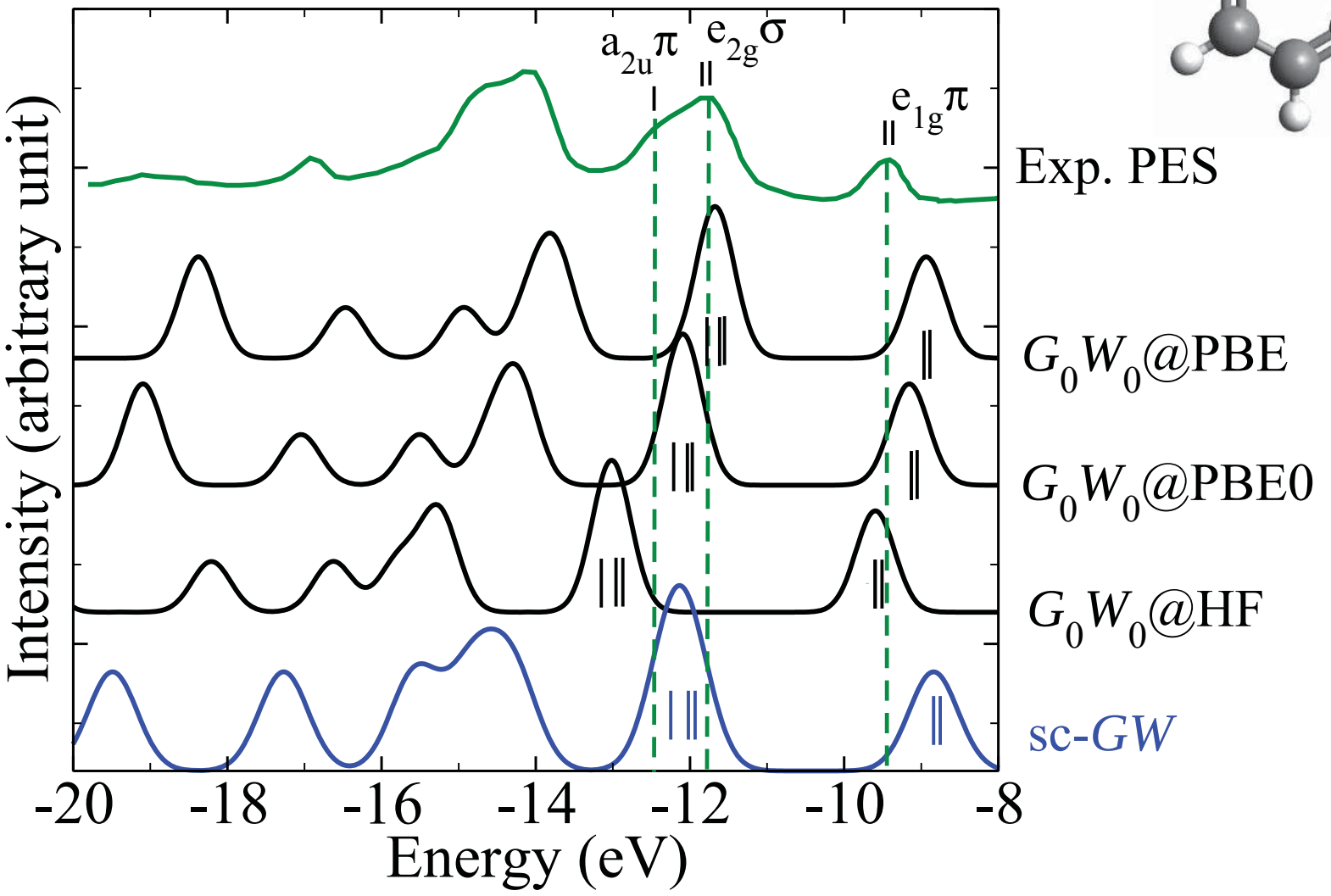
scGW and ionization potentials



deviation from exp.	
PBE	40%
G_0W_0@PBE	6%
G_0W_0@HF	4%
scGW	2%

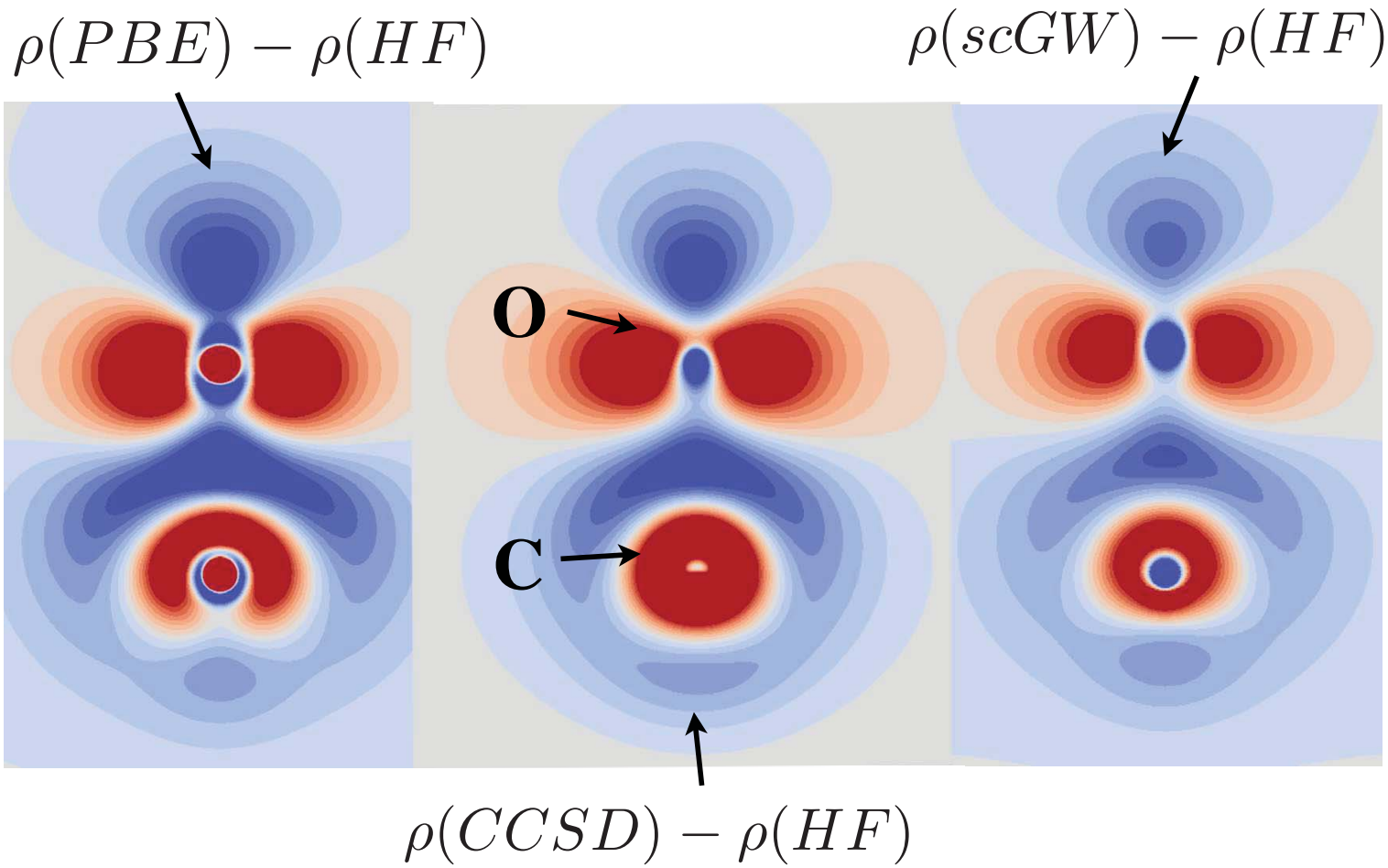
set taken from Rostgaard, Jacobsen, and Thygesen, PRB **81**, 085103, (2010)

GW spectra for benzene



N. Marom, F. Caruso, X. Ren, O. Hofmann, T. Körzdörfer, J. R. Chelikowsky, A. Rubio, M. Scheffler, and P. Rinke, Phys. Rev. B **86**, 245127 (2012)

The scGW density



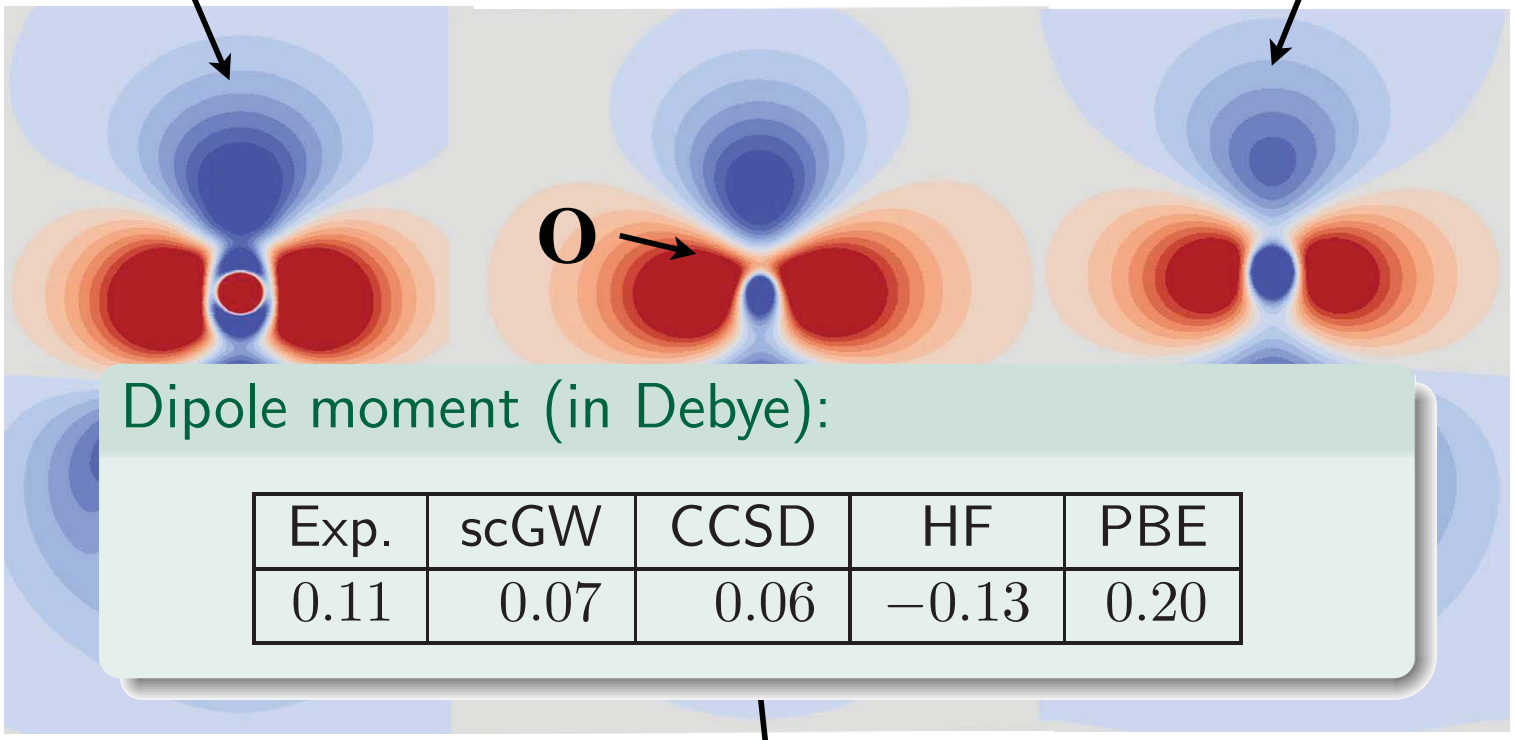
- density from Green's function: $\rho(\mathbf{r}) = -i \sum_\sigma G_{\sigma\sigma}(\mathbf{r}, \mathbf{r}, \tau = 0^+)$

Caruso, Ren, Rinke, Rubio, Scheffler, Phys. Rev. B 86, 081102(R) (2012)

The scGW density

$\rho(PBE) - \rho(HF)$

$\rho(scGW) - \rho(HF)$



Dipole moment (in Debye):

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

$\rho(CCSD) - \rho(HF)$

- 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, Phys. Rev. B 86, 081102(R) (2012)

Total energy in GW

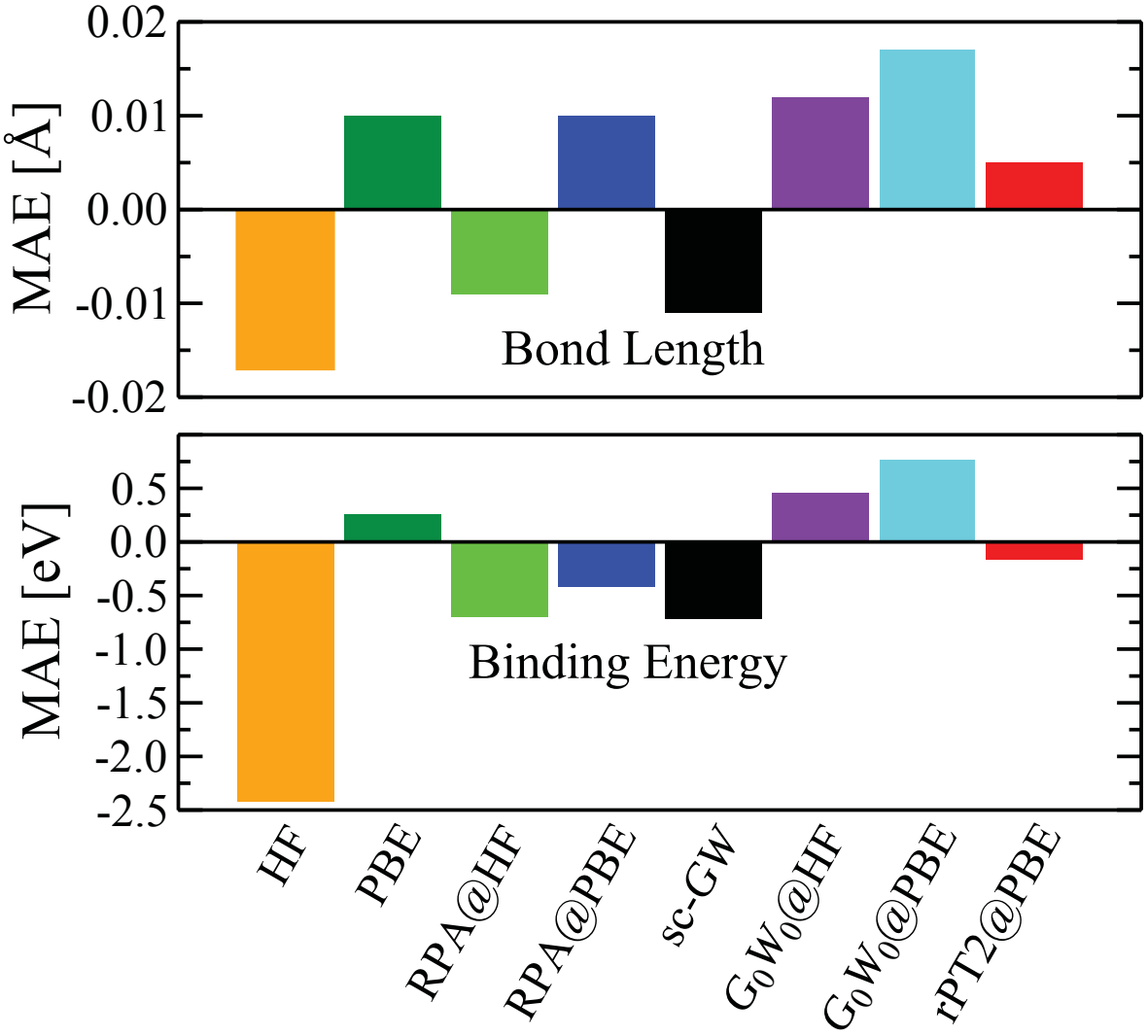
Galitskii-Migdal formula:

$$E_{\text{tot}}^{\text{GM}} = -i \int d\mathbf{r}\, dt \lim_{\mathbf{r}' \to \mathbf{r}} \lim_{t' \to t^+} \left[i\frac{\partial}{\partial t} - \frac{\nabla_{\mathbf{r}}^2}{2} + v_{\text{ext}}(\mathbf{r}) \right] G(\mathbf{r}t, \mathbf{r}'t')$$

or rearranged:

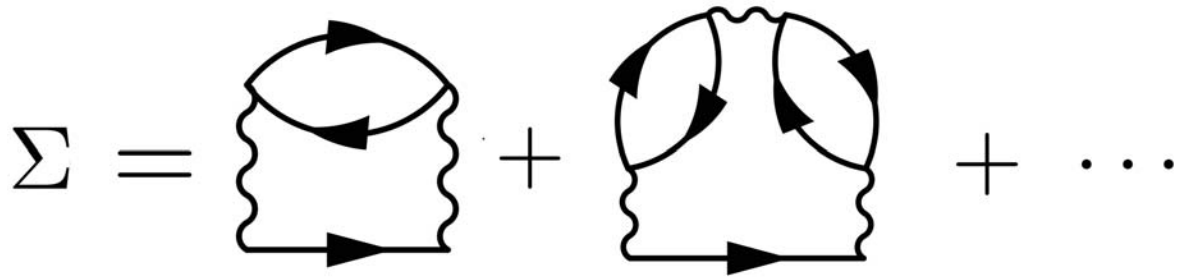
$$\begin{aligned} E_{\text{tot}}^{\text{GM}} &= -i \sum_{ij} \left[2t_{ij} + 2v_{ij}^{\text{ext}} + v_{ij}^{H} + \Sigma_{ij}^{x} \right] G_{ij}(t = 0^-) \\ &\quad -i \sum_{ij} \int \frac{d\omega}{2\pi}\, \Sigma_{ij}^{c}(\omega) G_{ij}(\omega) e^{i\omega\eta} \\ &= T + E_{\text{ext}} + E_H + E_x + E_c^{GW} \end{aligned}$$

GW total energy in comparison



set of 6 dimers: LiH, LiF, HF, CO, H_2 and N_2

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):

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

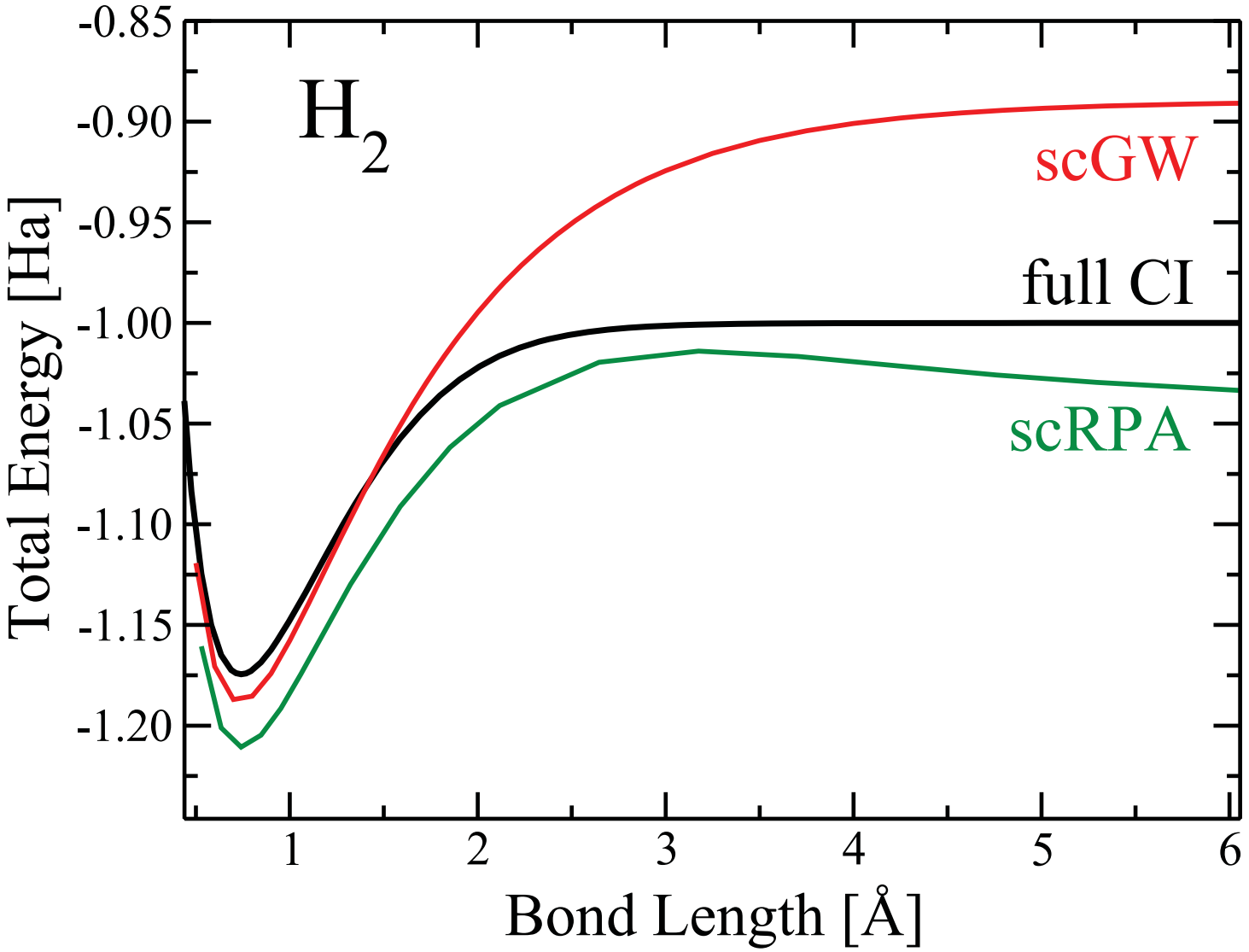
RPA and GW – a consistent pair

scGW versus scRPA:

- RPA also iterated to self-consistency (scRPA)

Do MBPT and DFT differ for the same diagrams?

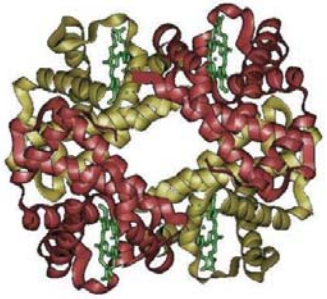
The most strongly correlated system



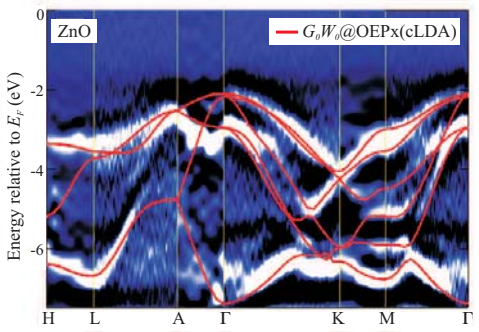
full CI: L. Wolniewicz, J. Chem. Phys. **99**, 1851 (1993)

Wish list for "optimum" electronic structure approach

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



(bio)molecules



RPA and GW for ground and excited states:

- ✔ scGW
  - ✔ is starting-point independent
  - ✔ gives new density
  - ✔ consistent ground and excited states
  - ✔ spectra not as good as "right" G_0W_0
- ✔ RPA performs better for strong correlation
- ✔ rPT2 still gives best overall performance
- ✔ more benchmarking required

Acknowledgements

Volker Blum

Noa Marom

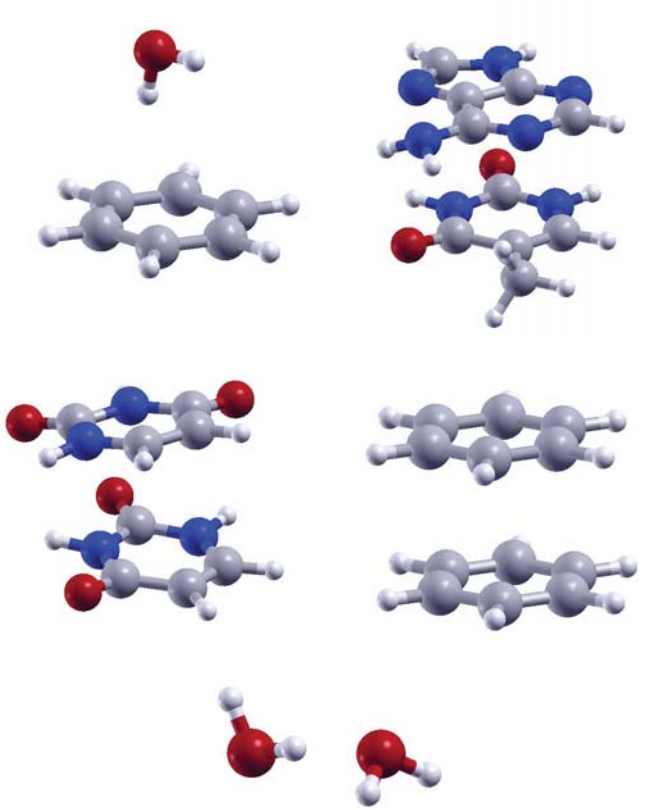
Angel Rubio

Matthias Scheffler

Van der Waals interactions - the S22 benchmark set

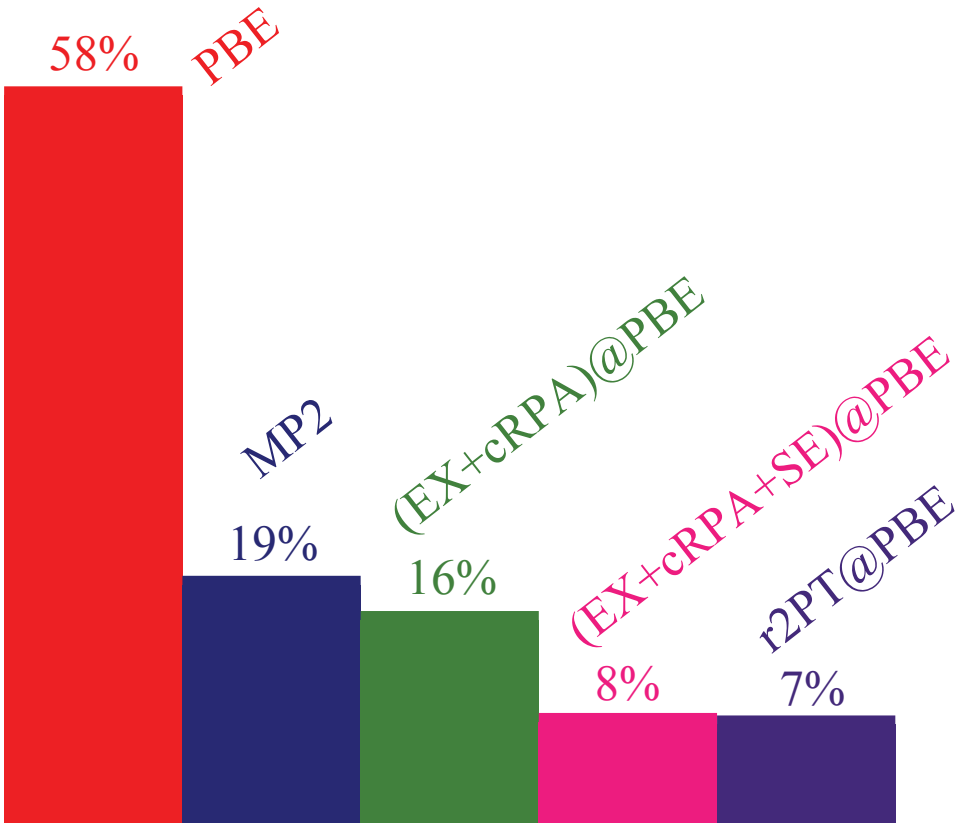
S22 set of binding energies

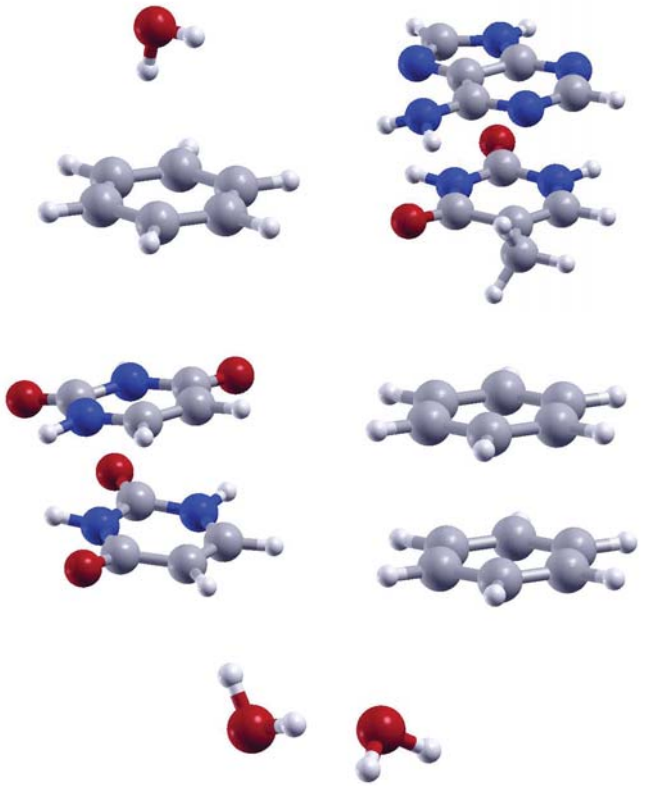
- 22 representative dimers:
  - 7 hydrogen bonded
  - 8 dispersion bonded
  - 7 mixed character
- CCSD(T) ("gold standard") reference values



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

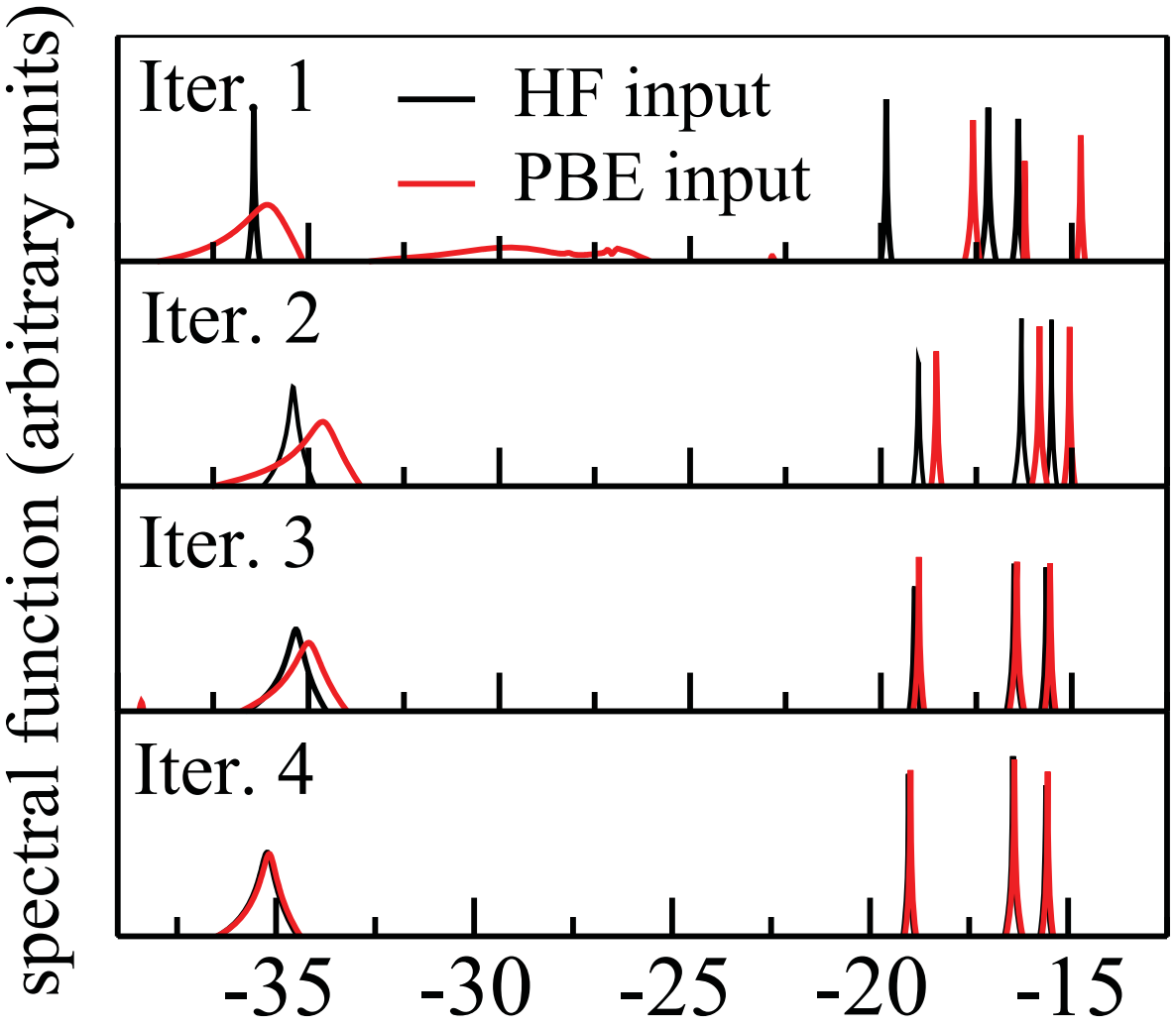
Van der Waals interactions - the S22 benchmark set





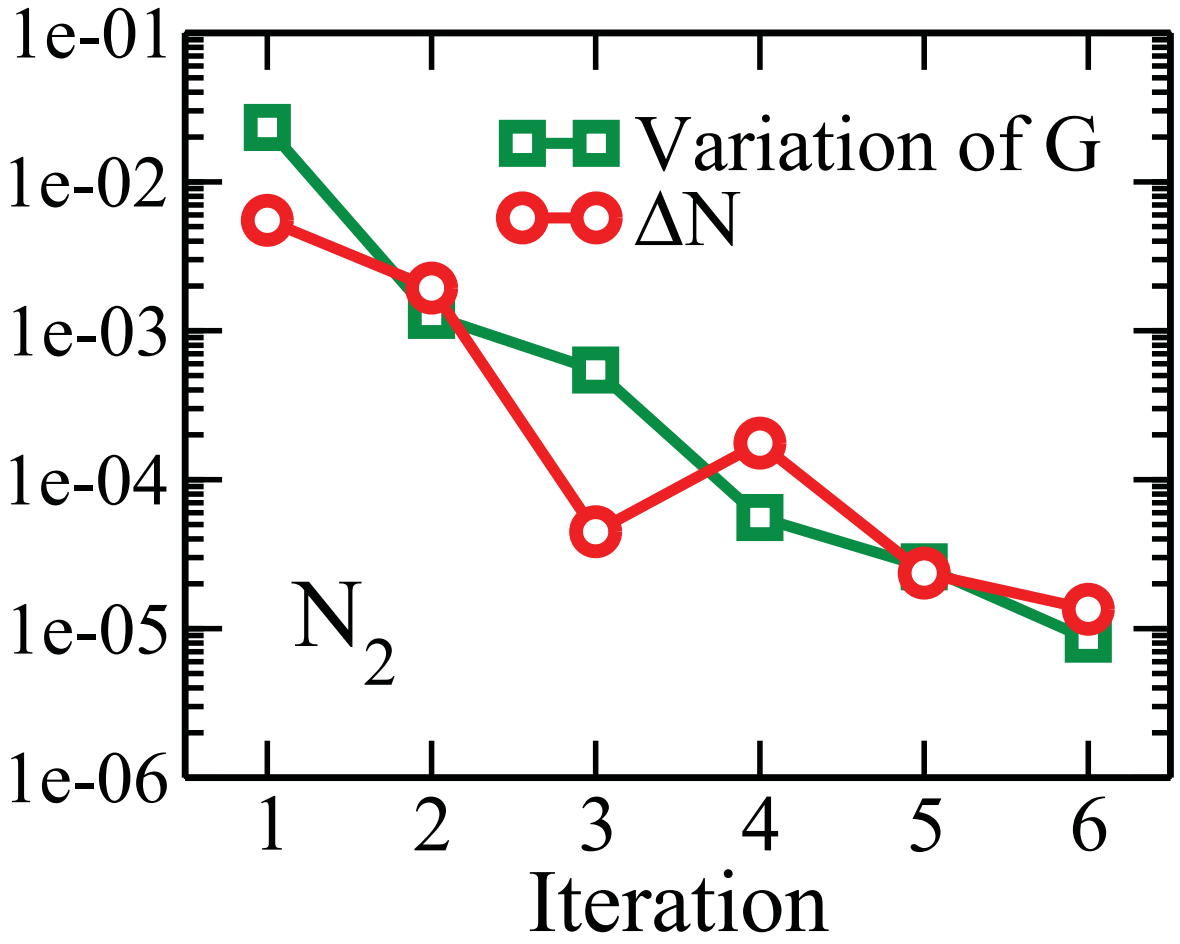
X. Ren, P. Rinke, A. Tkatchenko, M. Scheffler,
Phys. Rev. Lett. **106**, 153003 (2011)

Unique solution in self-consistent GW



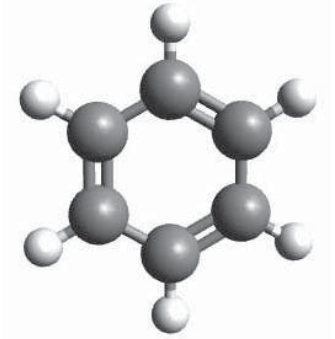
- sc-GW solution is independent of starting point

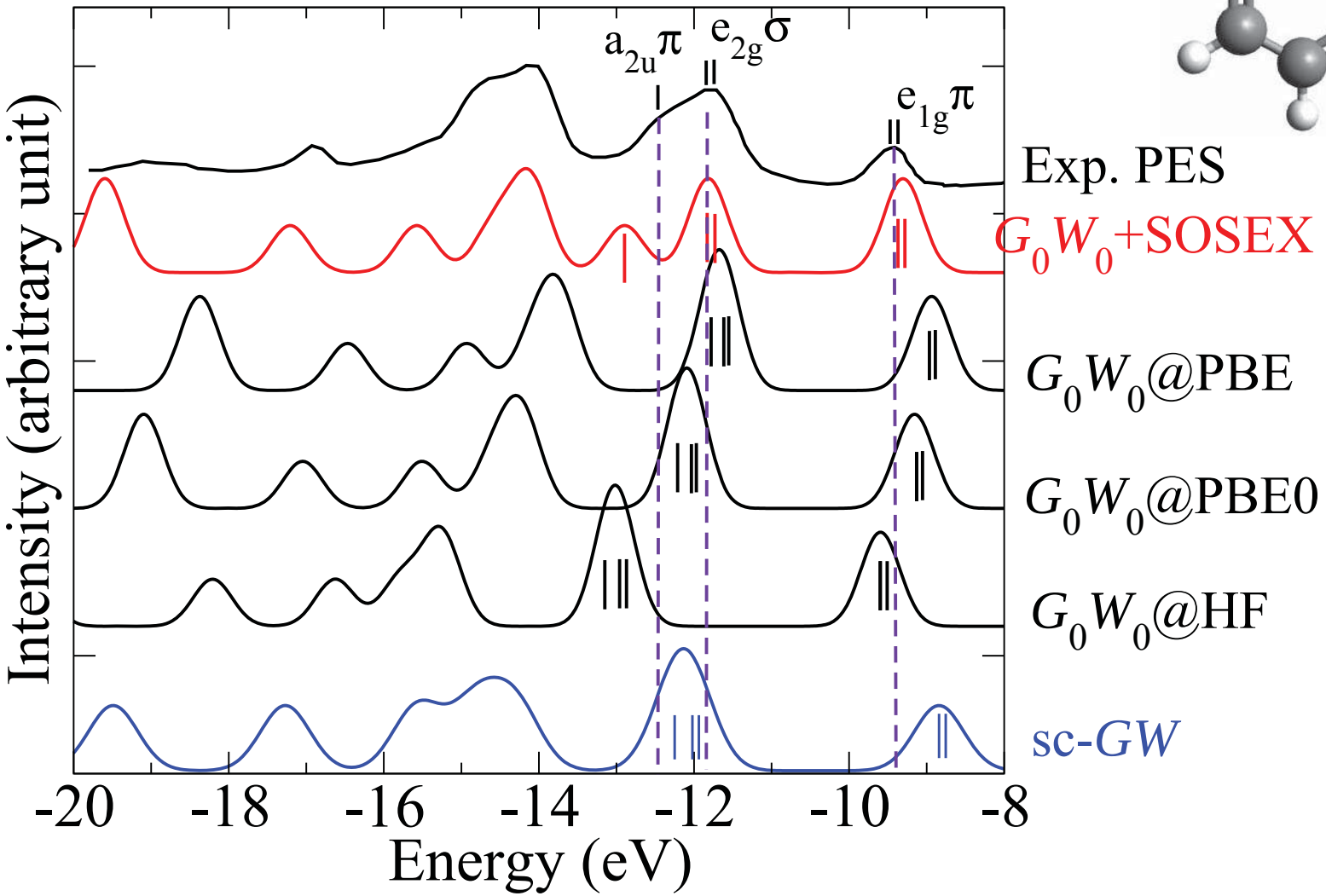
Unique solution in self-consistent GW



- sc-GW solution converges exponentially fast
- sc-GW conserves particle number

GW spectra for benzene

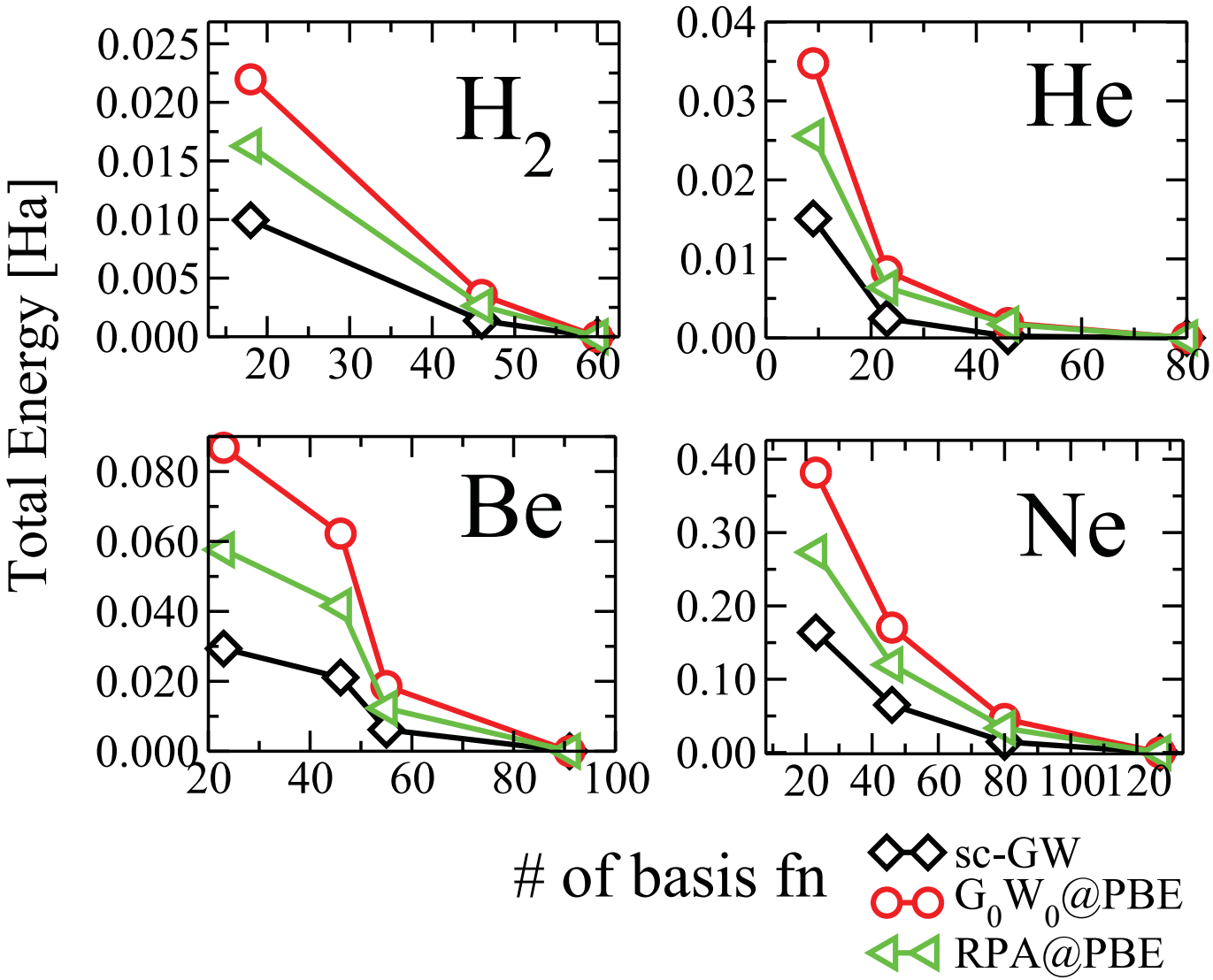




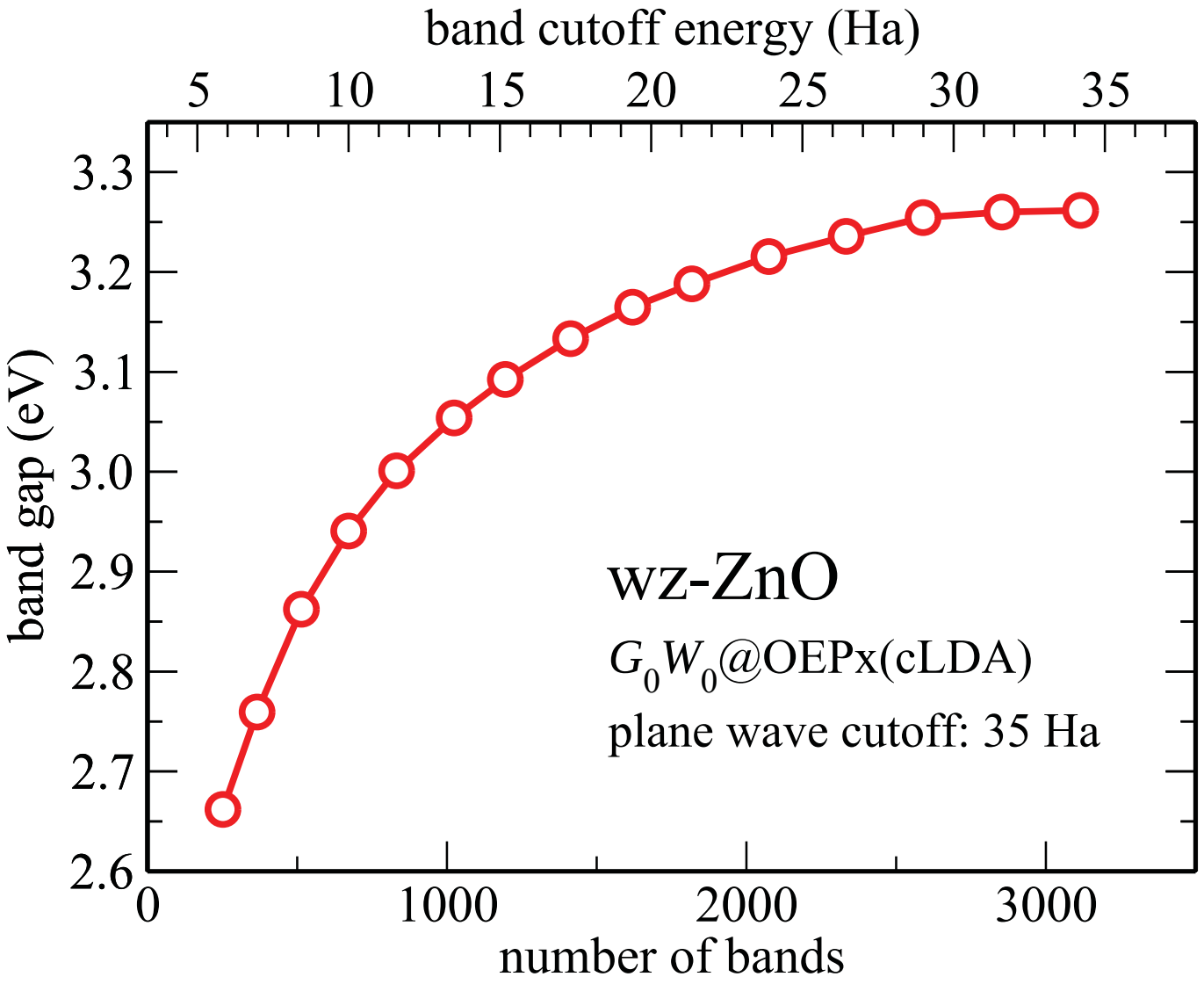
N. Marom, F. Caruso, X. Ren, M. Scheffler, and P. Rinke, in preparation

Basis set convergence with NAO: **sc-GW total energies**

aug-cc-pV*N*Z gaussian basis sets ($N = D, T, Q, 5$)



wurtzite ZnO – convergence of G_0W_0



see also related work by Shih, Xue, Zhang, Cohen and Louie, PRL **105**, 146401 (2010)