Beyond RPA and *GW*: renormalized second-order perturbation theory for ground-state and excited-state calculations

Xinguo Ren

Fritz Haber Institute, Berlin, Germany

FHI-aims Developers' and Users' Meeting,
Berlin, Germany, August 28-31, 2012

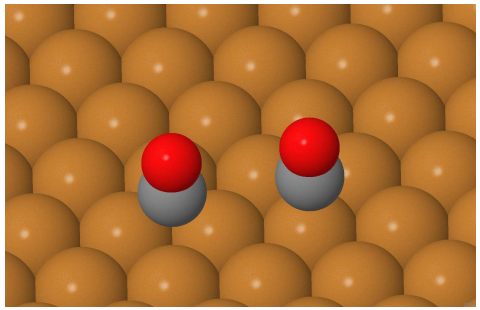
In collaboration with

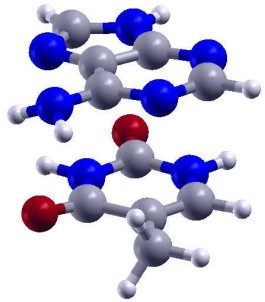
Patrick Rinke, Matthias Scheffler, Joachim Paier, Gustavo Scuseria

Thanks to all FHI-aims people

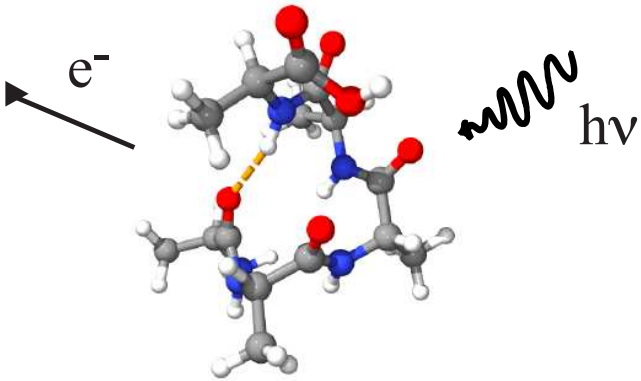
Ground state and excited states of condensed matters

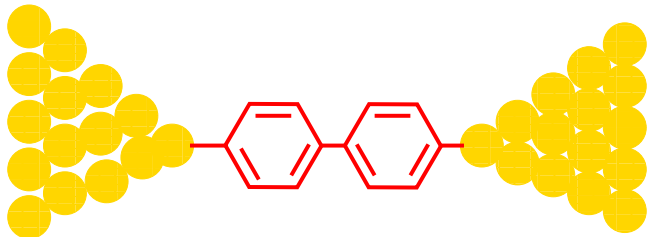
- Ground-state energy $\Longrightarrow$ structures, interaction strengths, cohesive properties, etc.





- Excitation energies $\Longrightarrow$ Photoemission spectroscopy, transport properties, etc.





State-of-the-art first-principles methods

- Ground-state energies:

  Density-functional theory (DFT) with advanced exchange-correlation functionals: hybrid functionals, random-phase approximation (RPA), double hybrids.

- Single-particle excitation energies (self-energy!) :

  $\epsilon_s = E(N,0) - E(N-1,s)$ and $\epsilon_t = E(N+1,t) - E(N,0)$

  The *GW* method

State-of-the-art first-principles methods

- Ground-state energies:

  Density-functional theory (DFT) with advanced exchange-correlation functionals: hybrid functionals, random-phase approximation (RPA), double hybrids.

- Single-particle excitation energies (self-energy!) :

  $\epsilon_s = E(N,0) - E(N-1,s)$ and $\epsilon_t = E(N+1,t) - E(N,0)$

  The *GW* method

For certain problems, one even needs to go beyond RPA and *GW*.

Diagrammatic technique $\Longrightarrow$
renormalized 2nd-order perturbation theory (rPT2)
to correct RPA and *GW*.

The Fritz Haber Institute *ab initio molecular simulations* package (FHI-aims)

Local atom-centered basis

$$\varphi_{i[lm]}(\mathbf{r}) = \frac{u_i(r)}{r} Y_{lm}(\Omega)$$

Standard DFT (LDA, GGA)

- all-electron
- periodic, cluster systems on equal footing
- favorable scaling (system size and CPUs)

Beyond standard DFT all based on "resolution of identity"

- Hartree-Fock, hybrid functionals (PBE0, HSE, B3LYP), MP2, double hybrids, RPA, rPT2
- quasiparticle self-energies: *GW*, MP2, fully self-consistent *GW*

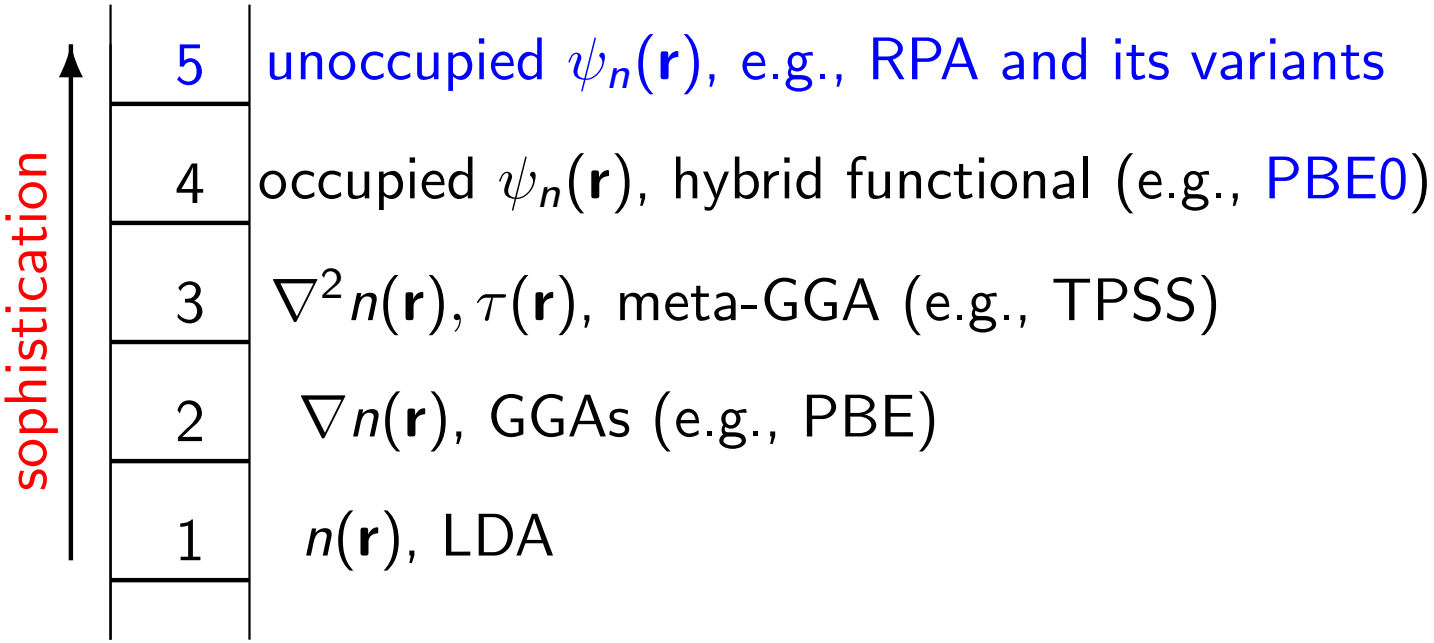
V. Blum *et al.*, Comp. Phys. Comm. **180**, 2175 (2009).

X. Ren *et al.*, New J. Phys. **14**, 053020 (2012).

See F. Caruso' talk

Jacob's ladder in DFT (John Perdew)

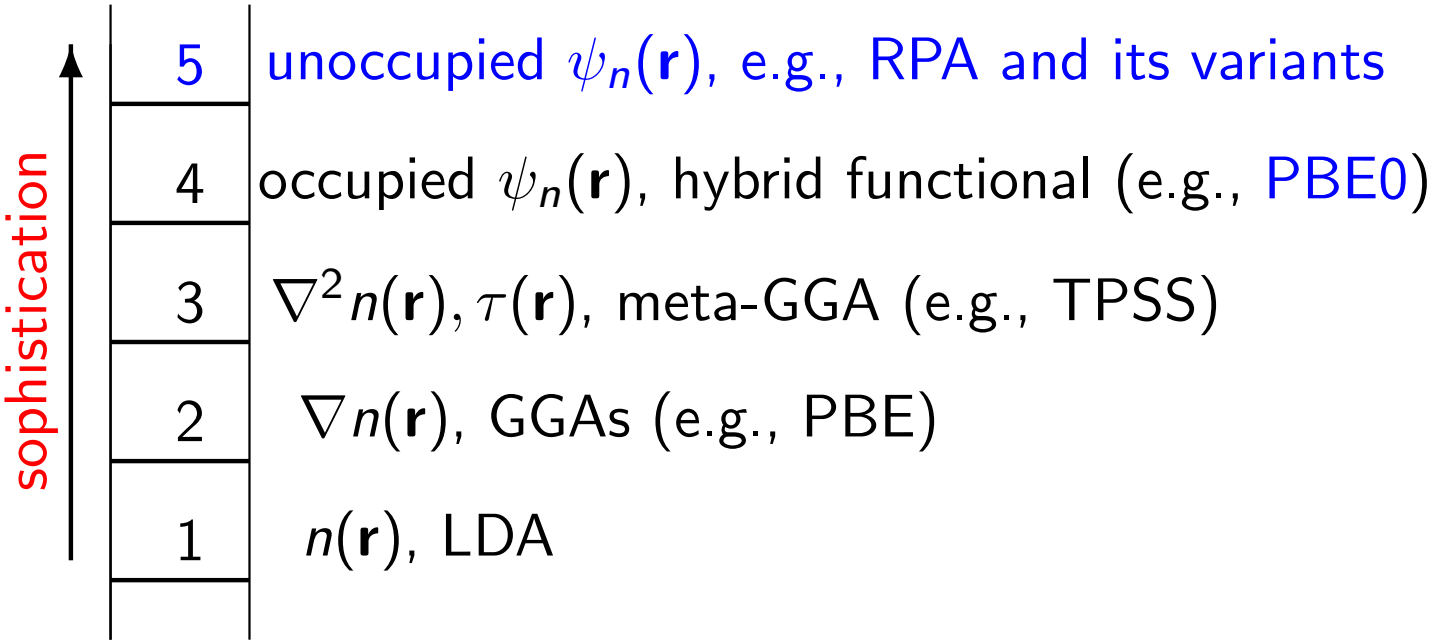
The exchange-correlation functional



Bohm & Pines (1953); Gell-Mann & Brueckner (1957);
Langreth & Perdew (1977); Furche (2001)

Jacob's ladder in DFT (John Perdew)

The exchange-correlation functional



- Level 1-4 are lacking the long-range vdW tails
- RPA and beyond hold promise to describe (nearly) all bonding situations

Bohm & Pines (1953); Gell-Mann & Brueckner (1957);
Langreth & Perdew (1977); Furche (2001)

Attractive features of RPA:

- Compatible with exact exchange, including which (EX+cPRA) cancels the self-interaction errors present in the Hartree energy. (not self-correlation free though)
- Automatic and seamless inclusion of van der Waals interactions
- No intrinsic limitations $\Longrightarrow$ applicable to (bio)molecules, insulators & metals, surfaces and interfaces, etc.
- Static correlation is (partly) captured (e.g, H_2 bond breaking well described)

Furche, Phys. Rev. B **64**, 195120 (2001).

Review: X. Ren, P. Rinke, C. Joas, M. Scheffler, J. Mater. Sci. **47**, 7447 (2012)

RPA calculations in practice

In practical calculations, RPA is done perturbatively on a LDA/GGA reference (e.g., RPA@PBE)

The "standard" RPA scheme:

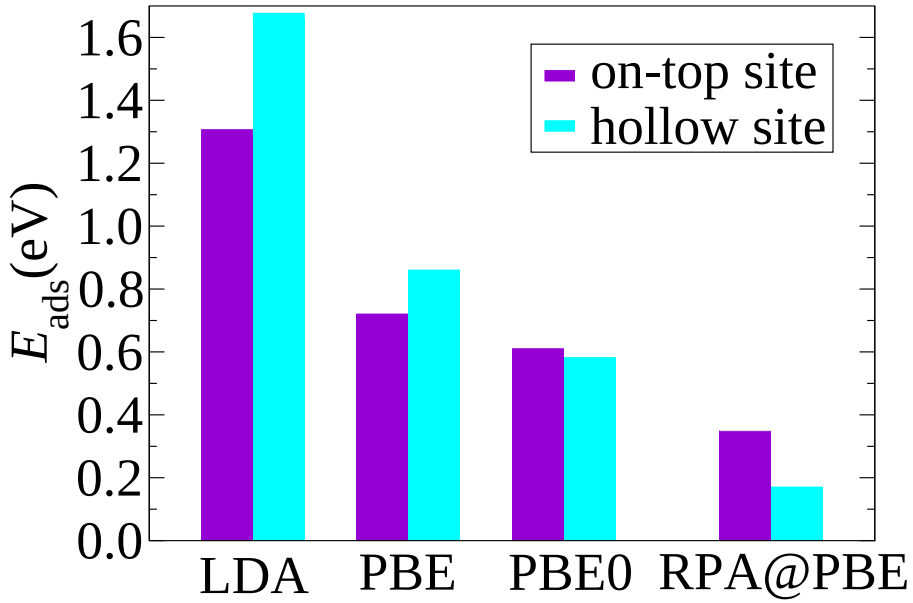
$$
\begin{aligned}
E^{\text{RPA@PBE}} &= E^{\text{PBE}} - E_{\text{xc}}^{\text{PBE}} + \left(E_{\text{x}}^{\text{exact}} + E_{\text{c}}^{\text{RPA}} \right) \text{@PBE} \\
&= \left(E_{\text{kin}} + E_{\text{ext}} + E_{\text{Hartree}} + E_{\text{x}}^{\text{exact}} + E_{\text{c}}^{\text{RPA}} \right) \text{@PBE} \\
&= E^{\text{EX@PBE}} + E_{\text{c}}^{\text{RPA@PBE}}
\end{aligned}
$$

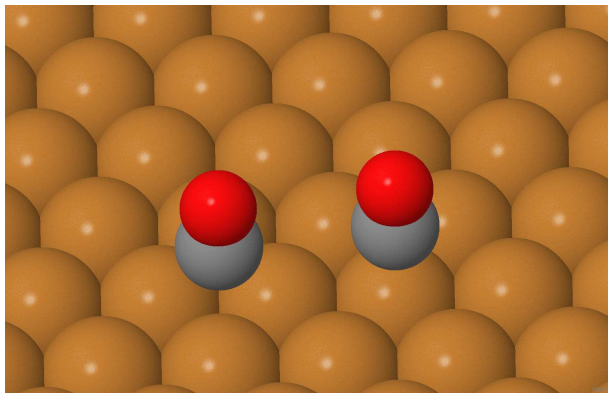
$E^{\text{EX@PBE}}$: non-self-consistent Hartree-Fock energy (exchange-only total energy) evaluated with PBE orbitals.

$E_{\text{c}}^{\text{RPA@PBE}}$: RPA correlation energy evaluated with PBE orbitals.

RPA applied to surface adsorption problem

"CO adsorption puzzle"





CO@Cu(111)

LDA/GGAs : hollow site

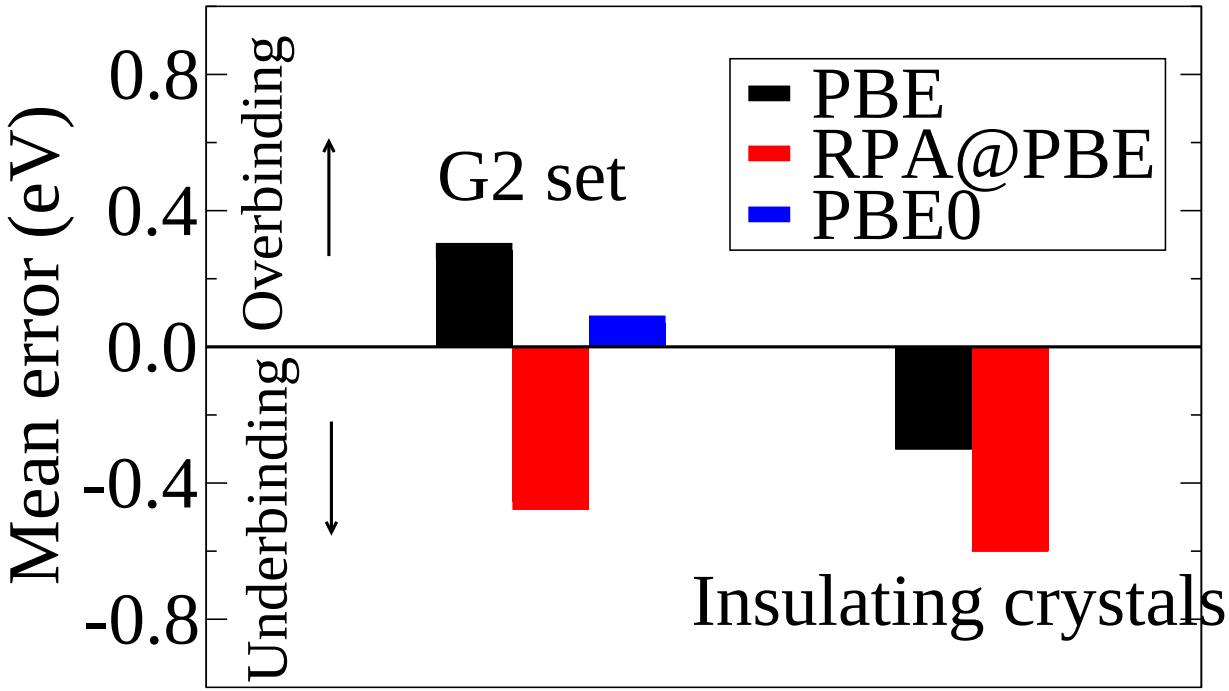
RPA/Exp. : on-top site

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

And also

The $\alpha - \gamma$ phase transition of Ce (M. Cacadei et al, PRL, in print)

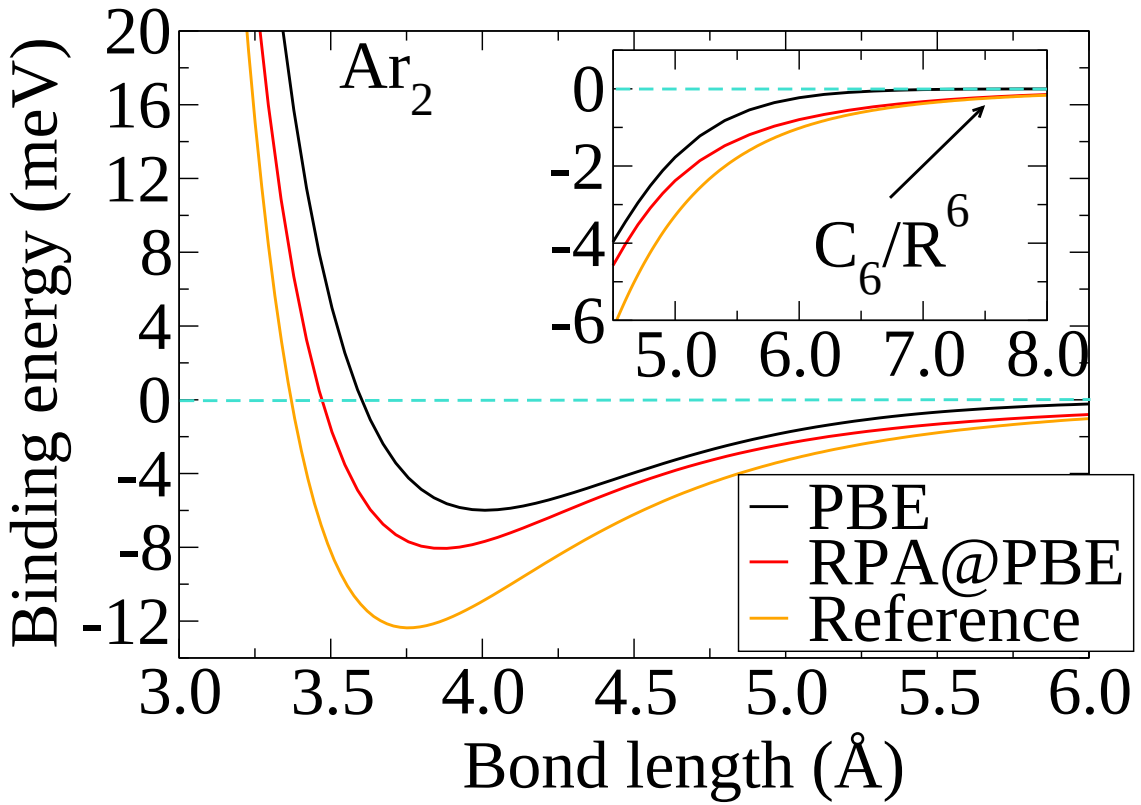
However, standard RPA shows a general tendency to underbind



Paier *et al.*, J. Chem. Phys. **132**, 094103 (2010); Erratum: **133**, 179902 (2010).

Harl, Schimka, and Kresse, Phys. Rev. B **81**, 115126 (2010).

RPA for describing the van der Waals interactions



Reference: Tang and Toennies, J. Chem. Phys. **118**, 4976 (2003)

\+ Correct asymptotic behavior, crucial for large molecules

– Underbinding around the equilibrium distance

Attempts for going beyond RPA

- "RPA+" and "RPA++": correct RPA using local and/or non-local density functional correlations.

  Z. Yan, J. P. Perdew, and S. Kurth, Phys. Rev. B **61**, 16430 (2000); A. Ruzsinszky, and J. P. Perdew, and G. I. Csonka, J. Chem. Theory Comput. **6**, 127 (2010).

- Range-separated RPA: only the long-range part of RPA is incorporated.

  B. G. Janesko, T. M. Henderson, and G. E. Scuseria, J. Chem. Phys. **130**, 081105 (2009). J. Toulouse *et al.*, Phys. Rev. Lett. **102**, 096404 (2009).

- SOSEX: complement RPA with second-order screened exchange.

  D. L. Freeman, Phys. Rev. B **15**, 5512 (1977).

  A. Grüneis *et al.*, J. Chem. Phys. **131**, 154115 (2009).

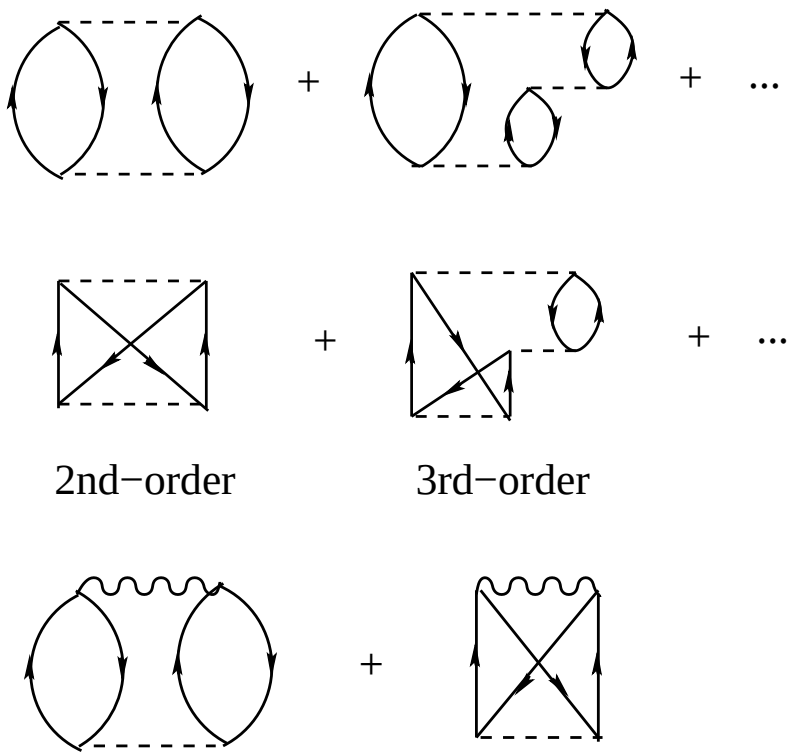
- SE correction: add a single-excitation (SE) contribution to cRPA.

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

The second-order screened exchange correction to RPA

Diagrammatic (Goldstone) representation (originally motivated from the coupled cluster context)

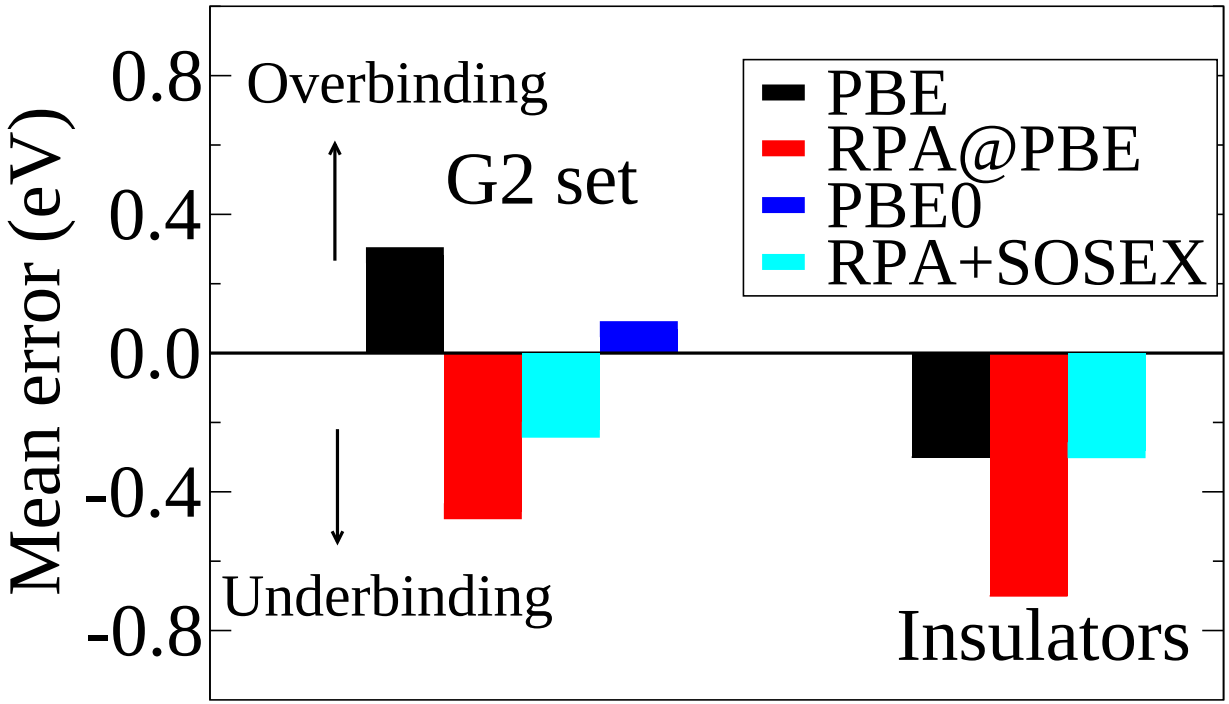
$E_c^{\mathrm{RPA+SOSEX}} =$



- Arising from the anti-symmetric nature of 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).

Atomization energies within RPA+SOSEX



J. Paier *et al.*, J. Chem. Phys. **132**, 094103 (2010); Erratum: **133**, 179902 (2010)
J. Harl, L. Schimka, and G. Kresse, Phys. Rev. B **81**, 115126 (2010).
J. Paier, X. Ren, P. Rinke, G. Scuseria, G. Kresse, M. Scheffler, New J. Phys. **14**, 043002 (2012).

SOSEX correction alleviates the underbinding problem of RPA !

The concept of single excitation (SE) correction

Rayleigh-Schrödinger perturbation theory:

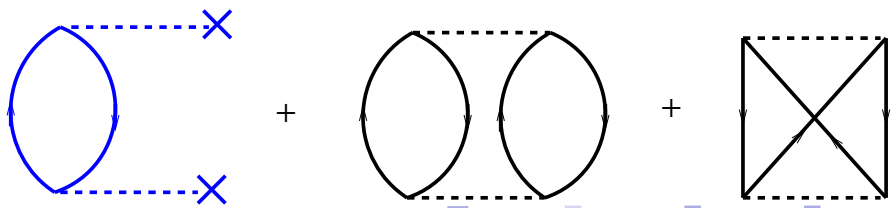
$$\hat{H} = \hat{H}^0 + \hat{H}'$$

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

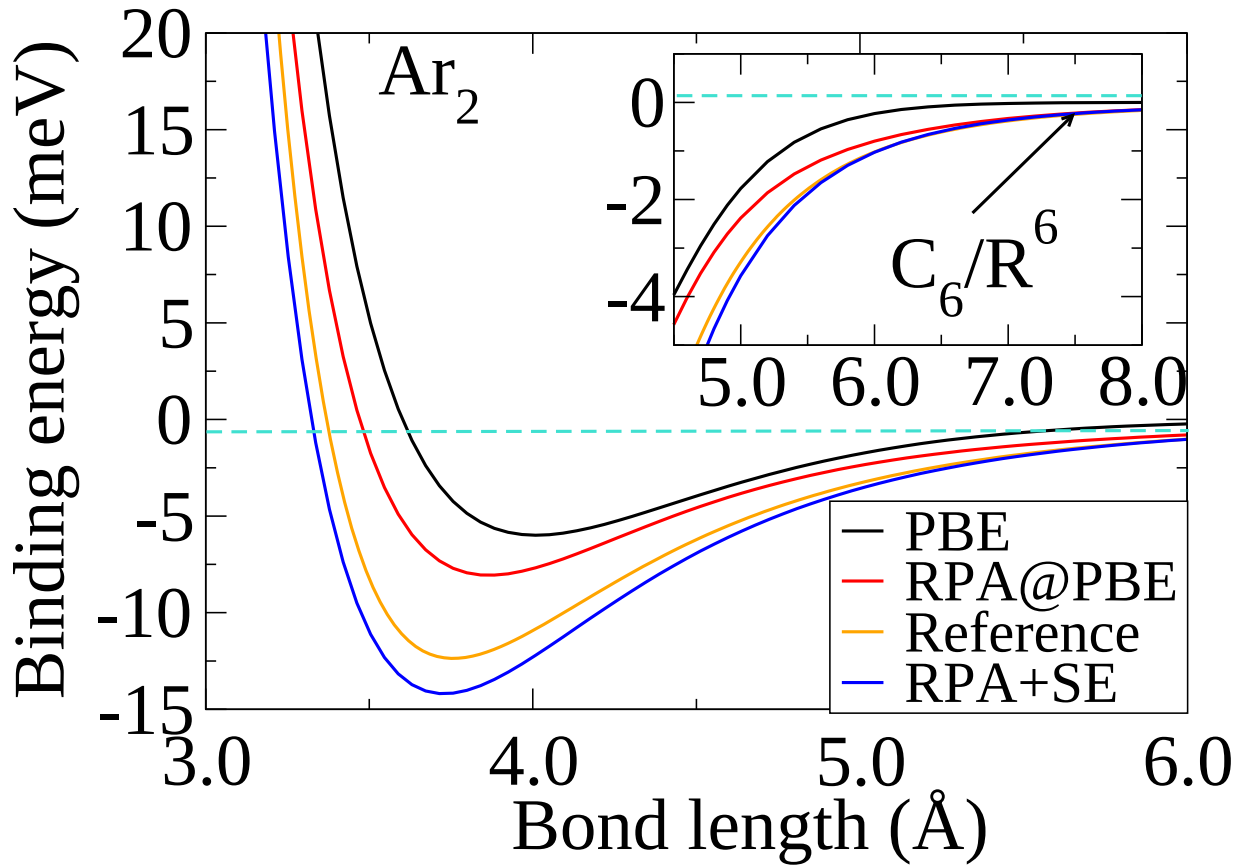
- zeroth-order: $E_0^{(0)} = \langle \Phi_0 | \hat{H}^0 | \Phi_0 \rangle$
- 1st order: $E_0^{(1)} = \langle \Phi_0 | \hat{H}' | \Phi_0 \rangle$
- 2nd order:

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

SE accounts for the orbital relaxation effect.

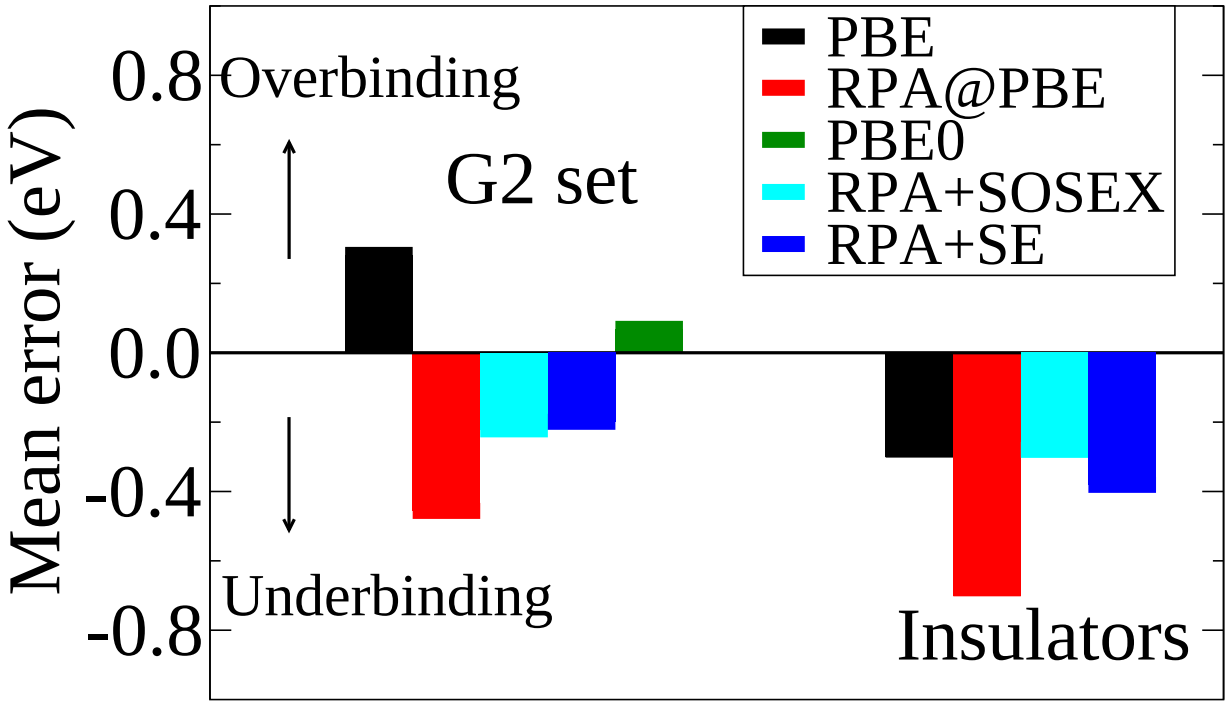


Performance of RPA+SE for Ar_2



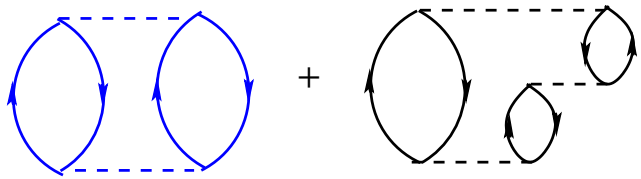
X. Ren, A. Tkatchenko, P. Rinke, and M. Scheffler, Phys. Rev. Lett. **106**, 153003 (2011).

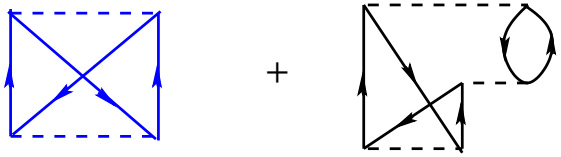
Performance of RPA+SE for atomization energies

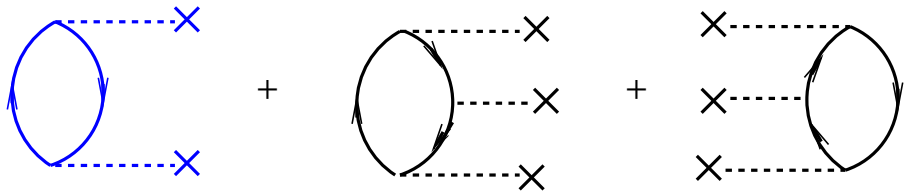


J. Paier, X. Ren, P. Rinke, G. Scuseria, A. Grüneis, G. Kresse, and M. Scheffler, New J. Phys. **14**, 043002 (2012).

The concept of Renormalized 2nd-order Perturbation Theory (rPT2)

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

$+$  $+ \cdots \quad (= \text{SOSEX})$

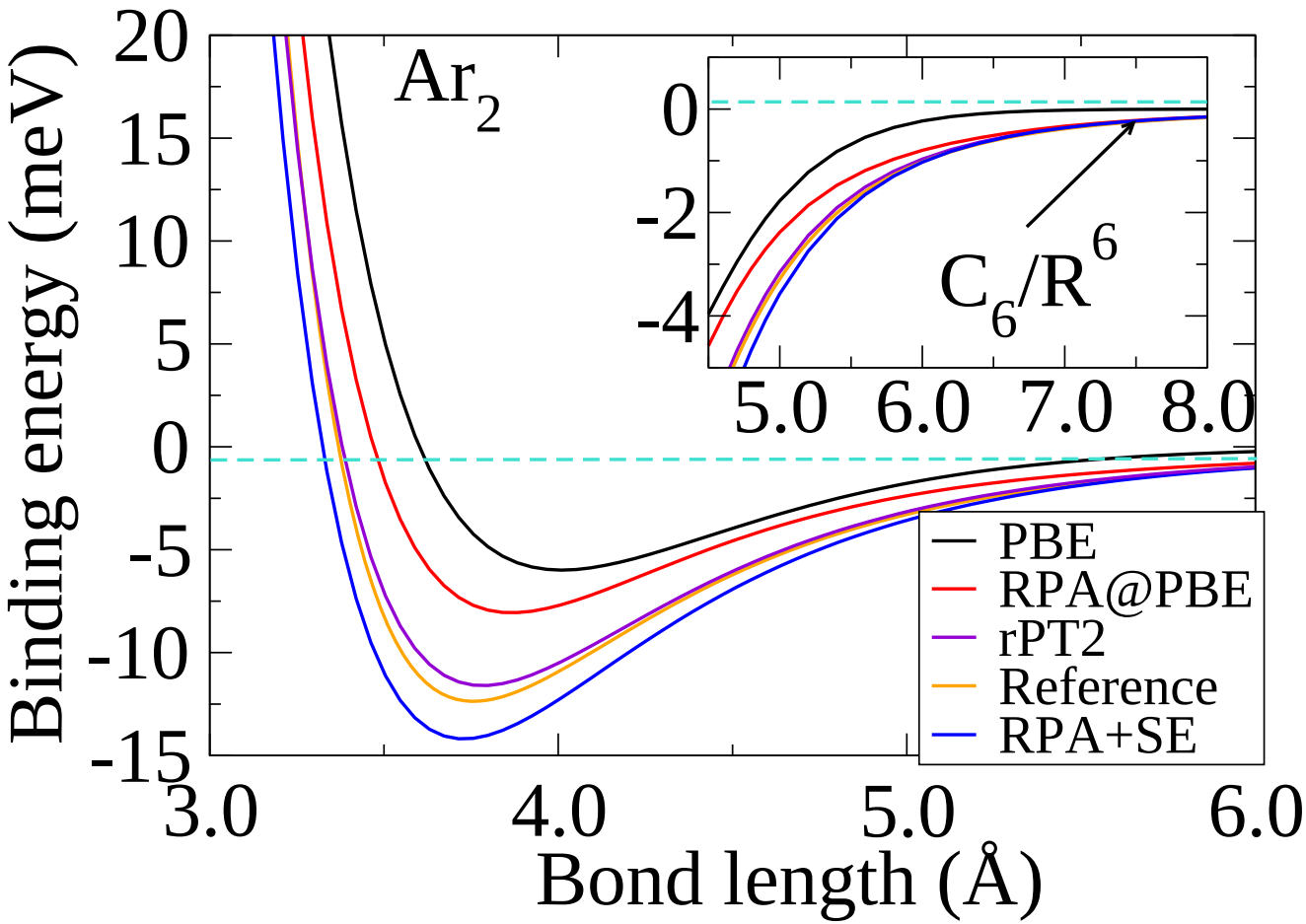
$+$  $+ \cdots \quad (= \text{rSE})$

2nd−order 3rd−order

$(= \text{2PT})$

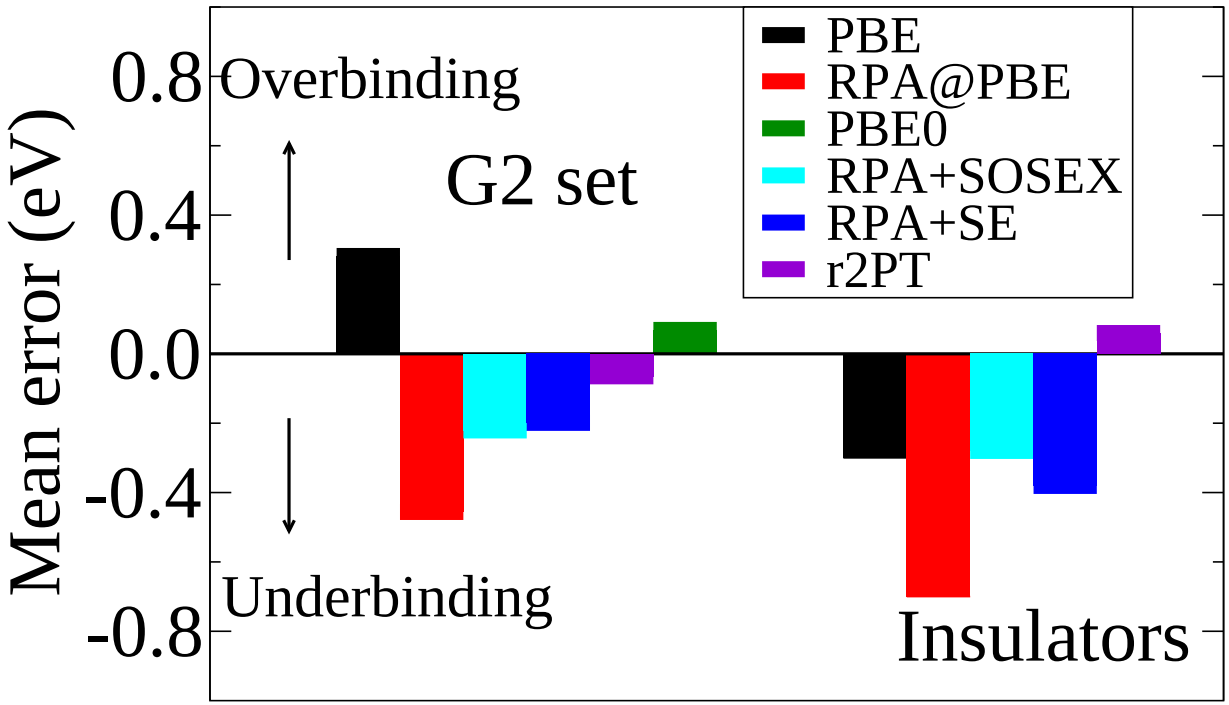
"rPT2" = "RPA+SOSEX+rSE"

Performance of rPT2 for Ar_2



X. Ren, P. Rinke, C. Joas, and M. Scheffler, J. Mater. Sci. **47**, 7447 (2012).

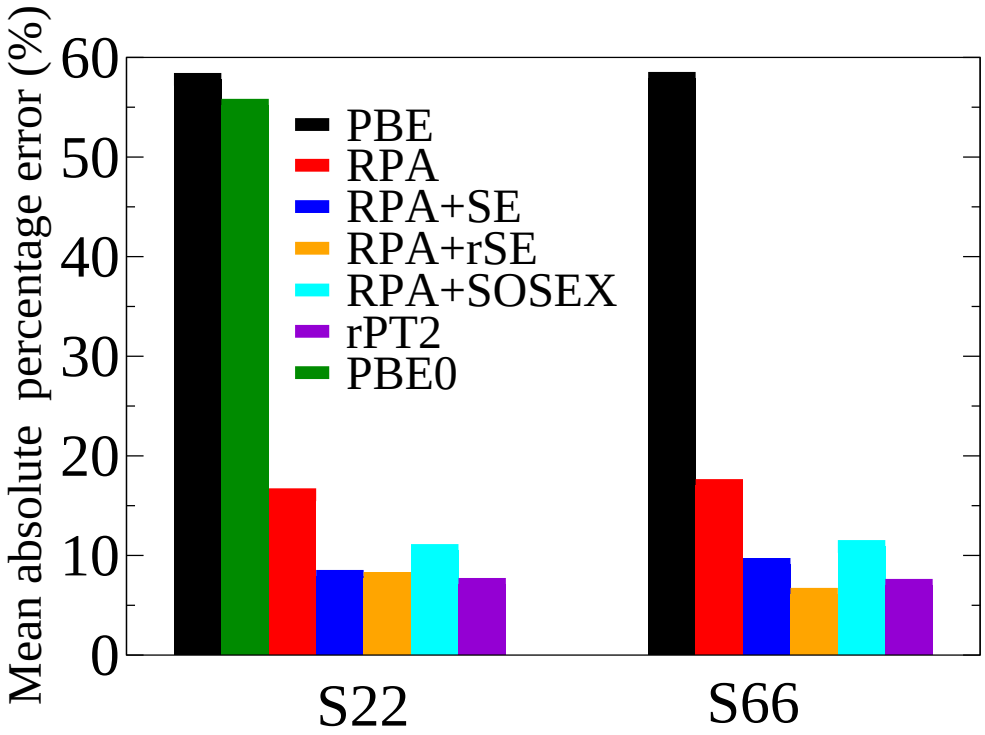
Atomization energies within rPT2



J. Paier, X. Ren, P. Rinke, G. Scuseria, A. Grüneis, G. Kresse, and M. Scheffler, New J. Phys. **14**, 043002 (2012).

Performance of rPT2 for non-covalent interactions

Interaction energies for S22 and S66 sets



X. Ren, P. Rinke, G. Scuseria, M. Scheffler, in preparation

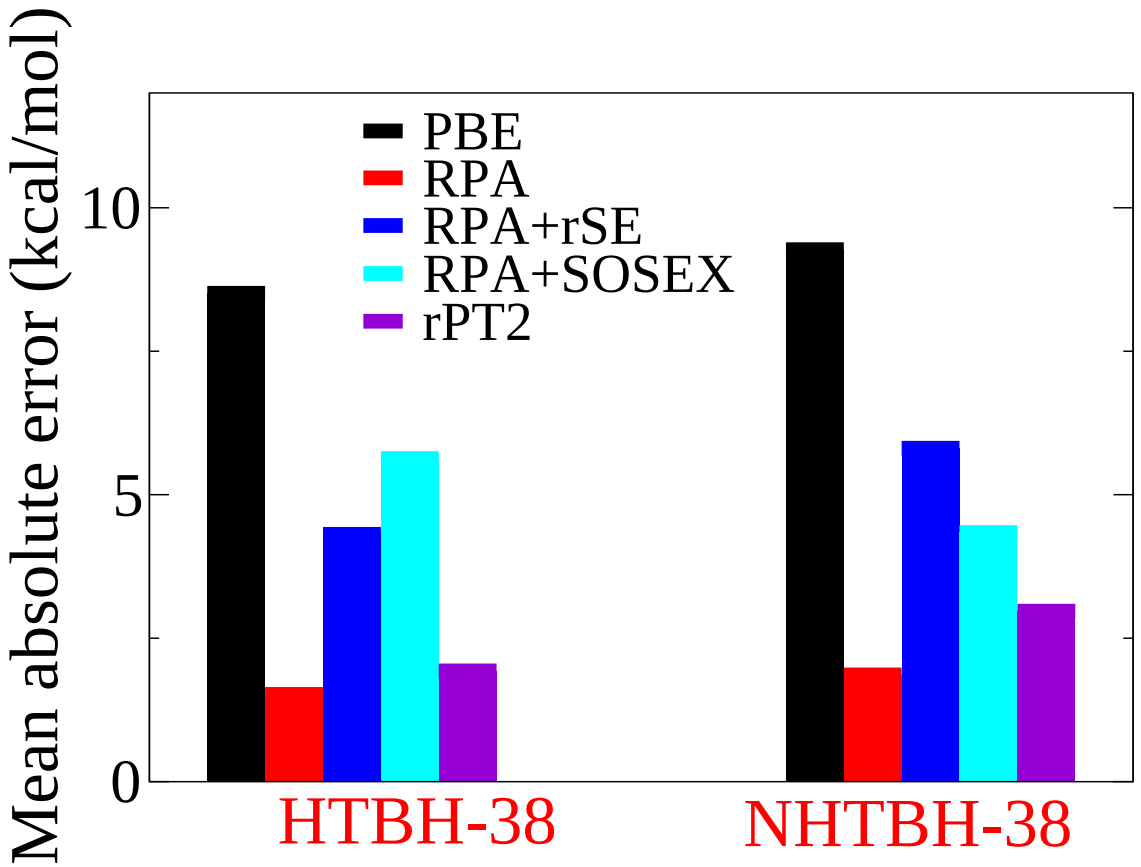
Bonding type	hydrogen	dispersion	mixed
S22 [1]	7	8	7
S66 [2]	23	23	20

[1] Jurečka, Šponer, Černý, and Hobza, PCCP **8**, 1985 (2006).

[2] Rezac, Riley, and Hobza, J. Chem. Theo. Comp. **7** 2427 (2011).

Performance of rPT2 for chemical reaction barrier heights

38 hydrogen-transfer barrier heights (HTBT-38) and 38 non-hydrogen-transfer barrier heights (NHTBH-38)



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

Part II:

Second-order screened exchange correction to the *GW* self-energy

The *GW* method

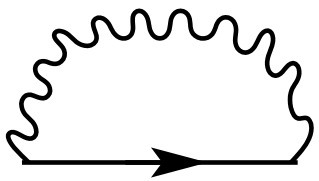
- Quasiparticle equation for interacting many-electron systems

$$H_0\psi_n^{\mathrm{QP}}(\mathbf{r}) + \int d\mathbf{r}'\Sigma(\mathbf{r},\mathbf{r}',\varepsilon_n^{\mathrm{QP}})\psi_n^{\mathrm{QP}}(\mathbf{r}') = \varepsilon_n^{\mathrm{QP}}\psi_n^{\mathrm{QP}}(\mathbf{r})$$

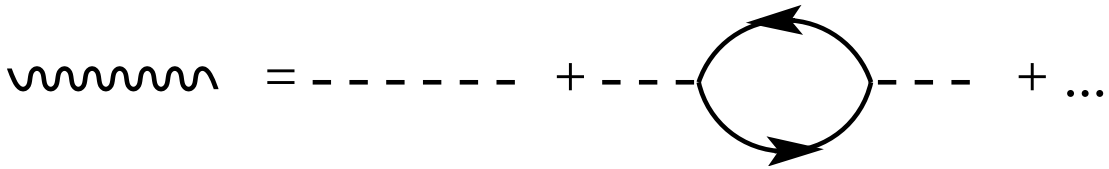
- *GW* approximation

$$\Sigma(\mathbf{r},\mathbf{r}',i\omega) = \frac{i}{2\pi}\int d\omega' G(\mathbf{r},\mathbf{r}',i\omega+i\omega')W(\mathbf{r},\mathbf{r}',i\omega')$$

$$W = v/(1-\chi v) = v + v\chi v + \cdots$$

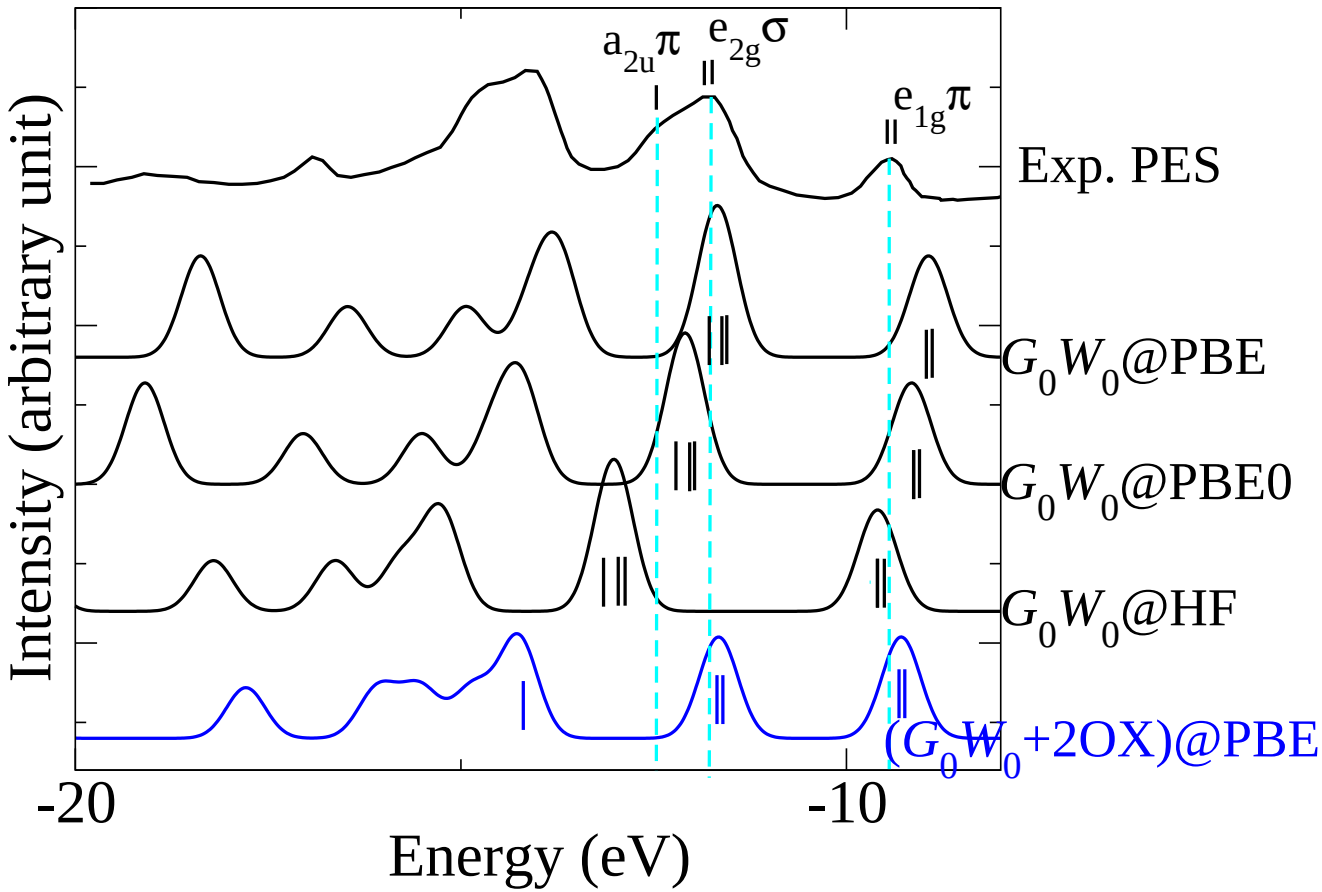


Feynman diagram



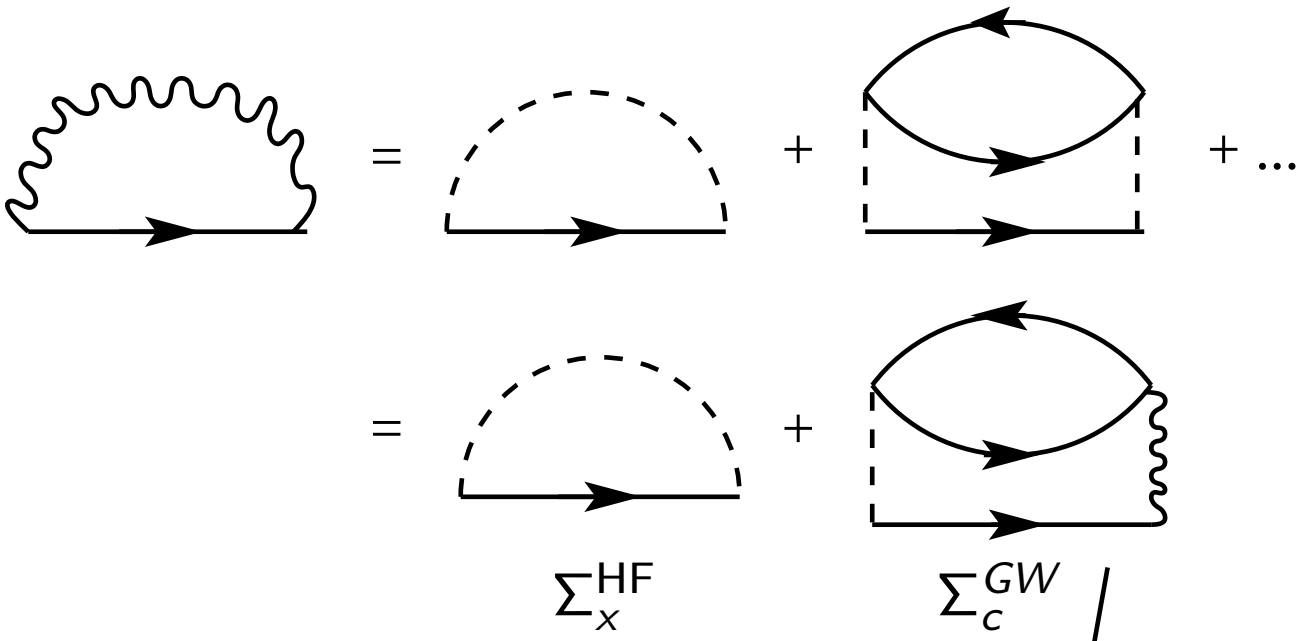
L. Hedin, Phys. Rev. **139** A796 (1965).

Photoemission spectra of benzene

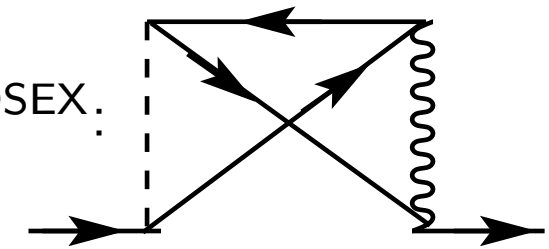


N. Marom et al., in preparation.

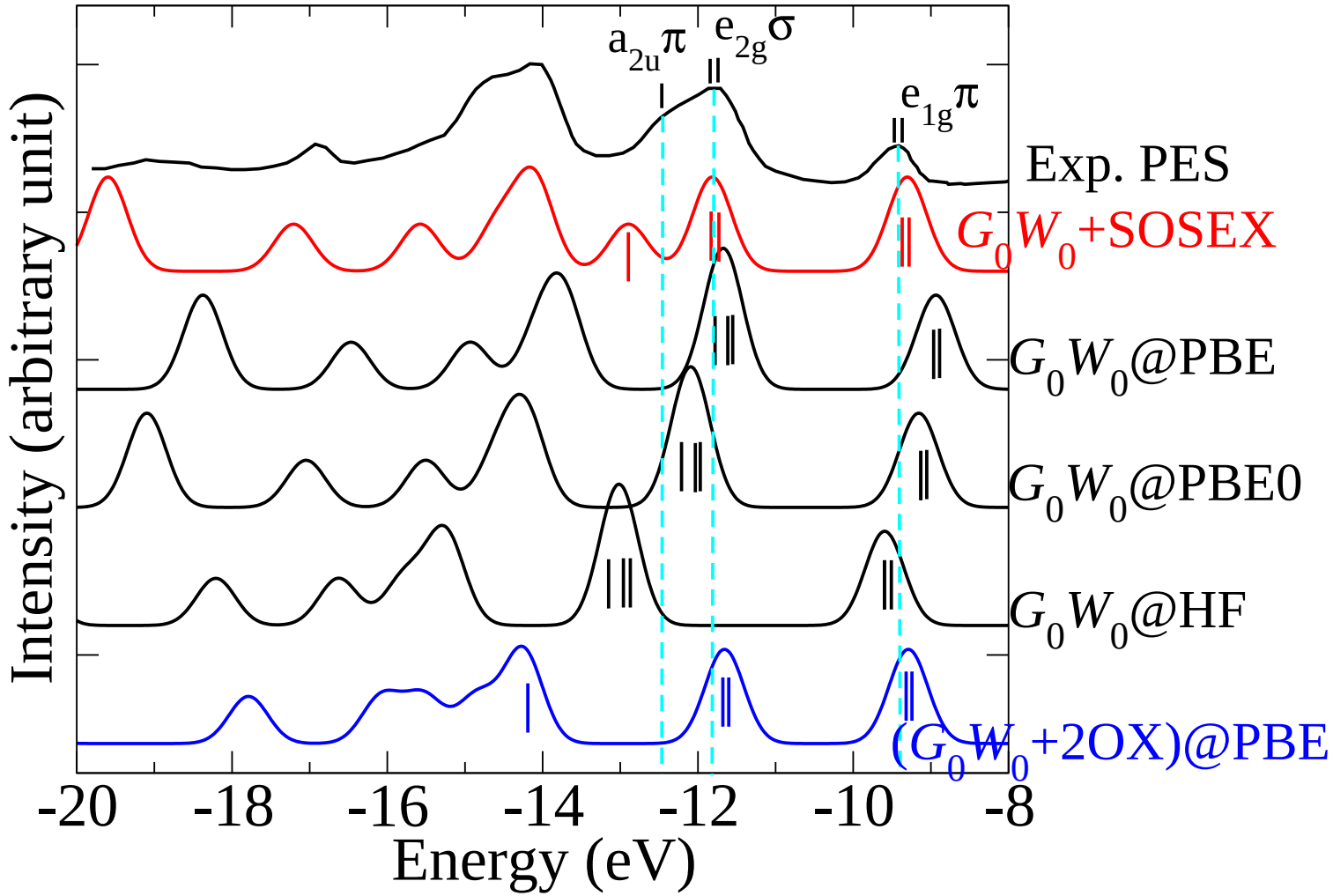
Diagrammatic representation of the screened 2nd-order exchange self-energy



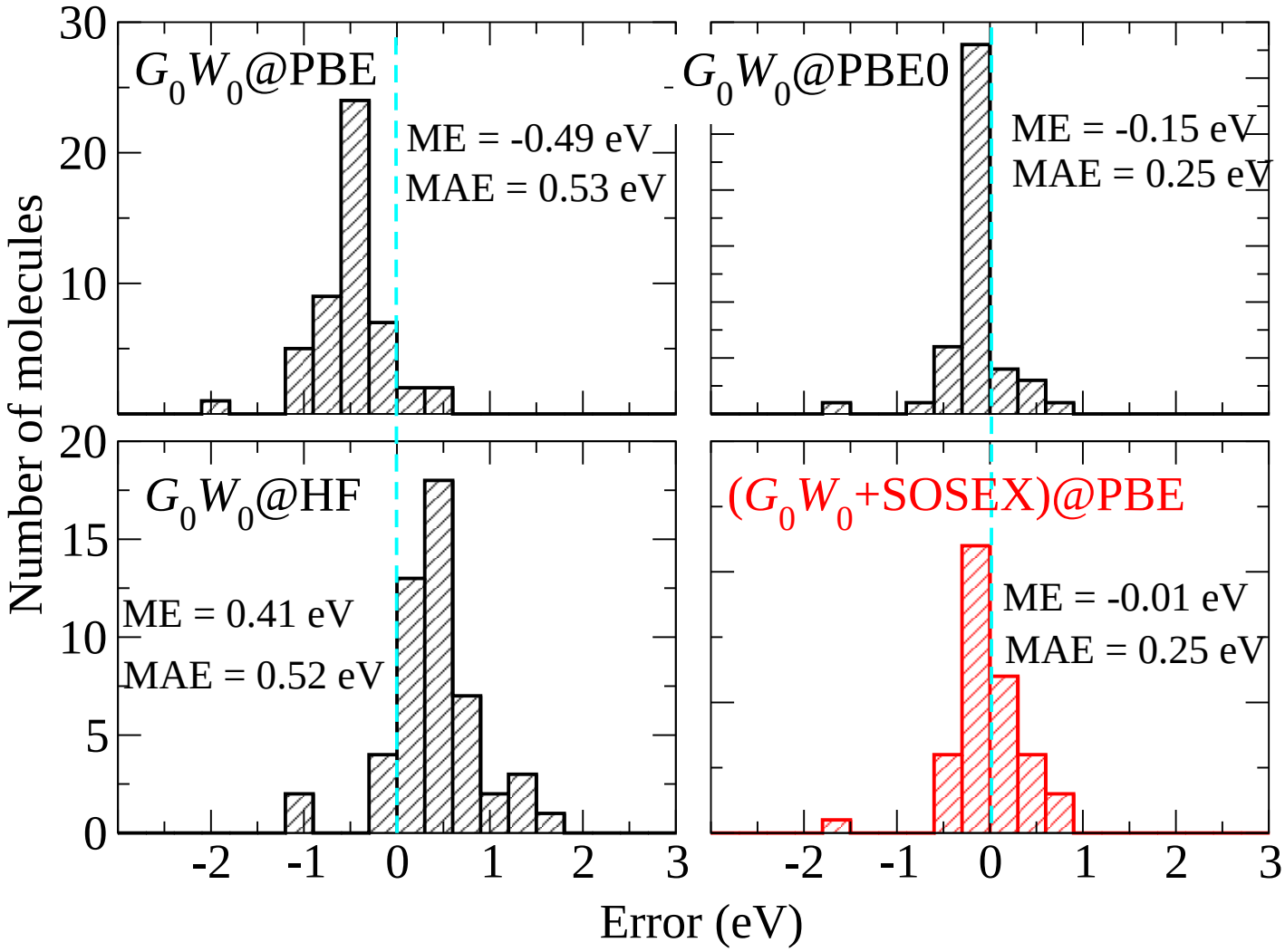
Screened second-order exchange $\Sigma_c^{\mathrm{SOSEX}}$:
(to reduce the "self-correlation")



Photoemission spectra of benzene

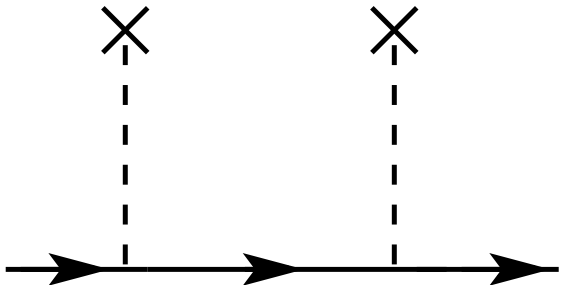


Error analysis for 50 atoms and molecules



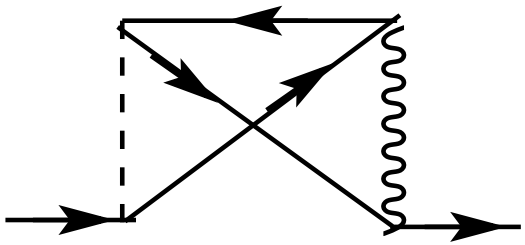
Some final remarks

- Is there a single-excitation contribution to the self-energy?



Improper (reducible) self-energy

- Screened second-order exchange versus second-order self-energy in terms of W



vs