

Random-phase approximation and beyond for materials: concepts, practice, and future perspectives

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Success and limitations of DFT in computational materials science

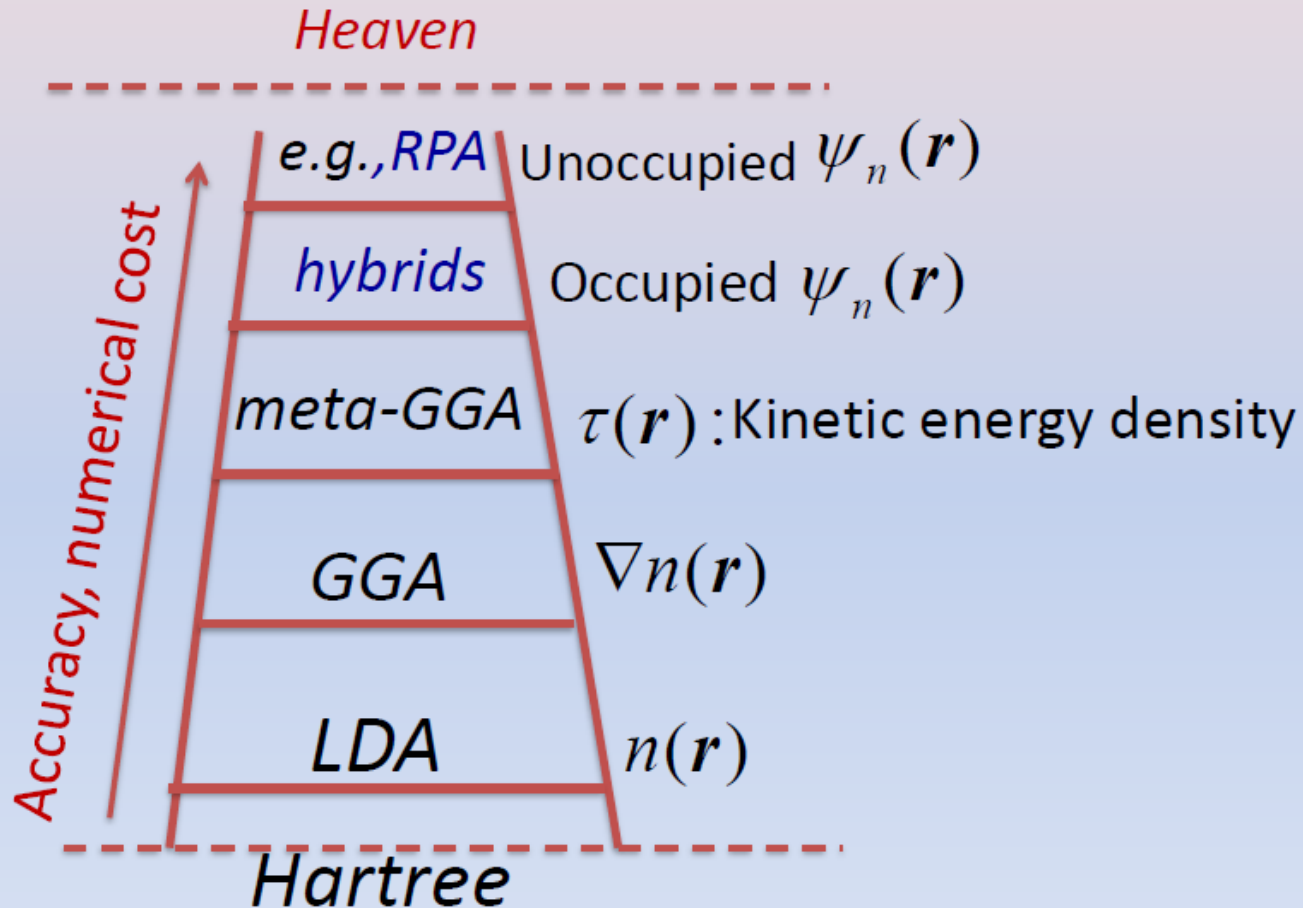
Density functional theory (DFT) in its semi-local approximations is enormously successful in simulating materials' properties and in materials designs, **but has certain (intrinsic) limitations.**

Typical situations:

- Systems with mixed bonding characteristics
- Systems with near degeneracy (“strong correlation”)
- Systems where both ground-state energies and charge excitation energy gaps are important.
- Heterogeneous systems
(different dielectric property in different subsystems)

.....

Jacob's ladder of DFT



J. Perdew & K. Schmidt, *Density functional theory and its application to materials*, edited by V. Van Doren et al. (2001)

A zoo of electronic-structure methods

Workhorse

LDA/GGAs

Deficiencies

Lack of van der Waals;
Self-interaction errors

Lack of functional derivative
discontinuity; Insufficiency
of KS spectrum

Consequences

Inaccuracy for ground-
state energies

Inaccuracy for quasi-particle
excitation energies

Possible fixes

MP2

RPA

CCSD(T)

DFT+*U*

SIC-LDA

GW

vdW-DF

Hybrid functionals

Double hybrids

LDA+DMFT

DFT+vdW

DFT-D

DFT+G

.....

Brief history of RPA

- Correlation energy of homogeneous electron gas (HES):
 - Divergence problem of “order-by-order” perturbation theory
- Separation of collective modes and quasiparticle modes:
 - First appearance of the RPA concept (Bohm & Pines, 1950)
- Self-consistent field approach to HES
 - Lindhard function (Lindhard, 1954)
- RPA = “sum of ring diagrams to infinite order”
 - (Brueckner & Gell-Mann, 1957)
- The concept of screened Coulomb interaction W
 - (Hubbard, 1957)
- The GW approximation to the self-energy $\Sigma=iGW$
 - (Hedin, 1965)

RPA as a first-principles method

- ❖ With the framework of **adiabatic-connection fluctuation-dissipation (ACFD) theorem**, RPA can be formulated as an approximate, but fully nonlocal exchange-correlation (XC) energy functional.

The XC energy

The density response function

$$E_{xc} = -\frac{1}{2\pi} \int_0^1 d\lambda \int_0^\infty d\omega \iint d\mathbf{r} d\mathbf{r}' [\chi_\lambda(\mathbf{r}, \mathbf{r}', i\omega) - n(\mathbf{r})\delta(\mathbf{r} - \mathbf{r}')] v(\mathbf{r}, \mathbf{r}')$$

The coupling constant

Coulomb interaction

Langreth & Perdew, *Phys. Rev. B* **15**, 2884 (1977).

Gunnarsson & Lundqvist, *Phys. Rev. B* **13**, 4274 (1976).

Dyson equation for the response function:

$$\chi_\lambda^{\text{RPA}} = \chi_0 + \lambda \chi_0 v \chi_\lambda^{\text{RPA}}$$

Explicitly known in terms of KS orbitals (both occupied and virtual) and orbital energies

$$\implies E_c^{\text{RPA}} = E_c^{\text{RPA}}[\varepsilon_i, \psi_i]$$

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The XC energy

The RPA density response function

$$E_{\text{xc}}^{\text{RPA}} = -\frac{1}{2\pi} \int_0^1 d\lambda \int_0^\infty d\omega \iint d\mathbf{r} d\mathbf{r}' \left[\chi_\lambda^{\text{RPA}}(\mathbf{r}, \mathbf{r}', i\omega) - n(\mathbf{r})\delta(\mathbf{r} - \mathbf{r}') \right] v(\mathbf{r}, \mathbf{r}')$$

The coupling constant

Coulomb interaction

Langreth & Perdew, Phys. Rev. B **15**, 2884 (1977).

Gunnarsson & Lundqvist, Phys. Rev. B **13**, 4274 (1976).

- ❖ First application to real molecules.

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

Fuchs & Gonze, Phys. Rev. B **65** 235109 (2002).

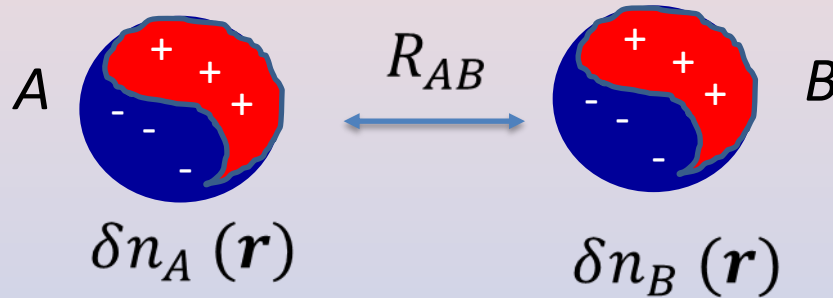
- ❖ Applications to molecules, solids, surfaces, and layered materials (2006-present).

For a review, see XR, *P. Rinke, C. Joas, and M. Scheffler, J. Mater. Sci.* **47**, 7447 (2012)

Why is RPA interesting?

- Automatic and seamless inclusion of van der Waals (vdW) interactions; non-additive, anisotropic, and many-body screening effects are properly accounted for.
- Self-interaction (delocalization) errors are reduced, by including exact-exchange.
- Different bonding (ionic, covalent, metallic, vdW) situations are treated on equal footings.
- Static correlation (partly) captured => excellent chemical reaction barrier heights

Theoretical description of vdW interactions



- vdW (dispersion) stems from the coupling between spontaneous quantum charge fluctuations at a distance.

The leading term $\Delta E_D \rightarrow \frac{C_6}{R_{AB}^6}$, for large R_{AB}

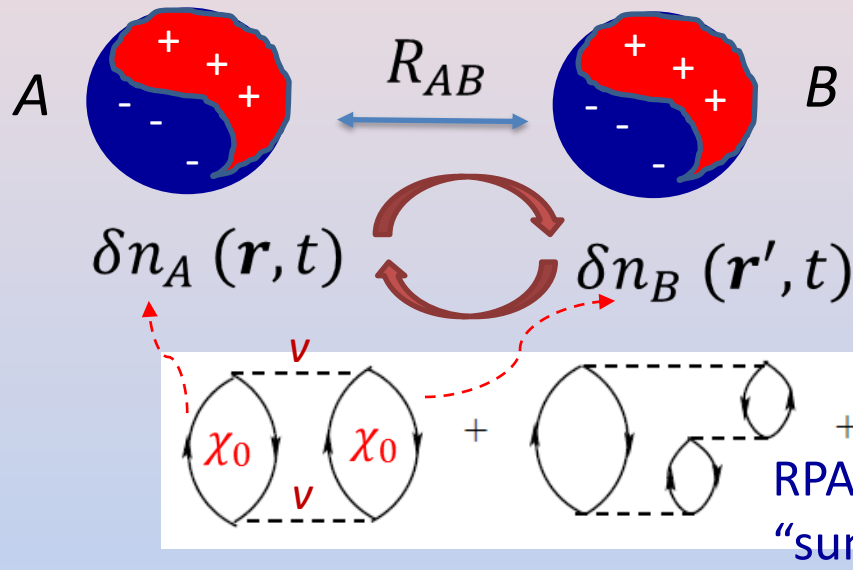
First principles description of vdW interactions is (computationally) a challenge!

CCSD(T) treats vdW accurately, but way too expensive.

Within the DFT context:

- DFT+ pairwise C_6/R^6 summation; DFT+ many-body dispersion
- Explicitly non-local density functionals: vdW-DF
- Orbital-dependent functionals, via the ACFD frameworks, e.g., RPA

RPA description of vdW interactions

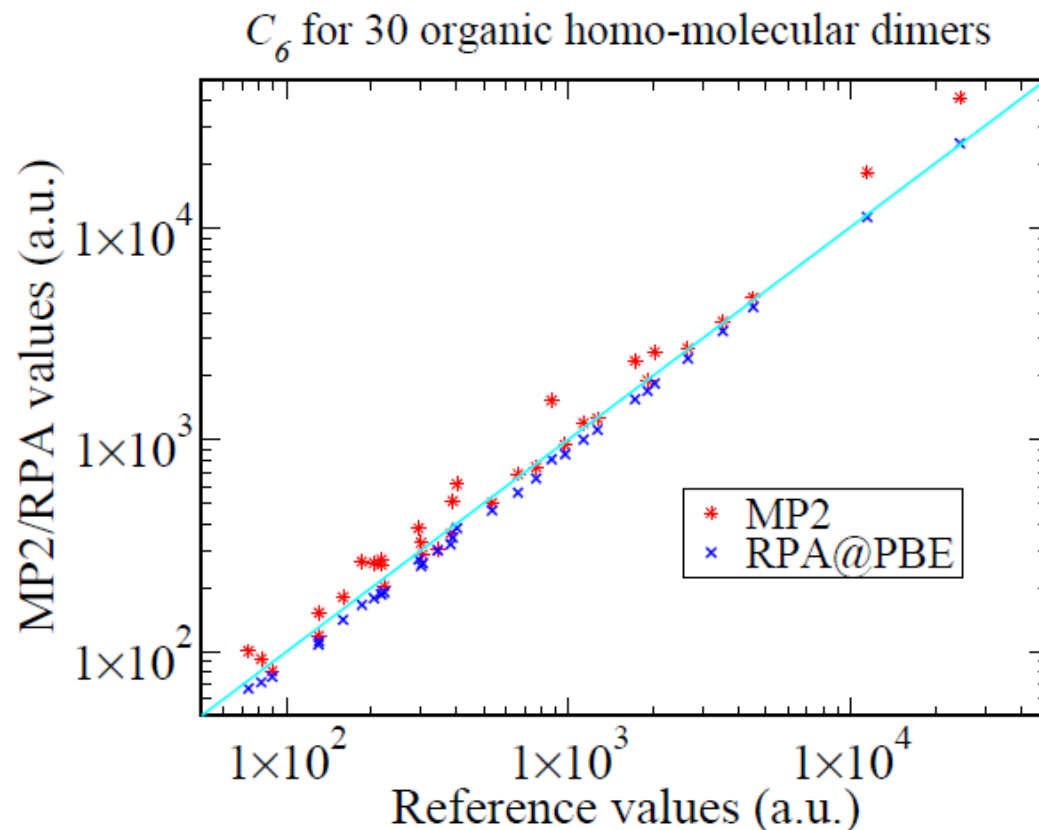


- RPA captures the **non-local coupling** between spontaneous quantum charge fluctuations separated in space.
- It can be shown analytically

$$\Delta E_c^{\text{RPA}} \rightarrow C_6^{\text{RPA}}/R^6 \quad \text{for large } R \rightarrow \infty$$

$$C_6^{\text{RPA}} = \frac{3}{\pi} \int d\omega \alpha_A^{\text{RPA}}(i\omega) \alpha_B^{\text{RPA}}(i\omega) \quad \text{“Dispersion consistent”}$$

RPA at the long range: quality of C_6 at the RPA level



Mean error in percentage:

MP2: 20%;

RPA@PBE: 10%

Reference values are obtained from the experimental data on “dipole oscillator strength distribution (DOSD)”

Reference data: G. D. Zeiss and W. J. Meath, *Molecular Physics*, **77**, 1155 (1977); **30**, 161 (1975). A. Tkatchenko and M. Scheffler, *PRL* **102**, 073005 (2009).

Basic formalism behind RPA

1. Kohn-Sham eigenvalues and eigenfunctions

$$\hat{h}_{\text{KS}}\psi_n(\mathbf{r}) = \varepsilon_n\psi_n(\mathbf{r})$$

2. Independent-particle (Kohn-Sham) response function

$$\chi^0(\mathbf{r}, \mathbf{r}', i\omega) = 2 \sum_{m,n} \frac{(f_m - f_n)\psi_m^*(\mathbf{r})\psi_n(\mathbf{r})\psi_n^*(\mathbf{r}')\psi_m(\mathbf{r}')}{\varepsilon_m - \varepsilon_n - i\omega}$$

3. Basis representation

$$\chi^0(\mathbf{r}, \mathbf{r}', i\omega) = \sum_{\mu,\nu} P_\mu(\mathbf{r})\chi_{\mu\nu}^0(i\omega)P_\nu(\mathbf{r}')$$

4. RPA correlation energy calculation

$$E_c^{\text{RPA}} = \frac{1}{2\pi} \int_0^\infty d\omega \text{Tr}[\ln(1 - \chi_0(i\omega)v) + \chi_0(i\omega)v]$$

RPA calculations in practice (so far ...)

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.

First-Principles code package

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

Numeric atom-centered basis functions

$$\varphi_{i[lm]}(\mathbf{r}) = u_{il}(r)Y_{lm}(\hat{\mathbf{r}})$$



Conventional DFT (LDA, GGAs)

- All-electron, full potential
- Periodic and finite systems on equal footing
- Favorable scaling
(w.r.t system size and CPU cores)

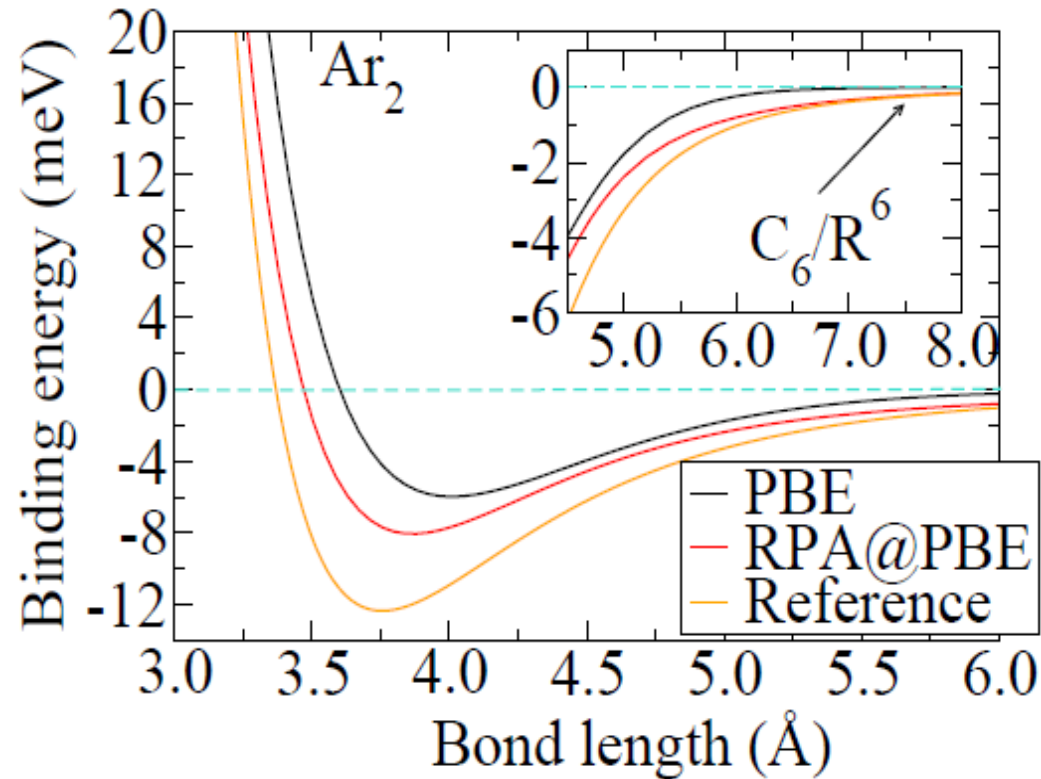
V. Blum *et al.*, *Comp. Phys. Comm.*
180, 2175 (2009)

“Beyond-DFT” methods

- Hybrid functionals, MP2, RPA and beyond
- Quasiparticle excitation energies: G_0W_0 , scGW, MP2, and beyond

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

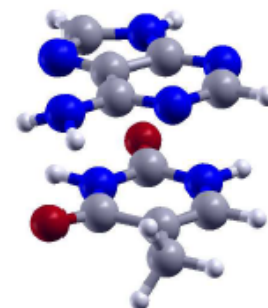
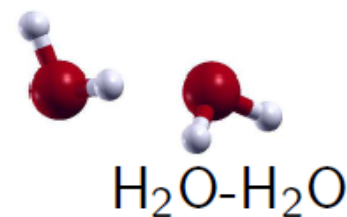
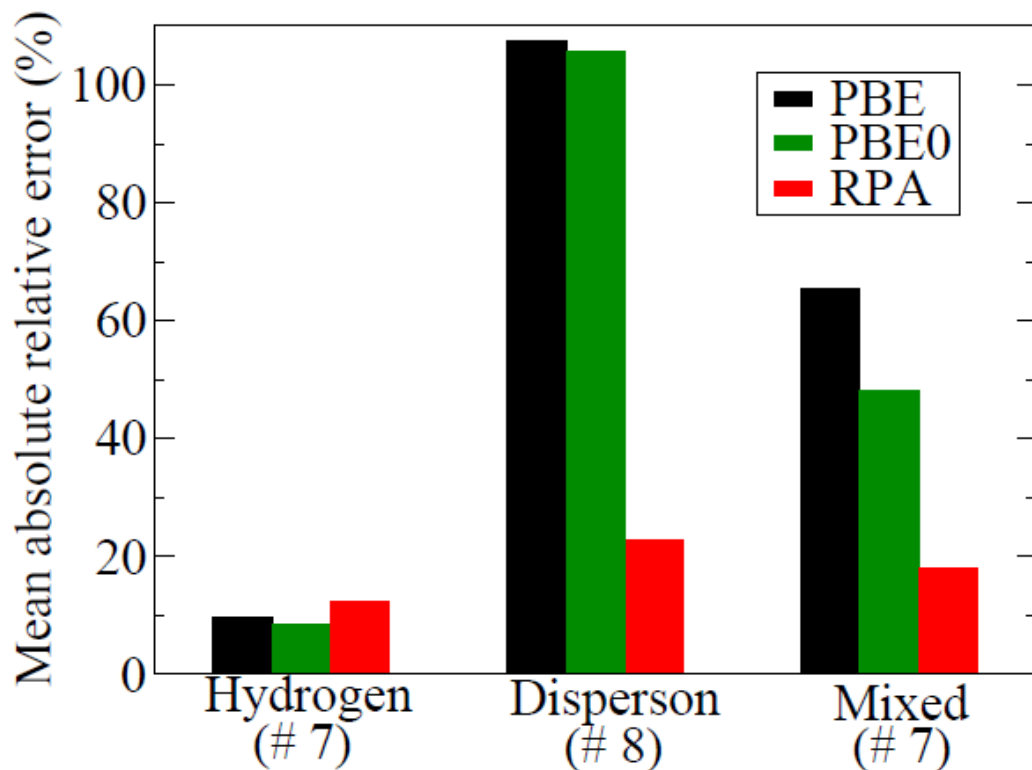
RPA for Ar₂



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

- + Correct asymptotic behavior, crucial for large molecules
- Underbinding around the equilibrium distance

RPA for S22 test set

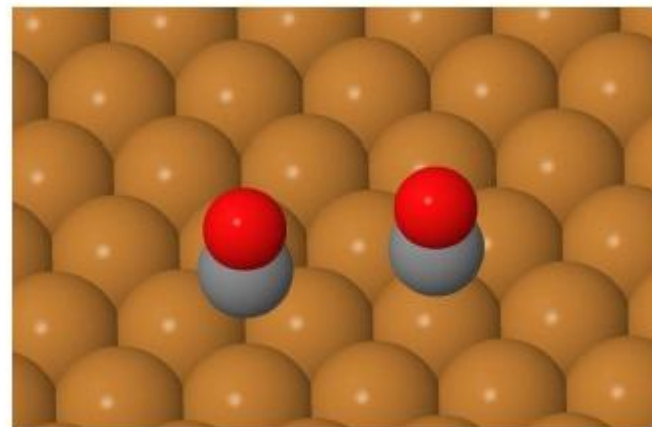
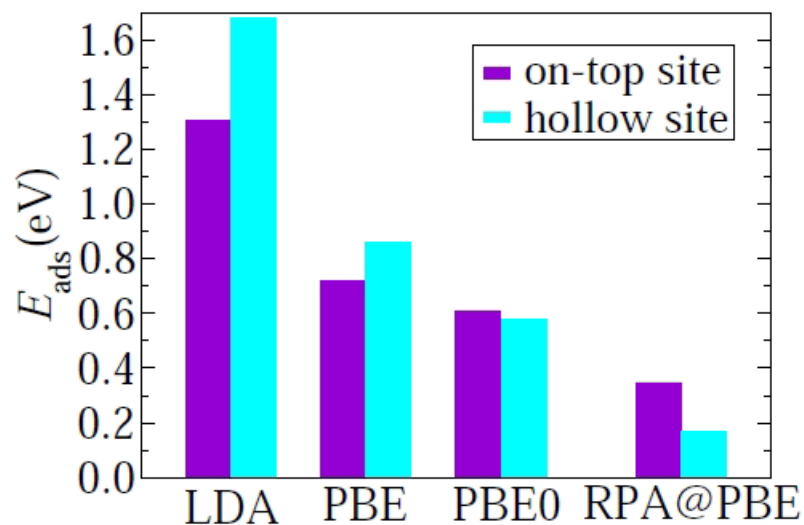


$\text{H}_2\text{O}-\text{C}_6\text{H}_6$

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

S22 test set: P. Jurečka, J. Šponer, J. Černý, and P. Hobza, Phys. Chem. Chem. Phys. **8**, 1985 (2006).

RPA applied to the “CO adsorption puzzle”



CO@Cu(111)

LDA/GGA => hollow site
Exp/RPA => on-top site

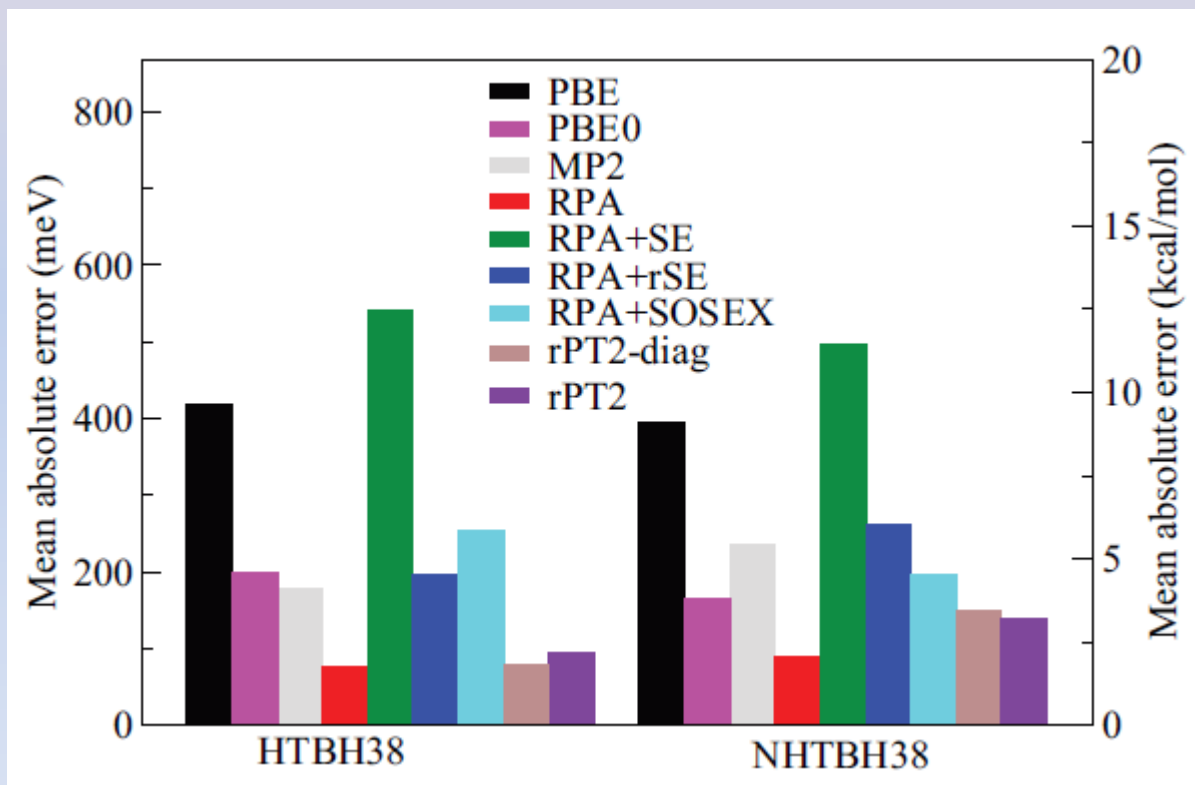
*XR, P. Rinke, and M. Scheffler,
Phys. Rev. B 80, 045402 (2009)*

See also *L. Schimka et al., Nature Materials 9, 741 (2010).*

RPA for Chemical reaction barrier heights

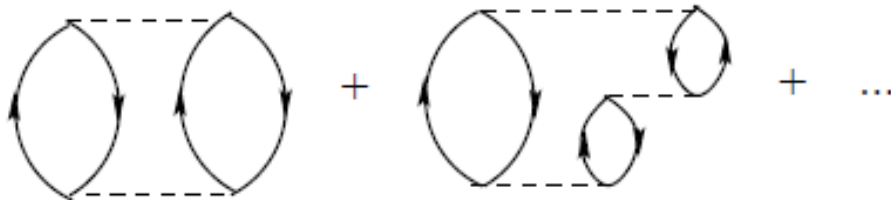
38 hydrogen transfer chemical reaction barrier Height (HTBH38)
and 38 non-hydrogen transfer Chemical reaction barrier height
(NHTBH38)

Ref. Data: Zhao, Gonzalez-Garcia, Truhlar, *J. Phys. Chem. A* 109, 2012 (2005)

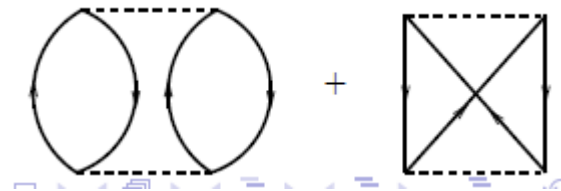


XR, P. Rinke, G.E. Scuseria, M. Scheffler, *Phys Rev. B* **88**, 035120 (2013).

Beyond RPA: insights from the Diagrammatic representation

$$E_c^{\text{RPA}} = \text{Diagram 1} + \text{Diagram 2} + \dots$$


Compare to

$$E_c^{\text{MP2}} = \text{Diagram 1} + \text{Diagram 2}$$


Screened second-order exchange

Diagrammatic representation (originally motivated from the coupled cluster context)

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

MP2

2nd-order 3rd-order

$$=$$

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

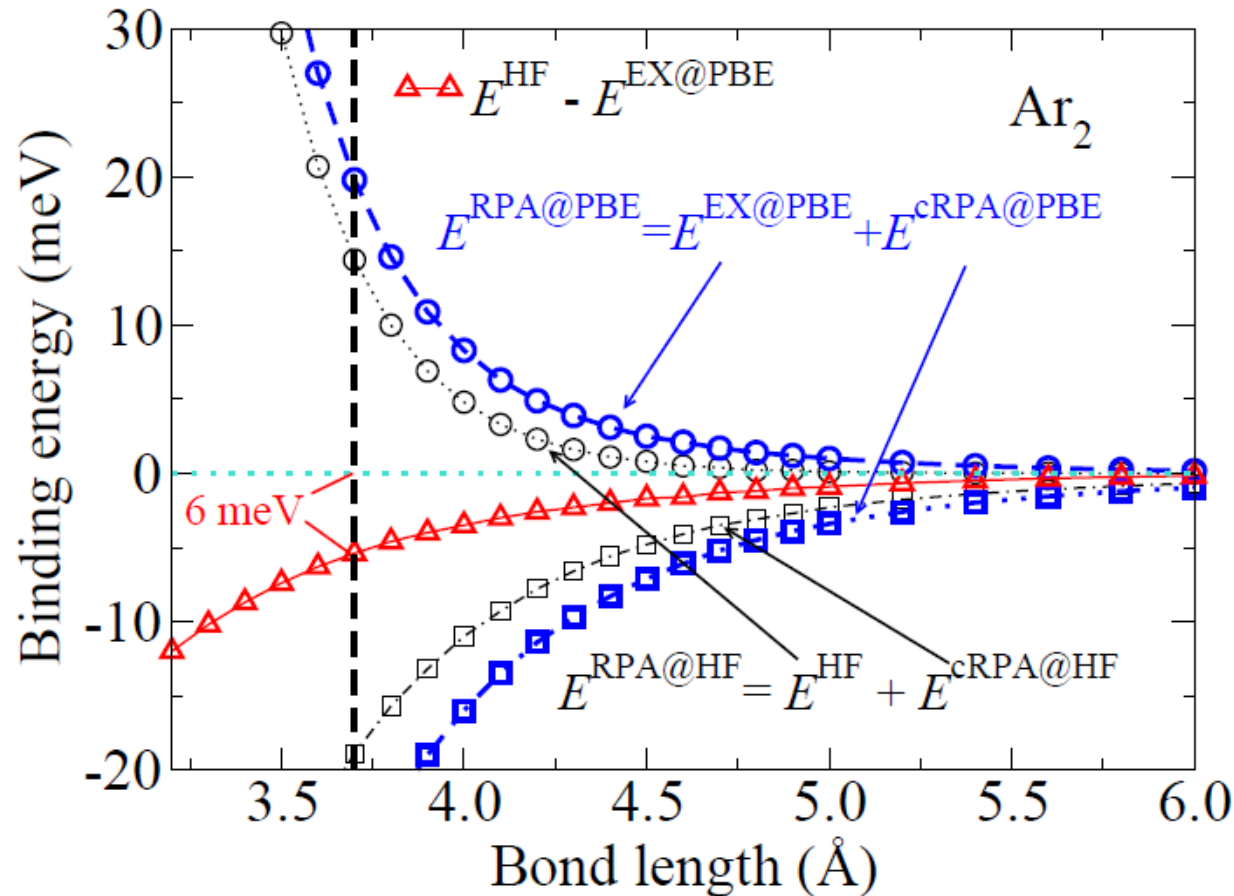
Screened second-order exchange

Diagrammatic representation (originally motivated from the coupled cluster context)



The SOSEX improves the atomization energy of covalently bound molecules, but does very little for vdW complexes.

Decomposing the RPA binding energy for Ar₂



Lennard-Jones

$$V_{\text{LS}}(r) = \frac{\alpha}{r^{12}} - \frac{\beta}{r^6}$$

Exact-exchange with Kohn-Sham orbitals has too strong Pauli repulsion!

There is yet another contribution: the singles

$$\hat{H}^e = \hat{H}_0^{\text{KS}} + \hat{H}_1, \quad \hat{H}_0^{\text{KS}} = \sum_{k=1}^N \left(-\frac{\nabla_k^2}{2} + v_{\text{ext}}(\mathbf{r}_k) + v_{\text{Hxc}}(\mathbf{r}_k) \right), \quad \hat{H}_0^{\text{KS}} |\Phi_n\rangle = E_n^{(0)} |\Phi_n\rangle$$

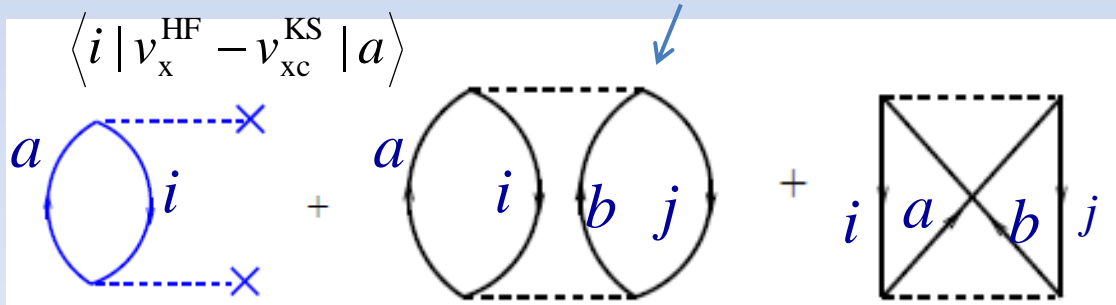
$$E_0^{(0)} = \langle \Phi_0^{\text{KS}} | \hat{H}_0 | \Phi_0^{\text{KS}} \rangle, \quad E_0^{(1)} = \langle \Phi_0^{\text{KS}} | \hat{H}' | \Phi_0^{\text{KS}} \rangle,$$

$$E_{\text{KS}}^{\text{EXX}} = E_0^{(0)} + E_0^{(1)}$$

Now

$$E_0^{(2)} = \sum_{i,a} \frac{|\langle \Phi_0^{\text{KS}} | H' | \Phi_i^a \rangle|^2}{\varepsilon_i - \varepsilon_a} + \sum_{i,j,a,b} \frac{|\langle \Phi_0 | H' | \Phi_{i,j}^{a,b} \rangle|^2}{\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b}$$

$\neq 0$



There is yet another contribution: the singles

$$E_c^{\text{SE}} = \sum_i^{\text{occ}} \sum_a^{\text{unocc}} \frac{\left| \langle \psi_i | \hat{f} | \psi_a \rangle \right|^2}{\varepsilon_i - \varepsilon_a}$$

Fock operator

Kohn-Sham orbitals

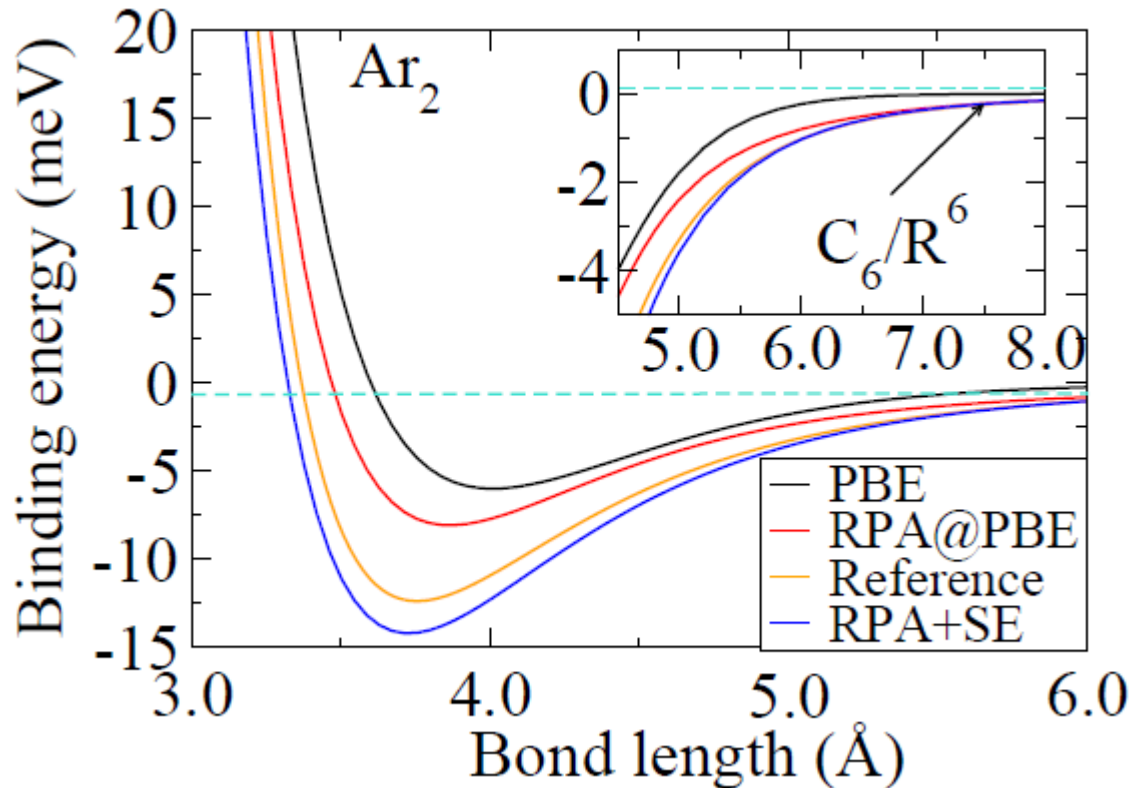
- Originally derived within the framework of Rayleigh-Schrödinger perturbation theory

XR, A. Tkatchenko, P. Rinke, M. Scheffler, PRL 106, 153003 (2011)

- Rederived within the framework of Adiabatic-connection fluctuation dissipation theorem **without freezing the density**

J. Klimes, M. Kaltak, E. Maggio, and G. Kresse, JCP 143, 102816 (2015)

RPA+SE for Ar₂



Singles contributions correct the too strong Pauli repulsion arising from the too extended GGA charge density.

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

Renormalized Singles Excitation (rSE) Contributions

$$E_c^{\text{rSE}} = \text{2nd-order} + \text{3rd-order} + \dots$$

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

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

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

“Semi-canonicalization”: Diagonalize f_{ij} and f_{ab} blocks separately $\rightarrow \tilde{f}_i, \tilde{f}_a$, and transform $f_{ia} \rightarrow \tilde{f}_{ia}$

The concept of renormalized second-order perturbation theory (rPT2)

$$E_c^{\text{RPA+SOSEX+rSE}} = \text{[Diagrams]} \quad (= \text{RPA})$$

$$+ \text{[Diagrams]} \quad (= \text{SOSEX})$$

$$+ \text{[Diagrams]} \quad (= \text{rSE})$$

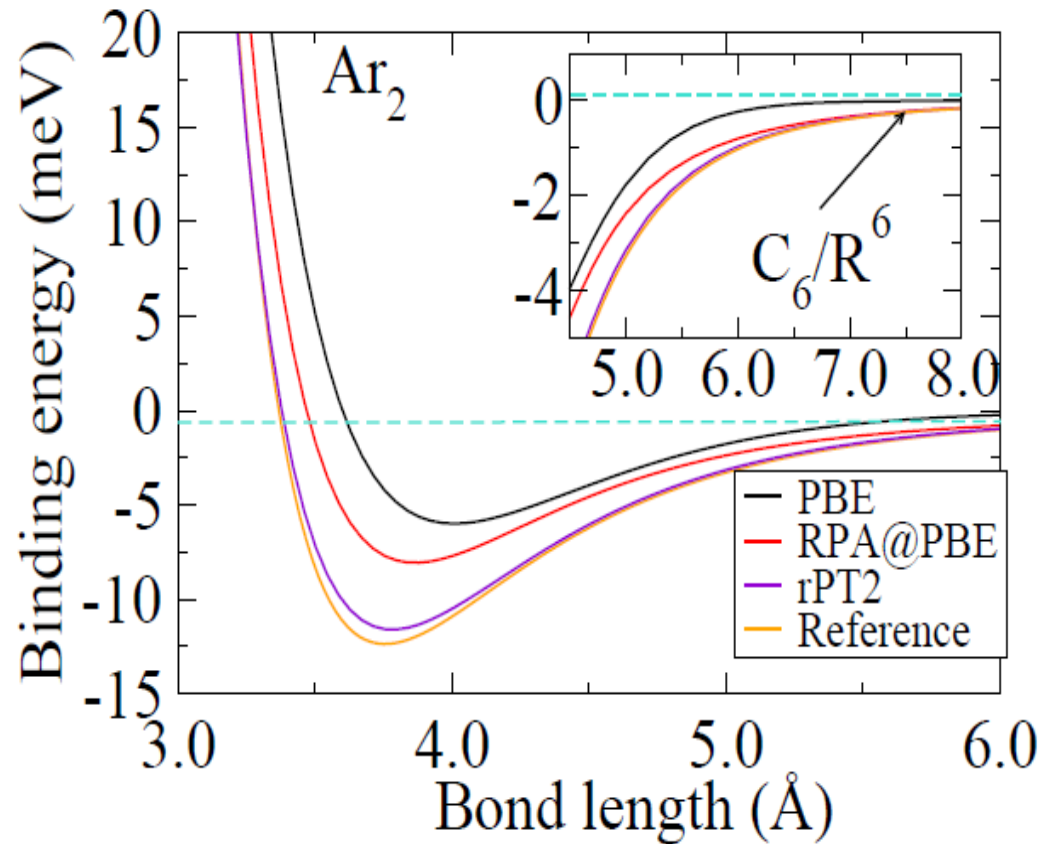
2nd-order 3rd-order

(PT2)

rPT2 = "RPA+SOSEX+rSE"

XR, P. Rinke, G.E. Scuseria, M. Scheffler,
Phys Rev. B **88**, 035120 (2013).

rPT2 for Ar₂



XR, P. Rinke, G.E. Scuseria, M. Scheffler,
Phys. Rev. B **88**, 035120 (2013).

The performance of rPT2

Van der Waals Cohesive energy Bond length Barrier heights

Method	S22 (%)	G2 (kcal/mol)	EBL10 (Å)	HTBH38 (kcal/mol)	NHTBH38 (kcal/mol)
PBE	57.8	8.2	0.044	9.7	8.9
PBE0	55.2	3.0	0.056	4.4	3.6
MP2	18.7	6.5	0.020	3.9	5.2
RPA	16.1	10.5	0.032	1.5	1.9
RPA + rSE	7.7	7.1	0.018	4.3	5.8
RPA + SOSEX	10.5	5.7	0.038	5.6	4.3
rPT2	7.1	3.1	0.019	1.9	3.0

rPT2: most balanced approach for atomization energy, van der Waals interaction, and chemical reaction barrier heights !

RPA + Singles for Solids

THE JOURNAL OF CHEMICAL PHYSICS **143**, 102816 (2015)

Singles correlation energy contributions in solids

Jiří Klimeš,^{1,2} Merzuk Kaltak,³ Emanuele Maggio,³ and Georg Kresse^{3,a)}

The random phase approximation to the correlation energy often yields highly accurate results for condensed matter systems. However, ways how to improve its accuracy are being sought and here we explore the relevance of singles contributions for prototypical solid state systems. We set out with a derivation of the random phase approximation using the adiabatic connection and fluctuation dissipation theorem, but contrary to the most commonly used derivation, the density is allowed to vary along the coupling constant integral. This yields results closely paralleling standard perturbation theory. We re-derive the standard singles of Görling-Levy perturbation theory [A. Görling and M. Levy, Phys. Rev. A **50**, 196 (1994)], highlight the analogy of our expression to the renormalized singles introduced by Ren and coworkers [Phys. Rev. Lett. **106**, 153003 (2011)], and introduce a new approximation for the singles using the density matrix in the random phase approximation. We discuss the physical relevance and importance of singles alongside illustrative examples of simple weakly bonded systems, including rare gas solids (Ne, Ar, Xe), ice, adsorption of water on NaCl, and solid benzene. The effect of singles on covalently and metallicly bonded systems is also discussed. © 2015 Author(s). All article content, except where otherwise noted, is licensed under

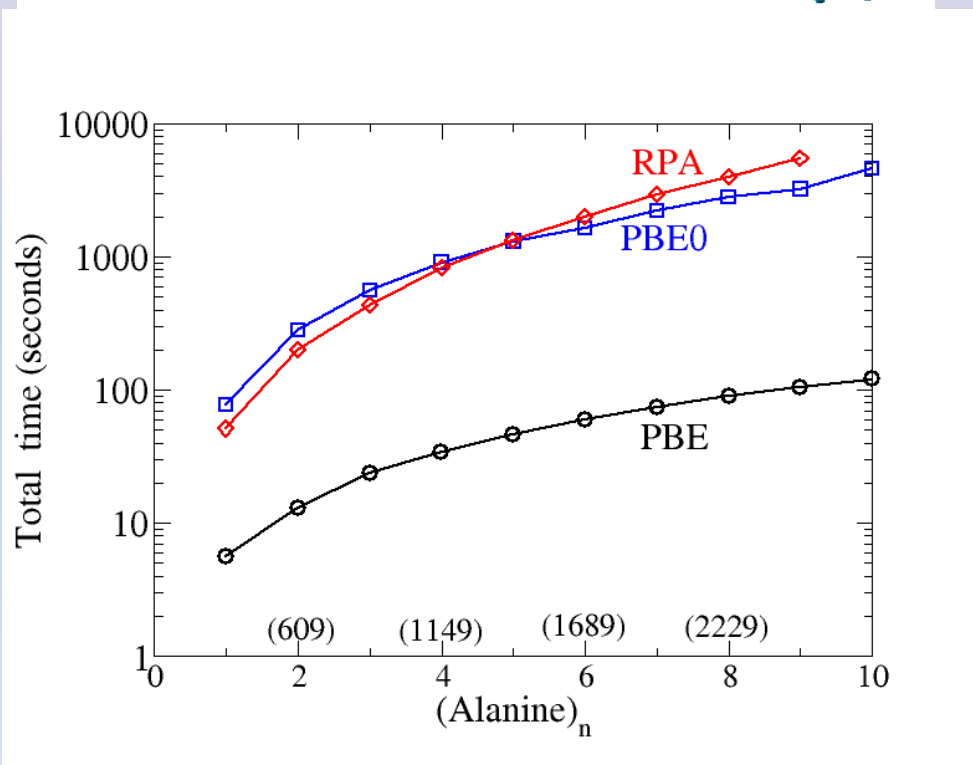
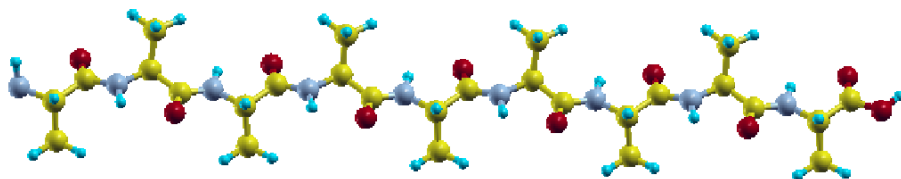
rSE fixed the problem of RPA!

What prevents RPA-based methods from widespread use?

- Computationally RPA is **2-3 orders of magnitude more expensive** than semi-local GGA DFT, for a system with $O(100)$ atoms.
→ **severely limited in the systems that can be tackled**
- Need to mind about unoccupied states
→ **tough basis set convergence problem**
- RPA Gradient is not readily available
→ **Production RPA calculations are only done with fixed geometry**
(I'd love to have the RPA geometry of molecules on metal surfaces!)
- No uniquely defined self-consistency scheme
→ **No well-defined RPA orbitals or RPA densities**

We will work on these issues in the Partner Group !

Computational times



- FHI-aims “tier 2” basis set.
- The situation gets more severe since RPA needs bigger basis set to converge.

Kohn-Sham theory versus Green function theory

Kohn-Sham theory

Green-Function theory

Basic variable

$$n(\mathbf{r})$$

$$G(\mathbf{r}, \mathbf{r}', \omega)$$

Harris-Foulkes functional

Luttinger-Ward functional

$$E[n] = \sum_i^{\text{occ}} \varepsilon_i - E_{\text{H}}[n] - \int v_{\text{xc}}(\mathbf{r})n(\mathbf{r}) + E_{\text{xc}}[n]$$

$$E[G] = -\text{Tr}[\ln(-G^{-1})] - E_{\text{H}}[n] - \text{Tr}[\Sigma G] + \Phi[G]$$

$$\frac{\delta E[n]}{\delta n} = 0 \Rightarrow \text{Kohn-Sham Eq.}$$

$$\frac{\delta E[G]}{\delta G} = 0 \Rightarrow \text{Dyson Eq.}$$

$$\left(-\frac{\nabla^2}{2} + v_{\text{ext}}(\mathbf{r}) + v_{\text{H}}(\mathbf{r}) + v_{\text{xc}}(\mathbf{r})\right)\psi_i(\mathbf{r}) = \varepsilon_i\psi_i(\mathbf{r})$$

$$G_0^{-1} - \Sigma = G^{-1}, \quad G_0^{-1} = \omega + \frac{\nabla^2}{2} - v_{\text{ext}}(\mathbf{r}) - v_{\text{H}}(\mathbf{r})$$

Effective XC potential:

$$V_{\text{xc}}[n] = \frac{\delta E_{\text{xc}}[n]}{\delta n}$$

Self-energy

$$\Sigma_{\text{xc}}[G] = \frac{\delta \Phi[G]}{\delta G}$$

Self-consistency issue

A self-consistent Green function theory can be formulated and implemented at the *GW* level, **that gives both ground-state energy and quasiparticle spectrum.**

(see, e.g., *F. Caruso, P. Rinke, XR, A. Rubio, M. Scheffler, Phys. Rev. B* **88**, 075105 (2012))

However,

- too expensive for materials
- binding energies are not great
- very difficult to go beyond *GW*

Practical way to go:

Formulating self-consistent theory in terms of the density matrix.

A dreamed theory (?)

A self-adapted vdW-inclusive hybrid functional

- ✓ Computationally similar to the HSE-type hybrid functional.
- ✓ The “mixing” and “screening” parameters are adjusted “on-the-fly” based on the dielectric property of the system.
- ✓ Including seamlessly a vdW part
(a non-local vdW functional based on density matrix should be possible, as Langreth-Lundquist vdW-DF is only based density)

Applicable to most materials of mixed bonding characters?



Patrick Rinke
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Volker Blum
(Duke U.)



Gustavo Scuseria
(Rice U.)