

# Basics and Recent Progress of Random Phase Approximation for Electronic Ground-State Energy Calculations

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第一性原理计算方法系列讲座

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# Outline

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- Concept and history of random phase approximation (RPA) as an approach to compute correlation energy of interacting electrons
- Selected examples of applications in materials science
- Efforts of going beyond RPA to further improve its accuracy
- Current (community-wide) activities and future perspectives

# Success and limitations of conventional DFT in computational materials science

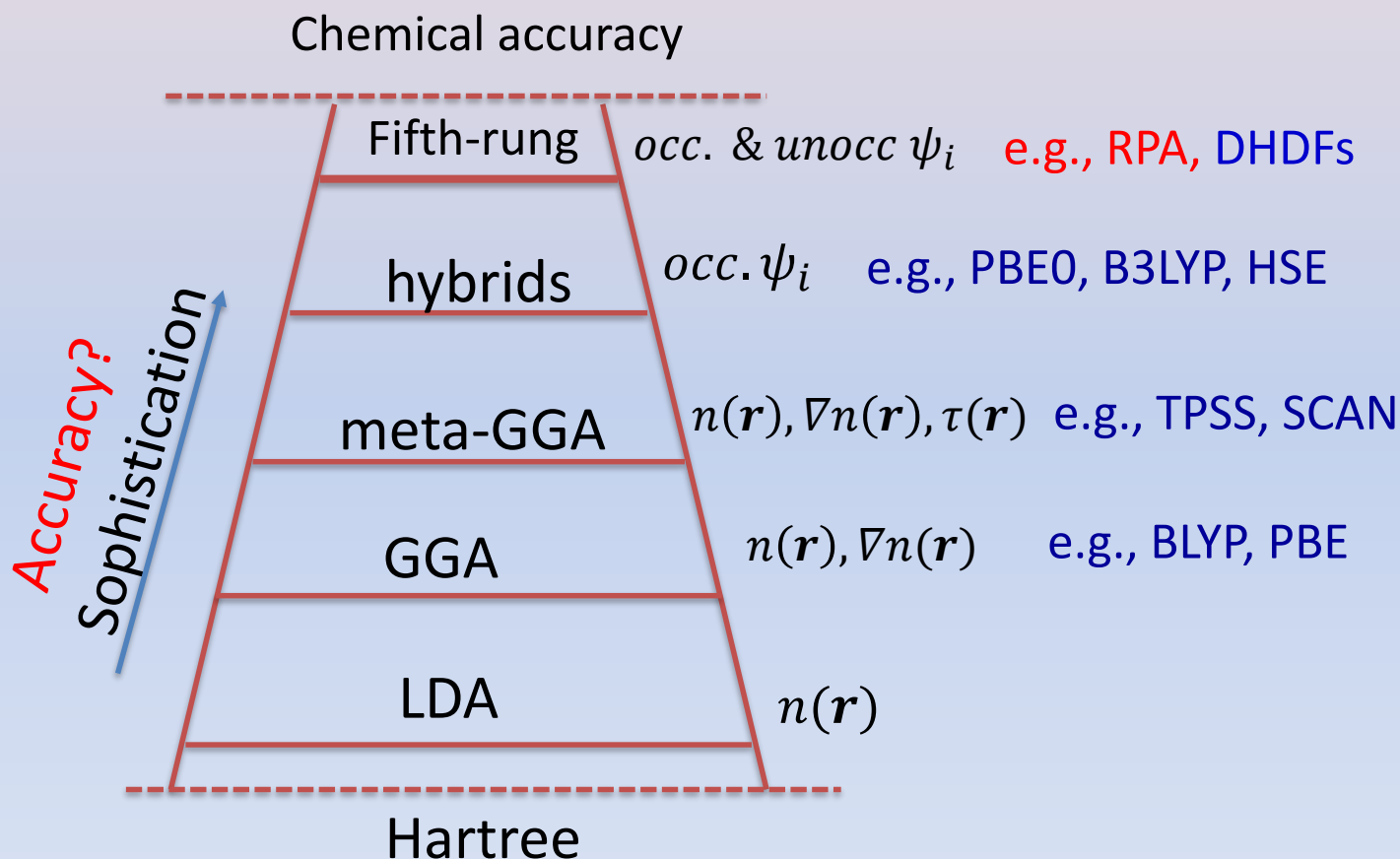
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Density functional theory (DFT) in its semi-local approximations is enormously successful in simulating materials' properties, **but has certain (intrinsic) limitations.**

Typical situations:

- **Systems with mixed bonding characteristics**  
(e.g., mixed physisorption and chemisorptions of molecules on metal surfaces, organic/inorganic interfaces, ...)
- **Systems where both ground-state energy and charge excitation energy gap are important.**  
(e.g., point defects in wide-gap insulators, ...)
- **Systems with near degeneracies (“strong correlation”)**  
(multi-configurational in nature, e.g., bond breaking, transition states, transition-metal oxides, *f*-electron systems, ...)

# Jacob's ladder in DFT



*J. Perdew & K. Schmidt, in Density functional theory and its application to materials, edited by 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

meta-GGA

DFT+vdW

DFT-D

DFT+G

.....

# Early history of RPA

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- Correlation energy of homogeneous electron gas (HES):
  - Divergence problem of “order-by-order” perturbation theory
- Separation of collective modes and internal modes of motion:
  - First appearance of the RPA concept (Bohm & Pines, 1950's)  
*“A Collective Description of Electron Interactions (I-IV)”* -- Bohm-Pines quartet  
*For a review, see D. Pines, Rep. Prog. Phys. 79, 092501 (2016).*
- Self-consistent field approach to HES
  - Lindhard function (Lindhard, 1954)
- RPA = “sum of ring diagrams to infinite order”
  - (Brueckner & Gell-Mann, 1957)
- The introduction of screened Coulomb interaction  $W$ 
  - (Hubbard, 1957)
- The  $GW$  approximation to the self-energy  $\Sigma=iGW$ 
  - (Hedin, 1965)

# The concept of RPA

We distinguish between two kinds of response of the electrons to a wave. One of these is in phase with the wave, so that the phase difference between the particle response and the wave producing it is independent of the position of the particle. This is the response which contributes to the organized behavior of the system. The other response has a phase difference with the wave producing it which depends on the position of the particle. **Because of the general random location of the particles, this second response tends to average out to zero** when we consider a large number of electrons, and **we shall neglect the contributions arising from this**. This procedure we call the “**random phase approximation**”.

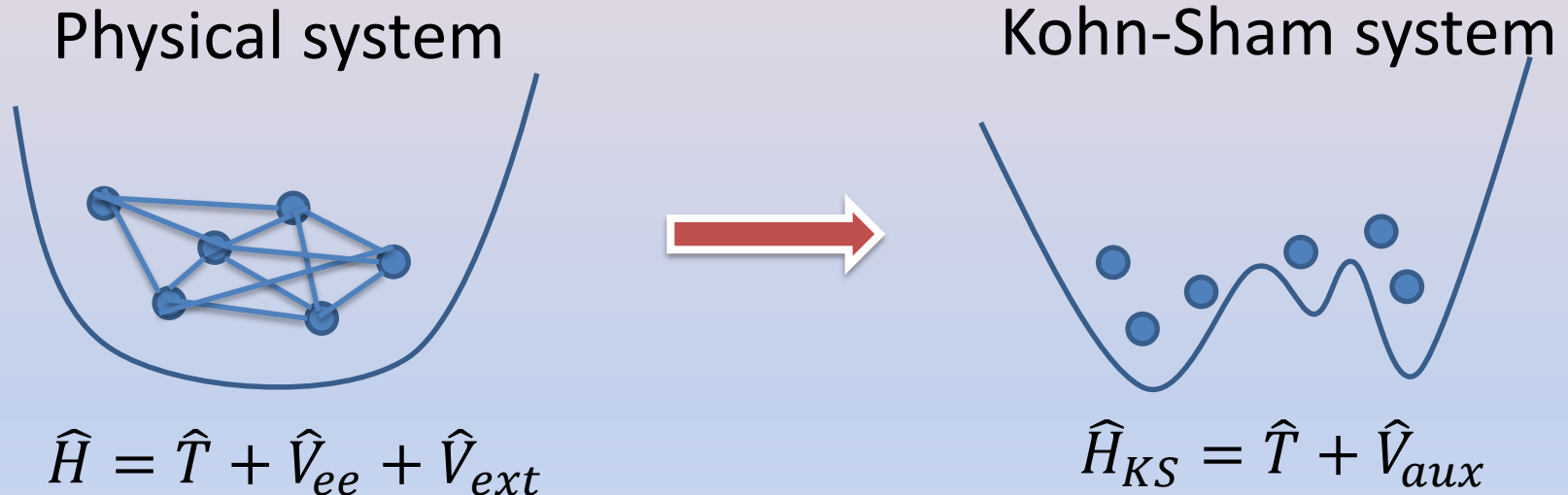
D. Bohm and D Pines, Phys. Rev. **82**, 625 (1950).

$$\frac{d^2 \rho_q}{dt^2} = -\omega_p^2 \rho_q - \sum_i \left( \mathbf{q} \cdot \frac{\partial \mathbf{x}_i}{\partial t} \right)^2 \exp[-i\mathbf{q} \cdot \mathbf{x}_i] \quad \left( \rho_q = \sum_i \exp[-i\mathbf{q} \cdot \mathbf{x}_i] \right)$$

$$- \sum_{i,j,k \neq q} \frac{4\pi^2}{mk^2} \mathbf{q} \cdot \mathbf{k} \underbrace{\exp[i(\mathbf{k} - \mathbf{q}) \cdot \mathbf{x}_i] \exp[-i\mathbf{k} \cdot \mathbf{x}_j]}_{\text{Average out to zero.}}$$

Average out to zero.

# The adiabatic connection construction



Define a series of fictitious systems with scaled interparticle interactions:

$$\hat{H}_{\lambda} = \hat{T} + \lambda \hat{V}_{ee} + \hat{H}_{ext}^{\lambda}$$

$$\hat{H}_{\lambda=1} = \hat{H}$$

$$\hat{H}_{\lambda=0} = \hat{H}_{KS}$$

The electron density  $n(r)$  is kept fixed for  $0 \leq \lambda \leq 1$ .



# 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 linear response function:

$$\chi_\lambda = \chi_0 + \lambda \chi_0 (v + f_{xc}) \chi_\lambda, \quad f_{xc} = 0 \rightarrow \chi_\lambda \approx \chi_\lambda^{\text{RPA}}$$

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

$$\Rightarrow E_c^{\text{RPA}} = E_c^{\text{RPA}}[\epsilon_i, \psi_i]$$

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

*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, molecules on surfaces, and layered materials (2006-2012).

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

# RPA for chemistry and materials science, as noted by Pines

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*Sixty-plus years later, the RPA continues to play a significant role in nuclear physics [66], bosonic field-theory [67], the quark-gluon plasma [68], many-fermion solvable models [69], and especially in computational chemistry and materials science. A recent review by Ren et al [70], to which the interested reader is referred, describes the impact of the RPA in the theoretical chemistry and materials science community, cites some thirty articles that indicate the renewed and widespread interest in the RPA during the period 2001–2011, discusses how it enables one to derive the  $1/r^6$  interaction between spatially separated closed shell electron systems, and, shows, in some detail, how the RPA enables one to go beyond density functional theory in computing ground state energies.*

-- David Pines, emergent behavior in strongly correlated electron systems, *Rep. Prog. Phys.* **79**, 092501 (2016)

# Why is RPA interesting for materials science?

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- Automatic and seamless inclusion of van der Waals (vdW) interactions; non-additive, anisotropic, and many-body screening effects are properly accounted for.
- Compatible with exact exchange; exact exchange plus RPA correlation makes the self-interaction error insignificant.
- Different bonding (ionic, covalent, metallic, vdW) types are treated on an equal footing.
- Static correlation (partly) captured => Correct dissociation of  $\text{H}_2$ ; excellent chemical reaction barrier heights

# RPA calculations in practice (so far ... )

In practical calculations, RPA is most often carried out as a single-point post-SCF approach, based on references from a preceding semi-local (or hybrid) calculation.

$$E^{\text{RPA}} = \langle \Phi_0 | \hat{H} | \Phi_0 \rangle + E_c^{\text{RPA}}[\epsilon_i, \psi_i]$$

RPA correlation energy

Hartree-Fock energy  
with (generalized) KS orbitals

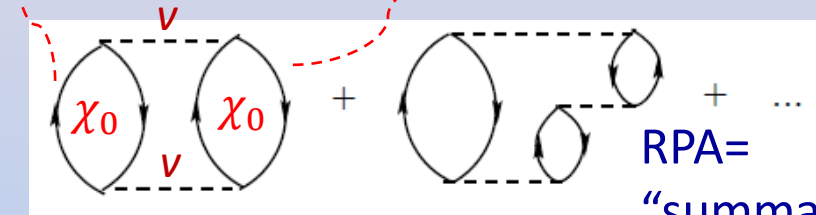
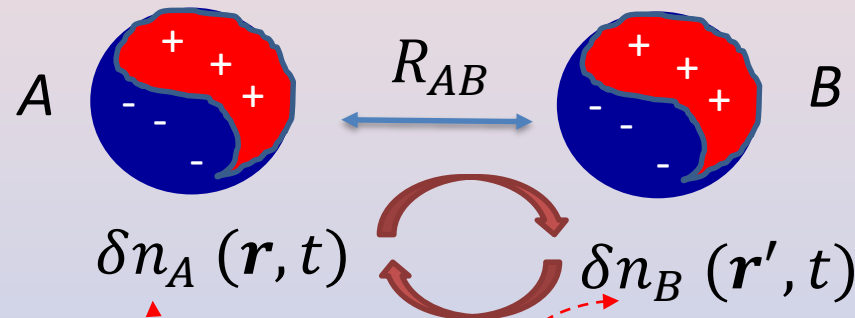
$\epsilon_i, \psi_i$ : (generalized) Kohn-Sham orbitals and orbital energies

$\Phi_0$ : Slater determinant formed with occupied  $\psi_i$

Typical choices for reference: LDA, PBE, TPSS, PBE0, HSE

Consequently, RPA results show a slight dependence on the starting point, denoted e.g., by “RPA@PBE”.

# RPA description of vdW interactions



“summation of ring diagrams”

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

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

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

# 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

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

# Matrix representation of $\chi^0$

A real-space grid representation of  $\chi^0(\mathbf{r}, \mathbf{r}', i\omega)$  is not tractable!

( **Nonlocal in space!**  $\mathbf{r}$  is restricted within one unit cell,  
where  $\mathbf{r}'$  extends over the entire solids.)

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

Expanding  $\chi^0$  in terms of a set of **auxiliary** basis functions.

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

Distinguish  $\{P_\mu(\mathbf{r})\}$  from the orbital basis set  $\{\varphi_i(\mathbf{r})\}$  to expand the KS orbitals

$$\psi_n(\mathbf{r}) = \sum_i c_{i,n} \varphi_i(\mathbf{r})$$



# Matrix representation of $\chi^0$

$$\begin{aligned}\chi^0(\mathbf{r}, \mathbf{r}', i\omega) &= 2 \sum_{m,n} \frac{(f_m - f_n) \psi_m^*(\mathbf{r}) \psi_n(\mathbf{r}) \psi_n^*(\mathbf{r}') \psi_m(\mathbf{r}')}{\varepsilon_m - \varepsilon_n - i\omega} \\ &= \sum_{\mu, \nu} P_\mu(\mathbf{r}) \chi_{\mu\nu}^0(i\omega) P_\nu(\mathbf{r}')\end{aligned}$$

Suppose

$$\psi_m^*(\mathbf{r}) \psi_n(\mathbf{r}) = \sum_{\mu} C_{mn}^{\mu} P_{\mu}(\mathbf{r})$$

Fermi Occupation factor

Then

$$\chi_{\mu\nu}^0(i\omega) = 2 \sum_{\mu} \frac{(f_m - f_n) C_{mn}^{\mu} C_{mn}^{\nu}}{\varepsilon_m - \varepsilon_n - i\omega}$$

# 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 rPT2, etc.
- Quasiparticle excitation energies:  $G_0W_0$ , scGW, MP2, and beyond

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

# First-Principles code package

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

Num

RPA implementations are also available in

- VASP
- Turbomole
- CP2K

Com

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Methods

CP2, RPA

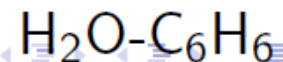
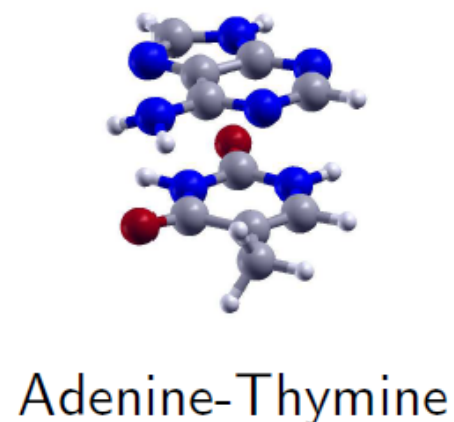
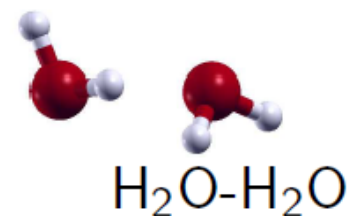
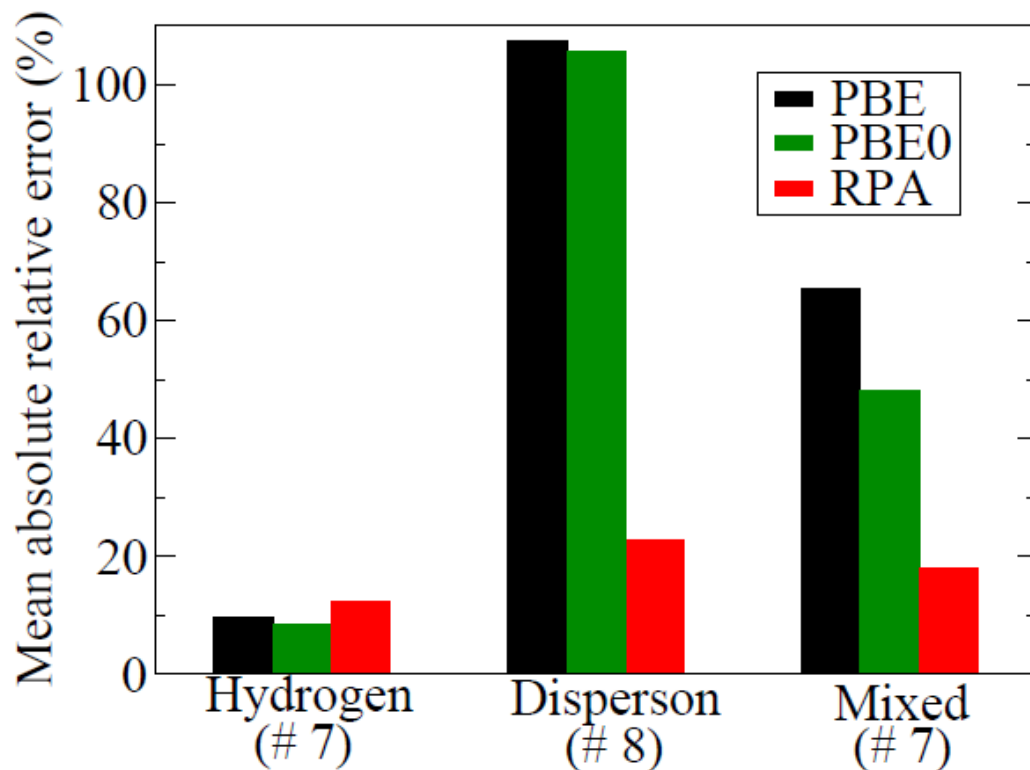
on energies:

beyond

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

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

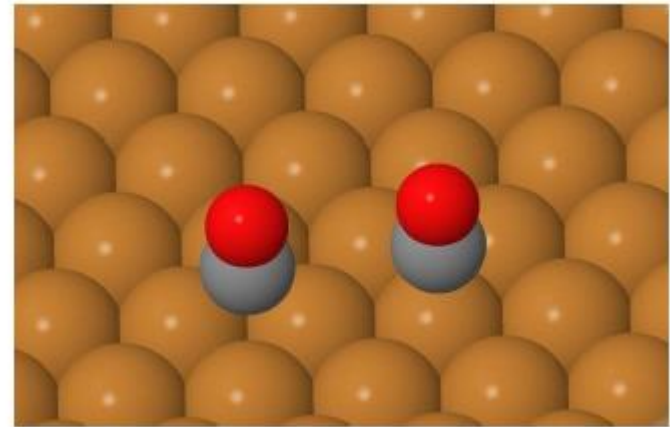
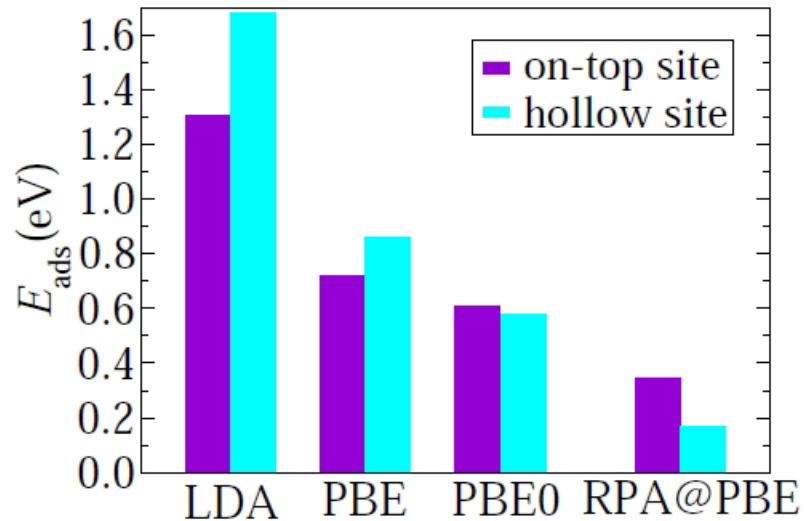
# RPA for the S22 test set



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)

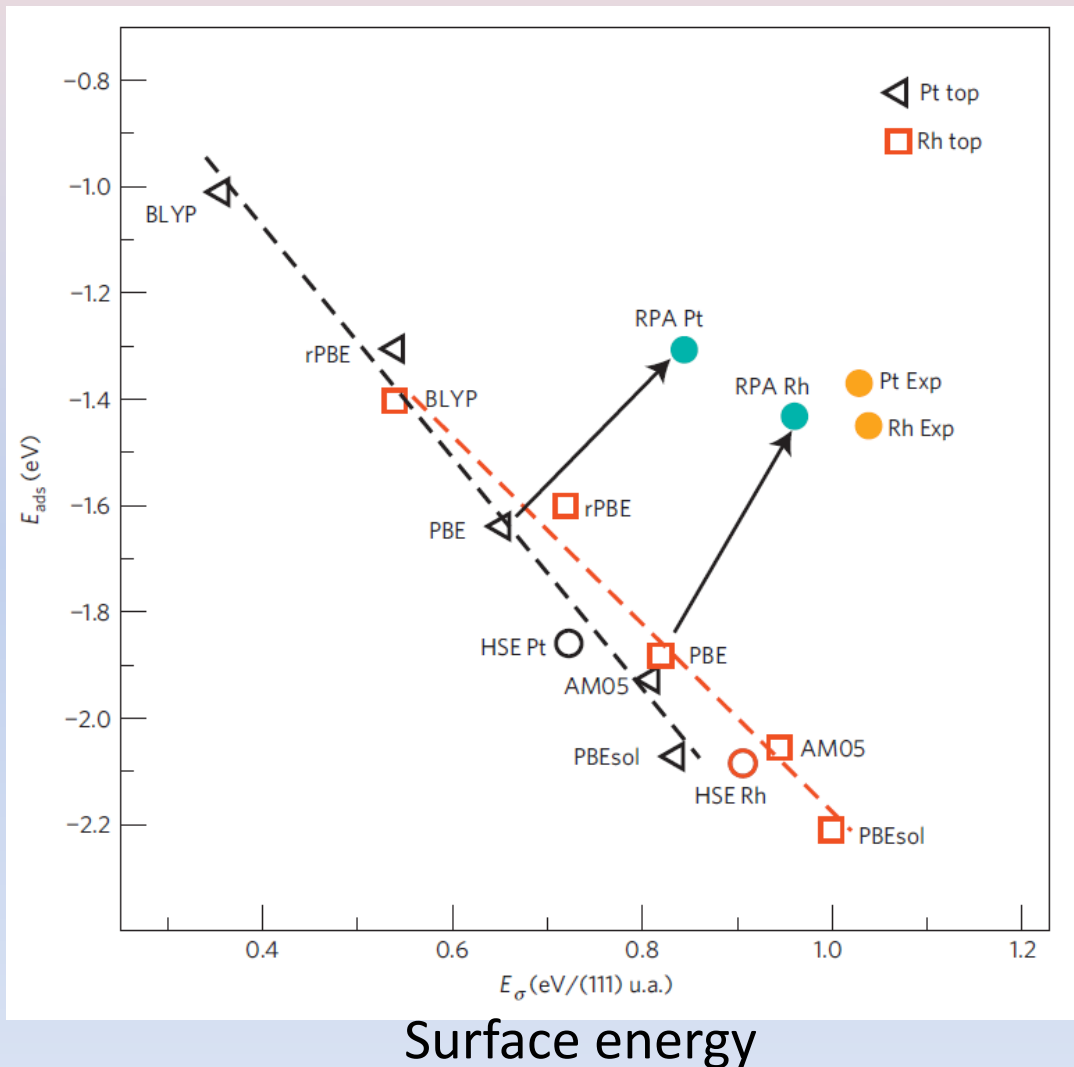
LDA/GGA => hollow site  
Exp/RPA => on-top site

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

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

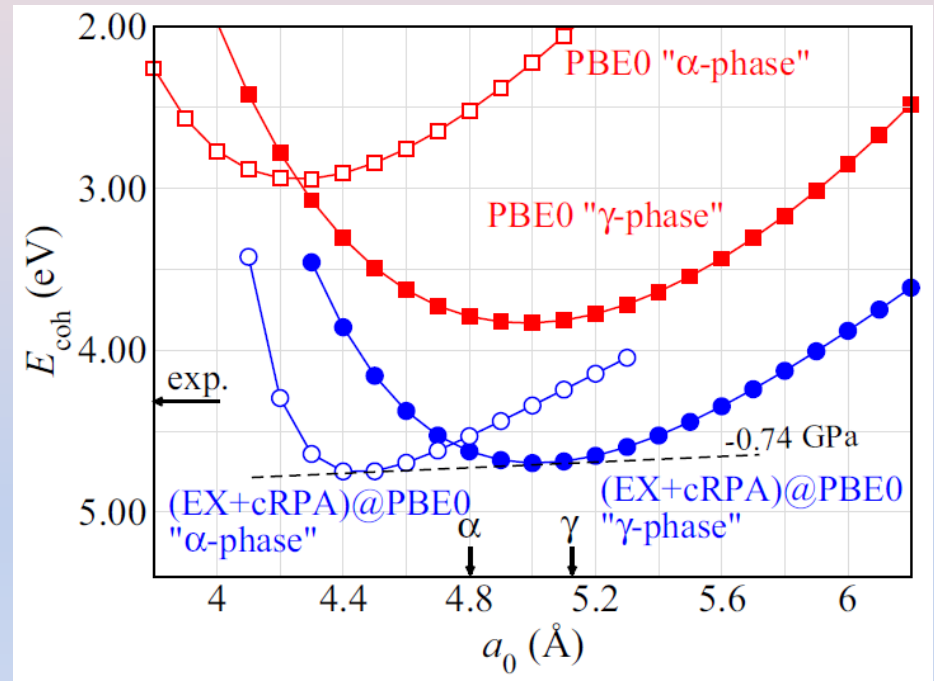
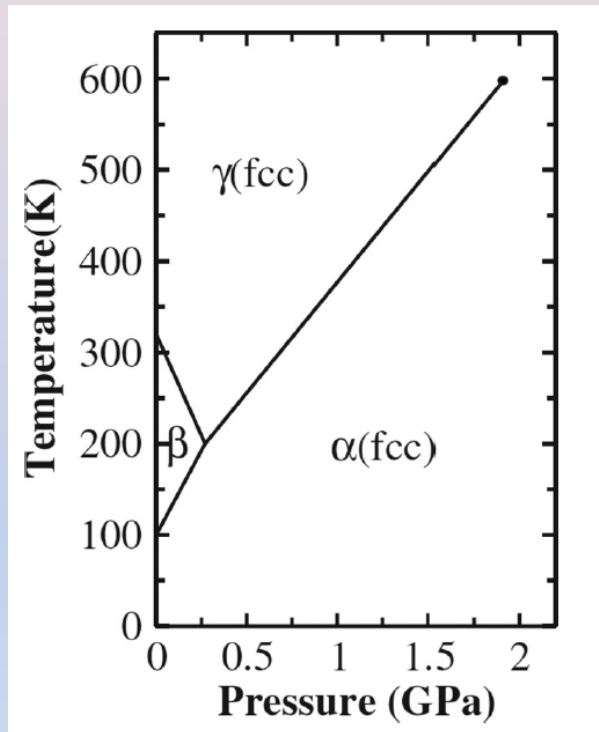
# CO adsorption energy versus surface energy

Adsorption energy



*L. Schimka, J. Harl, A. Stroppa, A. Grüneis, M. Marsman, F. Mittendorfer, and G. Kresse, Nature Materials* **9**, 741 (2010)

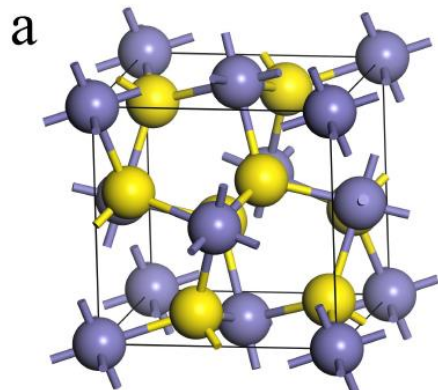
# The $\alpha - \gamma$ phase transition of Ce



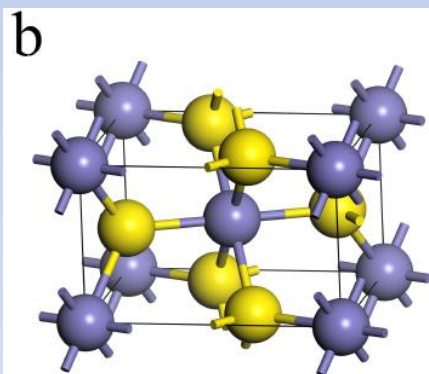
“Exact exchange” (EX) is crucial to produce two distinct solutions, corresponding to the two phases. Further adding the RPA correlation is necessary to yield the quantitatively correct stability of two phases.

*M. Casadei, XR, P. Rinke, A. Rubio, and M. Scheffler,  
Phys. Rev. Lett. 109, 146402 (2012); Phys. Rev. B 93, 075153 (2016)*

# The phase stability of FeS<sub>2</sub> polymorphs



Pyrite (P)

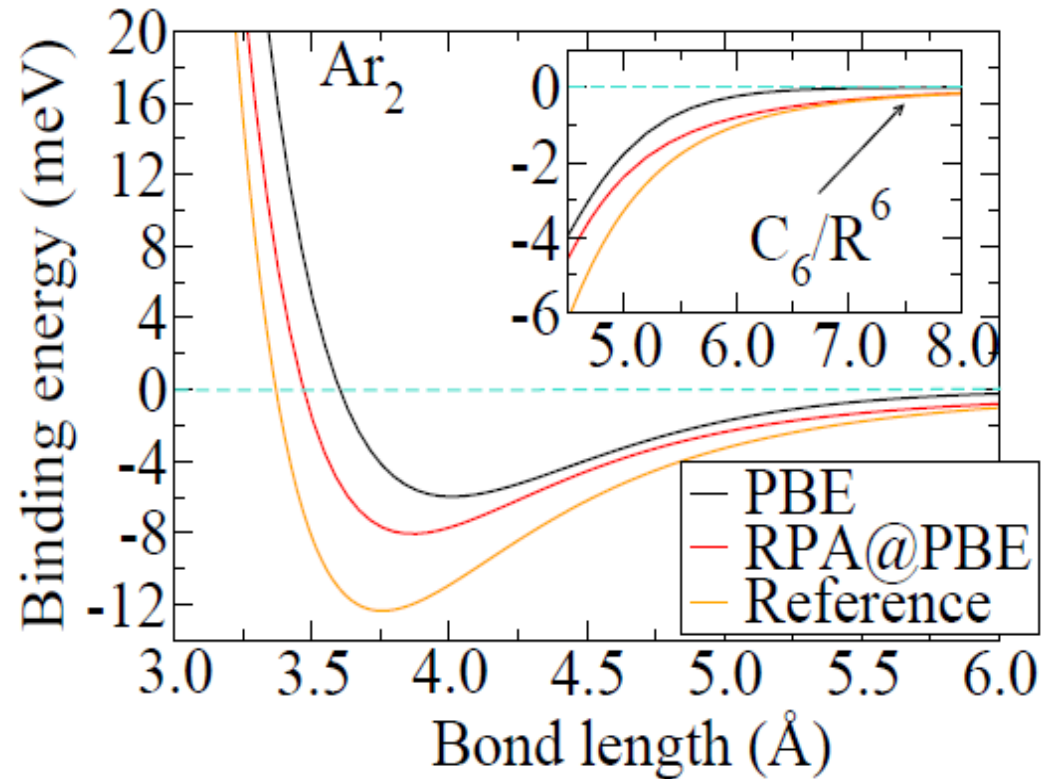


Marcasite (M)

Method	$\Delta E_{P-M}$ (meV/f.u.)	$\Delta H_{P-M}$ (meV/f.u.)
LDA	-7.3	-5.9
PBE	27.9	29.5
PBEsol	-4.5	-3.1
PBE+ <i>U</i>	28.3	
PBEsol+ <i>U</i>	4.4	
HSE06	-5.2	
PBE-D3	16.0	
optB88-vdW	25.5	
SCAN	31.7	
RPA@LDA	-30.7	-29.3
RPA@PBE	-24.0	-22.4
RPA@PBEsol	-25.2	-23.8
RPA@PBE+ <i>U</i>	-19.1	[-17.5]
RPA@HSE06	-15.9	[-14.3]
Exp.		$-42.9 \pm 0.2^d$



# RPA for $\text{Ar}_2$



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

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

# The singles correction: A many-body perturbation analysis

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

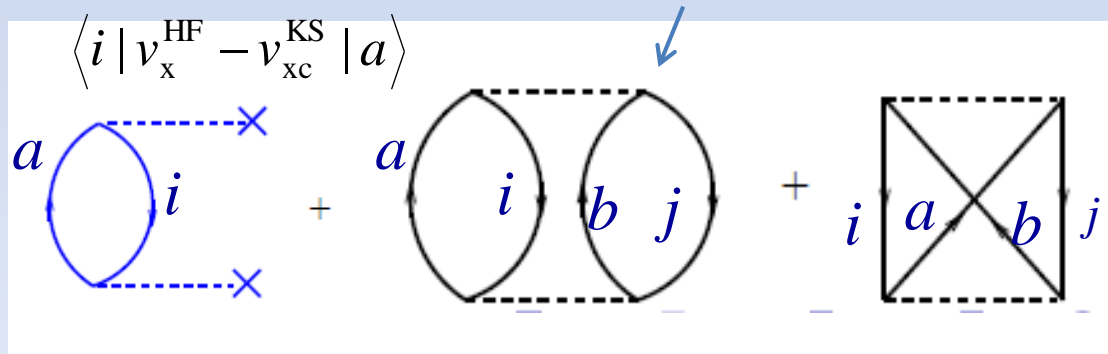
$$E_0^{(0)} = \langle \Phi_0^{\text{KS}} | \hat{H}_0 | \Phi_0^{\text{KS}} \rangle, \quad E_0^{(1)} = \langle \Phi_0^{\text{KS}} | \hat{H}' | \Phi_0^{\text{KS}} \rangle,$$

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

Now

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

$\neq 0$



# The computation of singles correction

Fock operator

$$E_c^{\text{SE}} = \sum_i^{\text{occ}} \sum_a^{\text{unocc}} \frac{\left| \langle \psi_i | \hat{f} | \psi_a \rangle \right|^2}{\epsilon_i - \epsilon_a} = \sum_i^{\text{occ}} \sum_a^{\text{unocc}} \frac{\left| \langle \psi_i | V_x^{\text{HF}} - V_x^{\text{KS}} | \psi_a \rangle \right|^2}{\epsilon_i - \epsilon_a}$$

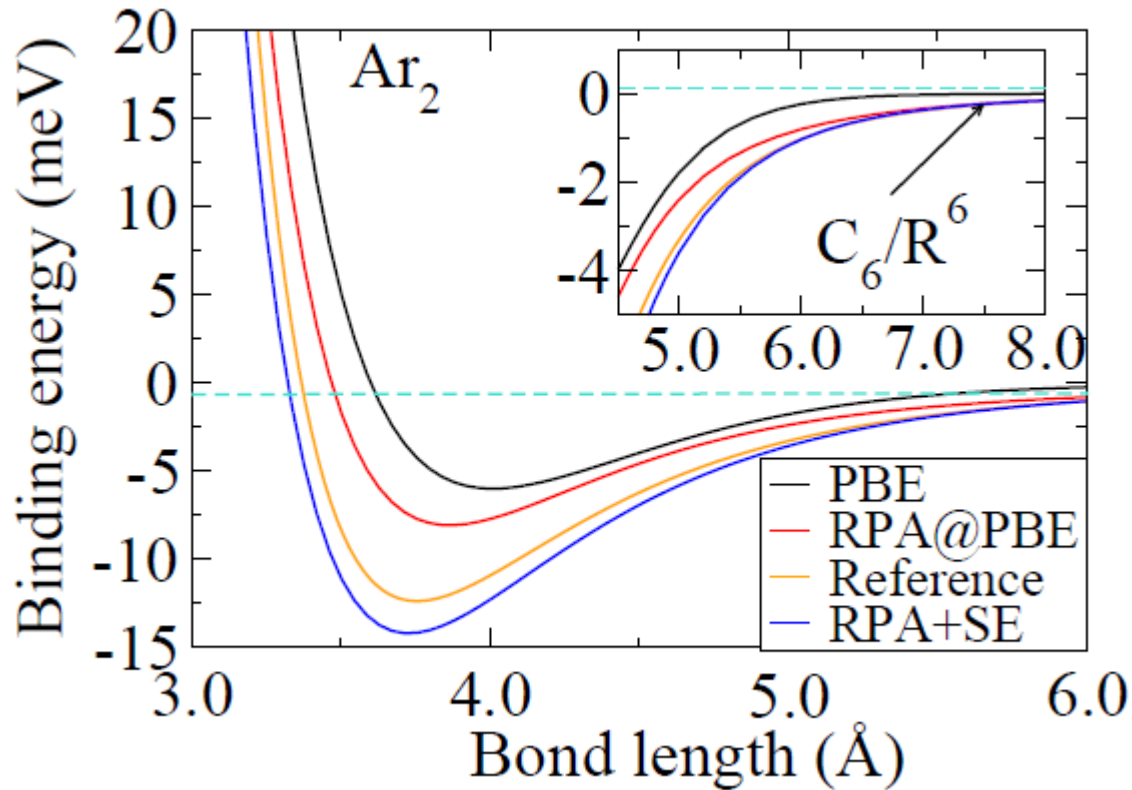
Kohn-Sham orbitals

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

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

- This term accounts for the fact that the orbitals used in RPA calculations are not “optimal”.

# RPA+SE for Ar<sub>2</sub>



Singles contributions correct the too strong Pauli repulsion arising from the too extended semi-local DFT charge density.

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

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

$$\begin{aligned}
 E_c^{\text{RPA+SOSEX+rSE}} = & \quad \text{[RPA diagrams]} + \dots \quad (= \text{RPA}) \\
 & + \text{[SOSEX diagrams]} + \dots \quad (= \text{SOSEX}) \\
 & + \text{[rSE diagrams]} + \dots \quad (= \text{rSE})
 \end{aligned}$$

2nd-order
3rd-order

(PT2)

rPT2 = “RPA+SOSEX+rSE”

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)

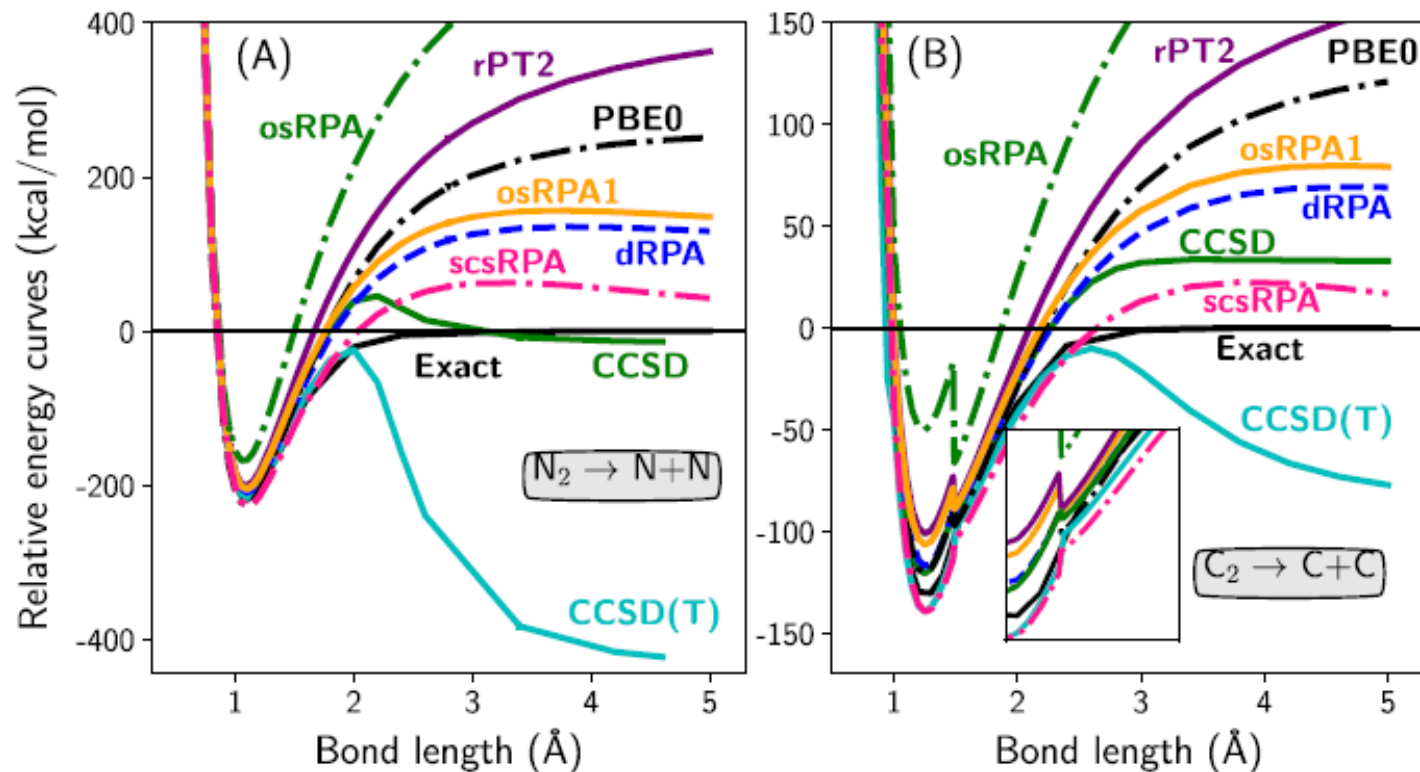
## Singles correlation energy contributions in solids

Jiří Klimeš,<sup>1,2</sup> Merzuk Kaltak,<sup>3</sup> Emanuele Maggio,<sup>3</sup> and Georg Kresse<sup>3,a)</sup>

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 metallically bonded systems is also discussed. © 2015 Author(s). All article content, except where otherwise noted, is licensed under

rSE fixed the problem of RPA!

# Spin component scaled direct RPA (scsRPA)



- Spin-pair distinctive error analysis
- Simultaneous reduction of the self-interaction error and non-dynamical error

*I. Y. Zhang and X. Xu, J. Phys. Chem. Lett. 10, 2617 (2019)*



# On-going community-wide activities

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- Low-scaling [ $O(N^3)$ ] RPA algorithm and implementations
  - Georg Kresse (VASP), up to 256 Si atoms
  - Joerg Hutter (CP2K), up to 500 water molecules
- Analytical gradient of RPA energy, allowing for geometry determination
  - Filipp Furche (Turbomole) for molecules
  - Georg Kresse (VASP) for solids
- Self-consistent RPA within a generalized Kohn-Sham (GKS) framework
  - Weitao Yang, optimizing the orbitals for RPA (similar to the Bruckner theory)
  - Filipp Furche, GKS-RPA, defining a static “RPA Hamiltonian”

A conceptually rigorous and practically useful self-consistency scheme, based on the variational principle has to be worked out, that yields

- Self-consistently determined charge densities and dipole moments
- Ground-state energy and quasi-particle energy levels in a unified framework
- Improved dielectric, optical, and magnetic properties

# Perspectives

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With the rapid advance of new concepts and algorithms, we hope (and believe), RPA can be developed into a viable approach in the near future which can

- bridge the conventional DFT and quantum-chemistry methods
- routinely tackle system size of a few hundred atoms
- provide unprecedented accuracy for computational materials science