

Random-Phase Approximation and Beyond for Materials: Concept, Practice, and Future Perspectives.

Xinguo Ren

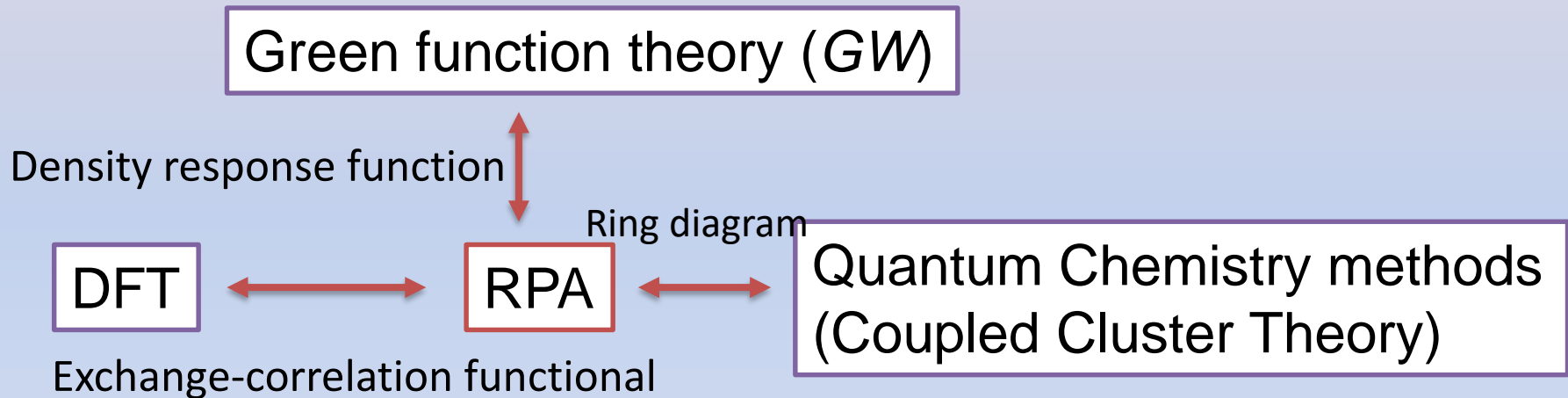
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Hands-on DFT and Beyond: High-Throughput Screening and Big-data Analytics, Towards Exascale Computational Materials Science

*University of Barcelona, Spain,
September 2, 2019*

What is random phase approximation (RPA)?

RPA plays a special role in modern electronic structure theory.



- RPA naturally captures non-local electron correlation effects, while conventional density functional approximation fail to do so.
- Bridges DFT, GW, and Quantum chemistry methods.

Outline

- Concept, history, and formulation of random phase approximation (RPA) as an approach to compute the 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

Density functional theory (DFT) in its conventional (e.g., LDA, GGA, hybrid) 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, ...)

A zoo of electronic-structure methods

Workhorse

LDA/GGAs

Deficiencies

Lack of van der Waals;
Delocalization errors

Insufficiency of KS-LDA/GGA
energy levels to describe one-
electron excitation energies

Consequences

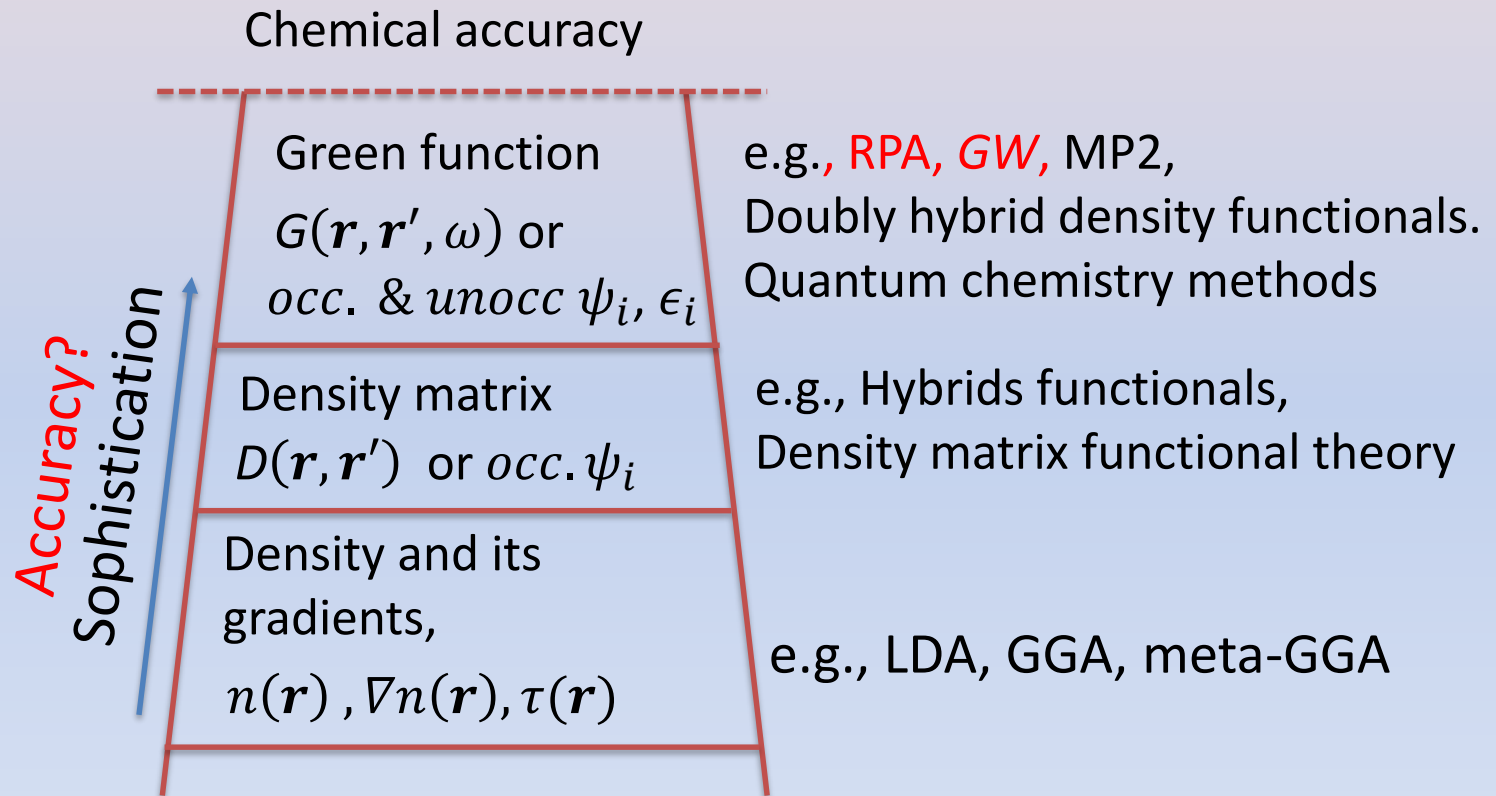
Inaccuracy for ground-
state energies

Underestimated band gaps;
distorted band structures

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 LOSC-DFT

Hierarchy of electronic structure theories



Early history of RPA

- 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 derive RPA
 - Lindhard function (Lindhard, 1954; Introduction of a frequency and momentum dependent dielectric function)
- 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**”.

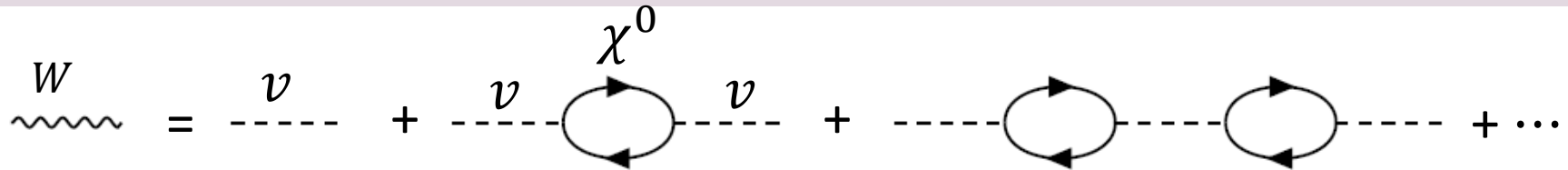
D. Bohm and D Pines, Phys. Rev. **82**, 625 (1950).

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

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

Average out to zero.

Diagrammatic representation of RPA



$$W(q, \omega) = v(q) + v(q)\chi^0(q, \omega)v(q) + \dots$$

$$= \frac{v(q)}{1 - v(q)\chi^0(q, \omega)} = \varepsilon^{-1}(q, \omega)v(q)$$

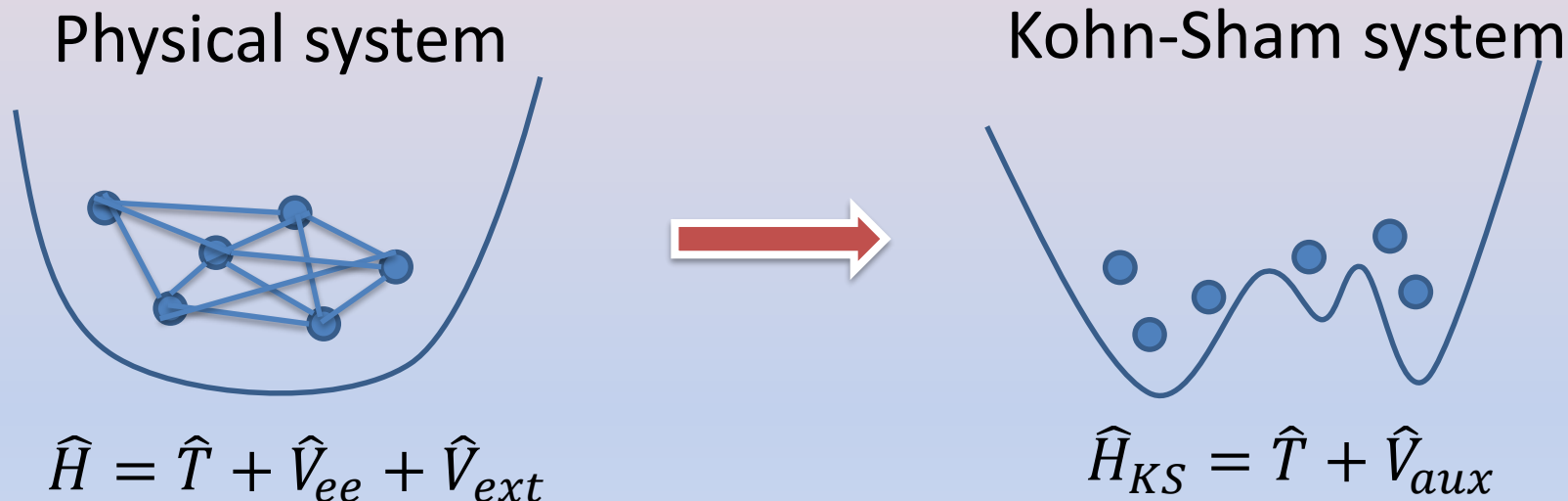
$\varepsilon(\mathbf{q}, \omega)$: momentum and frequency dependent dielectric function

$\chi^0(\mathbf{q}, \omega)$: Lindhard function; analytical form was first derived by Lindhard for the homogeneous electron gas (1954)

RPA correlation energy:

$$E_c^{\text{RPA}} = \frac{1}{2} \int_0^1 \frac{d\lambda}{\lambda} \frac{1}{\pi} \int_0^\infty d\omega \int \frac{d\mathbf{q}}{(2\pi)^3} \sum_{n=2}^{\infty} [\lambda v(\mathbf{q})\chi^0(\mathbf{q}, i\omega)]^n$$

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

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

The coupling constant *The density response function* *Coulomb interaction*

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

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

Dyson equation for the response function (**linear response TDDFT**):

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

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

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

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The RPA density response function

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 (2006-2012).

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

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)

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

Why is RPA interesting for materials science?

- 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 mitigates the many-body self-interaction error.
- Different bonding (ionic, covalent, metallic, vdW) situations are treated on an equal footing.
- Static correlation (partly) captured => Correct dissociation of H₂; excellent chemical reaction barrier heights

RPA calculations in practice (so far ...)

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

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

Hartree-Fock energy
with (generalized) KS orbitals

RPA correlation energy

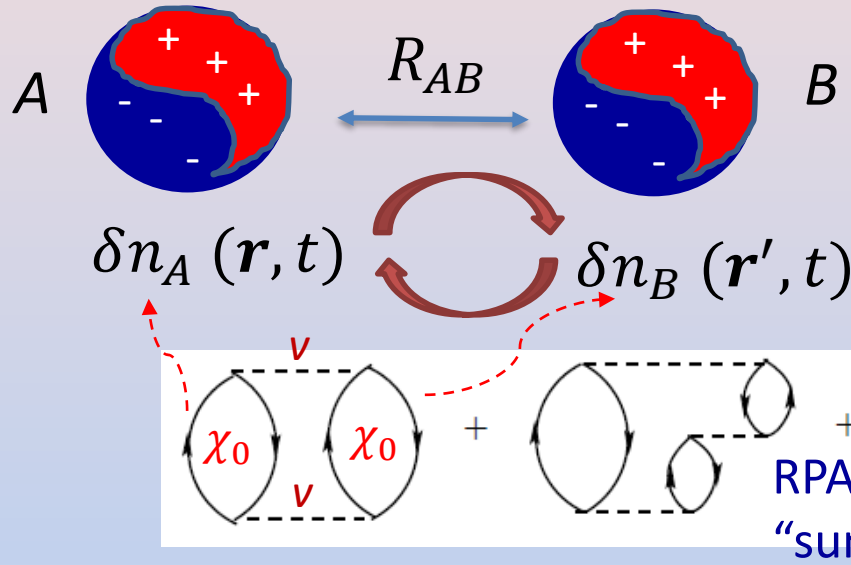
ϵ_i, ψ_i : (generalized) Kohn-Sham orbitals and orbital energies

Φ_0 : Slater determinant formed with occupied ψ_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



- RPA captures the **non-local coupling** between spontaneous charge fluctuations well separated in space.

- It can be shown analytically $\left(\alpha^{RPA}(i\omega) = \frac{1}{3} \sum_{j=1}^3 \iint x_j \chi^{RPA}(\mathbf{r}, \mathbf{r}', i\omega) x_j d\mathbf{r} d\mathbf{r}' \right)$

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

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

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 χ^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 χ^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 χ^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

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

Computational expression for RPA

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

$$\chi_{\mu\nu}^0(i\omega) = 2 \sum_{m,n} \frac{(f_m - f_n) C_{mn}^{\mu} C_{nm}^{\nu}}{\epsilon_m - \epsilon_n - i\omega}$$

$$V_{\mu\nu} = \int d^3r d^3r' \frac{P_{\mu}(\mathbf{r}) P_{\nu}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}$$

Define

$$\Pi_{\mu\nu}(i\omega) = [V^{1/2} \chi^0(i\omega) V^{1/2}]_{\mu\nu}$$

The RPA correlation energy:

$$\begin{aligned} E_c^{\text{RPA}} &= \frac{1}{2\pi} \int_0^{\infty} d\omega \text{Tr}[\ln(1 - \Pi(i\omega)) + \Pi(i\omega)] \\ &= \frac{1}{2\pi} \int_0^{\infty} d\omega [\ln(\det(1 - \Pi(i\omega))) + \text{Tr}(\Pi(i\omega))] \end{aligned}$$

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

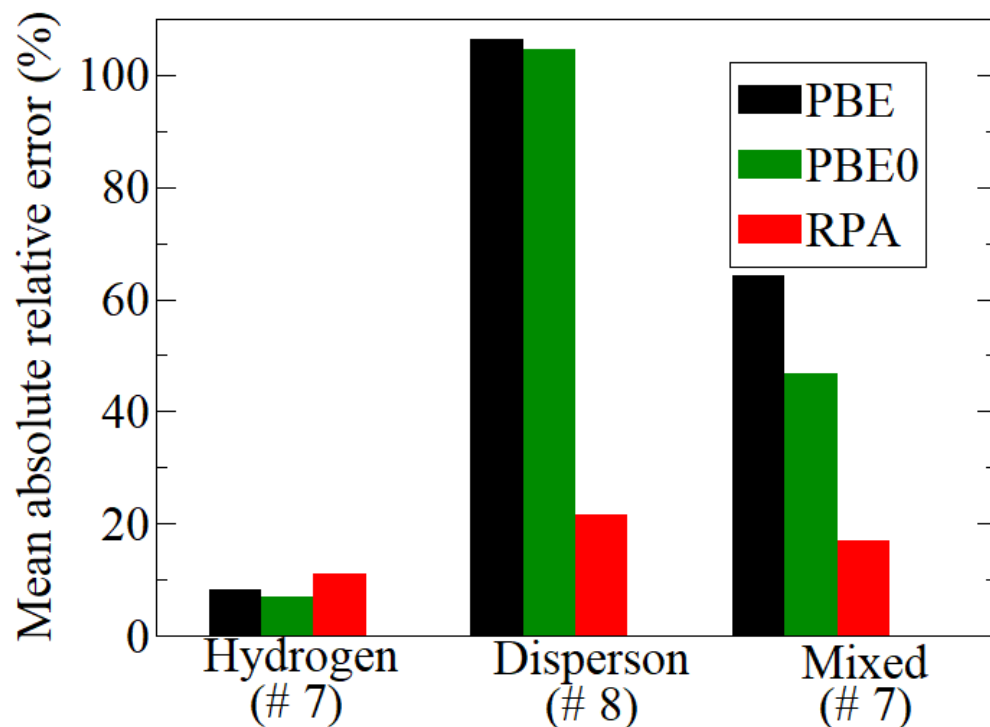
- Hybrid functionals, MP2, RPA and rPT2, etc.
- Quasiparticle excitation energies: G_0W_0 , scGW, MP2, and beyond

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

Outline

- Concept, history, and formulation of random phase approximation (RPA) as an approach to compute the 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

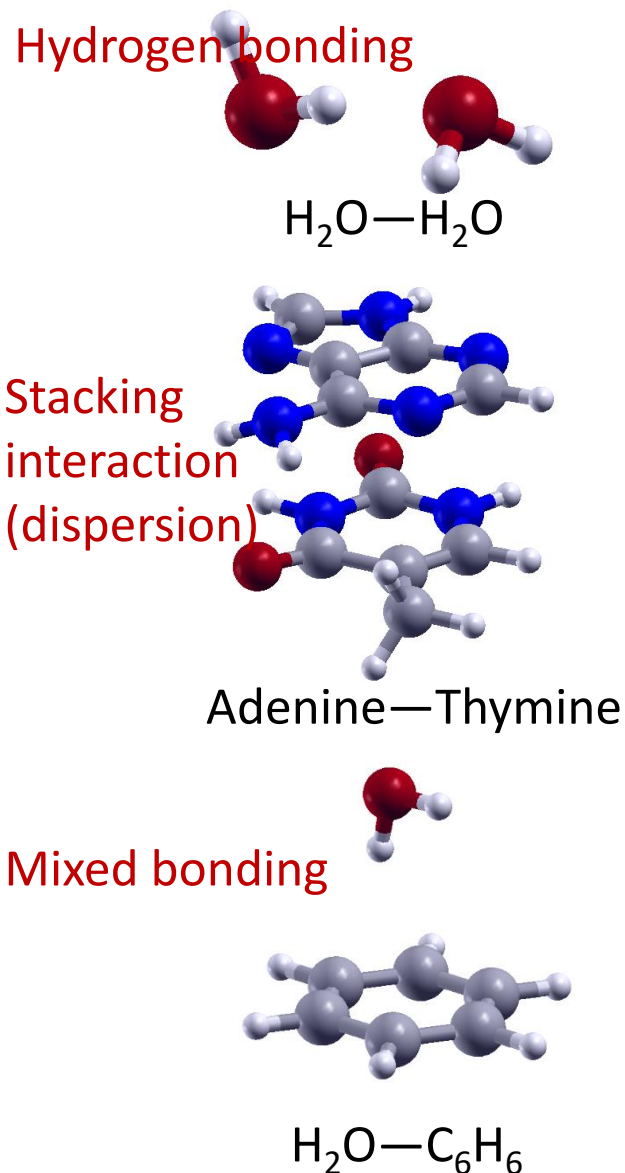
RPA for the S22 test set



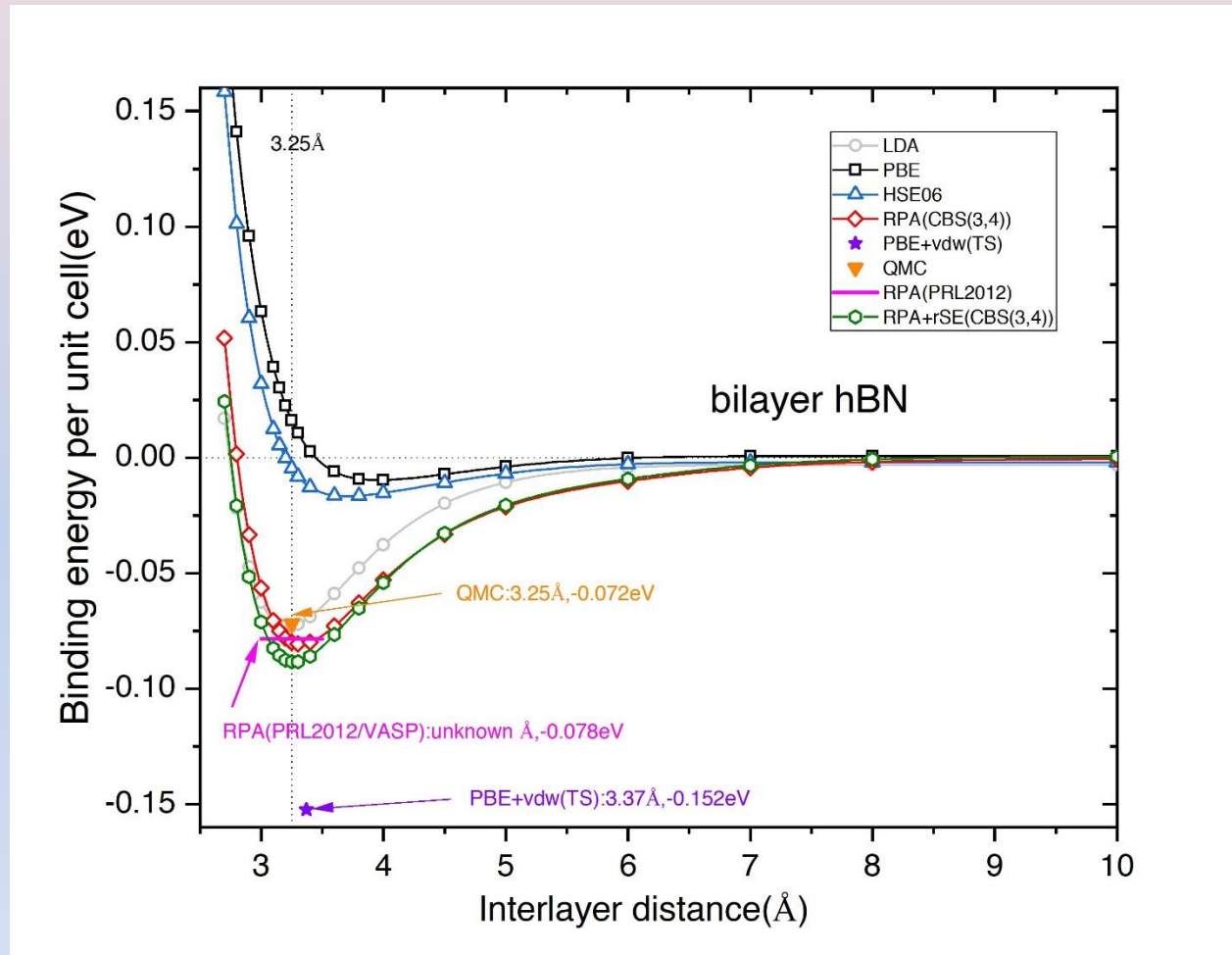
XR, A. Tkatchenko, P. Rinke, and M. Scheffler, *Phys. Rev. Lett.* **106**, 153003 (2011)

S22 set: 22 weakly bonded molecular complex, CCSD(T)/CBS reference data available

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



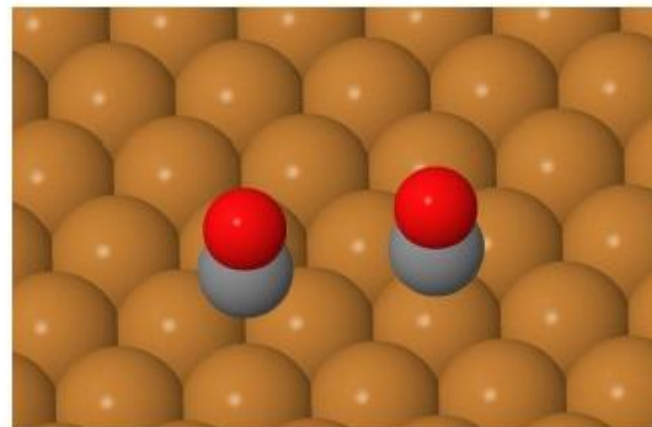
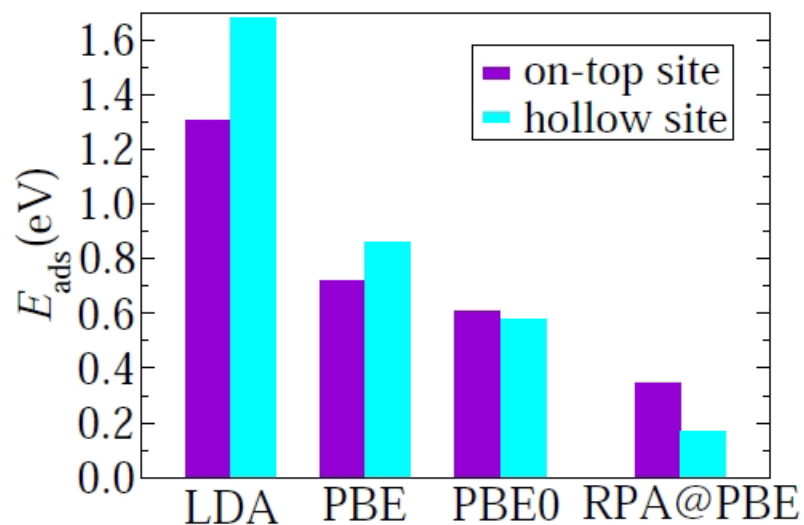
RPA binding energy curve for bilayer hBN



QMC: C.-R. Hsing et al., *New J. Phys* **16**, 113015 (2014).

PBE+vdW: N. Marom et al., *New J. Phys.* **105**, 046801 (2011)

RPA applied to the “CO adsorption puzzle”



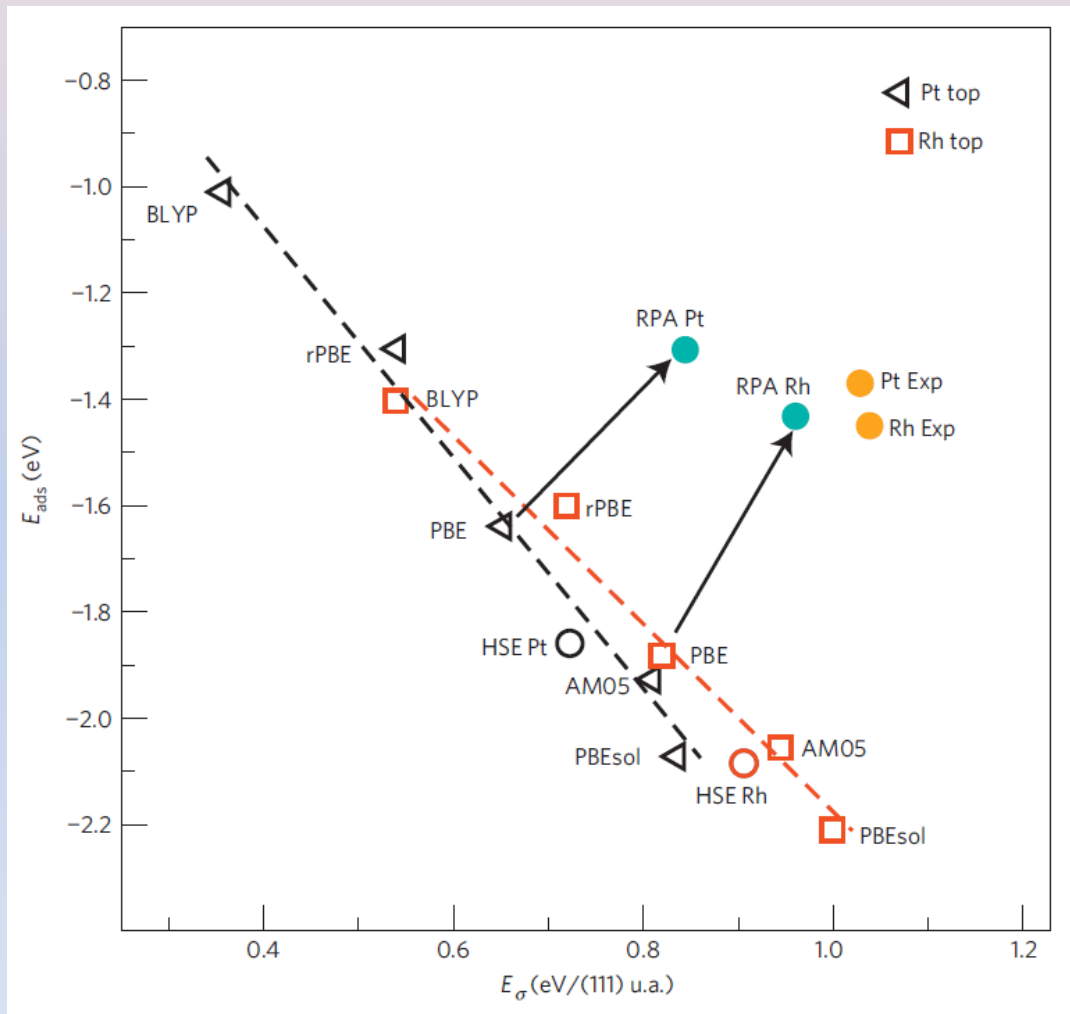
CO@Cu(111)

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

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

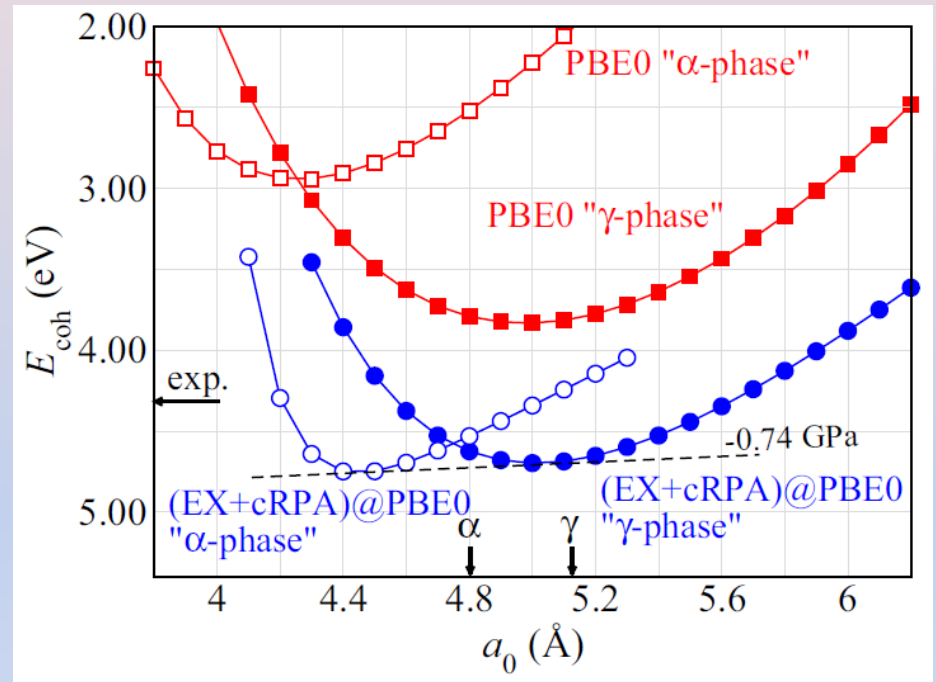
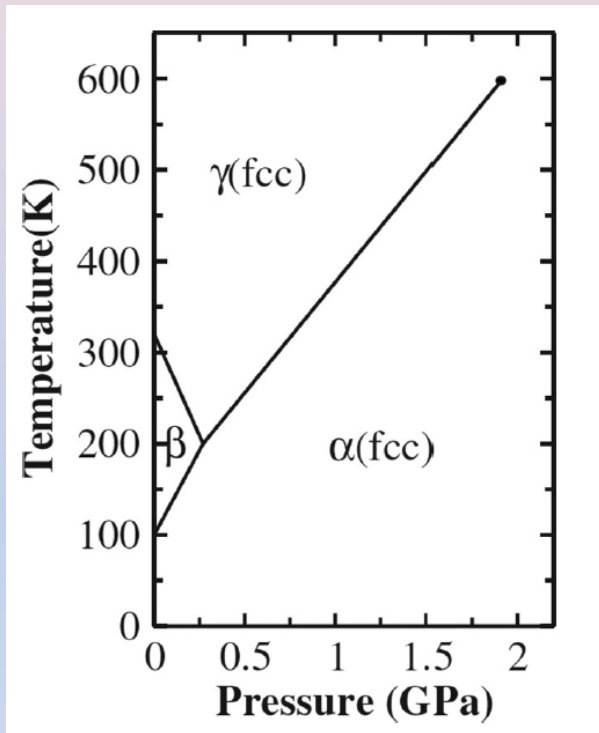
See also *L. Schimka et al., Nature Materials 9, 741 (2010).*

CO adsorption energy versus surface energy



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

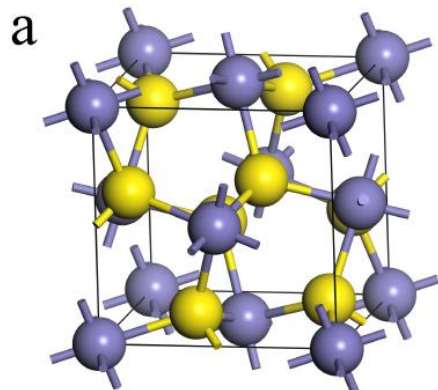


“Exact exchange” (EX) is crucial to produce two distinct solutions, corresponding to the two phases. Adding further the RPA correlation is necessary to yield the quantitatively correct stability of two phases.

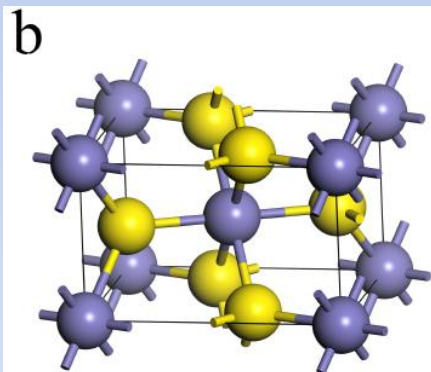
M. Casadei, XR, P. Rinke, A. Rubio, and M. Scheffler,

Phys. Rev. Lett. 109, 146402 (2012); Phys. Rev. B 93, 075153 (2016)

The phase stability of FeS₂ polymorphs



Pyrite (P)



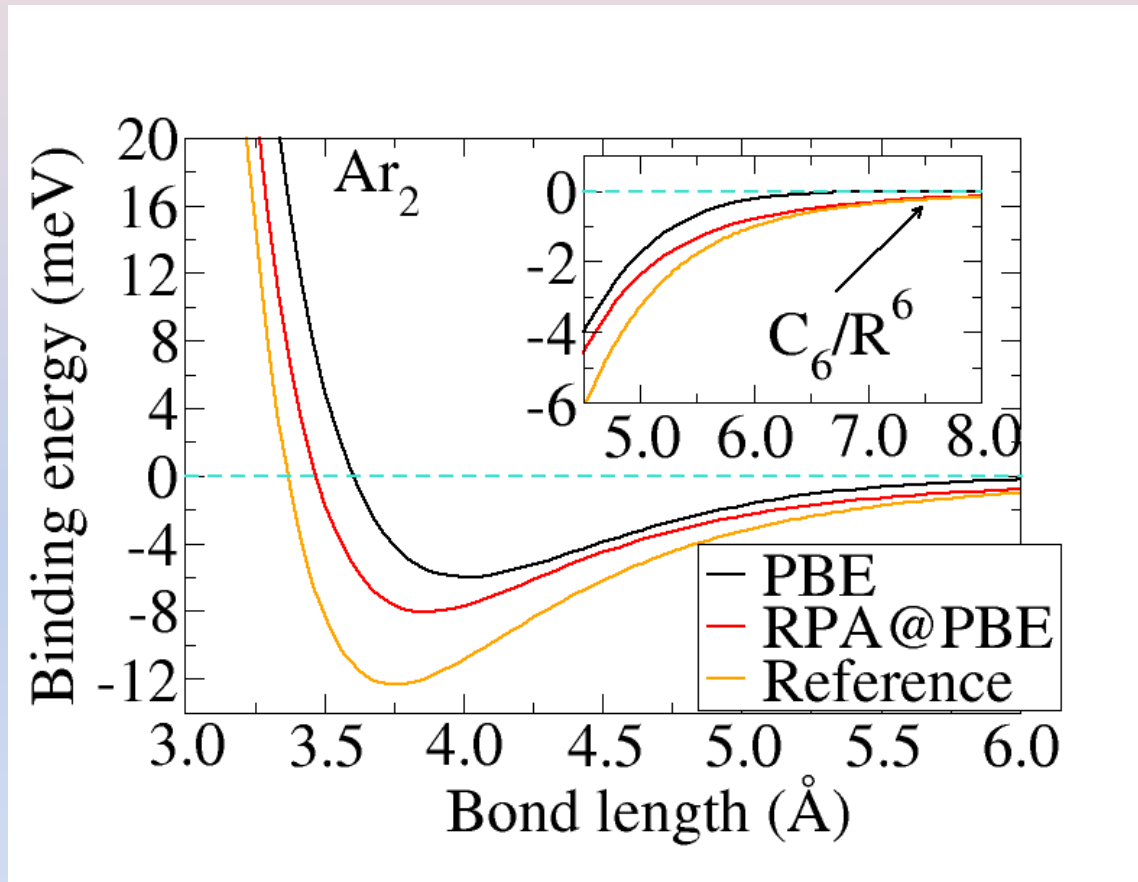
Marcasite (M)

Method	ΔE_{P-M} (meV/f.u.)	ΔH_{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 ± 0.2^d

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RPA for Ar₂



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

- Correct asymptotic behavior, crucial for large molecules.
- Substantial underbinding around the equilibrium distance.

The singles correction: A many-body perturbation analysis

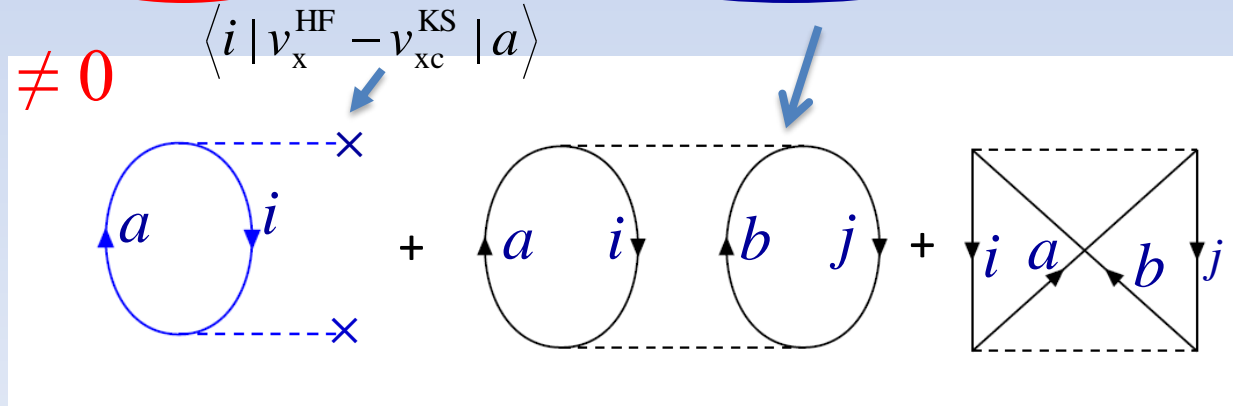
$$\hat{H}^e = \hat{H}_0^{\text{KS}} + \hat{H}_1, \quad \hat{H}_0^{\text{KS}} = \sum_{k=1}^N \left(-\frac{\nabla_k^2}{2} + v_{\text{ext}}(\mathbf{r}_k) + v_{\text{Hxc}}(\mathbf{r}_k) \right), \quad \hat{H}_0^{\text{KS}} |\Phi_n\rangle = E_n^{(0)} |\Phi_n\rangle$$

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

$$E^{\text{HF@KS}} = \langle \Phi_0^{\text{KS}} | \hat{H}^e | \Phi_0^{\text{KS}} \rangle = E_0^{(0)} + E_0^{(1)}$$

Now

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



The computation of singles correction

Fock operator

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

Kohn-Sham orbitals

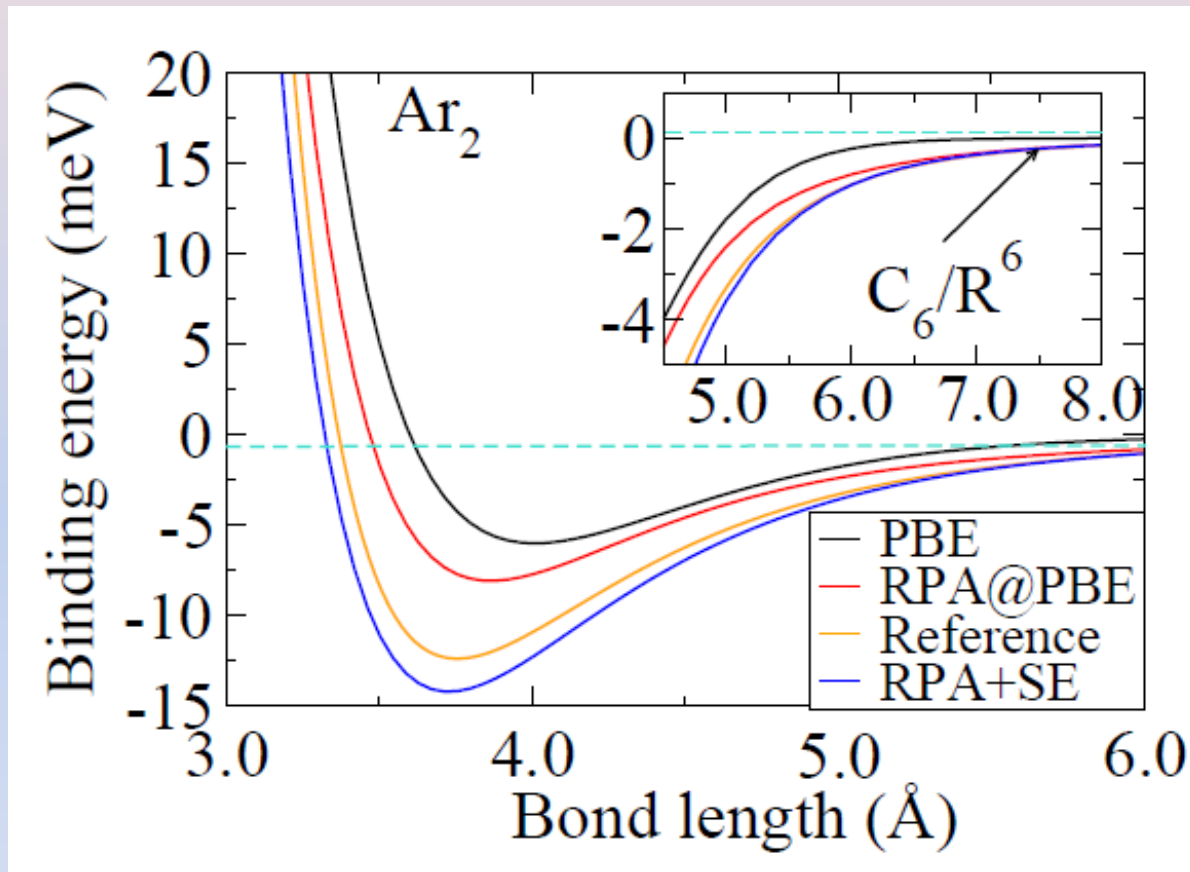
- Originally derived within the framework of Rayleigh-Schrödinger perturbation theory

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”.
- Singles contributions can be effectively included via an orbital optimization procedure

See Y. Jin, D. Zhang, Z. Chen, N. Q. Su, and W. Yang, J. Phys. Chem. Lett. 8, 4746 (2017).

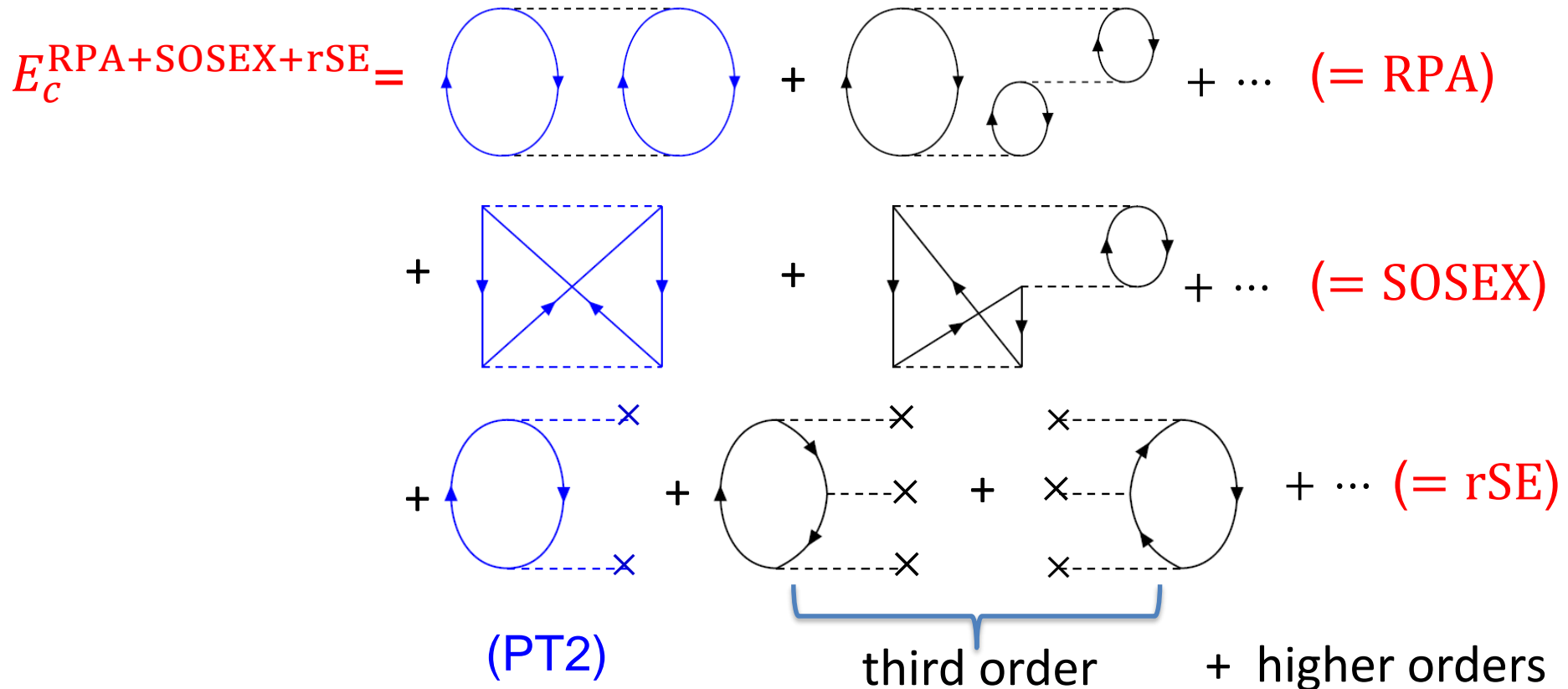
RPA+SE for Ar₂



- 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)



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

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Singles correlation energy contributions in solids

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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!

Outline

- Concept, history, and formulation of random phase approximation (RPA) as an approach to compute the 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**

On-going community-wide activities

- 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

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