Lecture on First-principles Computations (19): The Random Phase Approximation
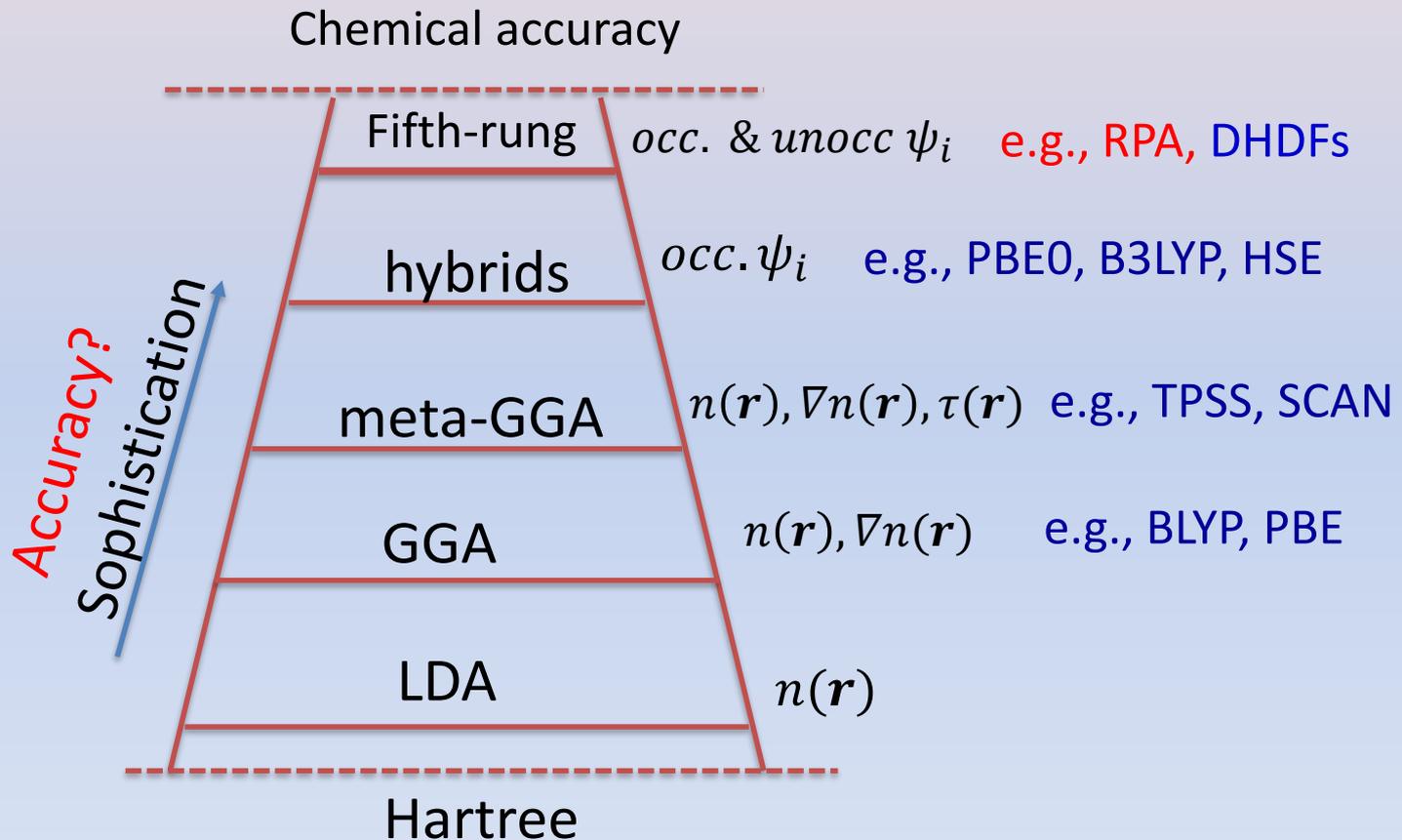
任新国 (Xinguo Ren)

中国科学技术大学
量子信息重点实验室

Key Laboratory of Quantum Information, USTC

Hefei, 2018.11.21

Jacob's ladder in DFT

Chemical accuracy

Fifth-rung — $occ.\ \&\ unocc\ \psi_i$ — e.g., RPA, DHDFs

hybrids — $occ.\ \psi_i$ — e.g., PBE0, B3LYP, HSE

meta-GGA — $n(\boldsymbol{r}), \nabla n(\boldsymbol{r}), \tau(\boldsymbol{r})$ — e.g., TPSS, SCAN

GGA — $n(\boldsymbol{r}), \nabla n(\boldsymbol{r})$ — e.g., BLYP, PBE

LDA — $n(\boldsymbol{r})$

Hartree

Accuracy?
Sophistication

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

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).*

Correlation energy of the homogeneous electron gas

Bohr radius

$$\frac{4\pi}{3} r_s^3 a_0^3 = 1/n$$

Electron density

Second-order exchange

$$E_0(r_s) = \frac{2.21}{r_s^2} - \frac{0.916}{r_s} - 0.096 + 0.062\ln(r_s) + \cdots [Ryd]$$

Kinetic energy

Exchange energy

RPA correlation energy

The concept of RPA has found broad applications

- Friedel oscillation (3D metals)

- Kohn anomaly (electron-phonon coulping)

- Peierls instability (1D atomic chain)

- Magnetic susceptibility (Spin systems)

- Nuclear physics

- ……

Focus: RPA as a first-principles method

-- An approximate functional within the Kohn-Sham DFT framework

Adiabatic-connection fluctuation-dissipation (ACFD) theorem

Kohn-Sham density-functional theory

- Hohenberg-Kohn theorem (Levy-Lieb constrained search)

$$E_{\text{HK}}[n] = F[n] + \int d\,\boldsymbol{r} v_{ext}(\boldsymbol{r}) n(\boldsymbol{r})$$

Universal functional

$$F[n] = \min_{\Psi \to n} \langle \Psi \mid \hat{T} + \hat{V}_{ee} \mid \Psi \rangle$$

$$E_{\text{HK}}[n] \geq E^0 = E_{\text{HK}}[n^{\text{GS}}]$$

$$= T[n] + J[n] + U_{\text{xc}}[n]$$

- Kohn-Sham scheme

$$E_{\text{KS}}[n] = T_s[n] + J[n] + E_{\text{xc}}[n] + \int d\,\mathbf{r} v_{ext}(\mathbf{r}) n(\mathbf{r})$$

$$E_{\text{xc}}[n] = T[n] - T_s[n] + U_{\text{xc}}[n] = T_c[n] + U_{\text{xc}}[n]$$

Treat $T_s[n]$ exactly via auxiliary single-particle orbitals!

The exchange-correlation energy

$$E_{xc} = E_x + E_c$$

$$E_x = \langle \Phi_{\text{KS}} | \hat{V}_{ee} | \Phi_{\text{KS}} \rangle - J[n] = -\frac{1}{2} \sum_{i,j}^{occ} \iint d\boldsymbol{r} d\boldsymbol{r}' \frac{\psi_i^*(\boldsymbol{r})\psi_j(\boldsymbol{r})\psi_j^*(\boldsymbol{r}')\psi_i(\boldsymbol{r}')}{|\boldsymbol{r} - \boldsymbol{r}'|} := E_x^{\text{EX}}$$

$$E_c = \langle \Psi_0 | \hat{T} + \hat{V}_{ee} | \Psi_0 \rangle - \langle \Phi_{\text{KS}} | \hat{T} + \hat{V}_{ee} | \Phi_{\text{KS}} \rangle = T_c + U_c$$

$$T_c = \langle \Psi_0 | \hat{T} | \Psi_0 \rangle - \langle \Phi_{\text{KS}} | \hat{T} | \Phi_{\text{KS}} \rangle = T - T_s = T_c$$

$$U_c = \langle \Psi_0 | \hat{V}_{ee} | \Psi_0 \rangle - \langle \Phi_{\text{KS}} | \hat{V}_{ee} | \Phi_{\text{KS}} \rangle = \langle \Psi_0 | \hat{V}_{ee} | \Psi_0 \rangle - J[n] - E_x^{\text{EX}}$$

❑ Explicitly density-dependent form of E_x must involve approximations ➔ Self-interaction error.

❑ E_x and E_c are often approximated together to achieve error compensation.

❑ If E_x is treated exactly, one must invoke a sophisticated (non-local) approximation to E_c to be compatible with E_x.

The adiabatic connection

Design a path connecting the KS state and the full many-body state

$$\widehat{H}_\lambda = \widehat{T} + \lambda \widehat{V}_{ee} + \widehat{V}_{aux}^\lambda, \quad \widehat{V}_{aux}^\lambda = \int d^3 r v_{aux}^\lambda \widehat{n}(\boldsymbol{r}) \quad \text{and} \quad \widehat{V}_{ee} = \sum_{i<j}^{N} \frac{1}{|\boldsymbol{r}_i - \boldsymbol{r}_j|}$$

$v_{aux}^\lambda(\mathbf{r})$ is chosen such that :

$$\widehat{H}_{\lambda=0} = \widehat{H}_{KS} = \widehat{T} + \int d^3 r v_{eff}(\boldsymbol{r}) \widehat{n}(\boldsymbol{r}) \quad \text{(the KS system)}$$

$$\widehat{H}_{\lambda=1} = \widehat{H} = \widehat{T} + \widehat{V}_{ee} + \int d^3 r v_{ext}(\boldsymbol{r}) \widehat{n}(\boldsymbol{r}) \quad \text{(the Interacting system)}$$

The electron density is kept fixed at the physical $n(\boldsymbol{r})$ for 0<λ<1.

The exact XC energy: $E_{xc}^{\text{exact}} = \int_0^1 d\lambda U_{xc}^\lambda$

$$U_{xc}^\lambda = \langle \Psi_0^\lambda | \widehat{V}_{ee} | \Psi_0^\lambda \rangle - \frac{1}{2} \iint d\boldsymbol{r} d\boldsymbol{r}' \frac{n(\boldsymbol{r})n(\boldsymbol{r}')}{|\boldsymbol{r} - \boldsymbol{r}'|} \quad \text{where} \quad \widehat{H}_\lambda |\Psi_0^\lambda\rangle = E_\lambda^0 |\Psi_0^\lambda\rangle$$

Adiabatic connection fluctuation-dissipation theorem

- Exact XC energy via "adiabatic connection formula"

$$E_{xc}^{\text{exact}} = \int_0^1 d\lambda\, U_{xc}^{\lambda}$$

U_{xc}^{λ} is connected to the density-density fluctuation of the system.

- The fluctuation-dissipation theorem

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

$$\chi_{\lambda}(\boldsymbol{r}, \boldsymbol{r}', t - t') = \frac{\delta n(\boldsymbol{r}, t)}{\delta v_{ext}^{\lambda}(\boldsymbol{r}', t')} : \text{ density response function}$$

(The imaginary part of χ_{λ} describes the dissipation property of the system)

$\Longrightarrow$ Open a new route to construct approximate E_{xc} .

*D. C. Langreth and J. P. Perdew, Phys. Rev. B **15**, 2884 (1977).*
*O. Gunnarsson and B. I. Lundqvist, Phys. Rev. B **13**, 4274 (1976).*

RPA within the ACFD framework

- Dyson equation for χ_λ

$$\chi_\lambda = \chi_0 + \chi_0(\lambda v + f_{xc}^\lambda)\chi_\lambda$$

$$f_{xc}^\lambda(\boldsymbol{r}, \boldsymbol{r}', t - t') = \frac{\delta v_{xc}^\lambda(\boldsymbol{r}, t)}{\delta n(\boldsymbol{r}', t')} \qquad (f_{xc} \text{ kernel})$$

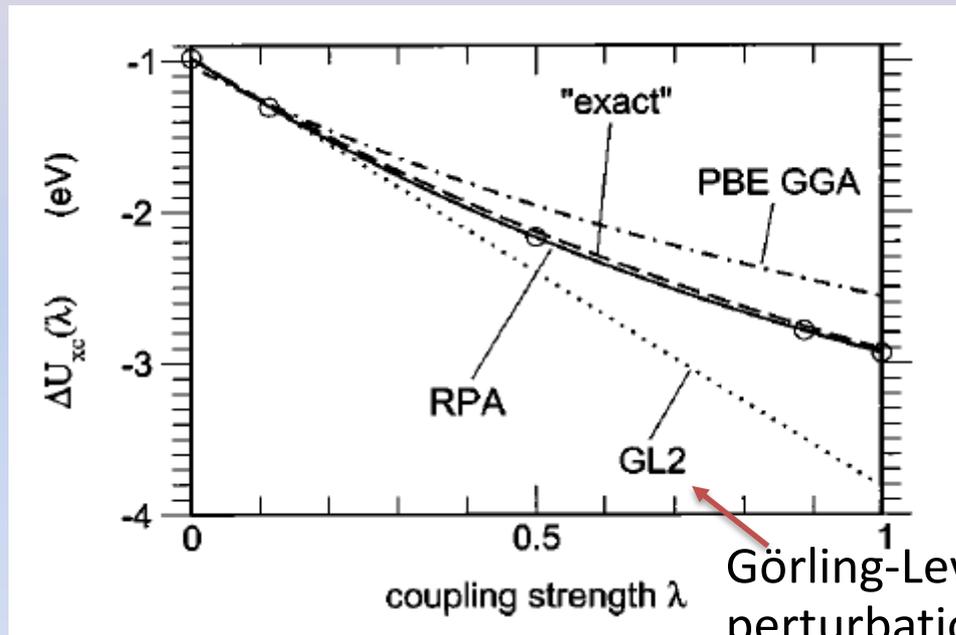Linear response time-dependent density functional theory

- RPA: $f_{xc} = 0$

$$E_{xc}^{\text{RPA}} = E_x^{\text{exact}} + E_c^{\text{RPA}}$$

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

$$\chi_0 v(\boldsymbol{r}, \boldsymbol{r}') = \int d\boldsymbol{r}''\chi_0(\boldsymbol{r}, \boldsymbol{r}'', i\omega)v(\boldsymbol{r}'', \boldsymbol{r}')d\boldsymbol{r}''$$

Behavior of U_{xc}^{λ} for stretched H_2 (d=1.4 Å)

$$\Delta U_{xc}^{\lambda} = U_{xc}(H_2) - 2U_{xc}(H)$$

Görling-Levy (GL) second-order perturbation theory

*M. Fuchs & X. Gonze, J. Chem. Phys. **122**, 094116 (2005)*

RPA calculations in practice

- RPA calculations are mainly done perturbatively based on GGA or hybrid functional reference states

$$E^{\text{RPA@PBE}} = E^{\text{PBE}} - E_{xc}^{\text{PBE}} + E_x^{\text{EX@PBE}} + E_c^{\text{RPA@PBE}}$$

$$= E^{\text{HF@PBE}} + E_c^{\text{RPA@PBE}}$$

Hartree-Fock energy with PBE orbitals

RPA correlation energy with PBE orbitals

Compare to hybrid functional PBE0

$$E_{xc}^{\text{PBE0}} = 0.25 E_x^{\text{EX}} + 0.75 E_x^{\text{PBE}} + E_c^{\text{PBE}}$$

The computation of RPA correlation energy

Kohn-Sham eigenvalues and eigenfunctions:

$$\epsilon_n, \psi_n$$

Independent-particle response function:

$$\chi^0(\mathbf{r}, \mathbf{r}', i\omega) = \sum_{m,n} \frac{(f_m - f_n)\psi_m^*(\mathbf{r})\psi_n(\mathbf{r})\psi_n^*(\mathbf{r}')\psi_m(\mathbf{r}')}{\epsilon_m - \epsilon_n - i\omega}$$
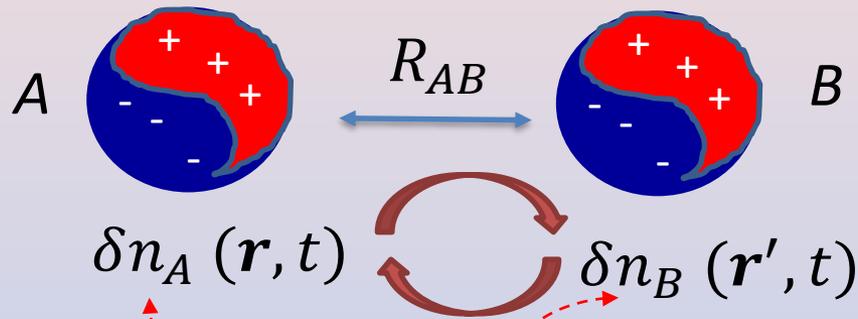
RPA correlation energy:

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

Why is RPA interesting?

- Compatible with exact-exchange, including which cancels the self-interactions in the Hartree energy

- Automatic and seamless inclusion of van der Waals (vdW) interactions

- Treating different bonding situations (ionic, covalent, metallic, vdW) on an equal footing

- Static correlation (partly) captured =>
  excellent chemical reaction barrier heights
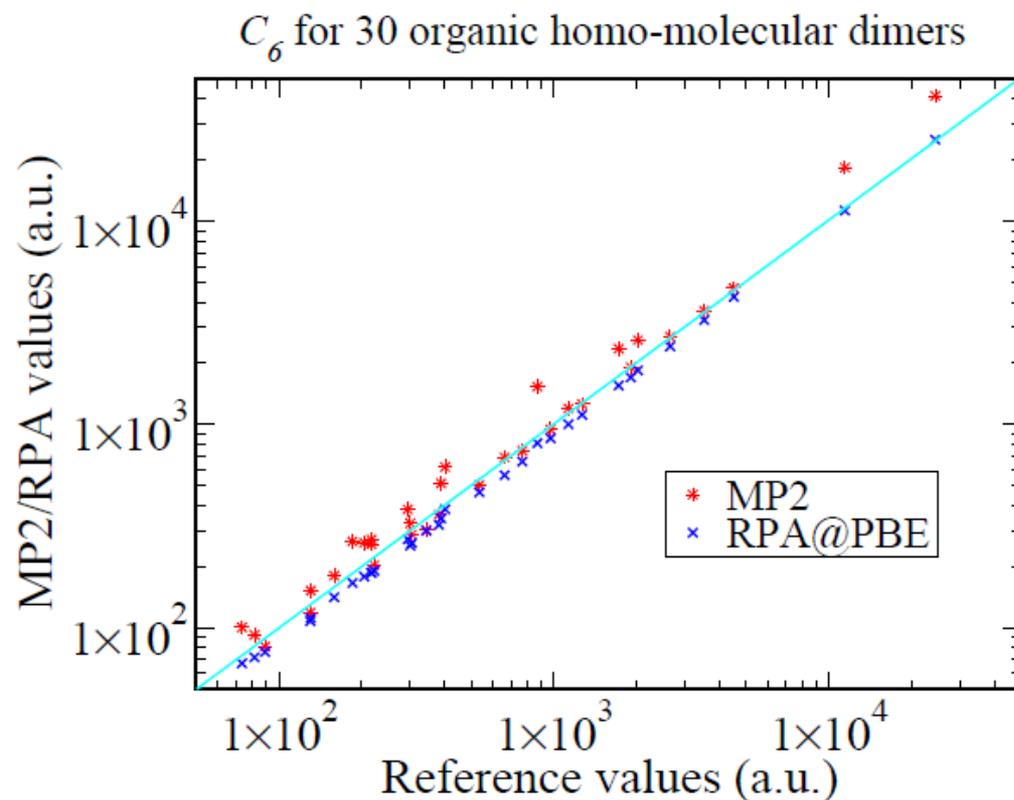
RPA description of vdW interactions
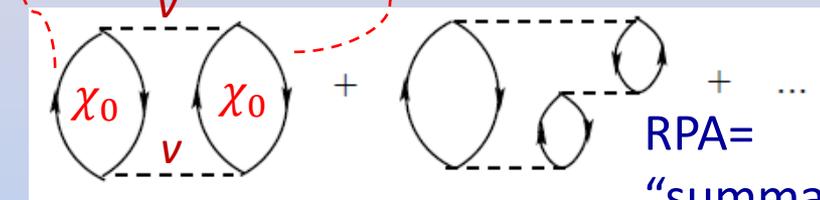
- RPA captures the non-local coupling between spontaneous quantum charge fluctuations separated in space.

- It can be shown analytically

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

$$C_6^{RPA} = \frac{3}{\pi} \int d\omega\, \alpha_A^{RPA}(i\omega)\, \alpha_B^{RPA}(i\omega) \qquad \text{"Dispersion consistent"}$$

J. Dobson, in "Topics in Condensed Matter Physics", Ed. M. P. Das (Nova, New York, 1994)

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

C_6 for 30 organic homo-molecular dimers
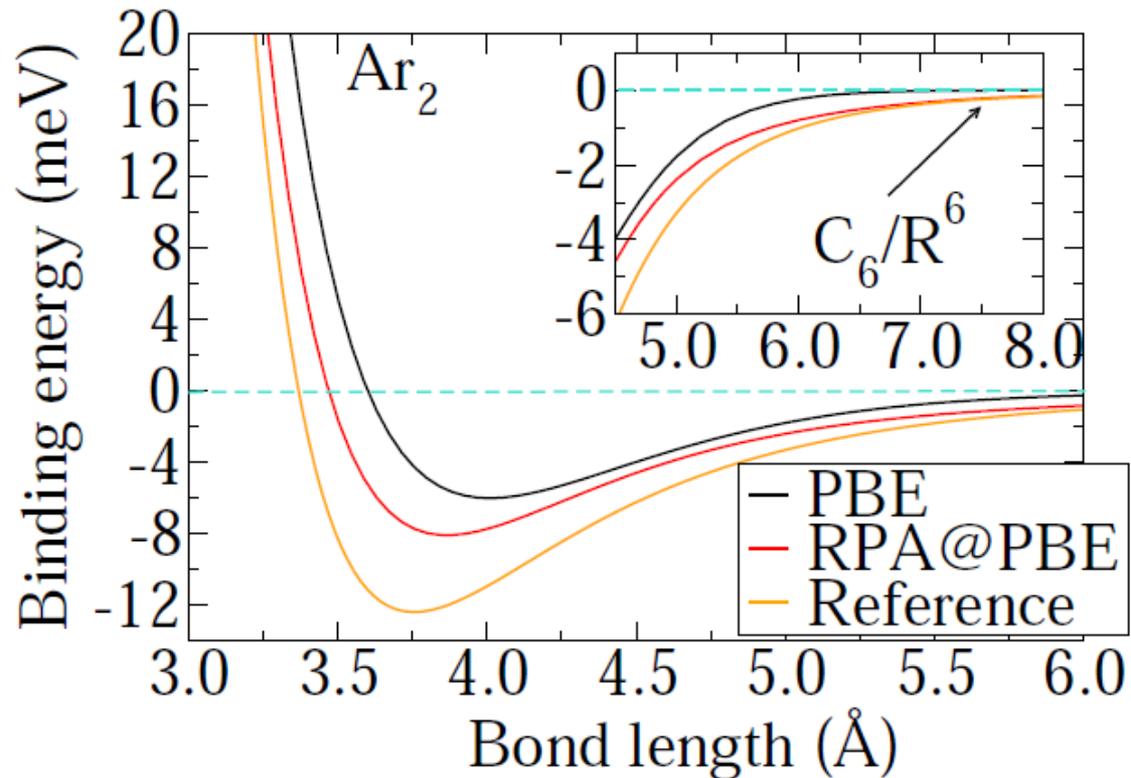
Mean error in percentage:
MP2: 20%;
RPA@PBE: 10%

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).
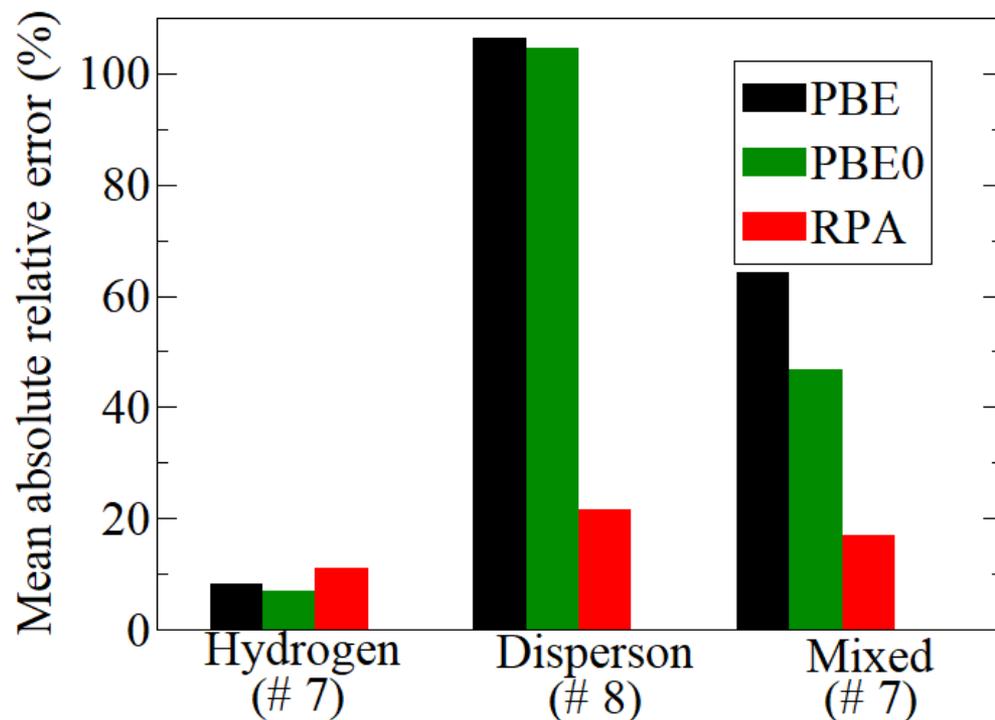
vdW interactions within RPA

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

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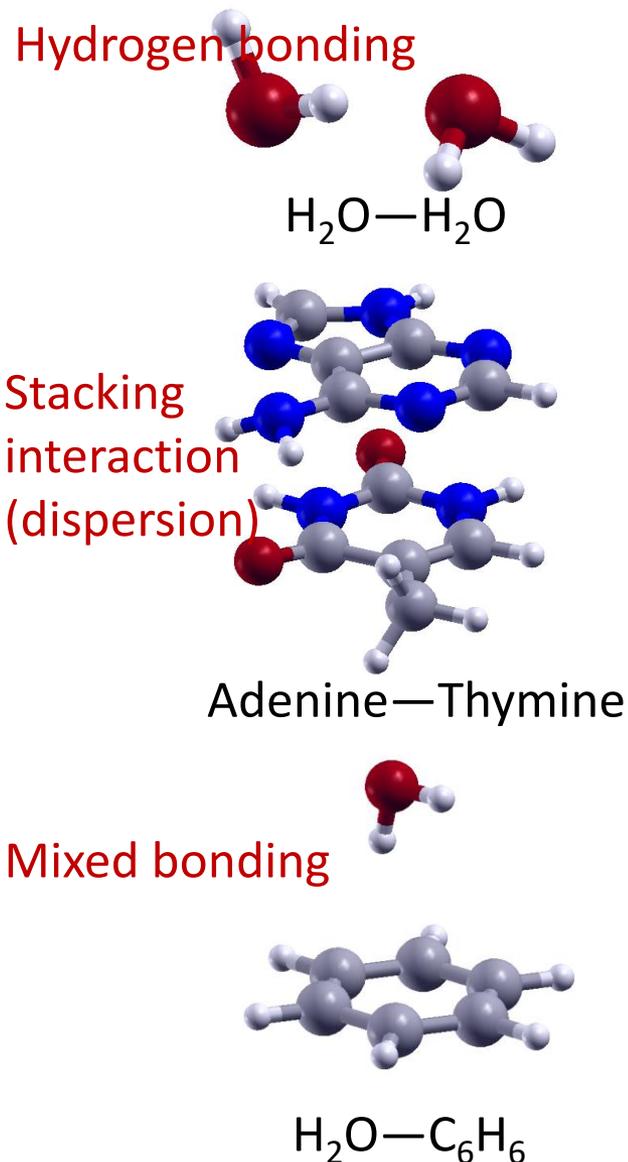
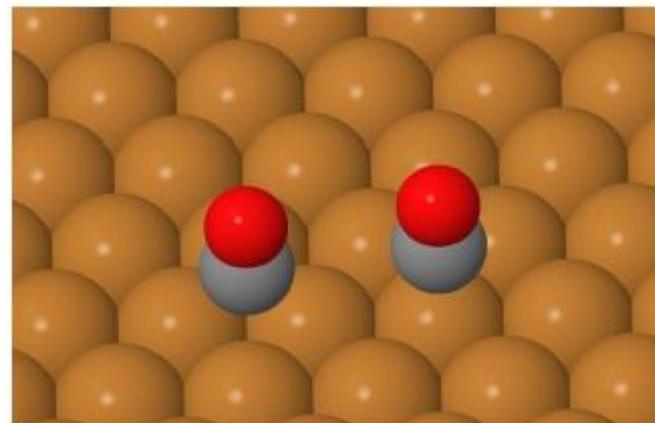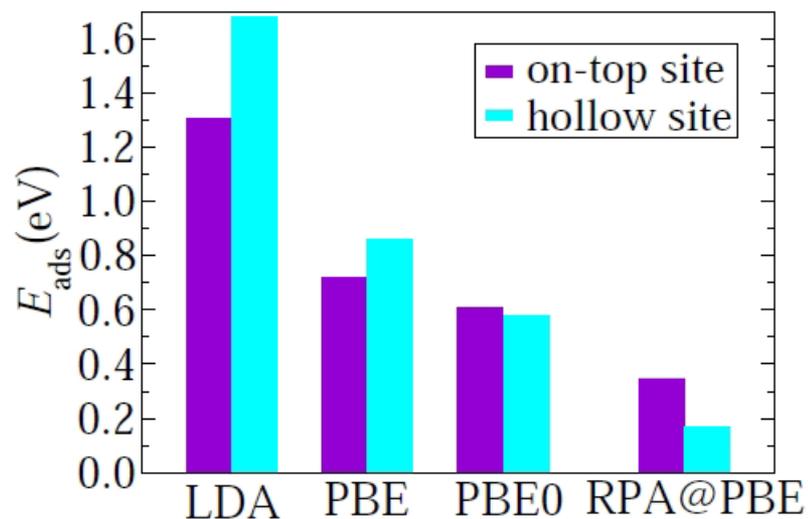− Underbinding around the equilibrium distance

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. Černy, and P. Hobza, Phys. Chem. Chem. Phys. **8**, 1985 (2006)*

Hydrogen bonding

H_2O—H_2O

Stacking interaction (dispersion)

Adenine—Thymine

Mixed bonding

H_2O—C_6H_6

RPA applied to the "CO adsorption puzzle"

CO@Cu(111)

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

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

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

CO adsorption energy versus surface energy

Graphene@Ni(111)
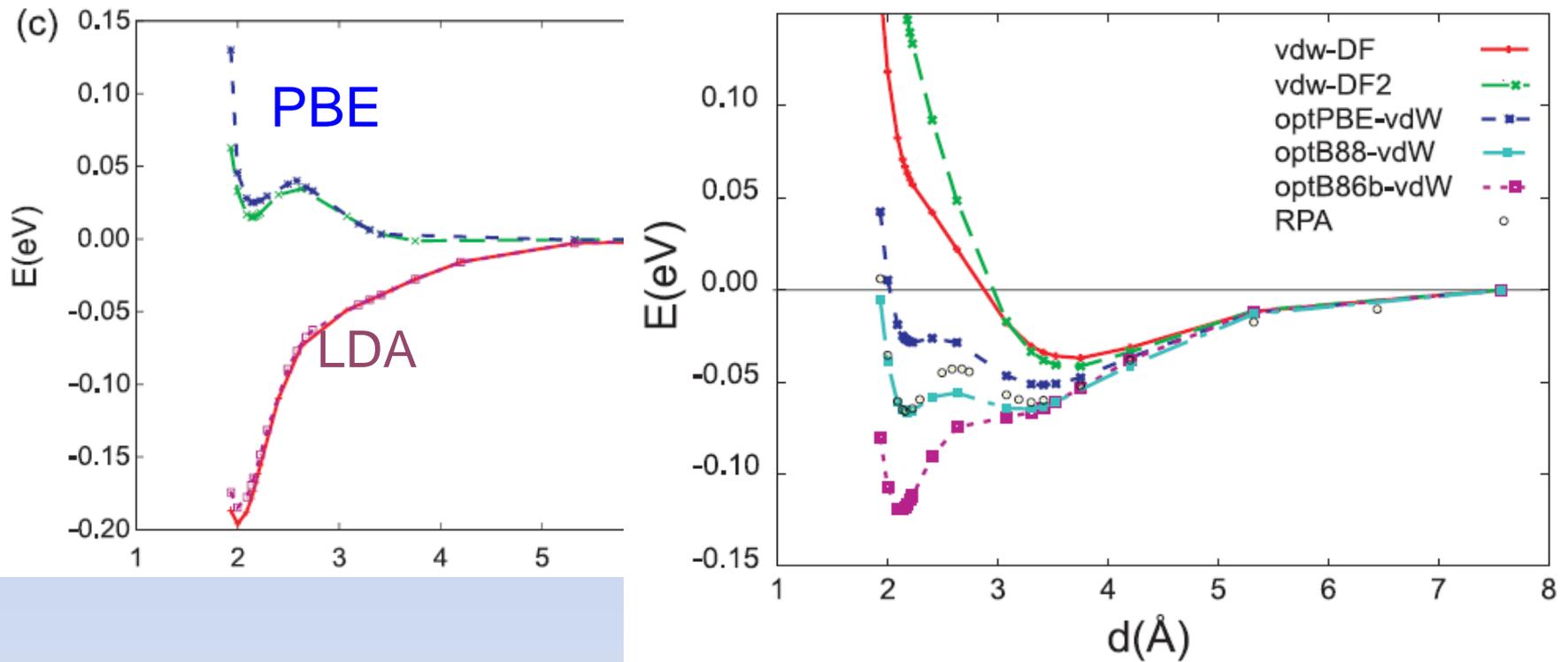
Mittendorfer et al., Phys. Rev. B 84 201401(R) (2011)

Binding energy of AB stacking graphite
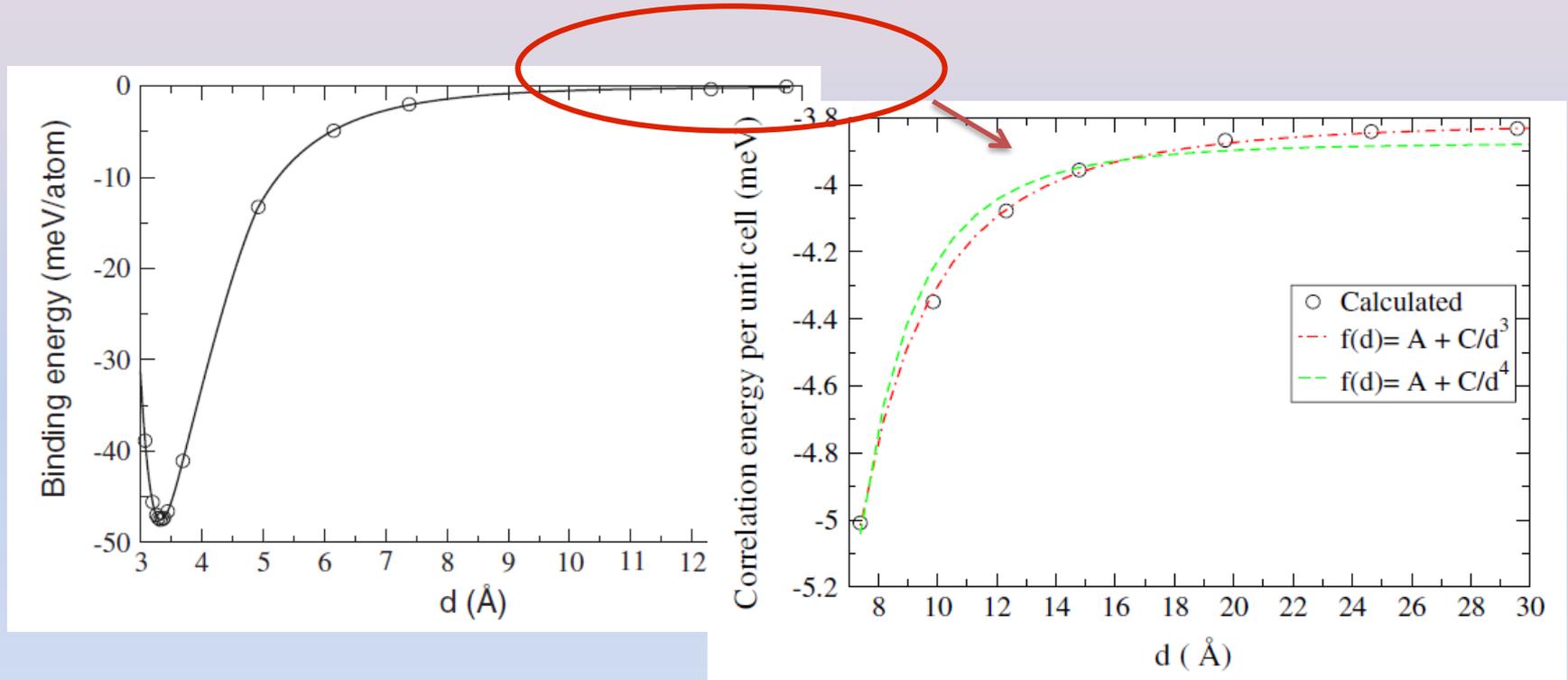
Lebegue, Harl, Could, Angyan, Kresse, and Dobson
Phys. Rev. Lett. 105 196401 (2010)

RPA applied to crystalline solids

Atomization energies

	ME (eV)	MAE (eV)	MAPE (%)	MaxAPE (%)
LDA	−0.74	0.74	18.0	32.7
PBE	0.15	0.17	4.5	15.4
RPA	0.30	0.30	7.3	13.5

Lattice constants

	ME (Å)	MAE (Å)	MAPE (%)	MaxAPE (%)
LDA	−0.045	0.045	1.0	3.7
PBE	0.070	0.072	1.4	2.7
RPA	0.016	0.019	0.4	0.9

Bulk moduli

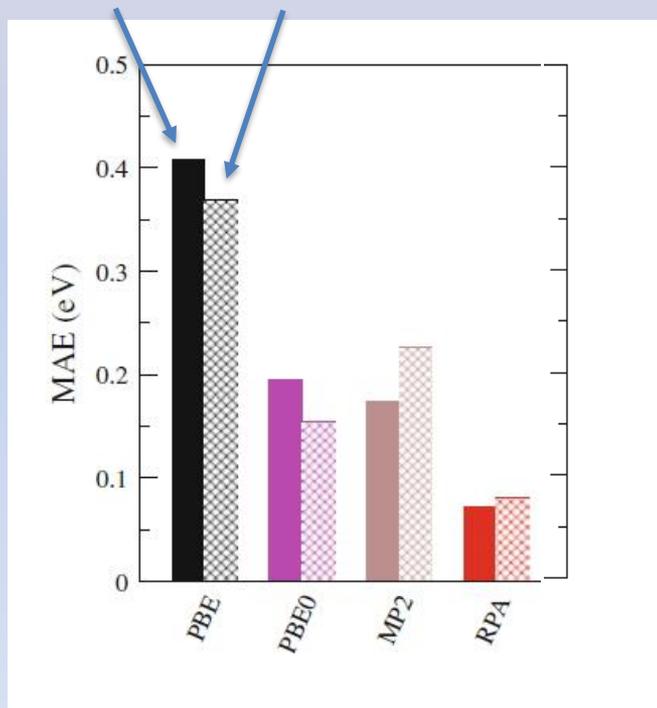|	ME (GPa)	MAE (GPa)	MAPE (%)	MaxAPE (%)
LDA	9	11	9.6	31.0
PBE	−11	11	10.7	23.7
RPA	−1	4	3.5	10.0

24 solids, including metals, insulators, and semiconductors

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

Chemical reaction barrier heights

HTBH38   NHTBH38

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

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

Perspectives

When feasible, RPA and beyond should be ideal for describing heterostructures, organic-inorganic hybrid systems, layered materials, or any systems that have mixed bonding characters.

- Implementation of $O(N^3)$ scaling RPA has been recently reported (Kresse group), and application to systems of a few hundard atoms is forseeable in the near future.

- Geometry relaxation is now possible, and molecular dynamics is foreseeable. Generally good for describing dynamical process.

Review papers

- [1] *H. Eshuis, J. E. Bates, and F. Furche, Theor. Chem. Acc.* **131**, *1084 (2012)*
- [2] *X. Ren, P. Rinke, C. Joas, M. Scheffler, J. Mater. Sci.* **47**, *7447 (2012)*

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)*