Wave function based correlation in solids: RPA, RPA+SOSEX

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Motivation

- Bulk properties (lattice constants, atomization energies)
- Surface energies
- Interactions of molecules with surfaces (adsorption energies)

$\rightarrow$ ACFDT-RPA as total energy method

- Band gaps
- Defect and Vacancy energies

$\rightarrow$ GW-RPA as Quasiparticle energy method

ACFDT-RPA: the random phase approximation

Using the adiabatic-connection fluctuation-dissipation theorem, the correlation energy may be written as

$$E_{\mathrm{RPA}}^c = -\int_0^1 d\lambda \iint d\mathbf{r}d\mathbf{r}' \int_0^\infty \frac{d\omega}{2\pi} \Big(\chi^\lambda(\mathbf{r},\mathbf{r}';i\omega) - \chi^0(\mathbf{r},\mathbf{r}';i\omega) \Big)$$

where χ^0 is the density response of the system w.r.t. a change in the Kohn-Sham potential ($\delta\rho/\delta V_{\mathrm{KS}}$), or "irreducible polarizability in the independent particle picture":

$$\chi^0(\mathbf{r},\mathbf{r}';i\omega) = -2\sum_i^{\mathrm{occ}}\sum_a^{\mathrm{virt}} \psi_a^*(\mathbf{r})\psi_i(\mathbf{r})\psi_i^*(\mathbf{r}')\psi_a(\mathbf{r}') \frac{2(\epsilon_a - \epsilon_i)}{(\epsilon_a - \epsilon_i)^2 + \omega^2}$$
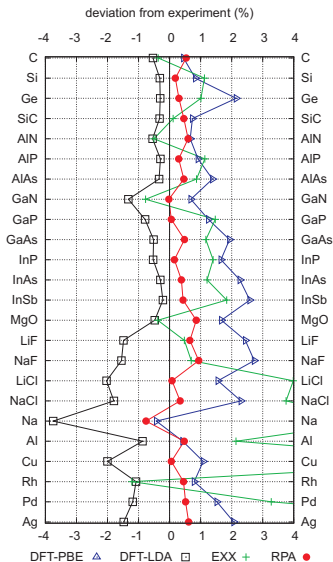
and the λ-interacting irreducible polarizability in the Random-Phase-Approximation is given by a Dyson equation

$$\chi^\lambda = \chi^0 + \lambda\chi^0\nu\chi^\lambda$$

where ν is the Coulomb kernel.

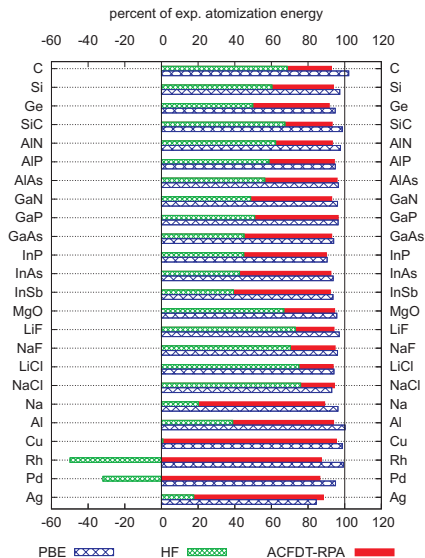N.B.: The $\{\psi,\epsilon\}$ are DFT (e.g. LDA or PBE) one-electron (Bloch) orbitals and eigenenergies.

RPA lattice constants

deviation from experiment (%)

	Deviations w.r.t. experiment	
	(corrected for zero-point vibrations)	
	MRE (%)	MARE (%)
PBE	1.2	1.2
HF	1.1	1.1
RPA	0.5	0.4

Harl *et al.* (Phys. Rev. Lett. **1**03, 056401 (2009)).

Grüneis, Marsman, Harl, Schimka, Kresse

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RPA atomization energies

percent of exp. atomization energy

	MAE (eV)	MARE (%)
PBE	0.17	5
LDA	0.74	18
RPA	0.30	7

PBE ⋈⋈⋈ HF ⬡⬡⬡ ACFDT-RPA ▬▬

Harl *et al.* (Phys. Rev. Lett. **1**03, 056401 (2009)).

RPA heats of formation
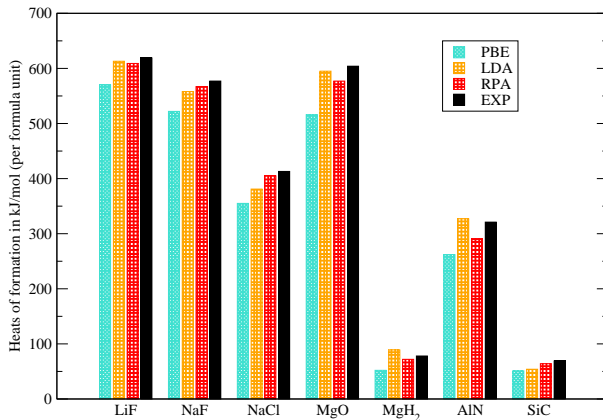
Harl *et al.* (Phys. Rev. Lett. **1**03, 056401 (2009)).

CO adorption on Pt(111) and Rh(111)

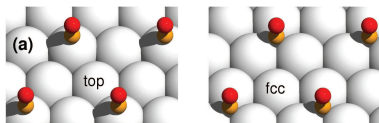Too small surface energies and too large adsorption energies!

FIG. 1: **Atop CO adsorption and surface energies for Pt(111) and Rh(111).** (a) Considered CO adsorption geometries for a (2×2) surface cell. Semi-local functionals predict CO to adsorb in the fcc hollow site coordinated to three metal atoms on Pt and Rh, whereas experiments unequivocally show adsorption atop a metal atom. (b) Atop adsorption energies versus surface energies for Pt(111) and Rh(111). Various semi-local functionals were used: AM05[10], PBEsol[11], PBE[8], rPBE[12] and BLYP[13], in order of increasing gradient corrections. Furthermore the hybrid functional HSE[18] based on the PBE functional was used.
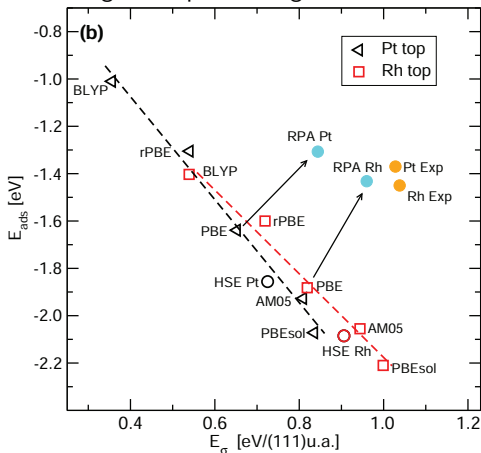
Schimka *et al.* (in preparation).

CO adorption summary

FIG. 3: **Surface energies, lattice constants and adsorption energies.** (a) Surface energies (E_σ) for PBEsol, BLYP and RPA. Experimental data are from Ref. 24. (b) Lattice constants for PBEsol, RPA and BLYP. Experimental data with error bars are from Ref. 25. (c) Adsorption energies for the atop and hollow sites on Cu, late $4d$ metals and Pt for PBEsol and RPA and BLYP. Experimental data with error bars are from Ref. 25.
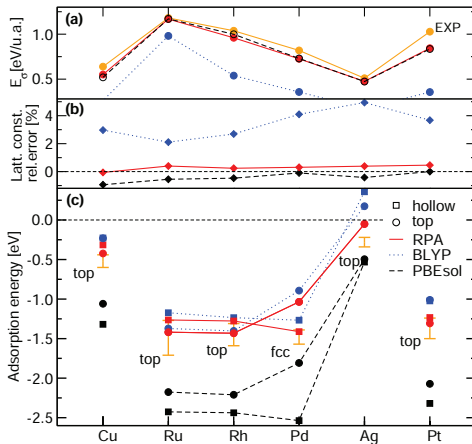
RPA:

Right site preference

Good adsorption energies

Excellent lattice constants

Good surface energies

Schimka *et al.* (in preparation).

- Advantages of the RPA
    - Accurate lattice constants and heats of formation
    - Similar quality for all bonding situations (including vdW)
    - low computational complexity
- Shortcomings of the RPA
    - Inaccurate absolute correlation energies (Error$\approx$30-50%)
    - underestimate bond strength
    - self-correlation

$\rightarrow$ *RPA+, RPA hybrids, range separation, include "exchange-like" diagrams in RPA*
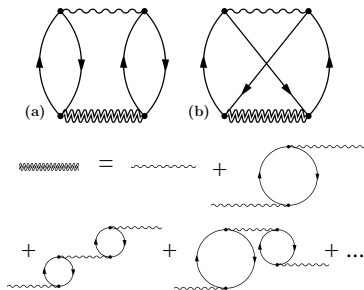
Second-order screened exchange

Solve

$$\langle ij|ab\rangle + t_{ij}^{ab}(\epsilon_a + \epsilon_b - \epsilon_i - \epsilon_j) + \langle ic|ak\rangle t_{kj}^{cb} + t_{ik}^{ac}\langle cj|kb\rangle + t_{ik}^{ac}\langle cd|kl\rangle t_{lj}^{ab} = 0$$

for the amplitudes t_{ij}^{ab}.

$$E_c = \sum_{ijab}\frac{1}{2}\langle ij|ab\rangle (t_{ij}^{ab})^* - \sum_{ijab}\frac{1}{2}\langle ij|ba\rangle (t_{ij}^{ab})^*$$

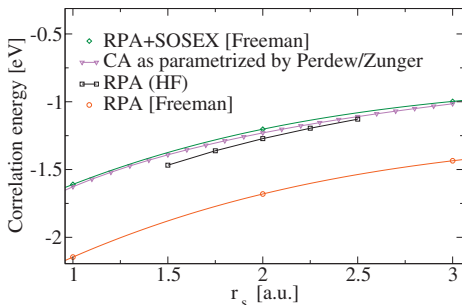proposed by D. L. Freeman, Phys. Rev. B **15**, 5512 (1977)

SOSEX: Jellium

FIG. 3. Correlation energy of jellium evaluated using various approximations: exact from QMC (Ref. 25), RPA and RPA+SOSEX values are from Freeman (Ref. 15) and were obtained using Kohn–Sham orbitals and one-electron energies, whereas the RPA(HF) values were calculated using HF orbitals and one-electron energies using VASP.

Grüneis *et al.* J. Chem. Phys. **131**, 154115 (2009).
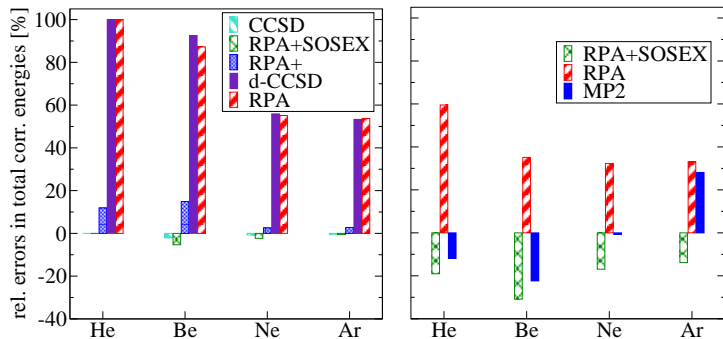
SOSEX: atoms

FIG. 2. Relative errors of absolute correlation energies evaluated using vari-ous approximations with respect to "exact" nonrelativistic results from Ref. 23: CCSD, RPA+SOSEX, RPA+ (from Ref. 22), CCSD using direct terms only (d-CCSD), and RPA. For CCSD, HF orbitals were used. On the left KS orbitals were used in the RPA calculations, whereas on the right HF orbitals were used for all calculations.

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

SOSEX: lattice constants and atomization energies (solids)

$MARE(a_0)$ = 0.2 %
$MAE(E_{at})$ = 0.070 eV
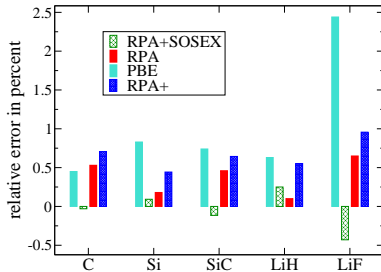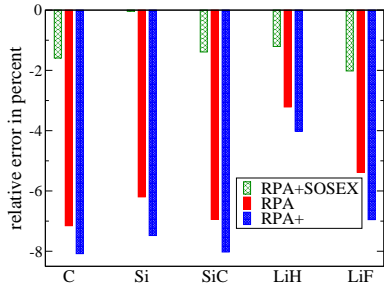
Grüneis et al. J. Chem. Phys. **131**, 154115 (2009).

Conclusions

- RPA:
  Good lattice constants
  Reasonable energy differences
  Similar quality for all bonding situations (including vdW)

- RPA+SOSEX:
  Good lattice constants
  Excellent atomization energies for solids
  Very reasonable absolute correlation energies
  Looks promising, but very expensive (scales as N^5)

- What's next: ???
  SCRPA
  Which diagrams are missing?

THANKS for your attention!

CO adorption on Pt(111) DOS

FIG. 2: **Electronic density of states (DOS) for CO adsorbed atop a Pt atom on Pt(111)**. The DOS is evaluated using density functional theory (PBE), the random phase approximation (GW-RPA) and a hybrid functional (HSE). Experimental data for the $2\pi^*$ state are from Ref. 19, for the 5σ and 1π state from Ref. 20.

DFT:
d-metal well described
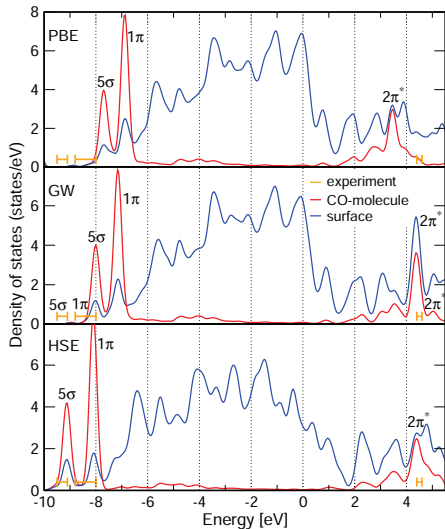CO orbitals too close to Fermi level

HSE:
CO well described
d-metal bandwidth too large

GW-RPA:

d-metal well described

CO reasonable ($2\pi*$ good, 5σ and 1π underbound)

Schimka *et al.* (in preparation).