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Spring College on Computational Nanoscience

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At the Fifth Rung of Jacob's Ladder: A Discussion of Exact Exchange plus Local- and Nonlocal-density Approximations to the Correlation Functional

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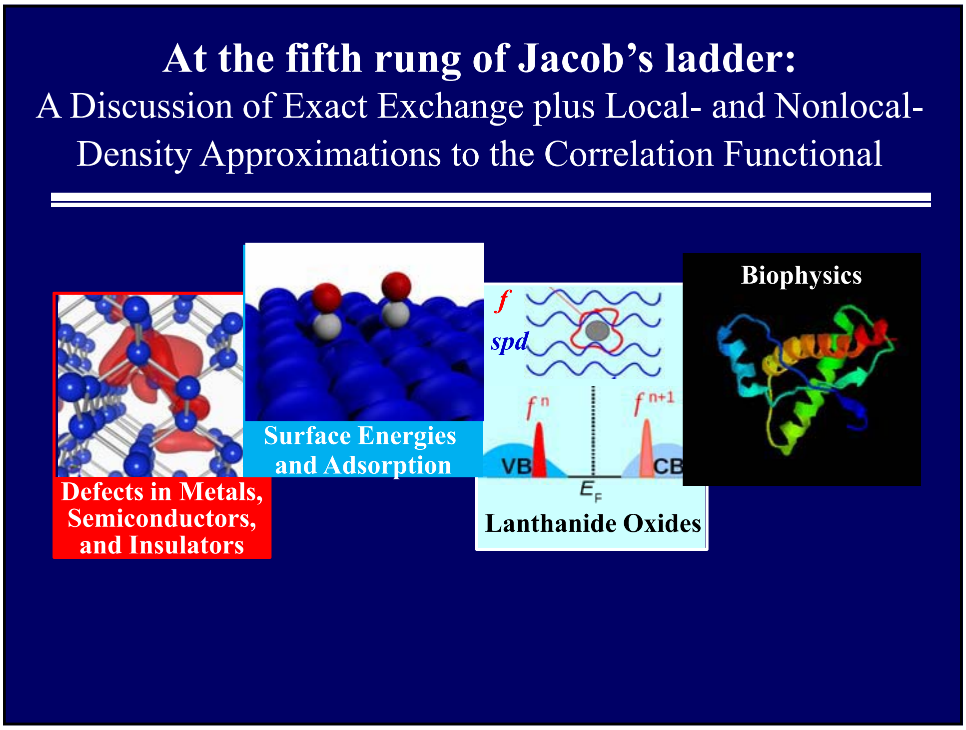


At the fifth rung of Jacob's ladder:

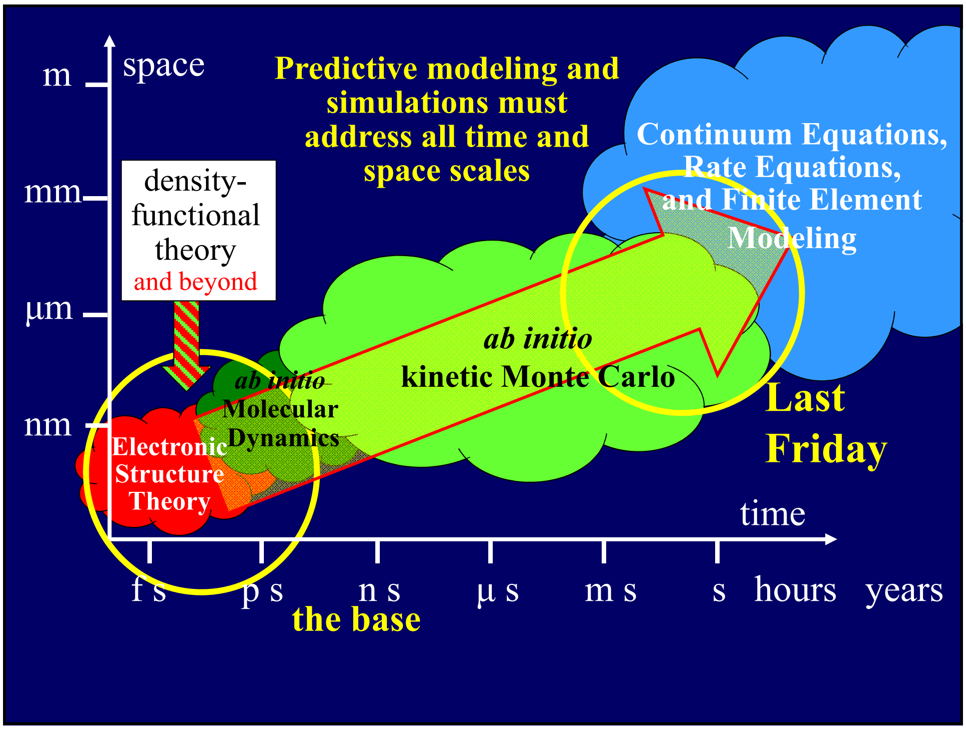
A Discussion of Exact Exchange plus Local- and Nonlocal-Density Approximations to the Correlation Functional

Defects in Metals, Semiconductors, and Insulators

Surface Energies and Adsorption

Lanthanide Oxides

Biophysics



Predictive modeling and simulations must address all time and space scales

density-functional theory and beyond

Electronic Structure Theory

ab initio Molecular Dynamics

ab initio kinetic Monte Carlo

Continuum Equations, Rate Equations, and Finite Element Modeling

Last Friday

the base

Approximate xc functionals (e.g. LDA and GGAs) have been very successful but there are problems

- **for certain bonding situations (vdW, hydrogen bonding, certain covalent bonds)**
- **for highly correlated situations, and**
- **for excited states.**

The zoo of approximate xc functional is getting hardly comprehensible. -- Patchwork or sound science?

HL ● VWN ● BP86 ● PKZB ● PW91 ● PBE ● r-PBE ● RPBE ● revPBE ● B88 ● PBE0

How to clean up this mess?

The challenges: Find *practical* ways to correct the xc approximation and/or to control the errors.

Efficient all-electron code; DFT also with hybrid functionals and TDDFT, Hartree-Fock +MP2, EX+cRPA, *GW* selfenergies, etc.

Perdew’s Dream: Jacob’s Ladder in DFT

accuracy ?

computational cost ↑

5	unoccupied $\psi_i(\mathbf{r})$,	e.g., ACFD-RPA
4	occupied $\psi_i(\mathbf{r})$,	hybrid functional (e.g., B3LYP, PBE0)
3	τ ($\mathbf{r}$),	meta-GGA (e.g., TPSS)
2	$\nabla n(\mathbf{r})$,	GGA (e.g., PBE)
1	$n(\mathbf{r})$,	LDA

$\tau(\mathbf{r})$:	KS kinetic energy density
ACFD :	adiabatic connection fluctuation dissipation theorem (Bohm, Pines (1953); Gell-Mann, Brueckner (1957); Langreth, Perdew (1977); Gunnarsson, Lunqvist (1975, 1976)
RPA :	random phase approximation

RPA in a Nutshell

- Adiabatic connection:

$$E_{\mathrm{XC}}^{\mathrm{exact}} = \int_0^1 \frac{d\lambda}{\lambda} U_{\mathrm{XC}}^{\lambda}$$

- Fluctuation-dissipation theorem

$$U_{\mathrm{XC}}^{\lambda} = -\frac{1}{2}\int d\mathbf{r}\int d\mathbf{r}' v(\mathbf{r}-\mathbf{r}')\left[-\frac{1}{\pi}\int_0^{\infty} d\omega \,\mathrm{Im}\chi_{\lambda}(\mathbf{r},\mathbf{r}',\omega) - n(\mathbf{r})\delta(\mathbf{r}-\mathbf{r}')\right]$$

- Dyson equation for χ_λ (χ_0: non-interacting response function)

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

- Random phase approximation (RPA): $f_{\mathrm{xc}} = 0$

$$E_{\mathrm{xc}}^{\mathrm{RPA}} = E_{\mathrm{x}}^{\mathrm{exact}} + E_{\mathrm{c}}^{\mathrm{RPA}}$$

Exact Exchange plus Correlation in RPA

$$E_x = -\frac{1}{2}\sum_{nm}^{occ}\iint d\mathbf{r}\, d\mathbf{r}' \frac{\psi_n^*(\mathbf{r})\psi_m(\mathbf{r})\psi_m^*(\mathbf{r}')\psi_n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}$$

The orbitals for evaluating E_x are different in Hartree-Fock and Kohn-Sham DFT. --The numerical technique to evaluate E_x is the same.

Adding correlation:

- on top of Hartree-Fock exchange: Møller-Plesset perturbation theory (MP2)
- on top of “DFT exact exchange”: random phase approximation (RPA)

RPA Formulated within DFT Framework

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

$$E_c^{\mathrm{RPA}} = \frac{1}{2\pi}\int_0^\infty du \mathrm{Tr}\left[\ln\left(1 - \chi_0(iu)v\right) - \chi_0(iu)v\right]$$

χ_0 == dynamical-response function of the Kohn-Sham system

$$\chi_0(\mathbf{r},\mathbf{r}',iu) = 2\sum_{mn}\frac{(f_m - f_n)\psi_m^*(\mathbf{r})\psi_n(\mathbf{r})\psi_n^*(\mathbf{r}')\psi_m(\mathbf{r}')}{iu + \epsilon_n - \epsilon_m}$$

The approach gives total energies but no information on how the Kohn-Sham energies, ϵ_n , i.e. spectroscopy, will change. This (corresponding) change is given by the *GW* self-energy.

Pros and Cons of EX+cRPA

The good aspects:

- Exchange is treated at the "exact exchange" level (so far with PBE or PBE0 orbitals)
- vdW interactions are included (automatically; seamlessly).
- Screening is taken into account. Thus EX+cRPA works for metals/small gap systems -- in contrast to MP2.
- Right decay behavior at metal surfaces (Rohlfing, Bredos, PRL **101** (2008).

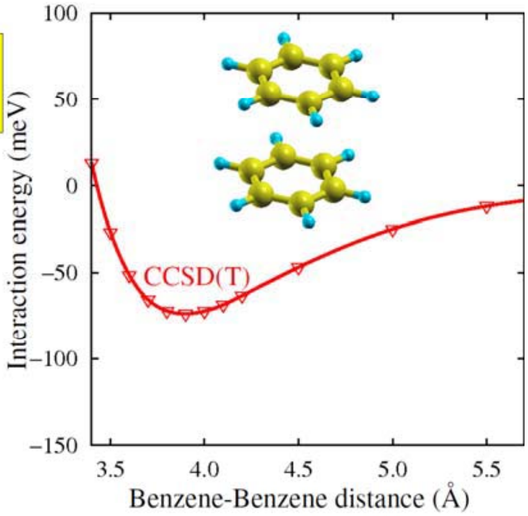
An "A" is still there!

- In contrast to LDA and GGA, EX+cRPA does not benefit from (fortuitous) error cancellation between the exchange and correlation terms.
- The "A" clearly shows up in atomization energies of small molecules: A non-selfconsistent (PBE-based) RPA does not always improve over hybrid functionals, e.g. B3LYP or PBE0.

The RPA and vdW interactions in Comparison with Other Methods

Methods

CCSD(T):
Quantum chemistry
"gold standard" (20-40 atoms)



The RPA and vdW interactions in Comparison with Other Methods

Methods

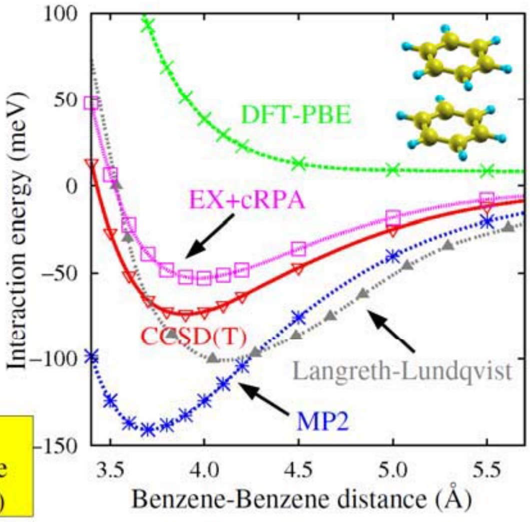
CCSD(T):
Quantum chemistry
"gold standard" (20-40 atoms)

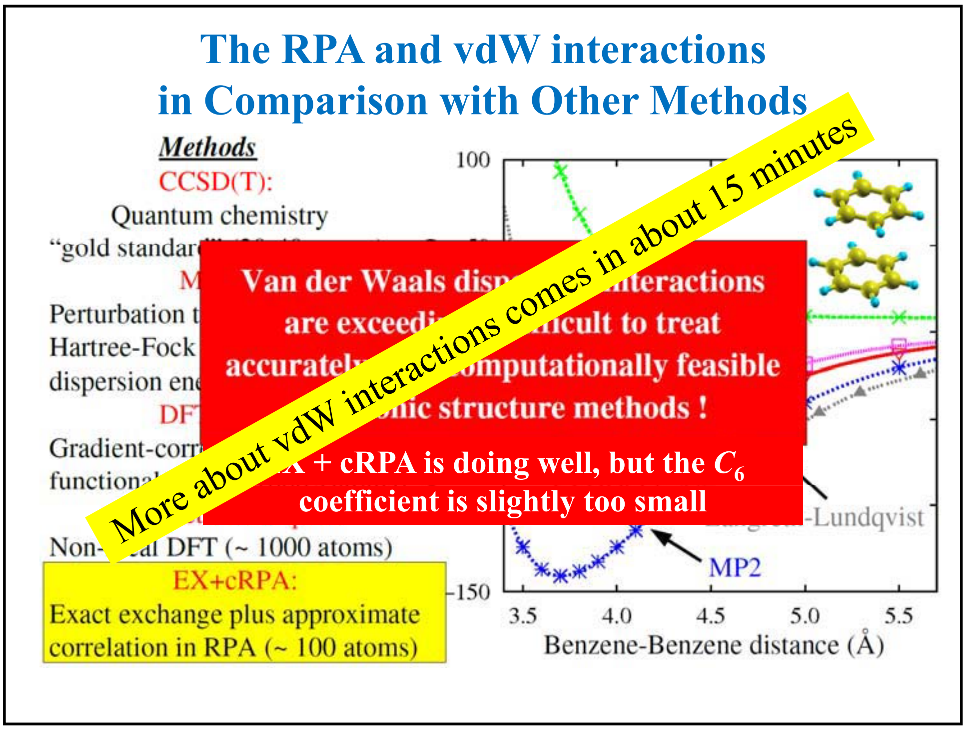
MP2:
Perturbation theory based on Hartree-Fock with approximate dispersion energy (~ 200 atoms)

DFT-PBE:
Gradient-corrected density-functional theory (1000's atoms)

Langreth-Lundqvist:
Non-local DFT (~ 1000 atoms)

EX+cRPA:
Exact exchange plus approximate correlation in RPA (~ 100 atoms)





The RPA and vdW interactions in Comparison with Other Methods

Methods

CCSD(T):

Quantum chemistry

"gold standar

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Perturbation t

Hartree-Fock

dispersion ene

DF

Gradient-corr

functiona

Non-   al DFT (~ 1000 atoms)

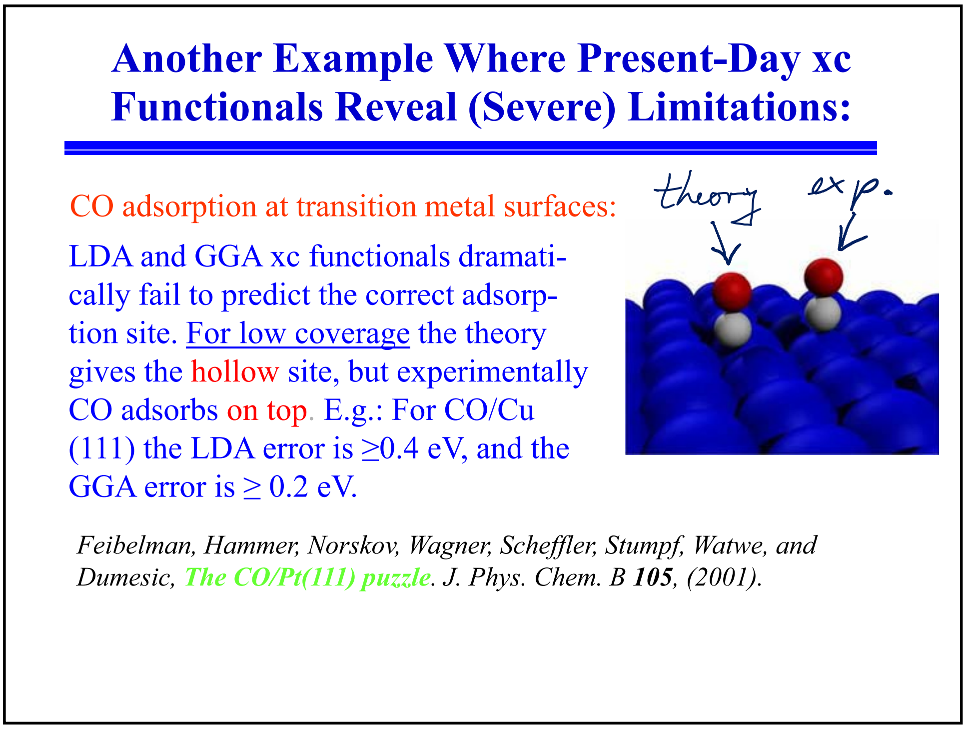
EX+cRPA:

Exact exchange plus approximate correlation in RPA (~ 100 atoms)

Van der Waals disp   nteractions are exceedi   ficult to treat accuratel   omputationally feasible   onic structure methods !

X + cRPA is doing well, but the C_6 coefficient is slightly too small

More about vdW interactions comes in about 15 minutes



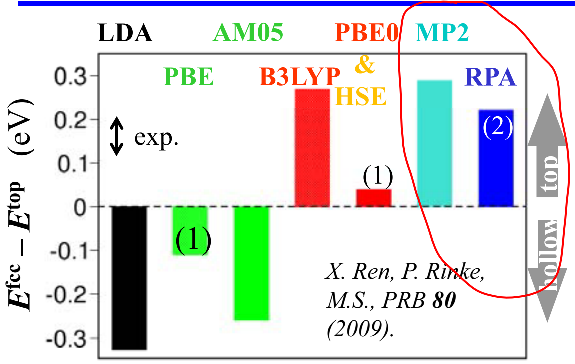
Another Example Where Present-Day xc Functionals Reveal (Severe) Limitations:

CO adsorption at transition metal surfaces:

LDA and GGA xc functionals dramatically fail to predict the correct adsorption site. For low coverage the theory gives the hollow site, but experimentally CO adsorbs on top. E.g.: For CO/Cu (111) the LDA error is ≥0.4 eV, and the GGA error is ≥ 0.2 eV.

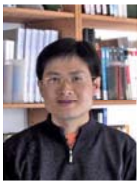
Feibelman, Hammer, Norskov, Wagner, Scheffler, Stumpf, Watwe, and Dumesic, ***The CO/Pt(111) puzzle****. J. Phys. Chem. B* ***105****, (2001).*

EX+cRPA, MP2, and Others for the CO Adsorption Puzzle



*X. Ren, P. Rinke, M.S., PRB **80** (2009).*

RPA was evaluated with LDA, PBE and PBE0 orbitals. The difference is only 0.02 eV.



Xinguo Ren

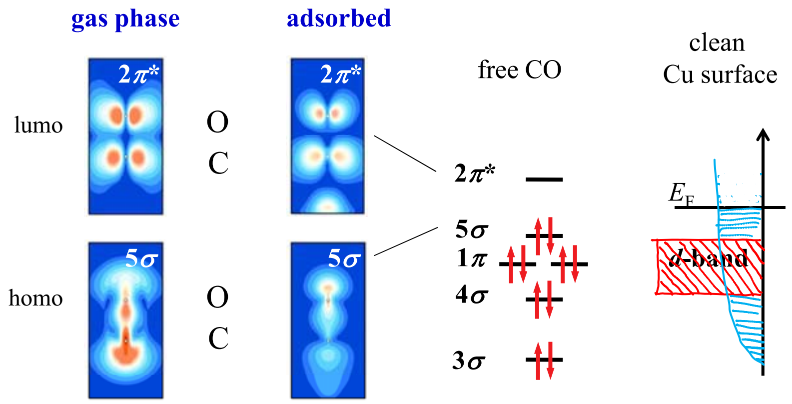
Patrick Rinke

[1] *Difference to Stroppa et al. PRB **76**(2007) is less than 0.04 eV.*

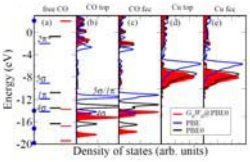
[2] *Harl and Kresse, PRL **103** (2009) only 0.12 eV*

Wrong preference for the hollow site in LDA and GGA (PBE, AM05)
… possibly corrected with hybrid XC's (B3LYP, PBE0, HSE03)
… definitely corrected by RPA (and also by MP2).

The CO Adsorption Puzzle

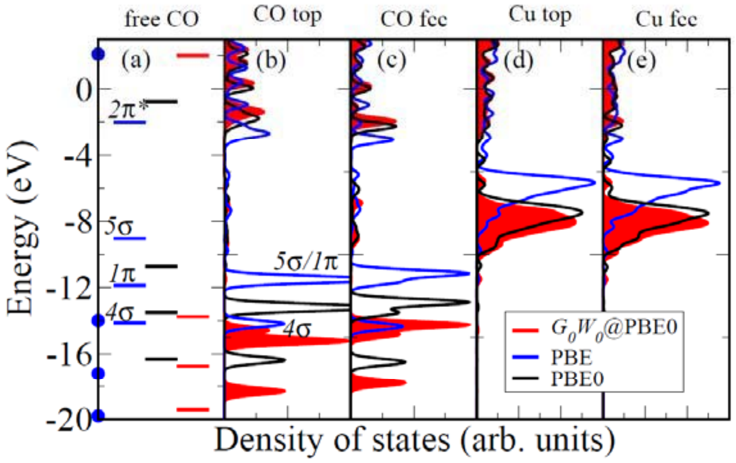


GW results:



For details (RPA and *GW*) see *X. Ren, P. Rinke, M.S., PRB **80** (2009).*

CO@Cu(111) Spectra (for Cu$_{16}$ cluster)

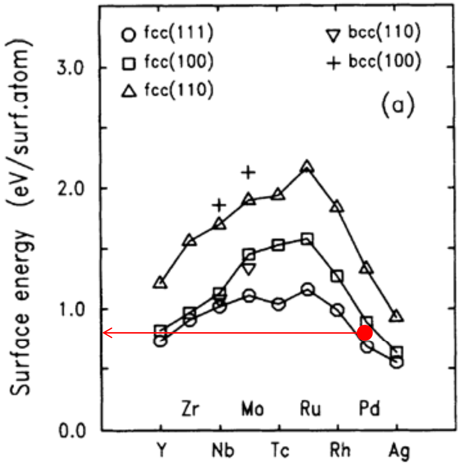


X. Ren, P. Rinke, and M. Scheffler PRB **80**, 045402 (2009)

(see also C. Freysoldt *et al.* PRL **103**, 056803 (2009) for CO@NaCl/Ge)

Surface Energies from Y to Ag

Theory: DFT-LDA



M. Methfessel, D. Hennig, and M. S., *Phys. Rev. B* **46**, 4816 (1992)

The trend in cohesive energies and surface energies is well understood (since long).

Uncertainties in experimental estimates are significant (extrapolation from surface tension of liquids). For example, for Pd (111) the experimental value is 0.8 ± 0.15 eV/surface atom.

Surface Energies from Y to Ag

Aloysius Soon

We evaluate the total energy from a difference$^{(1)}$

$$E^{\text{better-than-LDA}} = E^{\text{LDA}} + \Delta E^{\text{xc}} .$$

The total energy of a poly-atomic system can be written as

$$E = \sum_N C_N E_N .$$

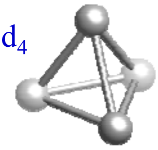
C_N is the number of atoms that are N-fold coordinated and E_N is the energy contribution of each N-fold coordinated atom. **We are not using this equation in full** but only for the xc correction:

$$\Delta E^{\text{xc}} = \sum_N C_N \left[E_N^{\text{cluster}}(\text{xc-better}) - E_N^{\text{cluster}}(\text{LDA}) \right]$$

(1) *Q.-M. Hu, K. Reuter, and M. S., PRL* ***98****, 176103 (2007); and* ***99****, 169903(E) (2007).*

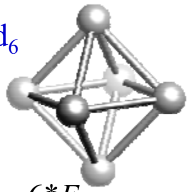
Some of the considered clusters:

Pd_4



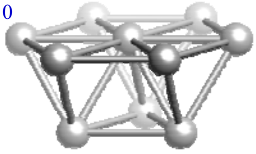
$E = 4^*E_3$

Pd_6



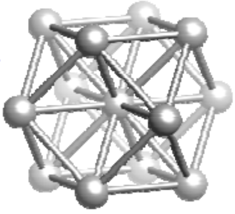
$E = 6^*E_4$

Pd_{10}



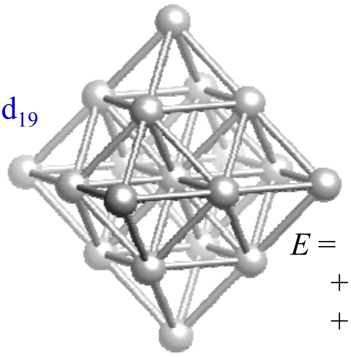
$E = 6^*E_4 + 3^*E_5 + E_9$

Pd_{13}

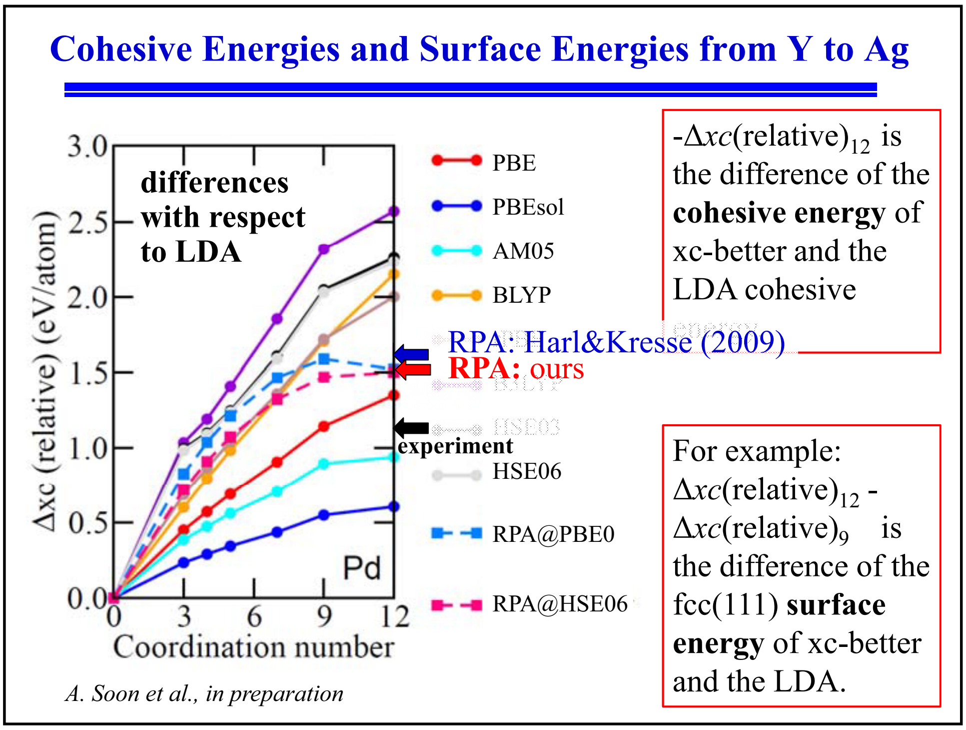


$E = 12^*E_5 + E_{12}$

Pd_{19}



$E = 6^*E_4 + 12^*E_7 + 1^*E_{12}$



Cohesive Energies and Surface Energies from Y to Ag

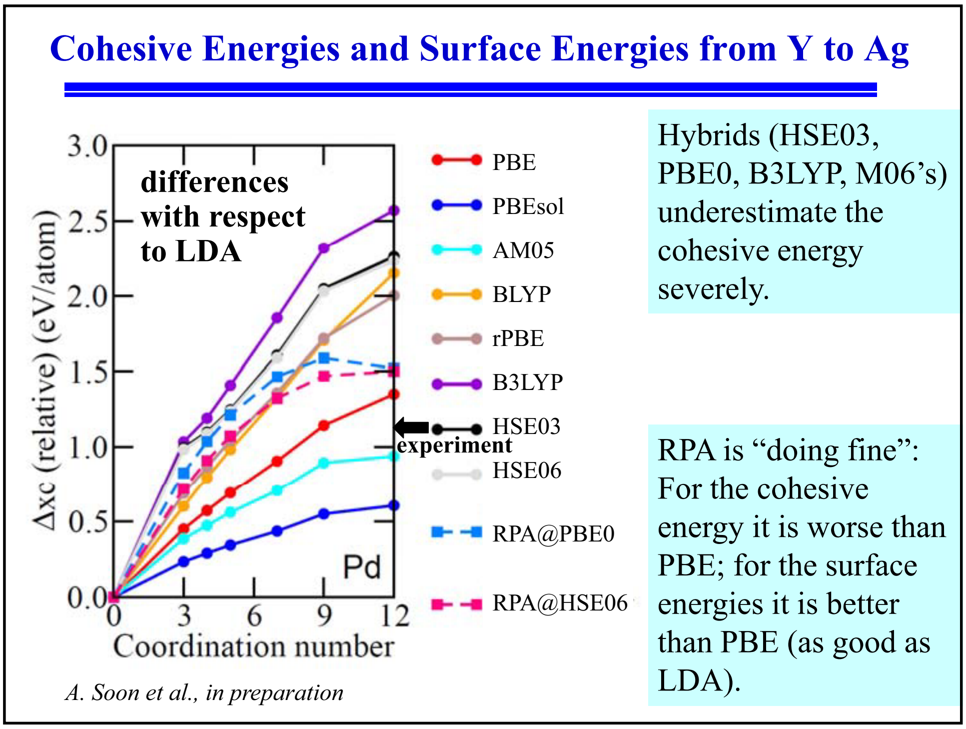
RPA: Harl&Kresse (2009)

RPA: ours

A. Soon et al., in preparation

-Δxc(relative)$_{12}$ is the difference of the **cohesive energy** of xc-better and the LDA cohesive energy

For example: Δxc(relative)$_{12}$ - Δxc(relative)$_9$ is the difference of the fcc(111) **surface energy** of xc-better and the LDA.



Cohesive Energies and Surface Energies from Y to Ag

A. Soon et al., in preparation

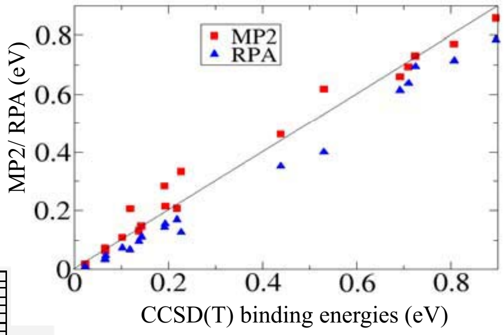
Hybrids (HSE03, PBE0, B3LYP, M06's) underestimate the cohesive energy severely.

RPA is "doing fine": For the cohesive energy it is worse than PBE; for the surface energies it is better than PBE (as good as LDA).

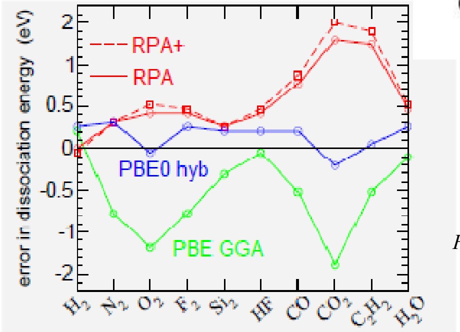
… how about molecules?

Jurecka, Sponer, Cerny, Hobza
PCCP 8, 1985 (2006)

Hydrogen bonds and dispersion: S22



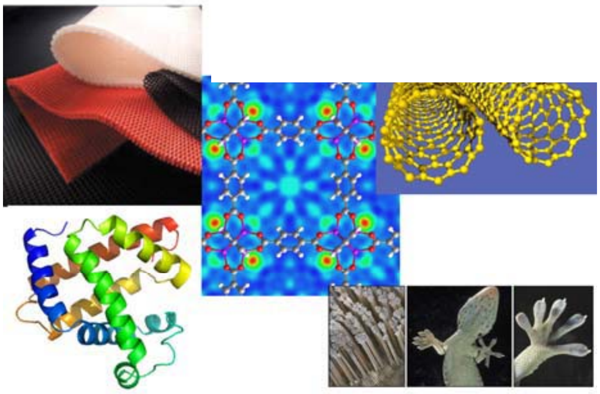
Covalent bonds: small molecules



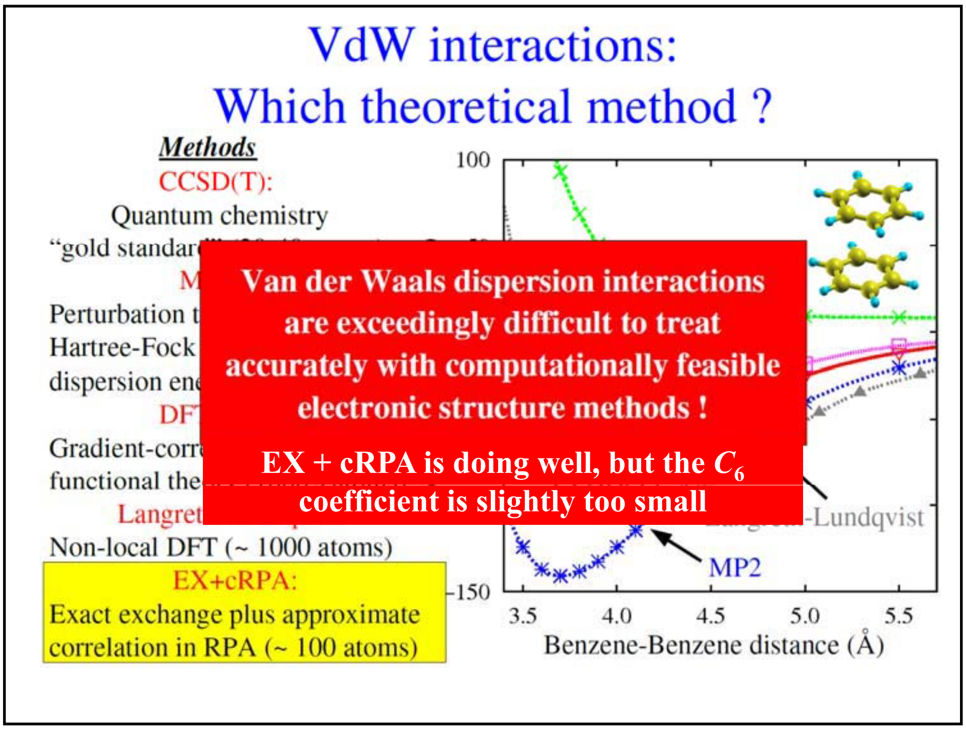
There is opportunity beyond the RPA …

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

The Role of vdW Forces in Organic Materials and Biophysics



Alexandre
Tkatchenko



VdW interactions: Which theoretical method ?

Methods

CCSD(T):
Quantum chemistry
“gold standar

M

Perturbation t
Hartree-Fock
dispersion ene

DF

Gradient-corr
functional the

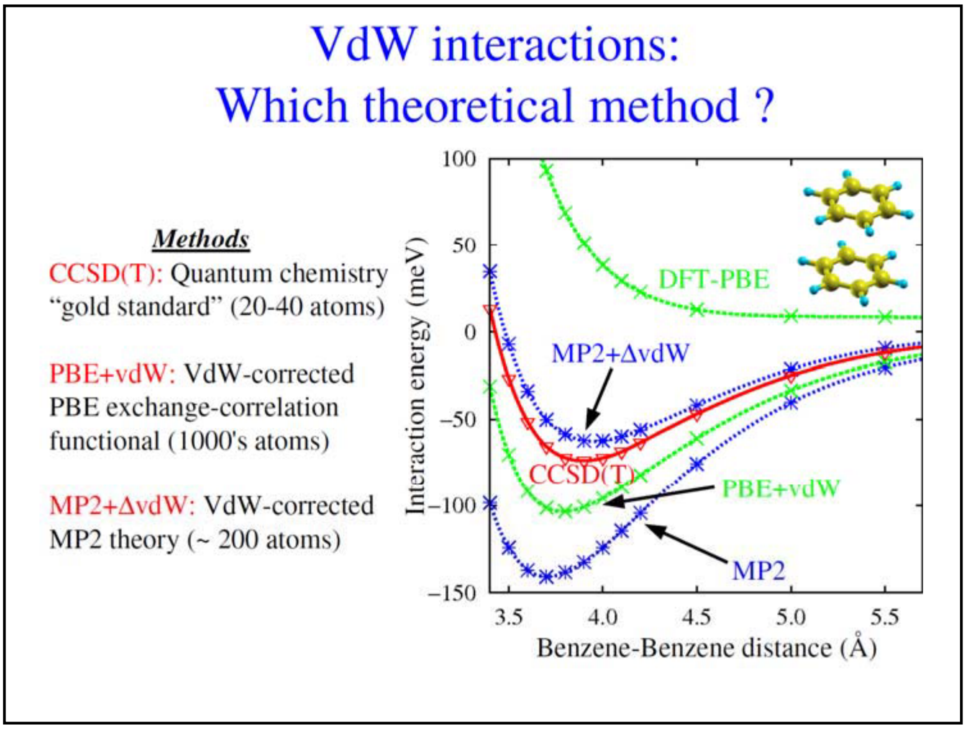
Langret

Non-local DFT (~ 1000 atoms)

EX+cRPA:
Exact exchange plus approximate correlation in RPA (~ 100 atoms)

Van der Waals dispersion interactions are exceedingly difficult to treat accurately with computationally feasible electronic structure methods !

EX + cRPA is doing well, but the C_6 coefficient is slightly too small



VdW interactions: Which theoretical method ?

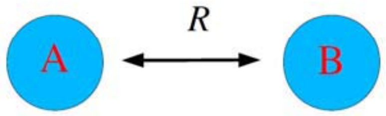
Methods

CCSD(T): Quantum chemistry “gold standard” (20-40 atoms)

PBE+vdW: VdW-corrected PBE exchange-correlation functional (1000's atoms)

MP2+ΔvdW: VdW-corrected MP2 theory (~ 200 atoms)

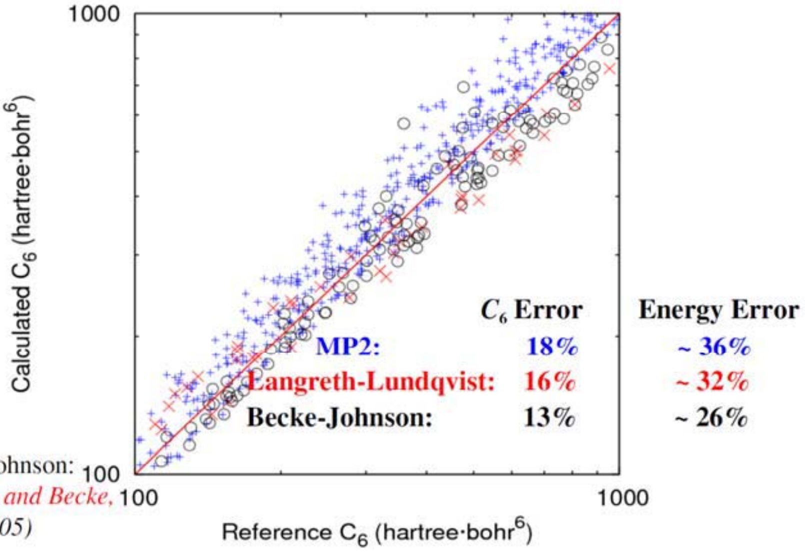
Are vdW asymptotics important for real systems?



No orbital overlap (large enough ***R***):

$$E_{\mathrm{A-B}}(R) = -\left(\frac{C_6}{R^6} + \frac{C_8}{R^8} + \frac{C_{10}}{R^{10}} + \ldots\right)$$

Can we get accurate dispersion coefficients from ground-state theory ?



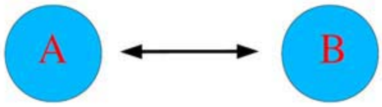
	C_6 Error	Energy Error
MP2:	**18%**	**~ 36%**
Langreth-Lundqvist:	**16%**	**~ 32%**
Becke-Johnson:	**13%**	**~ 26%**

Becke-Johnson:
Johnson and Becke,
JCP *(2005)*

Can we calculate
dispersion coefficients
within density-functional theory
to better than 5% ?

Atom-atom dispersion energy

$\Psi_A^{(0)}, \Psi_A^{(1)}, \Psi_A^{(2)}, \ldots, \Psi_A^{(\infty)}$



$\Psi_B^{(0)}, \Psi_B^{(1)}, \Psi_B^{(2)}, \ldots, \Psi_B^{(\infty)}$

No multipole moments on ***A*** and ***B*** ⇒ $E_{int} = E_{disp}$

$$E_{disp} = - \sum_{i \neq 0, j \neq 0} \frac{\langle 00 | H' | ij \rangle \langle ij | H' | 00 \rangle}{\epsilon_i^A + \epsilon_j^B - \epsilon_0^A - \epsilon_0^B}$$

To leading order (long-range approximation):

$$E_{disp}^{\infty} = - \frac{6}{R_{AB}^6} \sum_{i \neq 0, j \neq 0} \frac{\langle 0 | \mu^A | i \rangle^2 \langle 0 | \mu^B | j \rangle^2}{\epsilon_i^A + \epsilon_j^B - \epsilon_0^A - \epsilon_0^B}$$

***C*₆** coefficient

TS-vdW method: Basic ingredients

1) *Relative ab initio* atom-in-a-molecule / free-atom polarizability– avoiding inaccurate absolute polarizability of (semi-)local DFT.

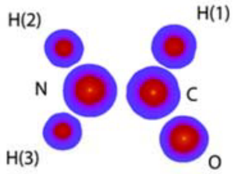
2) *Ab initio free-atom* polarizability and C_6 coefficients (*Chu and Dalgarno*): Excited state information only for free atoms !

3) Merging ground-state DFT treatment for molecules and excited-state treatment for free atoms is the key to accuracy:

$$C_{6AA}[n(\mathbf{r})] = \left(\frac{V_A[n(\mathbf{r})]}{V_A^{free}[n^{free}(\mathbf{r})]} \right)^2 C_{6AA}^{free}$$

Tkatchenko and Scheffler, ***PRL*** (2009).

Molecular C_6 coefficients



$$w_A(\mathbf{r}) = \frac{n_A^{free}(\mathbf{r})}{\sum_B n_B^{free}(\mathbf{r})}$$

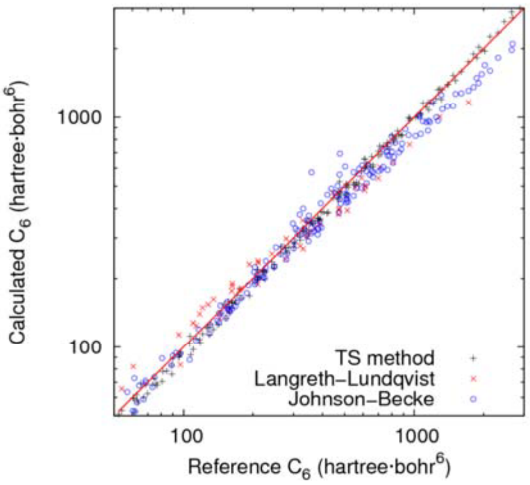
$$\kappa_A \frac{\alpha_A^{eff}}{\alpha_A^{free}} = \frac{V_A^{eff}}{V_A^{free}} = \left(\frac{\int r^3 w_A(\mathbf{r}) n(\mathbf{r}) d^3\mathbf{r}}{\int r^3 n_A^{free}(\mathbf{r}) d^3\mathbf{r}} \right)$$

$$C_{6AA}^{eff} = \boxed{\frac{\eta_A^{eff}}{\eta_A^{free}} \left(\frac{1}{\kappa_A} \right)^2} \left(\frac{V_A^{eff}}{V_A^{free}} \right)^2 \boxed{C_{6AA}^{free}}$$

set to **1**, Does this work ?

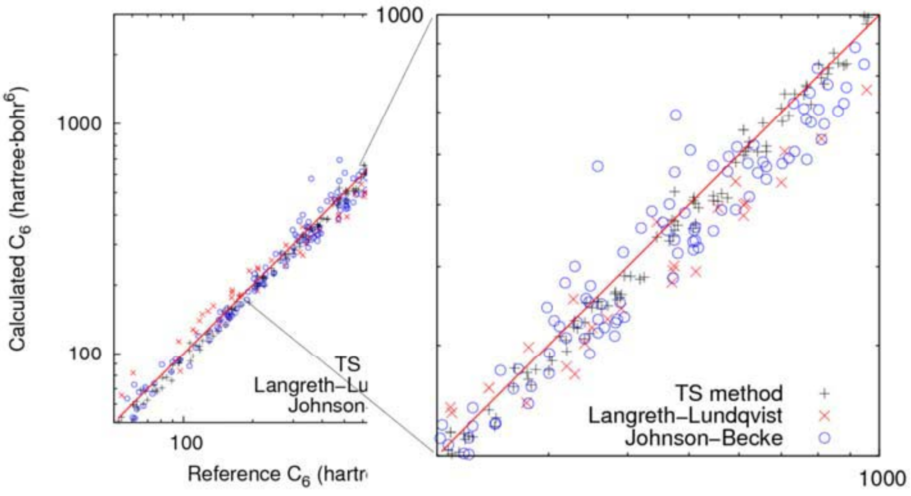
Chu and Dalgarno ***JCP*** 121, 4083 (2004)

Performance of TS-vdW for molecules



Mean absolute error of 5.5% for 1225 molecular C_6 from reference DOSD data of *W. J. Meath et al.*

Performance of TS-vdW for molecules



Results depend negligibly (1% deviation) on the employed *xc* functional

DFT+vdW$^{(1)}$ & *MP2+ΔvdW*$^{(2)}$

Leading dispersion term (or ΔC_6 term) is added to DFT or MP2 total energy, damped at short interatomic distance,

$$E_{vdW} = -\sum_A \sum_{B>A} f_{damp}(R_{AB}, R_A^0, R_B^0) C_{6AB} R_{AB}^{-6}$$

$$R_{eff}^0 = \left(\frac{V^{eff}}{V^{free}}\right)^{1/3} R_{free}^0$$

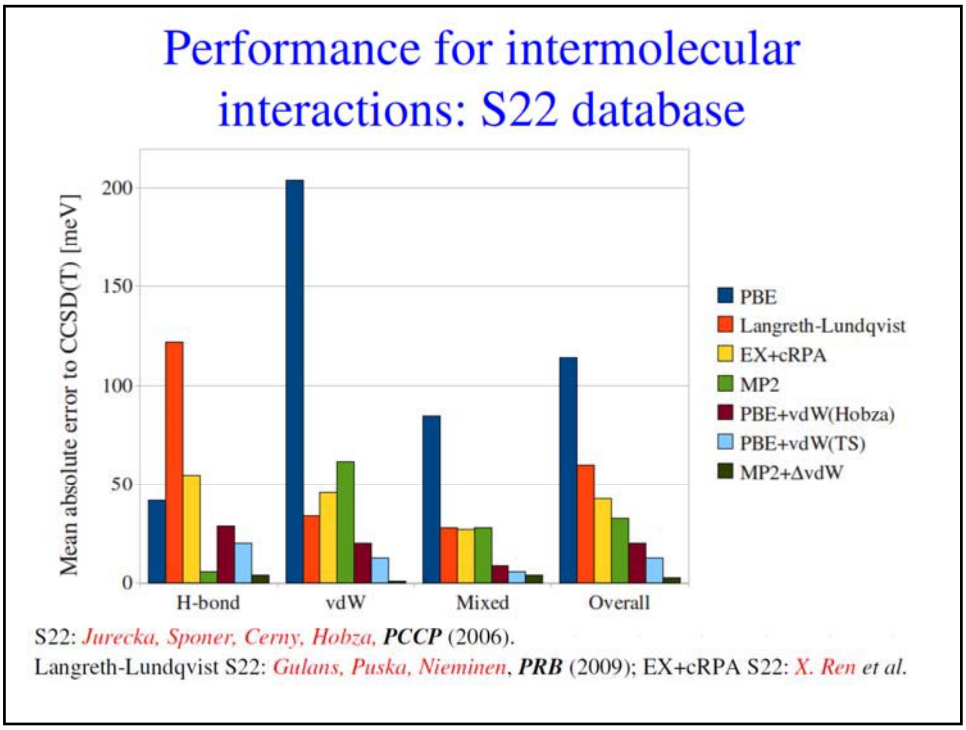
- Effective vdW parameters are functionals of the electron density:

$$C_6 = C_6[n(\boldsymbol{r})], \quad R_{\mathrm{vdW}} = R_{\mathrm{vdW}}[n(\boldsymbol{r})]$$

(1)***DFT+vdW:*** *Tkatchenko and Scheffler,* ***PRL*** (2009)
(2)***MP2+ΔvdW:*** *Tkatchenko, DiStasio Jr., Head-Gordon, Scheffler,* ***JCP (2009)***

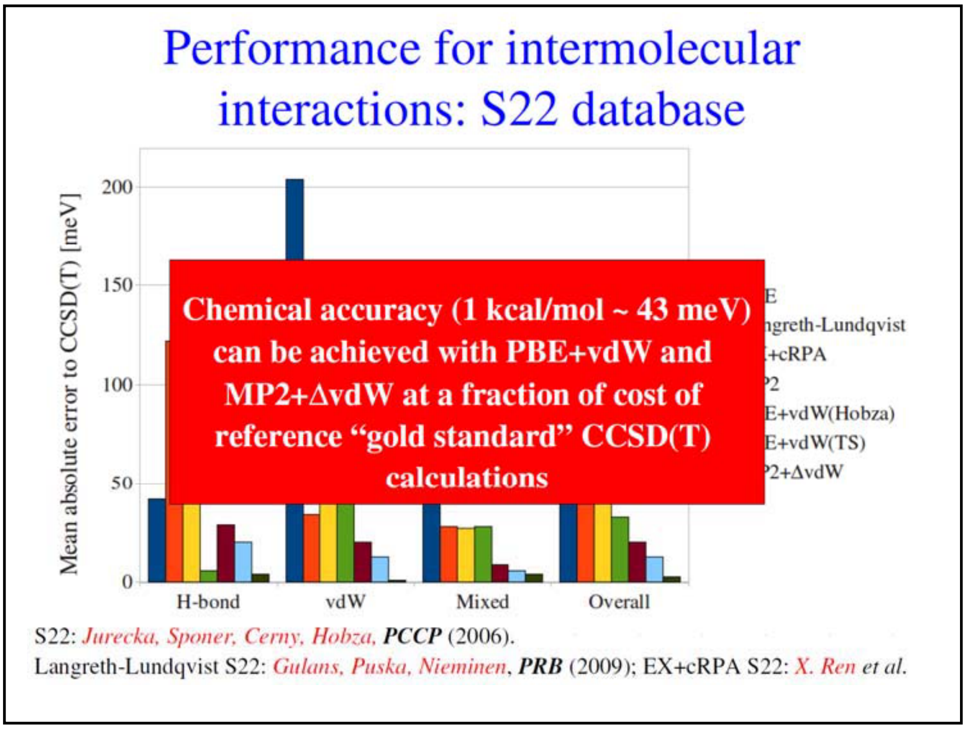
Short-range damping function: The only (slightly) weak point

- Analytical form known for spherical atoms (*Koide, Meath, Tang, Toennies, …*).
- Fitted to high-level reference databases when used with DFT (*Yang, Grimme, Hobza, ...*).
- Consistently accurate results for inter- and intra- molecular interactions with a single fitted parameter.
- Similar performance for different functionals: PBE, PBE-hybrid, B3LYP.



Performance for intermolecular interactions: S22 database

S22: *Jurecka, Sponer, Cerny, Hobza*, ***PCCP*** (2006).
Langreth-Lundqvist S22: *Gulans, Puska, Nieminen*, ***PRB*** (2009); EX+cRPA S22: *X. Ren et al.*



Performance for intermolecular interactions: S22 database

Chemical accuracy (1 kcal/mol ~ 43 meV) can be achieved with PBE+vdW and MP2+ΔvdW at a fraction of cost of reference "gold standard" CCSD(T) calculations

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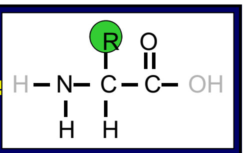
Why does the TS scheme work well ?

- No hidden approximations – the long-range dispersion is described (almost) perfectly and the rest is left to the (semi)-local functional.
- Local approximation (Langreth – Lundqvist, Vydrov – van Voorhis, etc.) *NOT* needed. Non-local contributions to polarizability are (approximately) accounted for by the virtue of Hirshfeld partitioning.

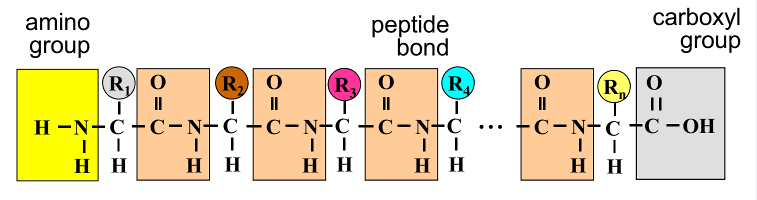
However, there are problems when applying the TS approach to bulk metals,

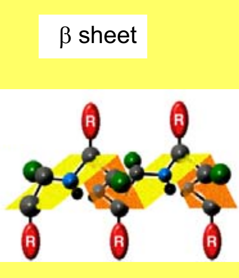
as there are problems for all the other schemes, except EX+cRPA.

Stability of the α-helix

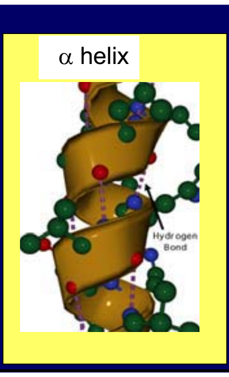


structure of proteins (peptide chains):



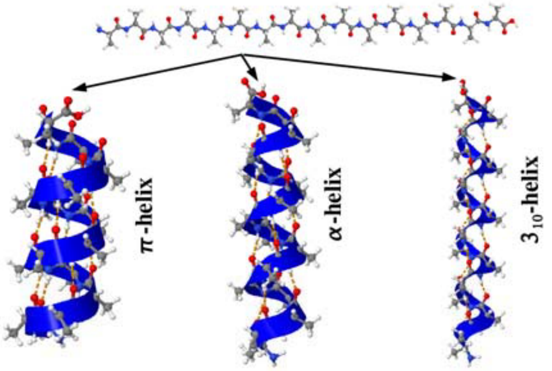


secondary structure

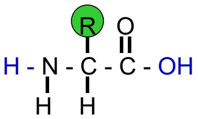


The Critical Role of vdW Intereactions: Structure and Stability of Polypeptides

Fully extended structure (FES)



peptide:



$$\mathrm{H-\underset{\displaystyle H}{N}-\overset{\displaystyle R}{\underset{\displaystyle H}{C}}-\overset{\displaystyle O}{C}-OH}$$

Alanine: R = CH_3

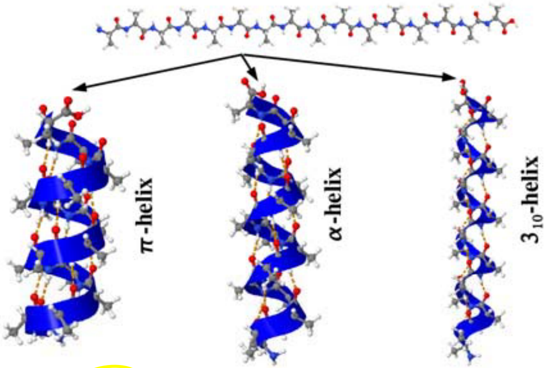
Mariana Rossi Carvalho

Volker Blum

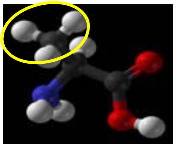
Alexandre Tkatchenko

Structure and Stability of Polypeptides

Fully extended structure (FES)



peptide:
C, N, O



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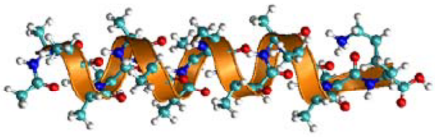
Polypeptides *in vacuo*

- *In vacuo* “clean room” conditions allow to study ***intrinsic*** polypeptide stability and quantify the stabilizing intramolecular interactions
- Same concept used in experimental studies by *Jarrold, Rizzo, von Helden, ...*
- Ever-growing number of experimental ion mobility and vibrational spectroscopy studies *in vacuo*

$Ala_{15}LysH^+$: Perfect test case for first-principles simulations

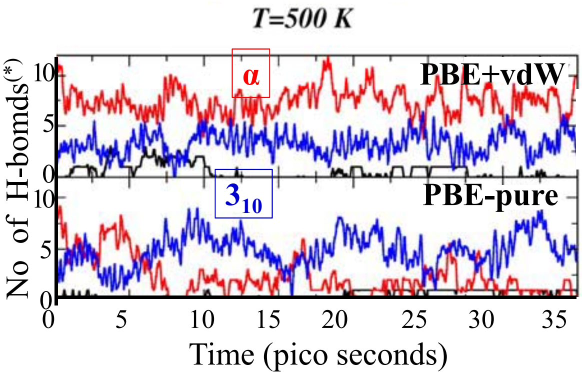


- $Ala_{15}LysH^+$ forms stable helices *in vacuo* up to ~ 750 K (in solution only up to ~ 340 K)
- Direct first-principles folding simulation are not feasible, but unfolding dynamics could provide similar insight !

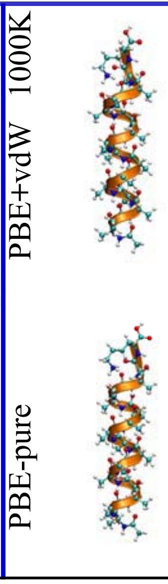
Experiments:

Kohtani, Jones, Schneider, Jarrold, ***JACS*** (2004)
Stearns, Sealby, Boyarkin, Rizzo, ***PCCP*** (2009)

Role of vdW Interaction on (Un)folding; Comparing α, 3_{10}, and π Helices for Ac-$Ala_{15}LysH^+$



(*)H-bond = 2.5 Å between CO and NH groups

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Volker Blum


Alexandre Tkatchenko

Summary

- Developed accurate and efficient first-principle method for the long-range van der Waal interaction.
- The method can be coupled with DFT (e.g., PBE+vdW) and MP2 (MP2+ΔvdW).
- Application for example to (un)folding dynamics of polyalanine helices:
  - vdW forces increase the stability of polyalanine helices by ~ 100%.
  - Qualitative differences in unfolding dynamics between PBE-pure and PBE+vdW.
  - Remarkable stability of polyalanine helices *in vacuo* is attributed to synergy between H-bonds and vdW forces.

Summary

EX+cRPA is promising. Though the improvement over lower-level xc functionals is (in principle) systematic, agreement with experiment is not always better.

There is room (need) for improvements; we have to go to self-consistent RPA (in some cases) and to higher order in the expansion.

An estimate of errors due to the xc approximation is becoming possible.