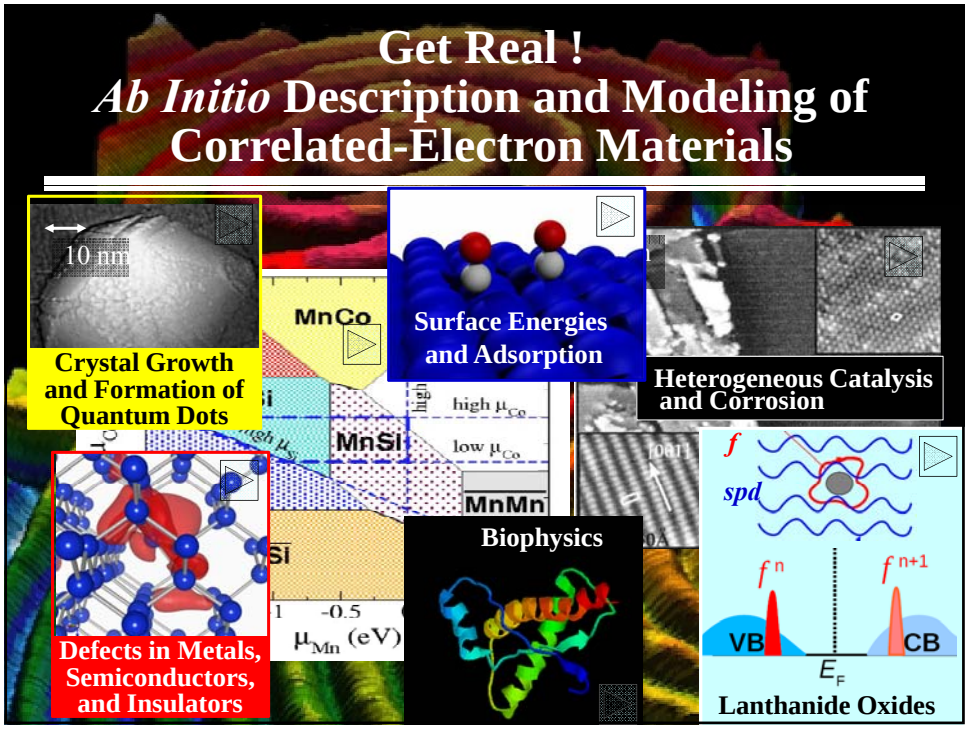
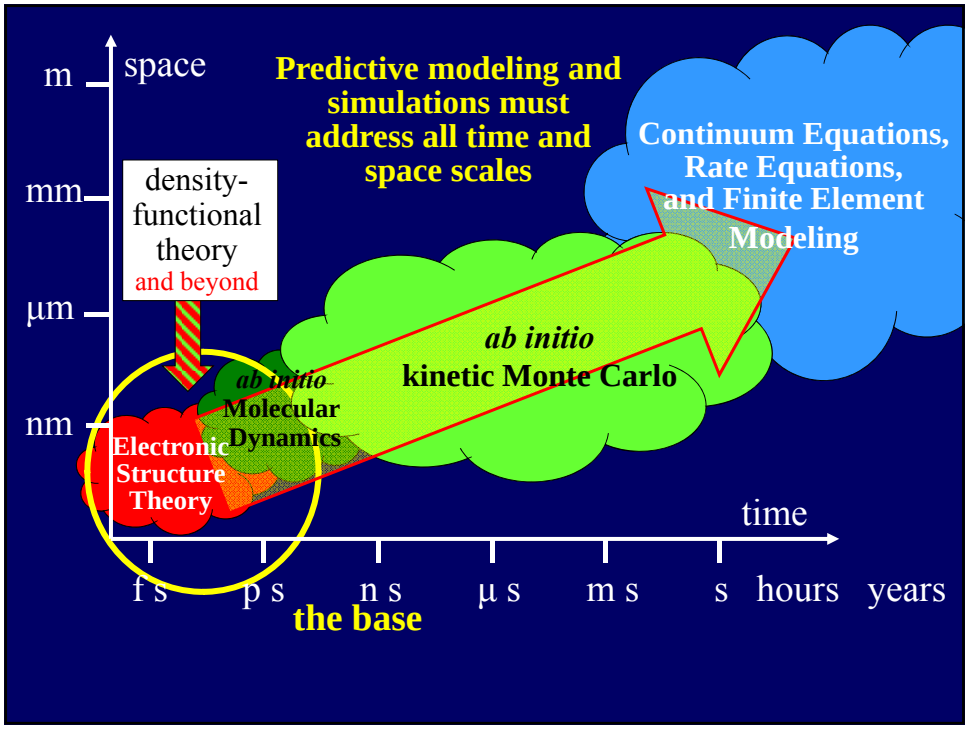

Get Real !
Ab Initio Description and Modeling of Correlated-Electron Materials
10 nm
Crystal Growth and Formation of Quantum Dots
Surface Energies and Adsorption
Heterogeneous Catalysis and Corrosion
MnCo
MnSi
MnMn
high μ_{Co}
low μ_{Co}
Si
1
-0.5
μ_{Mn} (eV)
Defects in Metals, Semiconductors, and Insulators
Biophysics
f
spd
f^n
f^{n+1}
VB
CB
E_F
Lanthanide Oxides


m
mm
µm
nm
space
density-functional theory and beyond
Predictive modeling and simulations must address all time and space scales
Continuum Equations, Rate Equations, and Finite Element Modeling
ab initio kinetic Monte Carlo
ab initio Molecular Dynamics
Electronic Structure Theory
time
f s
p s
n s
µ s
m s
s
hours
years
the base

DFT and Beyond

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.

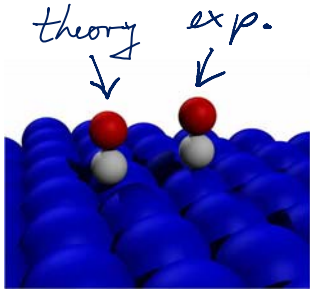
The challenges: Find *practical* ways to correct the xc approximation and/or to control the errors.

DFT also with hybrid functionals and TDDFT, Hartree-Fock +MP2, $E_X^{\text{exact}} + E_C^{\text{RPA}}$, *GW* selfenergies

One 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).*

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

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

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

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.

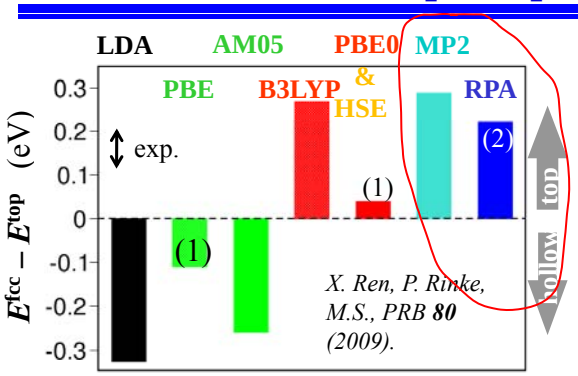
Attractive features of the RPA

$$E_{\text{tot}}^{\text{RPA}} = T_s + E_{\text{ext}} + E_H + E_x^{\text{exact}} + E_c^{\text{RPA}}$$

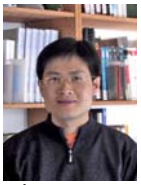
- "Exact exchange" (with Kohn-Sham orbitals)
  - self-interaction error considerably reduced
- vdW interactions included automatically and seamlessly
- Screening taken into account
  - applicable to metals/small gap systems (in contrast to MP2)

Critical assessment of the RPA is emerging.

RPA, MP2, and Others for the CO adsorption puzzle



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

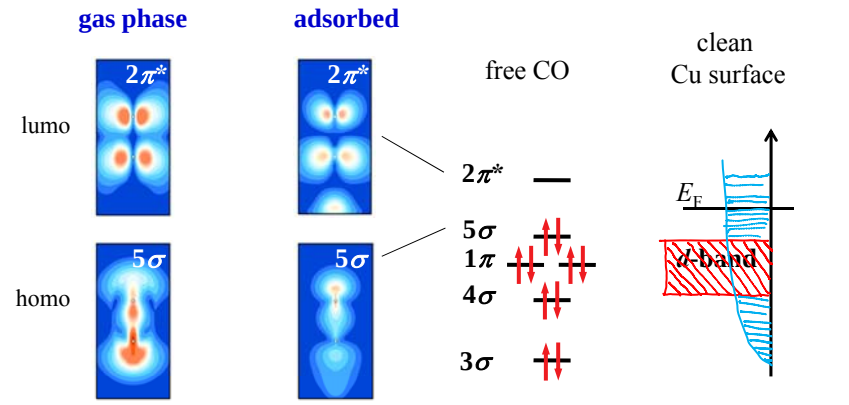

Xinguo Ren

Patrick Rinke

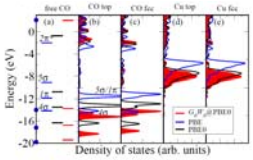
(1) *Difference to Stroppa et al. PRB* ***76****(2007) is less than 0.04 eV.*
(2) *Harl and Kresse, PRL* ***103*** *(2009) only 0.12 eV*

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).*

December 10, 2007 in Stockholm

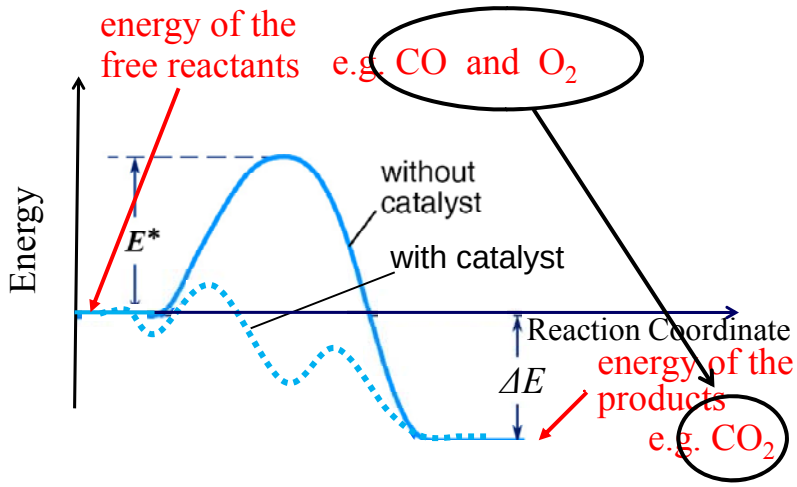
"for his studies of chemical processes on solid surfaces"

Jöns Jakob Berzelius
1779-1848

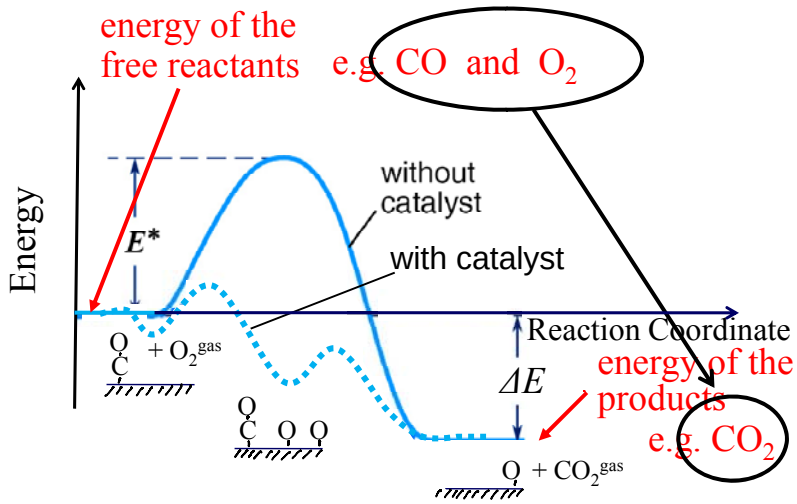
Wilhelm Ostwald
1853-1932
Nobel Prize in
Chemistry 1909

A catalyst is a substance that accelerates the rate of a chemical reaction without being part of its final product.

Heterogeneous Catalysis

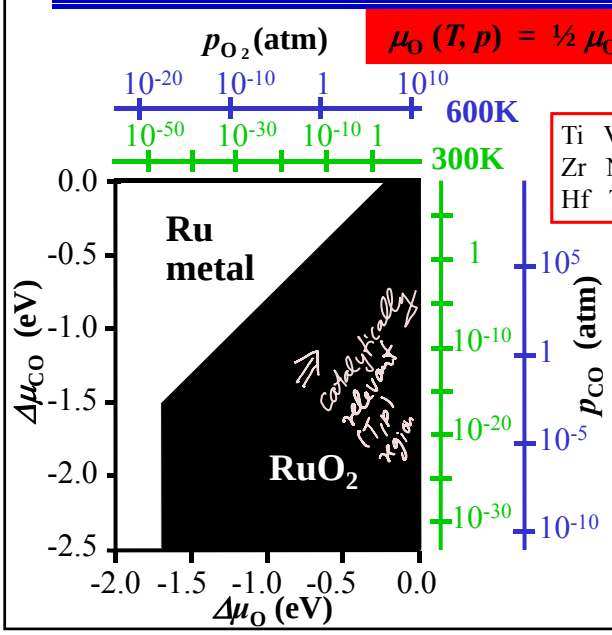


Heterogeneous Catalysis



Stability of TMs at Catalytic Conditions

$\mu_O(T, p) = \frac{1}{2}\mu_{O_2}(T, p^0) + \frac{1}{2} kT \ln(p/p^0)$



Ti	V	Cr	Mn	Fe	Co	Ni	Cu
Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag
Hf	Ta	W	Re	Os	Ir	Pt	Au

K. Reuter and M. S. Scheffler, Appl. Phys. A 78, 793 (2004)

Karsten Reuter

Stat. Mech. of Catalysis from First Principles

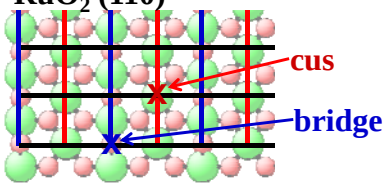
example: $CO + \frac{1}{2} O_2 \rightarrow CO_2$ at RuO_2

1. Analysis of all *possibly relevant* processes using density-functional theory
2. Calculate the rates of all important processes
   $\Gamma^{(i)} = \Gamma_0^{(i)} \exp(-\Delta E^{(i)} / k_B T)$
3. Statistical mechanics approach to describe
   -- adsorption/desorption of O_2 and CO
   -- diffusion of O and CO
   -- surface reactions between
   $CO^{br} + O^{cus}$, $CO^{cus} + O^{cus}$
   $CO^{br} + O^{br}$, $CO^{cus} + O^{br}$

Altogether: 26 processes.

For the general concepts see: Reuter, Stampfl, M.S. in: Handbook of Materials Modeling, ed. by Sidney Yip. Springer, Berlin Heidelberg, 2005.

RuO_2 (110)

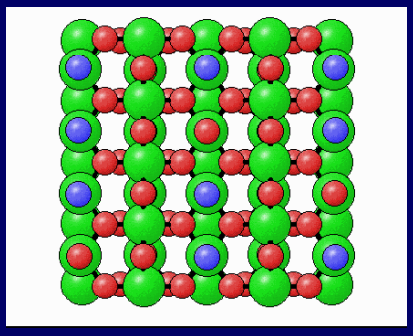


➡ **extended kinetic Monte Carlo**
(coarse-graining molecular dynamics)

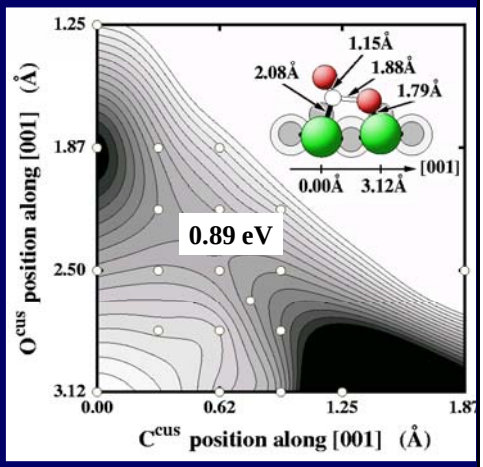
kMC Summary

- kMC is a coarse-grained technique for condensed-matter dynamics.
- It is a numerical solution of the master equation.
- It gives essentially the same information as MD -- but can simulate time spans $>10^{12}$ times longer.
- It can be linked to *ab initio* rate processes: free energy barriers, and their T dependence. Often transition state theory can be applied. Configurational entropy and resulting (kinetic) barriers are obtained by the kMC simulation.

CO_2 Formation Recation; Here the Example $CO_{cus} + O_{cus} \rightarrow CO_2$

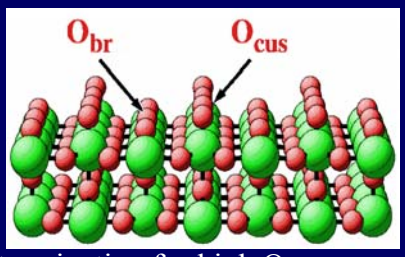


oxygen oxygen of CO

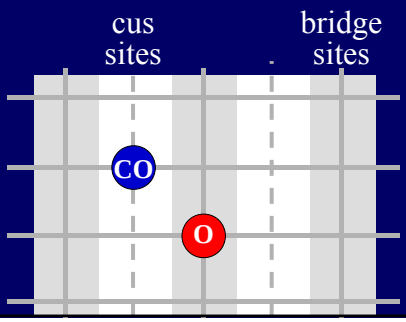


K. Reuter & M.S., PRL ***90****, 046103 (2003) and PRB* ***68****, 045407 (2003).*

Oxidation catalysis at RuO_2 (110)

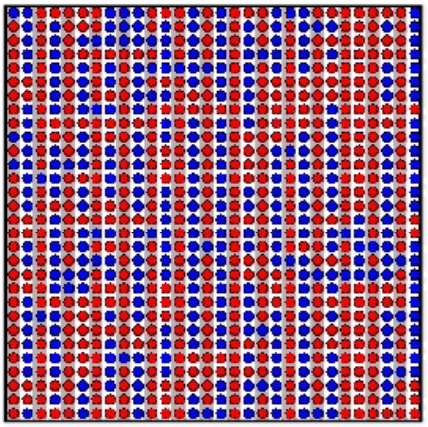


termination for high O_2 pressure

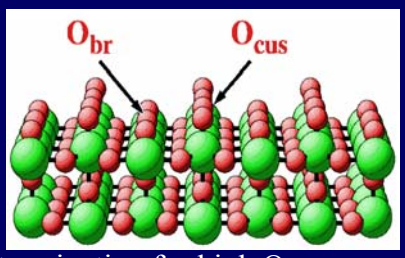


$p(O_2)$ = 1 atm, $p(CO)$ = 10 atm

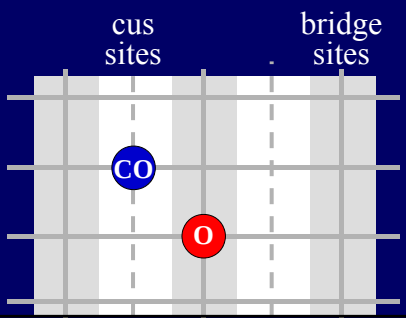
T = 600 K t = 5 mscc



Oxidation catalysis at RuO_2 (110)

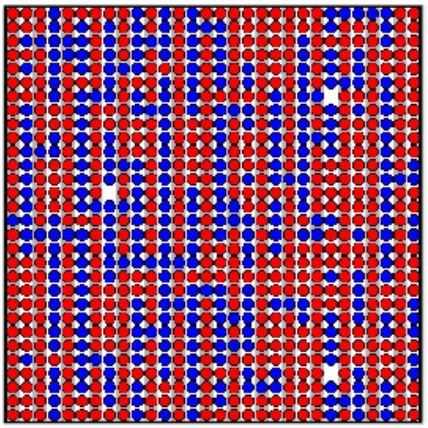


termination for high O_2 pressure

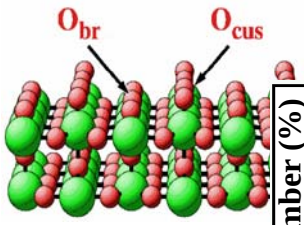


$p(O_2)$ = 1 atm, $p(CO)$ = 10 atm

T = 600 K t = 2 nscc



Site Occupation Statistics at the Steady State (Strong Fluctuations)



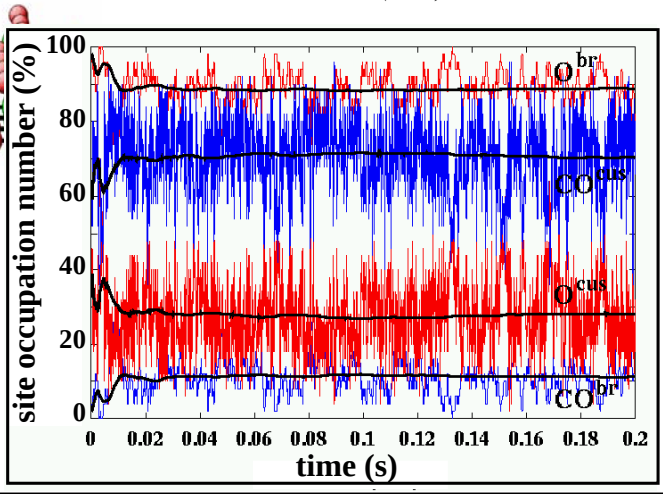
K. Reuter, D. Frenkel, M.S., PRL 93, 116105 (2004),
K. Reuter, M.S., PRB 73 (2006).

Reaction energy barriers (eV)

$CO^{br} + O^{cus}$: 0.8

$CO^{cus} + O^{cus}$: 0.9
$CO^{cus} + O^{br}$: 1.2

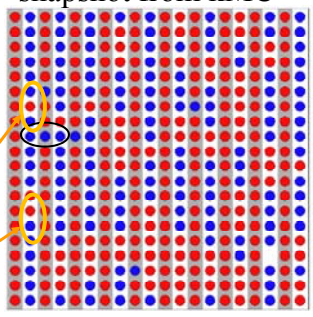
$CO^{br} + O^{br}$: 1.5



What kills the lowest-energy process?

The surface structure / composition is not in thermal equilibrium. The kinetics creates a non random structure.

snapshot from kMC



The action is here.

oxygen CO

cus sites: white background
bridge sites: grey background

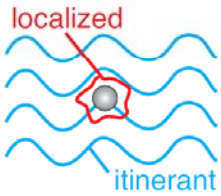
The $CO^{br} + O^{cus}$ reaction has the lowest energy barrier

Temel, Meskine, Reuter, Scheffler, and Metiu, J. Chem. Phys. ***126****, 204711 (2007)*
Meskine, Matera, Scheffler, Reuter, and Metiu, Surf. Sci. (2009).

Conclusions (of Part I): Get Real

- A careful linkage of electronic structure theory and statistical mechanics is necessary in order to describe the *system chemistry* and to understand the properties and function at the catalyst surface under realistic (*T, p*) conditions.
- Short time spans (< μs) show interesting MD processes. However, they most likely will miss the important ones.
- A catalyst is a *dynamical* ("living") material. Its *active state* is typically *a novel compound*, created in the realistic environment (atmospheric pressure of various reactive chemicals, high temperatures) under operating conditions.
- Structural instability and fluctuations are important. They enable a high dynamics and healing of (locally) poisoned regions.

f-Electron Systems – Lanthanide Oxides

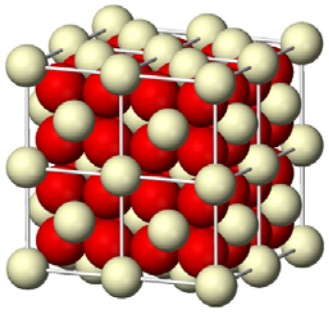


- localized and itinerant electrons

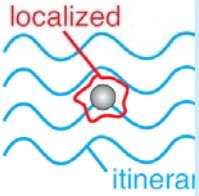
⇒ rich physics and chemistry

- LDA/GGA often not adequate
- often termed *strongly correlated*

- Ln_2O_3 (Ln=lanthanide series)
- technologically important materials e.g. catalysis



f-Electron Systems – Lanthanide Oxides



How well will *GW* perform?

- exact exchange
  - ➢ essential for localized electrons
- screening
  - ➢ essential for itinerant electrons
- answers from new LAPW-based GW code

Hong Jiang

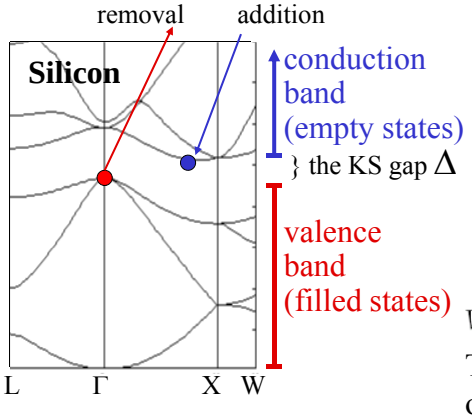
Patrick Rinke

Ricardo Gomez-Abal

Why Do We Need *GW*? Why Do We Need To Go Beyond DFT

Kohn-Sham band gap: $\Delta = \epsilon_{CB} - \epsilon_{VB}$ of the *N*-particle system

The measured (optical) band gap is something else:



$$E_{\text{gap}} = I - A \quad ,$$
$$A = E^{N} - E^{N+1}$$
$$I = E^{N-1} - E^{N}$$
$$E_{\text{gap}} = E^{N-1} + E^{N+1} - 2E^{N}$$
$$= \Delta + \Delta_{\text{xc}}$$

$$V_{\text{xc}}([n_{N+1}];\boldsymbol{r}) = V_{\text{xc}}([n_N];\boldsymbol{r}) + \Delta_{\text{xc}}$$

There is a discontinuity in V_{xc} that occurs upon addition of an electron.

We don't know how to determine Δ_{xc} within DFT

Many-Body Perturbation Theory; The Self-Energy

Occupied and unoccupied states and their energies are obtained from the quasiparticle equation

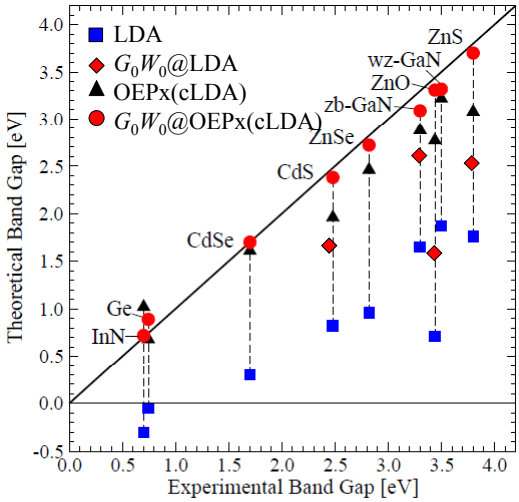
$$\left[-\frac{1}{2}\nabla^2 + V_{\rm ext}(\boldsymbol{r}) + V_{\rm H}(\boldsymbol{r})\right]\psi_{N,j}(\boldsymbol{r}) + \int \Sigma_{\rm xc}(\boldsymbol{r},\boldsymbol{r}',\epsilon_{N,j})\psi_{N,j}(\boldsymbol{r}')\,{\rm d}^3r' = \epsilon_{N,j}\psi_{N,j}(\boldsymbol{r})\ .$$

The self-energy $\Sigma_{\rm xc}$ incorporates all contributions from exchange and correlation processes. In contrast to the xc-potential of DFT, it is nonlocal, energy-dependent and has a finite imaginary part. We evaluate $\Sigma_{\rm xc}$ in the G_0W_0 approximation:

$$\Sigma_{\rm xc}(\boldsymbol{r},\boldsymbol{r}';t \quad t') = \lim_{\eta\to+0} {\rm i}G_0(\boldsymbol{r},\boldsymbol{r}';t \quad t')W_0(\boldsymbol{r},\boldsymbol{r}';t \quad t'+\eta)$$

W_0 is the screened Coulomb interaction; we employ the random-phase approximation, taking the full frequency-dependence of the dielectric function into account.

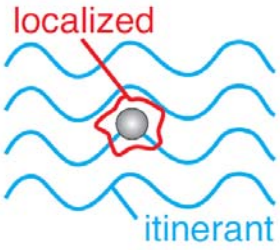
G_0W_0 band gaps

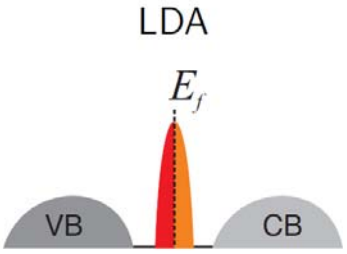


The starting point can be important. If we start too far from the final answer, first order perturbation theory (G_0W_0) will fail.

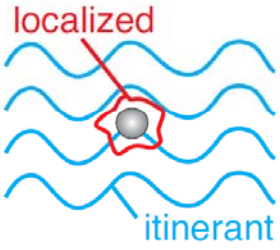
Rinke et al. New J. Phys. 7, 126 (2005), phys. stat. sol. (b) 245, 929 (2008)

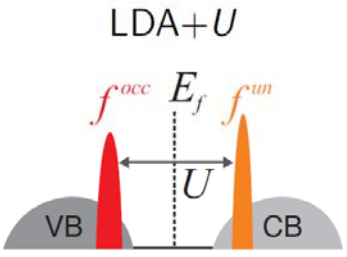
Ce_2O_3 - Localized vs Itinerant States





Ce_2O_3 - Localized vs Itinerant States

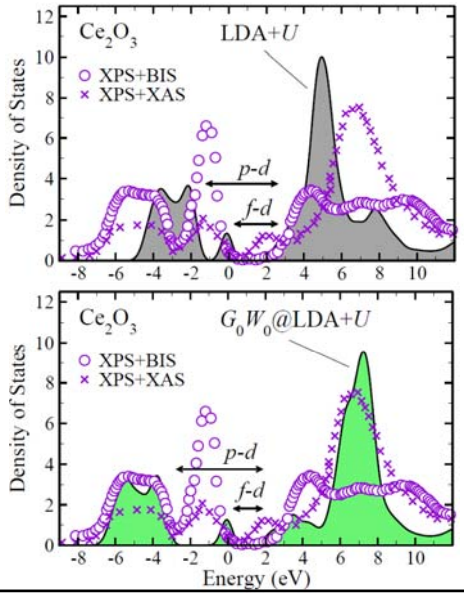




$$E^{\mathrm{LDA}+U}[\rho(\mathbf{r}), \hat{n}_I^a] = E^{\mathrm{LDA}}[\rho(\mathbf{r})] + E^{\mathrm{ee}}[\hat{n}_I^a] - E^{\mathrm{dc}}[\hat{n}_I^a]$$

E^{ee} : screened HF-like interaction between localized electrons
E^{dc} : double counting correction

Ce_2O_3 in LDA+U and in G_0W_0@LDA+U

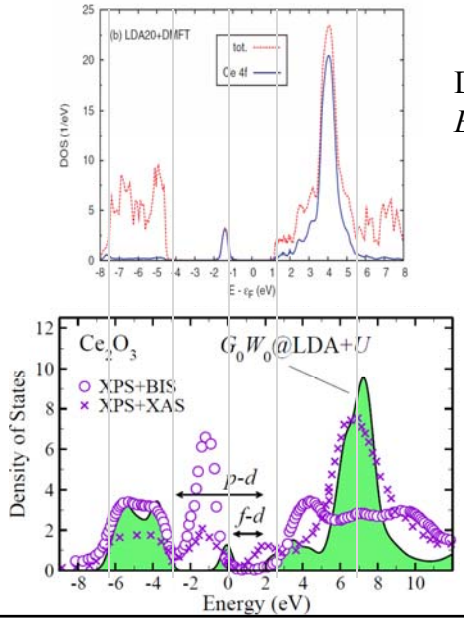


LDA+U splits f-peaks and opens gap

G_0W_0@LDA+U reproduces main peaks and gaps

H. Jiang et al., PRL ***102*** *(2009)*

Ce_2O_3 in LDA+U and in G_0W_0@LDA+U

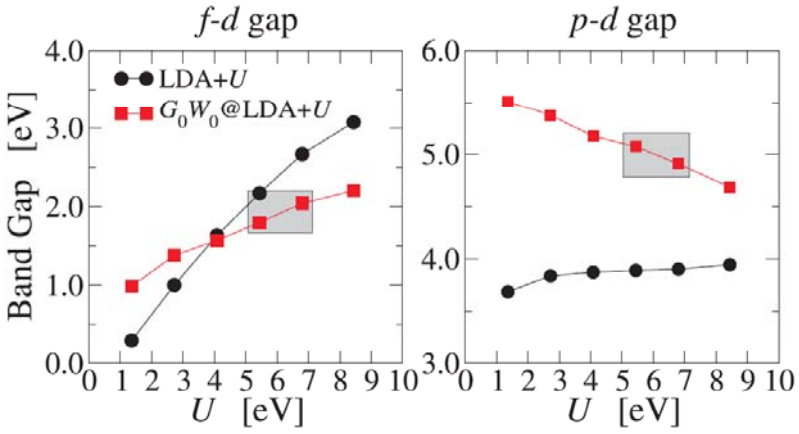


D. Jacob, K. Haule, G. Kotliar, *EPL* **84** (2008)

G_0W_0@LDA+U reproduces main peaks and gaps

H. Jiang et al., PRL ***102*** *(2009)*

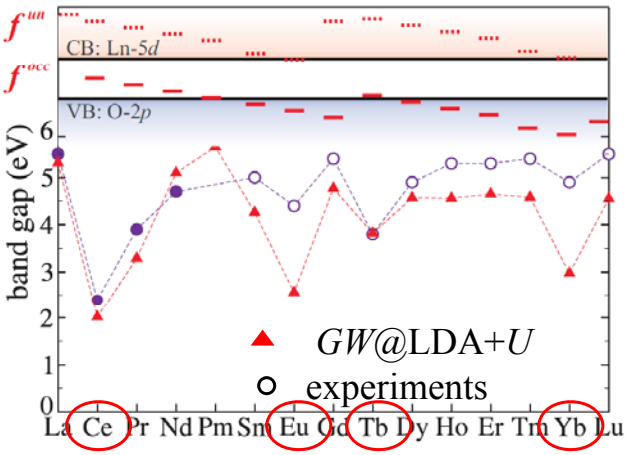
Ce_2O_3 – U-dependence in G_0W_0@LDA+U



- G_0W_0@LDA+U: small U-dependence in "physical range"

H. Jiang, et al., PRL ***102*** *(2009)*

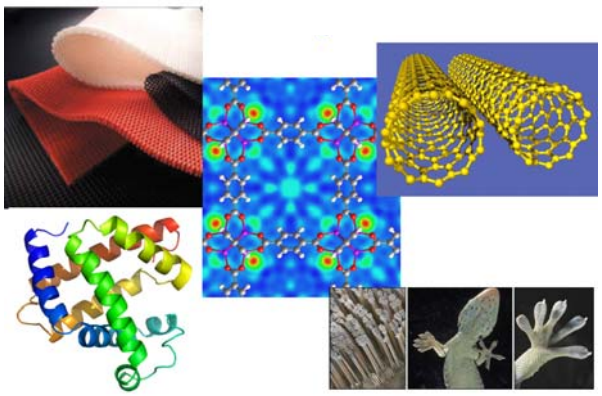
Lanthanide Sesquioxide Series



H. Jiang, et al., PRL ***102*** *(2009)*

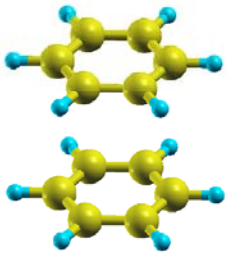
... And More About Correlation: vdW Forces = 100% Correlation

The Role of vdW Forces in Physics, Chemistry, and Biology



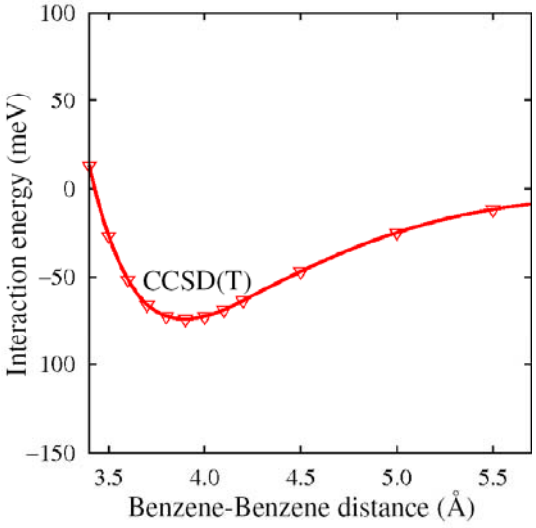
Alexandre Tkatchenko

VdW interactions: Which theoretical method ?

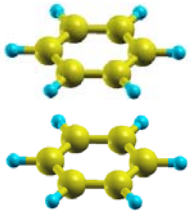


Methods

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

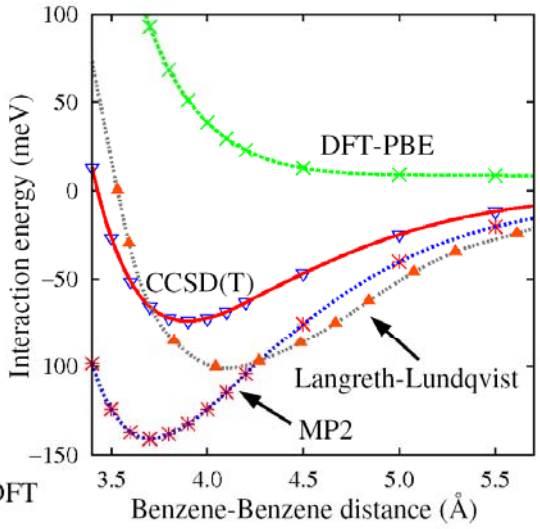


VdW interactions: Which theoretical method ?



Methods

CCSD(T) – Quantum chemistry "gold standard" (20-40 atoms)
MP2 – Perturbation theory incl. approximate dispersion energy
DFT-PBE – (semi)-local density-functional theory
Langreth-Lundqvist: Non-local DFT



VdW interactions: Which theoretical method ?

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

"gold

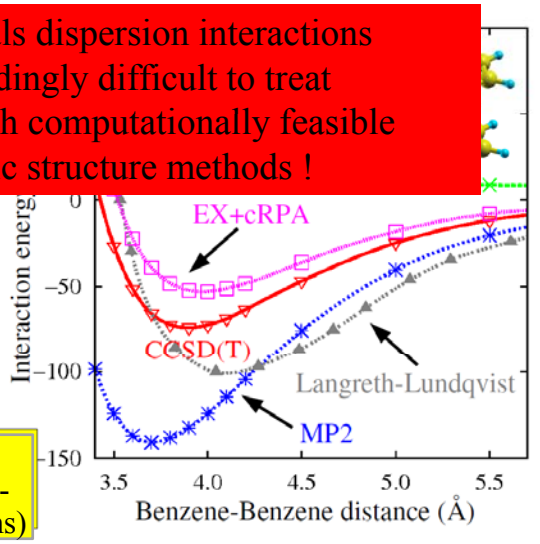
Pertu

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)

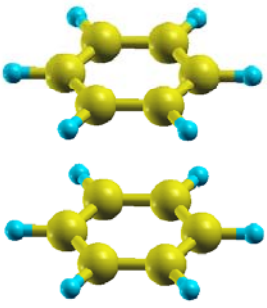
EX + cRPA
exact exchange plus correlation in the RPA (~ 100 atoms)



20% error in the C_6 coefficients implies a ~40% error in the vdW contribution to the binding energy

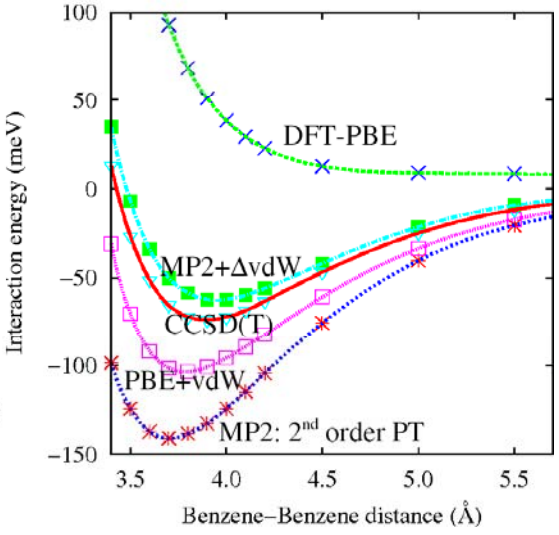
Can we get dispersion coefficients within density-functional theory to better than 5% ?

VdW interactions: Which theoretical method ?



Methods

CCSD(T): Up to 20-40 atoms
MP2: Up to ~ 200 atoms
DFT: 1000's atoms



TS-vdW method: Basic ingredients

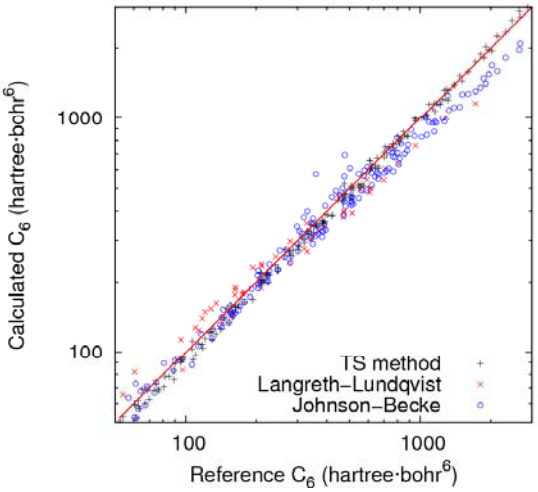
1) Only *relative* atom-in-a-molecule / free-atom polarizability is used – avoiding inaccurate absolute polarizability of (semi-)local DFT.

2) *Ab-initio free-atom* polarizability and C_6 database (*Chu and Dalgarno*)

⇨ C_6 coefficients are a functional of the density

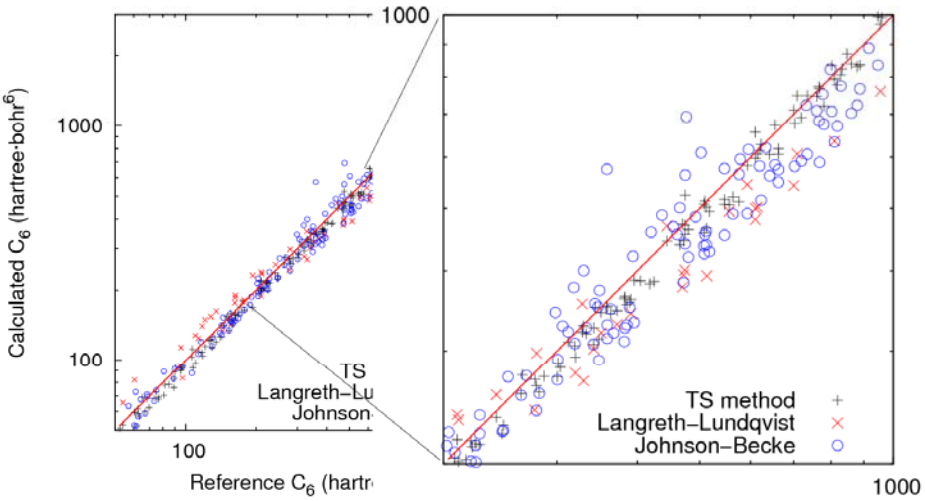
A. Tkatchenko and M. Scheffler, PRL (2009)

Performance of TS-vdW for molecules



Mean absolute error of 5.5% for 1225 molecular pairs from DOSD reference 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,

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

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

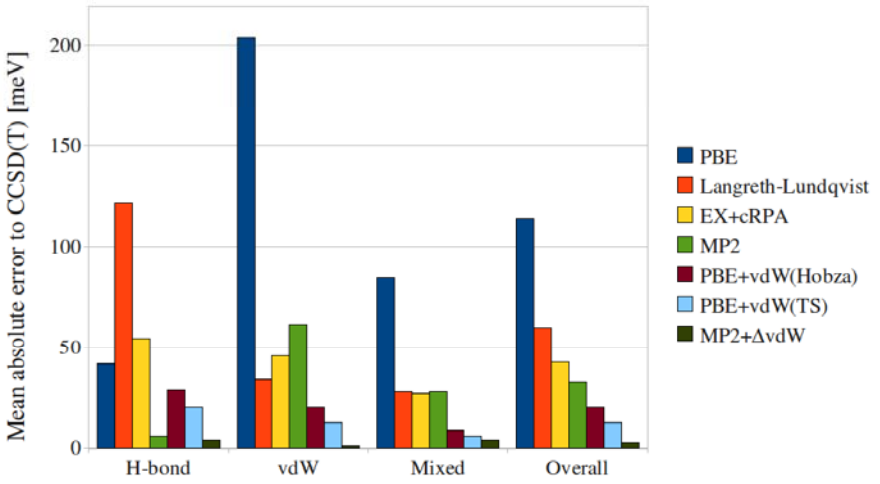
- Effective vdW parameters are functionals of the electron density:

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

- One damping parameter for DFT (for each functional) fitted to quantum-chemical reference data, no parameters for MP2

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

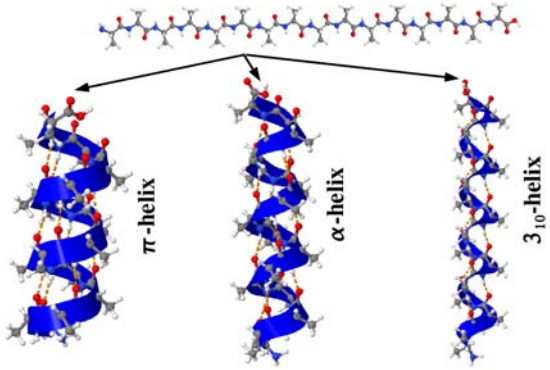
Performance for intermolecular interactions: S22 database

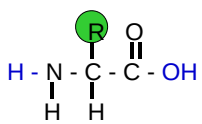


S22: *Jurecka, Sponer, Cerny, Hobza,* ***PCCP*** (2006).
Langreth-Lundqvist S22: *Gulans, Puska, Nieminen*, ***PRB*** (2009); EX+cRPA S22: *X. Ren et al.*

Structure of Alanine Polypeptides

Fully extended structure (FES)



peptide: 

Mariana Rossi Carvalho

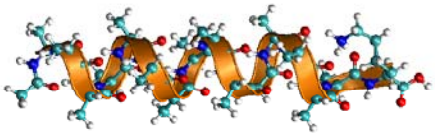
Volker Blum

Alexandre Tkatchenko

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



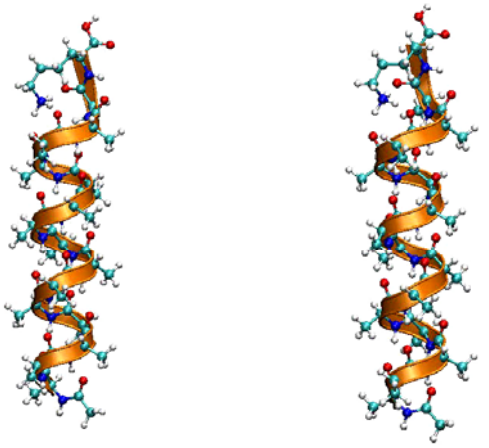
- $Ala_{15}LysH^+$ forms stable helices *in vacuo* up to ~ 750 *K* (in solution only up to ~ 340 *K*)
- Direct first-principles folding simulation are not feasible, but unfolding dynamics could provide similar insight !

Experiments:

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

"DFT-PBE pure" and "DFT+vdW" Molecular Dynamics for 30 ps at 1000K

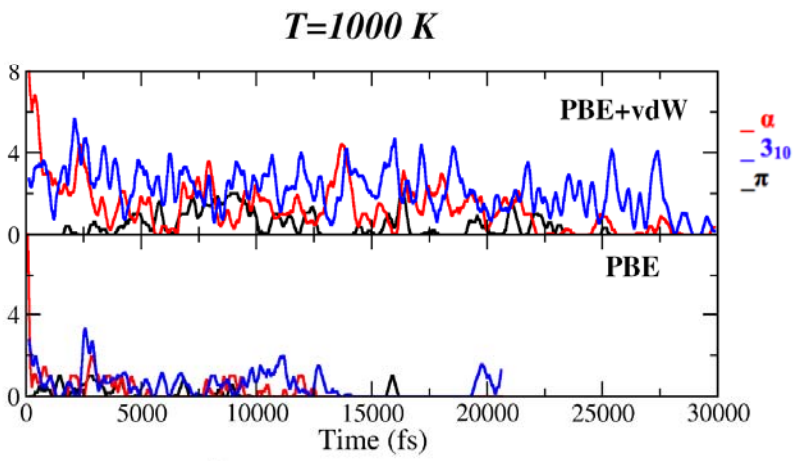
pure PBE



PBE +vdW

$Ala_{15}LysH^+$: Role of vdW on unfolding, comparing α, 3_{10} and π

With *M. Rossi, V. Blum, J. Ireta, M. Scheffler*

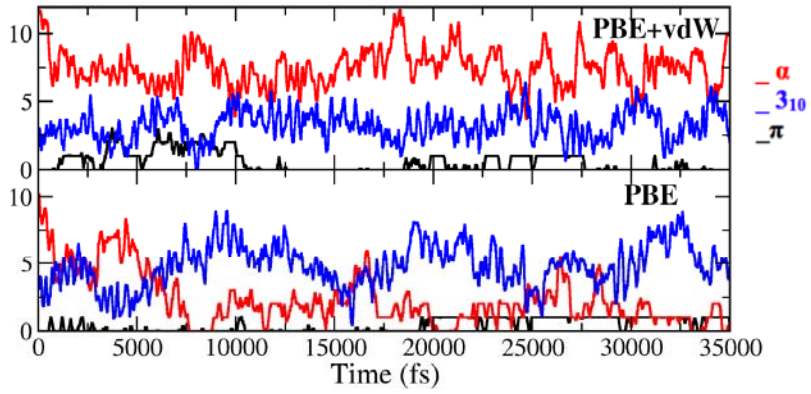


H-bond: 2.5 Å distance between CO and NH groups

$Ala_{15}LysH^+$: Role of vdW on unfolding, comparing α, 3_{10}, and π

With *M. Rossi, V. Blum, J. Ireta, M. Scheffler*

T=500 K

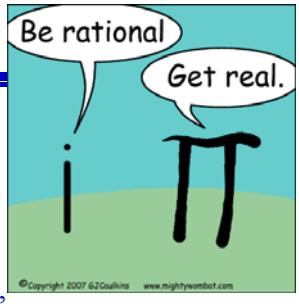


H-bond: 2.5 Å distance between CO and NH groups

Polyalanine Unfolding: Conclusions

- VdW forces increase the stability of polyalanine helices by ~ 100%
- Qualitative differences in unfolding dynamics bteween PBE-pure and PBE+vdW
- Remarkable stability of polyalanine helices *in vacuo* attributed to synergy between Hbonds and vdW forces

Final Conclusions: We need



- continue to worry about "strong" correlations and van der Waals interactions; *GW* works better (and for more systems) than we had expected.
- theory to describe non-adiabatic effects,
- theory to describe heat transport and dissipation, mass transport,

- more experimental information about the (temporary) formation of the (novel) compounds that form under real-life conditions,
- more experimental information on the role of *fluctuations* and the *correlated* adsorption and reaction *dynamics* at high pressure.