Plenary Talk PV XXIV Fri 8:30 H 0105

Role of van der Waals Interactions in Physics, Chemistry, and Biology — •Matthias Scheffler — Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Germany

Van der Waals (vdW) interactions are crucial for the formation, stability, and function of many molecules and materials. They typically dominate in regions where the overlap of electron densities is small. Interestingly, the commonly applied implementations of density-functional theory (LDA, GGAs, hybrids) are completely lacking the vdW tail.

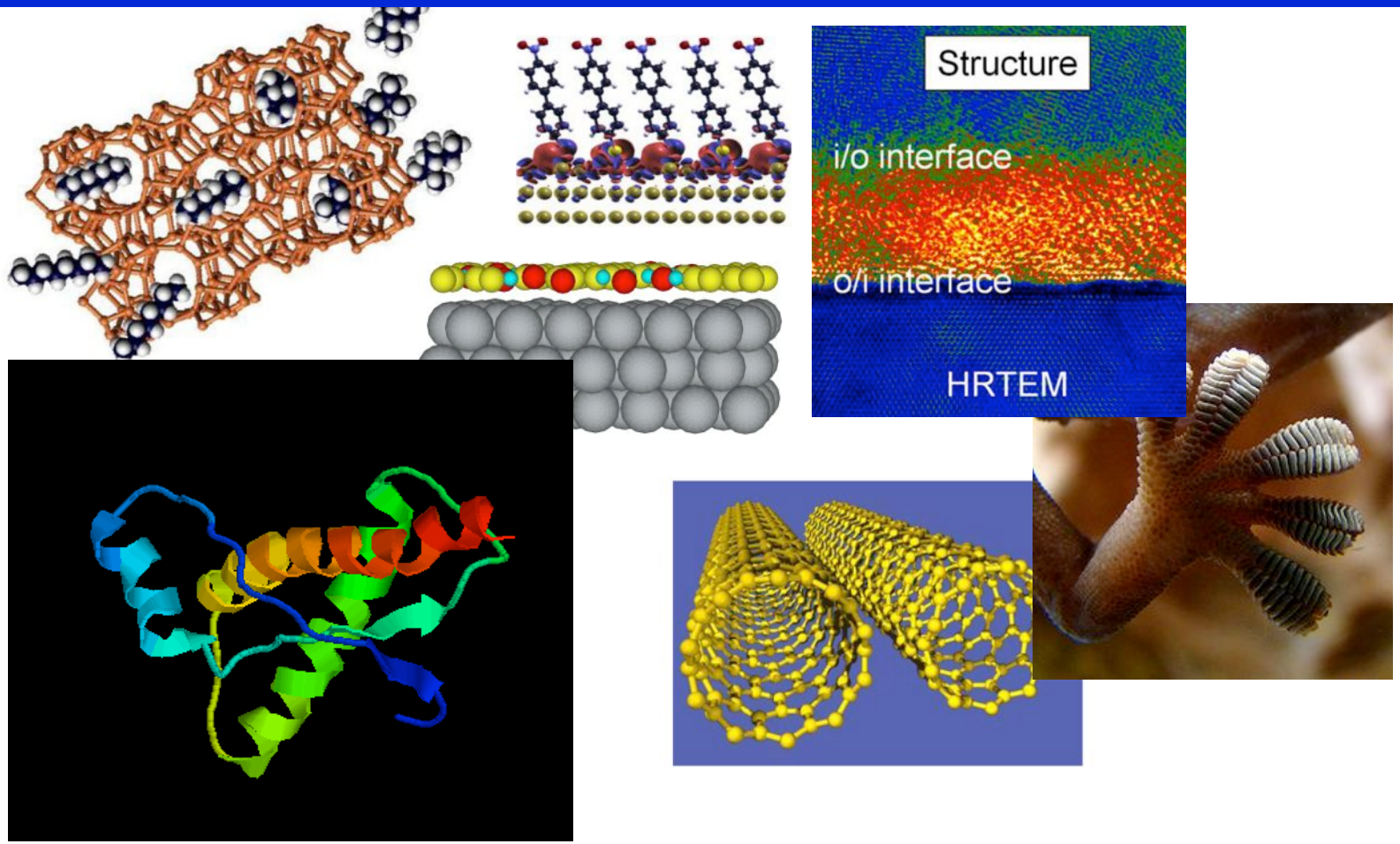
In this talk, I will review recent advances in electronic-structure theory; in particular, I will highlight the "exact exchange random-phase approximation to correlation (cRPA)" approa cent corrections to cRPA. Furthermore, I will discuss appr that are computationally more efficient and enable the tr large systems or long time-scale molecular dynamics. The of the talk will deal with representative applications, e.g.,

* The noticeable role of vdW interactions in the cohesio metals and semiconductors and in the intermolecular inte water and ice.

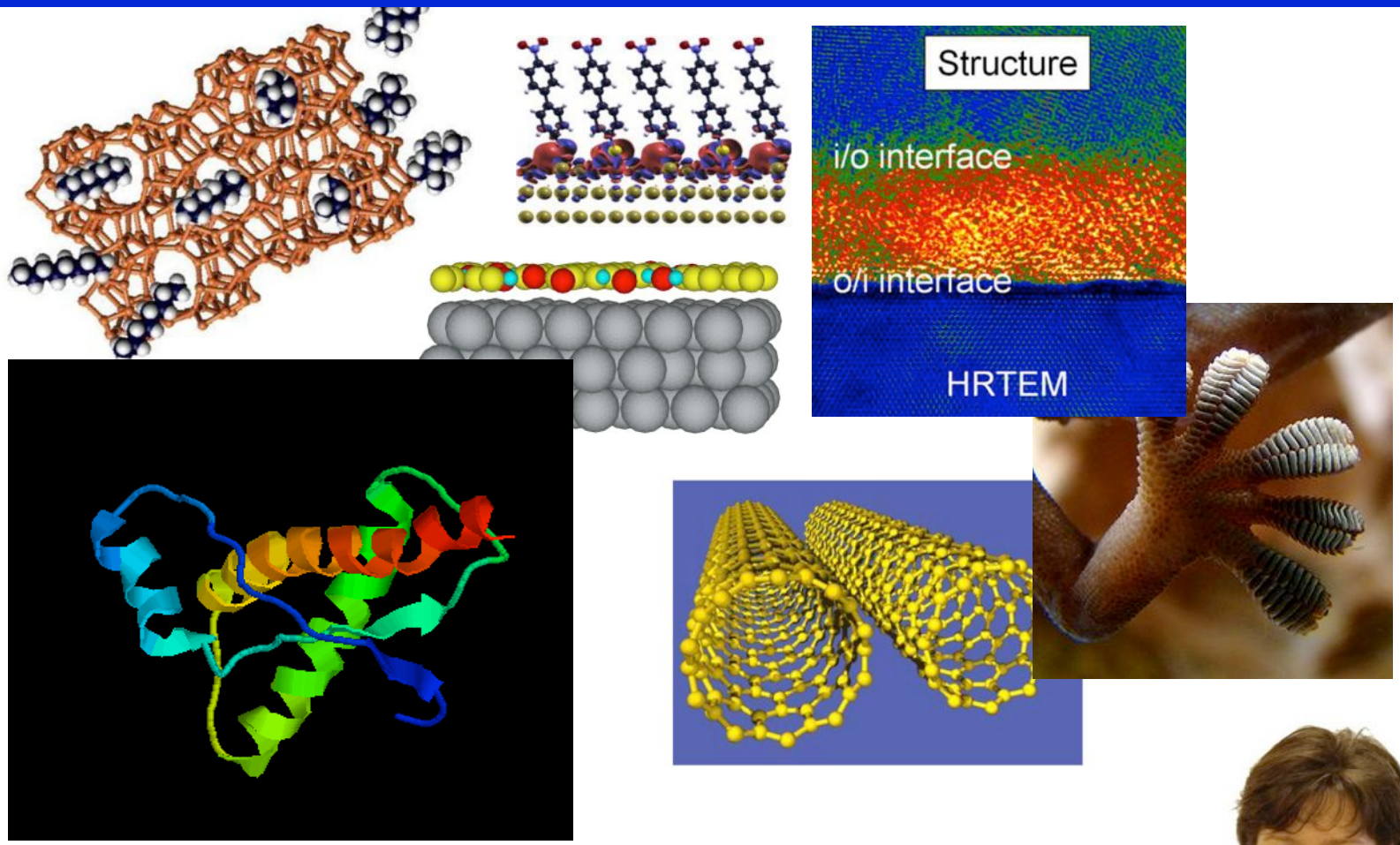
* Particular focus will be put on the adsorption of organic at metals and semiconductors, and on tuning the workfunc inorganic substrate by molecular acceptors.

* Regarding biophysics, I will show how vdW interacti the conformational landscape, stabilize the helical hydrogen work compared to plain DFT-GGA calculations, and thus e thermal stability of helical structures by several hundred K

Role of van der Waals Interactions in Physics, Chemistry, and Biology

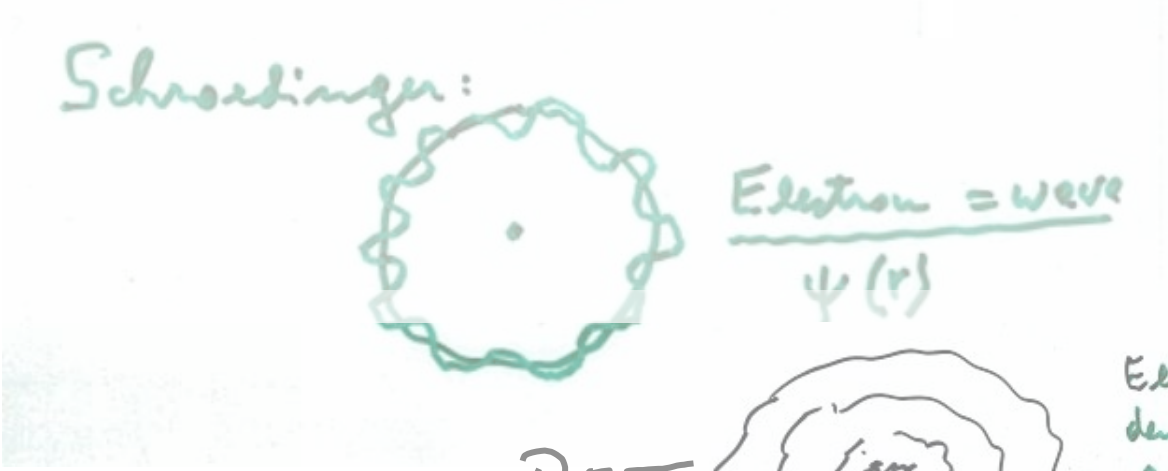


Role of van der Waals Interactions in Physics, Chemistry, and Biology



Karin Jacobs: “Take van der Waals forces into account in theory, simulations, and experiment!”

The Kohn-Sham Ansatz of Density-Functional Theory



Walter Kohn

The Kohn-Sham Ansatz of Density-Functional Theory

- Kohn-Sham (1965): Replace the original many-body problem by an independent electron problem **that can be solved!**

$$E_{\mathrm{v}}[n] = T_s[n] + \int \mathrm{v}(\mathbf{r})\, n(\mathbf{r})\, d^3\mathbf{r} + E^{\mathrm{Hartree}}[n] + E^{\mathrm{xc}}[n]$$

- With $T_{\mathrm{s}}[n]$ the kinetic energy functional of independent electrons, and $E^{\mathrm{xc}}[n]$ the unknown functional.
- The challenge is to find useful, approximate xc functionals.

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The Kohn-Sham Ansatz of Density-Functional Theory

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Approximate xc functionals have been very successful

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The Kohn-Sham Ansatz of Density-Functional Theory

Approximate xc functionals have been very successful but there are problems

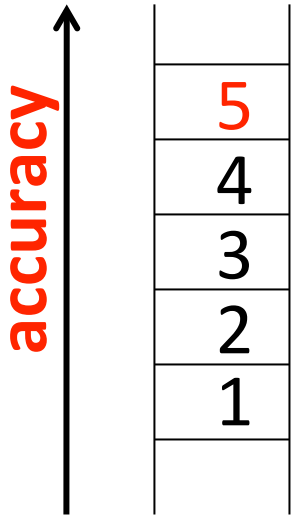
- for certain bonding situations (vdW, hydrogen bonding, certain covalent bonds)
- for highly correlated situations, and
- for excited states.

- The challenge is to find useful, approximate xc functionals.

Perdew's Dream: Jacob's Ladder in Density-Functional Theory

The exchange-correlation functional

our favorite



unoccupied $\psi_i(\mathbf{r})$,	EX + cRPA, as given by ACFD
occupied $\psi_i(\mathbf{r})$,	hybrids (B3LYP, PBE0, HSE, …)
$\tau\,(\mathbf{r})$,	meta-GGA (e.g., TPSS)
$\nabla n(\mathbf{r})$,	Generalized Gradient Approx.
$n(\mathbf{r})$,	Local-Density Approximation

$\tau(\mathbf{r})$: Kohn-Sham kinetic-energy density

EX: exact exchange: $E_x = -\frac{1}{2}\sum_{occ}\int\int d\mathbf{r}\,d\mathbf{r}'\,\frac{\psi_n^*(\mathbf{r})\psi_m(\mathbf{r})\psi_m^*(\mathbf{r}')\psi_n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}$

cRPA : random-phase approximation for correlation

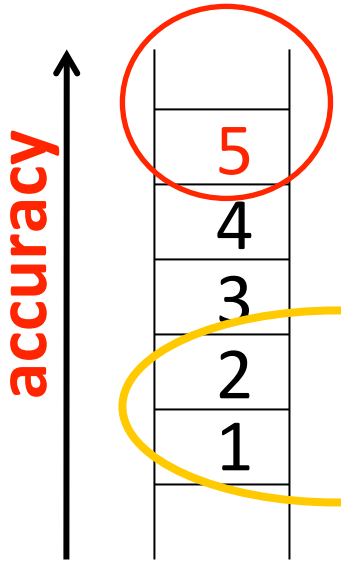
ACFD : adiabatic connection fluctuation dissipation theorem

Bohm, Pines (1953); Gell-Mann, Brueckner (1957); …;

X. Ren, et al., Invited Review in J Mater Sci (2012) -- arXiv: 1203.5536

Perdew's Dream: Jacob's Ladder in Density-Functional Theory

The exchange-correlation functional



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past and presence

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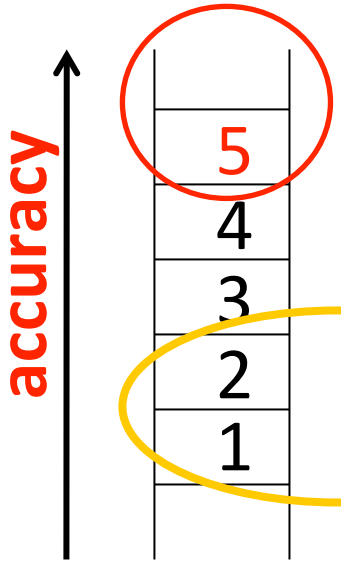

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unoccupied $\psi_i(\mathbf{r})$, EX + cRPA, as given by

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past and prese

Functionals of level 1, 2, 3, and 4 are lacking the long-range vdW tails.

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"Level 5 plus"
Viewed in the Many-Body Framework

Perturbation theory:

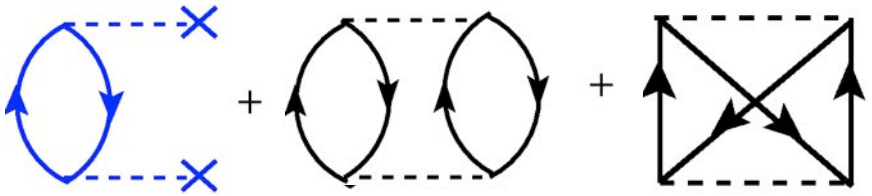
$H = H^0 + H'$ with $H^0|\varphi_n\rangle = E_n^{(0)}|\varphi_n\rangle$ and $|\varphi_n\rangle$ = Slater det.

$|\varphi_0\rangle$ = ground state, $|\varphi_{i,\,a}\rangle$ = single excitations, $|\varphi_{ij,\,ab}\rangle$ = double exci.

$$E_0^{(0)} = \langle\varphi_0|\, H^0\, |\varphi_0\rangle, \qquad E_0^{(1)} = \langle\varphi_0|\, H'\, |\varphi_0\rangle$$

$$E_0^{(2)} = \sum_{n\neq 0} \frac{|\langle\varphi_0|\, H'\, |\varphi_n\rangle|^2}{E_0^{(0)} - E_n^{(0)}} = \sum_{i,\,a} \frac{|\langle\varphi_0|\, H'\, |\varphi_{i,\,a}\rangle|^2}{E_0^{(0)} - E_{i,\,a}^{(0)}} + \sum_{ij,\,ab} \frac{|\langle\varphi_0|\, H'\, |\varphi_{ij,ab}\rangle|^2}{E_0^{(0)} - E_{ij,ab}^{(0)}}$$

single excitations double excitations



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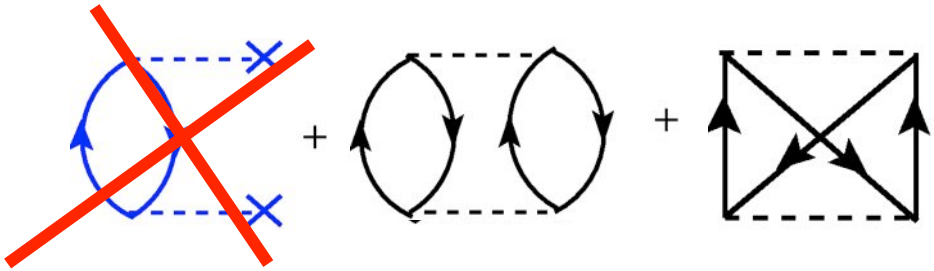
single excitations double excitations

Using HF input, this is Møller-Plesset pertur-bation theory, MP2



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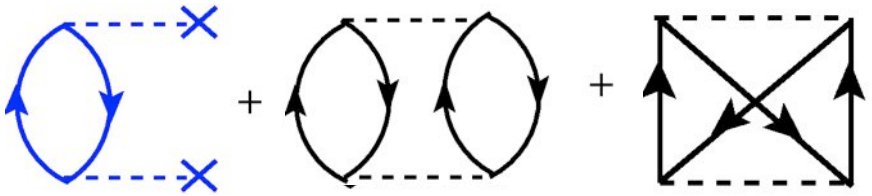
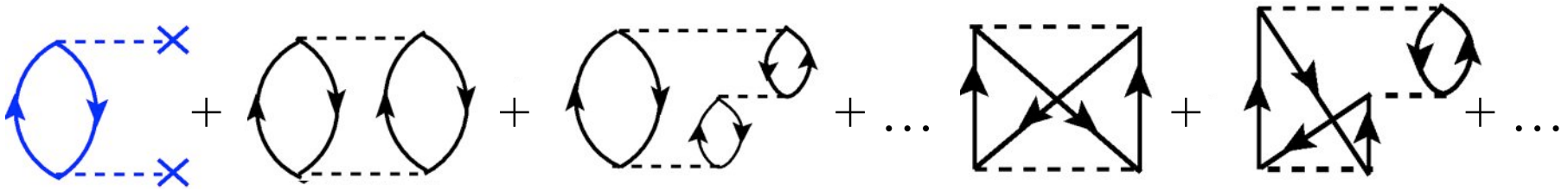


Adding all ring diagrams from higher order perturbations:

X. Ren, et al., Invited Review in J Mater Sci (2012) -- *arXiv: 1203.5536*

Renormalized second order perturbation theory sets the reference. However, it is quite costly and (at present) limited to about 100 atoms.
Can we find a method that is efficient AND accurate?
We need dispersion coefficients with an error ≤ 5%.

Adding all ring diagrams from higher order perturbations:



= single excitations + cRPA + SOSEX

*X. Ren, A. Tkatchenko, P. Rinke, and M.S., PRL **106**, (2011).*

J. Paier, X. Ren, P. Rinke, A. Grüneis, G. Kresse, G. E. Scuseria, M.S., NJP (2012).

X. Ren, et al., Invited Review in J Mater Sci (2012) -- arXiv: 1203.5536

C_6 Coefficients in the TS Scheme (schematic)

S. Grimme: add tails $E_{\mathrm{vdW}} = \Sigma'_{I,J}\, C_{6,I,J} / R^6_{I,J}$

$$C_{6AB} = \frac{3}{\pi}\int_0^\infty \alpha_A(i\omega)\alpha_B(i\omega)d\omega$$

...

$$C^{\mathrm{eff}}_{6AA} = \frac{\eta^{\mathrm{eff}}_A}{\eta^{\mathrm{free}}_A}\left(\frac{\kappa^{\mathrm{free}}_A}{\kappa^{\mathrm{eff}}_A}\right)^2\left(\frac{V^{\mathrm{eff}}_A}{V^{\mathrm{free}}_A}\right)^2 C^{\mathrm{free}}_{6AA}$$

*Chu and Dalgarno, JCP **212** (2004)*

Alexandre Tkatchenko

Calculated by DFT
– on the fly –

C_6 is a functional of the density, $C_6 = C_6[n]$.

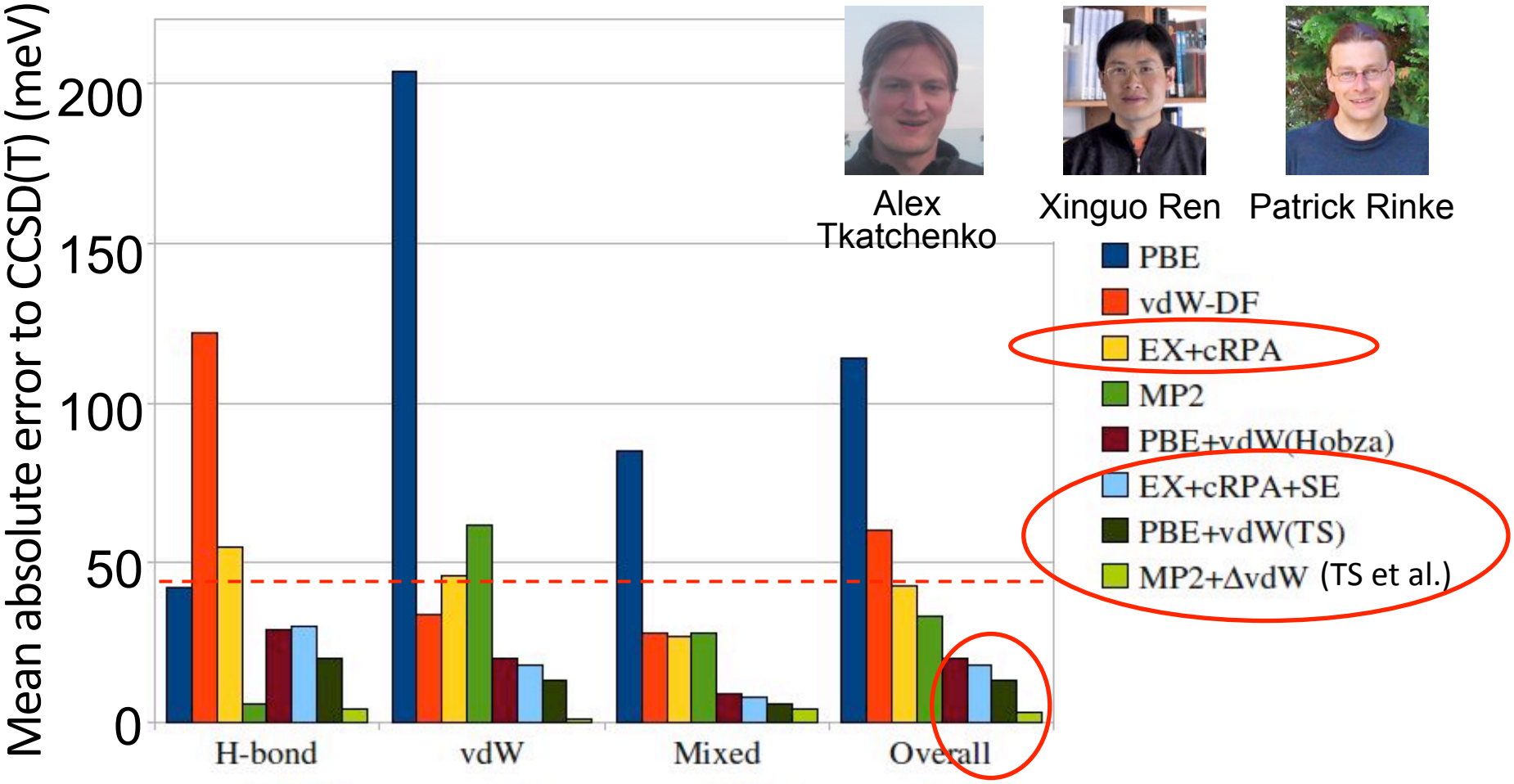
For details, see:

*DFT+vdW: A. Tkatchenko and M.S., PRL **102** (2009).*

MP2+ΔvdW: A. Tkatchenko, R. DiStasio, M. Head-Gordon, and M.S., JCP (2009) .

Excellent description – as long as the "pair-wise model" holds.

Performance for Intermolecular Interactions: S22 Test Set



S22: Jurecka, Sponer, Cerny, Hobza, ***PCCP*** *(2006).*
Langreth-Lundqvist S22: Gulans, Puska, Nieminen, ***PRB*** *(2009); EX+cRPA S22: X. Ren et al.* ***PRL*** *(2011);* ***TS****: A. Tkatchenko and M.S.,* ***PRL*** *(2009); A. Tkatchenko et al.,* ***JCP*** *(2009).*

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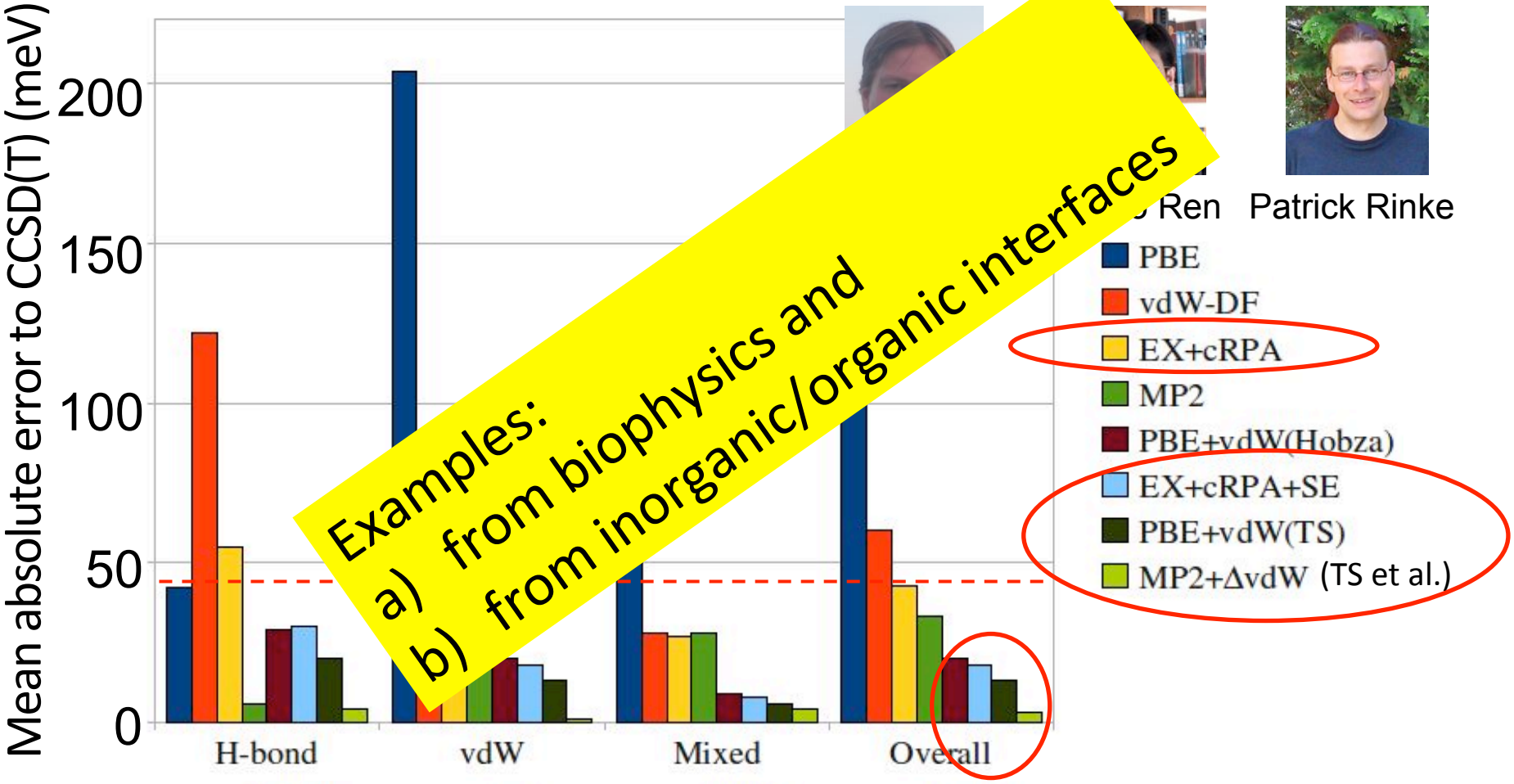

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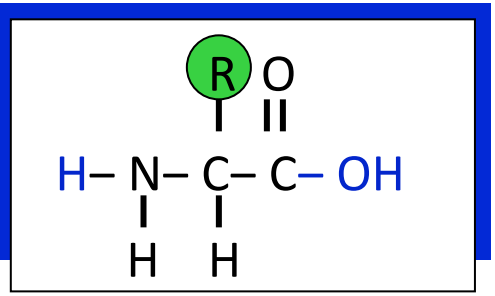
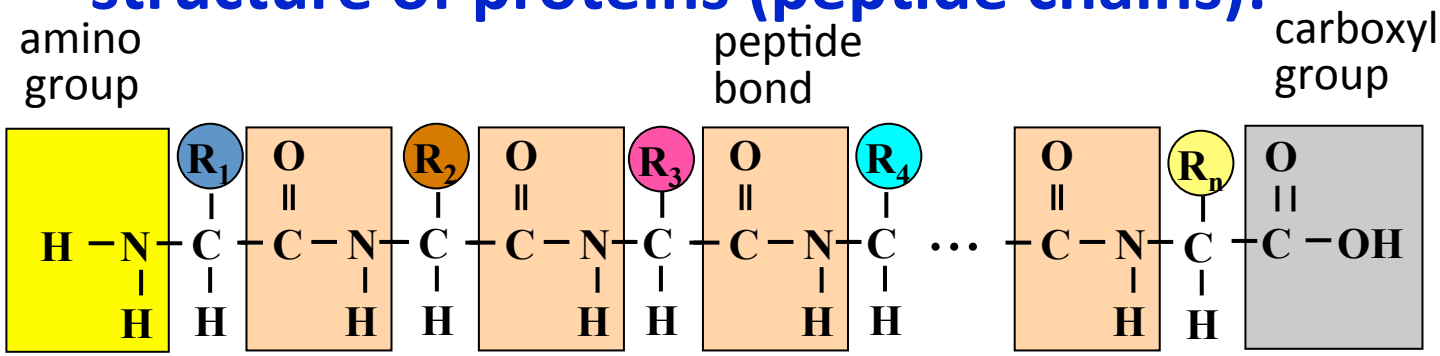
Stability of Secondary Structures

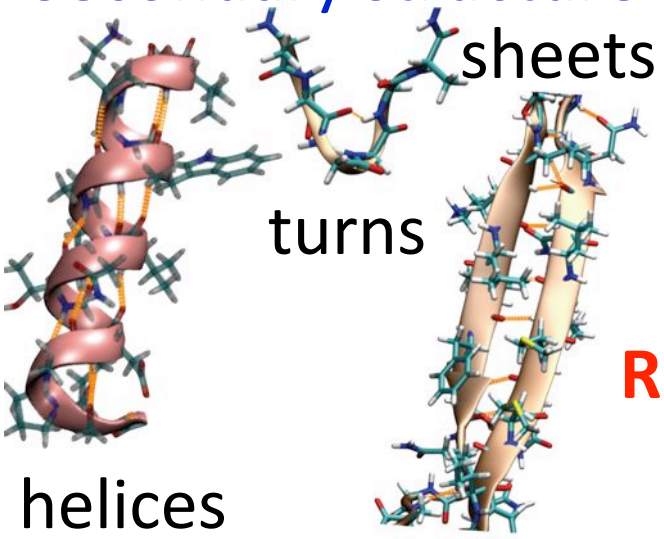


structure of proteins (peptide chains):



Mariana Rossi Carvalho

Secondary structure



R = CH_3 = alanine

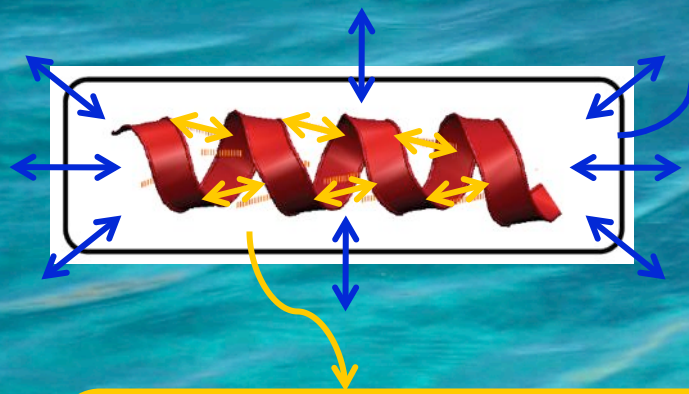
Tertiary structure

Volker Blum

Alexandre Tkatchenko

Secondary Structure from First Principles

Environment



Solute-environment interactions (dieletric, H-bonds, van der Waals, ...)

Intramolecular interactions (H-bonds, electrostatics, van der Waals)

Secondary Structure from First Principles

Intramolecular interactions
(H-bonds, electrostatics,
van der Waals)

Secondary Structure from First Principles

First (necessary) step:

Intramolecular interactions;

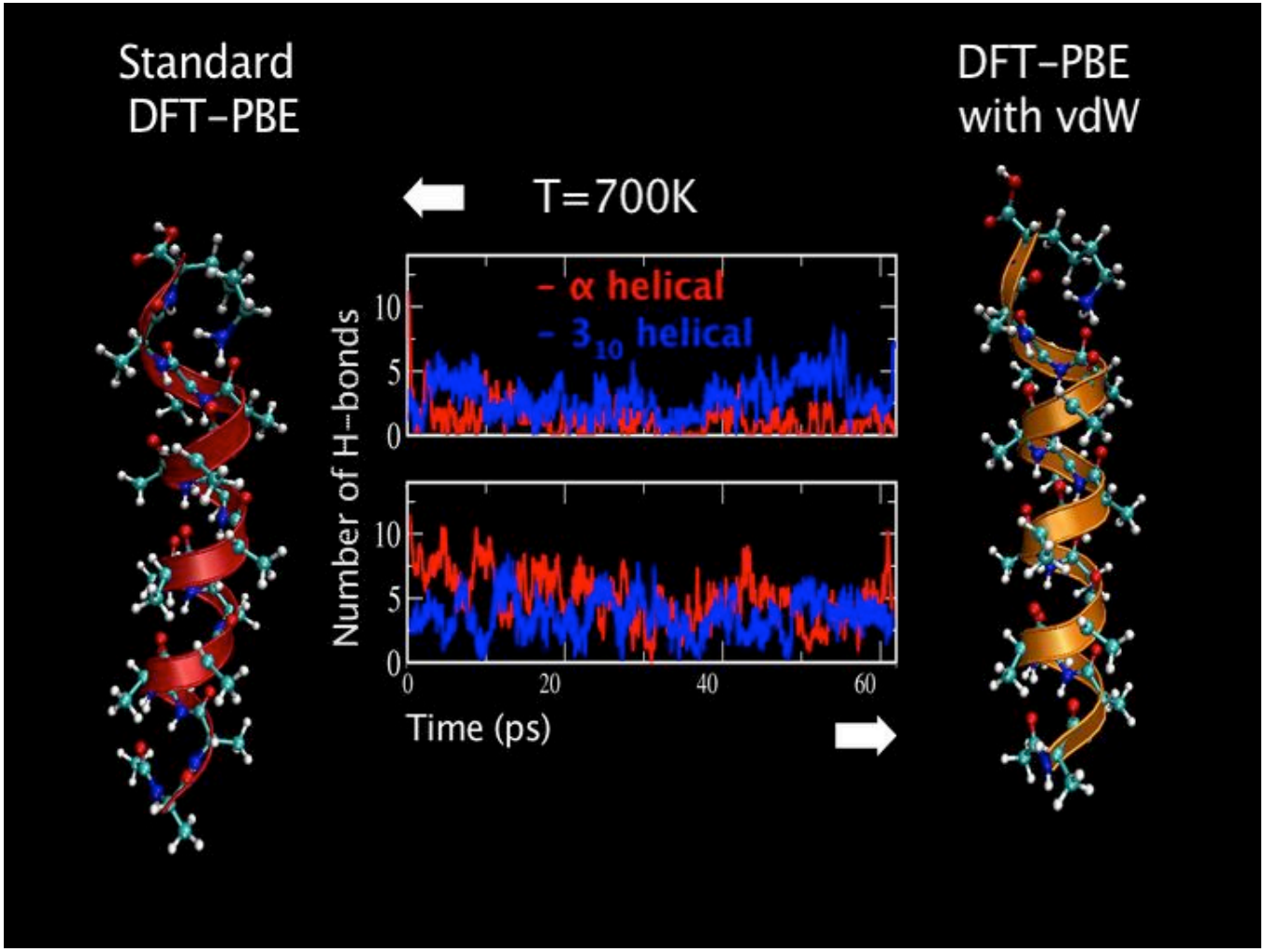
"Clean room" conditions: gas phase

Intramolecular interactions (H-bonds, electrostatics, van der Waals)

In the following: Ac-Ala$_n$-*LysH*$^+$, n = 1…15

Structure prediction: There are several hundred low energy structures

Role of vdW Interaction on (Un)folding; $Ac\text{-}Ala_{15}LysH^{+}$



Mariana Rossi
Carvalho

Volker Blum

Alexandre
Tkatchenko

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

http://www.youtube.com/watch?v=Y_7G8s26zzw

PRL ***106****, 118102 (2011)*

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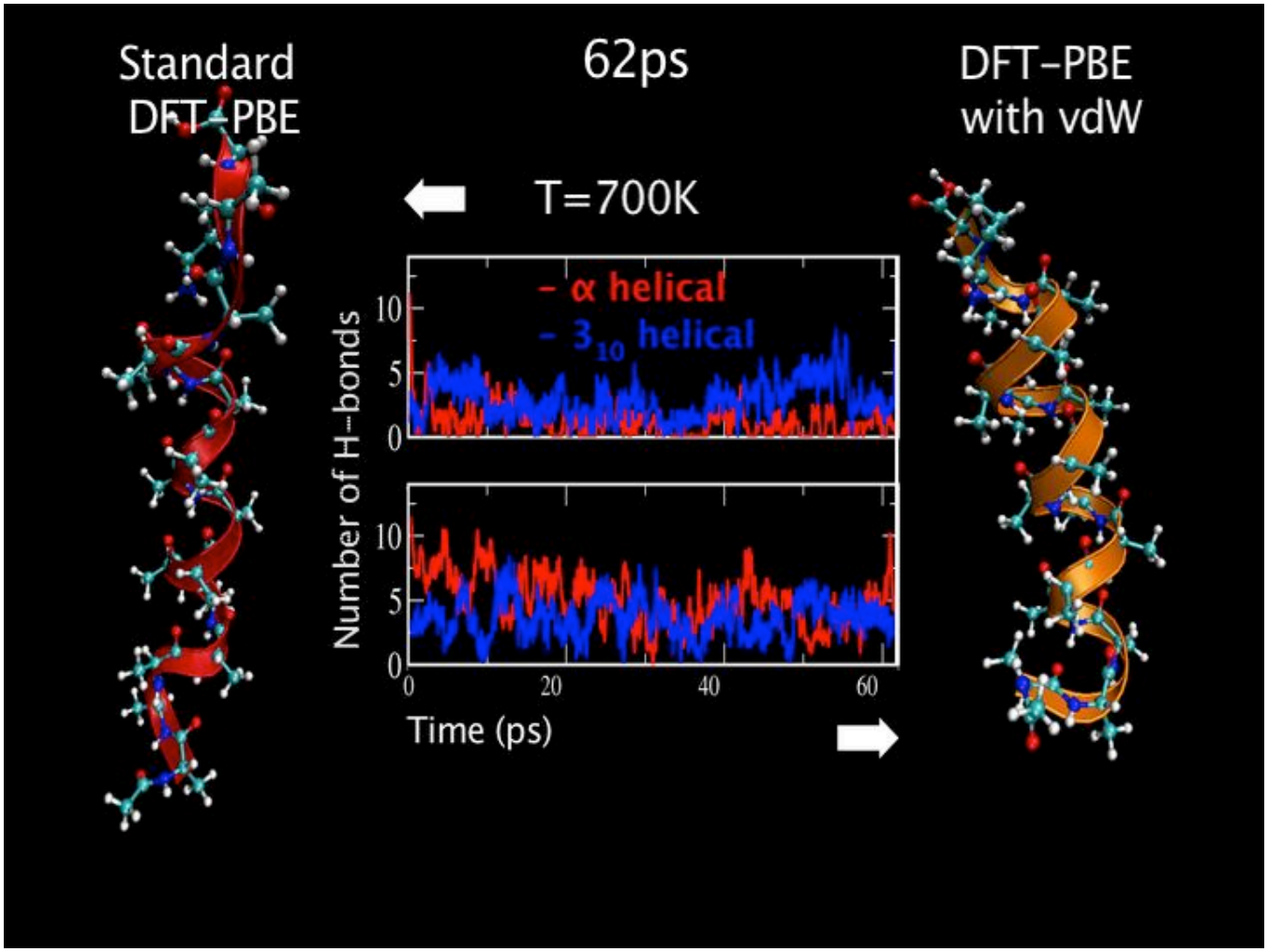

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What Did We Learn from Studying Polypeptides?

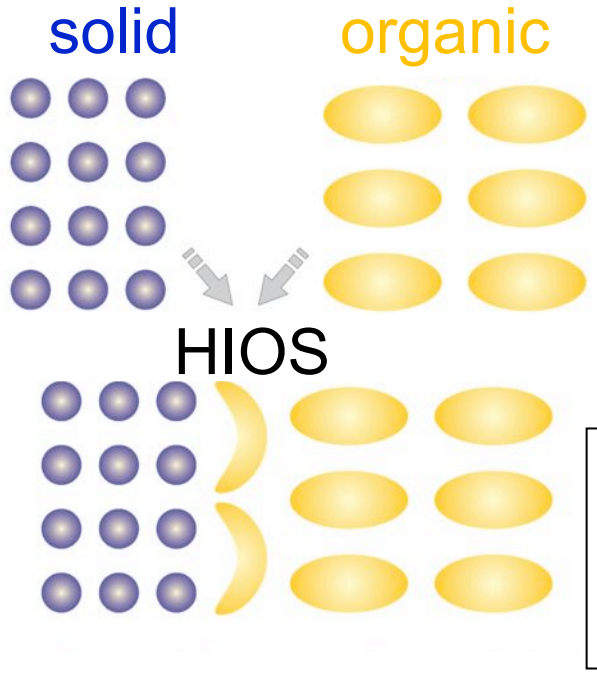
Density-functional theory (PBE+**vdW**) is able to:

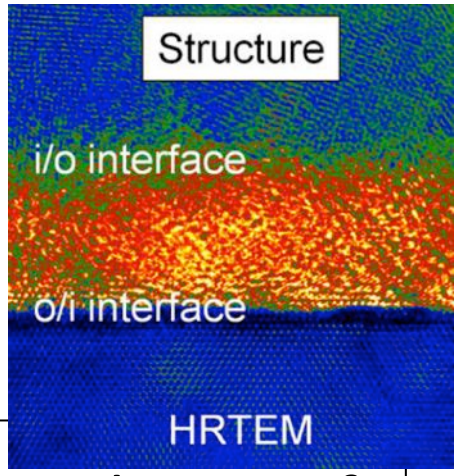
- Predict geometry and properties, analyze stability and unfolding:
  - hydrogen bonding,
  - vdW interaction, and
  - vibrational entropy.
- Verification of structure predictions against experiment (vibrational spectroscopy).

*M. Rossi, V. Blum, et al., JPCL **1** (2010).*
*A Tkatchenko, M Rossi, V Blum, J Ireta, M.S., PRL **106**, 118102 (2011)*

http://www.youtube.com/watch?v=Y_7G8s26zzw

2. Example: Hybrid Inorganic/Organic Systems (HIOS)





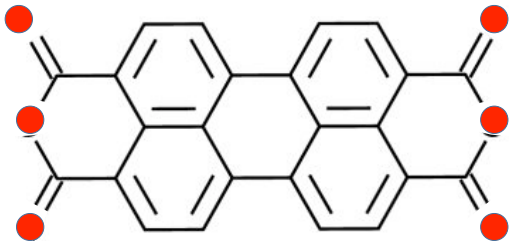
S. Blum-stengel et al.

HIOS: a novel type of material; new physics

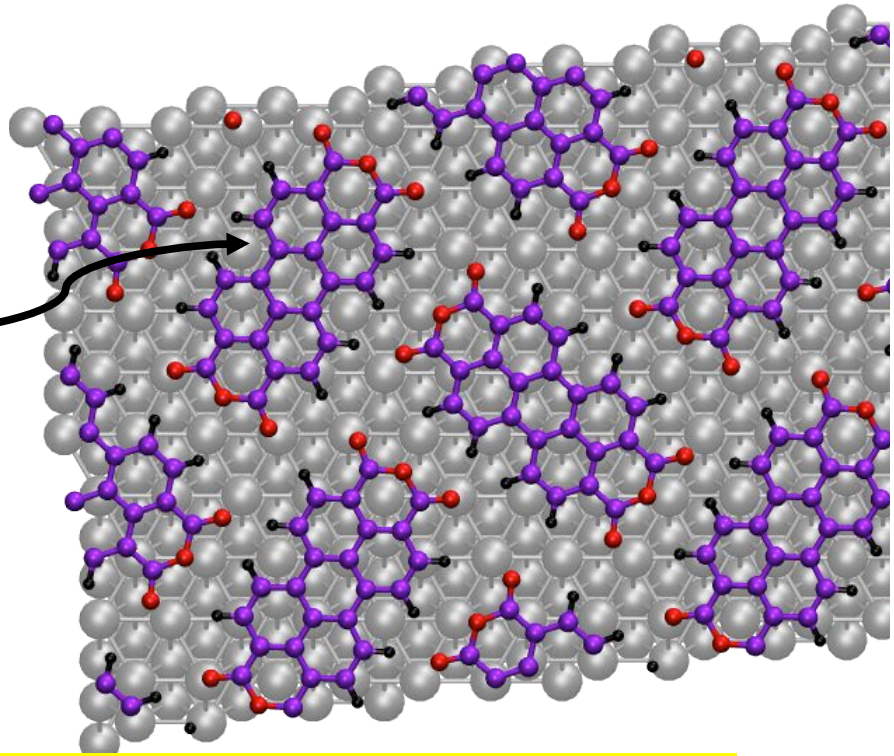
- What is the atomic structure of and at the interface?
- What are the electronic properties?
- What is the nature of charge carriers?

Van der Waals Interactions at Interfaces
The Example of PTCDA @ Me(111)

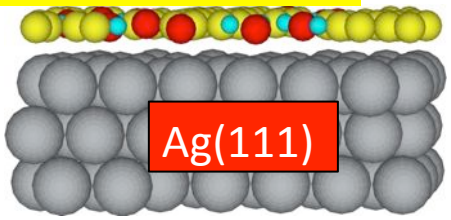
PTCDA



perylene-tetracarboxylic acid dianhydride ($C_{24}H_8O_6$)



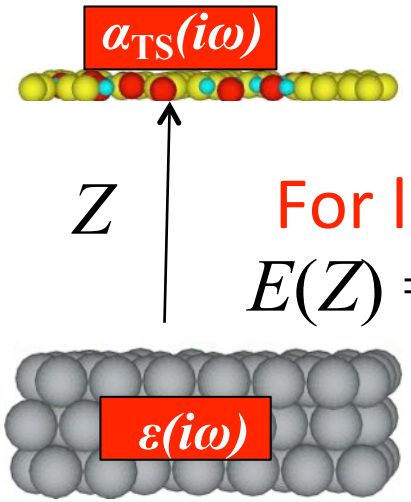
Which Theoretical Method?



Experiment: ***A. Hauschild et al., PRB 81 (2010)***

Theory review: L. Romaner, C. Draxl, et al. NJP (2009); A. Tkatchenko et al., MRS Bulletin (2010)

Molecule @ Metal Surfaces, Correct Long-Range Theory



The interaction energy is not additive; it is not a simple sum over pair-wise interactions.

For large Z:

$$E(Z) = C_3 / Z^3$$

$$C_3 = \frac{1}{4\pi}\int d\omega \alpha(i\omega)\frac{\varepsilon(i\omega)-1}{\varepsilon(i\omega)+1}$$

To be combined with the TS approach:

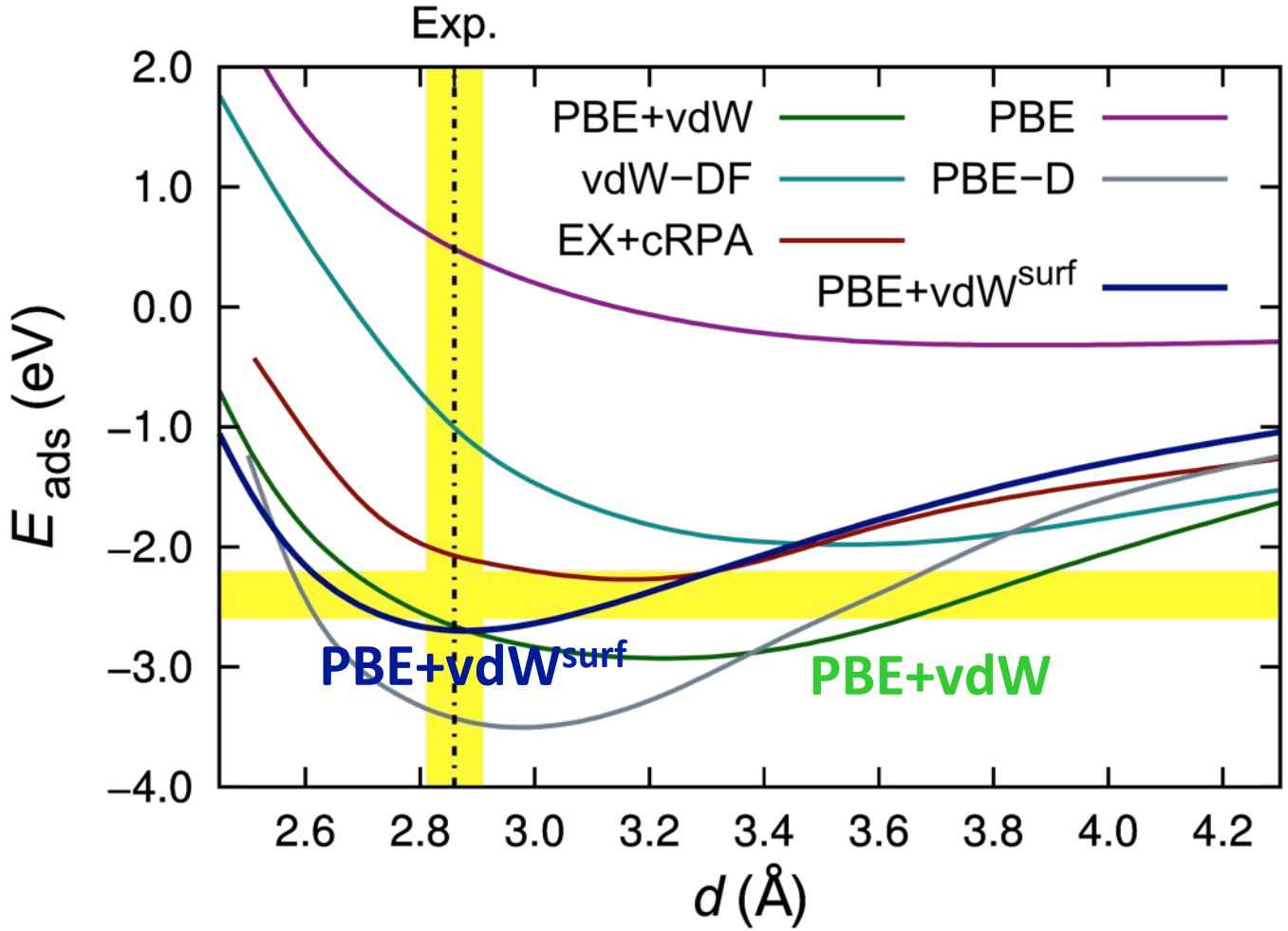
PBE + vdW^{surf}

I. E. Dzyaloshinskii, E. M. Lifshitz, and L. P. Pitaevskii, Adv. Phys. (1961); C. Mavroyannis, Mol. Phys. 6 (1963); A. D. McLachlan, Mol. Phys. 7 (1964); E. Zaremba and W. Kohn, PRB (1976).

*A. Tkatchenko and M.S. PRL **102** (2009).*

*V. G. Ruiz, W. Liu, E. Zojer, A. Tkatchenko, and M.S., PRL **108** (2012).*

PTCDA@Ag(111): PBE+vdW^{surf}



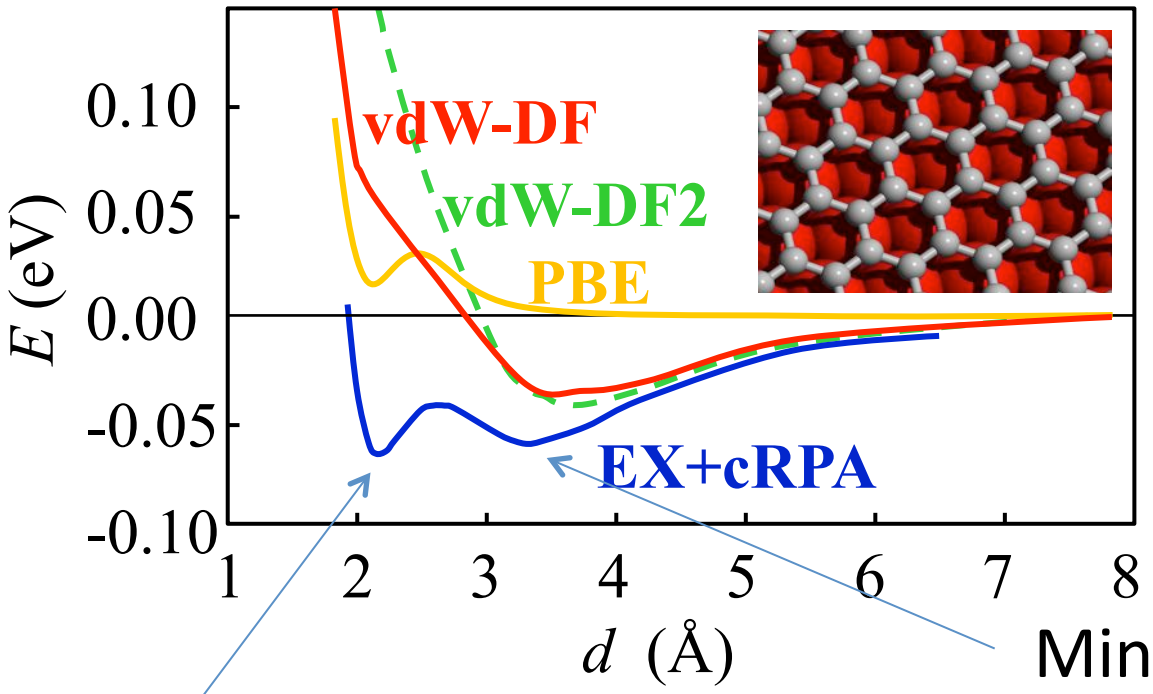

Alex Tkatchenko


Victor G. Ruiz


Egbert Zojer

Experiment: *A. Hauschild et al., PRB* ***81*** *(2010)*
EX+cRPA: *M. Rohlfing and T. Bredow, PRL* ***101*** *(2008).*
V. G. Ruiz, W. Liu, E. Zojer, M. S., and A. Tkatchenko, PRL ***108*** *(2012).*

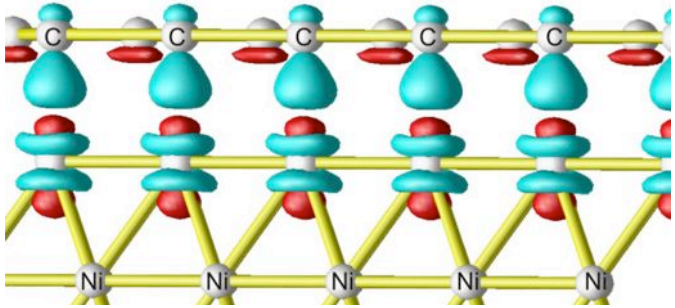
Graphene on Ni(111)
-- a novel bonding mechanism --



*F. Mittendorfer, A. Garhofer, J. Redinger, J. Klimes, J. Harl, G. Kresse, PRB **84** (2011).*

Minimum, actuated by vdW interaction.

Energy lowering due to change of orbital occupation which implies a reduction of EX energy: decrease in d_{z^2} and increase in Ni d_{xz} and d_{yz}.



Summary
Electronic-Structure Theory of Materials

- "Level 5 plus" = second order re-normalized perturbation theory provides a most balanced description of materials.
- For some issues (e.g. energy barriers) we need even better methods as well as self consistency.
- Need more efficient numerics (massive parallel, GPUs, hybrid-core, …)
- **Building a Materials Library of hitherto Unknown Materials**

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novel materials discovery

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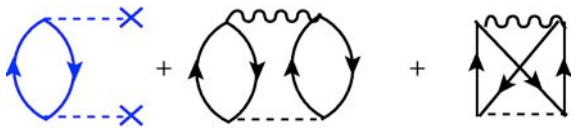
Electronic-Structure Theory of Materials
Where Are We? What Comes Next?

-  "Level 5 plus" = second order re-normalized perturbation theory provides a most balanced description of materials.
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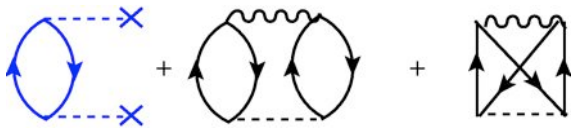
-  "Level 5 plus" = second order re-normalized perturbation theory provides a most balanced description of materials.
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