Density-fitted periodic local MP2. Application to molecular crystals and surface adsorbtion

Denis Usvyat

Institut für Physikalische und Theoretische Chemie, Universität Regensburg
Universitätsstraße 31, D-93040 Regensburg

September 13th, 2007, Dresden

CRYSCOR overview I

Provides a periodic local MP2 solutions on top of the HF reference, provided by the CRYSTAL code.

CRYSCOR takes (from CRYSTAL):

- The information on the **basis set, geometry, symmetry, etc**
- **Density and Fock matrices** of the **periodic HF** solution
- Symmetrized **Wannier functions**

CRYSCOR delivers:

- **periodic LMP2 energy**
- **periodic LMP2 density matrices** (presently without an orbital relaxation)

Density-fitted periodic local MP2. Application to molecular crystals and surface adsorbtion. LCC2007

CRYSCOR overview II

The DFP-LMP2 (**density fitted periodic local MP2**) method comprises:

- Molecular local correlation techniques: **PAOs for virtuals, excitation domains, orbital pairs**
- Extensive use of **symmetry**
- Two-step multipole-constrained **Density Fitting** approximation
- Distant-pair two-electron integrals – via **multipole expansion**
- The **contribution from the very distant pairs** – through evaluation of C_6 parameters

The CRYSCOR crew

Torino	Regensburg
Prof. Cesare Pisani	Prof. Martin Schütz
Dr. Lorenzo Maschio	Dr. Denis Usvyat
Dr. Silvia Casassa	
Migen Halo	

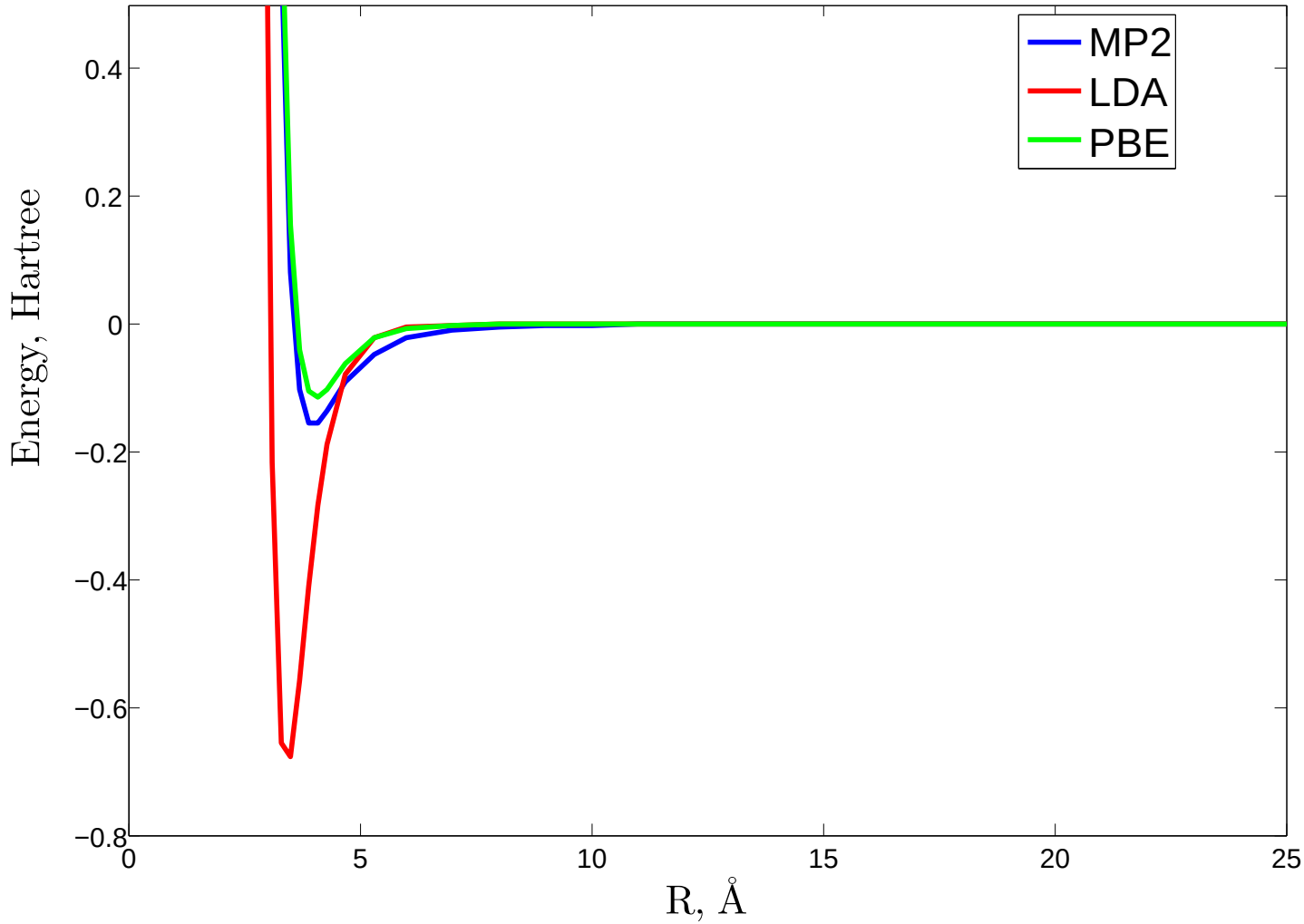
LMP2 and weakly bound systems

- **Unlike DFT LMP2 is able to treat dispersion**, which plays an important role in such systems!

- **Wannier functions are well localized** within the monomers $\Rightarrow$ the periodic LMP2 calculations are relatively not expensive.

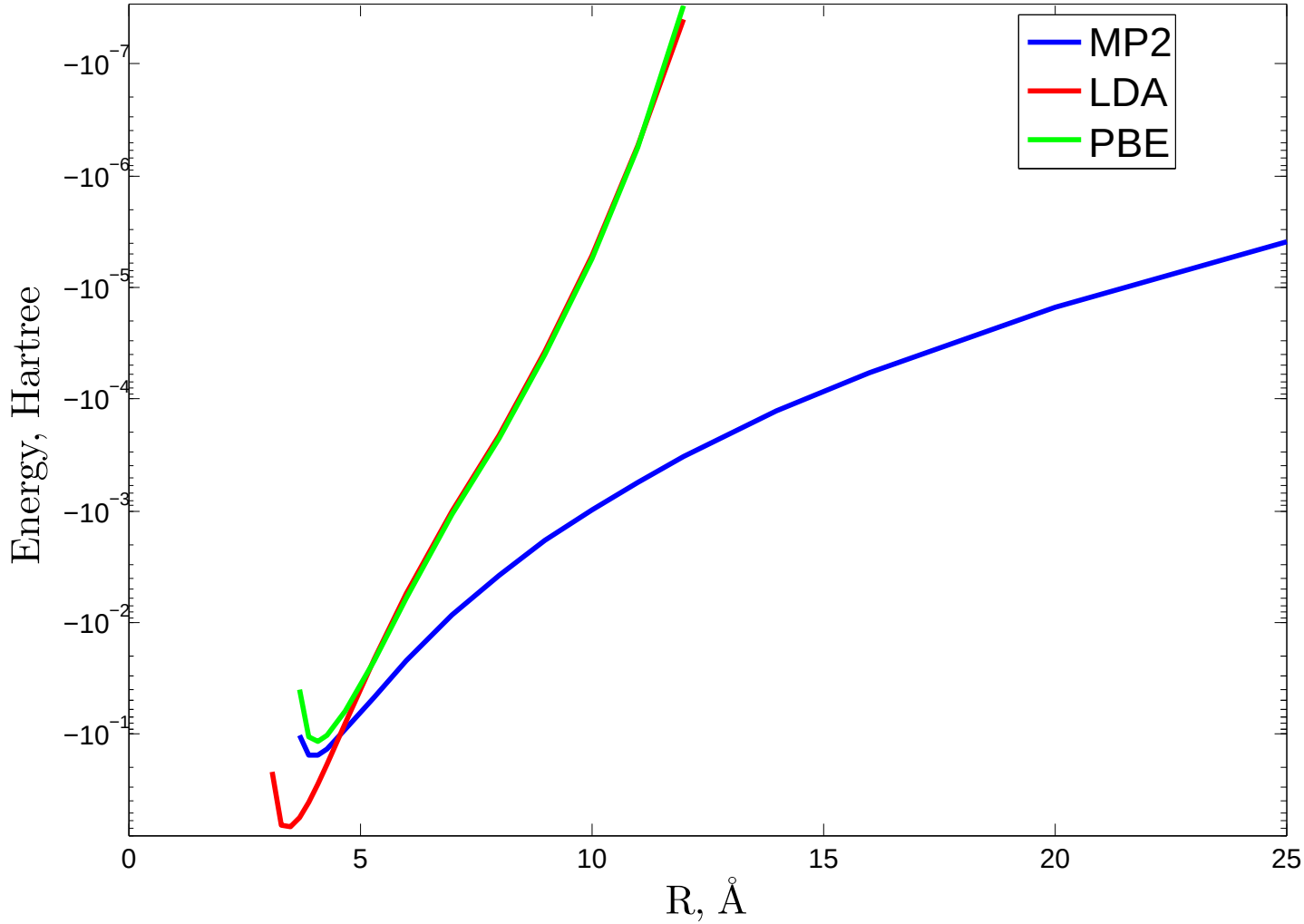
- **However**, for describing the weak binding **large basis sets are needed**.

DFT and dispersion, argon dimer



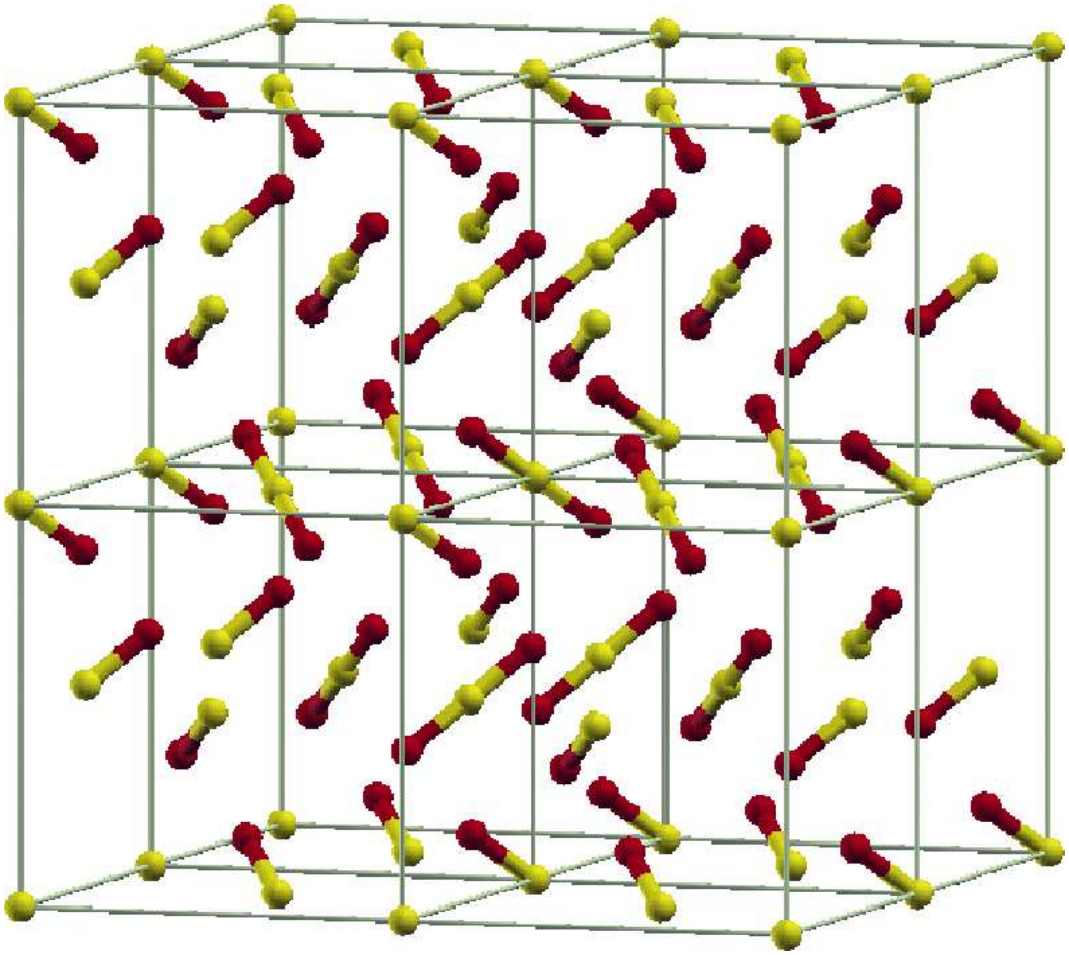
Density-fitted periodic local MP2. Application to molecular crystals and surface adsorbtion. LCC2007

DFT and dispersion, argon dimer



Density-fitted periodic local MP2. Application to molecular crystals and surface adsorbtion. LCC2007

CO_2 crystal



Density-fitted periodic local MP2. Application to molecular crystals and surface adsorbtion. LCC2007

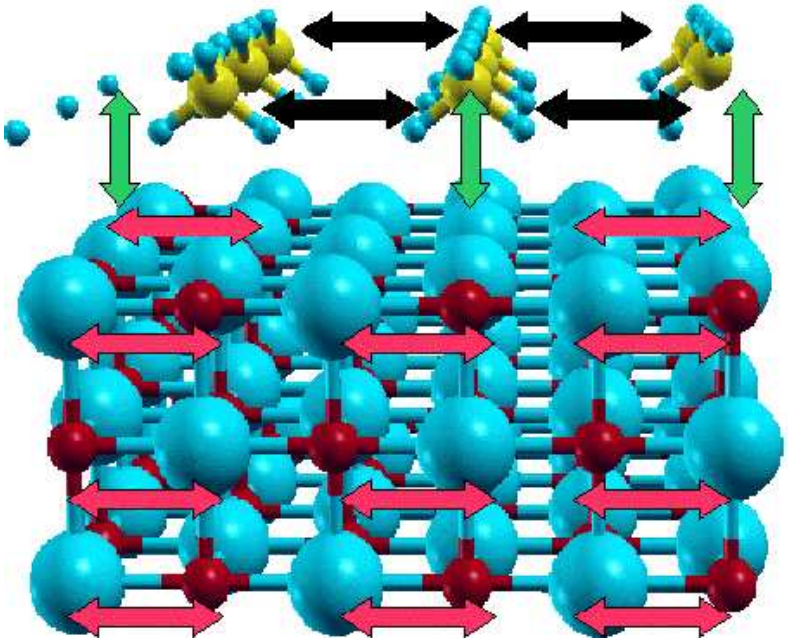
CO_2 crystal

Method	Formation energy kcal mol^{-1}	Lattice constant Å
HF, 6-21G*	2.59	6.09
HF, 6-311G(3D)	1.95	6.13
LDA, 6-21G*	7.46	5.26
LDA, 6-311G(3D)	8.48	5.28
B3LYP, 6-21G*	1.89	6.01
B3LYP, 6-311G(3D)	1.40	6.01
LMP2, 6-21G*	4.51	5.79
LMP2, 6-21G* $\rightarrow$ AVQZ	5.95	5.65
LMP2, 6-311G(3D)	**5.76**	**5.68**
LMP2, 6-311G(3D) $\rightarrow$ AVQZ	6.50	5.63
Experiment	**6.44**	**5.54**

Density-fitted periodic local MP2. Application to molecular crystals and surface adsorbtion. LCC2007

Physisorbtion on a surface.

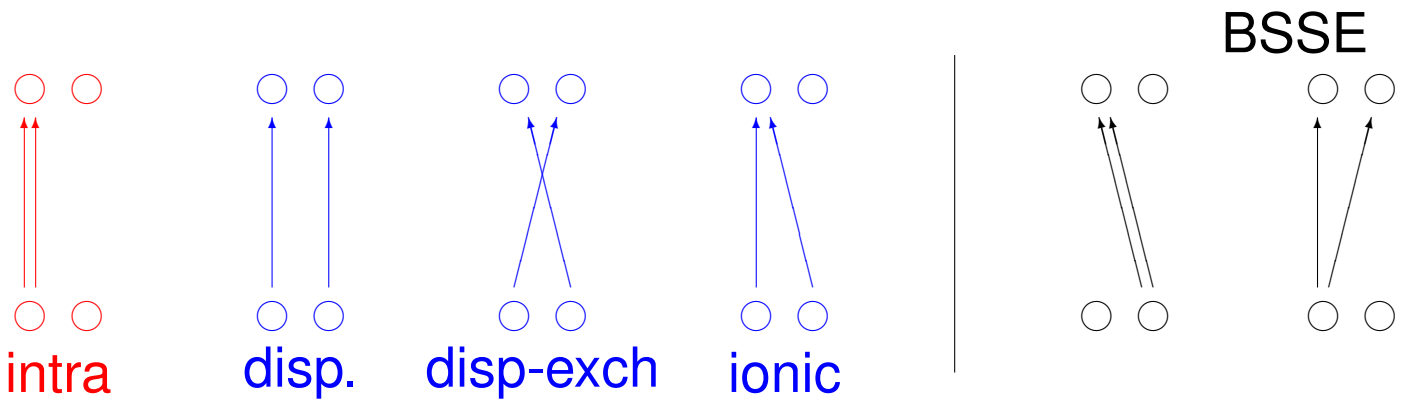
Pair Partitioning



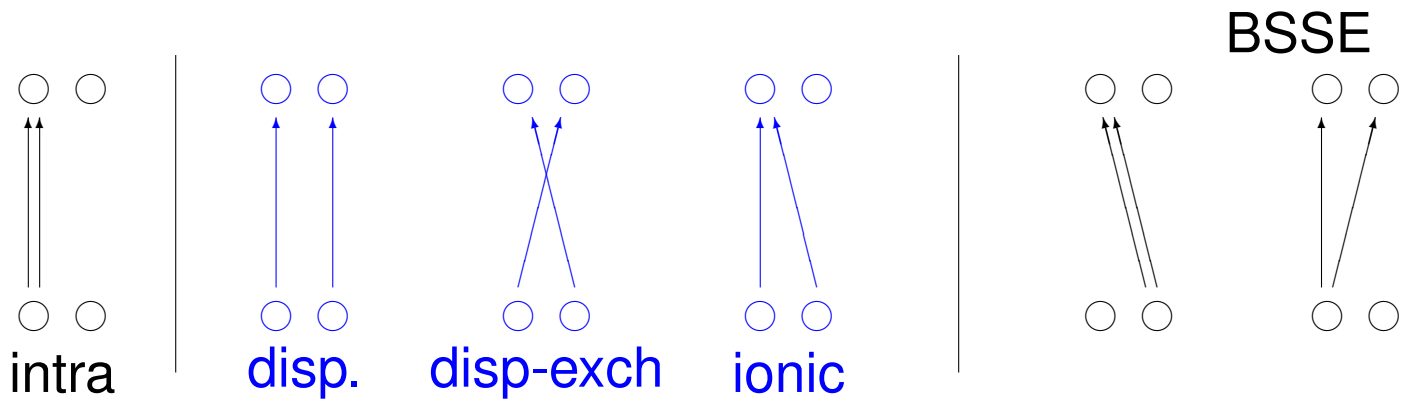
- Adsorbate - adsorbate pairs
- Adsorbate - slab pairs
- Within-slab pairs

New approximation: **Only important pairs** can be included in the calculations.
For example, **only slab-adsorbate pairs** can be taken into account.

What we lose:



What we lose:



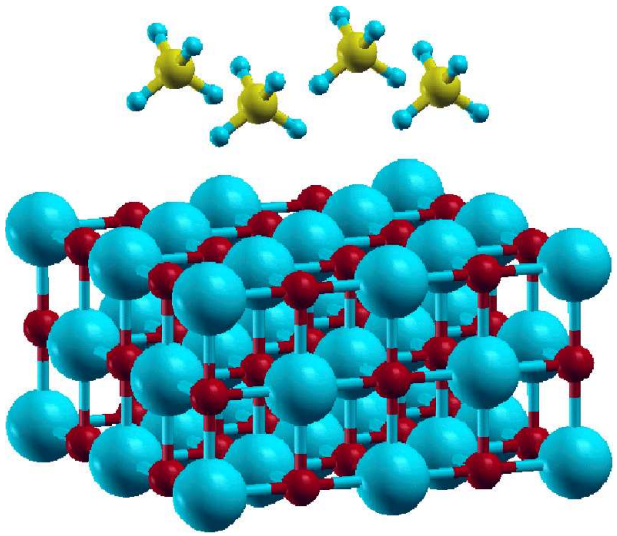
The electrostatic interaction remains at the HF level.

What we gain:

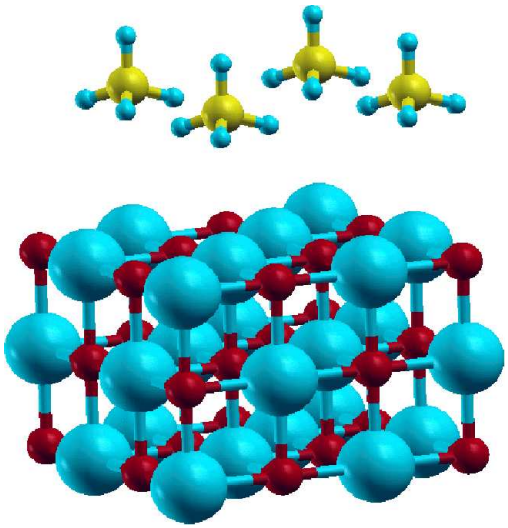
- **If electrostatic interaction doesn't dominate**, the approximation is fairly good. For adsorbtion of methane on MgO its error **is $\approx$0.5 kJ/mol**.
- **This error can be reduced further** by including just few adsorbate-adsorbate and within-slab pairs.
- The calculations become **essentially less consuming** without a large loss in accuracy.
- **No LMP2 BSSE** by construction.
- Possibility to treat molecular **adsorbtion on metallic surfaces**.

Methane on MgO

Dipod

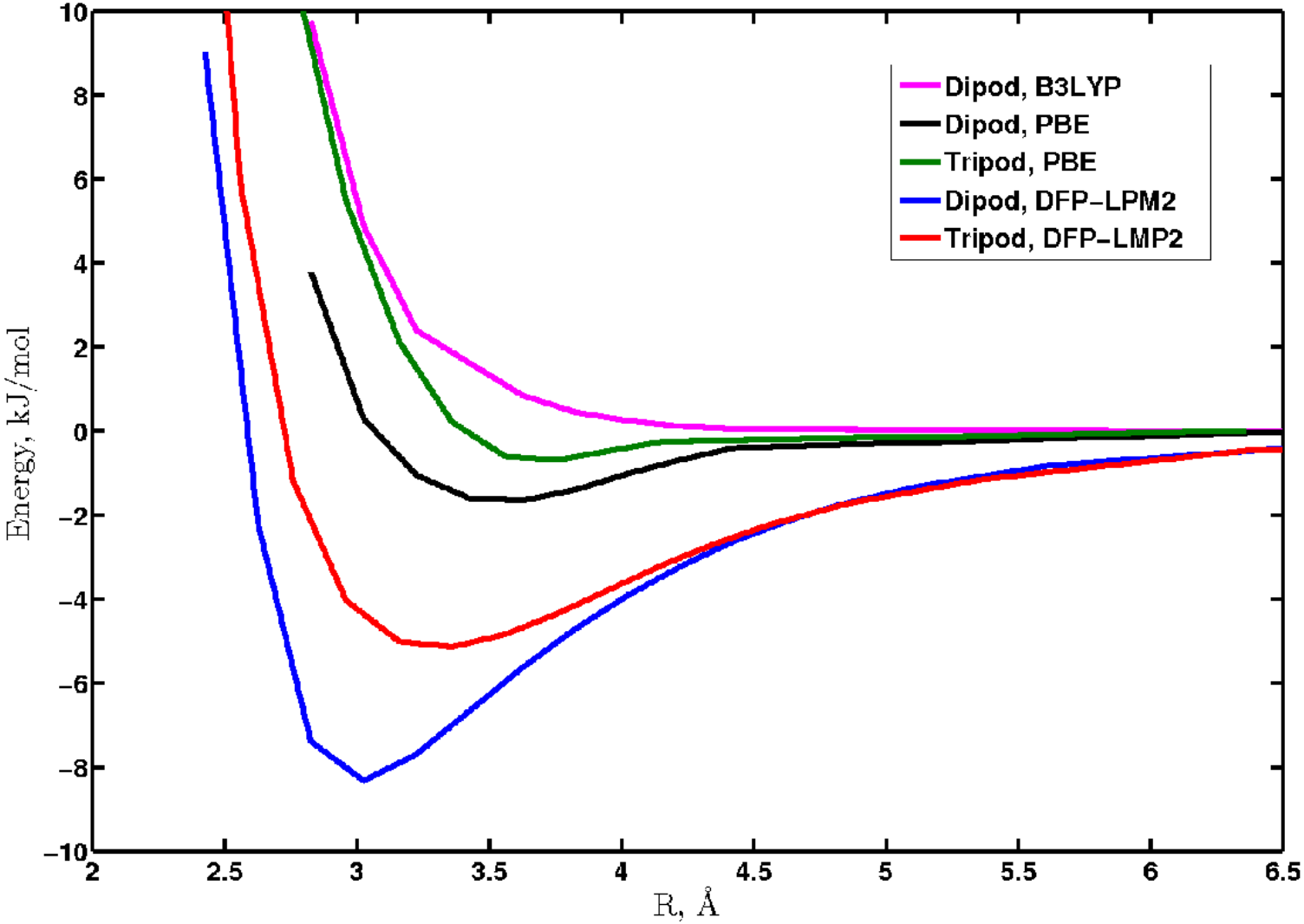


Tripod



Density-fitted periodic local MP2. Application to molecular crystals and surface adsorbtion. LCC2007

Methane on MgO



Density-fitted periodic local MP2. Application to molecular crystals and surface adsorbtion. LCC2007

Methane on MgO

Method	Preferable structure	Adsorption energy, kJ/mol
Semiempirical	Tripod	
PCI-extrapolated MCPF Methane on MgO cluster*	Dipod	8
DFT**	Dipod	
DFP-LMP2, 8-511G*(MgO)/6-311G(3d)(CH_4)	**Dipod**	**10.1**
Experiment	**Dipod**	**13.1**

*K. Todnem, K. J. Borve, M. Nygren, Surf. Sci. 421, 296 (1999)

**M. L. Drummond, B. G. Sumpter, W. A. Shelton, and J. Z. Larese, Phys. Rev. B 73, 195313 (2006)

Physisorbtion on a metallic surface

- HF is bad for metals
- MP2 is totally inappropriate for metals

But

- We are not interested in the metal but rather in the adsorbtion on it.
- DFT for dispersion is worse than HF for a metal.
- Adsorbate layer does not conduct

Therefore

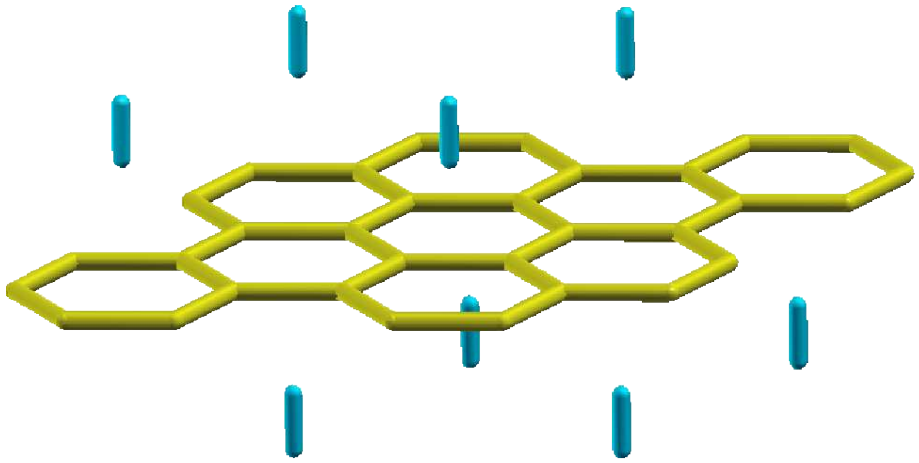
We can try to model the dispersion by MP2 by considering only the slab-adsorbate (and if needed adsorbate-adsorbate pairs)

Density-fitted periodic local MP2. Application to molecular crystals and surface adsorbtion. LCC2007

H_2 on graphene

H_2 physisorbed on graphene.

(A common work with together with Thomas Heine and Lyuben Zhechkov in the context of hydrogen storage)

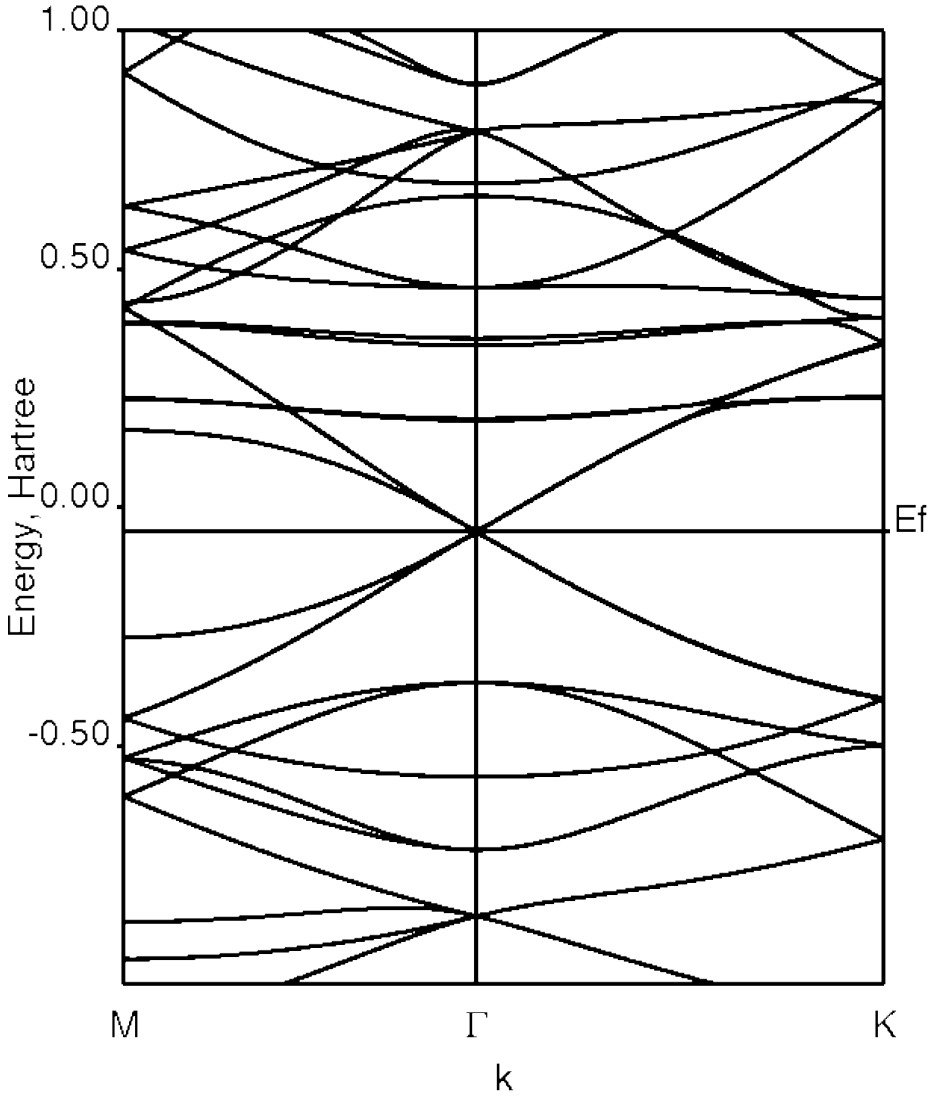


R.H. Lochan and M. Head-Gordon, PCCP, 8, 2006

H_2 on graphene

Graphene is a metal (semimetal)...

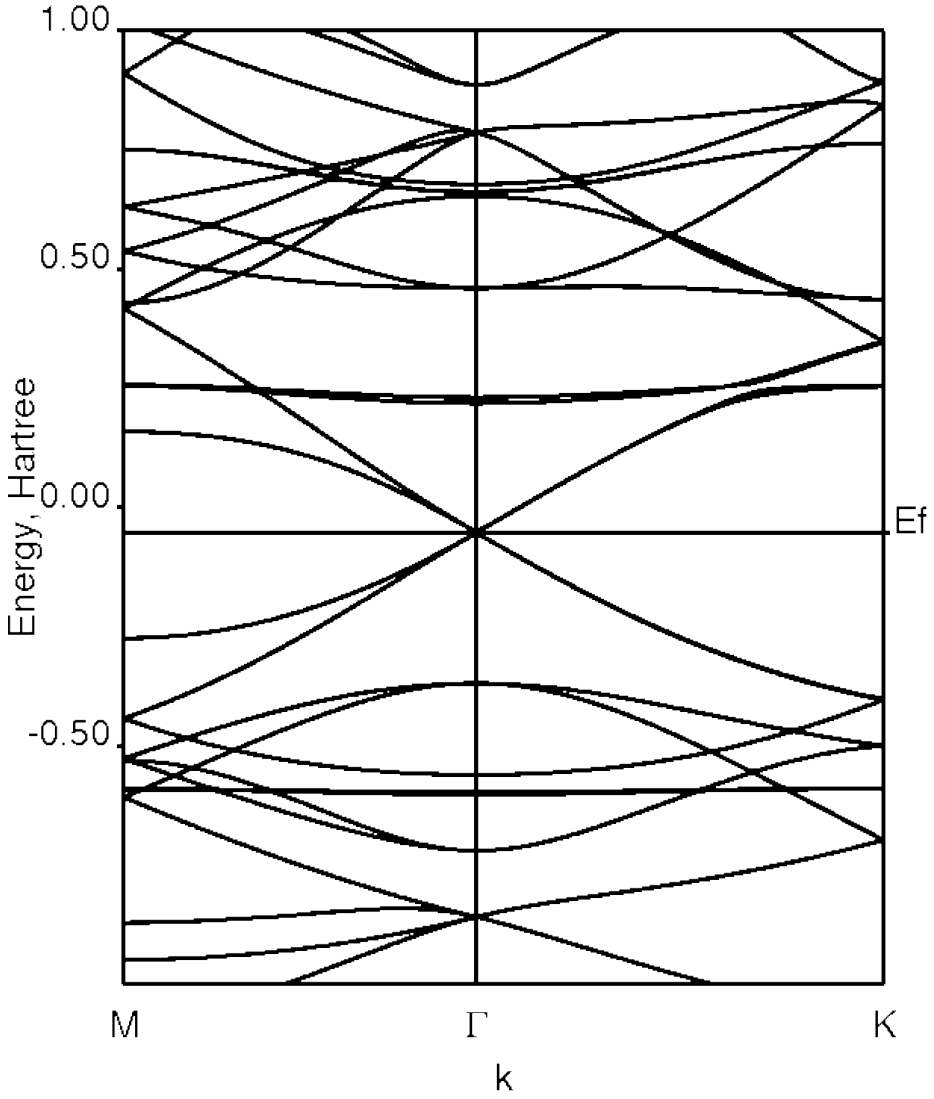
Band structure of graphene



H_2 on graphene

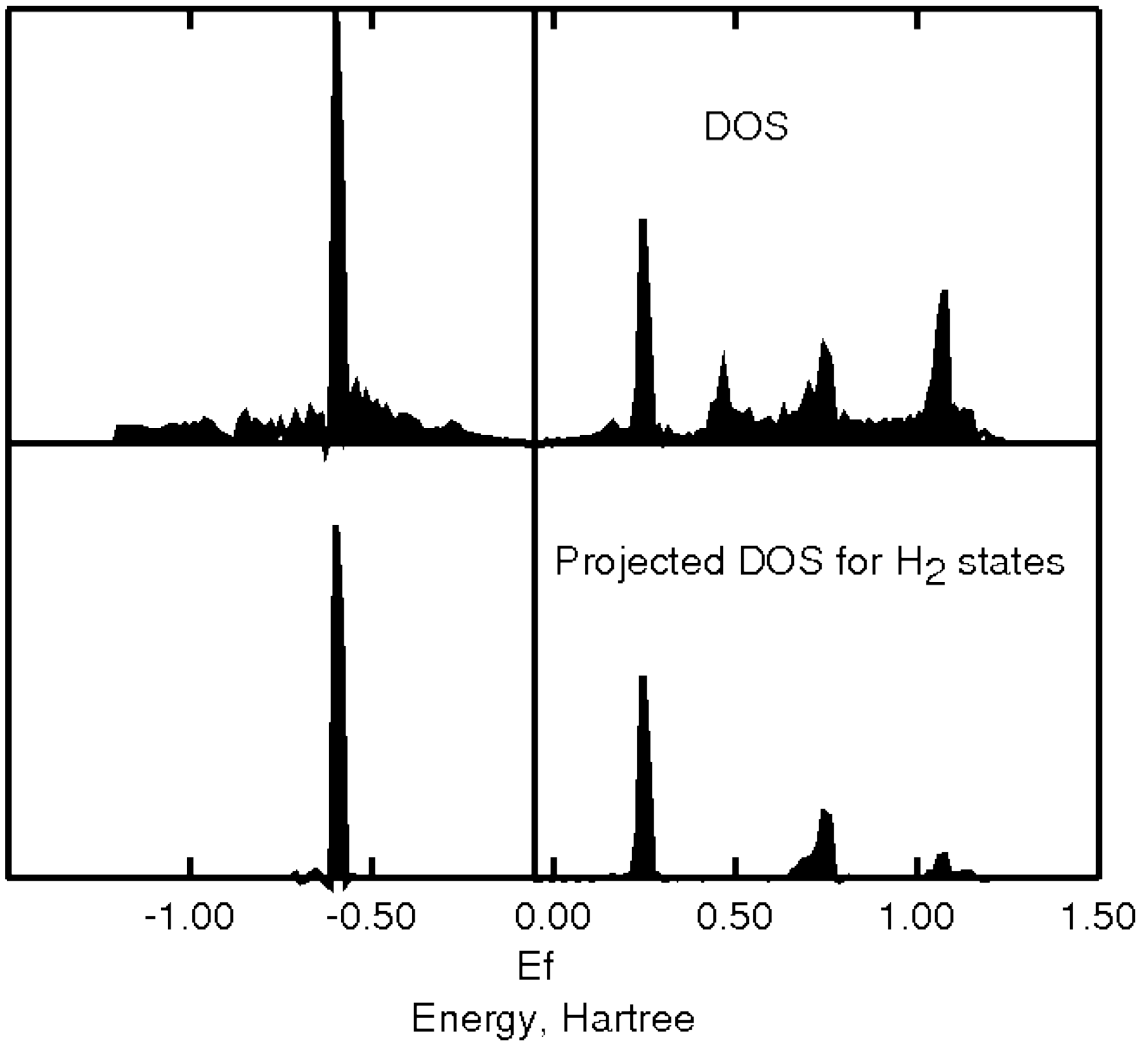
But the states of the adsorbed H_2 molecules form narrow bands with a band gap!

Band structure of H_2 on graphene



Density-fitted periodic local MP2. Application to molecular crystals and surface adsorbtion. LCC2007

DOS of H_2 on graphene

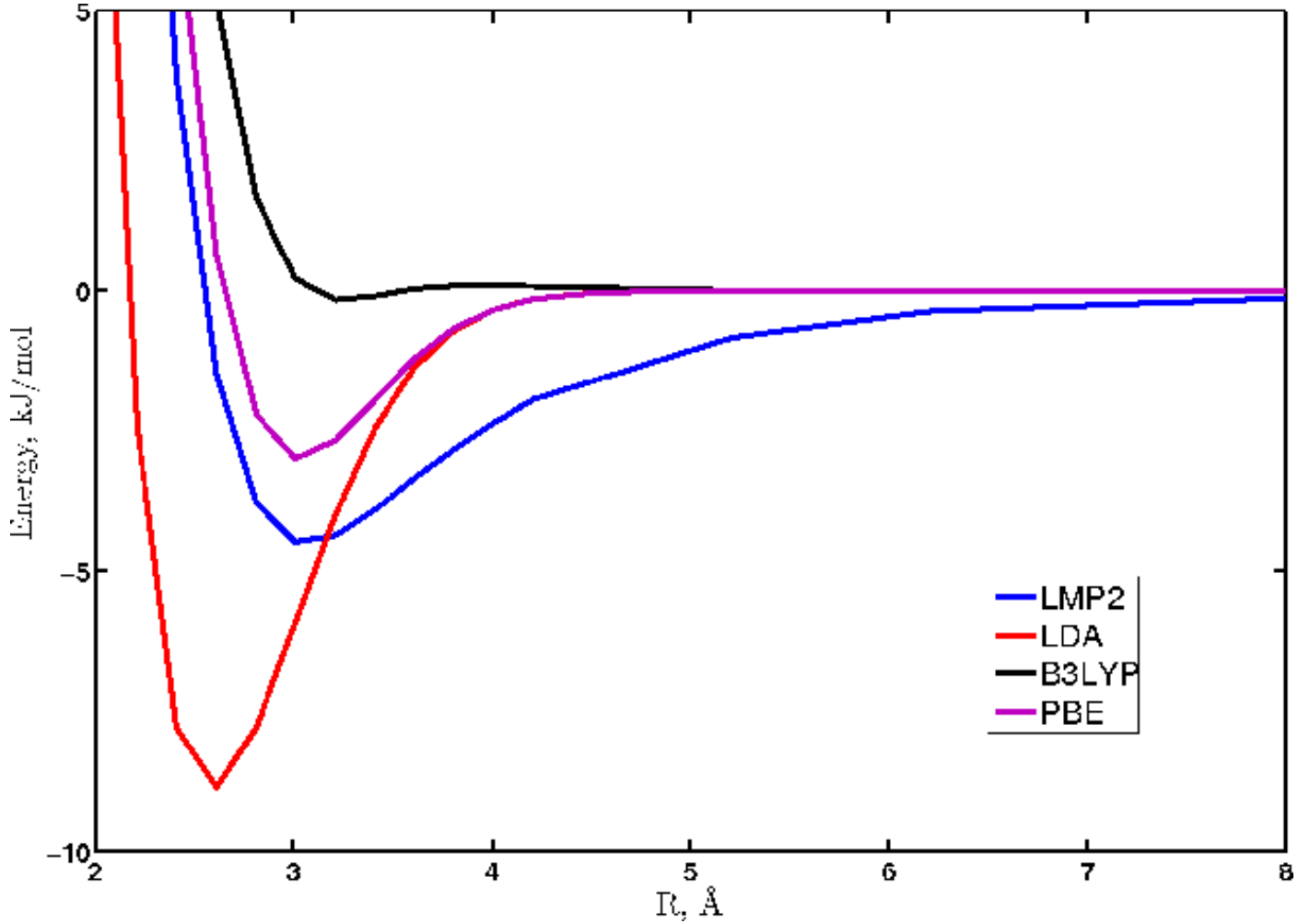


Density-fitted periodic local MP2. Application to molecular crystals and surface adsorbtion. LCC2007

H_2 on graphene

So the LMP2 method can be applied for H_2 physisorbed on graphene if within-slab pairs are not included.

H_2 on graphene



Density-fitted periodic local MP2. Application to molecular crystals and surface adsorbtion. LCC2007

Adsorbtion energies for H_2 on graphene and related structures

System	Method	Adsorption energy, kJ/mol
MP2/6-31G	H_2 on benzene	1
*MP2/6-311G**	H_2 on benzene	2.1
*MP2/aug-cc-pVQZ	H_2 on benzene	5
*MP2/aug-cc-pVQZ	H_2 on coronene	6.4
Experiment	H_2 on graphene	5
LMP2/6-31G*(C)/6-311G(H)**	**H_2 on graphene**	**2.4**

* *T. Heine, L. Zhechkov, G. Seifert, PCCP* **6** *(2004)*

Timings for DFP-LMP2 calculations

System and basis set	CPU time for HF, sec	CPU time for DFP-LMP2, sec
CO_2 crystal, 6-21G*	30	3500
CO_2 crystal, 6-311G(3d)	300	17000
CH_4 on MgO, 6-311G(3d)/8-511G*	4500	9500
H_2 on graphene, 6-311G**/6-31G*	700	5000

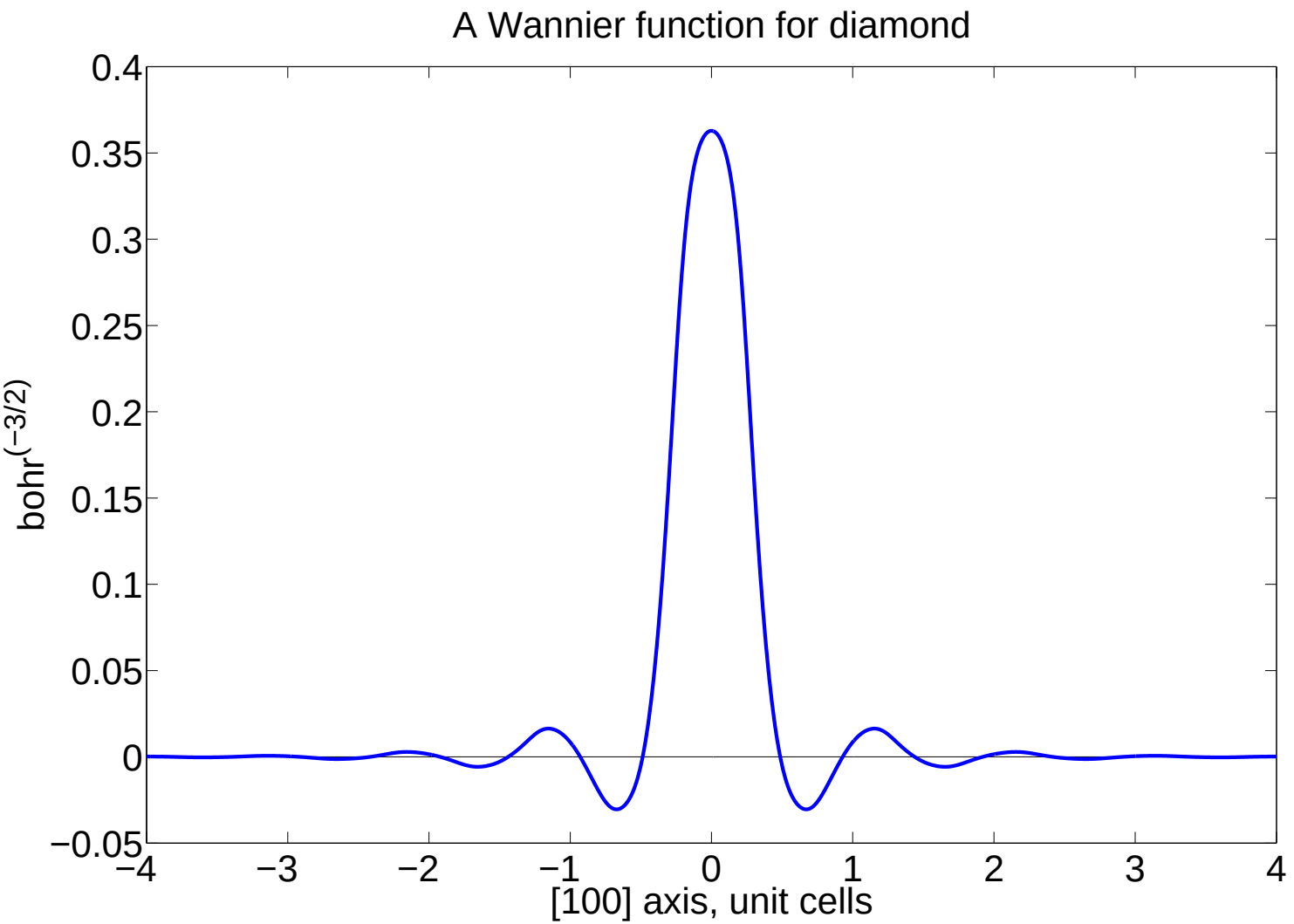
Conclusions and outlook

The DFP-LMP2 method, implemented in CRYSCOR code is evidently a **convenient and reliable tool** in studying weakly bound periodic systems.

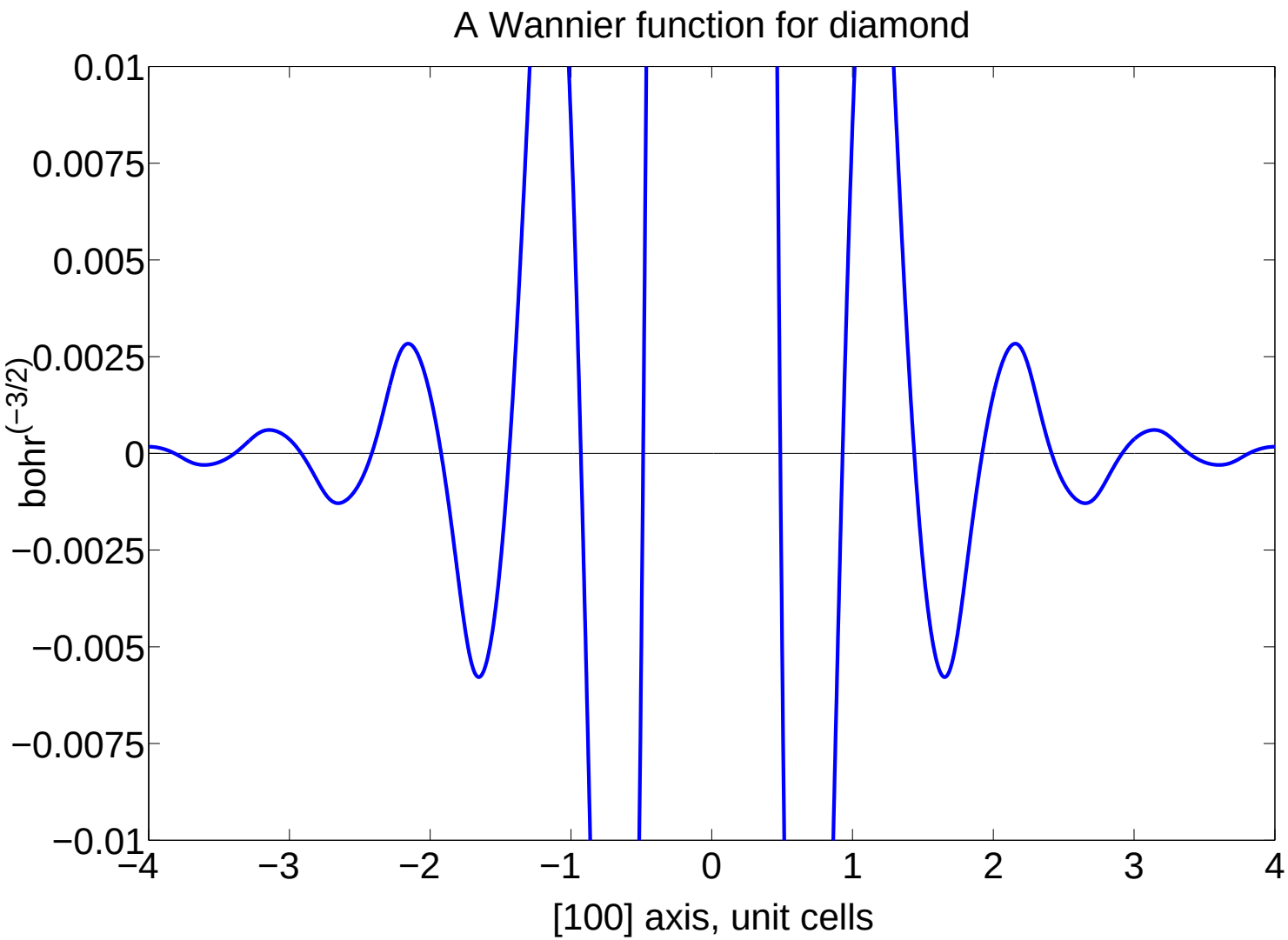
Problems:

- A need for larger basis sets $\Rightarrow$ **dual basis sets**, **F12-technique** (work in progress).
- Poorly localized Wannier functions in conducting slabs $\rightarrow$ Utilization of **finite-support Wannier functions**.

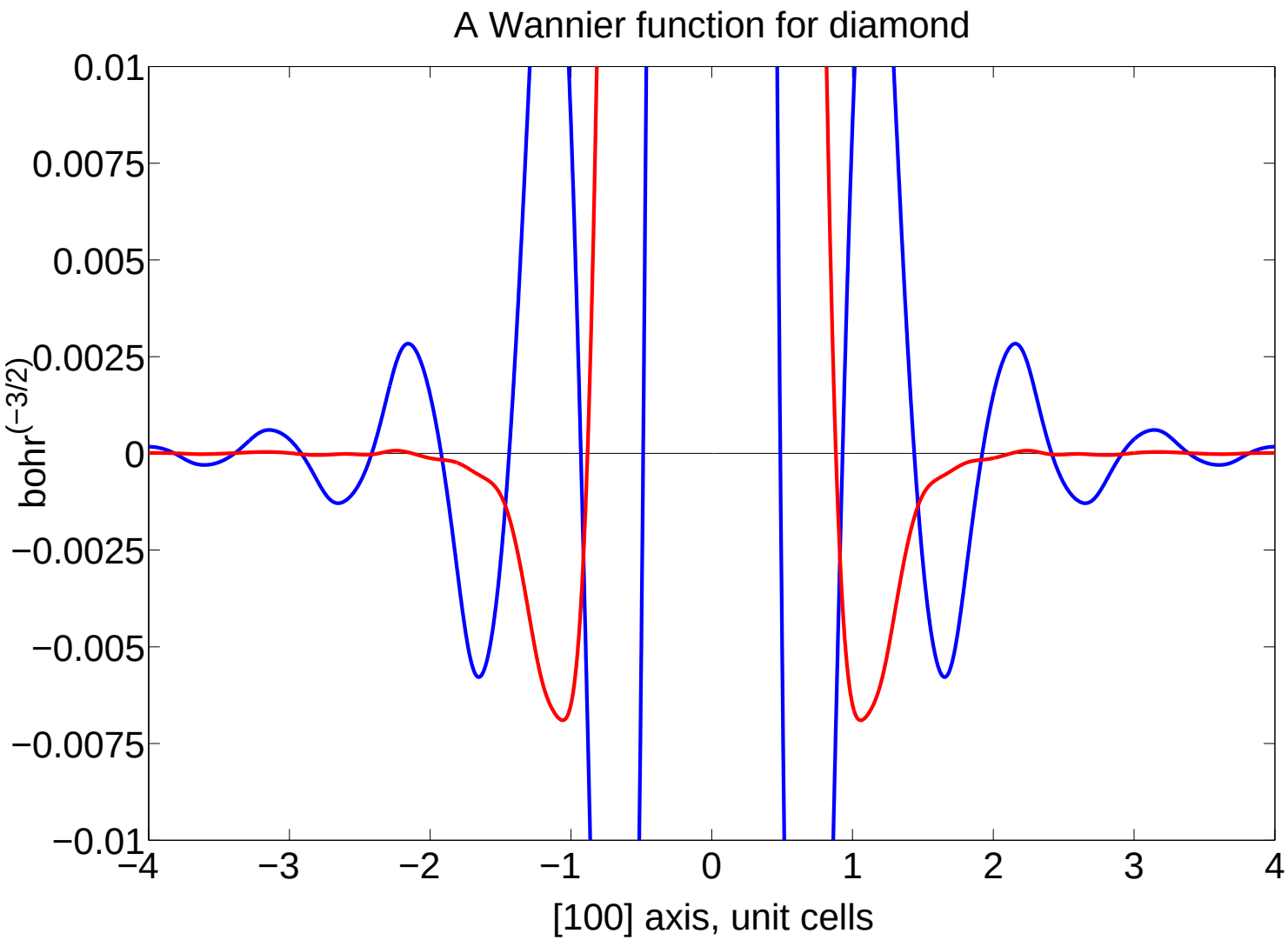
Localization of Wannier function



Localization of Wannier function



Localization of Wannier function



D. Usvyat and M. Schütz, TCA (2005)

Density-fitted periodic local MP2. Application to molecular crystals and surface adsorbtion. LCC2007

Acknowledgments

LCC207 organizers.

My collaborators:

- Regensburg theory group:
  Prof. Martin Schüetz
  Keyarash Sadeghian
  Danylo Kats
  Dominik Schemmel

- Cryscor Group in Torino:
  Prof. Cesare Pisani
  Dr. Lorenzo Maschio
  Dr. Silvia Casassa Migen Halo

Financial support from DFG