



The Method of Increments

A Wavefunction-based Correlation Methods for Solids and Surfaces

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0 Overview

1 Introduction

2 Method of increments

General formalism

3 Extension to metals

Results for group 2/12 metals

4 Extension to absorption on surfaces

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Results for H₂S adsorption on graphene

5 Summary and Outlook

1 Introduction

Aim: Ab initio calculation of the electronic correlations in solids with wavefunction-based quantum chemical methods

Electronic Hamiltonian (in atomic units):

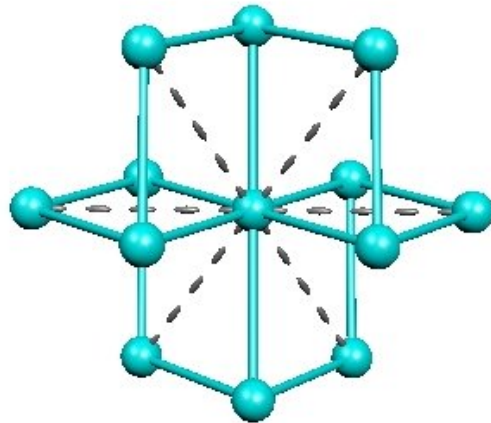
$$H = \sum_i \left(-\frac{1}{2} \Delta_i - \sum_{\alpha}^K \frac{Z_{\alpha}}{|\vec{r}_i - \vec{R}_{\alpha}|} \right) + \frac{1}{2} \sum_{i \neq j} \frac{1}{|\vec{r}_i - \vec{r}_j|}$$

Solving the problem in an effective single-particle picture:

Density-Functional Theory (DFT)

Lattice parameters for Hg

Rhombohedral
lattice structure:



	$a(\text{Å})$	$\alpha(^{\circ})$	$E_{\text{coh}}(\text{eV})$	$\frac{a(\text{n}2)}{a(\text{nn})}$
B3LYP	3.894	89.5	-0.044	1.408
PW91	3.535	61.2	-0.195	1.015
BP86	3.539	63.7	-0.078	1.044
PBE	3.540	60.9	-0.164	1.014
LDA	2.971	72.6	-0.918	1.182
Expt	3.005	70.53	-0.67	1.153

N. Gaston et al, Phys. Rev. B 74, 094102 (2006)

Hartree-Fock treatment for metals

Calculations with CRYSTAL, R. Dovesi et al. University of Torino

$E_{\text{coh}}(\text{eV})$	Mg	Zn	Cd	Hg
HF	-0.27 ¹	+0.09	+0.25	+0.98
Expt	-1.50	-1.37	-1.16	-0.67

¹ I. Baraille et al, J. Phys. Condens. Matter 10, 10969 (1998)

subsequent many-particle treatment possible
wavefunction-based (quantum chemical) correlation methods

2 Method of increments

How to apply quantum chemical correlation methods to infinite systems?

Idea: Electronic correlations are of short range: Far away electrons interact only via mean-field

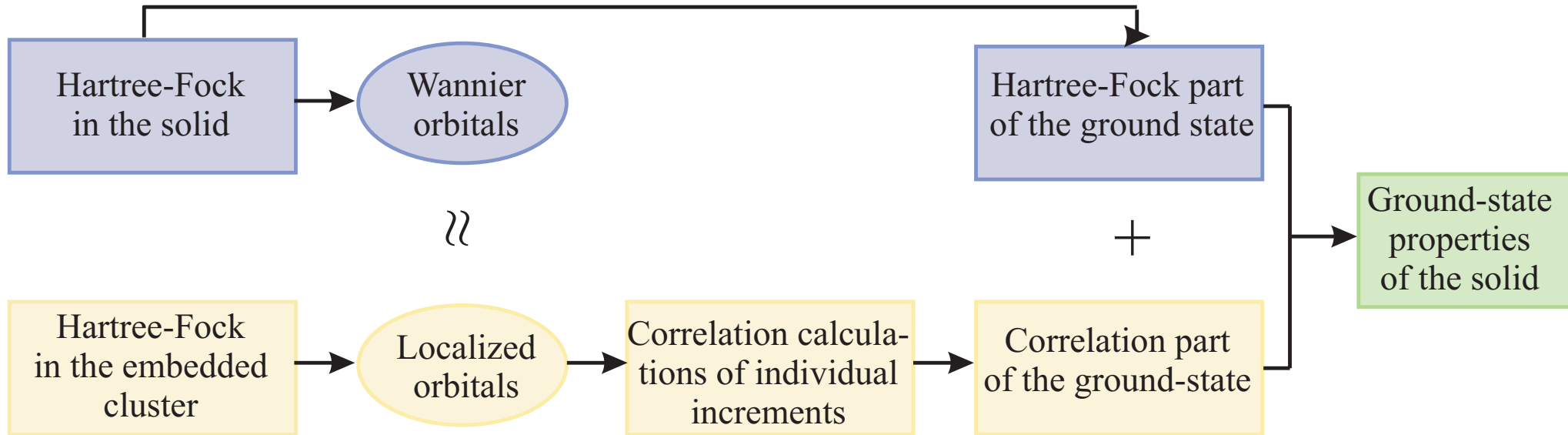
- Hartree-Fock calculation for the infinite solid
- Generating localized orbitals (e.g. Wannier orbitals)
- Correlations are short-range, but not local, typical extension in semiconductors up to 4th nearest neighbours ≈ 100 electrons

Too many electrons to be correlated simultaneously

- Dividing the correlation energy into contributions of localized orbitals or orbital groups

H. Stoll, Phys. Rev. B 46, 6700 (1992), H. Stoll, Chem. Phys. Lett. 191, 548 (1992).

Schematic overview of the method of increments:



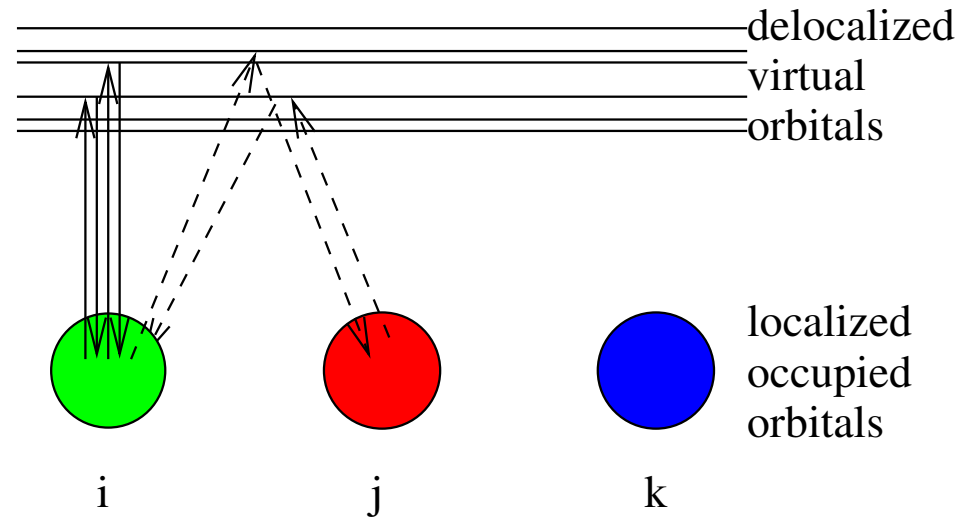
Coupled cluster ansatz for the ground-state wavefunction in terms of localized orbital groups:

$$|\Psi\rangle = e^{\Omega} |\Psi_{\text{HF}}\rangle \quad \text{with} \quad \Omega = \sum_{i,\mu} n_{i,\mu} c_{\mu}^{\dagger} c_i + \frac{1}{2} \sum_{ij\mu\nu} n_{ij}^{\mu\nu} c_{\mu}^{\dagger} c_{\nu}^{\dagger} c_i c_j + \dots$$

i, j, \dots label the **localized** orbitals at centre i, j

μ, ν, \dots label the virtual orbitals (delocalized)

Incremental scheme:



- Correlating (size-extensive method) orbitals at centre *i* (independent centres), e.g. excitations from *i* into the whole virtual space

$$\epsilon_i = E_i - E_{\text{HF}} = \langle \Psi_{\text{HF}} e^{-\Omega_i} | H_{\text{corr}} | e^{\Omega_i} \Psi_{\text{HF}} \rangle$$

$$\Rightarrow E_{\text{corr}}^{(1)} = \sum_{i \in \text{u.c.}} \epsilon_i$$

- Correlating localized orbitals at two centres i and j

$$\epsilon_{ij} = E_{ij} - E_{\text{HF}} = \langle \Psi_{\text{HF}} e^{-\Omega_{ij}} | H_{\text{corr}} | e^{\Omega_{ij}} \Psi_{\text{HF}} \rangle$$

Energy increment $\Delta\epsilon_{ij}$: non-additive contribution of the two centres i and j

$$\Delta\epsilon_{ij} = \epsilon_{ij} - (\epsilon_i + \epsilon_j)$$

- Correlating three centres i , j and k

$$\Delta\epsilon_{ijk} = \epsilon_{ijk} - (\epsilon_i + \epsilon_j + \epsilon_k) - (\Delta\epsilon_{ij} + \Delta\epsilon_{jk} + \Delta\epsilon_{ik})$$

- Correlation energy for the infinite system

$$E_{\text{corr}} = \sum_{i \in \text{u.c.}} \epsilon_i + \frac{1}{2!} \sum_{\substack{i \neq j \\ i \in \text{u.c.} \\ j \in \text{solid}}} \Delta\epsilon_{ij} + \frac{1}{3!} \sum_{\substack{i \neq j \neq k \\ i \in \text{u.c.} \\ j, k \in \text{solid}}} \Delta\epsilon_{ijk} + \dots$$

Incremental expansion will be useful if

- it converges with increasing distance of the localized orbitals
- it converges with respect to the order of the increments
- the increments can be calculated in small embedded clusters

The incremental method was applied and works well for:

- Semiconductors (H. Stoll, M. Albrecht, S. Kalvoda, F.-J. Shi, B.P.)
- Alkali halides and alkali-earth oxides (K. Doll, M. Dolg, H. Stoll)
- Transition metal oxides, rare-earth oxides and nitrides (K. Doll, K. Rościszewski, S. Kalvoda, M. Dolg, E. Voloshina, B.P.)
- Rare gas crystals (K. Rościszewski, B.P.)
- Polymers, graphite, fullerene (M. Yu, A. Abdurahman, M. Dolg, C. Willnauer, H. Stoll, B.P.)
- Hydrogen-bound systems: HF and HCl chains (C. Buth, B.P.)

Review: *Phys. Rep.* 428, 1 (2006)

3 Extension to Metals

Problems in Metals:

- Localized orbitals
- Mimic the band structure of a metal with finite clusters (i.e. vanishing gap at the Fermi level)

Solution:

Generate proper embedding to mimic a metal

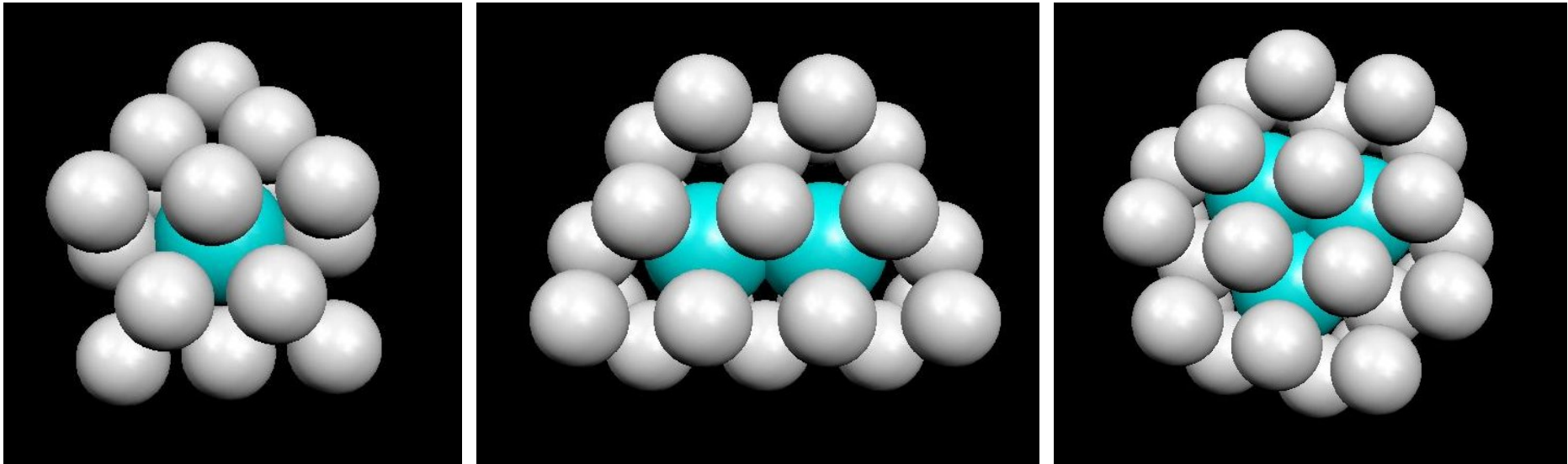
Suggested Procedure:

J. Chem. Phys. 126, 134115 (2007)

1. Selection of the fragment of the solid

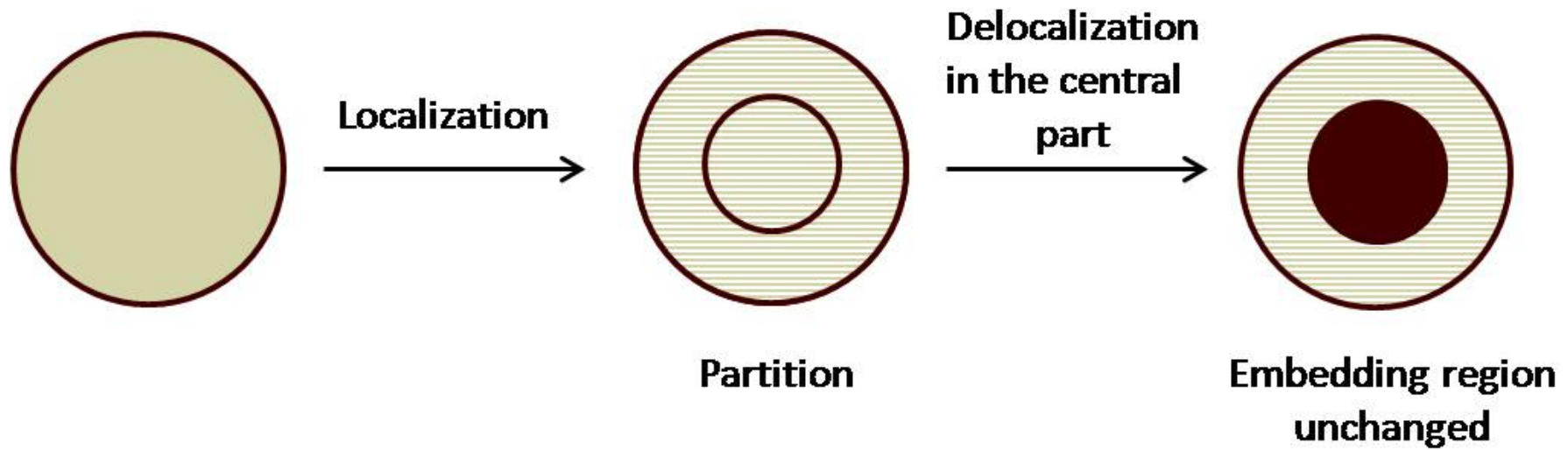
Must be done in a consistent way — definition of shells ($1.7 a_0$)

Separation into “correlation” and “embedding” atoms



2. Localization of the orbitals:

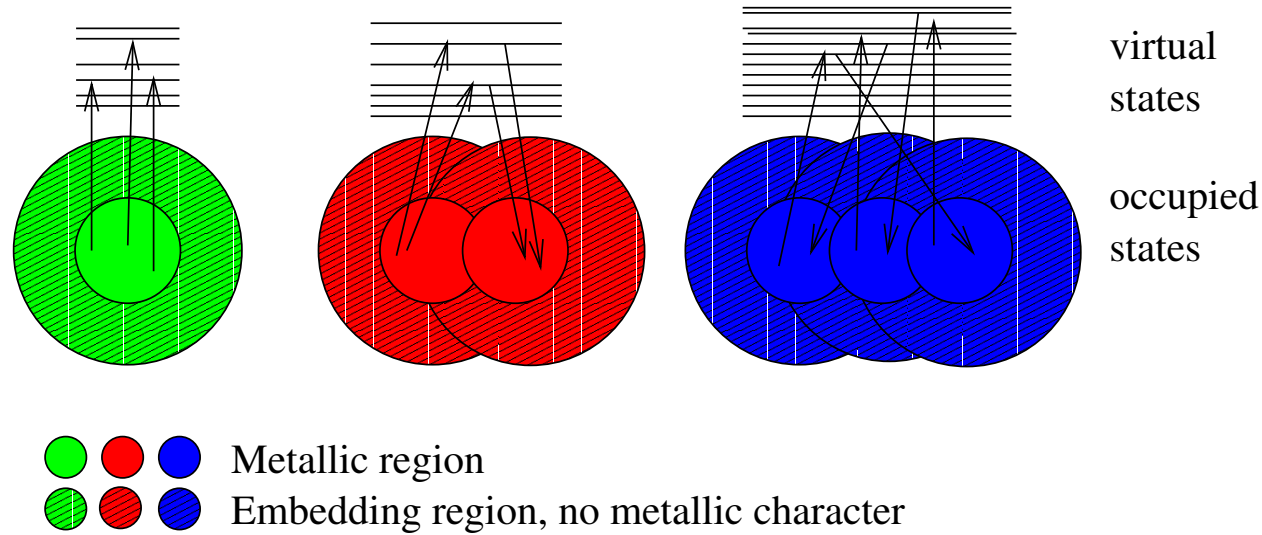
- Calculation of the whole cluster with a minimal valence basis set
- Localization of the orbitals possible
 - ⇒ Localized orbitals mimic the electrostatic and van der Waals interaction, no metallicity described
- Selecting the orbitals of the embedding region and of the atoms to be correlated
- Allowing for the delocalization in the central part (to be correlated)
(Reoptimization of the localized orbitals of the central part due to supply of polarization functions on the central atoms, while the orbitals of the embedding are kept fixed.)



⇒ Metallic-like orbitals in the central part — long-range tails of the metallic orbital are neglected

3. Correlation treatment of the central part:

Incremental expansion of the correlation energy:

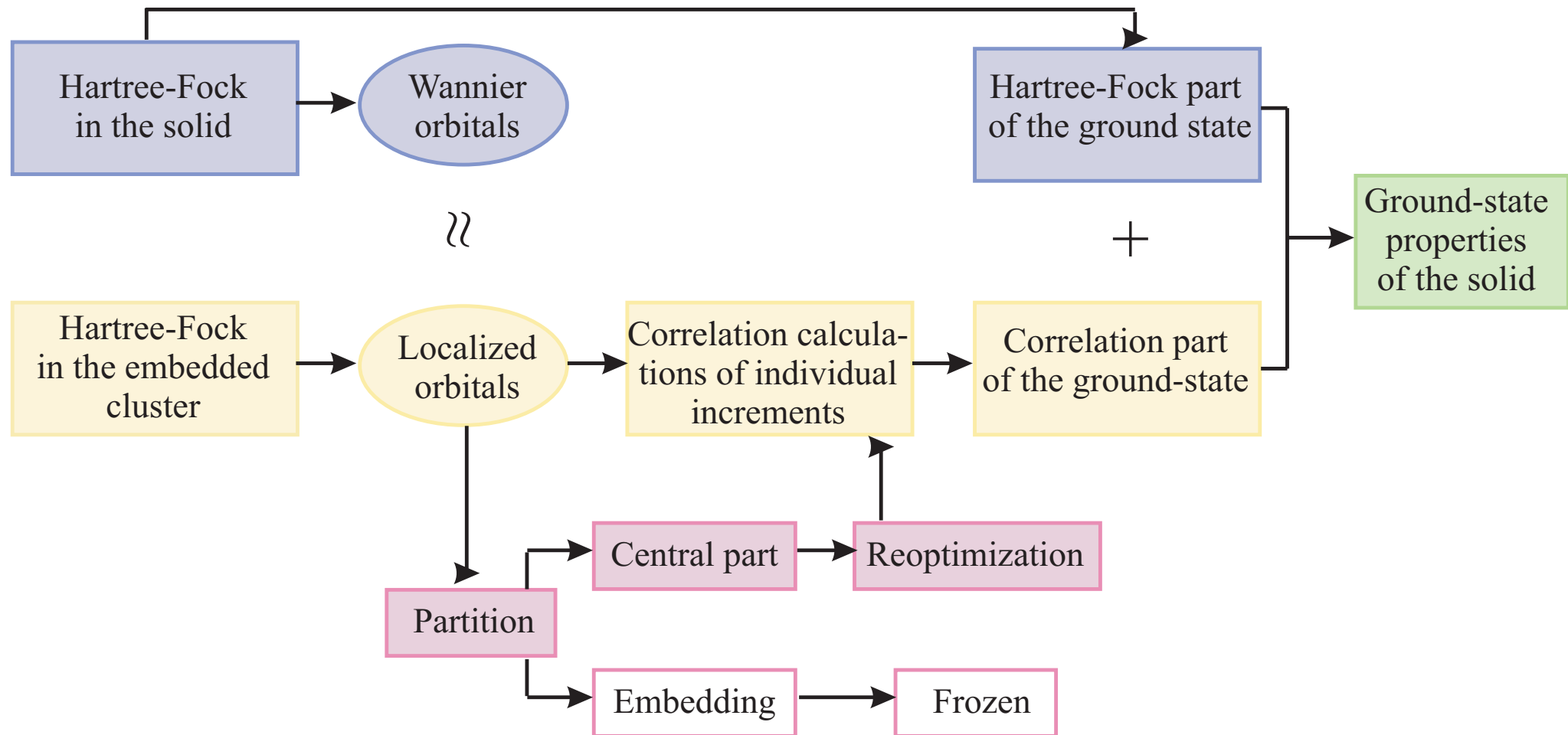


Correlation energy for the infinite system

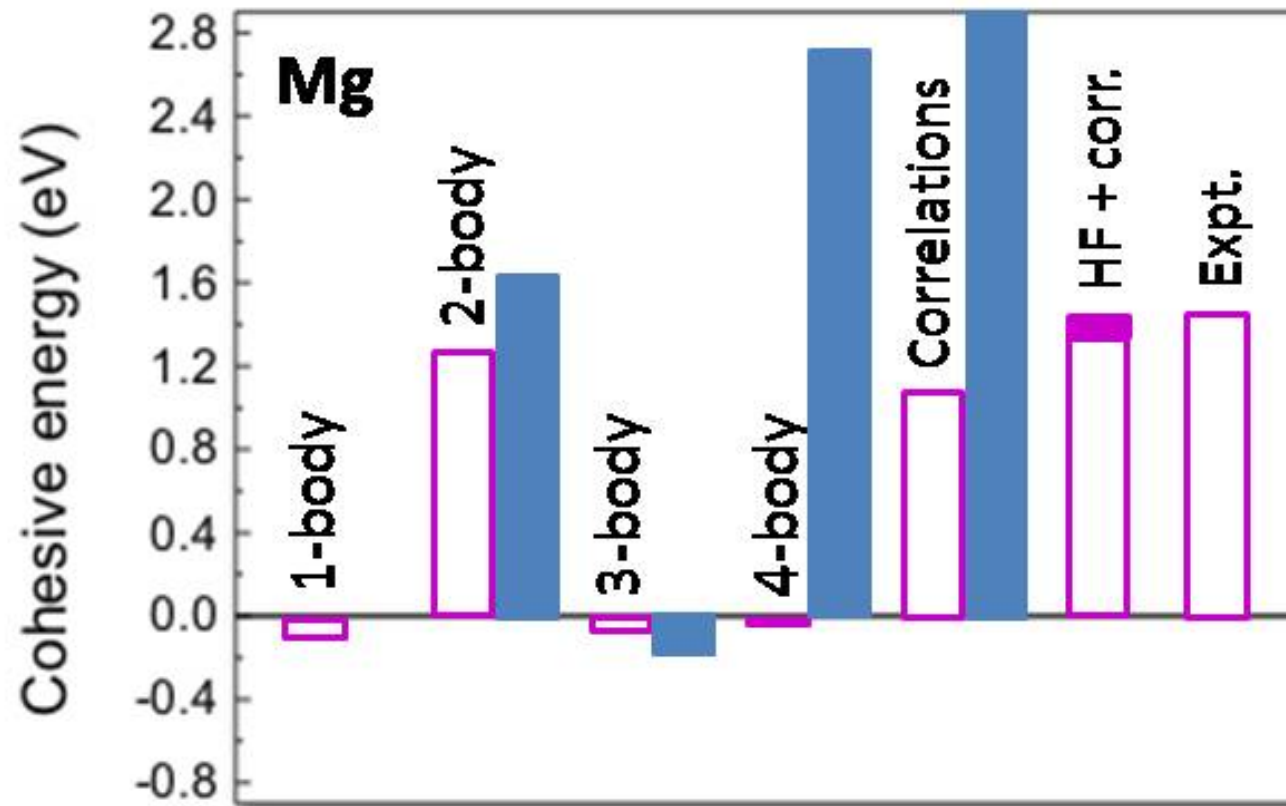
$$E_{\text{corr}} = \sum_{i \in \text{u.c.}} \epsilon_i + \frac{1}{2!} \sum_{\substack{i \neq j \\ i \in \text{u.c.} \\ j \in \text{solid}}} \Delta \epsilon_{ij} + \frac{1}{3!} \sum_{\substack{i \neq j \neq k \\ i \in \text{u.c.} \\ j, k \in \text{solid}}} \Delta \epsilon_{ijk} + \dots$$

In metals: $\Delta \epsilon_{ij}$ and $\Delta \epsilon_{ijk}$ include correlations and the non-additive effects of delocalization and correlation.

Schematic overview of the method of increments for metals:

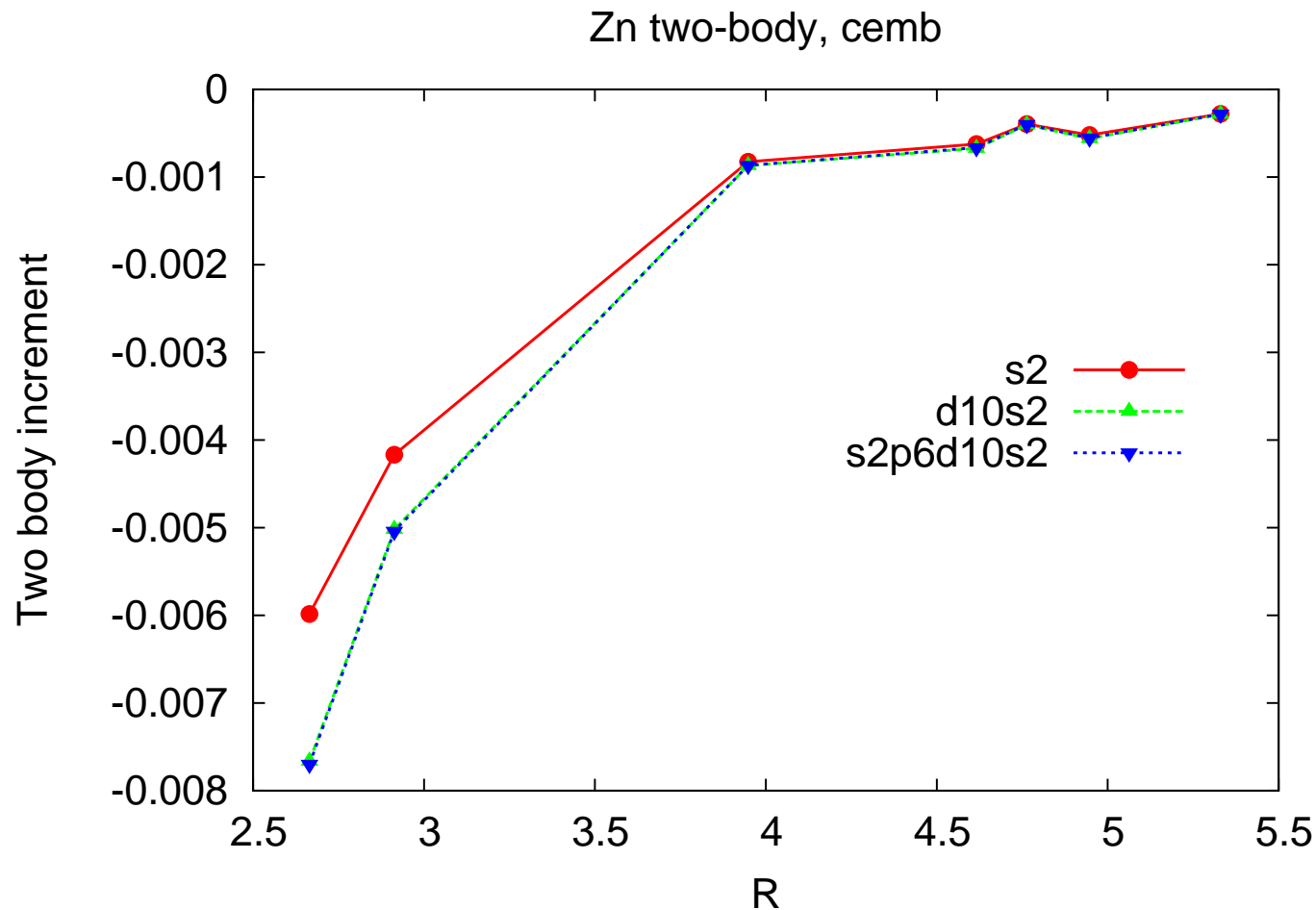


Comparison with and without embedding: Mol. Phys. 105, 2849 (2008)



Embedding is necessary for convergence of the incremental expansion

Convergence with distance of localized orbitals:



Nearest neighbour yield largest contribution

Decay with distance almost vdW-like (but screening in the metal)

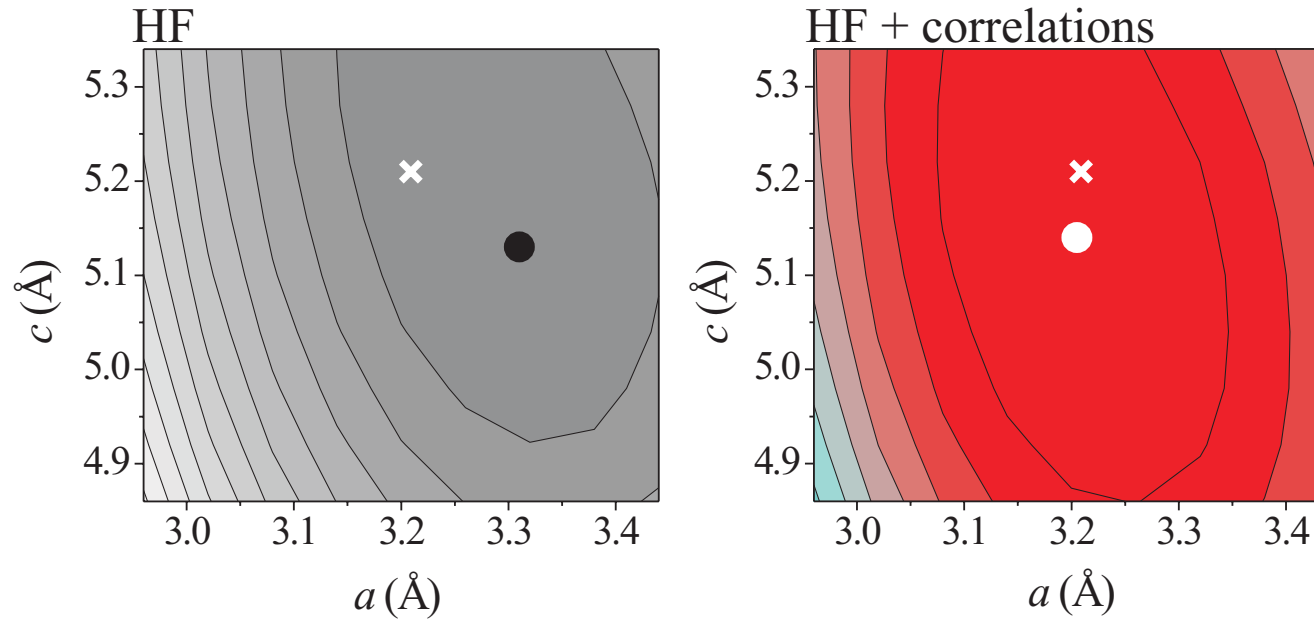


Cohesive energy for group 2/12 metals

E_{coh} (eV)	Mg	Zn	Cd	Hg
HF	-0.27	+0.09	+0.25	+0.98
one-body	+0.1019	-0.0302	-0.0026	+0.1170
two-body	-1.3646	-1.4517	-1.5248	-1.4760
three-body	+0.0580	+0.0344	+0.0974	-0.2740
four-body	+0.0153	+0.0002	+0.0002	+0.0820
total	-1.46	-1.36	-1.18	-0.57
exp	-1.50	-1.35	-1.16	-0.67

Lattice structure for magnesium

E. Voloshina et al, Phys. Rev. B 75, 245117 (2007)



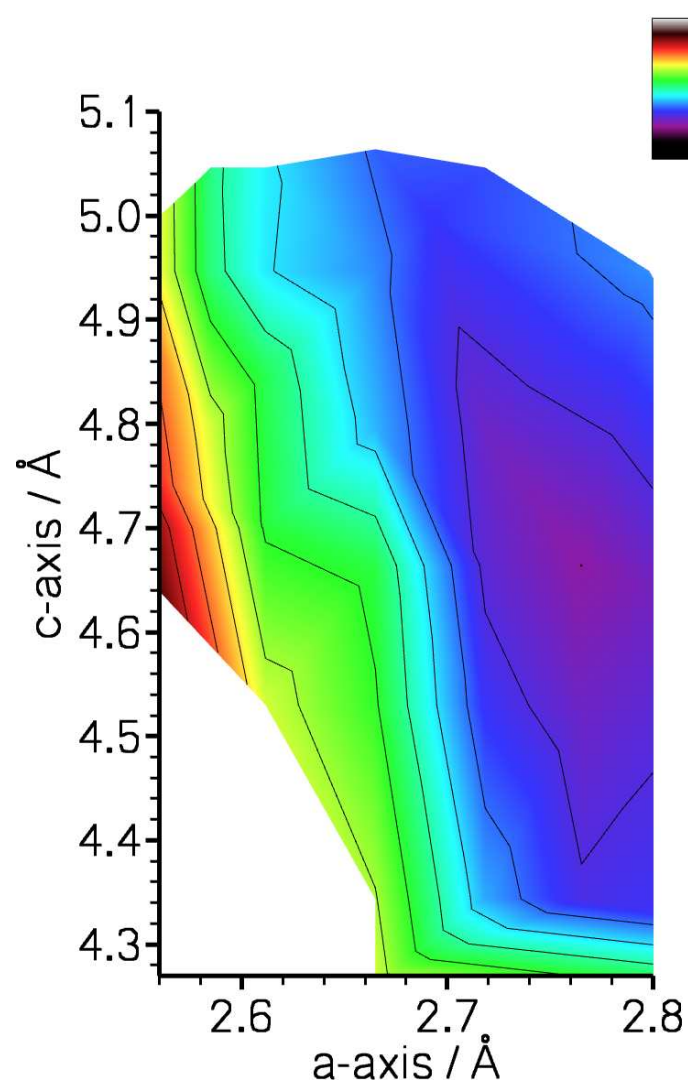
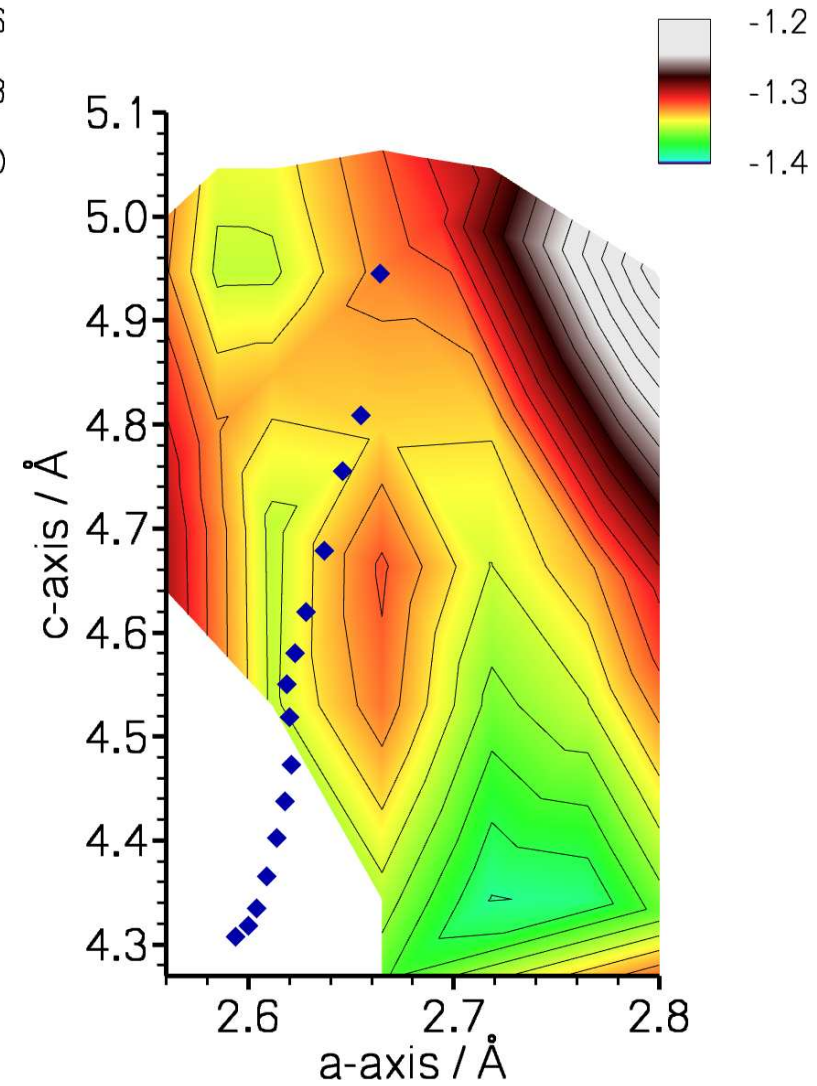
Mg	$a(\text{Å})$	$c(\text{Å})$	$\frac{c}{a}$	$B(\text{GPa})$
HF	3.310	5.131	1.550	37.0
HF+corr	3.205	5.141	1.604	35.1
exp	3.209	5.211	1.624	36.9

Lattice parameters for mercury

N. Gaston et al, Phys. Rev. B 74, 094102 (2006)

Method	$a(\text{\AA})$	$\alpha(^{\circ})$	$E_{\text{coh}}(\text{eV})$	B(Mbar)
LDA	2.97	72.6	-0.918	0.176
HF + 1- + 2-body-corr.	2.97	70.0	-0.375	0.132
+3-body: <i>s</i> -only	2.97	69.2	-0.561	0.383
+3-body: <i>sd</i> -corr	2.96	69.5	-0.649	0.360
Expt.	3.005	70.53	-0.670	0.382/0.322

Potential surface for zinc: (PRL 100, 226404 (2008))

without d correlationswith d correlations

Multiple Minima in the Zn potential surface:

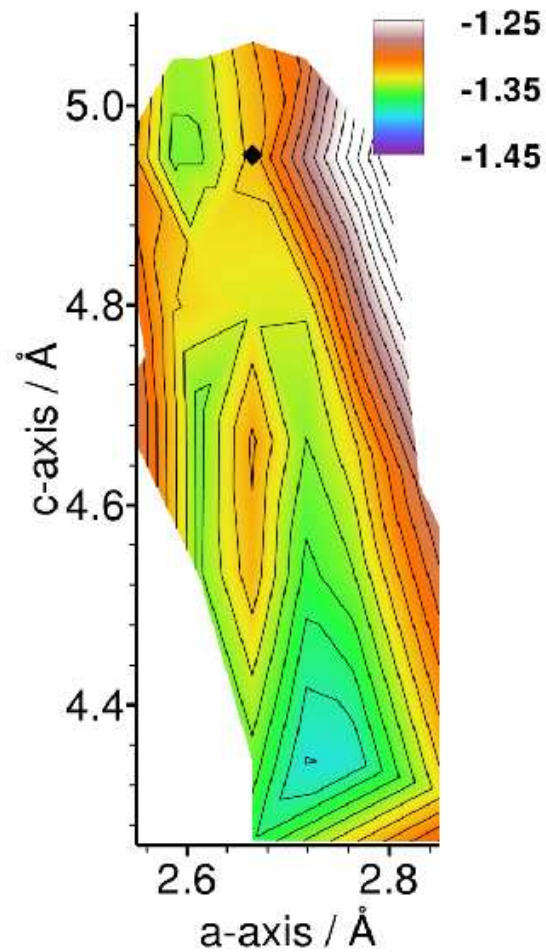
Zn	$a(\text{Å})$	$c(\text{Å})$	$\frac{c}{a}$	$E_{\text{coh}}(\text{eV})$	$V(\text{Å}^3)$
expt-like	2.61	4.98	1.91	-1.35	29.3
ideal-like	2.72	4.34	1.60	-1.39	27.8
min-3	2.61	4.70	1.80	-1.35	27.7
exp	2.67	4.95	1.86	-1.35	30.4
ideal			1.63		
sym. point in hcp			1.73		

Theoretically a magnesium-like zinc exists !

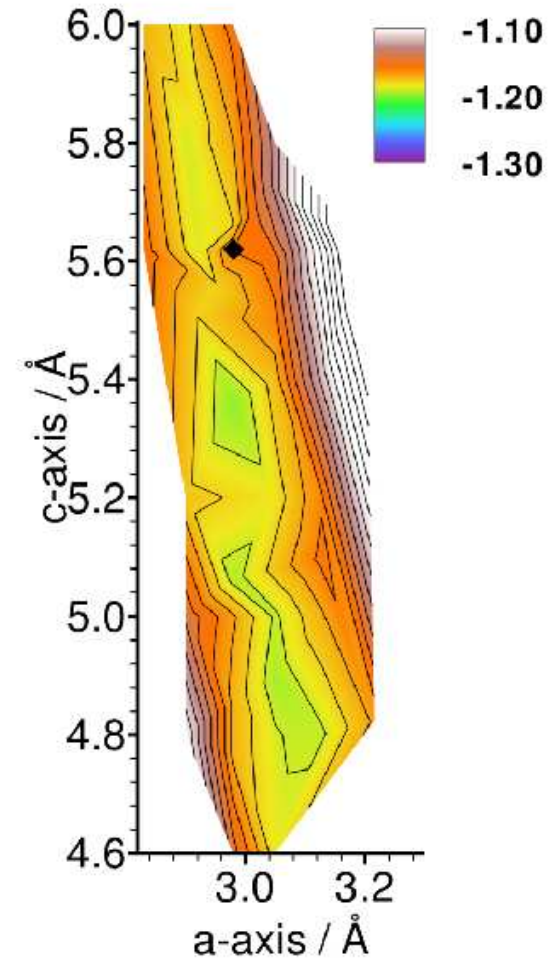
Can it be found experimentally ?

Potential surface for cadmium:

(N. Gaston, et al. PCCP in press)



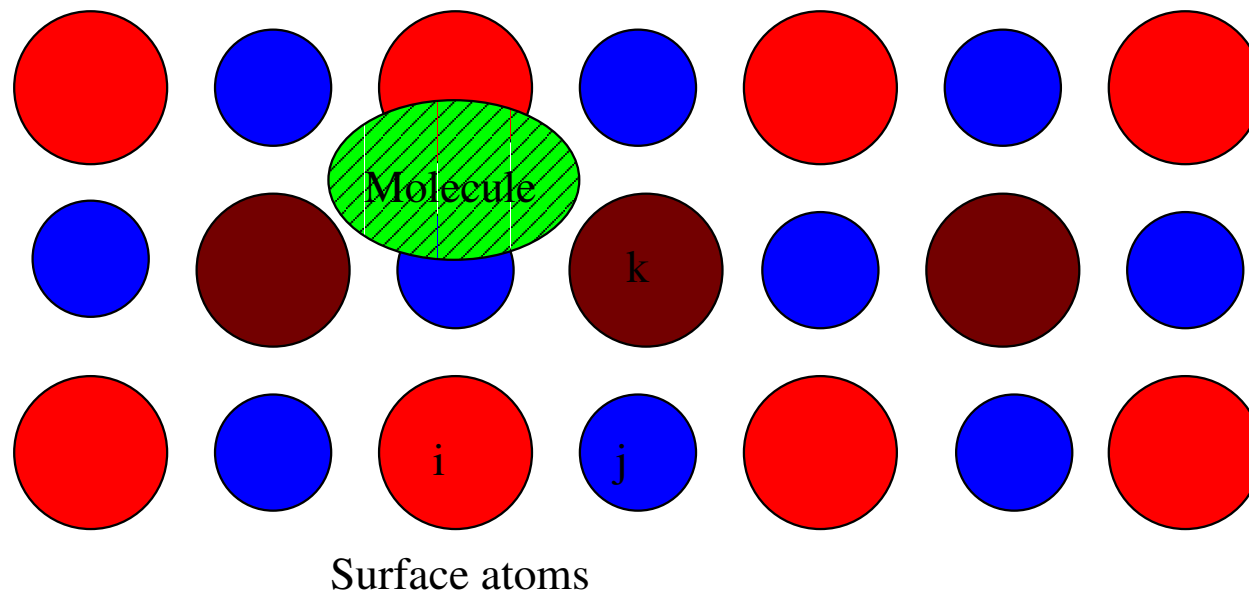
Zn: s + d correlation



Cd: s + d correlation

4 Method of increments for the adsorption on surfaces

Incremental expansion for the adsorption energy



Localized orbital groups:

- localized orbitals of the **adsorbed molecule**
- localized orbitals of the **individual ions in the surface**

Definition of the adsorption energy:

$$E^{\text{adsorb}} = E_{\text{joint system}} - E_{\text{surface}} - E_{\text{molecule}} = E_{\text{HF}}^{\text{adsorb}} + E_{\text{corr}}^{\text{adsorb}}$$

Incremental expansion for the correlation contribution to the adsorption energy:

$$E_{\text{corr}}^{\text{adsorb}} = \eta_{\text{mol}} + \sum_{i \in \text{surface}} \eta_i + \sum_{i \in \text{surface}} \eta_{\text{mol},i} + \frac{1}{2!} \sum_{\substack{i \neq j \\ i, j \in \text{surface}}} \eta_{ij} + \dots$$

with

η_{mol} change in correlation energy of the molecule due to adsorption

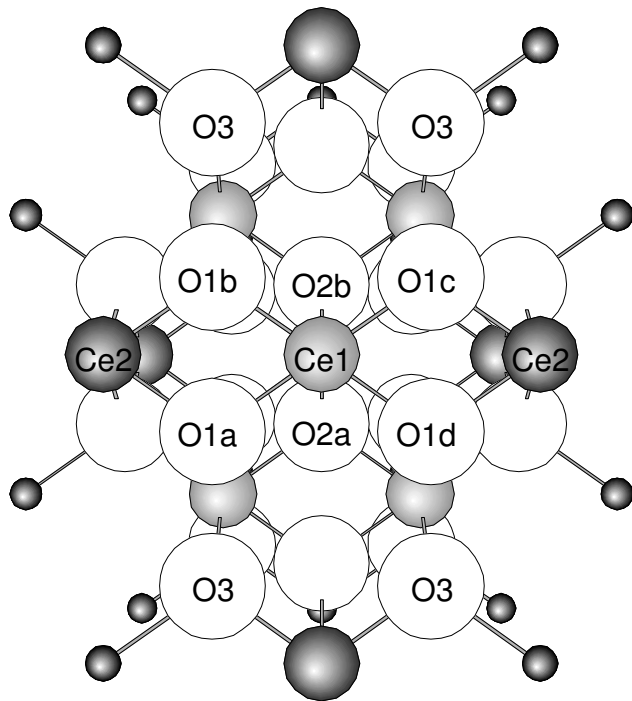
η_i change in the individual correlation increments of the surface

$\eta_{\text{mol},i}$ correlation energy increments between molecule and surface

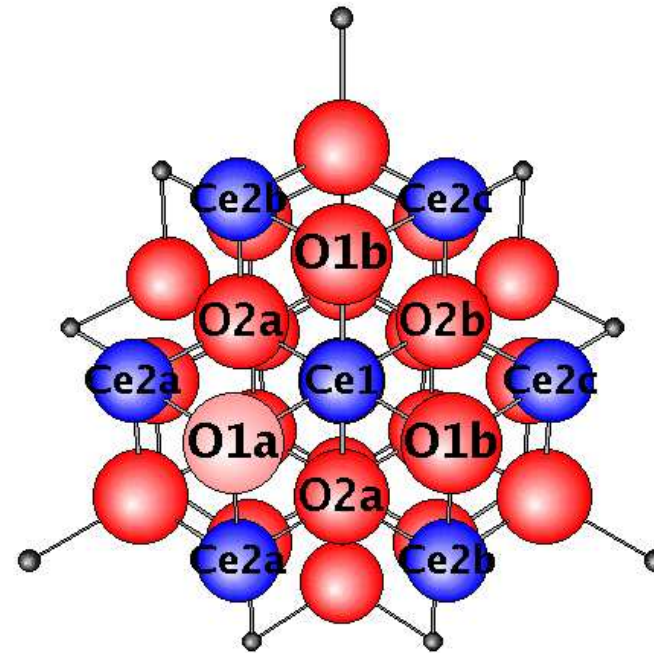
η_{ij} changes in the two-body increments of the surface

CO on the CeO_2 (110) surface and CeO_2 (111) surface:

(110) surface



(111) surface



CO on the Ce-site:

Adsorption geometry (Å) and adsorption energy (meV)

	$r_{\text{C-Ce}}$	E^{ads}	E^{ads}	E^{ads}	$E_{\text{corr}}^{\text{ads}}$	$E_{\text{corr}}^{\text{ads}}$
	B3LYP	B3LYP	HF	MP2	MP2	CCSD(T)
(110)	2.959	-104	-149	-244	-95	-52
(111)	2.856	-110	-48	-323	-275	-235

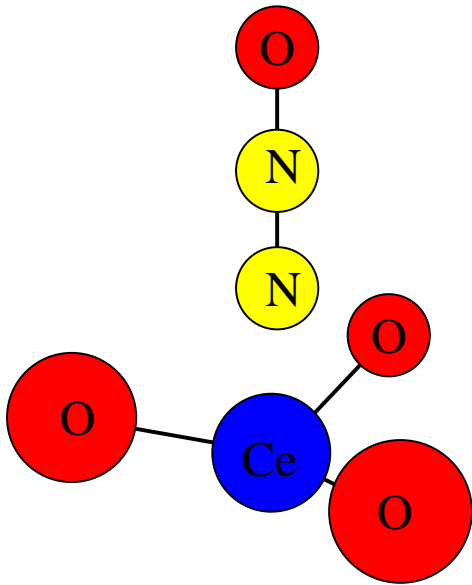
(J. Chem. Phys. 128, 214701 (2008), Surf. Sci. 603, 2619 (2009))

- Significant binding contribution from the semi-core $5s^2p^6$ shell of Ce ($\approx 40\%$)
- Difference between (110) and (111) surface mainly due to the CO-nearest neighbour oxygen increments, they are much nearer in the (111) surface and yield in sum about 200 meV lower correlation energy.

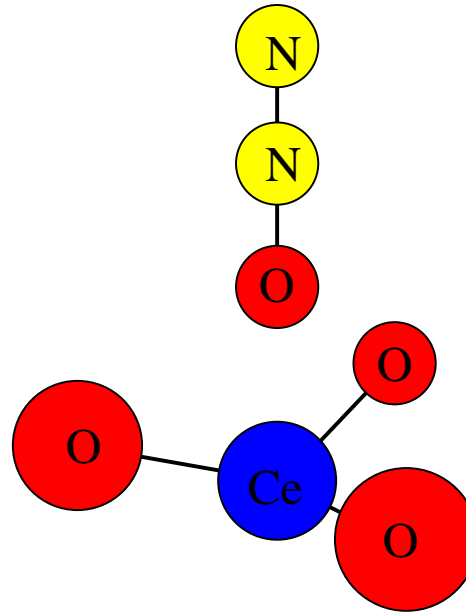
Results for N_2O on the CeO_2 (111) surface:

Different adsorption geometries on the Ce-site:

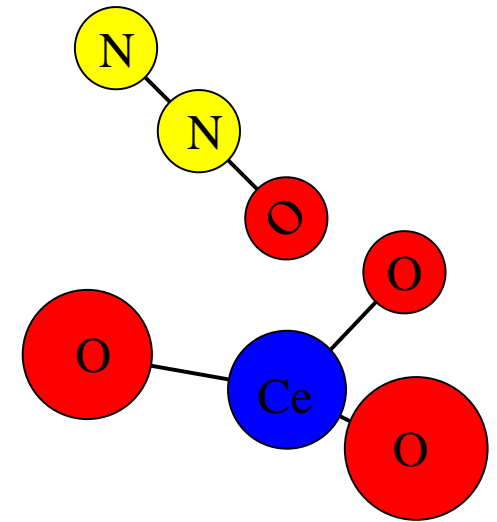
N-down



O-down (perp.)



O-down (tilted)



Adsorption energies with the method of increments

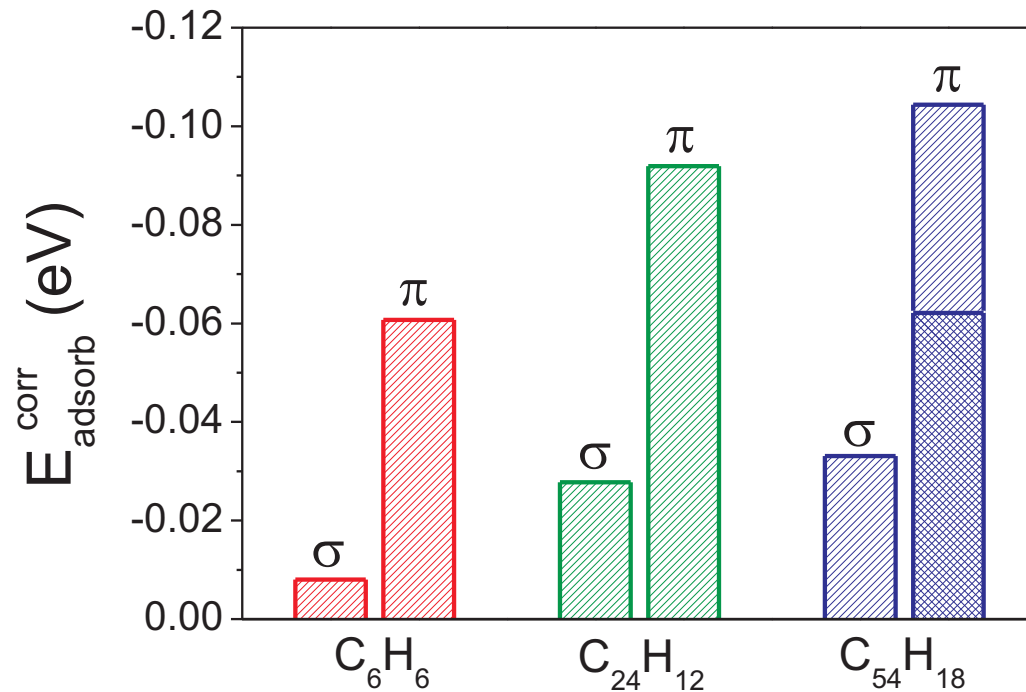
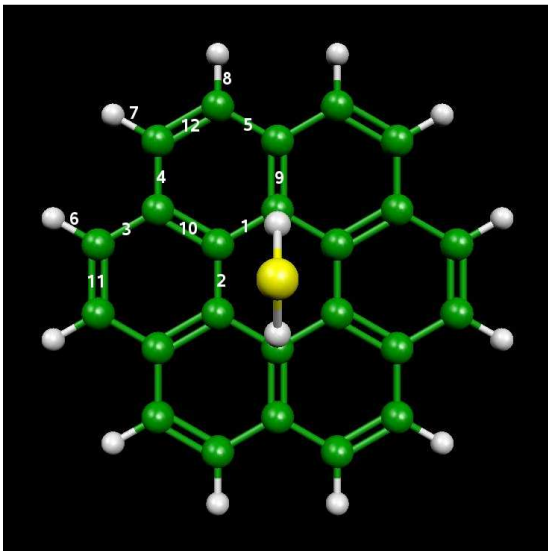
	HF	MP2	CCSD(T)
N-down	22 meV	-276 meV	-227 meV
O-down (perp)	4 meV	-142 meV	-133 meV
O-down (tilted)	-105 meV	-263 meV	-261 meV

(Chem. Phys. in press (2009))

- tilted O-down geometry is the most stable one in agreement with the experiment
- correlation energy stays nearly the same due to tilting, electrostatic interaction yields stronger binding
- in the N-down case binding entirely due to correlation

Adsorption on Graphene

Method of increments for H₂S on graphene-like Coronene



(Int. Journal of Quantum Chem. in press (2009))

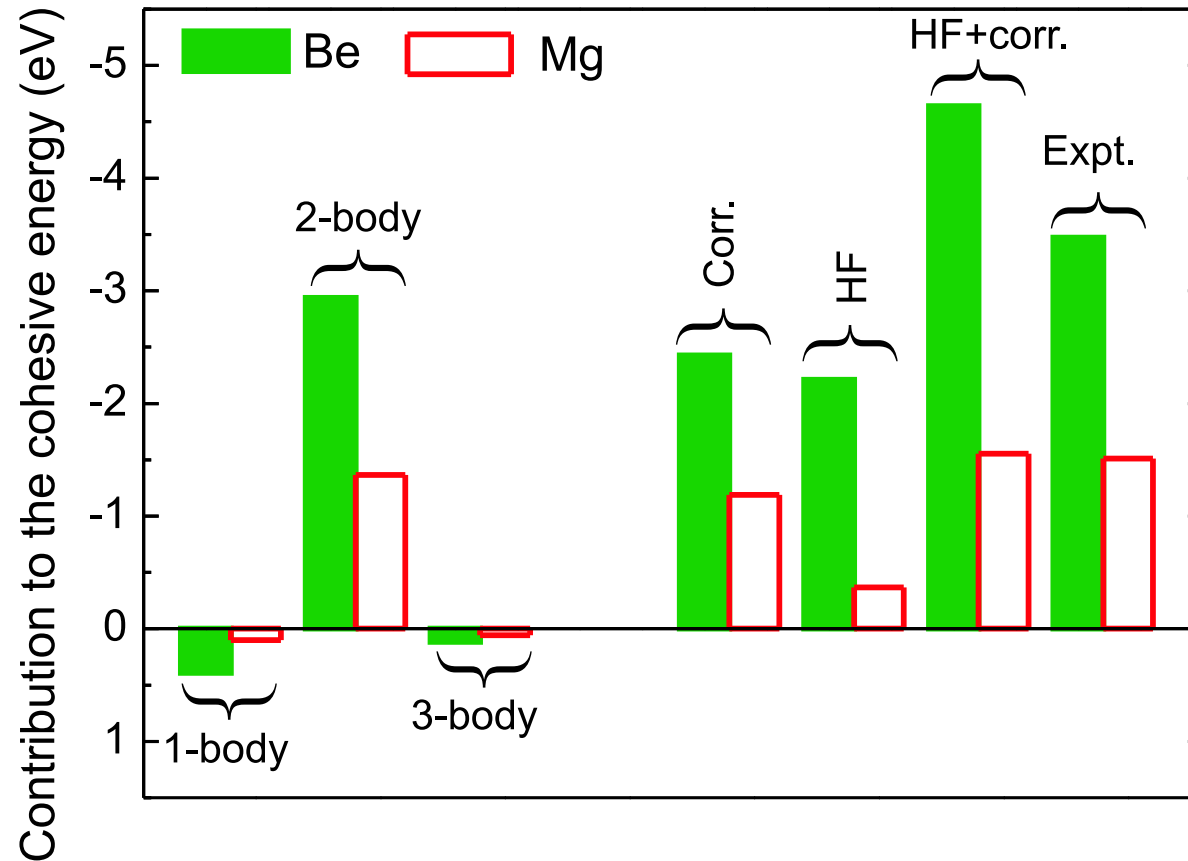
- Hartree-Fock yields no binding (slightly repulsive 0.2 eV)
- Localization and method of increments possible for delocalized π -systems
- About 30% of the binding due to σ bonds

5 Conclusion and Outlook

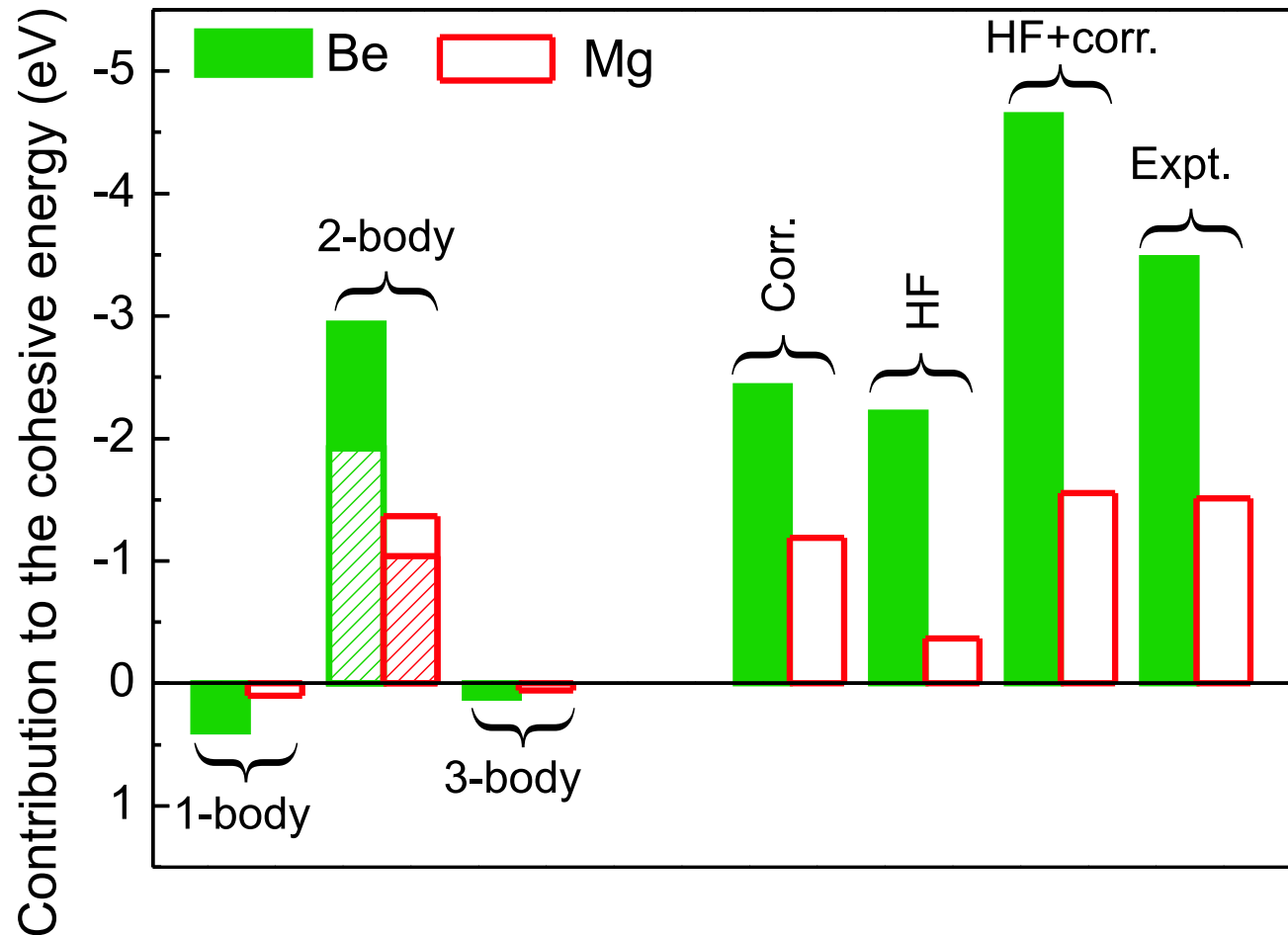
- Method of increments for metals:
 - Embedded clusters for the correlation calculation are necessary
 - The non-additive part of the metallic character and the electron correlation is treated via the incremental scheme
- Very good agreement of the ground-state properties of Mg, Zn, Cd and Hg with the experimental values
 - Binding is substantial due to electronic correlations, *d*-shell correlations important for Zn, Cd and Hg
 - Multiple minima in the potential surface of Zinc and Cadmium

Cohesive energy of beryllium — Work in progress

(J. of Phys. Conf. Series 117, 012029 (2008))

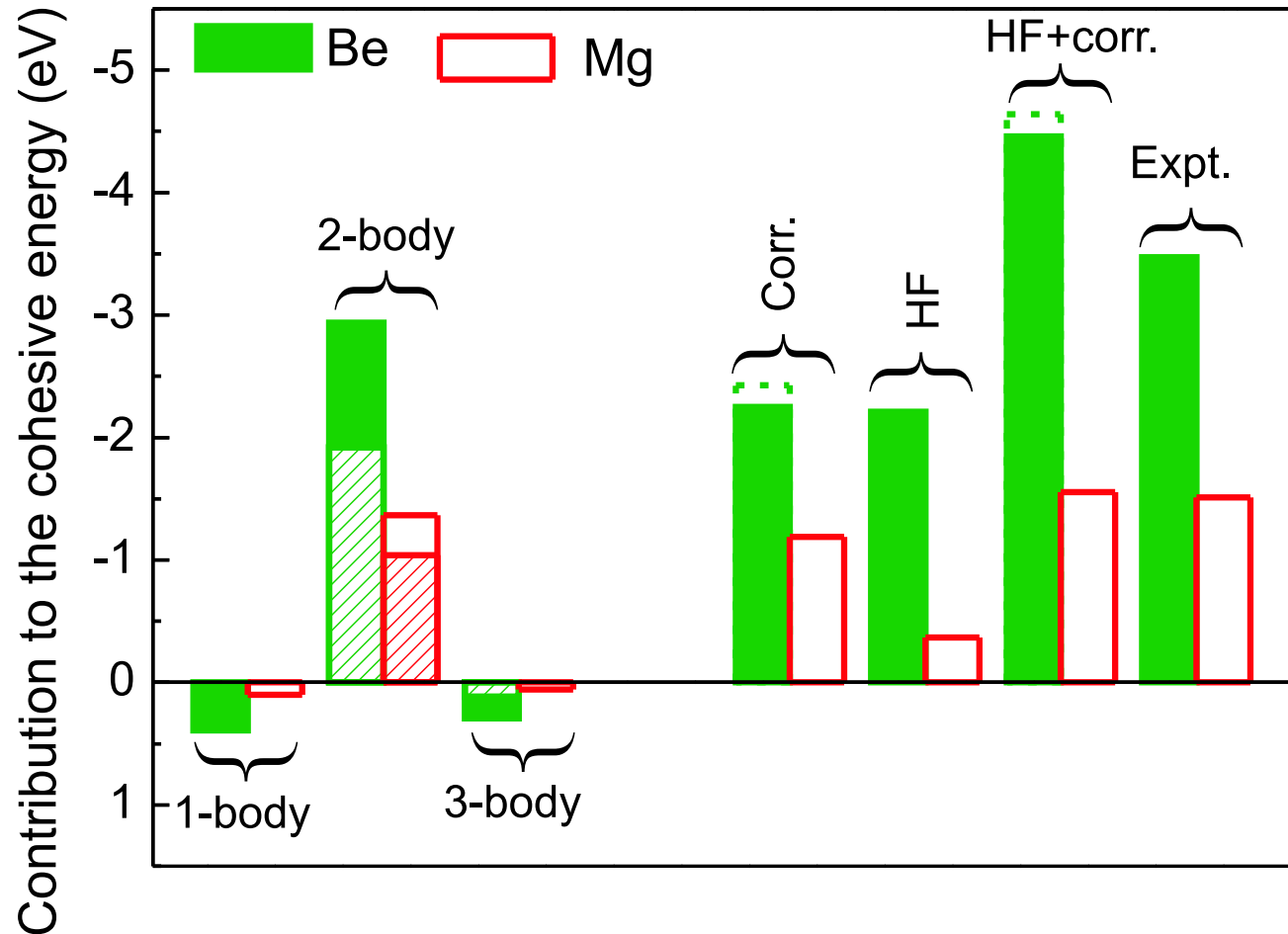


Remark: Hartree-Fock contribution to the cohesive energy in beryllium 55% in magnesium only 20%

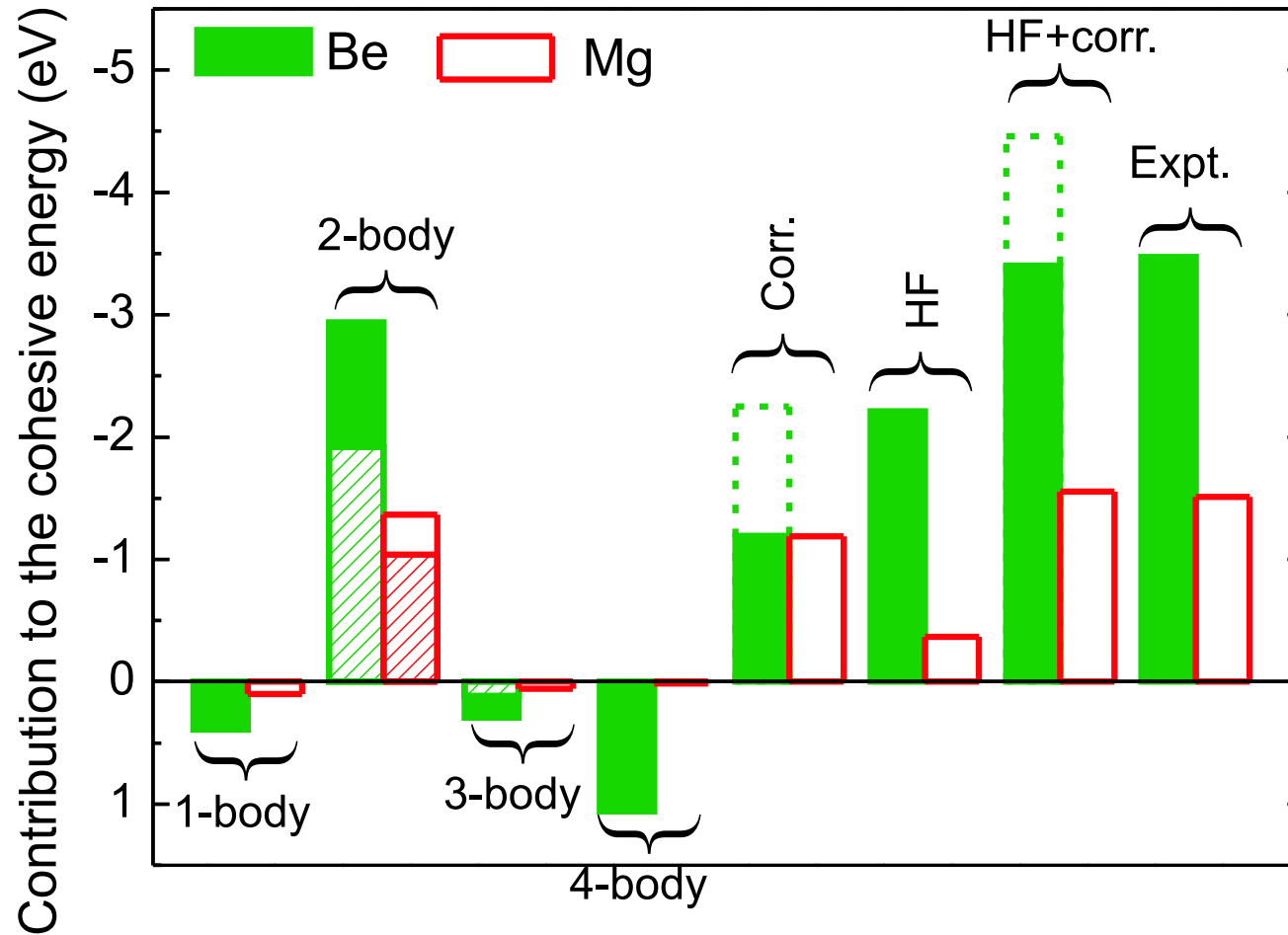


Whereas in magnesium 80% of the two-body correlations is from the nearest neighbour increment, it contributes only 60% in beryllium

⇒ further away contributions also in higher-body terms

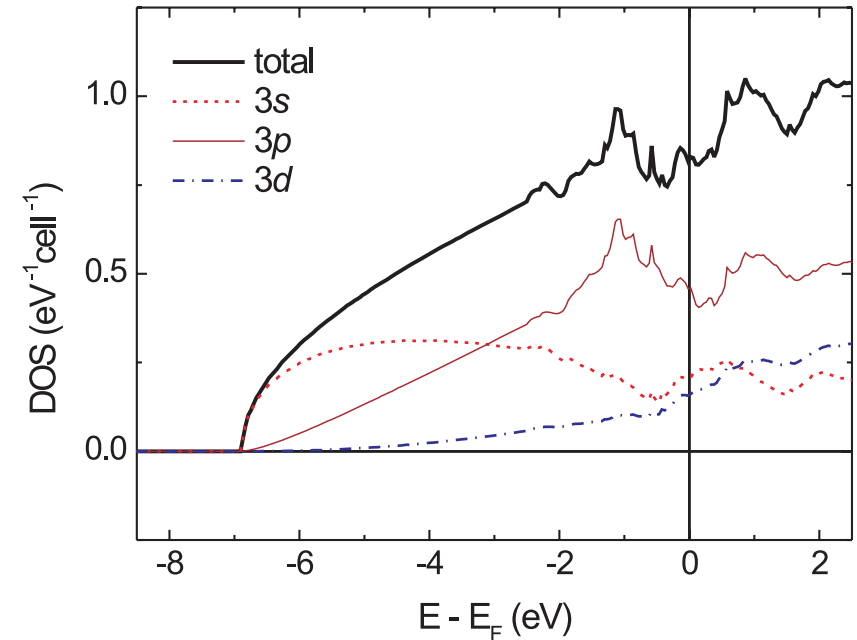
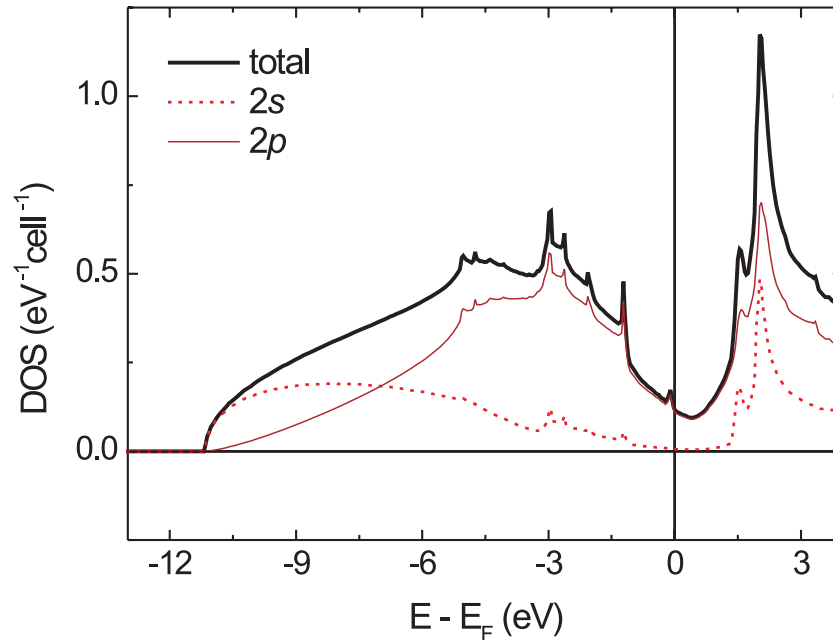


3-body increments up to second nearest neighbours are repulsive, but still too small to correct the overestimations of the calculated cohesive energy .



Four-body increments yield large repulsive contribution, good agreement with experiment

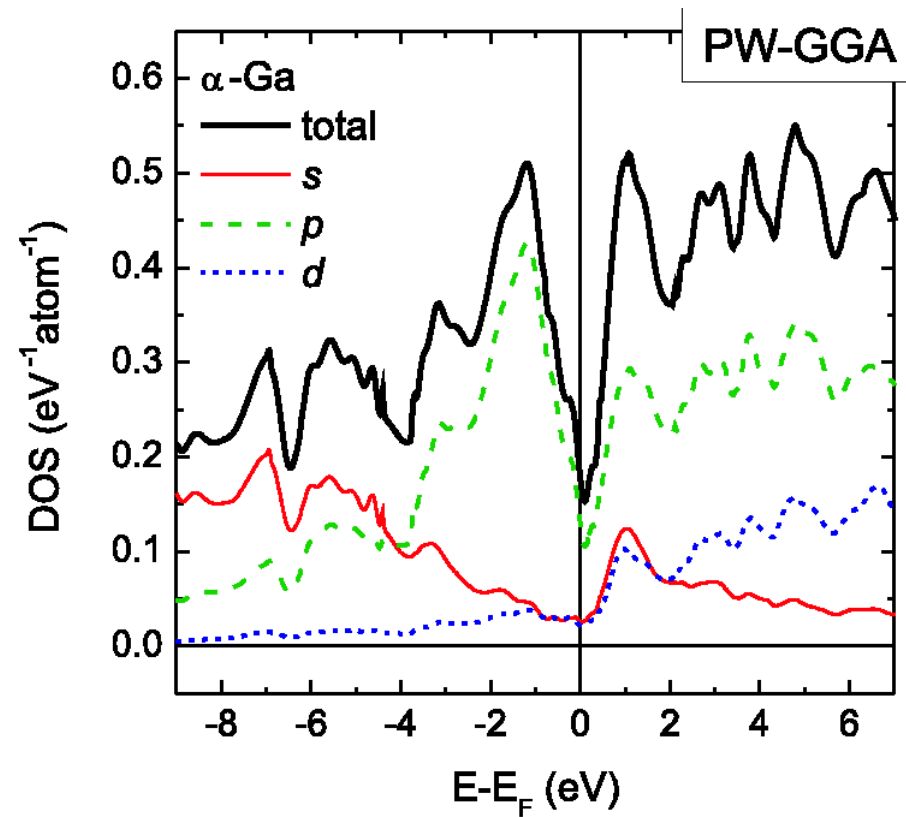
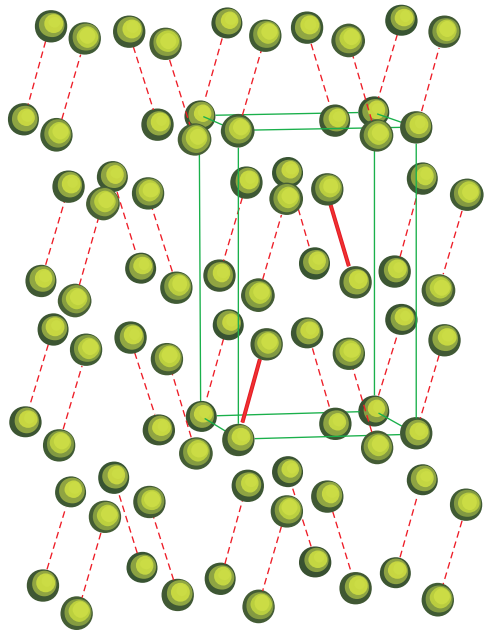
- bad convergence of the incremental scheme, if it is formulated for localized orbitals on atoms
- Density of states



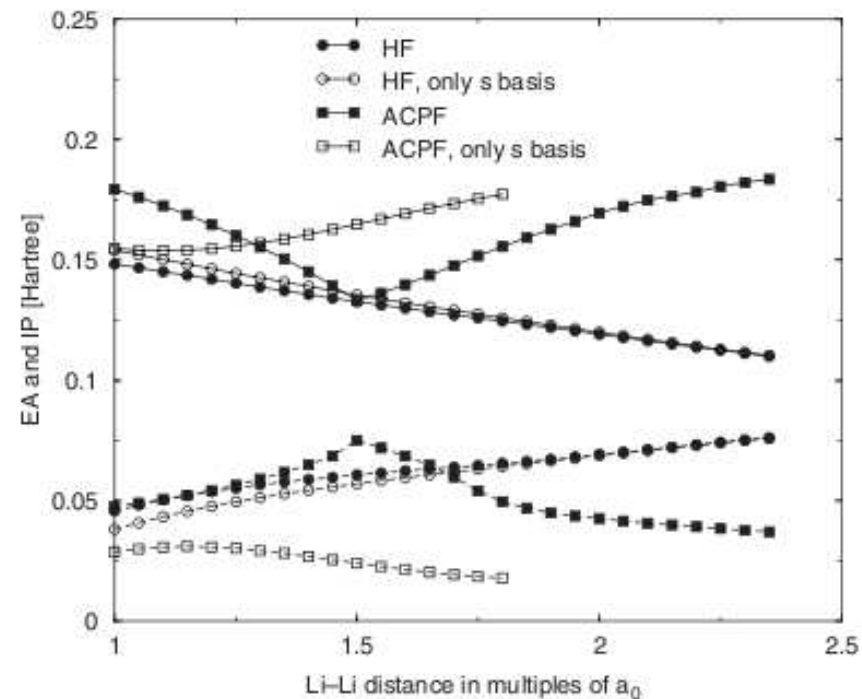
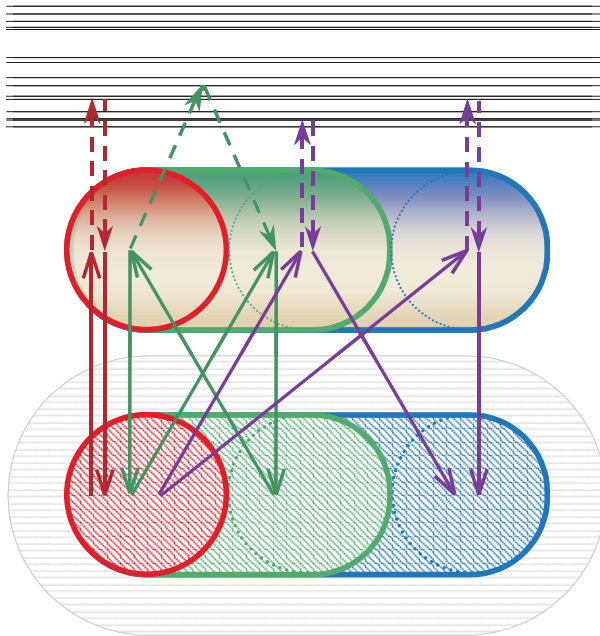
- Significant covalent binding in beryllium \Rightarrow the incremental expansion has to be formulated for larger entities, e.g. Be-tetraedrons

Local correlation treatment in metals:

- Gallium: Metal formed from Gallium dimers (Phys. Rev. B 79, 045113 (2009))



- Open shell metals (group 1/11):
 - Multi-reference method of increments (Chem. Phys. Lett. 317, 7 (2003))



- Metal-insulator transition with quantum chemical methods (Phys. Rev. B 68, 235115 (2003); Eur. J. Phys. B 40, 243 (2004))
- Special embedding for open-shell metals (Chem. Phys. Lett. 469, 90 (2009))

Adsorption on surfaces:

- Highly accurate correlation methods are applicable for adsorption energies
- Individual contributions to the binding can be discussed
- Good convergence for CO on CeO₂ surface, but large influence of change in 1- and 2-body increments of molecule and surface individually
- Further examples:
 - CO on CeO₂ 111 surface
 - N₂O on CeO₂ 111 surface in N-down and O-down geometry
 - H₂S on graphene-like Coronene
- Adsorption of open-shell molecules: NO on CeO₂ 111 surface
- Adsorption on metallic surfaces

Acknowledgement:

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Hermann Stoll (Stuttgart)

Peter Fulde (Dresden)

Peter Schwerdtfeger (Auckland)

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