The method of increments

Wave-function based correlation calculations for the lattice structures of the anisotropic hcp metals, zinc and cadmium

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Acknowledgements

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Outline

Local correlation methods

1. Question: How can we apply quantum chemical methods for correlation to infinite systems?
2. Idea: (Dynamical) electron correlations are short ranged
   - 2.1 Local Ansatz (Stollhoff and Fulde, 1977)
   - 2.2 Local correlation method by Pulay (Pulay, 1983)
     - 2.2.1 Implemented into MOLPRO for molecules (MP2, CCSD(T))
     - 2.2.2 Implemented into CRYSCOR for periodic solids (MP2)
   - 2.3 Method of increments (Stoll, 1992)
3. All use localised orbitals for the wavefunction-based correlation calculation

The Method of Increments

Decompose the system into a sum of interactions between parts:

$$\begin{aligned} \epsilon &= \Delta\epsilon_1 + \Delta\epsilon_2 + \Delta\epsilon_3 + \dots \\ \Delta\epsilon_2 &= \sum_{ij} \Delta\epsilon_2(i,j) \\ \Delta\epsilon_2 &= \Delta\epsilon_2(1,2) + \Delta\epsilon_2(1,3) + \Delta\epsilon_2(1,4) + \dots \end{aligned}$$

$\Rightarrow$ for metals, use Hartree-Fock energy from CRYSTAL calculations

$$\begin{aligned} \epsilon_{corr} &= \epsilon_{1,corr} + \epsilon_{2,corr} + \epsilon_{3,corr} + \dots \\ E(\text{total}) &= E_{\text{HF}} + \epsilon_{corr} \end{aligned}$$

$\Rightarrow$ need well localised orbitals for each correlation increment which should be as close to the true orbitals in the metal as possible

The Method of Increments

Decompose the system into a sum of interactions between parts:

$$\epsilon = \Delta\epsilon_1 + \Delta\epsilon_2 + \Delta\epsilon_3 + \ldots$$

Important properties of the method of increments:

1. Correlations short range, but in solids important up to 4th nearest neighbours (at least): usually no chance of simultaneous correlation of all electrons
2. The localised orbital groups should be physically reasonable
3. Size extensive method i.e. (CCSD(T))

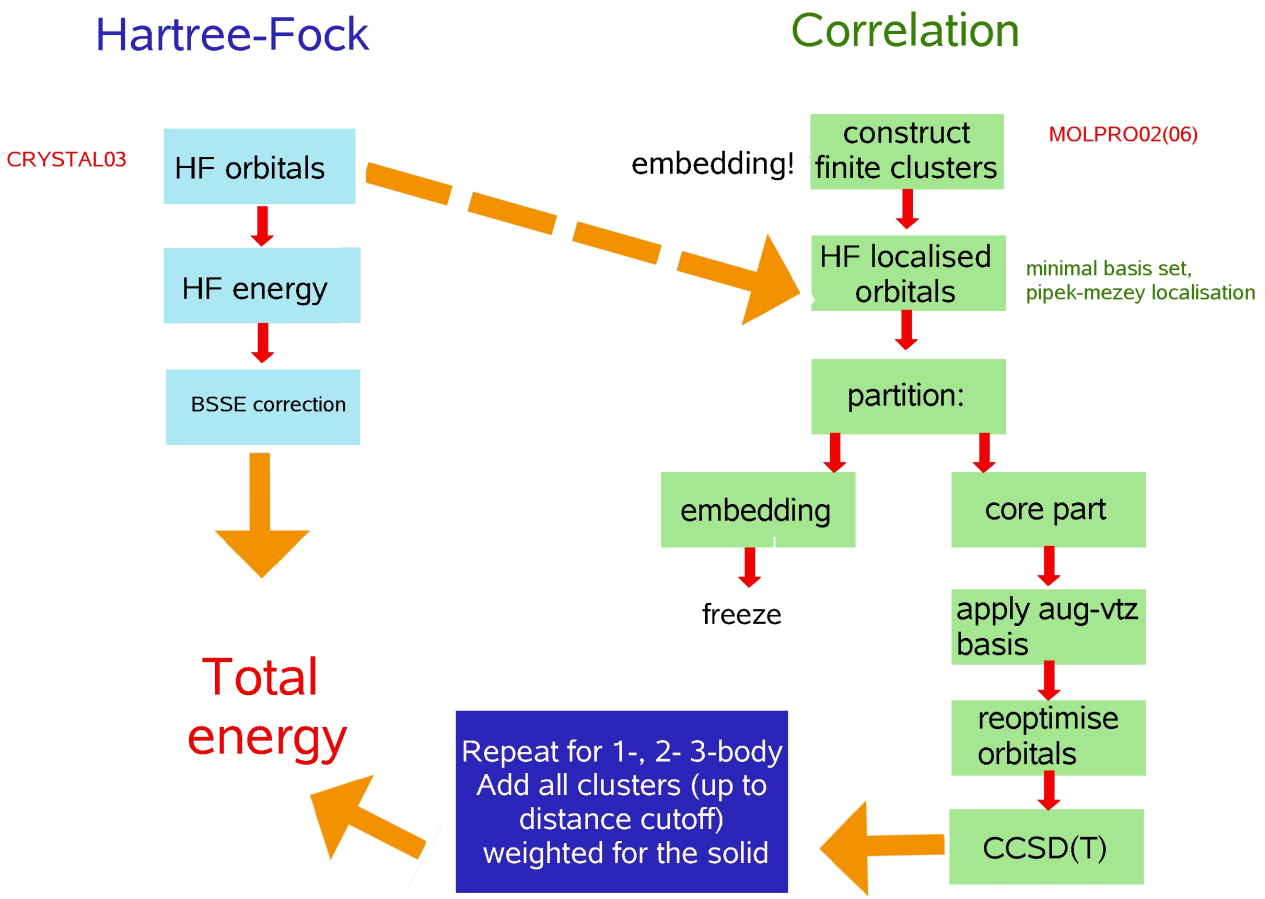
The Method of Increments

Applications to date:

1. Semiconductors
2. Alkali halides and alkali earth oxides
3. Transition metal oxides, rare earth oxides and nitrides
4. Rare gas crystals
5. Polymers, graphite, fullerene
6. hydrogen-bound systems: HF and HCl chains

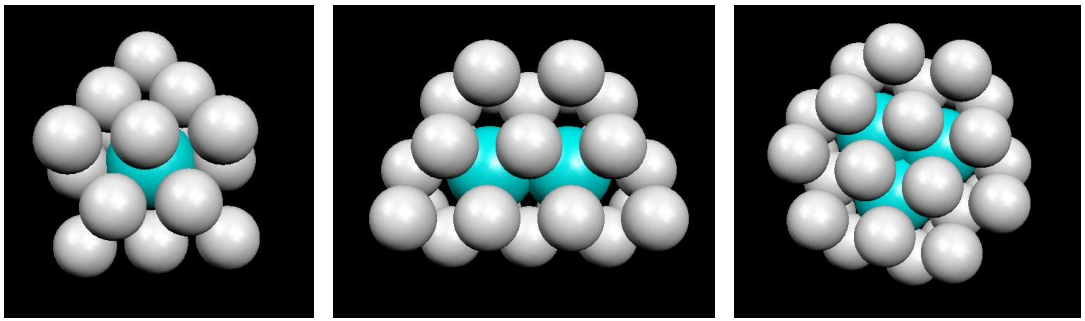
Review article: B. Paulus, Phys. Rep. 428, 1, 2006

The Method of Increments for Metals



Embedding of finite increments

1. Must be done in a consistent way — definition of shells (1.7 a_0)
2. Separation into "correlation" and "embedding" atoms
3. Need to have convergence with respect to:
   - 3.1 Number of "correlation" atoms
   - 3.2 Number of "embedding" atoms



Technical details

Definition of the "embedding" atoms

1. Large core pseudopotential (only explicit s^2 valence)
2. Minimal basis for the valence (4s)/[1s] optimised within large cluster:

Definition of the "correlation" atoms

1. Small core pseudopotential (leaving $s^2p^6d^{10}s^2$ electrons)
2. augmented TZ (strongly decontracted $(10s9p8d3f2g)/[8s7p6d3f2g]$) basis set used throughout (Peterson, PP website)
3. CCSD(T) calculations of the correlation energy
   - 3.1 Can compare the influence of pure 'valence' (s^2) correlation and the importance of the underlying d-shell

Description of metallic character

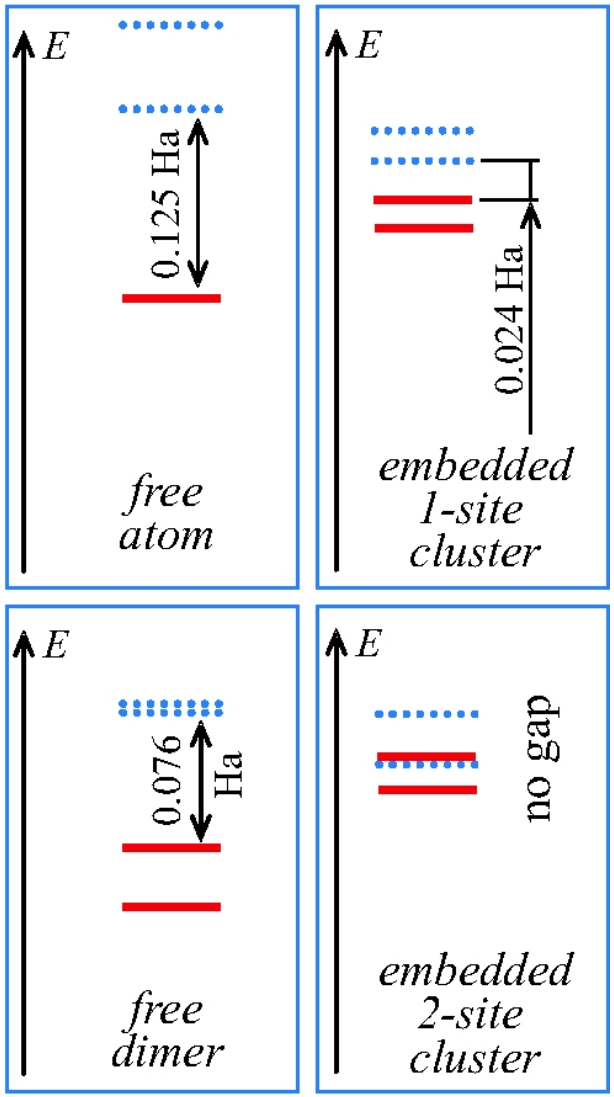
1. Embedding must enable:
   1.1 localization of the orbitals
   1.2 neutrality of atoms to be correlated
   1.3 correct description of virtual space (band gap)
2. In metallic clusters the electrons move to the surface of the cluster even for cluster sizes up to 1000 atoms
3. This charge is compensated by a positive charge in the center of the cluster
4. vanishing gap at the Fermi-level: i.e. the HOMO-LUMO gap has to approach zero

Charge characteristics of clusters

Size of cluster (atoms)	13	19	1	13
Size of embedding (atoms)	—	—	12	62
Charge on central atom	+1.59	+1.82	-0.21	-0.001
Averaged charge on the first shell	-0.15	-0.18	—	+0.026
Charge on embedding			+0.02	-0.008

Charge characteristics of symmetric Mg clusters of 13 and 19 atoms compared with an embedded cluster of 13 atoms (embedding cutoff 1.5 a_0) as obtained with a Mulliken population analysis. All atoms are described by a large-core pseudopotential and corresponding basis set.

Simulation of band gap closure

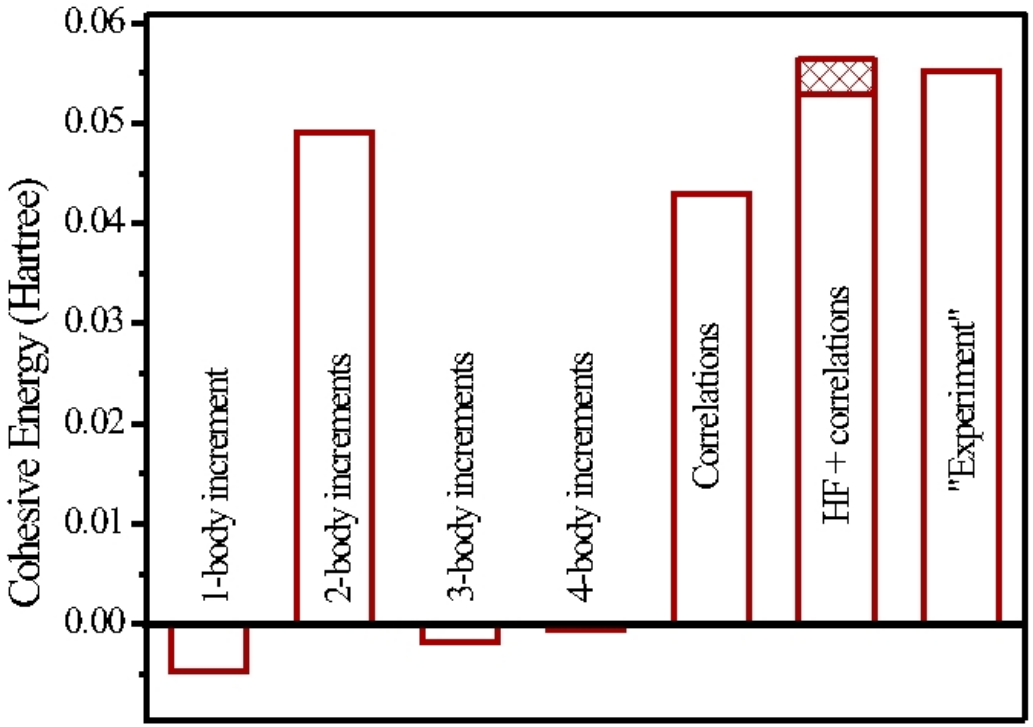


occupied MO
unoccupied MO

1. Tested (LDA-SVWN level) change of HOMO-LUMO gap
   - 1.1 For the atom, the HOMO-LUMO gap is reduced from 0.125 Hartree to 0.024 Hartree by the embedding
   - 1.2 For the dimer (at NN Mg-Mg distance in solid) the HOMO-LUMO gap is 0.076 Hartree for the free dimer, but closed for embedded dimer.

Geometry optimisation of Mg

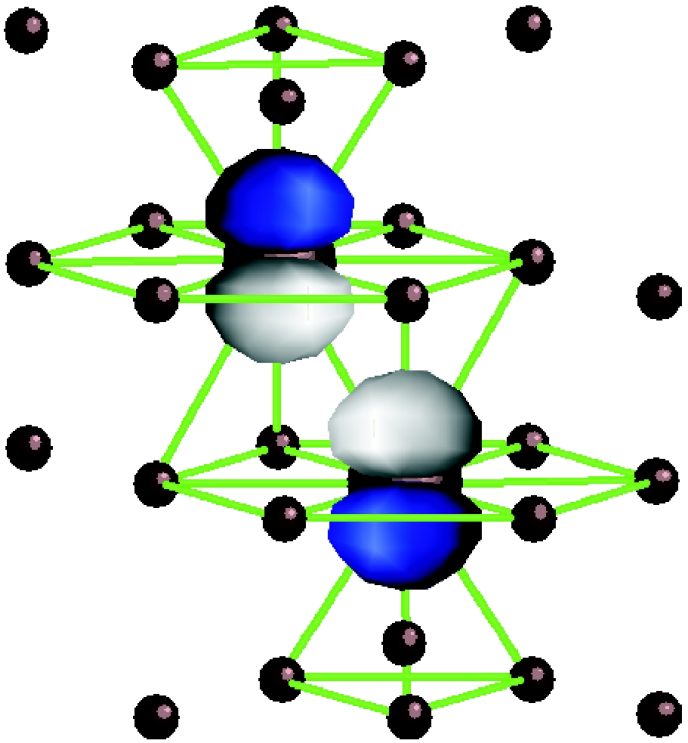
E. Voloshina



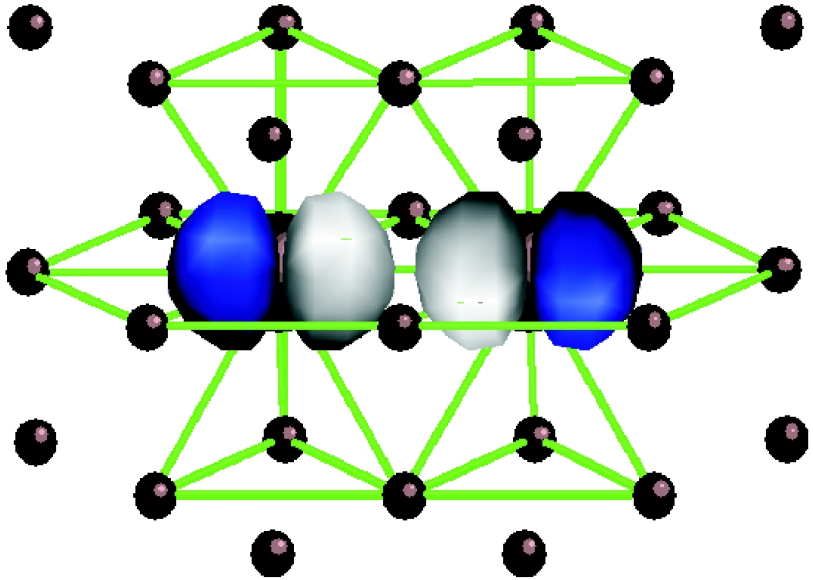
1. HF underbound
2. 1-body correlations repulsive
3. 2-body correlations make most of the binding

Geometry optimisation of Mg

E. Voloshina



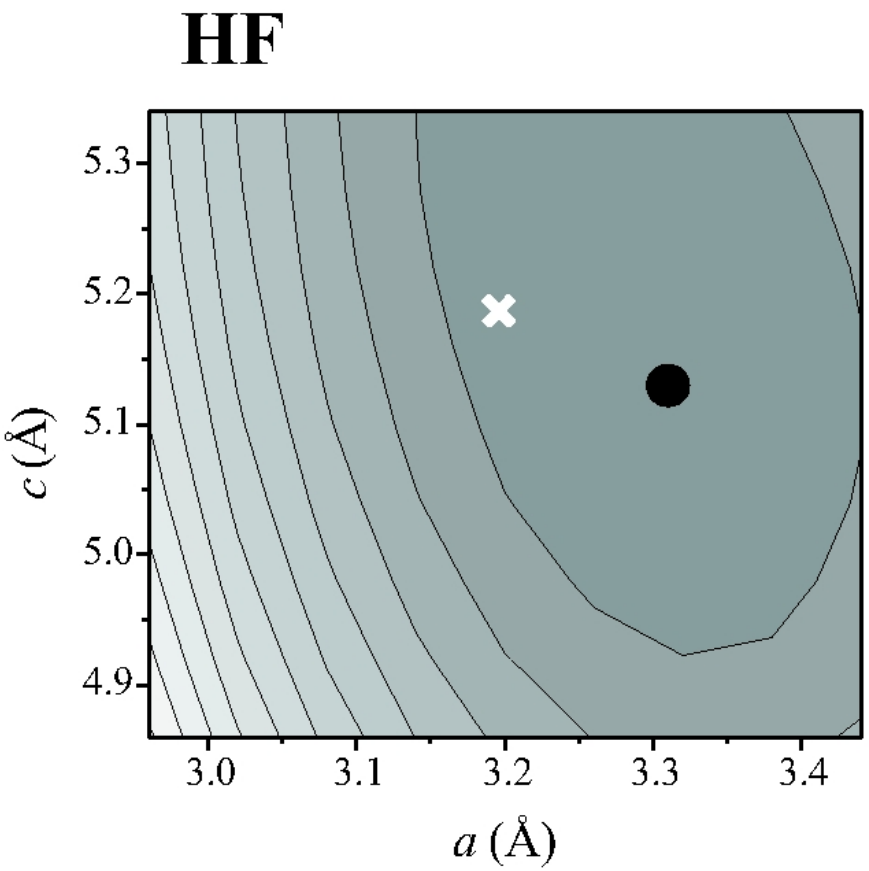
(a)

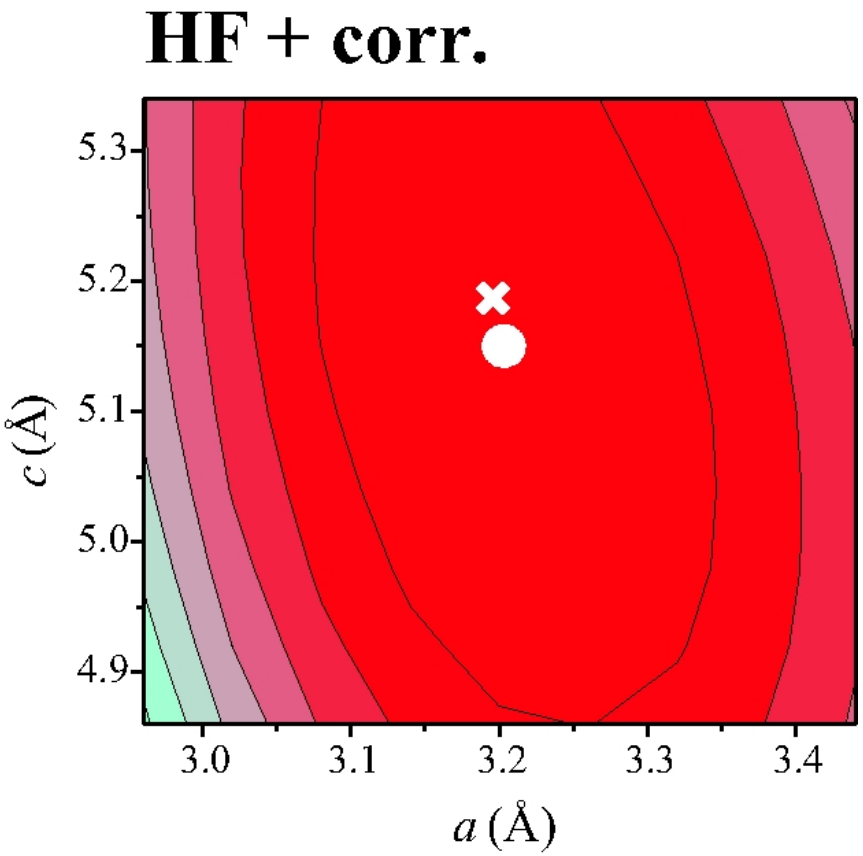


(b)

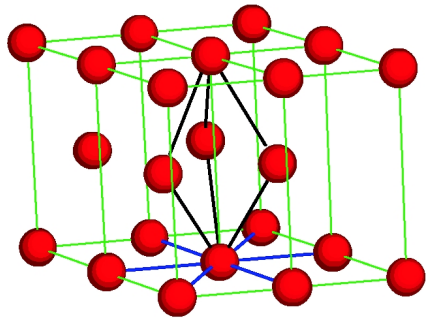
Geometry optimisation of Mg

E. Voloshina



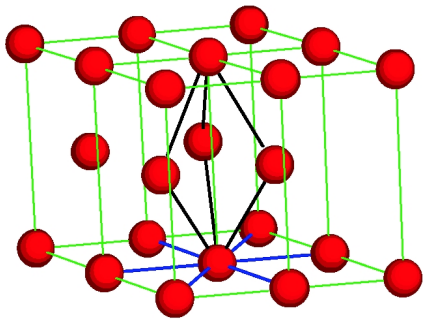


Structural anisotropy in Zn, Cd, Hg



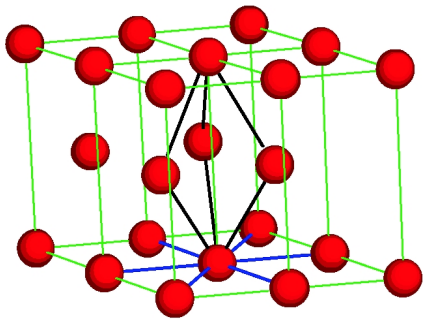
Structure	a(n2)/a(nn)	layering	α
hcp (ideal)	1.000	ABA	60.00
magnesium (hcp)	0.996	ABA	59.87
zinc (hcp)	1.093	ABA	62.78
cadmium (hcp)	1.106	ABA	63.12
mercury (rhomb)	1.155	ABC	70.50
fcc (ideal)	1.000	ABC	60.00

Lattice parameters for Zn



	a(Å)	c(Å)	E(eV)
LDA	2.56	4.88	-1.65
BP86	2.63	5.34	-0.77
PBE	2.65	5.12	-0.97
B3LYP	2.65	5.74	-0.29
B3PW	2.65	5.10	-0.82
EXPT	2.66	4.94	-1.35

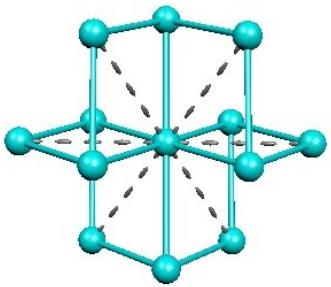
The effect of the *d*-shell in Zn, Cd, Hg



Lattice parameters for Cd

	a(Å)	c(Å)	E(eV)
LDA	2.93	5.22	-1.52
BP86	3.03	5.58	-0.62
PBE	3.02	5.52	-0.77
B3LYP	3.01	6.04	-0.19
B3PW	2.98	5.68	-0.67
EXPT	2.98	5.62	-1.16

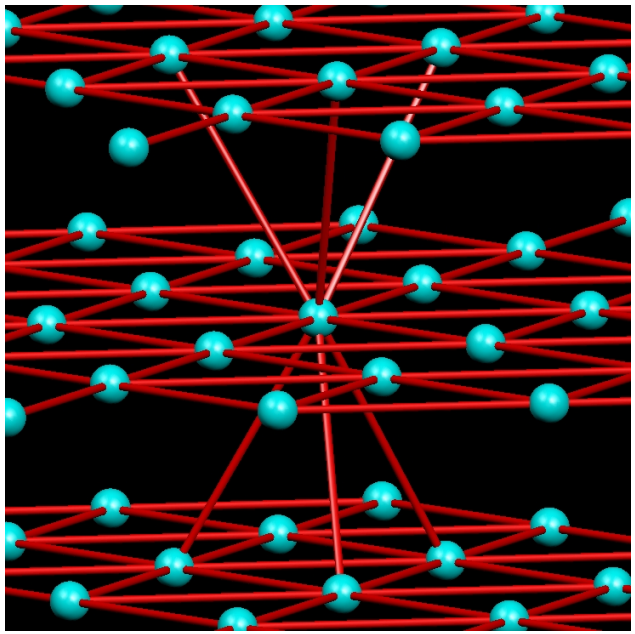
The effect of the *d*-shell in Zn, Cd, Hg

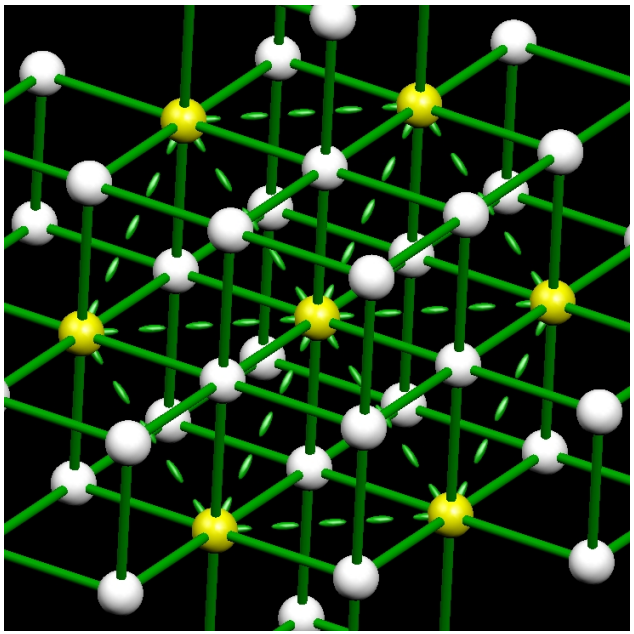


Lattice parameters for Hg

	a(Å)	$\alpha(^o)$	E(eV)	a(n2)/a(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

Structural anisotropy in Zn, Cd, Hg

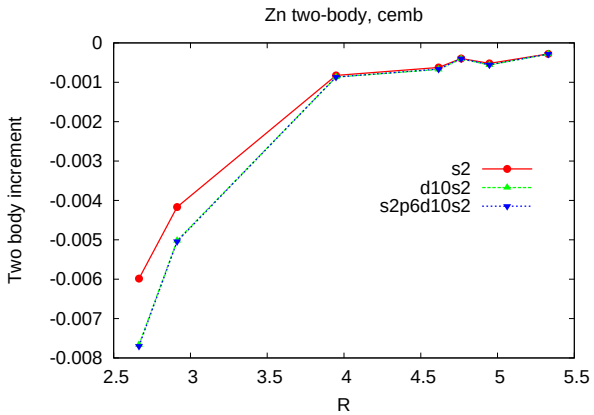


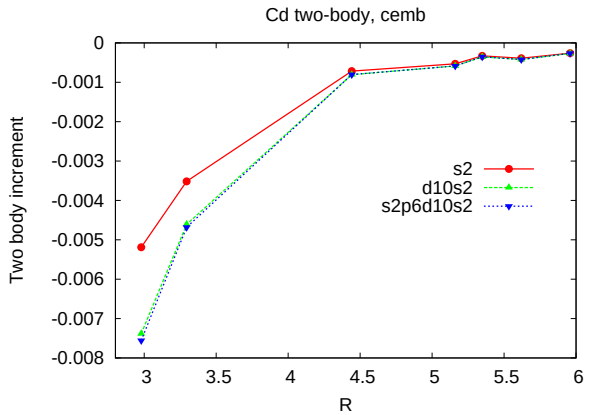


Results - Two body increments

Two-body increment

zinc

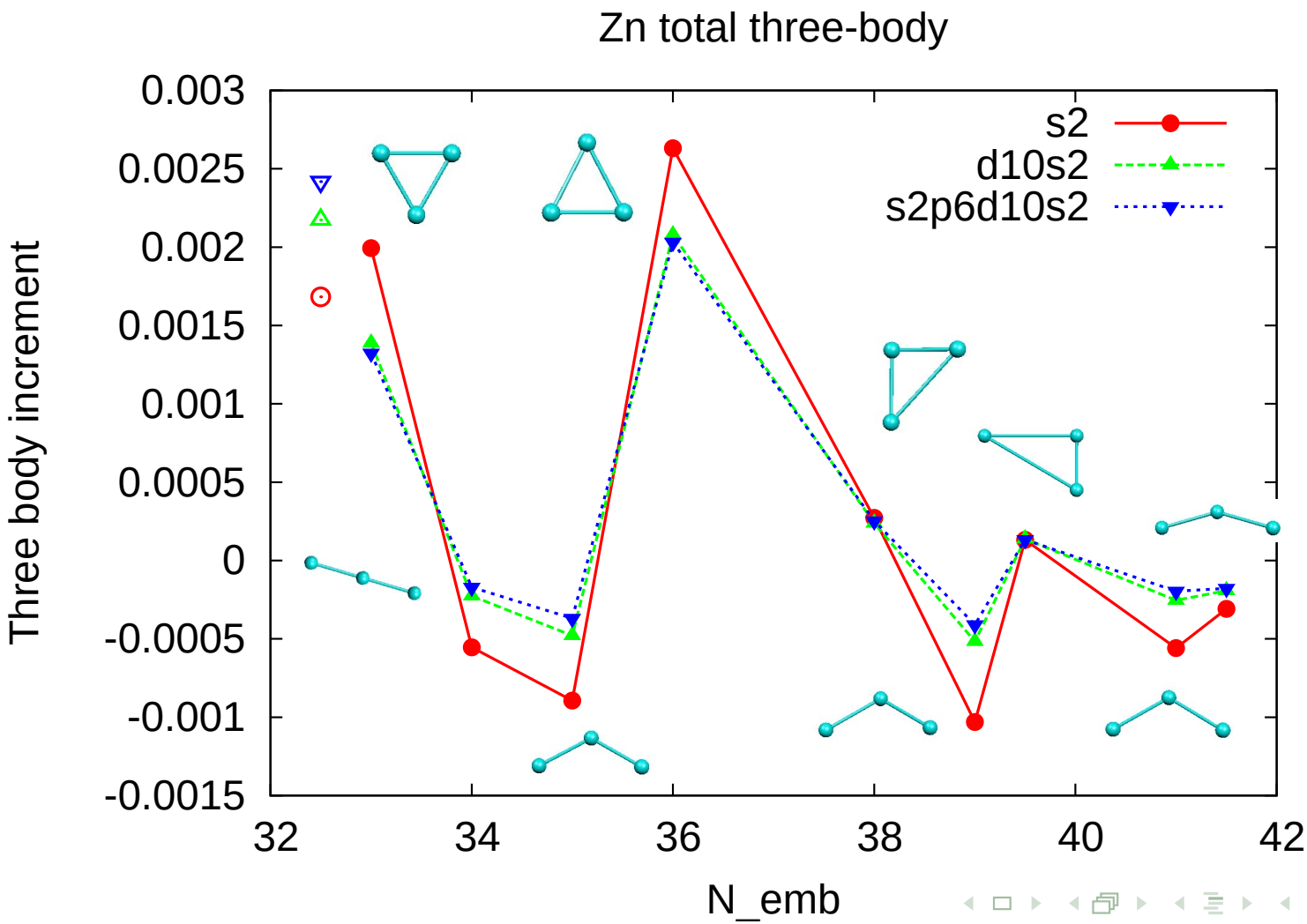




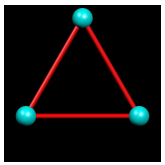
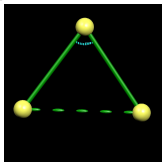
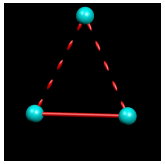
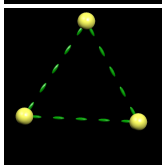
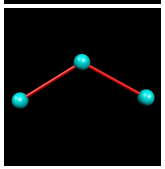
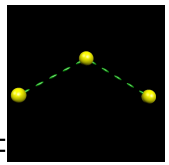
cadmium

1. two-body increments always attractive
2. nearest neighbour largest contribution, decay with distance almost vdW-like (but screening in the metal)

Results - Three body increments



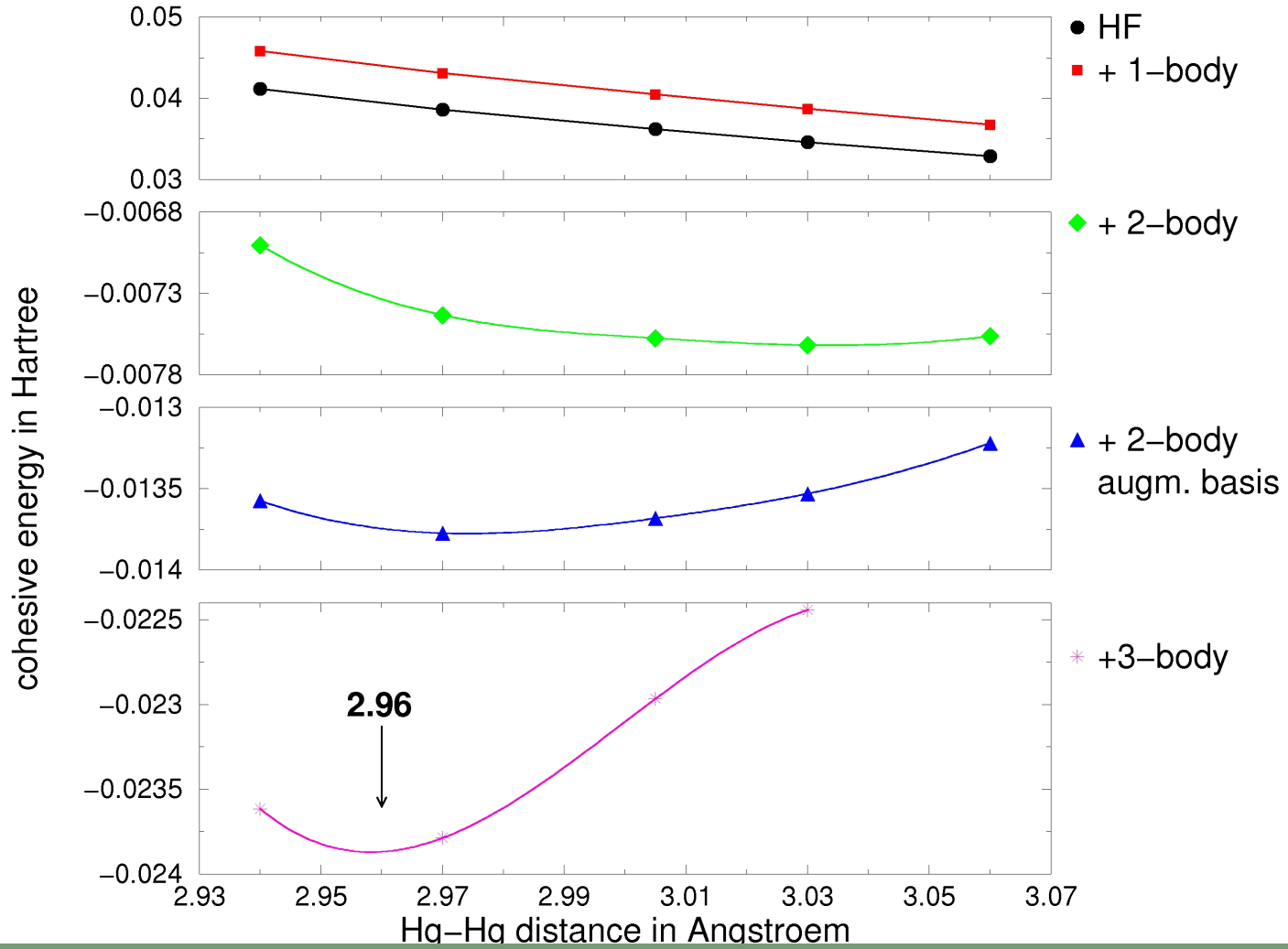
Angular dependence of 3-body increments

HCP	Cohesive Energy /meV	Zn	Cd	Hg	Rhomb
	First 3-body	34.9 (2)	27.6 (2)	-100.8 (6)	
	Second 3-body	52.9 (6)	46.8 (6)	10.2 (2)	
	3-body (120°)	-11.1 (6)	-24.5 (6)	-21.6 (6)	

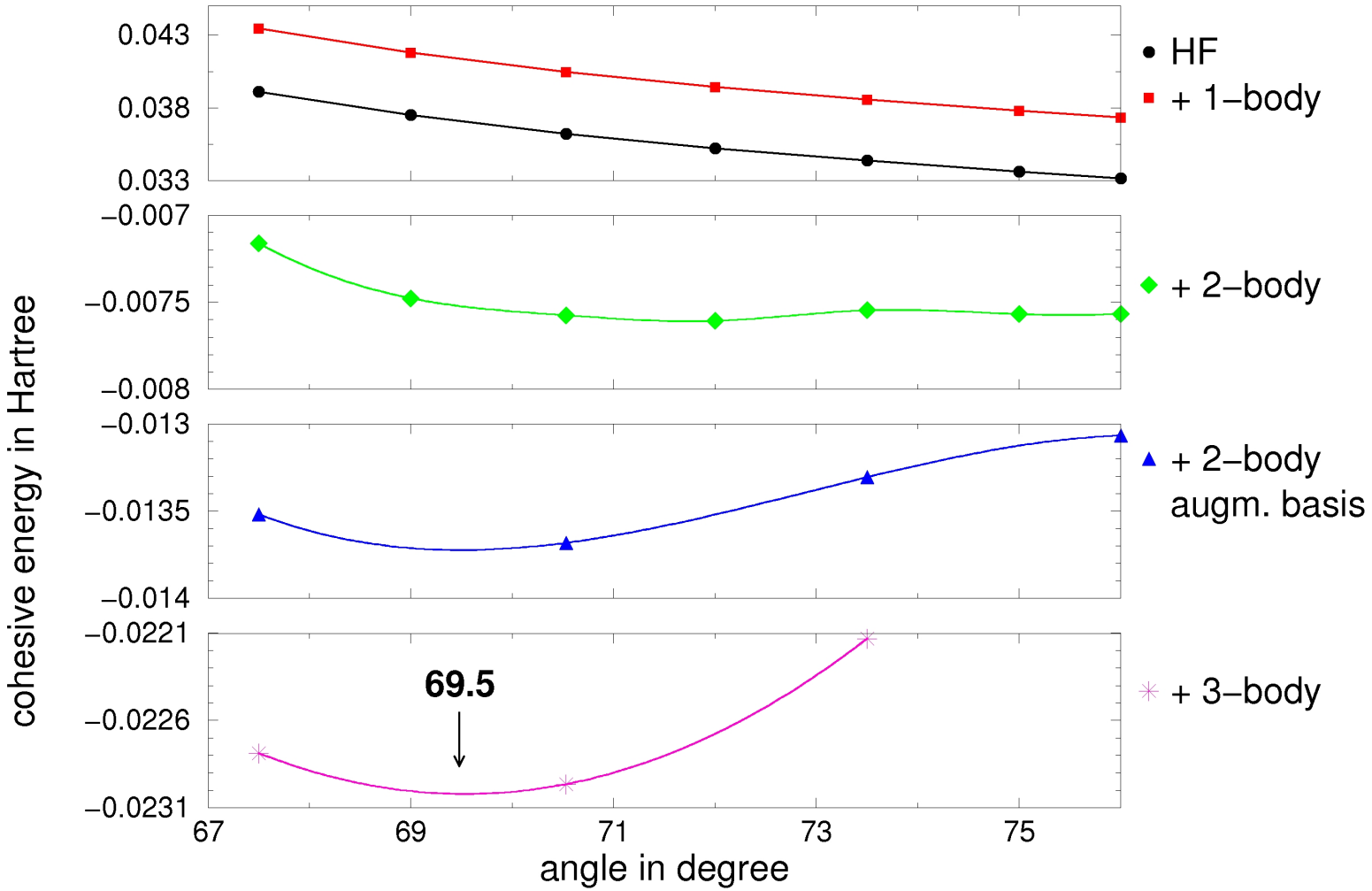
Results - Summary

Cohesive energy (in eV)	**Zinc**	**Cadmium**	**Mercury**
Hartree-Fock (bsse)	**0.089**	**0.266**	**0.985**
$\Delta\epsilon_i^{\mathrm{coh}}$	**-0.030**	**-0.003**	**0.117**
2-body	**-1.452**	**-1.525**	**-1.541**
3-body	**0.087**	**0.097**	**-0.315**
4-body (vTZ-basis)	**0.011**	**0.005**	**0.082**
calculated BE	**-1.30**	**-1.16**	**-0.67**
experimental BE	**-1.35**	**-1.16**	**-0.67**

Results - Structure: Hg - lattice constant



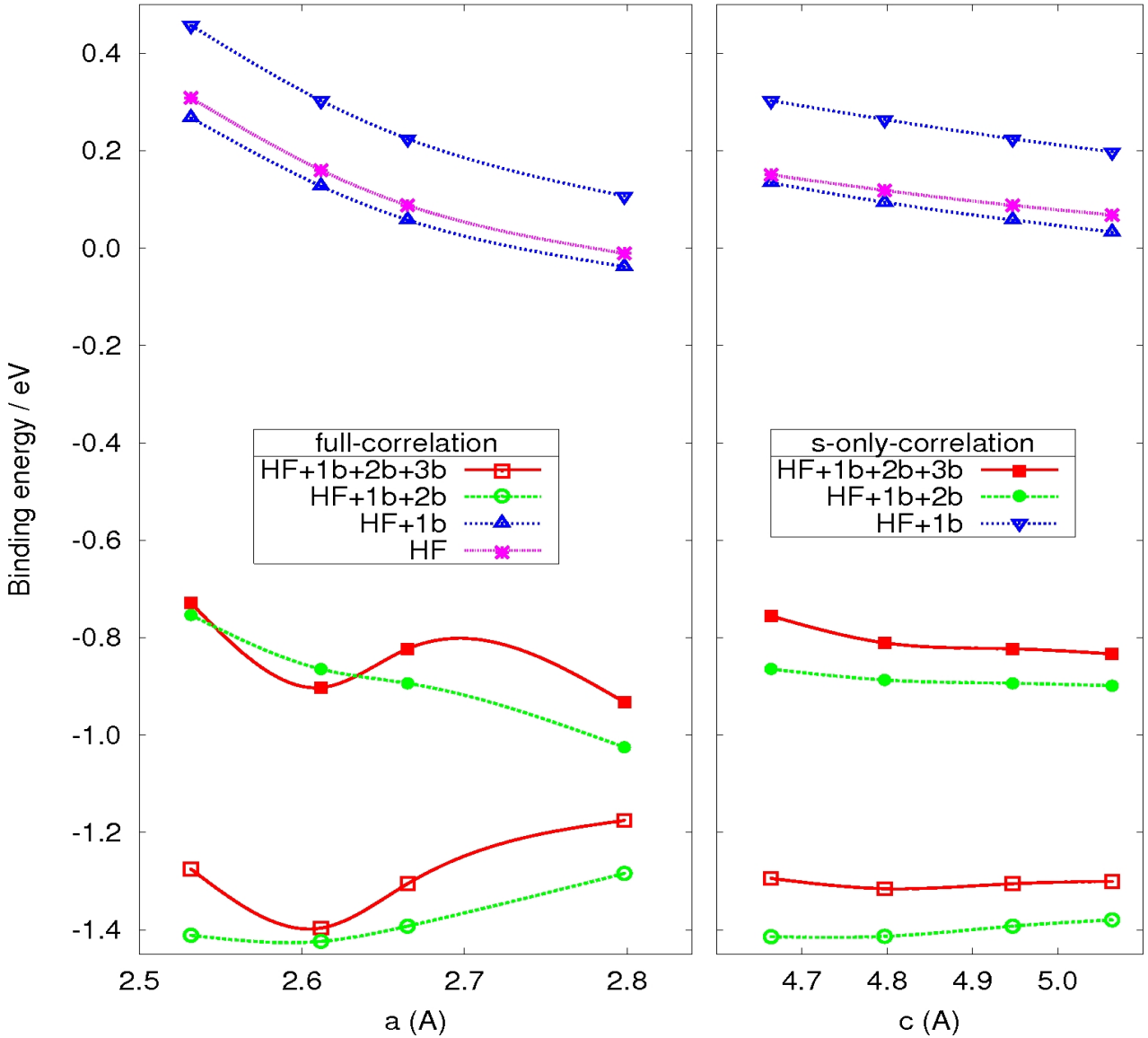
Results - Structure: Hg - rhombohedral angle



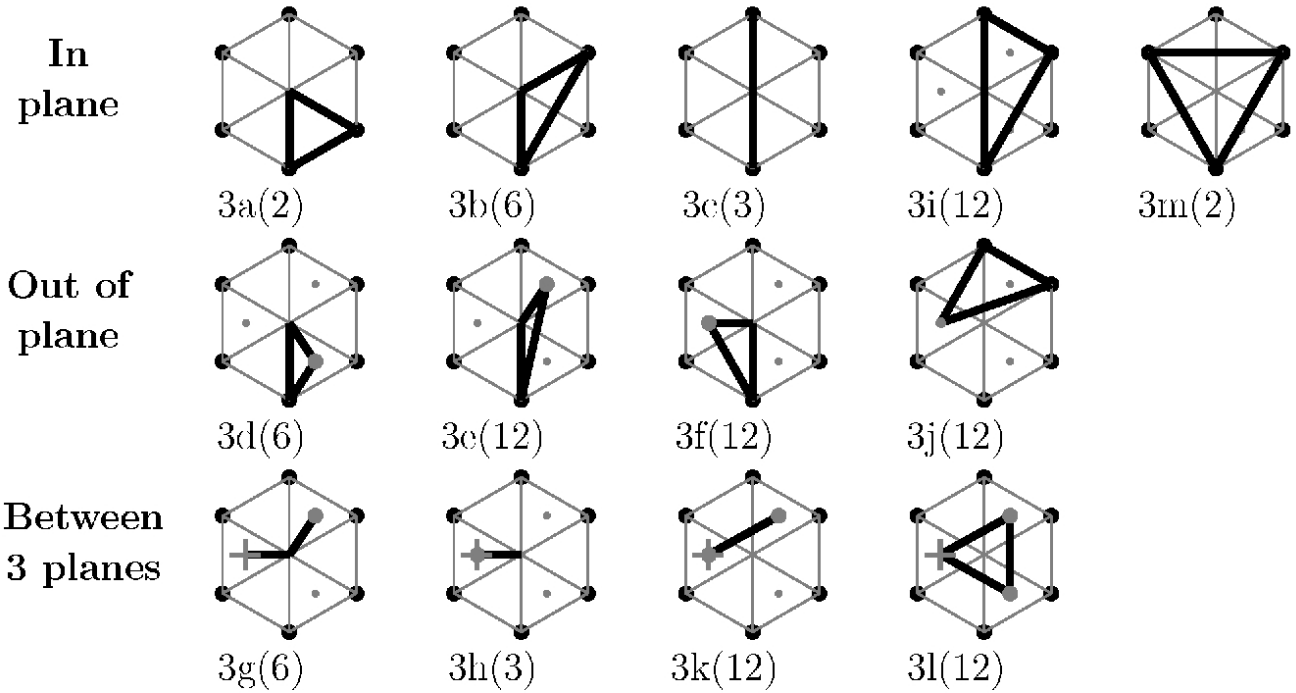
Results - Structure: Hg - bulk modulus

Method	a (Å)	$\alpha(^{o})$	E_{coh}	B (Mbar)
NR-LDA	3.10	60.0	-0.930	0.353
LDA	2.97	72.6	-0.918	0.187
LDA (hcp)	3.06	60.0	-0.813	0.190
Inc. correlation (2b:aug. basis)	2.97	70.0	-0.375	0.132
Inc. correlation (3b:*s*-only)	2.97	69.2	-0.561	0.383
Inc. correlation (3b)	2.96	69.5	-0.649	0.360
Expt CRC Handbook (97)	3.005	70.53	-0.670	
(LMTO):fcc PRL **72**, 2446 (94)	5.03	60.0		0.48
(LMTO):hcp PRL **72**, 2446 (94)	3.58	60.0		0.21
Expt PRL **72**, 2446 (94)				0.382
Expt Sol. St. Phys. **7**, 282 (1958)				0.322

Results

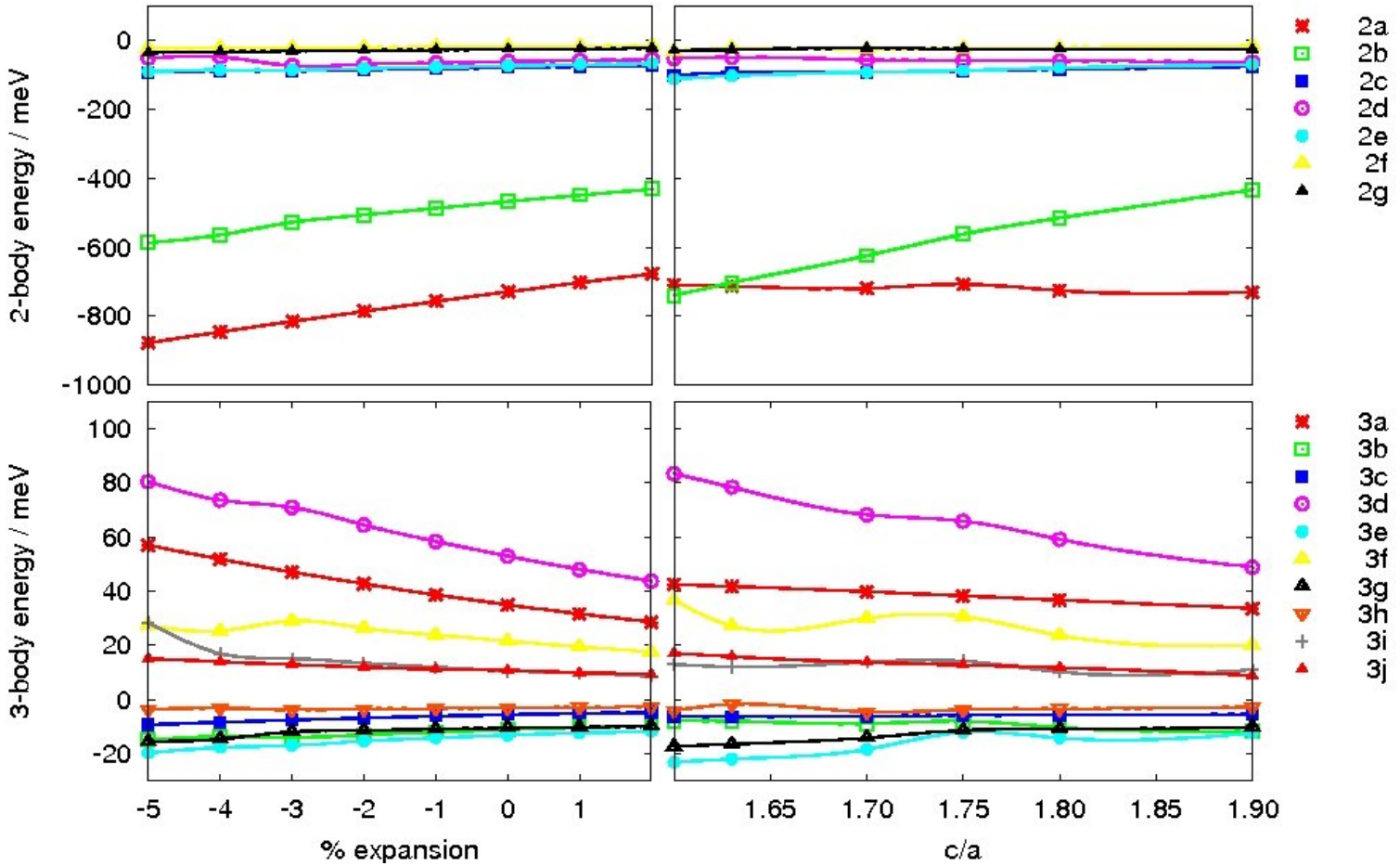

Binding energy / eV
0.4
0.2
0.0
-0.2
-0.4
-0.6
-0.8
-1.0
-1.2
-1.4
full-correlation
HF+1b+2b+3b
HF+1b+2b
HF+1b
HF
s-only-correlation
HF+1b+2b+3b
HF+1b+2b
HF+1b
2.5
2.6
2.7
2.8
a (A)
4.7
4.8
4.9
5.0
c (A)

Results - Structure: Zn - 3-body?

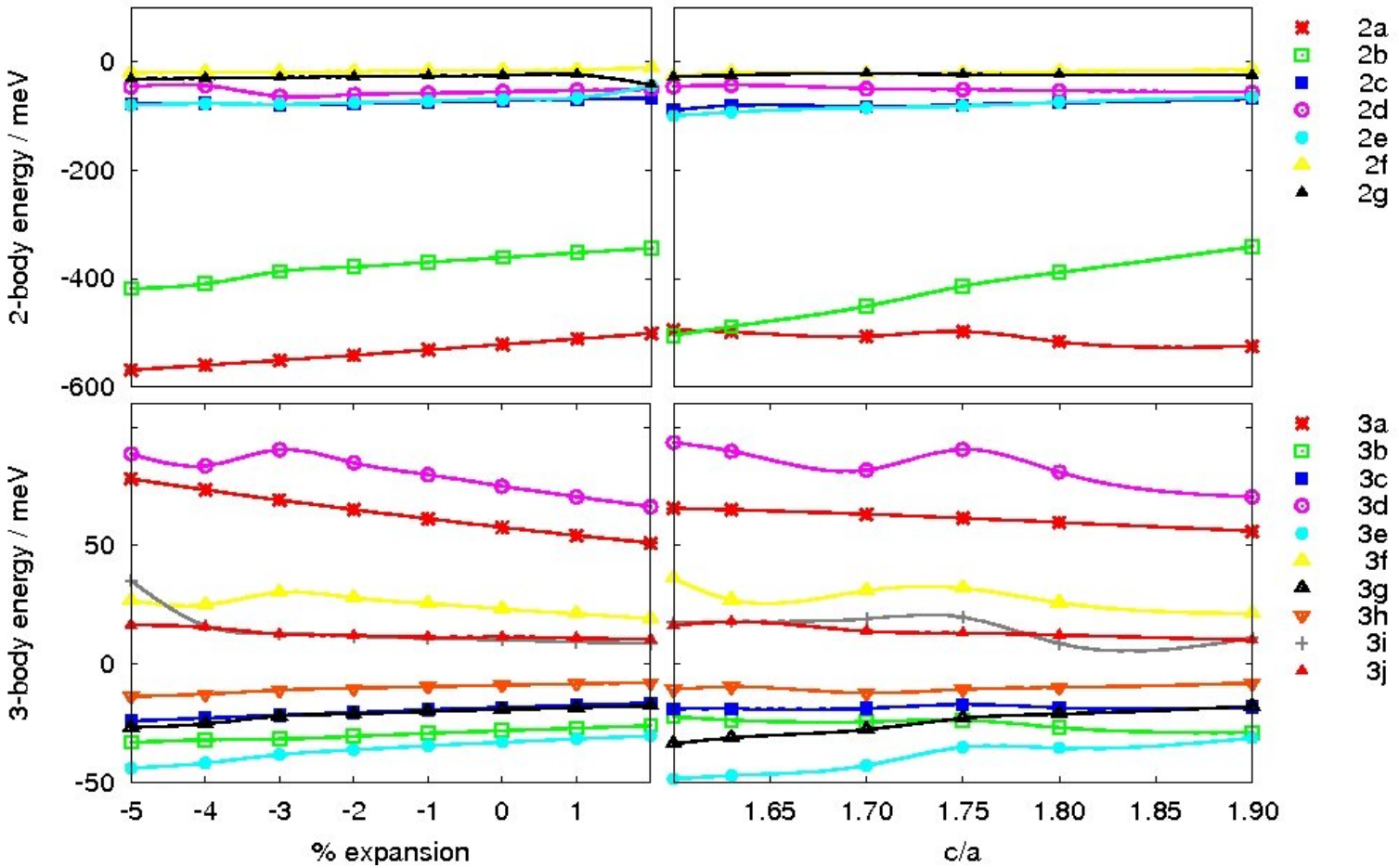


Topological treatment: changing importance of different contributions as lattice parameters change - must keep same geometries to have smooth change of energy

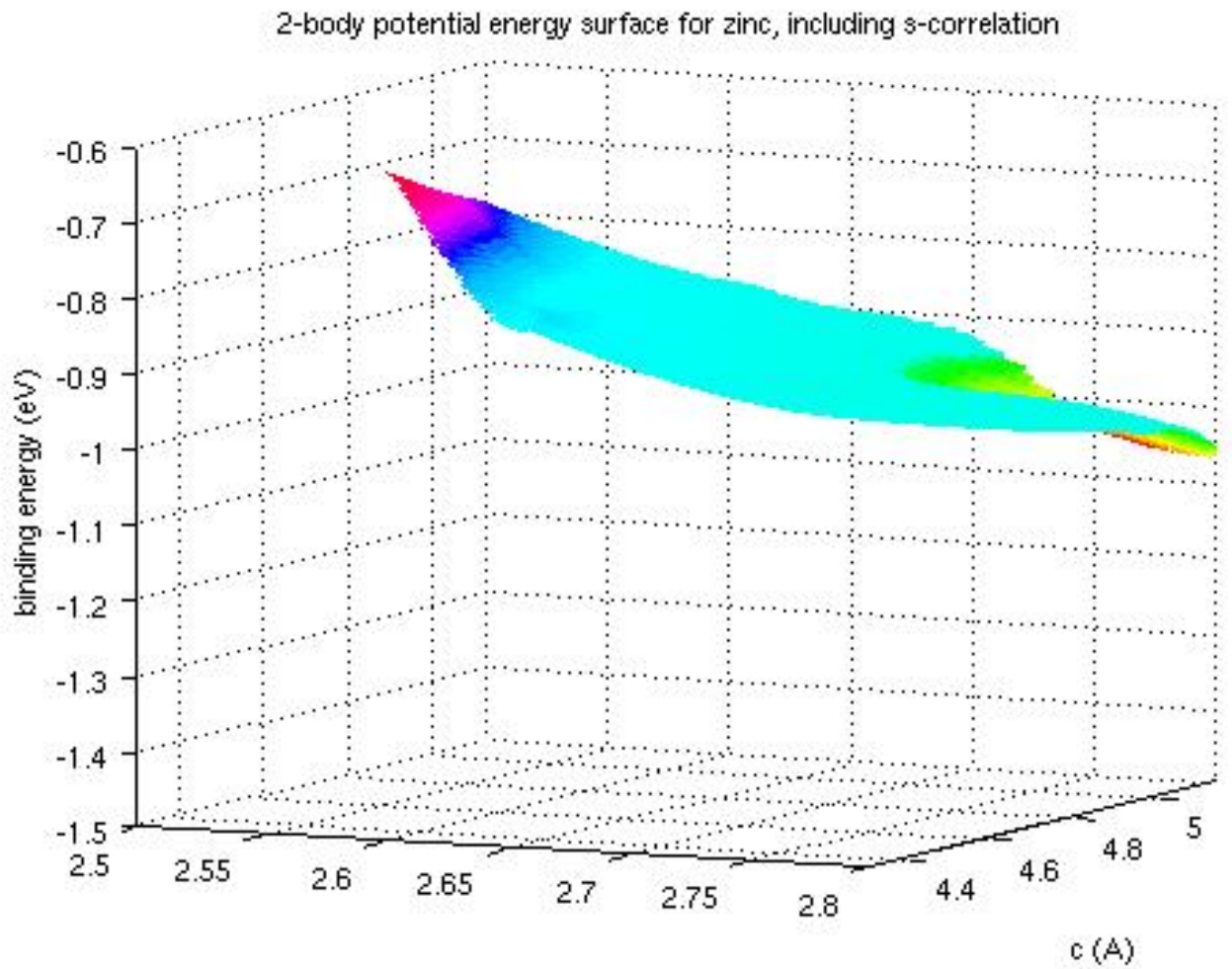
Results - Structure: Zn - individual contributions



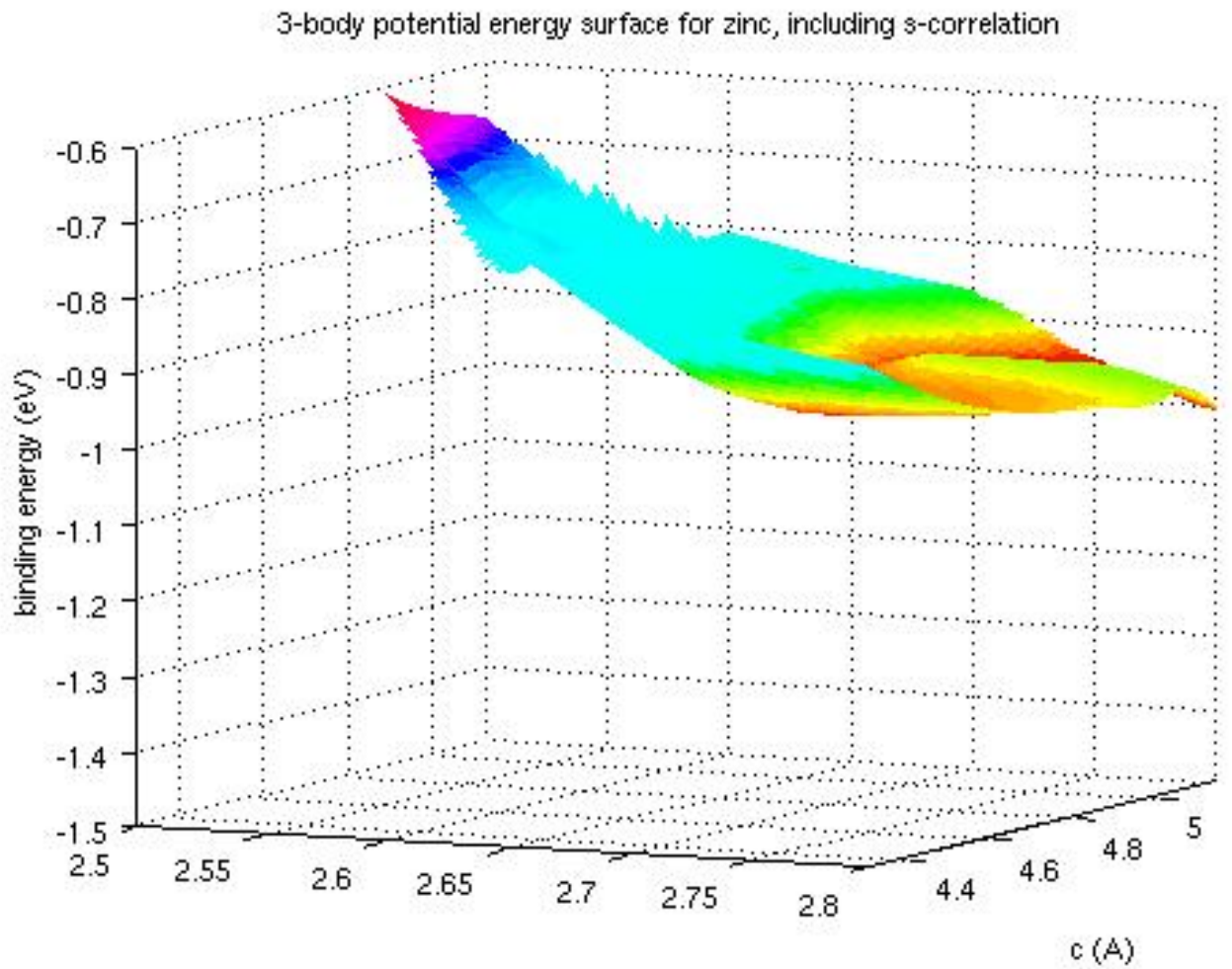
Results - Structure: Zn - individual contributions (s-correlation)



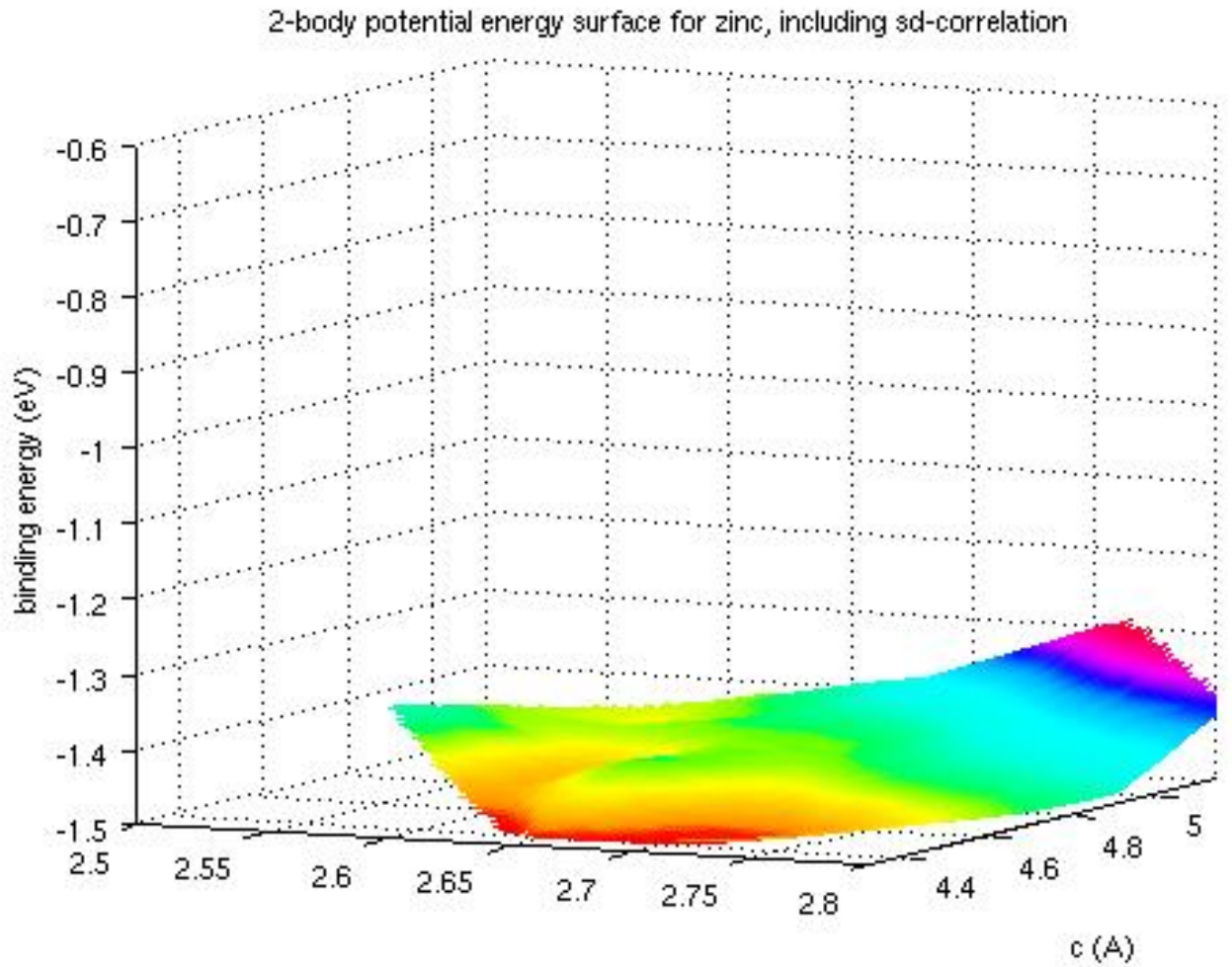
Results - Structure: Zn - PES 2-body s-correlation



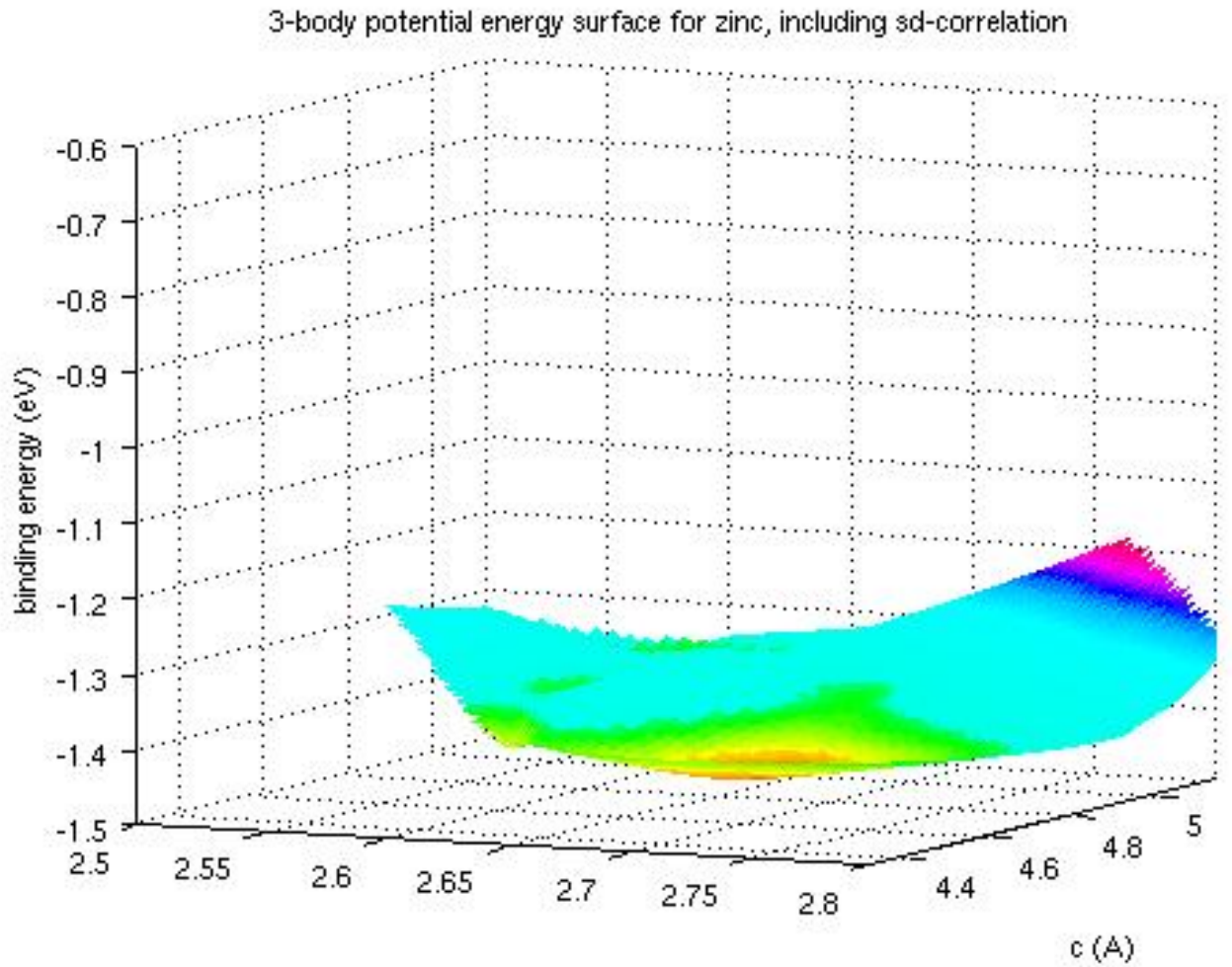
Results - Structure: Zn - PES 3-body s-correlation



Results - Structure: Zn - PES 2-body sd-correlation



Results - Structure: Zn - PES 3-body sd-correlation



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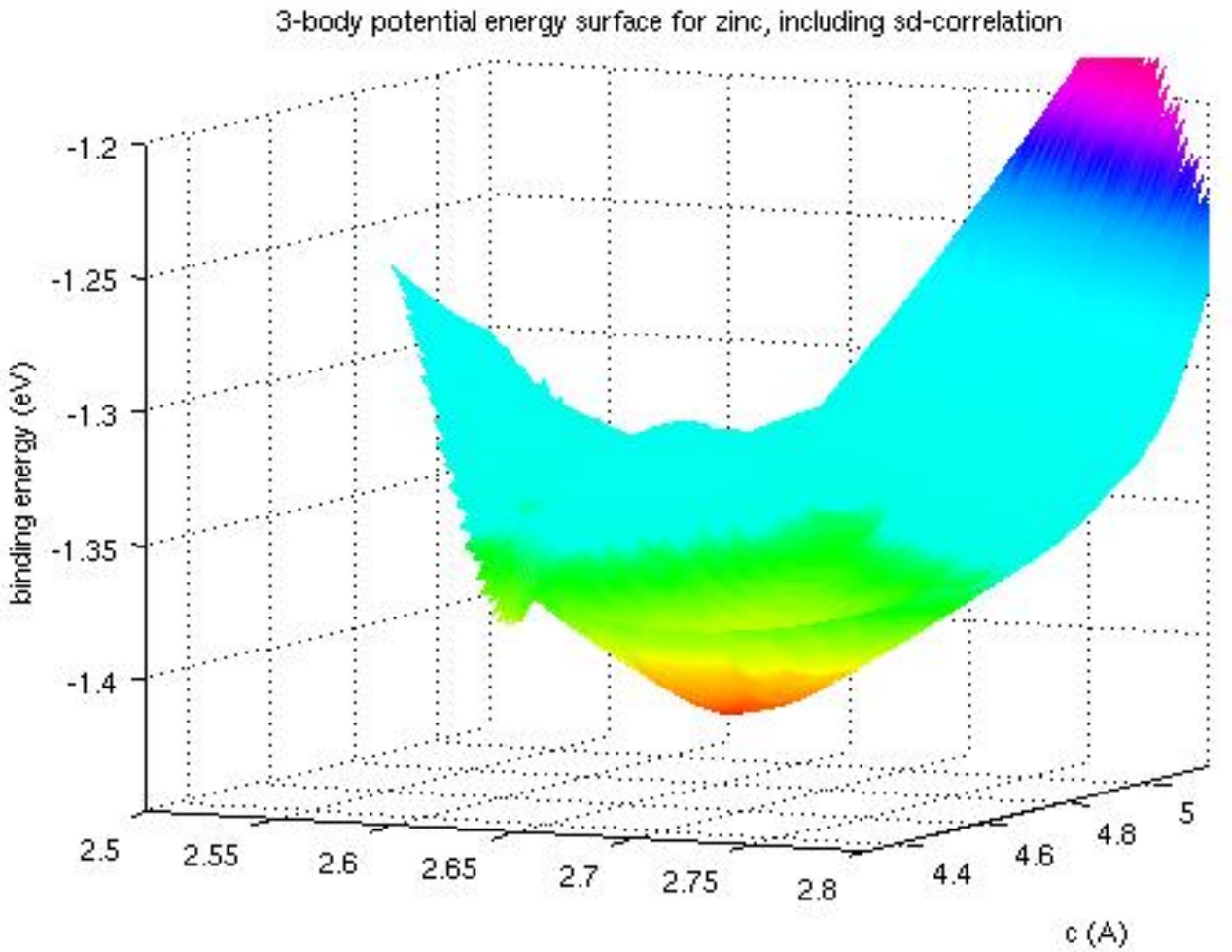

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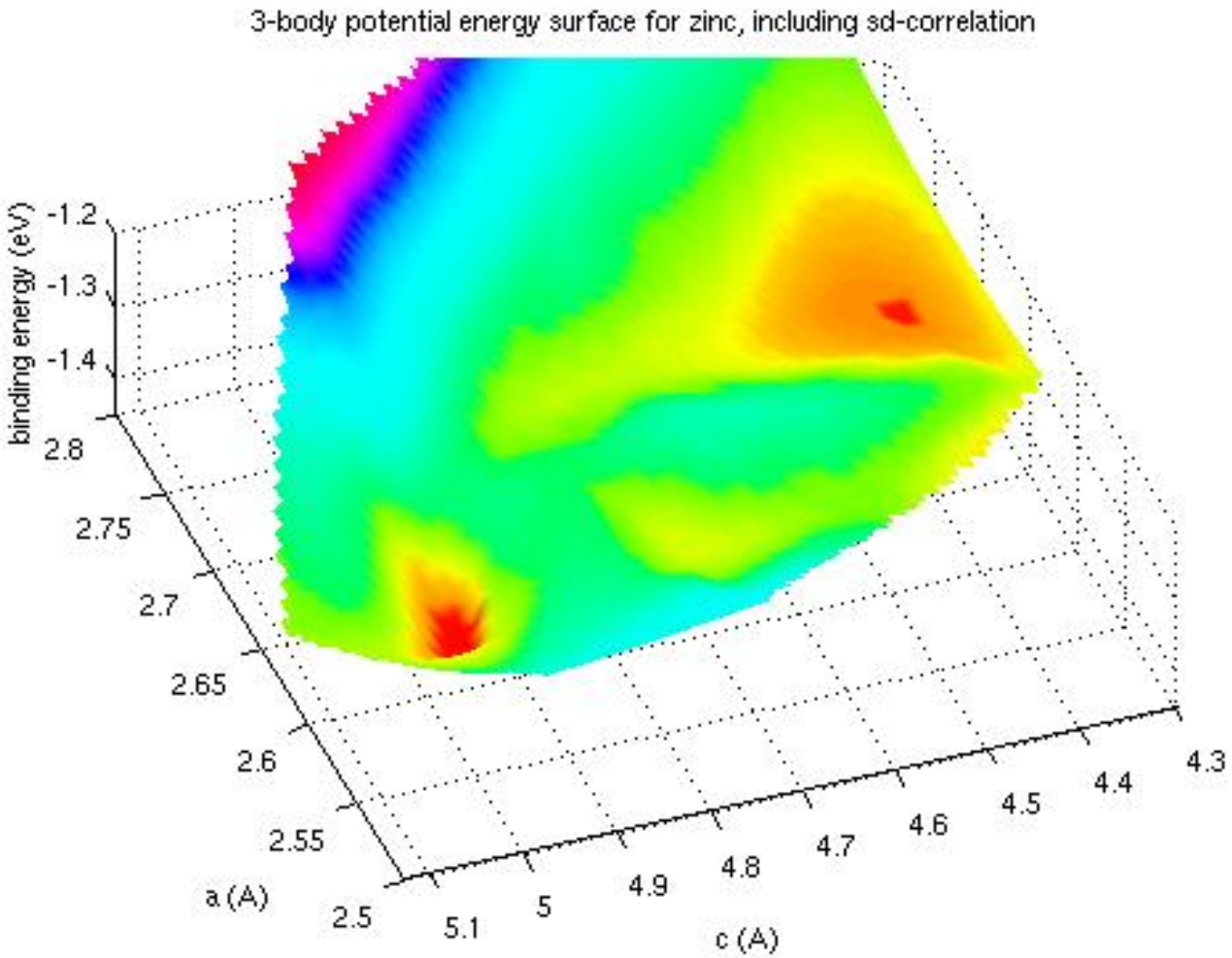

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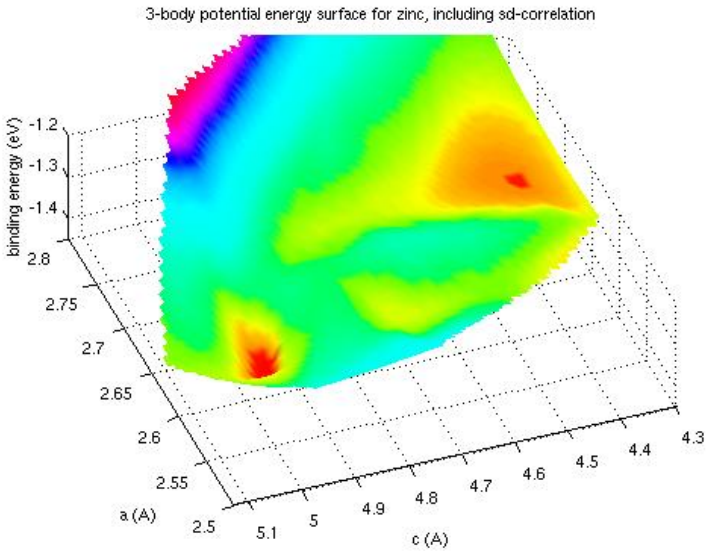
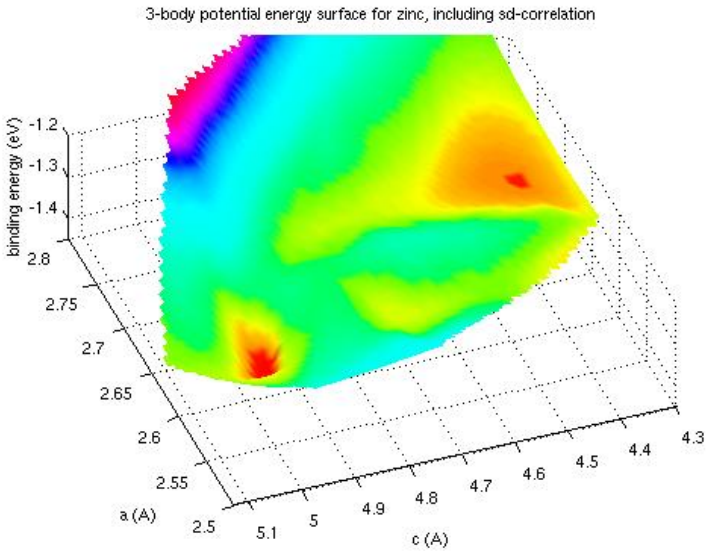


	$a/$Å	$c/$Å	c/a	E_{coh}/eV
Expt	2.66	4.94	1.86	1.35
min 1	2.62	4.96	1.89	1.42
min 2	2.72	4.37	1.61	1.40
max	2.64	4.89	1.85	1.32

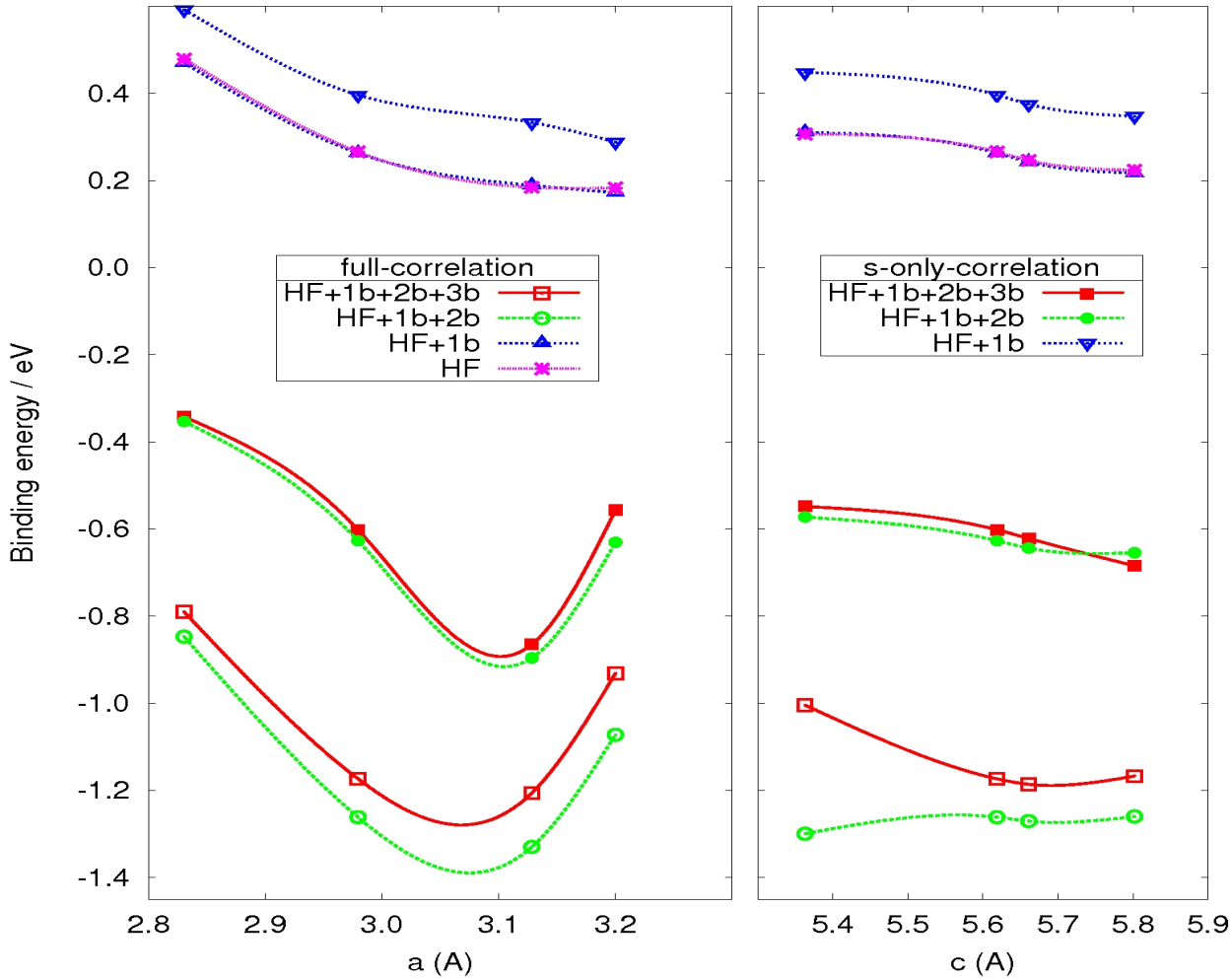
Results - Structure: Zn - PES 3-body sd-correlation



Barrier height $\approx$ 0.09 eV $\approx$ 1200 K

	$a/$Å	$c/$Å	c/a	E_{coh}/eV
Expt	2.66	4.94	1.86	1.35
min 1	2.62	4.96	1.89	1.42
min 2	2.72	4.37	1.61	1.40
max	2.64	4.89	1.85	1.32

Results : Cadmium



Conclusions — method of increments

1. can reproduce the binding energy of magnesium, zinc, cadmium, and mercury quantitatively using *ab initio* (CCSD(T)) correlation calculations
2. all lattice parameters in good agreement with experiment
3. have good convergence of the incremental scheme
4. each higher order of increments contributes about an order of magnitude less (4-body same magnitude as ZPVE contribution)

Conclusions — the group IIB metals

1. The equilateral triangle is repulsive in all cases
2. The hcp distortion (large c/a) reduces this repulsion
3. *d*-correlation adds about 35-50% of the cohesive energy, proportionately more in 3-body
4. The change of structure from hcp to rhombohedral for Hg makes the total 3-body contribution more cohesive
5. The attractive 3-body interaction for mercury due to close proximity of the *d*-orbitals, caused both by the strong contraction of the Hg-Hg distance relative to the dimer, and the relativistic expansion of the 5*d*-orbitals

Conclusions — the c/a anisotropy

1. The experimental (anisotropic) minimum comes from the 3-body terms
2. This is partly described by *s*-correlation, but overall the wrong slope
3. *d*-correlation absolutely vital for total energy and slope of PES
4. The two-body terms would give an ideal hcp structure (which remains as a local minimum with 3-body)
5. The barrier between the anisotropic and ideal hcp forms of zinc can be estimated to be of the order of 1000 K, well over the melting point of zinc (692.68 K), which may explain why it has never been observed