

The scheme of local increments for calculating adsorption energies of molecular adsorbates at solid surfaces

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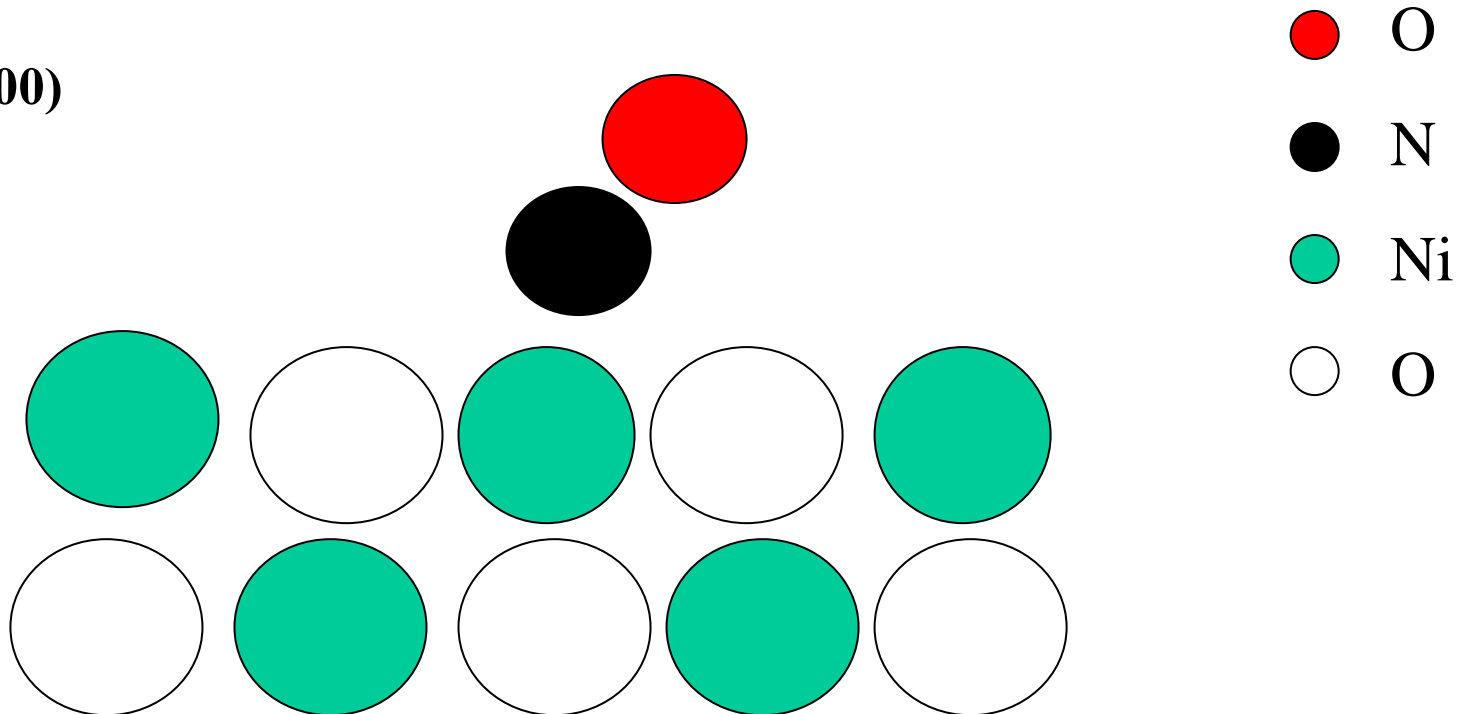
LCC2007, Dresden, 12.-15.Sept. 2007

J.-T. Hoefft, M. Kittel, M. Polcik, S. Bao, R. L. Toomes, J.-H. Kang,
D. P. Woodruff, M. Pascal, and C. L. A. Lamont

Molecular Adsorption Bond Lengths at Metal Oxide Surfaces: Failure of Current Theoretical Methods

Phys. Rev. Lett. 87, 086101 (2001)

NO/NiO(100)



Adsorption energy for CO/MgO(001)

Experiment

Theory

Method	MgO model	E_{ads}/eV	Reference
Temperature programmed desorption (TPD)	Single crystal MgO(100) surface	0.14	73
Infrared (IR) spectroscopy	Thin MgO film	0.43	74
IR spectroscopy	MgO microcrystals	0.13	75
IR spectroscopy	MgO powder samples	0.15 – 0.17	76,77
SCF (without BSSE correction)	Embedded MgO_5^{8-} cluster	0.20	78
DFT LDA functional	Embedded Mg_9O_9 cluster	0.97	79
DFT BLYP functional (BSSE corrected)	Free $\text{Mg}_{25}\text{O}_{25}$ cluster	0.09	80,81
SCF (BSSE corrected) Correlated (BSSE corrected)	Embedded MgO_5^{8-} cluster	0.014 0.066	83
DFT PW91 functional	Embedded Mg_9O_9 cluster	0.288	82
DFT B3LYP functional	Periodic approach (1×4) coverage	0.034	72
DFT, B3LYP functional, and perturbation estimate	Mg_9O_9 cluster	0.137	84

Review: V. Staemmler

Top. Organomet..Chem 12,
219 (2005)

References therein

HAS

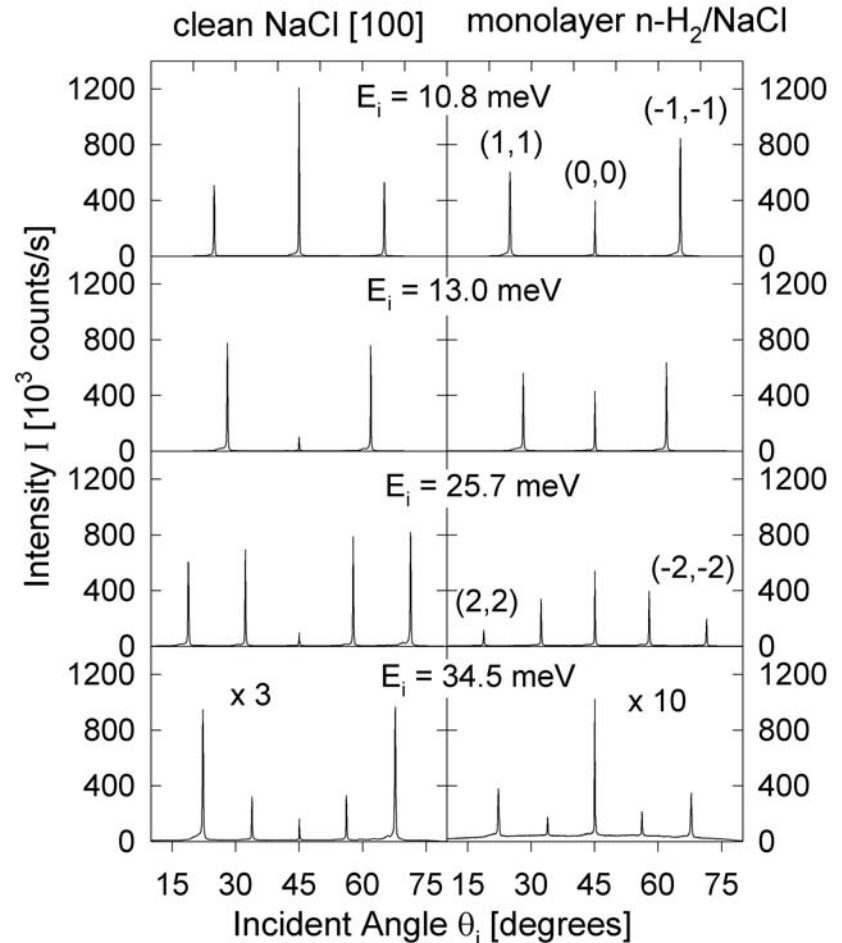
Helium Atom Scattering

Surface analysis

(Bochum: Wöll, Witte, Traeger)

He/MgO

- > weak interaction, ~ 10 meV
- > full 3D potential energy surface
- > conventional CC methods too expensive
- > Stoll's method of increments ?



F.Traeger, Bochum, private communication

Outline

- I. Method of increments
- II. Pure Van der Waals system:
He/MgO(001)
- III. CO/MgO(001)
- IV. Cu atoms in O and Zn defects
at ZnO surfaces
- V. Conclusions

Method of increments

$$E_{korr} = \sum_{i=1}^n I_1(N_i) + \sum_{i<j}^n I_2(N_i, N_j) + \sum_{i<j<k}^n I_3(N_i, N_j, N_k) + \dots$$

$$I_1(N_i) = E_{korr}(N_i)$$

$$E_{korr}(N_1, N_2) = I_1(N_1) + I_1(N_2) + I_2(N_1, N_2)$$

$$I_2(N_1, N_2) = E_{korr}(N_1, N_2) - I_1(N_1) - I_1(N_2)$$

$$I_3(N_1, N_2, N_3) = E_{korr}(N_1, N_2, N_3) - I_1(N_1) - I_1(N_2) - I_1(N_3) \\ - I_2(N_1, N_2) - I_2(N_1, N_3) - I_2(N_2, N_3)$$

$$I_n(N_1, N_2, \dots, N_n) = E_{korr}(N_1, N_2, \dots, N_n) - \sum_{i=1}^{n-1} I_i(N_1, N_2, \dots, N_i)$$

H. Stoll, B. Paulus, P. Fulde, J. Chem. Phys. 123, 144108 (2005)

B. Paulus, Phys. Rep. 428, 1 (2006)

Method of calculation

> Embedded cluster model

Quantum cluster, boundary region, extended point charge field

> MCCEPA

(„multi configuration coupled electron pair approximation“)

approximate multi reference CCSD

exactly size consistent, scales as $n_{\text{occ}}^2 \times N^4$

start with ROHF (closed or open shell)

localization of the occupied orbitals (Foster-Boys)

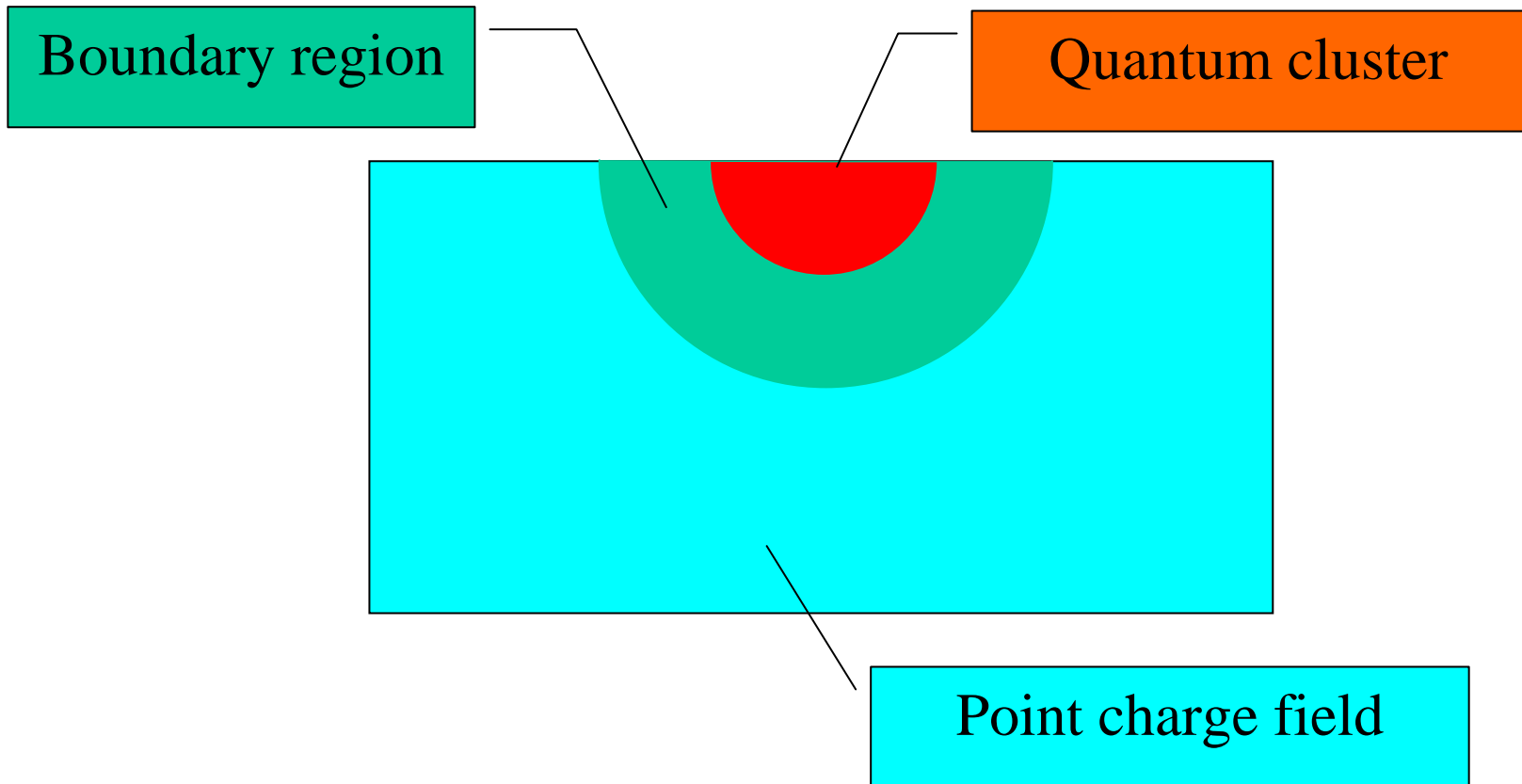
use of pair natural orbitals (PNOs): automatic localization of the virtual orbitals, truncation according to an energy criterion

R. Fink, V. Staemmler, Theor. Chim Acta 87, 129 (1993)

> Medium to large basis sets

600-800 basis functions

Embedded cluster model



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I. Method of increments

II. Pure Van der Waals system:
He/MgO(001)

III. CO/MgO(001)

IV. Cu atoms in O and Zn defects
at ZnO surfaces

V. Conclusions

Theoretical treatment of van der Waals interactions

DFT:

exact XC functional: exact solution
including dispersion

local functionals: no dispersion,
overbinding

semi-empirical: KSDD:
 $\sim D \cdot C_6 / R^6$

improved functionals: ????

Wave function based approaches:

SCF: all interactions, no dispersion

semi-emp.: HFDD

(HF+damped dispersion)

MP2: reasonable, size consistent,
 $\sim N^5$, overbinding

CISD: not size consistent, $\sim N^6$

CCSD: reasonable, $\sim N^6$

CCSD(T): very reliable, best method
time consuming, $\sim N^7$

alternative methods:

embedding (Torino group)

increments (Stoll, Paulus)

Details of the calculation

Embedded clusters:

MgO5, small basis

MgO5, large basis

Mg2O7, large basis

Mg18O17

fixed geometry, $a=7.96 a_0$

PP: Mg, Stuttgart group

PC field: 10206 PC

He position:

ontop Mg^{2+} , $R=6.00 a_0$

Subunits:

He

$\text{O}^{2-}(2s,2p)$, $\text{Mg}^{2+}(2s,2p)$

BSSE correction:

full Boys-Bernardi

Basis sets:

small: TZP(O)

TZ(Mg)

large: QZ3d1f (O,Mg)

7Z4p1d (He)

Mg18O17: TZ3d(O)

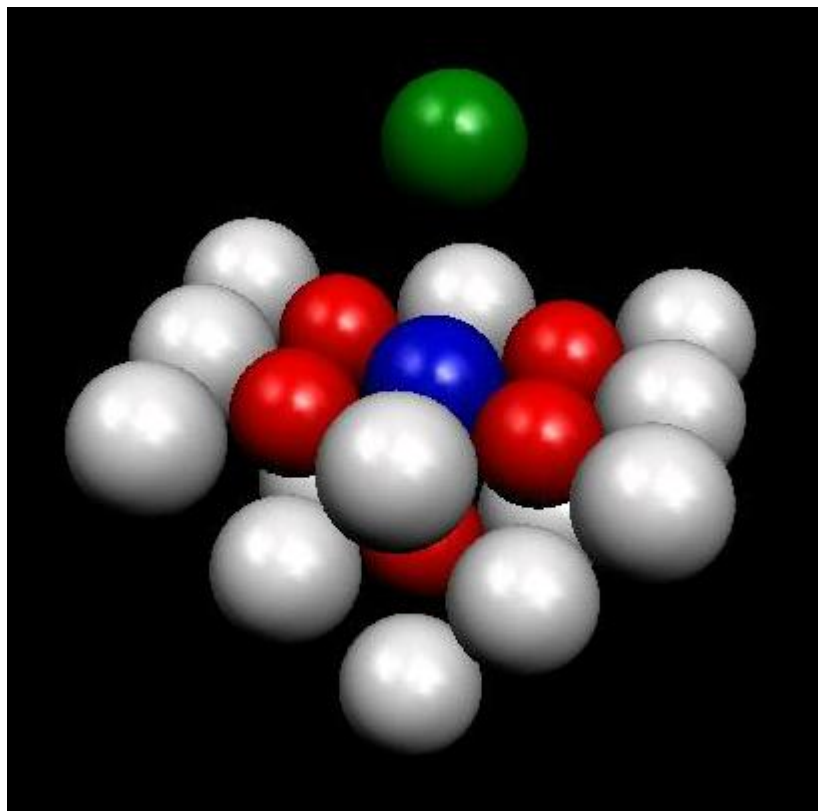
TZ(Mg)

Correlation:

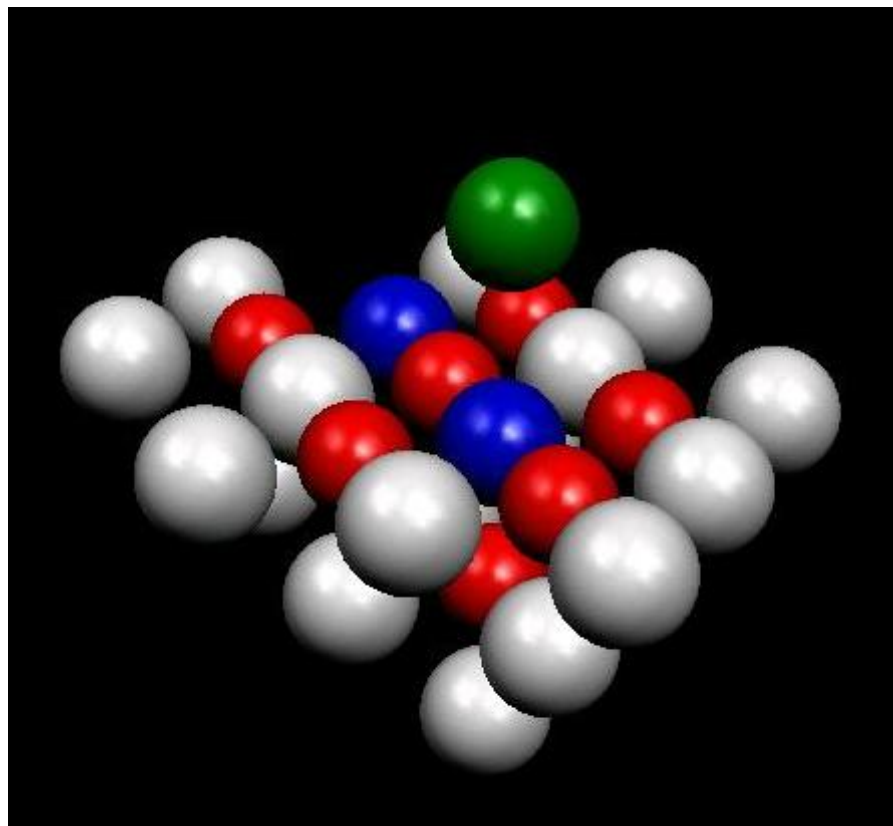
MCCEPA

CEPA-0

MgO clusters



He/MgO₅PP₁₃



He/Mg₂O₇PP₁₈

I. Convergence of the n-body increment expansion: He/MgO₅

Increments	Atoms	Small basis	Sum
1-body	He	-0.023631	-0.023631
	Os	-0.187475	
	Oss	-0.183861	-0.933742
2-body	He-Os	-0.000060	
	He-Oss	-0.000002	-0.000242
	Os-Os'	-0.002234	
	Os-Os''	-0.000254	
	Os-Oss	-0.002040	-0.017846
3-body	He-O-O	~ +0.000001	
	O-O-O	~ +0.000050	+0.000500
1,2,3-body			-0.974717
Full calculat.			-0.974737

Large basis	Sum
-0.037951	-0.037951
-0.244078	
-0.240585	-1.216920
-0.000097	
-0.000005	-0.000393
-0.002675	
-0.000294	
-0.002389	-0.021235
~ +0.000002	
~ +0.000060	+0.000596
	-1.275510
	-1.275532

Only O atoms correlated: Os, Os' = surface O atom
 Oss = subsurface O atom
 All entries in a.u.; not all increments are shown

II. Counterpoise correction: He/MgO₅

Increments	Atoms	CC (He+MgO)	Sum	Full system He/MgO	Sum
1-body	He	-0.037966	-0.037966	-0.037951	-0.037951
	Os	-0.244116		-0.244078	
	Oss	-0.240582	-1.217038	-0.240585	-1.216920
2-body	He-Os	-		-0.000097	
	He-Oss	-		-0.000005	-0.000393
	Os-Os'	-0.002673		-0.002675	
	Os-Os''	-0.000296		-0.000294	
	Os-Oss	-0.002391	-0.020848	-0.002389	-0.020848
3-body	He-O-O	-		~ +0.000002	
	O-O-O	~ +0.000050	+0.000502	~ +0.000060	+0.000596
1,2,3-body			-1.275350		-1.275510
Full: He+MgO			-1.275325		-1.275532

Large basis set; all entries in a.u..

III. Dispersion: Cluster size effect

Increment	Number of contributions/ distance $d(a_0)$	MgO5 small basis	MgO5 large basis	Mg2O7 large basis	Mg18O17
He-Os	4 / 7.20	-0.060	-0.097	-0.106	-0.126
He-Oss	1 / 9.98	-0.002	-0.005	-0.005	-0.012
He-Os'	8 / 13.36	-	-	-0.002	-0.005
He-Mg	1 / 6.00	-	-	-0.012	-0.021
Total disp.		-0.242	-0.393	-0.457	-0.577

All contributions in mH.

IV. Total interaction energy

	SCF	Dispersion	Correlation	Total
MgO5, small basis	+0.300	-0.242	-0.020	0.280
MgO5, large basis	+0.274	-0.393	-0.207	0.067
Mg2O7		-0.457		
Mg18O17, increments	+0.241	-0.577		(-0.150)
Mg18O17, full	+0.241	(-0.473)	(-0.293)	(-0.052)
MgO, periodic, 2L DZP basis	+0.285			
MgO, periodic, 2L DZP+diffsp(0.13)	+0.269			

All contributions in mH, with CC.
Values in parentheses: smaller basis,
not all electrons correlated

$$\text{SCF-repulsion} + \text{dispersion} = \text{total}$$
$$+ 0.241 - 0.577 = - 0.336$$

What did we learn?

- + Rapid convergence of n-body expansion
- ! 1-body increments yield repulsive contributions; „truncation of the correlation space“
- ! Inter-molecular 2-body increments (dispersion) converge slowly with increasing basis size
- Dispersion terms depend on cluster size (basis set effect?)
- ! Intra-molecular increments (2-body, 3-body,...) do not contribute much to interaction energy. Can be calculated with a smaller basis set.
- ? Accuracy: Very weak interaction, many very small contributions.
- ? Experiment: Our results for the binding energy of He/MgO so far 4-5 meV; experimental estimate ~ 10 meV (= 0.370 mH) (F. Traeger, private communication)

Scaling

1. Our MCCEPA scales like CCSD

as:

$$n_{\text{occ}}^2 \times N^4$$

2. One has to include at least 13 O, 5 Mg, 1 He for 1 meV accuracy.

3. $n_{\text{occ}} = 73$

therefore $\rightarrow \rightarrow \rightarrow$

4. Reduction by symmetry.

5. **Advantage:** One can calculate increments in smaller basis sets, by using the large basis only for the atoms to be correlated !!!

Full: $5329 \times N^4$

I_1 : $289 \times N^4$

I_2 , disp.: $450 \times N^4$

I_2 , He+MgO: $2448 \times N^4$

I_3 : too many

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Details of the calculation

Embedded clusters:

MgO5, large basis, one O

Mg2O7, large basis

Mg4O7, large basis

Mg18O17

fixed geometry, $a=7.96 a_0$

PP: Mg, Stuttgart group

PC field: 10206 PC

CO position:

ontop Mg^{2+} , $R=5.50 a_0$

Subunits:

CO

$\text{O}^{2-}(2s,2p)$, $\text{Mg}^2(2s,2p)$

BSSE correction:

full Boys-Bernardi

Basis sets:

large: QZ3d1f (O,Mg)

aQZ3d1f(C;O)

Mg18O17: TZ3d(O)

TZ(Mg)

MgO5: a5Z5d3f1g

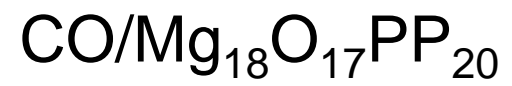
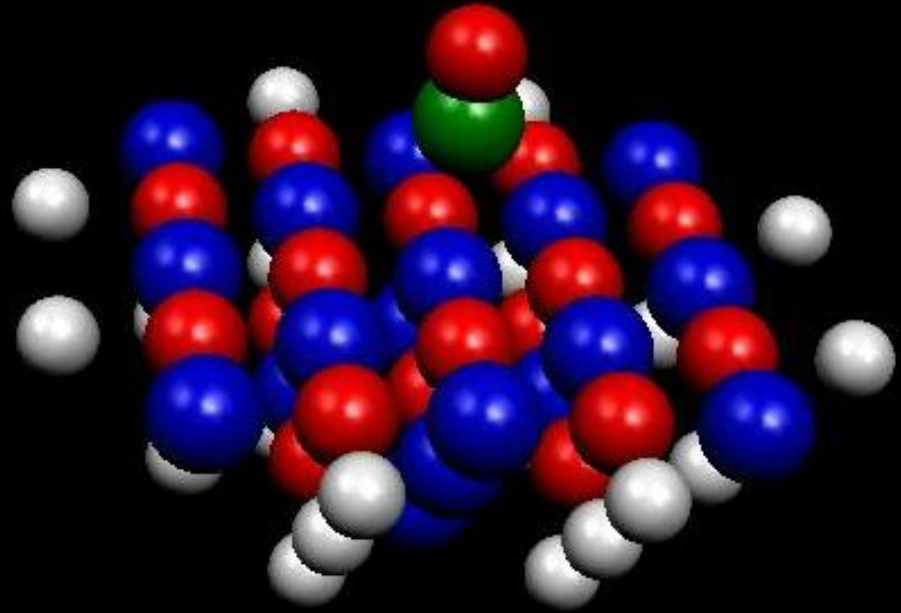
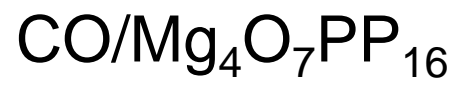
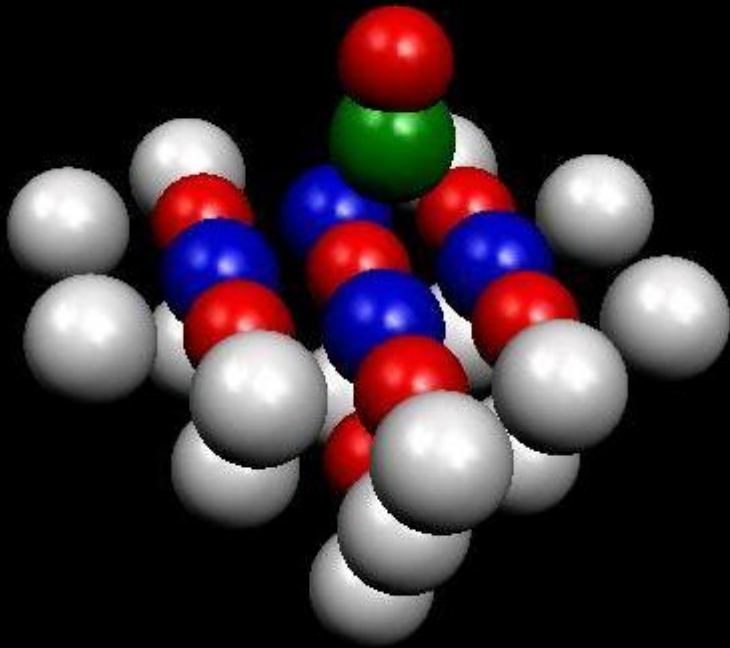
for one O atom

Correlation:

MCCEPA

CEPA-0

Clusters



I. Correlation energies: CO/Mg₁₈O₁₇

		CO	MgO	CO/MgO
1-body	CO	-0.340136		-0.340489
	Os		-0.232331	-0.232261
	Oss		-0.229133	-0.228695
2-body, disp.	CO-Os			-0.573716
	CO-Oss			-0.569258
2-body	Os-Os'		-0.467868	-0.467598
	Os-Os''		-0.465039	-0.464863
	Os-Oss		-0.464167	-0.463630
3-body			not calcul.	not calcul.

All values in a.u.

only 5 O atoms in MgO are correlated

II. Increments: CO/Mg₁₈O₁₇

		CC	CO/MgO	diff./a.u.	diff./eV
1-body	CO	-0.340136	-0.340489	-0.000353	
	MgO	-1.158457	-1.157739	+0.000718	
sum				+0.000365	+0.010
2-body, disp.	CO-O _s	---	-0.000966	-0.000966	
	CO-O _{ss}	---	-0.000074	-0.000074	
sum				-0.003938	-0.107
2-body	MgO	-0.024310	-0.023642	+0.000668	+0.018

IV. Dispersion: Cluster size effect

Increment	Number	Distance (a_0) from C	Cluster	$E_{\text{disp}}/\text{mH}$	$E_{\text{disp}}/\text{eV}$
CO-Os	4	6.78	Mg18O17	-0.966	-0.110
			Mg2O7	-0.983	
			MgO5	-1.015	
CO-Oss	1	9.48	Mg18O17	-0.074	-0.002
			Mg2O7	-0.077	
CO-Os'	8	10.46	Mg2O7	-0.031	-0.007
CO-Mg1	1	5.50	Mg4O7	-0.260	-0.008
CO-Mg2	4	7.87	Mg4O7	-0.007	
Total disp.				-4.673	-0.127

Total CO-MgO interaction

Method	Cluster	Energy contribution eV
SCF	Mg4O7	-0.011
	Mg18O17	-0.016
dispersion	Mg18O17	-0.107
	best	-0.127
1,2-body, intra	Mg18O17	+0.028
3,..-body		???
total		-0.115

$R(\text{Mg}^{2+}\text{-C}) = 5.50 a_0$; close to the equilibrium distance

M. A. Nygren et al., J. Chem. Phys. 100, 2010 (1994)

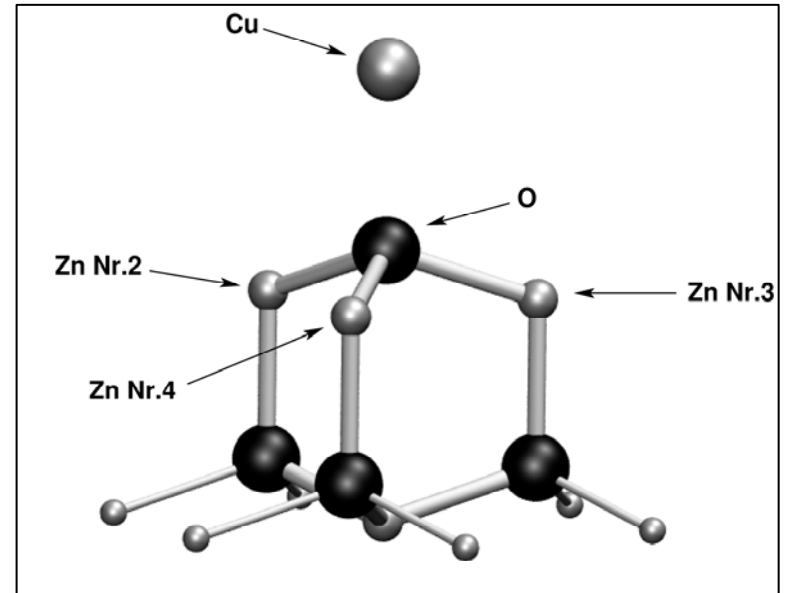
Outline

- I. Method of increments
- II. Pure van der Waals system:
He/MgO(001)
- III. CO/MgO(001)
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at ZnO surfaces
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Model system: Cu on Zn₄O₄

Details of the calculation:

- > Embedded Zn₄O₄ cluster:
hydrogen stabilized ZnO(000-1) surface,
12565 point charges,
PPs at all neighbors of the O²⁻ ions
- > Correlated atoms: Cu, O, Zn1, Zn2, Zn3:
5 atoms, 25 valence orbitals
- > single point calc., d(Cu-O) = 2.00 Å
- > Basis sets:
small core PPs for Cu and Zn (Stuttgart)
TZ2P+diffsp
- > 1 unpaired electron at Cu, ROHF start



Definition of the
increments not unique!

Correlation energy in Cu/Zn₄O₄

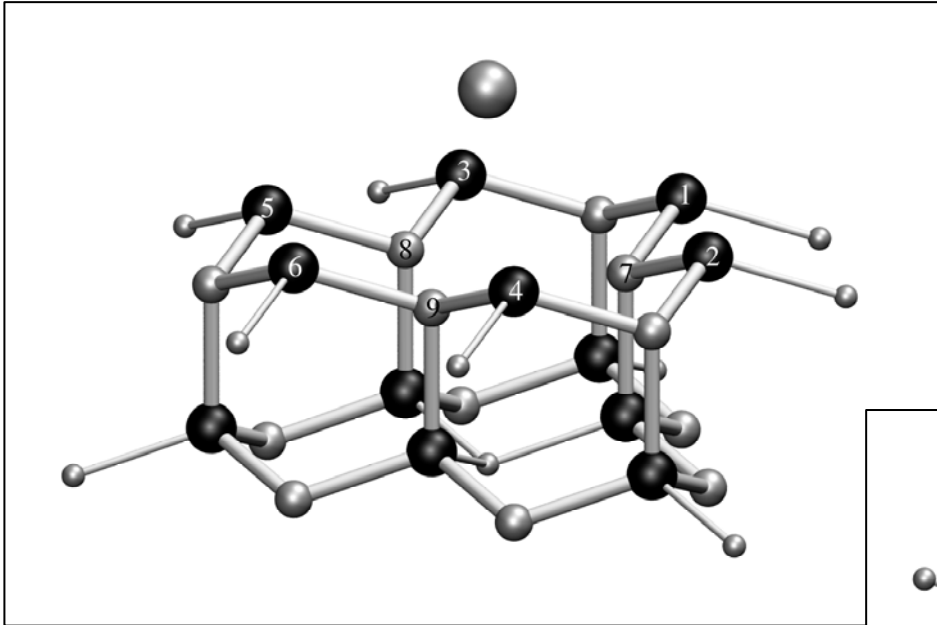
	Cu	ZnO	full	ΔE_{corr}
1-body	-0.290306	-1.160936	-1.449421	+0.001822
up to 2-body		-1.191810	-1.497044	-0.014927
up to 3-body		-1.191639	-1.497728	-0.015783
up to 4-body		-1.191639	-1.497205	-0.015260
Full MCCEPA		-1.191639	-1.497331	-0.015386

All entries in a.u.

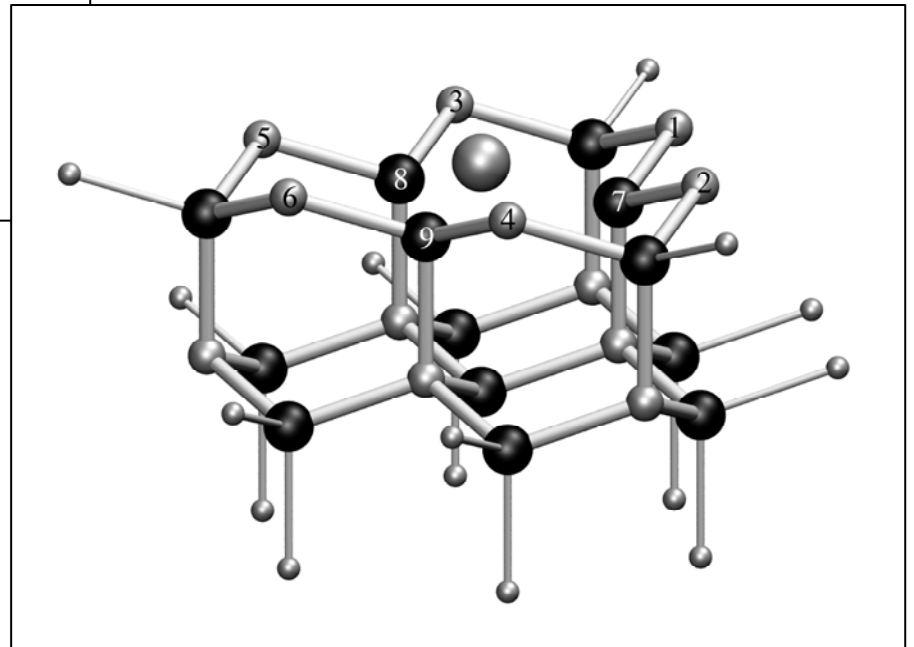
D_0 : SCF: -0.37 eV

Total: -0.79 eV

Cu at ZnO: defect sites

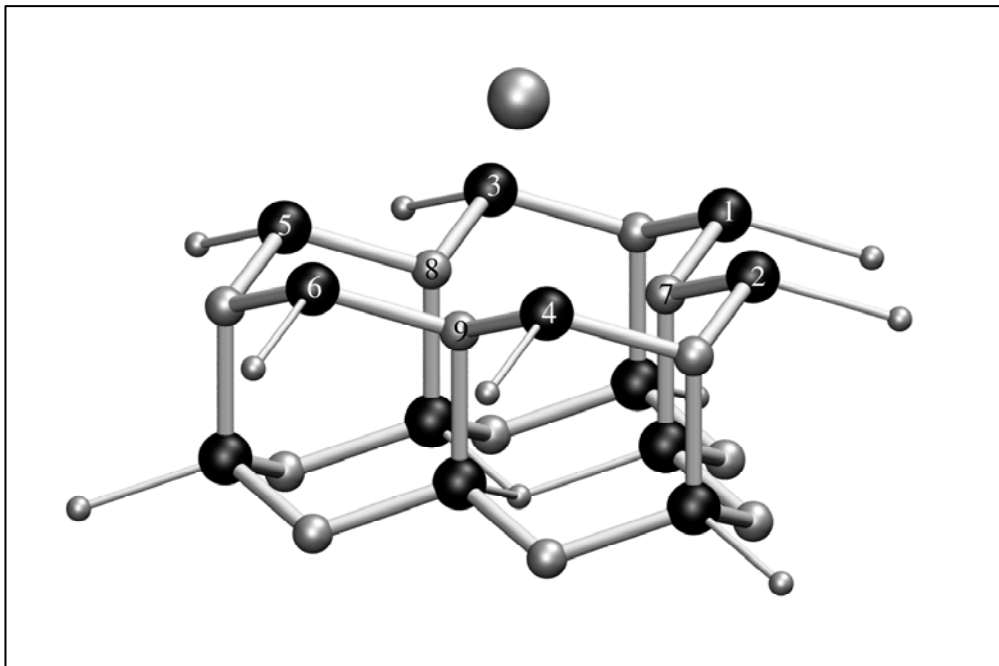


ZnO(000-1): O defect



ZnO(0001): Zn defect

Cu in an oxygen defect



Details:

O-ZnO(000-1) surface

R(Cu-surface): 2.01 Å

Embedding PC field with
~ 40000 PC

Correlated: Cu, 6 O, 3 Zn
(89 electrons)

Neutral system

BSSE corrected

	small basis	large basis
SCF(ROHF): D_0	-1.67 eV	-1.60 eV
MCCEPA: D_0	-1.11 eV	
MCCEPA Incr.: D_0		-1.43 eV

Cu in an oxygen defect: typical increments

	number	Cu, ZnO (CC)	Cu/ZnO	difference
$I_1(\text{Cu})$	1	-0.289292	-0.268175	0.021117
$I_1(\text{O1})$	6	-0.237604	-0.236782	0.000822
$I_1(\text{Zn})$	3	-0.305947	-0.304683	0.001264
$I_2(\text{Cu,O})$	6	-----	-0.003611	-0.003611
$I_2(\text{Cu,Zn})$	3	-----	-0.004359	-0.004359
$I_2(\text{O,O})$	15	-0.002576	-0.002402	0.000175
$I_2(\text{Zn,Zn})$	3	-0.000221	-0.000207	0.000013
$I_2(\text{O,Zn})$	18	-0.000329	-0.000262	0.000067
$I_3(\text{Cu,O,O})$	15	-----	0.000438	0.000438
$I_3(\text{O,O,O})$	many	-0.000300	-0.000317	0.000013

All contributions in a.u.; I. Hegemann, PhD thesis, Bochum 2007

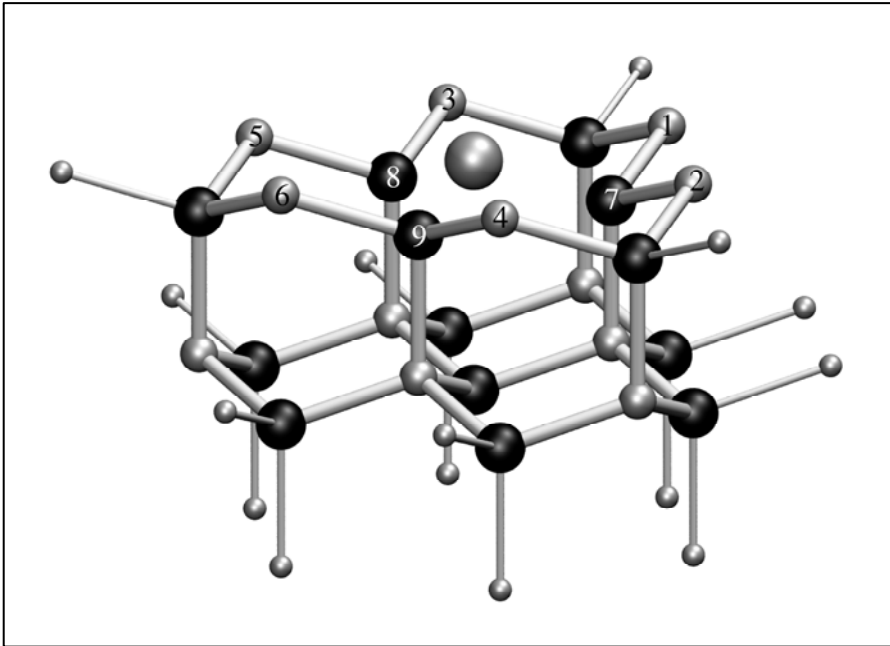
Correlation energy contributions for Cu in an O defect site

	Cu	ZnO	full	ΔE_{corr}
1-body	-0.289292	-2.343372	-2.602555	+0.030109
up to 2-body		-2.428345	-2.716221	+0.001416
+ some 3-body		-2.430526	-2.713592	+0.006226
Full MCCEPA (small basis)	-0.289242	-2.139385	-2.407916	+0.020711

Definition of the subunits??

All contributions in a.u.; I. Hegemann, PhD thesis, Bochum 2007

Cu in an Zn defect



Details:

Zn-ZnO(0001) surface

R(Cu-surface): 0.28 Å

Embedding PC field with
~ 40000 PC

Correlated: Cu, 3 O, 6 Zn
(95 electrons)

BSSE corrected

?????

Cu on ZnO

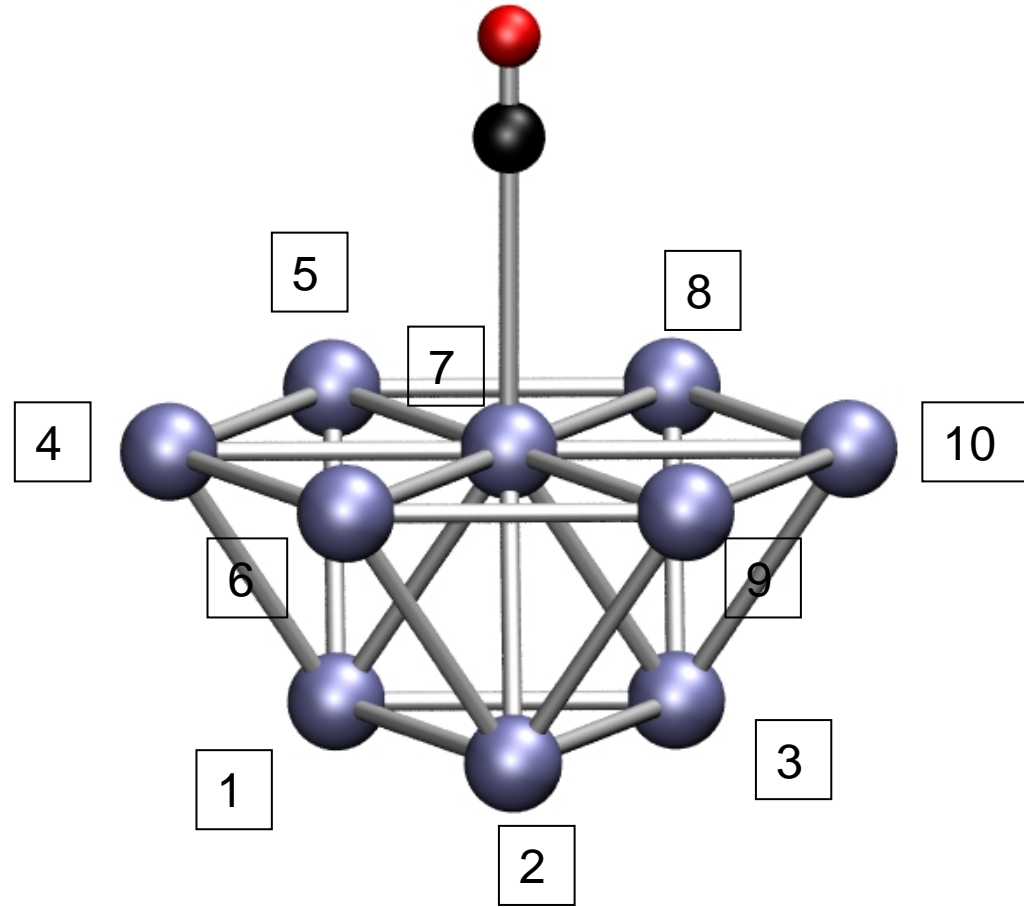
	SCF	SCF	SCF	MCCEPA	MCCEPA
	$d_0/\text{\AA}$	D_0/eV	q_{Cu}	$d_0/\text{\AA}$	D_0/eV
ontop Zn_4O_4	2.15	-0.37	-0.06	2.00	-0.79
O defect	1.94	-1.88	+0.87	2.01	-1.43
Zn defect	0.28	-3.06	+0.16		

Conclusions

1. Method of increments works very well for weak interactions
2. Timing: Big savings; calculations are feasible also in cases where a full CCSD calculation is not possible
3. One-body increments are the dominant contributions to the total correlation energy
4. One-body increments lower the binding energy („truncation of the correlation space“)
5. The main contributions to the binding energy are the two-body increments between the fragments (dispersion-type increments, „inter-molecular“ increments)
6. The „intra-molecular“ two-body increments are of little importance
7. The three-body increments are negligible (< 0.0001 a.u.) ??
8. Problems
 - a) localization of the valence orbitals always possible (metals) ?
 - b) localization of the valence orbitals is not unique
 - c) many many small calculations, book keeping ?

CO/Ar₁₀

Ar(7,3) cluster as a model for Ar(111)



The numbering of the Ar atoms corresponds to the tables shown later

Details of the calculation

1. Free Ar₁₀ cluster, no embedding
2. Fixed geometry of bulk fcc Ar, R(Ar-Ar) = 3.717 Å
3. Two basis sets: small (456), large (686)
4. Fixed CO-Ar(111) distance, z = 3.50 Å
(more precisely: R(C-Ar(111)) = 3.50 Å)
5. Steps in the calculation:
 - a) closed shell SCF
 - b) localization of the valence orbitals
 - c) MC-CEPA (= approximate CCSD)

Increment	Number	MCCEPA, full	MCCEPA, CC	ΔE
CO	1	-0.286998	-0.287047	+0.000049
Ar7	1	-0.129530	-0.129555	+0.000025
Ar4	6	-0.128730	-0.128731	+0.000006
Ar1	3	-0.128833	-0.128836	+0.000009
CO-Ar7	1	-0.000626		-0.000626
CO-Ar4	6	-0.000045		-0.000270
CO-Ar1	3	-0.000006		-0.000018
Ar7-Ar4	6 (nn)	-0.000305	-0.000304	
Ar7-Ar1	3 (nn)	-0.000307	-0.000307	
Ar4-Ar5	6 (nn)	-0.000293	-0.000292	
Ar1-Ar2	3 (nn)	-0.000284	-0.000286	
Ar1-Ar4	6 (nn)	-0.000285	-0.000286	
Ar1-Ar6	3 (nnn)	-0.000035	-0.000033	
Ar1-Ar9	6 (nnnn)	-0.000013	-0.000012	
Ar4-Ar9	6 (nnnn)	-0.000013	-0.000012	
Ar4-Ar10	3	-0.000003	-0.000002	

Increments:
CO/Ar10

small basis

all entries in a.u.

Increments:
CO/Ar10

large basis

Increment	Number	MCCEPA, full	MCCEPA, CC	ΔE
CO	1	-0.330281	-0.330210	+0.000029
Ar7	1	-0.157611	-0.157632	+0.000021
Ar4	6	-0.157555	-0.157610	+0.000055
Ar1	3	-0.157538	-0.157556	+0.000018
CO-Ar7	1	-0.000903		-0.000903
CO-Ar4	6	-0.000068		-0.000408
CO-Ar1	3	-0.000009		-0.000027
Ar7-Ar4	6 (nn)			
Ar7-Ar1	3 (nn)			
Ar4-Ar5	6 (nn)			
Ar1-Ar2	3 (nn)			
Ar1-Ar4	6 (nn)			
Ar1-Ar6	3 (nnn)			
Ar1-Ar9	6 (nnnn)			
Ar4-Ar9	6 (nnnn)			
Ar4-Ar10	3			

all entries in a.u.

Consequences

1. Method of increments works very well for weak interactions
2. Timing: Full calculation with large basis hardly possible, calculations for the increments rather fast
3. One-body increments are the dominant contributions to the total correlation energy
4. One-body increments lower the binding energy („truncation of the correlation space“)
5. The main contributions to the binding energy are the two-body increments between the fragments (dispersion-type increments, „inter-molecular“ increments)
6. The „intra-molecular“ two-body increments are of little importance
7. The three-body increments are negligible (< 0.0001 a.u.)
8. Problems
 - a) localization of the valence orbitals always possible (metals) ?
 - b) localization of the valence orbitals is not unique
 - c) many many small calculations