Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Electronic Supplementary Information

Chemically Accurate Adsorption Energies for Monolayers of Methane and Ethane on the MgO(001) Surface

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S1. Many-body expansions within hybrid QM:QM calculations

Part of the MonaLisa code[1] is an implementation of the fragment-based[2, 3] QM:QM scheme for large condensed-phase systems consisting of individual monomers. In our approach we combine a many-body expansion (MBE) at MP2 level with a periodic calculation at DFT+D2 level. The MBE is performed decomposing the periodic system into a certain number of monomers and it is truncated at the two-body terms. The method treats the monomers in the central unit cell and their short-range two-body interactions (with just one or both monomers belonging to the central unit cell) at MP2 level, while the long-range two-body interactions and the many-body interactions are described by a periodic DFT+D2 calculation. The hybrid energy is expressed via subtractive scheme:

$$E_{\mathrm{HL:LL}}(\mathrm{pbc}) = E_{\mathrm{LL}}(\mathrm{pbc}) - E_{\mathrm{LL,MBE}}(\mathrm{C}) + E_{\mathrm{HL,MBE}}(\mathrm{C}) \quad (1)$$

The low-level energy of the periodic system, $E_{\mathrm{LL}}(\mathrm{pbc})$, is corrected by subtracting two separated calculations: the high-level energy, $E_{\mathrm{HL,MBE}}(\mathrm{C})$, and the low-level energy, $E_{\mathrm{LL,MBE}}(\mathrm{C})$, both computed trough the same many-body expansion at MP2 and DFT+D2 level, respectively. The MBE energy

$$E_{\mathrm{MBE}}(\mathrm{C}) = \sum_{i}^{Z} E_i + \sum_{i}^{Z}\sum_{j>i}^{Z} \Delta E_{ij} + \frac{1}{2}\sum_{i}^{Z}\sum_{j_n}^{images} \Delta E_{ij_n} \quad (2)$$

is expressed as a sum of monomer energies, E_i, and two-body interaction energies,

$$\Delta E_{ij} = E_{ij} + E_i - E_j \quad (3)$$

where E_{ij} represents the energy of the dimer *ij*, composed of the *i*th and *j*th monomer. The *i* and *j* indices run over all *Z* monomers in the central unit cell and j_n runs over all periodic image monomers in the *n*th image cell. The summation includes all the two-body interactions within a cut-off in each lattice vector direction (at user's discretion) and creates a supercell of two-body interactions.

We compute many-body counterpoise corrected (MBCP) energies as suggested by Stein and Sauer.[4] The BSSE (ε) for a MBE truncated after two-body terms is given by:

$$\varepsilon = \sum_{i}^{Z} \sum_{j \neq i}^{Z} (E_{i\{j\}} - E_i) \qquad (4)$$

In the notation the subscript index "$i\{j\}$" refers to the ith monomer in presence of the basis set of the dimer ij. The counterpoise corrected many-body energy, E_{MBCP}, is obtained by:

$$E_{MBCP} = E_{MBE} + \varepsilon \qquad (5)$$

MonaLisa allows extrapolations to the CBS limit of counterpoise corrected many-body energies and gradients, according to the CPC-CBS scheme.

S2. DFT cluster calculations with VASP/plane waves and TURBOMOLE/Gaussian basis sets

Table S1 shows the PBE results for the adsorption cluster models obtained with VASP/plane waves and TURBOMOLE/Gaussian (def2-TZVP and def2-QZVP) basis set. The def2-QZVP adsorption energies are in good agreement to the plane waves ones, while def2-TZVP values deviate of -1.4 and -0.5 kJ/mol for $CH_4{\cdot}Mg_9O_9$ and $C_2H_6{\cdot}Mg_{12}O_{12}$, respectively. DFT calculations performed with def2-TZVP basis sets and with plane waves approach to the same low-level of theory within an uncertainty of -0.9 ± 0.4 kJ/mol.

Table S1 PBE adsorption energies, ΔE, for the $CH_4{\cdot}Mg_9O_9$ and $C_2H_6{\cdot}Mg_{12}O_{12}$ cluster cut out from the corresponding MP2:PBE+D2 equilibrium structures of the low coverage systems, in kJ/mol. Results obtained with plane waves (energy cut off, 600 eV and computational box, 15x15x25 Å) are compared to results with def2-TZVP and def2-QZVP Gaussian basis set.[a]

	$CH_4{\cdot}Mg_9O_9$[b]			$C_2H_6{\cdot}Mg_{12}O_{12}$[b]		
PBE	pw-600	def2-QZVP	def2-TZVP	pw-600	def2-QZVP	def2-TZVP
ΔE		-2.9	-3.2		-3.4	-5.3
ΔE_{CPC}	-2.5	-2.5	-1.1	-2.9	-2.9	-2.4

[a] Not BSSE- and BSSE-corrected results are reported when Gaussian basis sets are the computational choice. [b] At the hybrid MP2:PBE+D2 minima of the low coverage $CH_4{\cdot}MgO(001)$ and $C_2H_6{\cdot}MgO(001)$ system.

S3. Rumpling of the surface atoms

The PBE+D2 Mg-O equilibrium distance in the MgO(001) slab model compared to the PBE+D2 bulk optimized value (212 pm) increases to 215 pm for the terrace O^{2-} ions and decreases to 210 pm for terrace Mg^{2+} ions, which shows a surface relaxation effect and a small rumpling of the surface atoms of 1%, as also experimentally observed.[5] With the adsorption of the CH_4 monolayer, the PBE+D2 Mg-O distance for the occupied Mg^{2+} sites increases to 211 pm, and for the unoccupied ones it decreases to 209 pm corresponding to an even more complex surface rumpling effect. The surface O^{2-} ion positions are not altered, as also previously reported in the work of Tosoni and Sauer.[6]

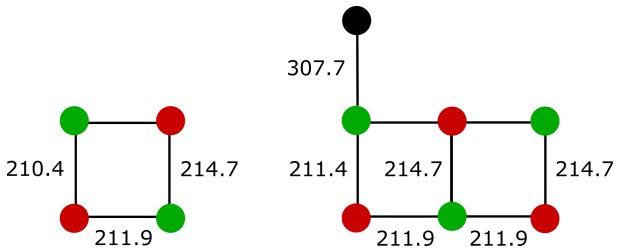

Fig. S1 Sketches of the rumpling effects (side view, distances in pm) of the MgO(001) slab on the left and of the CH_4(1ML)·MgO(001) system on the right. Color code: magnesium - green, oxygen - red and carbon - black.

S4. BLYP+D2 results

Bulk structure optimizations.

Table S2 Lattice parameters *a* and *R*(Mg-O) distances in Å obtained with PBE+D2 and BLYP+D2.

	PBE+D2	BLYP+D2	Exp[7]
a	4.239	4.252	4.210
R(Mg-O)	2.119	2.126	2.105

Adsorption energies.

Table S3 $R(Mg^{2+}\cdots C)$ distances in pm, adsorption energies, ΔE, dispersion energy contributions, ΔE_D, adsorbate-surface interactions, ΔE^*, and lateral interactions, ΔE_L obtained with BLYP+D2.

$\Theta = 1$	CH_4·MgO[a]	CH_4·MgO[b]	C_2H_6·MgO[b,c]
$R(Mg^{2+}\cdots C)$	313	312	322/322
ΔE	-9.5	-9.5	-19.6
ΔE_D	-20.0	-20.3	-43.7
ΔE^*	-6.2	-6.1	-8.7
ΔE_L	-3.3	-3.3	-10.9

[a] Computed for BLYP+D2 and [b] PBE+D2 lattice parameters. [c] Distances between the carbon atoms of the methyl groups pointing toward the surface and the closest terrace Mg^{2+} ions. Each distance is twice repeated.

Relaxed potential energy curves including high-level corrected lateral interactions. Fig. S2. shows the BLYP+D2 and MP2/CPC-CBS(D,T):BLYP+D2 adsorption energies for CH_4 and C_2H_6 as a function of the adsorbate monolayer-surface distance (R). For CH_4·MgO(001) the BLYP+D2 minimum is located at R =317 pm with ΔE = -9.4 kJ/mol and the MP2:BLYP+D2 minimum at R = 295 pm with ΔE = -18.8 kJ/mol. For C_2H_6·MgO(001) the BLYP+D2 minimum is found at R = 320 pm with ΔE = -19.6 kJ/mol and the MP2:BLYP+D2 minimum at R = 303 pm with ΔE = -30.0 kJ/mol. BLYP+D2 minima reproduce the results obtained by full BLYP+D2 optimizations in Table S3.

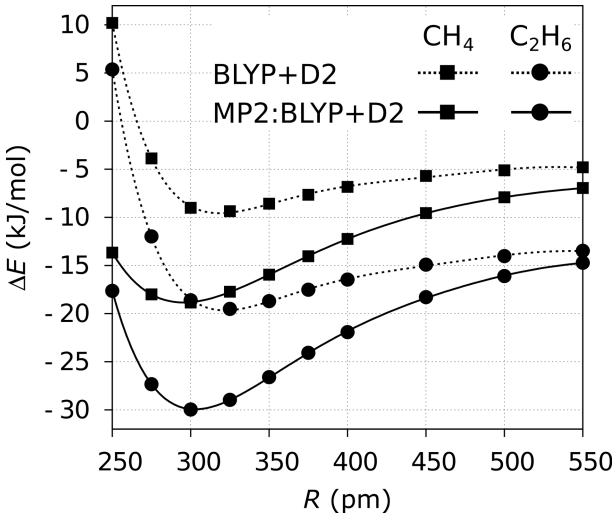

Fig. S2 BLYP+D2 and hybrid MP2/CPC-CBS(D,T):BLYP+D2 potential energy curves for high coverage CH_4·MgO(001) and C_2H_6·MgO(001) system as a function of the adsorbate monolayer-surface distance (*R*).

S5. Basis set extension effects on CCSD(T) results

In a previous work[8] on the CH_4·MgO(001) system, an attempt has been made to estimate the basis set extension effect using smaller clusters that are charged and, hence, require point charge embedding. The latter, in turn, suffers from over-polarization effects. Nevertheless, the result -0.9 kJ/mol (double-zeta for the embedded Mg_9O_9 cluster) plus -0.7 ± 0.1 kJ/mol (the increment for increasing the basis set to triple-zeta) gives -1.6 kJ/mol, that was 0.2 ± 0.1 kJ/mol larger than the double-zeta result for the non-embedded Mg_9O_9 cluster. In the current work CCSD(T)/T-zeta results could be completed only for the CH_4·Mg_9O_9 cluster at the MP2:PBE+D2 equilibrium structure of the high coverage CH_4·MgO(001) system. The CCSD(T) correction to the MP2 result increases of 0.5 kJ/mol with the basis set quality from double-zeta to triple-zeta, see Table S4.

Table S4 Counterpoise corrected MP2, CCSD and CCSD(T) adsorbate-surface interaction energies, ΔE^*, in kJ/mol of the high coverage CH_4·MgO(001) system calculated at the MP2:PBE+D2 equilibrium structure.[a]

	MP2	CCSD	CCSD -MP2	CCSD(T)	CCSD(T) - CCSD	CCSD(T) - MP2
D	-9.2	-9.6	-0.4	-11.5	-1.9	-2.3 (-0.9)[c]
T	-11.9	-12.2	-0.3	-14.7	-2.5	-2.7
CBS(D,T)	-13.1	-13.3	-0.2	-16.0	-2.7	-2.9
T-D	-2.7	-2.6	0.1	-3.2	-0.6	-0.5 (-0.7 ± 0.1)[c]

[a] The adsorbate-surface interactions are computed with the triple-zeta basis set level (aug'-cc-p(C)TZV).[b] Θ = 1, R = 312 pm. [c] In parenthesis results of Boese and Sauer[8] for point charge embedded clusters of the CH_4(Θ = 0.25)·MgO(001) system.

S6. Reference energies derived from experiment

As described in previously, [6, 9] desorption enthalpies, ΔH_T, are obtained from Arrhenius desorption barriers, E_A, according to[10]

$$\Delta H_T = E_A - RT. \quad (6)$$

Using statistical mechanics with vibrational energies obtained from DFT calculations desorption energies are obtained from observed enthalpies,

$$\Delta E = \Delta H_T - \Delta\Delta_T E - \mathrm{R}T - \Delta E_{\mathrm{ZPV}}, \quad (7)$$

which we use as reference values for assessing the calculated desorption energies.

For CH_4 we derive an adsorption energy of 15.0 kJ/mol from the experimental desorption barrier of 12.6 kJ/mol, with an uncertainty estimate of ± 0.6 kJ/mol. This we get from half of the difference between the vibrational corrections from refs. 8 and 6 (0.25 kJ/mol) and half of the difference of the ΔE values derived from the two different experiments (0.35 kJ/mol, see also ref. 6) Previous estimates[6, 8] fall into the uncertainty limit specified.

Table S5 Observed Arrhenius desorption barriers, E_A in kJ/mol, observed desorption temperatures, T in K, and desorption energies derived from experiment, ΔE, in kJ/mol for monolayer coverage ($\Theta = 1$).

	C_2H_6·MgO	CH_4·MgO			
	This work	This work	Ref. 8	Ref. 6	
E_A	22.76	12.63	12.63	12.6	13.1
RT *(T)*	0.62 (75)	0.39 (47)	0.39 (47)	0.4 (47)	0.3 (40)
$\Delta H_T = E_A - RT$ [a]	22.14	12.24	12.24	12.2	12.8
$\Delta H_0 = \Delta H_T - \Delta\Delta_T E - RT$ [b]	21.10	11.18	11.26	11.1	
ΔE_{ZPV} [c]	-3.32	-3.81	-3.56	-4.2	
$\Delta E = \Delta H_0$ - ΔE_{ZVP} [d]	24.42	14.98	14.82	15.3	16.0
ΔE, final estimate	24.4 ± 0.6	15.0 ± 0.6	15.1 ± 0.6	15.3 ± 0.4	

[a] Enthalpies at temperature T. [b] Enthalpies at 0 K, $\Delta\Delta_T E$ is the thermal energy change. [c] Zero-point vibrational energy. [d] Desorption energies derived from experiment.

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Structure files and energies contributions to the *hybrid MP2:(PBE+D2)ΔCC* values – high loading (1ML) systems

VASP POSCAR files are structured as follow:

- TITLE
- Cell scaling factor
- Lattice vector parameters
- Number of each atomic species
- Coordinates (Direct (fractional))

The energy contributions to the *hybrid MP2:(PBE+D2)ΔCC* energies are organized as follow:

- "pbc" stands for periodic boundary conditions
- "C1" is the CH_4/Mg_9O_9 cluster for the CH_4/MgO(001) system (see section 2.4)
- "C2" is the $C_2H_6/Mg_{16}O_{16}$ cluster for the C_2H_6/MgO(001) system (see section 2.4)
- "MBE" stands for two-body expansion of the lateral interactions (see section 2.5)
- All the PBE+D2/TURBOMOLE calculations are performed with Ahlrichs'def2-TZVP basis set (see section 3)
- D- and T-zeta basis sets are aug'-cc-p(C)VDZ and aug'-cc-p(C)VTZ, respectively (see section 3)
- CBS(D,T) stands for basis set extrapolation between D- and T-zeta basis set

Gas phase CH_4 molecule

```
CH4
1.00000000000000
15.0000000000000000  0.0000000000000000  0.0000000000000000
0.0000000000000000 15.0000000000000000  0.0000000000000000
0.0000000000000000  0.0000000000000000 25.0000000000000000
H C
4 1
Direct
0.3483473333333365  0.3683087800555711  0.7701447625877123
0.4081043908520883  0.3085826666666662  0.8208265780265265
0.3483473333333365  0.2488558866110964  0.7701447625877123
0.2885902758145846  0.3085826666666662  0.8208265780265265
0.3483473333333365  0.3085826666666662  0.7954941187715292
```

E(PBE+D2,VASP) = -24.065049 eV

E(PBE+D2,TURBOMOLE) = -1101.076767 eV

E(MP2/CBS(D,T)) = -1100.206992 eV

E(MP2/D-zeta) = -1098.461165 eV

E(CCSD(T)/CBS(D,T)) = -1100.916797 eV

E(CCSD(T)/D-zeta) = -1099.224376 eV

Gas phase C_2H_6 molecule

```
C2H6
1.00000000000000
15.0000000000000000  0.0000000000000000  0.0000000000000000
0.0000000000000000 15.0000000000000000  0.0000000000000000
0.0000000000000000  0.0000000000000000 25.0000000000000000
H C
6 2
Direct
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0.3250973191434170  0.2981496016042371  0.7984467017596089
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Energies:

E(PBE+D2,VASP) = -40.579336 eV

E(PBE+D2,TURBOMOLE) = -2169.659787 eV

E(MP2/CBS(D,T))= -2167.854084 eV

E(MP2/D-zeta)= -2164.694968 eV

E(CCSD(T)/CBS(D,T))= -2169.054210 eV

E(CCSD(T)/D-zeta) = -2165.966630 eV

Unloaded MgO(001) surface

```
unloaded MgO(001)
1.00000000000000
8.4774919999999998 0.0000000000000000  0.0000000000000000
0.0000000000000000 8.4774919999999998  0.0000000000000000
0.0000000000000000 0.0000000000000000 25.0000000000000000
Mg  O
32 32
Direct
0.3663629999999998  0.0460029999999989  0.4201219999999992
0.8663629999999998  0.0460029999999989  0.4201219999999992
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E(PBE+D2,pbc) = -378.678314 eV

E(PBE+D2,C1) = -67408.013926 eV

E(PBE+D2,C2) = -119844.052399 eV

E(MP2/CBS(D,T),C1) = -67401.328324 eV

E(MP2/CBS(D,T),C2) = -119832.967052 eV

E(MP2/D-zeta,C1) = -67334.995562 eV

E(MP2/D-zeta,C2) = -119715.174899 eV

E(CCSD(T)/D-zeta,C1) = -67337.513225 eV

E(CCSD(T)/D-zeta,C2) = -119719.901028 eV

CH_4(1ML)/MgO(001) system

```
CH4-MgO(001)
1.00000000000000
8.4774919999999998 0.0000000000000000  0.0000000000000000
0.0000000000000000 8.4774919999999998  0.0000000000000000
0.0000000000000000 0.0000000000000000 25.0000000000000000
Mg  O  H C
32 32 16 4
Direct
0.3663629999999998  0.0460029999999989  0.4201219999999992
0.8663629999999998  0.0460029999999989  0.4201219999999992
0.6163629999999998  0.2960029999999989  0.4201219999999992
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0.6163629999999998  0.0460029999999989  0.6738352893070925
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0.8663629999999998  0.7960029999999989  0.6734249998349018
0.3663629999999998  0.2960029999999989  0.6734249998349018
0.8663629999999998  0.2960029999999989  0.6734249998349018
0.1163629999999998  0.5460029999999989  0.6738352893070925
0.6163629999999998  0.0460029999999989  0.4201219999999992
0.1163629999999998  0.0460029999999989  0.4201219999999992
0.1163629999999998  0.5460029999999989  0.4201219999999992
```

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0.3663629999999998  0.7960029999999989  0.4201219999999992
0.8663629999999998  0.7960029999999989  0.4201219999999992
0.3663629999999998  0.2960029999999989  0.4201219999999992
0.8663629999999998  0.2960029999999989  0.4201219999999992
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0.3663629999999998  0.0460029999999989  0.5048969999999997
0.1163629999999998  0.2960029999999989  0.5048969999999997
0.1163629999999998  0.7960029999999989  0.5048969999999997
0.3663629999999998  0.5460029999999989  0.5048969999999997
0.6163629999999998  0.2960029999999989  0.5048969999999997
0.6163629999999998  0.7960029999999989  0.5048969999999997
0.8663629999999998  0.5460029999999989  0.5048969999999997
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0.1163629999999998  0.5460029999999989  0.5896175233336626
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0.8663629999999998  0.7960029999999989  0.5895871077766037
0.3663629999999998  0.2960029999999989  0.5895871077766037
0.8663629999999998  0.2960029999999989  0.5895871077766037
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0.1163629999999998  0.1527604377023753  0.7734557544335958
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0.1163629999999998  0.5460029999999989  0.7985272893070885
0.6163629999999998  0.0460029999999989  0.7985272893070885
```

E(PBE+D2,pbc) = -475.549059 eV

E(PBE+D2,C1) = -68509.229406 eV

E(PBE+D2,MBE) = -4404.512460 eV

E(MP2/CBS(D,T),C1) = -68501.670644 eV

E(MP2/D-zeta,C1) = -68433.552205 eV

E(MP2/CBS(D,T),MBE) = -4400.951030 eV

E(CCSD(T)/D-zeta,C1) = -68436.856529 eV

E(CCSD(T)/CBS(D,T),MBE) = -4403805103 eV

C_2H_6(1ML)/MgO(001) system

```
C2H6-MgO(001)
1.00000000000000
8.4774919999999998 0.0000000000000000  0.0000000000000000
0.0000000000000000 8.4774919999999998  0.0000000000000000
0.0000000000000000 0.0000000000000000 25.0000000000000000
Mg  O  H C
32 32 24 8
Direct
0.3663629999999998  0.0460029999999989  0.4201219999999992
0.8663629999999998  0.0460029999999989  0.4201219999999992
0.6163629999999998  0.2960029999999989  0.4201219999999992
0.3663629999999998  0.5460029999999989  0.4201219999999992
0.6163629999999998  0.7960029999999989  0.4201219999999992
0.8663629999999998  0.5460029999999989  0.4201219999999992
0.1163629999999998  0.2960029999999989  0.4201219999999992
0.1163629999999998  0.7960029999999989  0.4201219999999992
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0.6163629999999998  0.0460029999999989  0.5048969999999997
0.6163629999999998  0.5460029999999989  0.5048969999999997
0.3663629999999998  0.7960029999999989  0.5048969999999997
0.8663629999999998  0.7960029999999989  0.5048969999999997
0.3663629999999998  0.2960029999999989  0.5048969999999997
0.8663629999999998  0.2960029999999989  0.5048969999999997
0.1163629999999998  0.5460029999999989  0.5048969999999997
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0.8662271062770385  0.0459938827263927  0.5899238837618028
0.6165619875439040  0.2960078305019897  0.5899261852079100
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0.6165620361924737  0.7960078330774581  0.5899261977546409
0.8662270801896886  0.5459938212147299  0.5899238781883112
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0.1163310971393383  0.7960384440014689  0.5897644566856188
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0.8668149326293049  0.7961122749705186  0.6738352893000013
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0.8668148650037939  0.2961121453811326  0.6738352893000013
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0.6163629999999998  0.5460029999999989  0.4201219999999992
0.3663629999999998  0.7960029999999989  0.4201219999999992
0.8663629999999998  0.7960029999999989  0.4201219999999992
0.3663629999999998  0.2960029999999989  0.4201219999999992
0.8663629999999998  0.2960029999999989  0.4201219999999992
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0.3663629999999998  0.0460029999999989  0.5048969999999997
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0.1163629999999998  0.2960029999999989  0.5048969999999997
0.1163629999999998  0.7960029999999989  0.5048969999999997
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0.6163629999999998  0.2960029999999989  0.5048969999999997
0.6163629999999998  0.7960029999999989  0.5048969999999997
0.8663629999999998  0.5460029999999989  0.5048969999999997
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0.1169933917317355  0.7961015619319367  0.6754523236824691
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0.6547981445826027  0.0522534863152692  0.8327943373795773
0.4394026771190759  0.8397487523896866  0.8373894299026264
0.3575308902431323  0.0313638695458079  0.8461849513040143
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0.0518409178439470  0.5894505935092894  0.8373744047943696
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0.3398208423103722  0.4350480838892805  0.7837030982870251
0.4393415431372280  0.3397481518138694  0.8373826768195521
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0.5547211907296692  0.6402615399437175  0.7782388639364195
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0.6378164211908982  0.4469386381058922  0.7719786202051090
0.8506715679902686  0.1965266251124481  0.7727448353757451
0.8365112702556973  0.3018581137956038  0.8336589987810623
0.9342898377447646  0.3896516819208038  0.7785599050010523
0.0518496900952318  0.0894194455751382  0.8373712560078050
0.1488699861697189  0.1835979596432639  0.7829468031571796
0.1346316345304649  0.2809384243440485  0.8453348891606530
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0.0706907270111301  0.7035890791597301  0.8174439810999985
0.4197559133358284  0.4542500051035112  0.8177746174999996
0.5748037356097196  0.5276643781233409  0.7991762611000013
0.9149391670234384  0.2771657113318434  0.7996289622999981
0.0707059378517203  0.2035573108242176  0.8174418063000033
```

E(PBE+D2,pbc) = -541.984262 eV

E(PBE+D2,C2) =-122013.856343 eV

E(PBE+D2,MBE) = -8679.168470 eV

E(MP2/CBS(D,T),C2) = -122000.981899 eV

E(MP2/D-zeta,C2) = -121879.985002 eV

E(MP2/CBS(D,T),MBE) = -8671.747361 eV

E(CCSD(T)/D-zeta,C2) = -121886.007482 eV

E(CCSD(T)/CBS(D,T),MBE) = -8676.582964 eV