Single Molecule Magnets Grafted on Gold: Magnetic Properties From Ab Initio Molecular Dynamics. Supporting Information

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1 Models Benchmark

In order to correctly capture the Au(111)-molecule interaction we benchmarked our computational DFT set up. The meta-GGA TPSS functional has been tested over the calculation of Au bulk lattice constant, Au(111) Density of states (DOS) and surface energy convergence over slab's number of layers and finally over the cohesive energy of a benzene molecule physisorbed over Au(111).

1.1 Bulk Au

Au posses an fcc bulk crystalline cell with a lattice constant of 4.08 Å. Using our computational set up (see Section Methods) we studied the energy dependence over different lattice constant values. The model was made by a periodic orthorombic cell of 480 Au atoms. In conclusion TPSS+D3 correctly predicts the experimental lattice constant.

1.2 Au(111) Surface

Since the TPSS+D3 functional predicts an Au bulk lattice constant in agreement with the experimental value, we used it also for all surface models. In Fig. 1 are reported the DOS of the Au(111) slab for vaious number of layers, calculated with the TPSS functional over the TPSS+D3 optimized structures. Similar description of the electronic structure close to the Fermi Energy is achived by all the models. A little poorer description of the inner states has been evidenced for the 3 layers model, as expected (absence of internal bulk-like layers).

In Table 1 are reported the Au(111) surface energy values and their dependence by the number of layers which compose the slab surface model. The surface energy is defined as

$$\gamma = \frac{1}{2A}(E_S^N - N_{at}E_B) \tag{1}$$

where A is the surface area, E_S^N stands for the energy of the slab made of N layers, N_{at} is the number of atoms composing the slab and E_B is the bulk energy per atom. While the The E_S^N term was evaluated by direct calculation, E_B was extrapolated with the Fiorentini Method[1] as suggested in the work of Singh-Miller et al.[2].

The tested method slightly overestimates the experimental surface energy and an oscillating behavior is registered but it is quite more accurate with respect to bare GGA treatments[2]. In Table 2 are reported the

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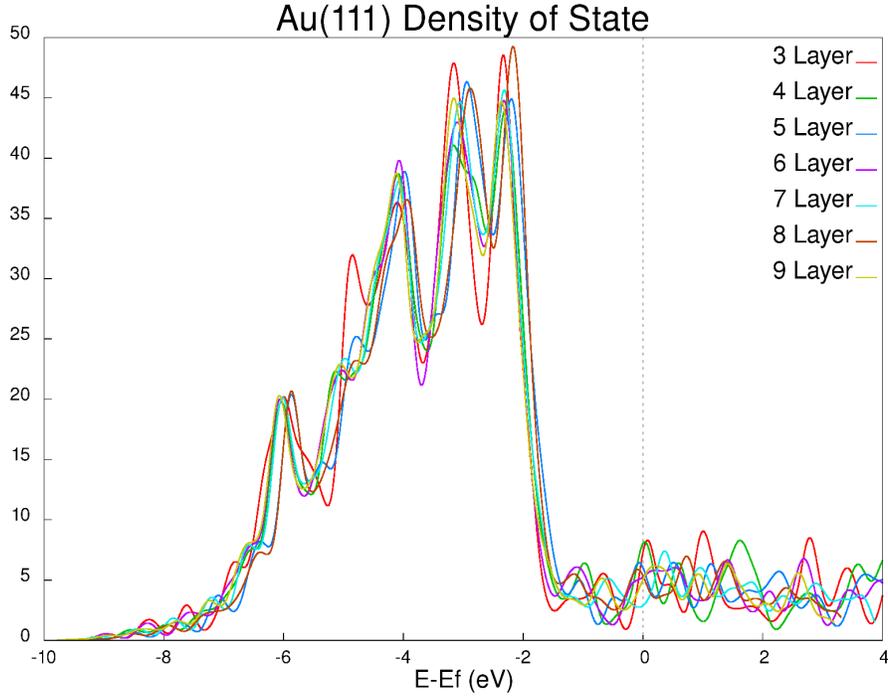
Fig. 1 Number of layers Au(111) slab DOS dependence.

Table 1 Au(111) Surface Energy

	EXP	3 layer	4 layer	5 layer	6 layer	7 layer	8 layer
TPSS+D3	1.48-1.52	-	1.84	1.86	1.82	1.80	1.84

All values are reported in J/m^2.

Au(111) inter-layer distances. The dependence by the number of layers which compose the slab surface model is also studied.

Table 2 Intelayer Spacing

	3 layer	4 layer	5 layer	6 layer	7 layer	8 layer	9 layer
d(1-2)	2.52	2.51	2.54	2.51	2.51	2.56	2.51
d(2-3)	2.52	2.40	2.41	2.38	2.40	2.42	2.39
d(3-4)	–	2.51	2.41	2.38	2.39	2.41	2.38
d(4-5)	–	–	2.55	2.38	2.39	2.41	2.39
d(5-6)	–	–	–	2.51	2.40	2.41	2.39

All values are reported in Å.

An accettable inner interlayer distance is observed starting from the 4 layer model which shows a deviation of only about 2% from the 2.35 Å bulk inter-layer distance. Taking into accounts all the data here presented is possible to conclude that the choice of a 4 layer slab is a good compromise between accuracy and system size.

1.3 Benzene@Au(111)

One of the main contribution to cohesive energy of physisorbed systems over metallic substrates is the dispersion energy. This particular kind of stabilization energy comes from long-range interactions and it is usually poorly captured by GGA functionals. In order to employ DFT for systems where dispersion forces play a crucial role, a lot of efforts have been done in order to correct such deficiency of current XC-functional adding to them a term which explicitly include van der Waals forces. We tested two different kind of vdW corrections: local semi-empirical Grimme's D3[3] corrections and non-local vdW-DF2[4] and rVV10[5,6] methods.

Table 3 Ph@Au(111) Absorption Energies

	EXP	D3	vdW-DF2	rVV10
TPSS	-17.1	-28.9	-29.8	-20.9

All values are reported in kcal mol^{-1}.

In Table 3 is possible to observe how the D3 method and the non-local vdW-DF2 method overestimate dispersion forces. The rVV10 vdW functional produces a good agreement with the experimental value. Since the non-local correction are particularly cumbersome from a computational point of view, we decided to utilize the D3 method, which gave reasonable results without additional computational costs.

2 Fe$_2$ Magneto Structural Correlations

A new magneto structural correlation inside μ-hydroxo bridged iron dimer have been examined. We studied the iron dimer [Fe$_2$(OMe)(dbm)$_2$]$_2$[7] without phenyl rings as a model (see Fig. 2) to investigate how the isotropic exchange interaction varies along the out of plane angle (ϕ) of the methoxy's carbon with respect to the Fe-O-Fe plane (see Figure 2).
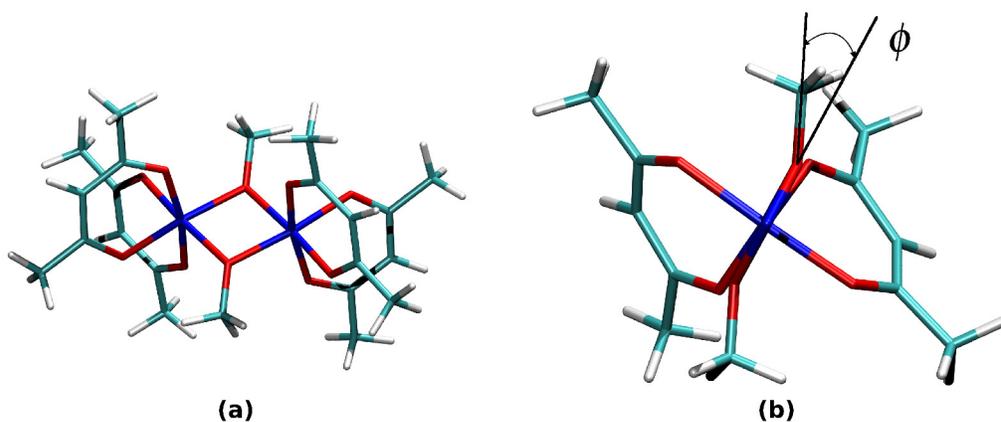
Fig. 2 (a): Complete Fe$_2$ model. (b): ϕ improper angle definition.

In Table 4 are reported the J values obtained with the PBE0 procedure explained in the Methods Section. A clear trend is observed and it supports the hypothesis made in the Results Section. Further calculations would be needed in order to completely characterize such evidence but they are beyond the scope of this work.

Table 4 *J* Magneto Structural Correlation

ϕ	148.3°	155.5°	162.1°
J	10.1 cm^{-1}	12.1 cm^{-1}	13.7 cm^{-1}

3 Fe Magnetic Moment

As the three Fe_p always posses the same magnetization and it is always found to be only $0.02\mu_B$ higher in absolute value with respect to the magnetic moment of Fe_c, we reported on Table 5 only the variation of the mean absolute value of iron ions' magnetic moments for different computational set up and models. All the walkers magnetic moments show exactly the same behavior and for this reason we only reported the magnetic moments of Walker1. The magnetic moment of iron ions has been monitored during all AIMD runs and it do not sensitively deviates from the values reported on Table 5. These values all refers to calculations done with CP2K software.

Table 5 Iron Magnetic Moment

	X-Ray	Opt-Bulk	Opt-Isol	Walker1@Au(111)	Walker1@Au(111)
PBE	4.15	4.17	4.16	4.07	4.14
PBE+U	4.36	4.36	4.36	4.35	4.35
PBE0	4.35	4.35	4.35	–	4.34

All values are reported in μ_B units.

The PBE functional predicts for all the models a slightly small value of magnetic moment with respect to the PBE0 and PBE+U functionals. This was expected as hybrid and hubbard corrected functionals solve (at least partially) the self interaction energy error and thus they enhance the localization of magnetic orbitals on paramagnetic ions. However, the magnetic moments are below the value of $5\mu_B$ as a consequence of delocalization of the density on ligands. Indeed a value of $\sim 4.4\mu_B$ is perfectly in line with S=5/2 paramagnetic ions. Moreover, this was expected as high spin Fe^{3+} ions in a weak octahedral crystal field are by far more stable than intermediate and low spin counterparts. From Table 5 it could also be noted that while PBE produces a depletion of magnetic moment passing from the Walker1@Au(111) to the Walker1@Au(111) model, the other more accurate functionals do not show the same behavior suggesting an absence of a transfer of magnetic moment from Fe_4C_5 to the surface.

References

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