Interaction between a single-molecule magnet Mn_{12} monolayer and a gold surface

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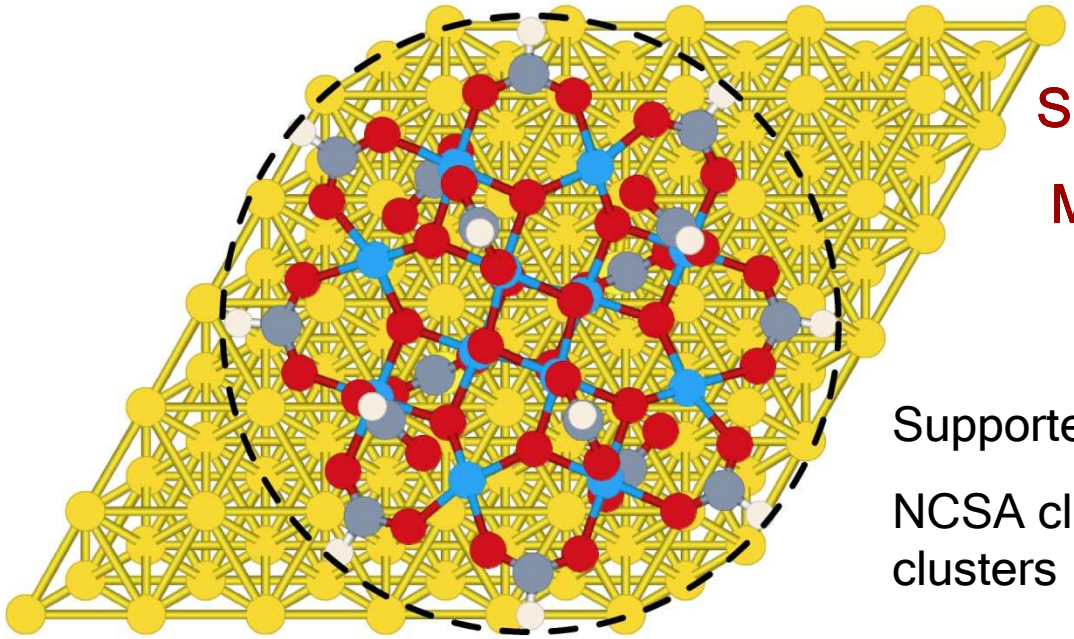


Salvador Barraza-Lopez (postdoc)

Michael C. Avery (undergraduate)

Supported by Jeffress Memorial Trust Fund

NCSA clusters, Virginia Tech System X, VT clusters

NCSA

VirginiaTech
Invent the Future

Outline

- What are single-molecule magnets (SMMs)?
- Motivation
- Methodology: density-functional theory (DFT)
- Review of properties of isolated SMM Mn_{12}
- SMM Mn_{12} deposited on a gold surface
  - Method and model
  - Changes in electronic structure (orbital broadening, charge transfer)
  - Changes in magnetic properties
- Beyond DFT: effect of Hubbard-like U term

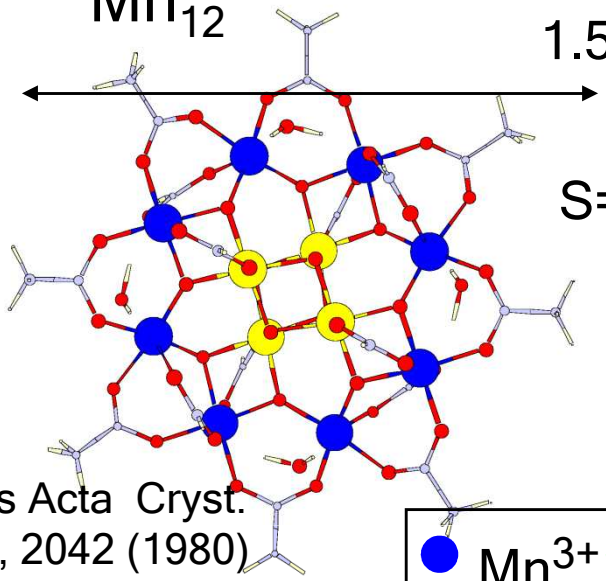
What are single-molecule magnets?

- Volume of one molecule: a few nm^3
- Single molecule: several transition metal ions strongly coupled via ligands
- Behaves as single-domain magnetic nanoparticle
- Large spin with large magnetization reorientation barrier
- Can form single crystals (*different molecules are well separated*)

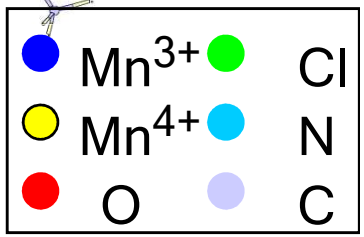
C & E news, Dec 13, 2004

- Examples: Mn_{12} , Mn_4 , Fe_4, Fe_8, Co_4, Ni_4, cyanide-bridged molecules, Mn_{84} torus, etc.

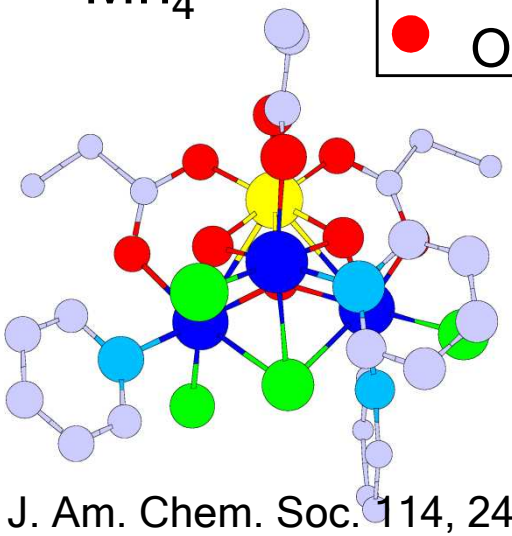
Mn_{12}



T.Lis Acta Cryst. B36, 2042 (1980)



Mn_4

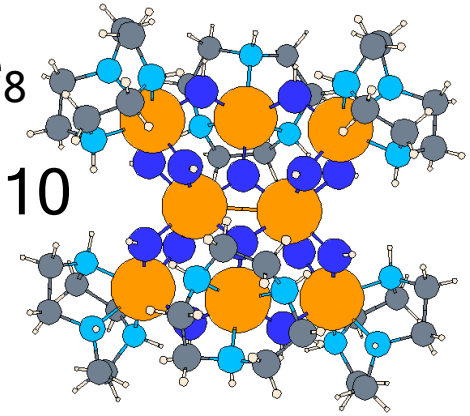


D. Hendrickson J. Am. Chem. Soc. 114, 2455 (1992)

Single-molecule magnets

Fe_8

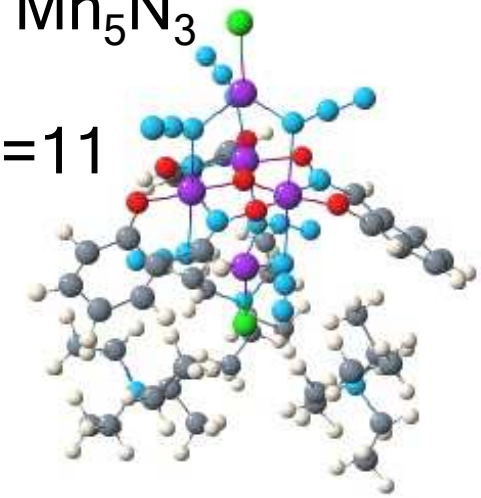
S=10



Wieghart et al., Angew. Chem. Int. Ed. Engl. 23, 77 (1984)

Mn_5N_3

S=11



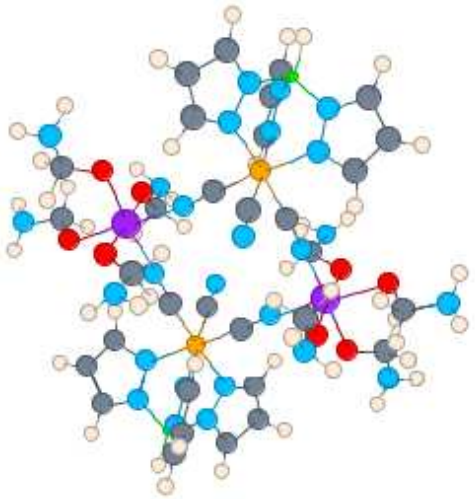
C.-I. Yang et al., J. Am. Chem. Soc. 129, 456 (2007)

S=6

Tasiopoulos et al, Angew. Chem. Int. Ed. 43, 2117 (2004)

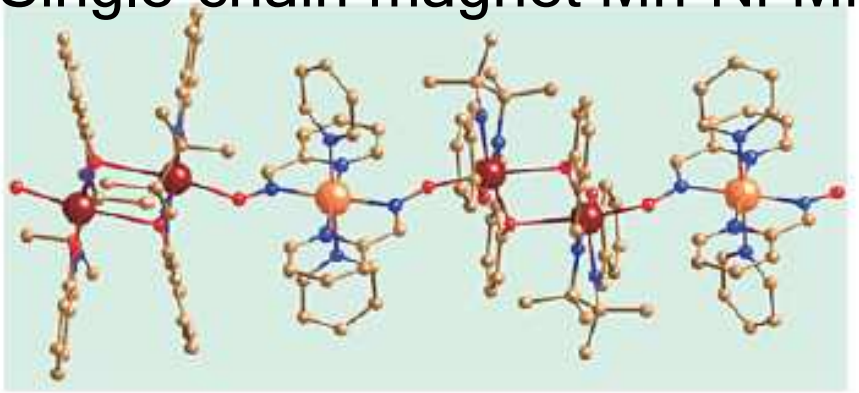
Fe_2Ni_2

S=3



Li et al., Inorg. Chem. 44, 4903 (2005)

Single-chain magnet Mn-Ni-Mn unit



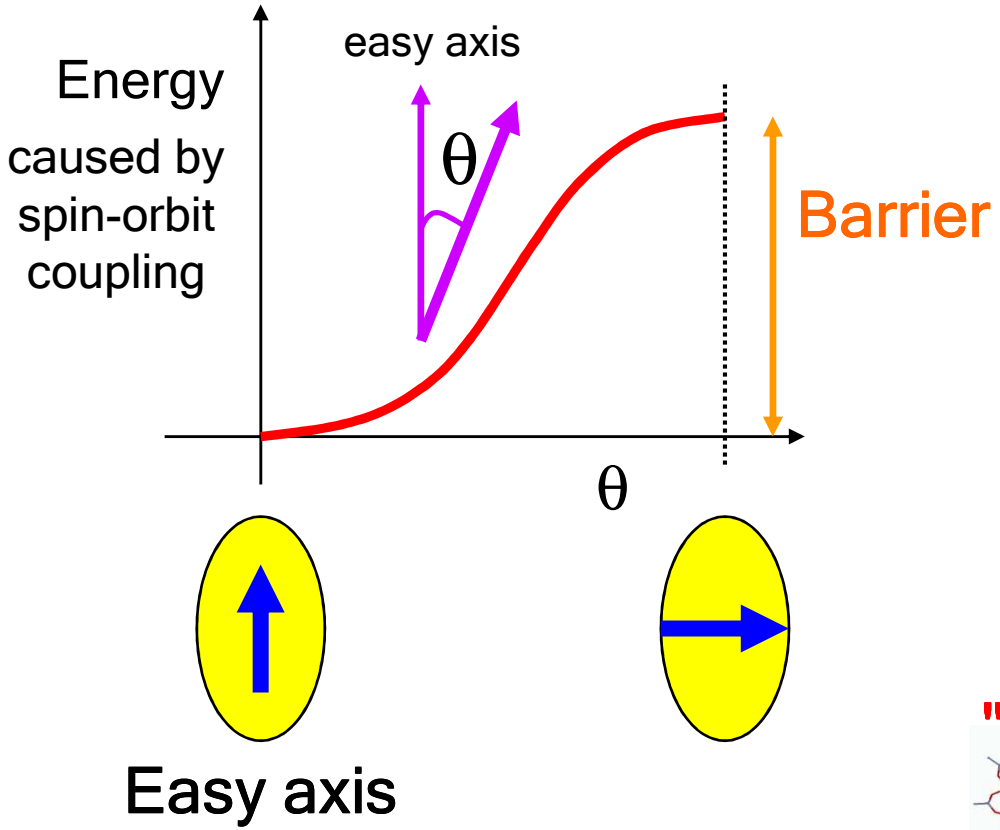
S=3

Coulon et al., PRB 69, 132408 (2004)

Magnetic Anisotropy Barrier & Easy Axis

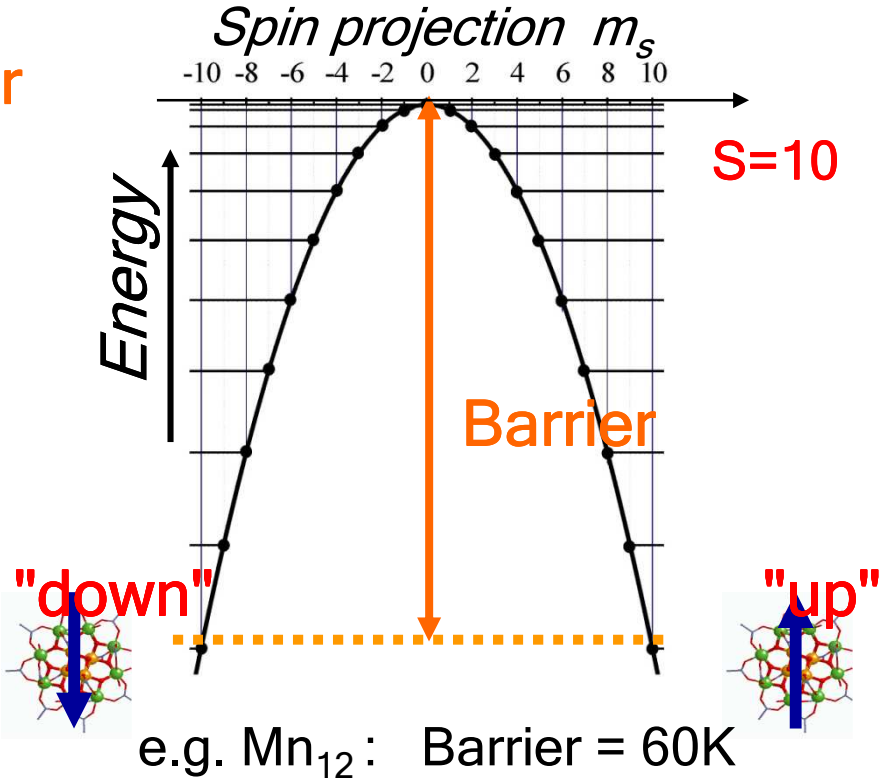
(magnetization reversal barrier)

Classical



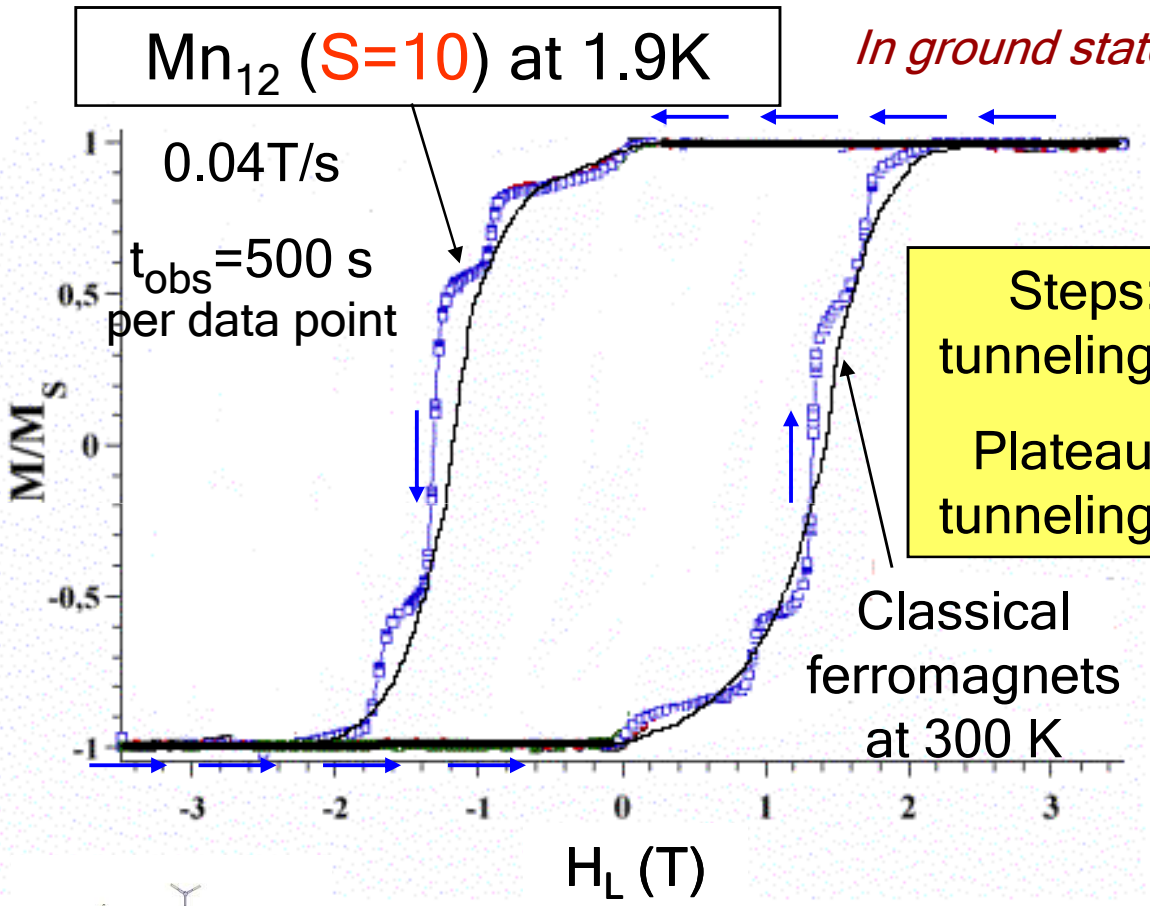
Quantum mechanical

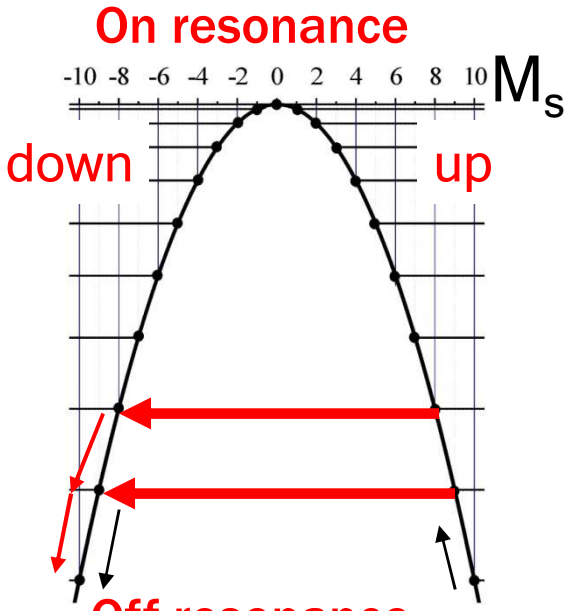
$Energy = -Dm_s^2; D > 0$ for B=0

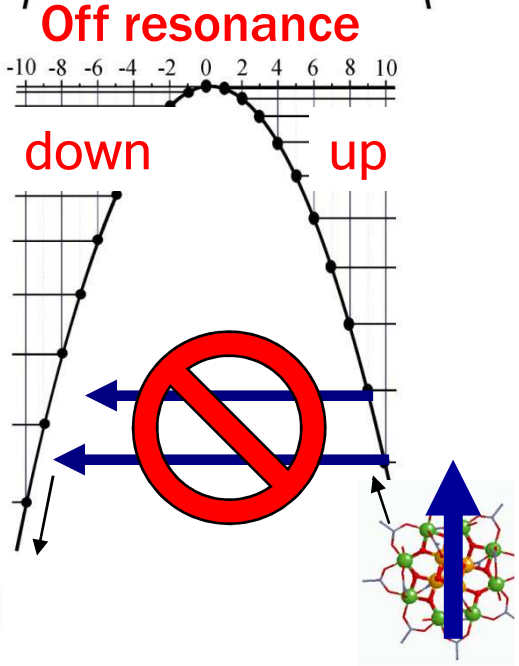


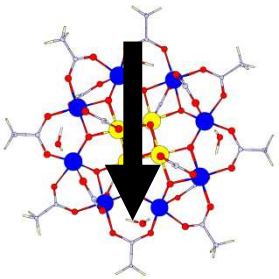
e.g. Mn_{12}: Barrier = 60K

Magnetic hysteresis: essence of quantum tunneling

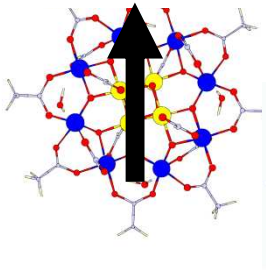




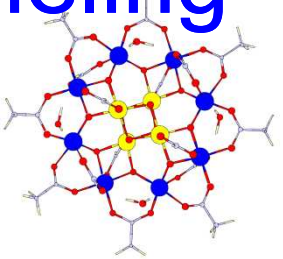




B. Barbara et al., J. Phys. Soc. Jpn. (2000); J. Friedman et al., PRL (1996); L. Thomas et al., Nature (1996)

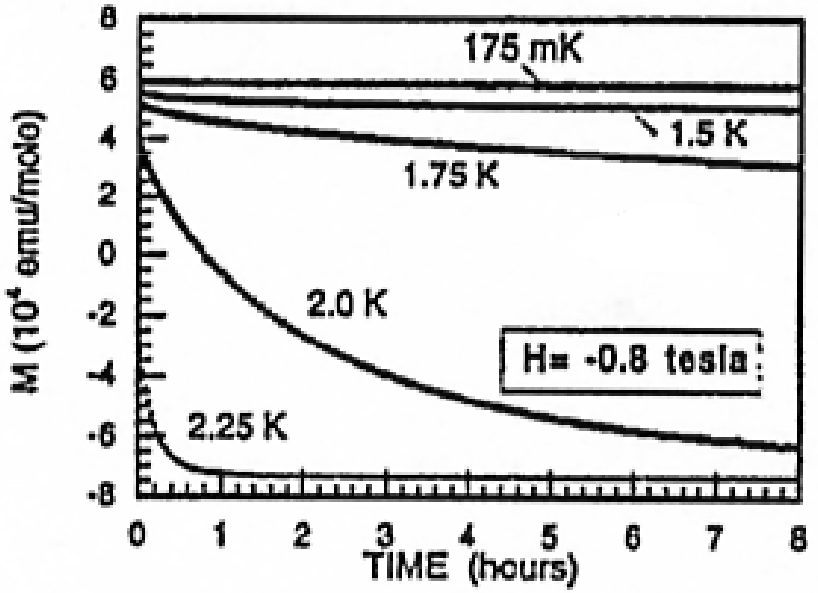


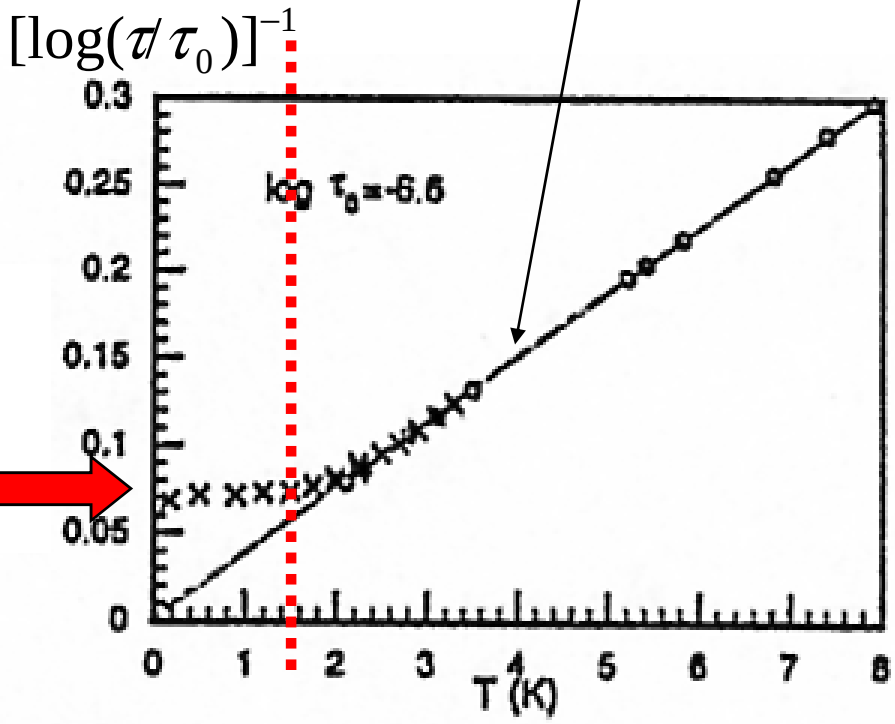
Another evidence of quantum tunneling



•Time dependence of magnetization becomes independent of temperature (T) as T → 0

$\tau = \tau_0 \exp(U/k_B T)$,





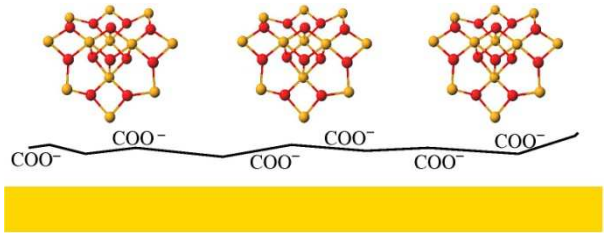
C. Paulsen et al., J. Mag. Mag. Mat. (1995)

A. Caneschi et al., Nature (1993)

Motivation: device applications

•Deposition of SMMs on a gold or silicon surface

Steckel et al., Nano Lett. (2004); Zobbi et al, Chem. Comm. (2005); Fleury et al., Chem. Comm. (2005).



•Magnetic measurement: Properties of Mn_{12} monolayers differ from those of bulk Mn_{12}

Naitabdi et al., Adv. Mater. 17. 1612 (2005)

Salman et al., Nano Lett. (2007)

•Photoemission spectra on Mn_{12} monolayers: Mn_{12} d orbitals in valence bands are similar to those for bulk Mn_{12}

STM image

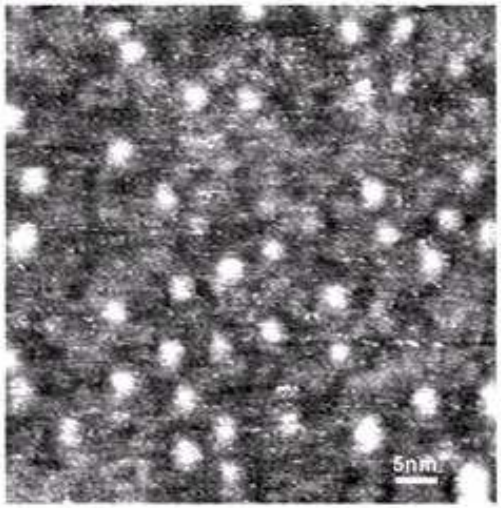
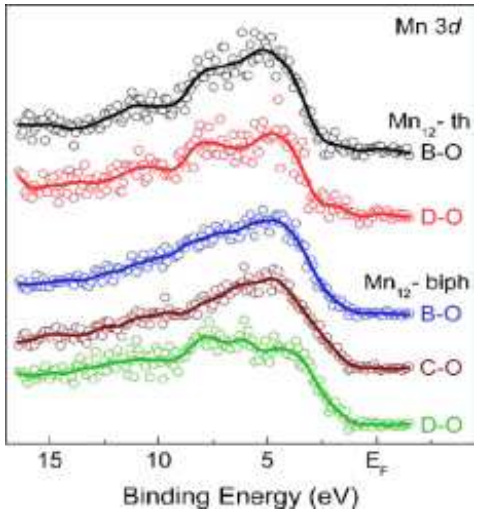
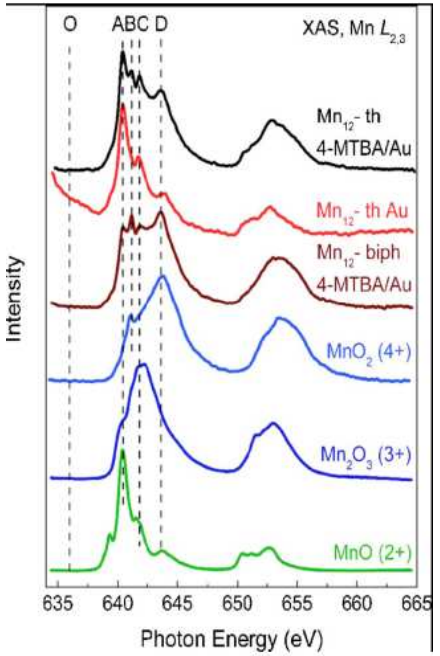


Fig. 4 (Bottom) Constant-current STM image of 2 assembled on the Au(111) surface (scan area 60 × 60 nm²). (Top) The distribution of diameters extracted from 400 measurements.** The best-fit gaussian distribution is shown as a light gray curve (R^2 = 0.97, x_c = 2.7 nm, σ = 0.5 nm).

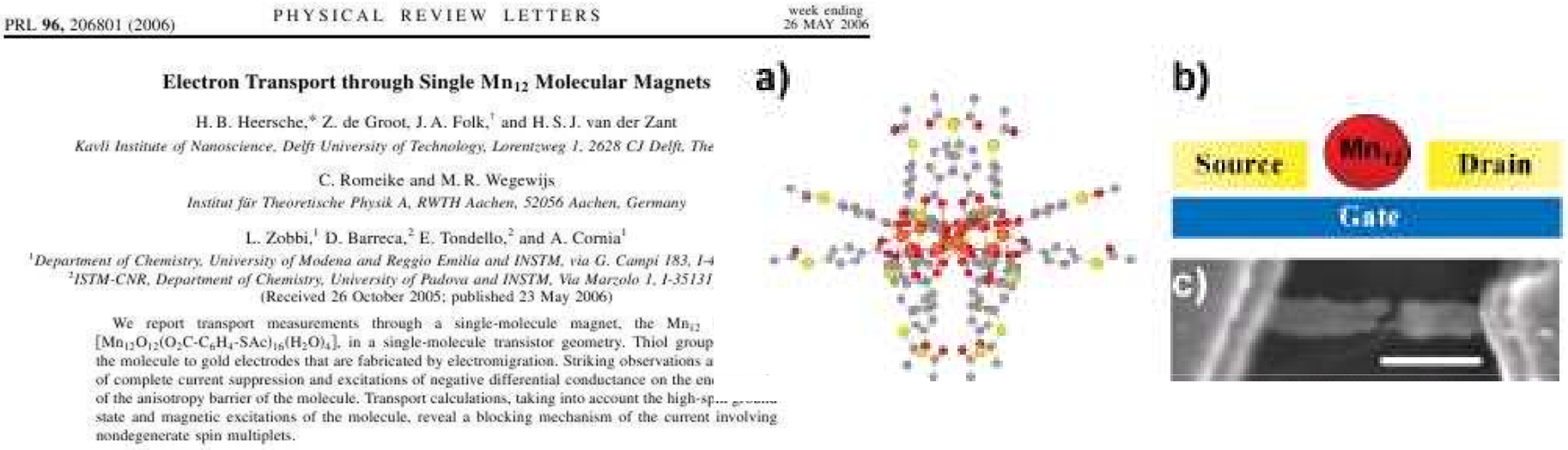


del Pennino et al., Surf. Sci. (2006); Voss et al., PRB (2007)



Motivation: device applications

- Electronic transport measurements through SMM Mn_{12}



PRL 96, 206801 (2006) PHYSICAL REVIEW LETTERS week ending 26 MAY 2006

Electron Transport through Single Mn_{12} Molecular Magnets

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(Received 26 October 2005; published 23 May 2006)

We report transport measurements through a single-molecule magnet, the Mn_{12} $[Mn_{12}O_{12}(O_2C\text{-}C_6H_4\text{-}SAc)_{16}(H_2O)_4]$, in a single-molecule transistor geometry. Thiol group the molecule to gold electrodes that are fabricated by electromigration. Striking observations a of complete current suppression and excitations of negative differential conductance on the en of the anisotropy barrier of the molecule. Transport calculations, taking into account the high-sp... state and magnetic excitations of the molecule, reveal a blocking mechanism of the current involving nondegenerate spin multiplets.

- Jo at el. Nano Lett (2006) - Henderson et al., J. Appl. Phys. (2007)

- Theories on transport through SMM:
  - G.H. Kim and T.S. Kim, PRL (2004).
  - Romeike et al. PRLs (2006)
  - Elste and Timm, PRB (2005), PRBs (2006)
  - Leuenberger and Mucciolo, PRL 97, 126601 (2006).
  - Misiorny and Barnas, cond-mat/0706.2315

No first-principles calculations on SMMs deposited on a surface or bridged between electrodes

How to solve many-body problems quantum mechanically using Density-Functional Theory(DFT)

Interacting many-electron problem: $H\Psi=E\Psi$

where $\Psi=\Psi(x_1,y_1,z_1,\ldots,x_N,y_N,z_N)$

$H = H_{kin} + H_{n\text{-}e} + H_{e\text{-}e}$

Cost: M^{3N} for M x M x M grids

(e.g.: 10^{30} for N=10, M=10)

DFT

Kohn & Pople (1998, Nobel prize in chemistry)

Total density of electrons is the same

N non-interacting single-electron problems: $H'\Phi_i=\varepsilon_i\Phi_i$ where $\Phi_i=\Phi_i(x,y,z)$

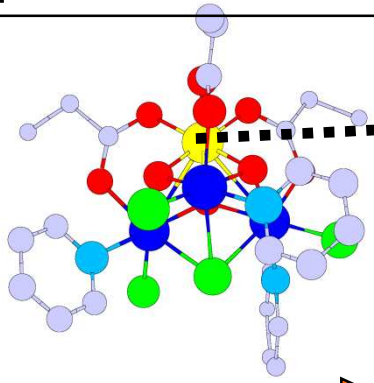
$H'=-\nabla^2/2+V_{eff}(\vec{r})$ where $V_{eff}(r)$ is an effective potential

Cost: NM^3 for M x M x M grids

(e.g.: 10 x10^3 for N=10, M=10)

How to do electronic structure calculations

Initial assignment (geometry, total charge, spin conf., total moment)



Place Gaussians on each atom as a basis set for an atomic wavefunction

$$\Psi(\vec{r}) = \sum C_k f_k \exp[-\alpha_k (\vec{r} - \vec{R}_k)^2]$$

Solve N **non-interacting** one-electron equations under **effective potential** self-consistently:

$V_{eff}(r) = V_{nucl} + V_H[\rho(r)] + V_{xc}[\rho(r)]$

$$[-\nabla^2/2 + V_{eff}(\vec{r})]\Psi_i = \varepsilon_i \Psi_i$$

Energy is converged?

NO

YES

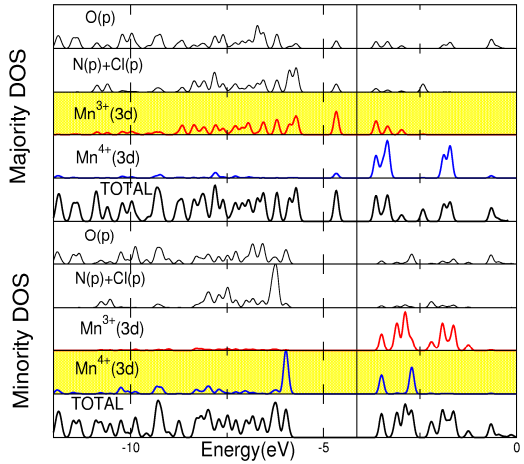
Calculate forces, ρ(r), geometry

Force is small?

NO

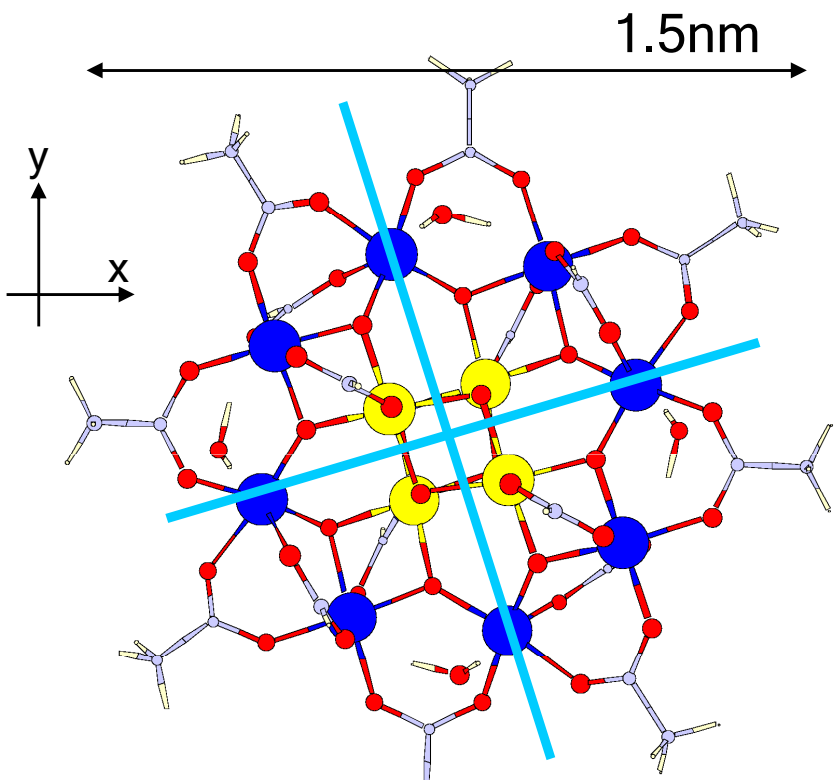
YES

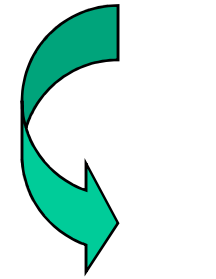
Geometry is optimized!

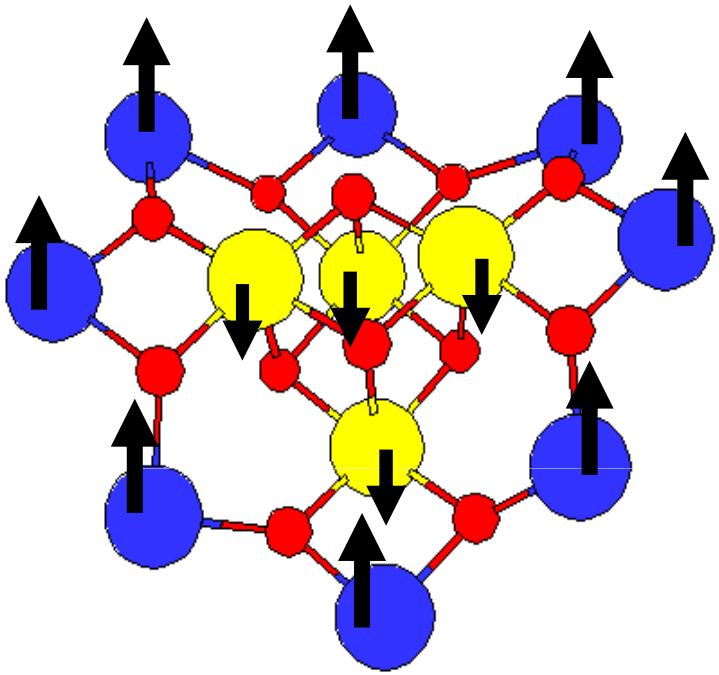


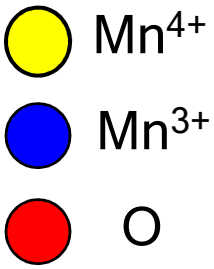
Mn_{12}: $[Mn_{12}O_{12}(O_2CCH_3)_{16}(H_2O)_4]$

T.Lis Acta Cryst. B36, 2042 (1980)









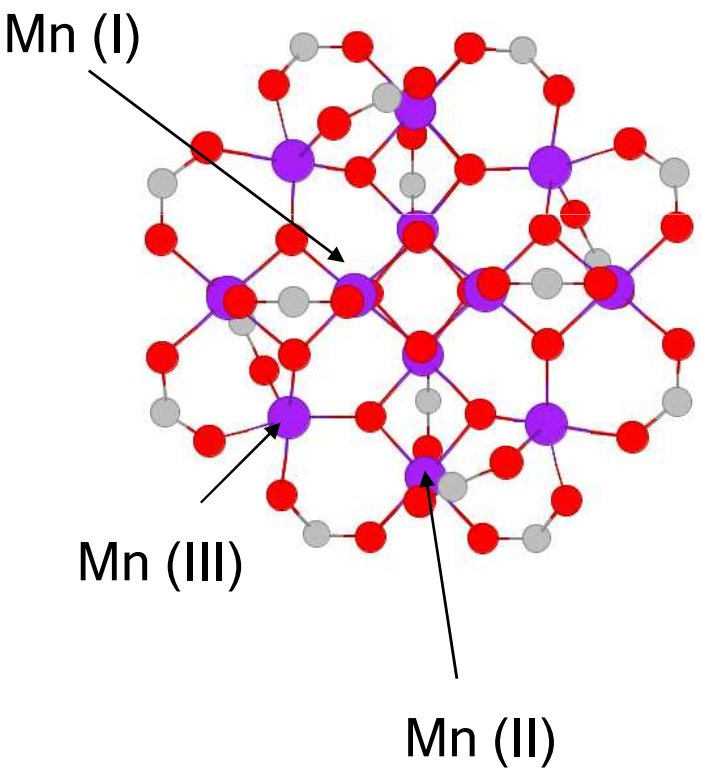
- Single molecule: S_4 symmetry
- 4 Mn^{4+} ($3d^3$,S=3/2) ions in cube
- 8 Mn^{3+} ($3d^4$,S=2) ions in outer crown
- Easy axis: z axis

- Total ground-state spin:
  S = 8 x 2 - 4 x 3/2 = 10

Electronic structure & Magnetic anisotropy for isolated Mn_{12}

M. R. Pederson & S. N. Khanna, PRB 60, 9566 (1999)

$[Mn_{12}O_{12}(O_2CH)_{16}(H_2O)_4]$



- All-electron density-functional theory (DFT) calculations using NRLMOL
- All ligands were included
- Total ground-state spin S=10
- Spin density is localized on Mn ions
- Majority HOMO-LUMO gap=0.45 eV
- Minority HOMO-LUMO gap=2.08 eV
- (2^{nd} order) magnetic anisotropy barrier =55.7 K

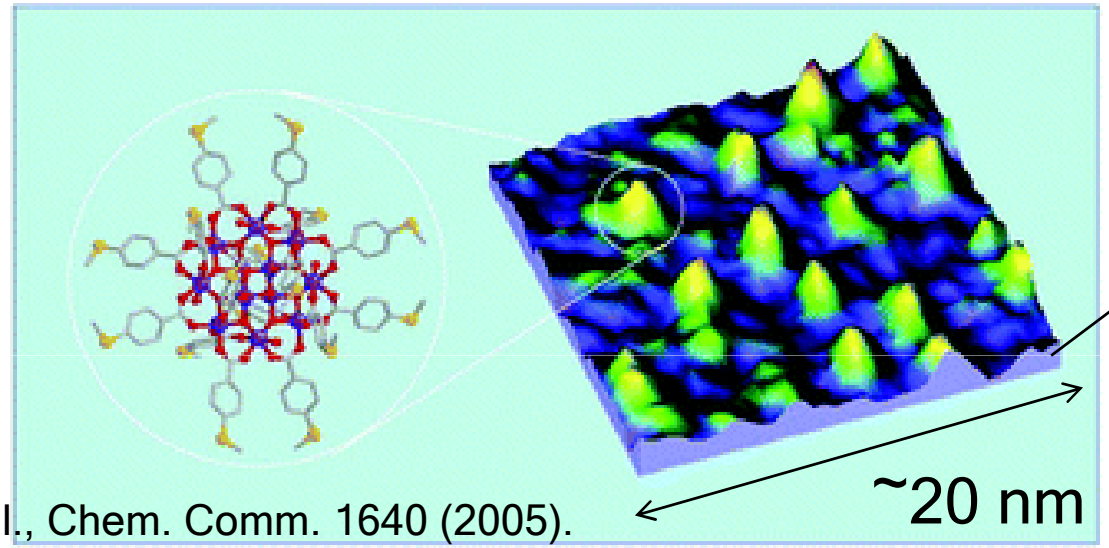
c.f. Expt: 55.6 K A.Fort et al., PRL (1998)

NRLMOL: M.R. Pederson & K.A. Jackson, PRB (1990); ibid, PRB (1991); K.A. Jackson & M.R. Pederson, PRB (1990); D. Porezag & M.R. Pederson, PRB (1996)

How does a metal surface affect electronic structure and magnetic anisotropy of Mn_{12}?

Experiment

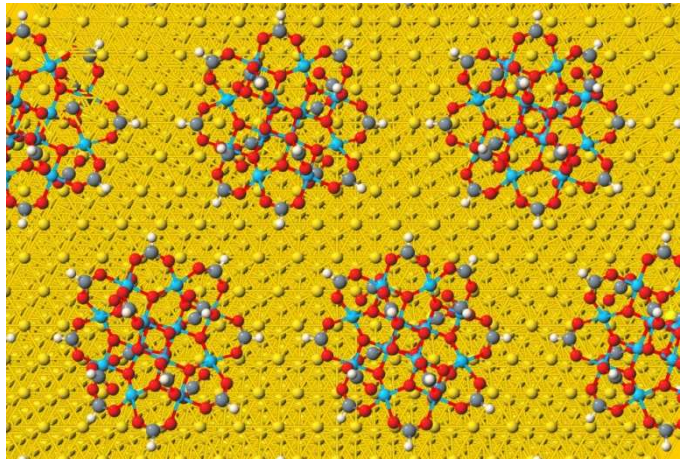
Monolayer of Mn12 on gold surface



L. Zobbi et al., Chem. Comm. 1640 (2005).

Theory

Consider slab calculation: Mn_{12}-S_2-gold surface



S. Barraza-Lopez et al., Phys. Rev. B (2007).

short link

Method & Model

- Spin polarized density-functional theory (DFT)
- Use Vienna ab-initio simulation package (VASP)
- PBE GGA for exchange-correlation potential
- Projector augmented-wave (PAW) pseudopotentials

[Blöchl, PRB (1994); Kresse & Joubert, PRB (1999)]

- All-electron wavefunctions are available
- To take into account spin-orbit coupling
- Accuracy is improved in magnetic materials

Au: s1 d10

Mn: 3p6 4s2 3d5

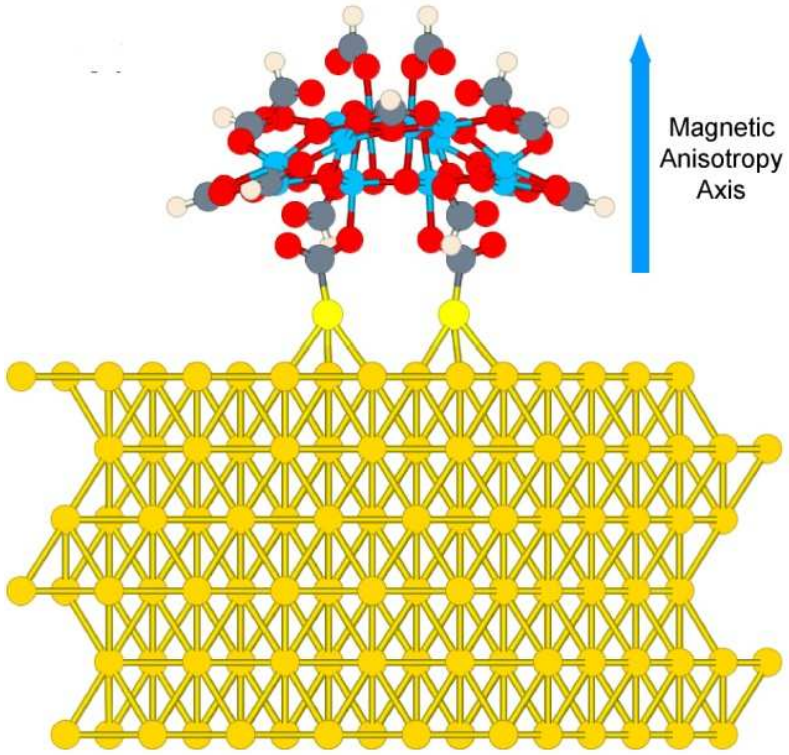
O: s2 p4

C: s2 p2

S: s2 p4

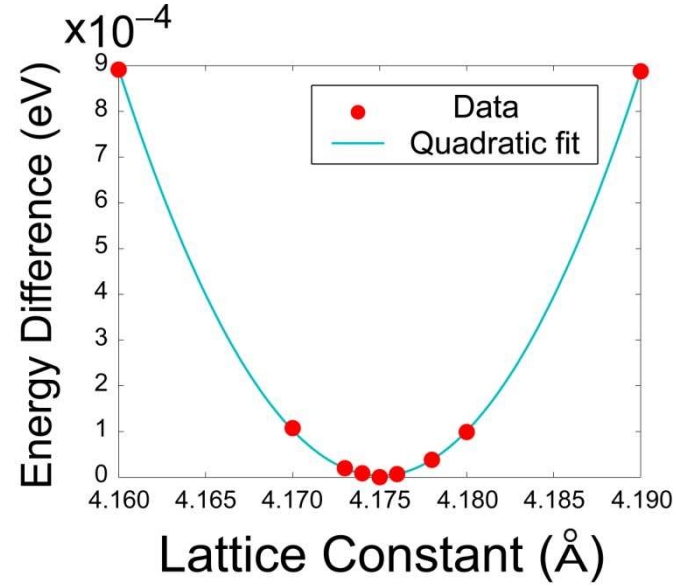
Method & Model (continued)

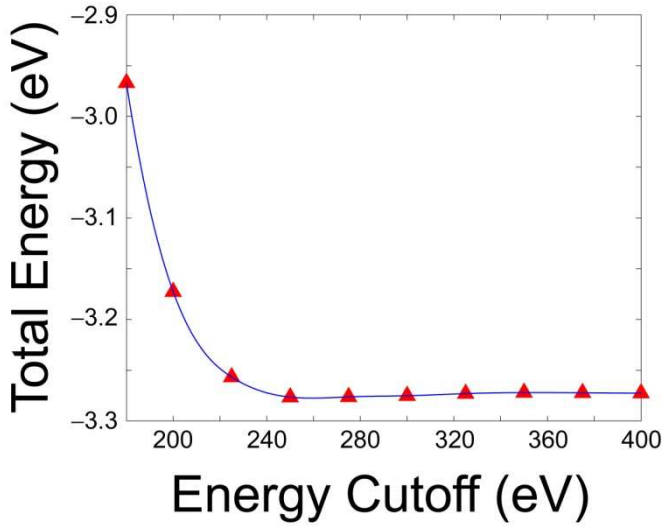
- No chemical bonding between Au and Mn_{12} so two S atoms link Mn_{12} to Au
- All ligands are included in our simulations
- Mn_{12}+linker+Au slab: Total 2886 valence electrons per unit cell
- Optimize Au slab and Mn_{12} separately to create a whole geometry



Au(111) slab

- Compute equilibrium lattice constant for bulk gold (4.175 Å)
- With the calculated lattice constant, we construct Au monolayers
- Check convergence with # of k points and energy cutoff for plane waves
- To cover Mn_{12}, at least 36 surface gold atoms per monolayer are needed
- Use six gold monolayers (36 x 6 = 216 gold atoms as a total)
- Relax gold slab (w/o molecule) until max forces are less than 0.01 eV/Å



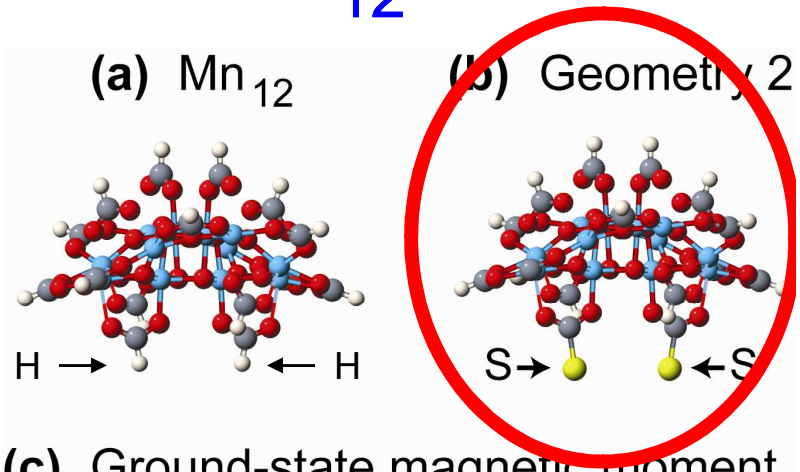


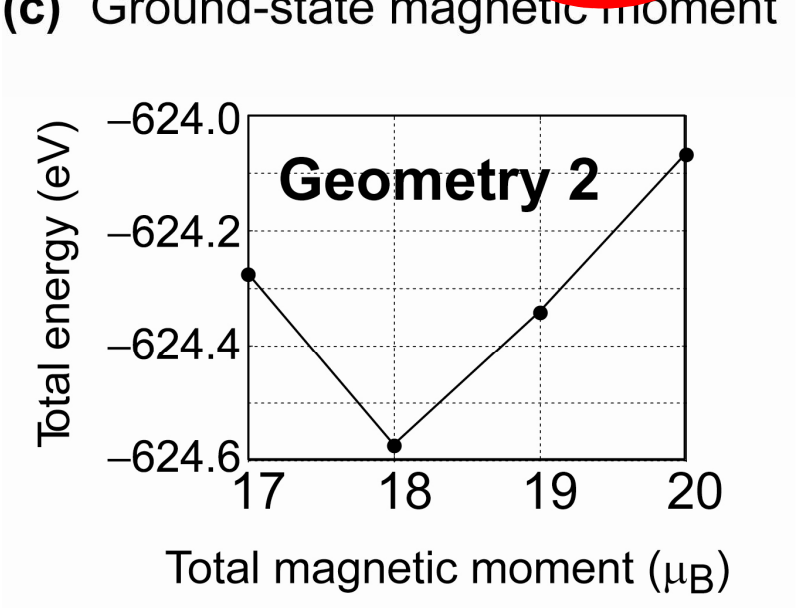
Isolated S-terminated Mn_{12}

- Mn_{12} with the lowermost H atoms replaced by S atoms, is adsorbed on Au

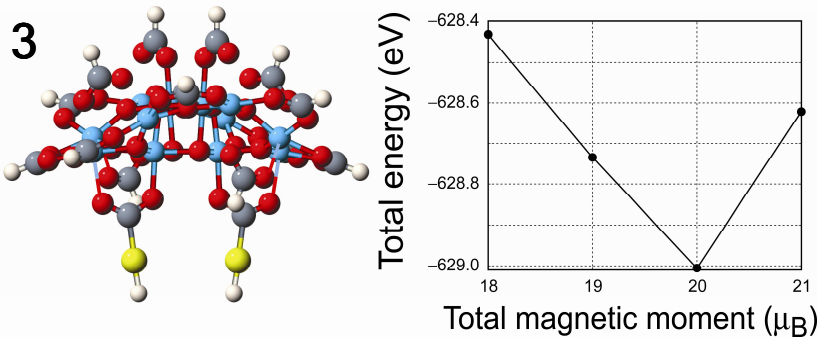
- Total magnetic moment of S-terminated Mn_{12} in ground state : 18 μ_B (c.f. ground state of Mn_{12}: 20 μ_B)

- By adding H below sulfur, the magnetic ground state goes back to 20 μ_B





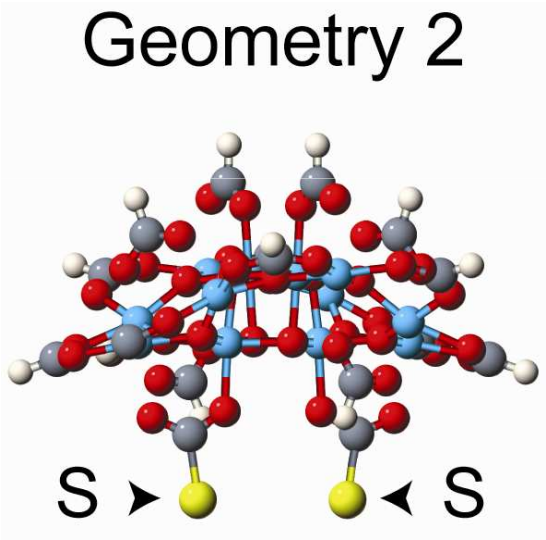
Geometry 3

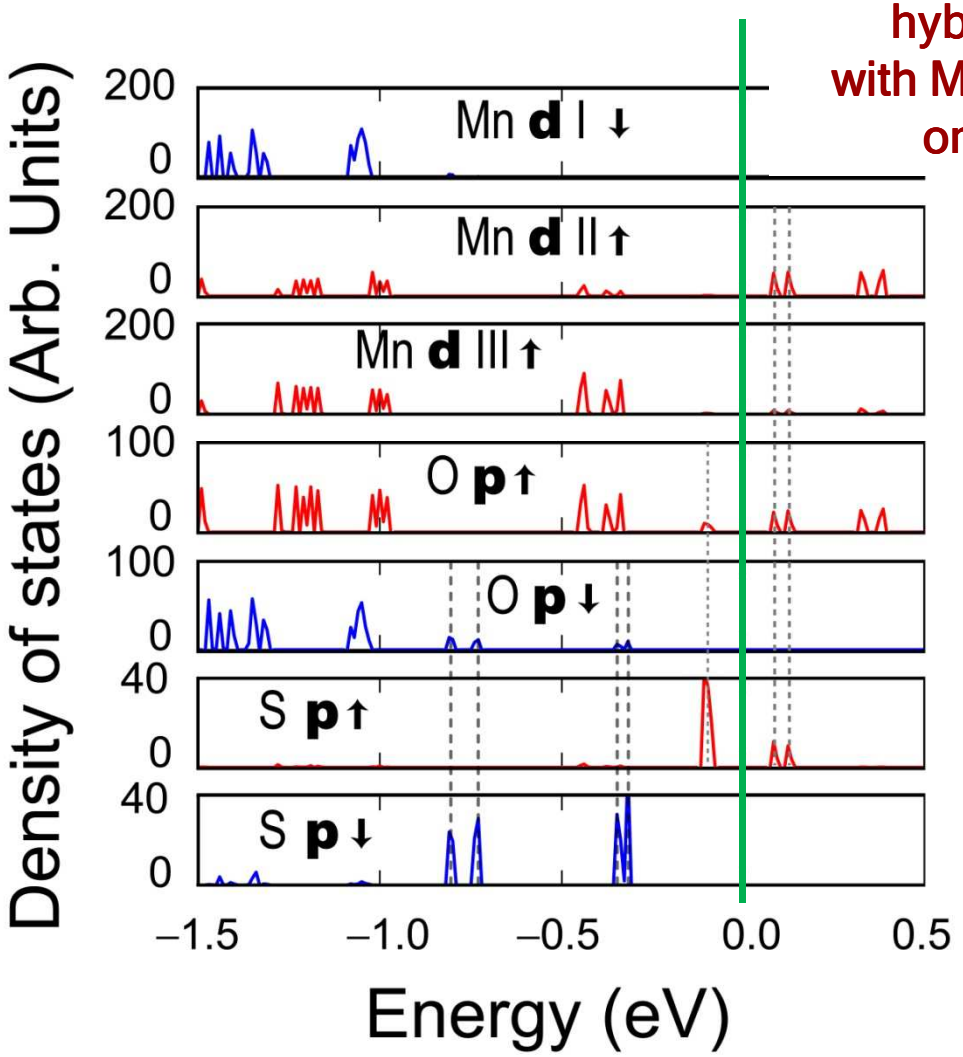


Density of States: Geometry 2

- **Spin polarization** of sulfur evident from the density of states (DOS)
- HOMO-LUMO **gap is created by sulfur p-orbitals**

Sulfur p-orbitals hybridized with Mn d-, O p-orbitals





Building whole structure

- Unit cell 17.7 x 17.7 x 34.0 Å^3

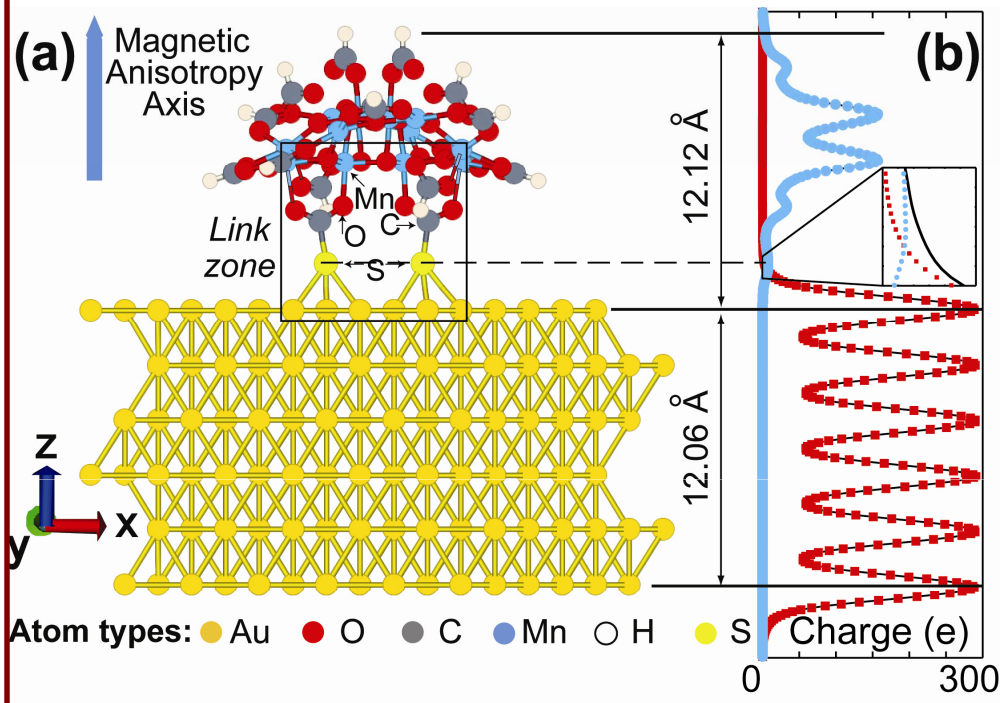
  6 Au layers + S_2 + Mn_{12} (Geo 2) + 10 Å vacuum

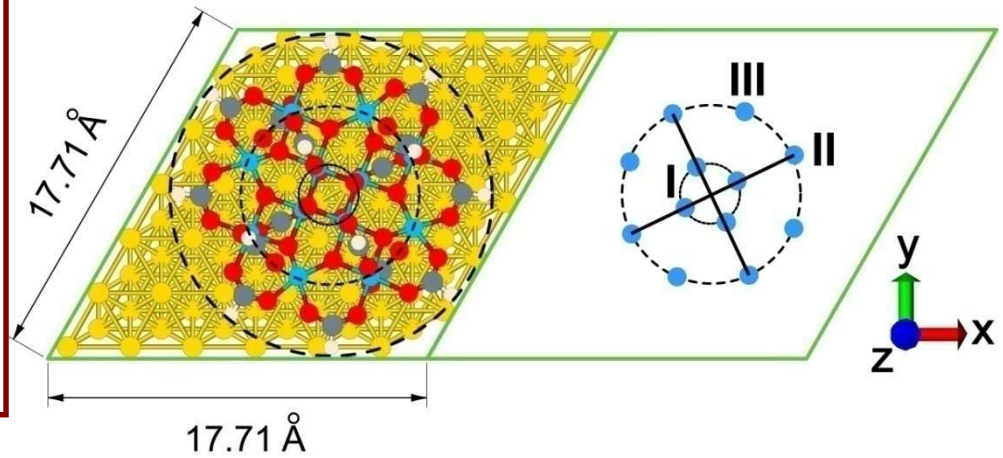
- Distance between closest H atoms in neighboring molecules: 3.35 Å. Interactions between molecules are weak.

- No further relaxation of the whole structure

- 4 k-points in 6x6x1 Au supercell

- Charge profile was computed; charge from Au slab has a tail going all the way to the lower section of magnetic molecule

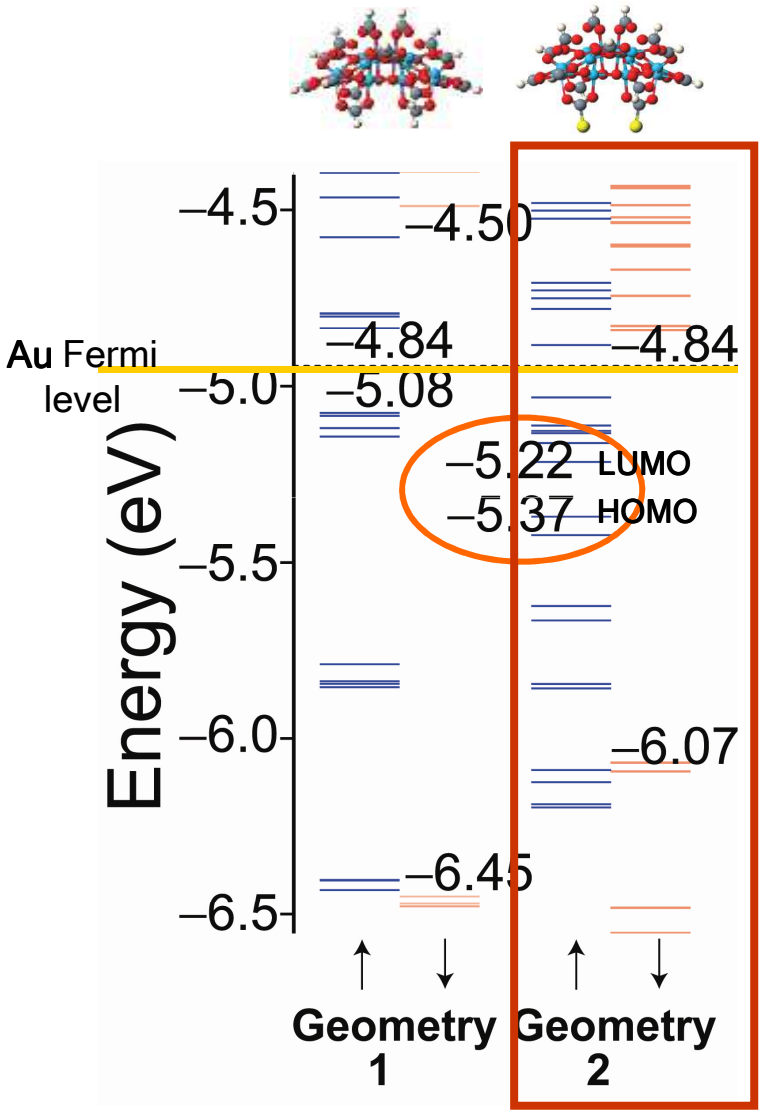




Energy levels around the Fermi level and charge transfer

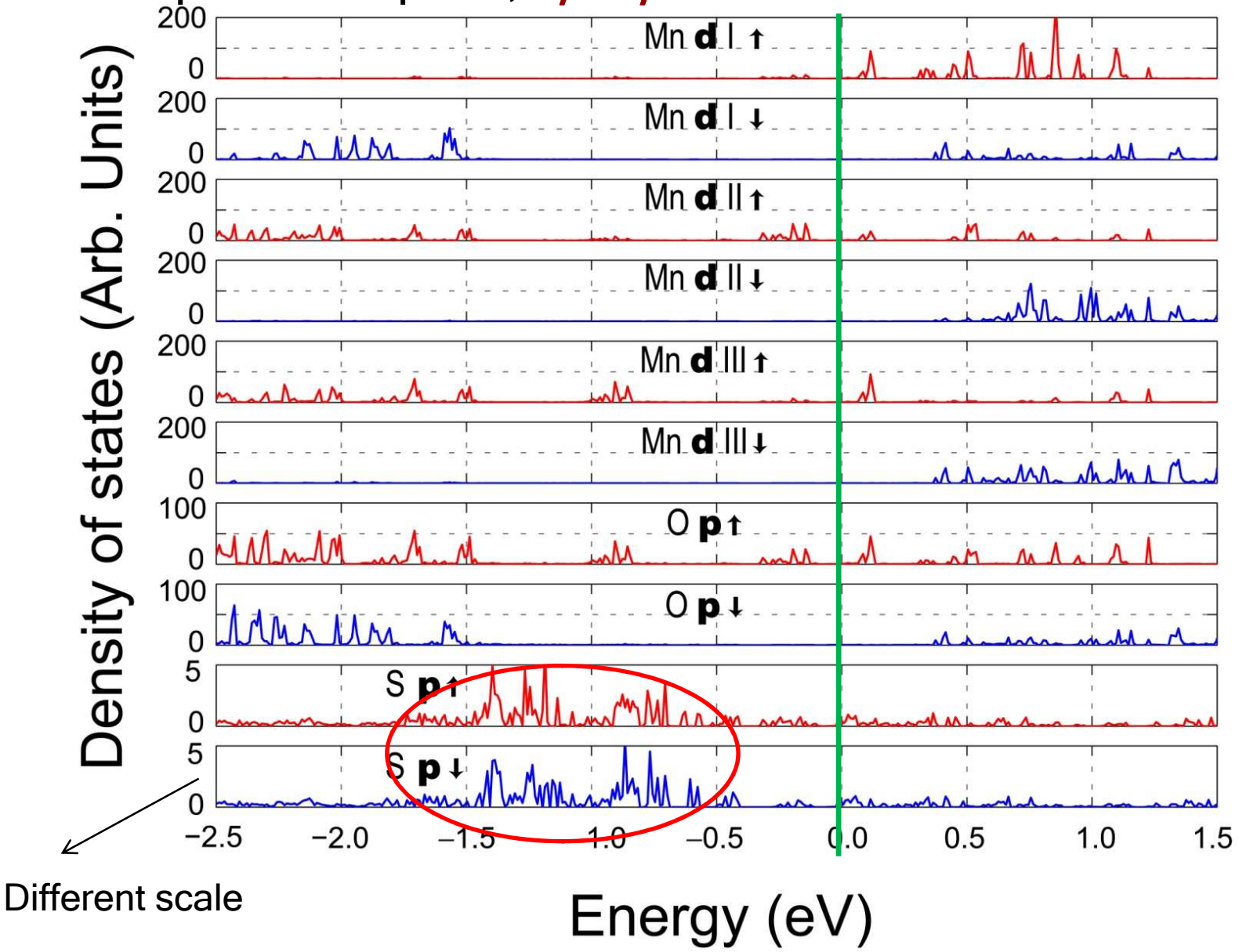
- The location of the HOMO-LUMO for the isolated S-terminated Mn_{12}, relative to the Fermi energy of bulk Au, determines the direction of charge transfer, from Au to the magnetic molecule

- Au Fermi level is above majority spin LUMO but below minority spin LUMO.



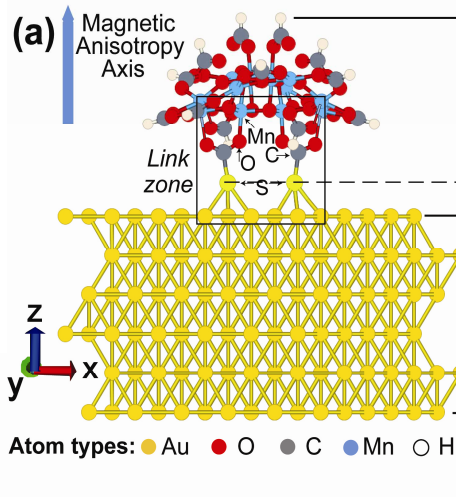
Density of states: Whole structure

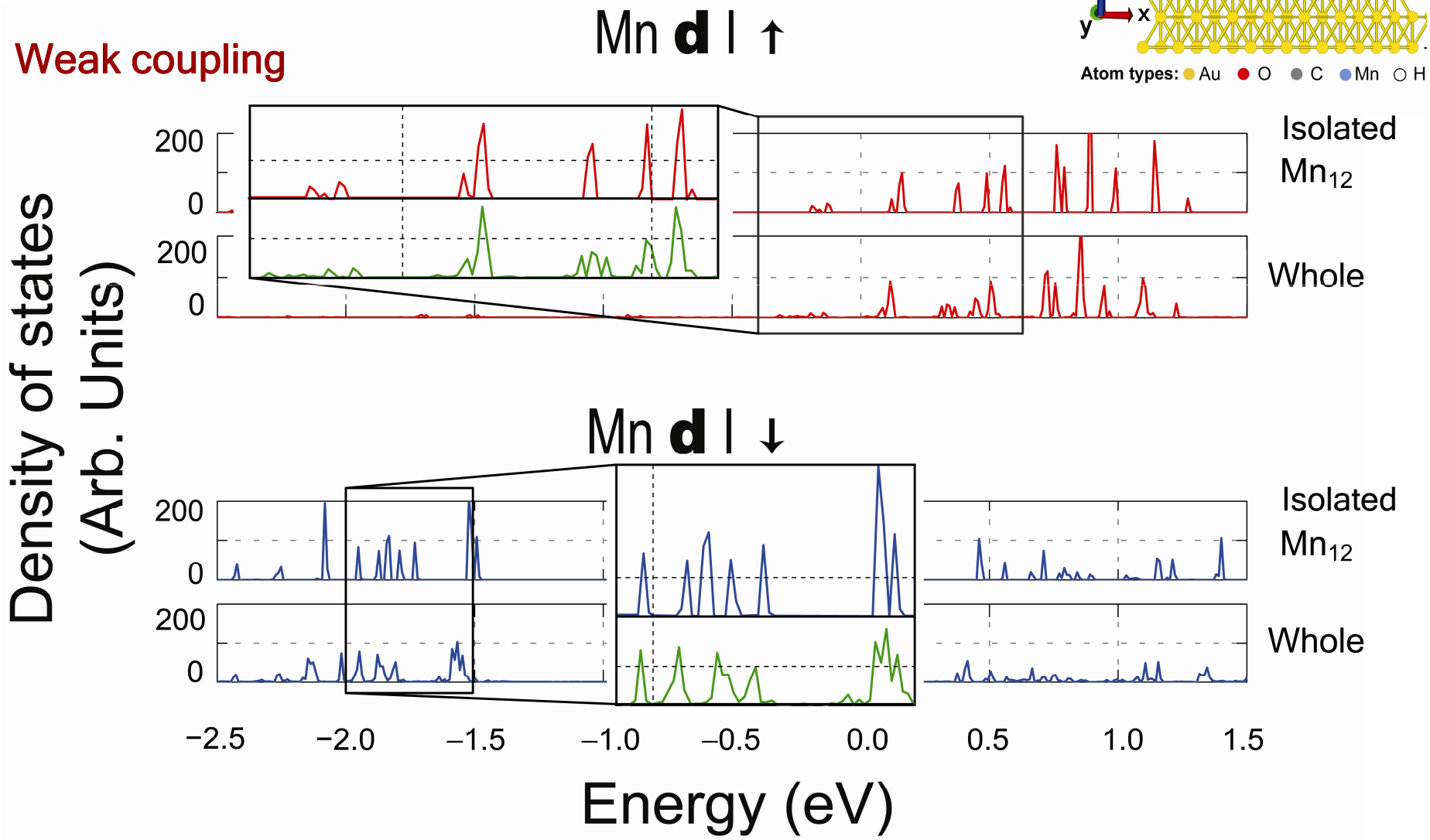
Upon adsorption, *spin polarization of S* atoms is *lost*



Orbital broadening

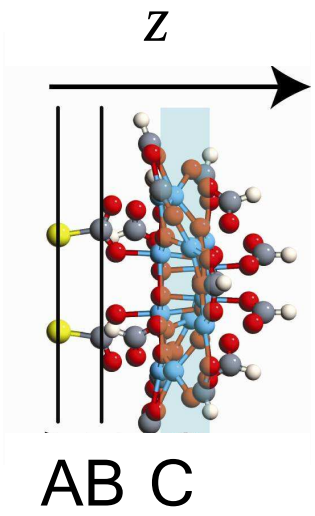
- Mn12 molecular orbitals broaden upon adsorption
- Orbital broadening is much less than charging energy

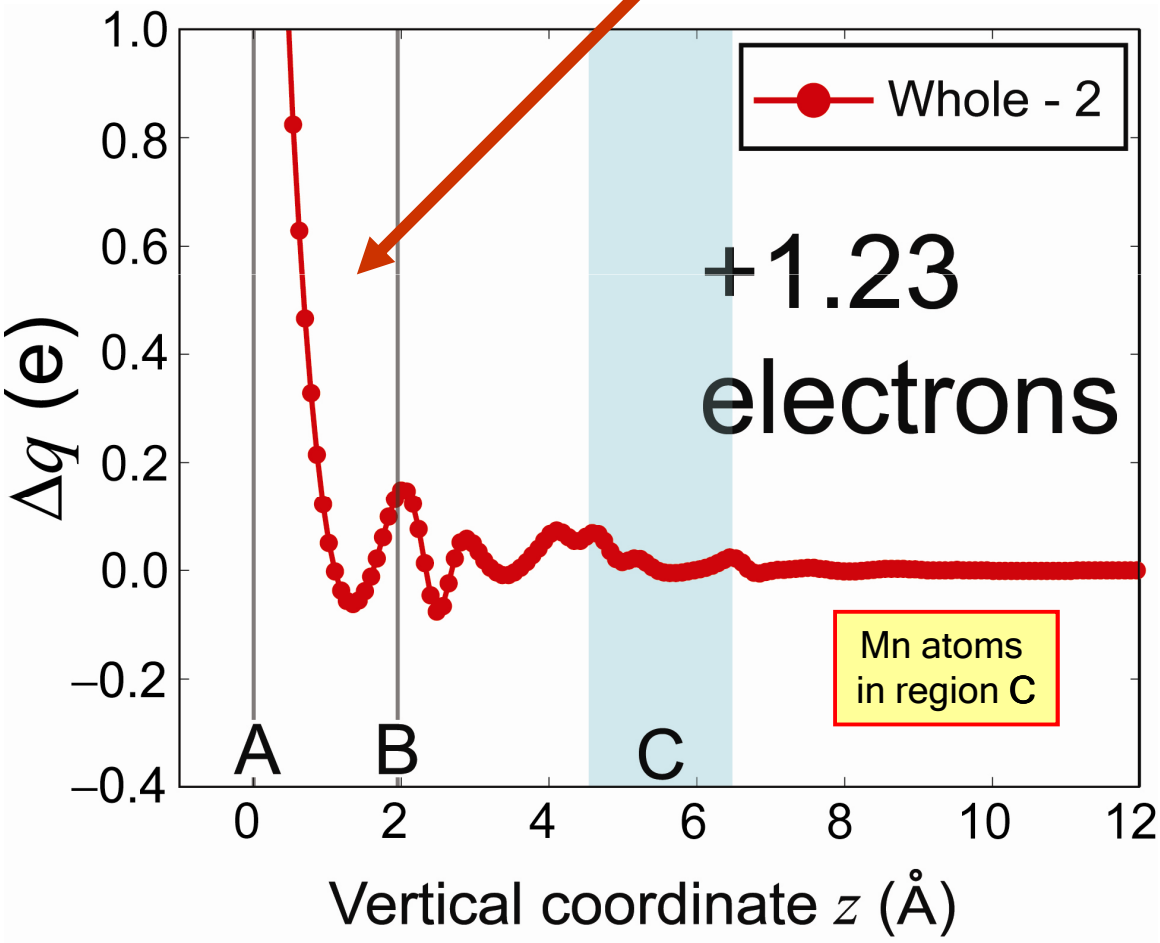




Charge transfer towards Mn_{12}

Determined via *in-plane* integration of the charge density for molecule with and without gold slab; 1.23 electrons; Au tail dominating.

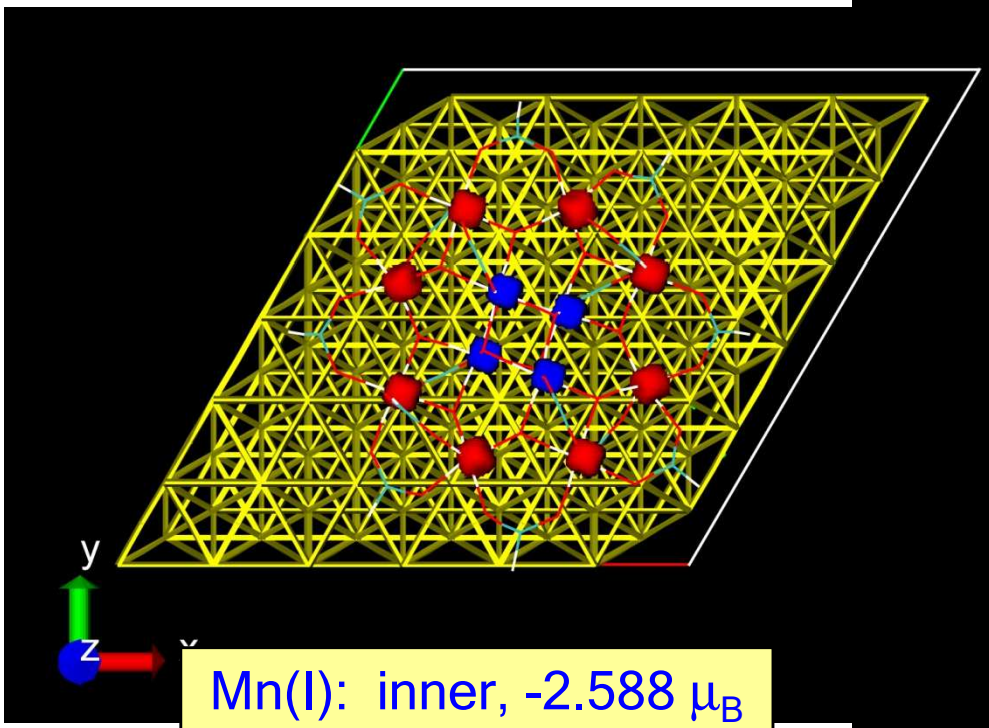




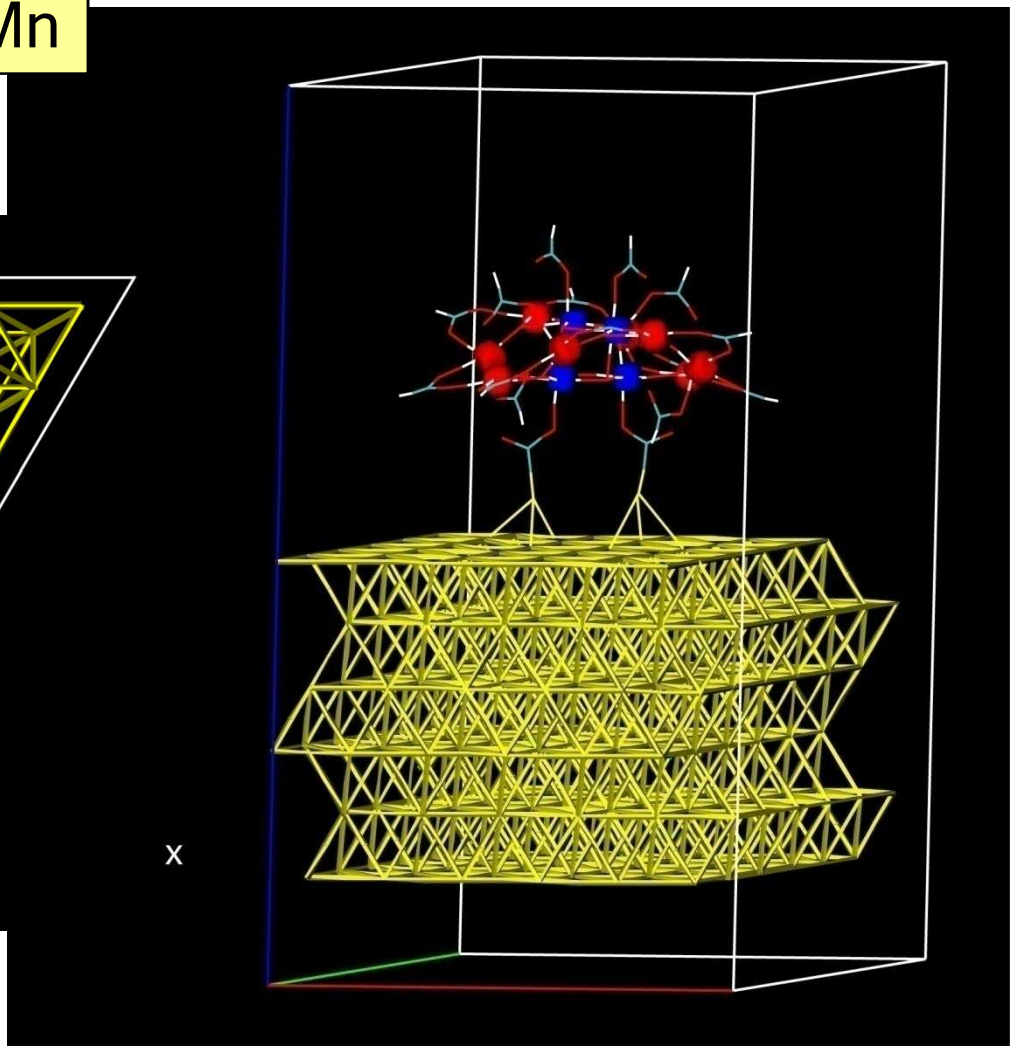
Calculated spin density

Spin density is localized on Mn

Top view Red: up Blue: down



Side view



Mn(I): inner, -2.588 μ_B

Mn(II): outer, 3.524 μ_B

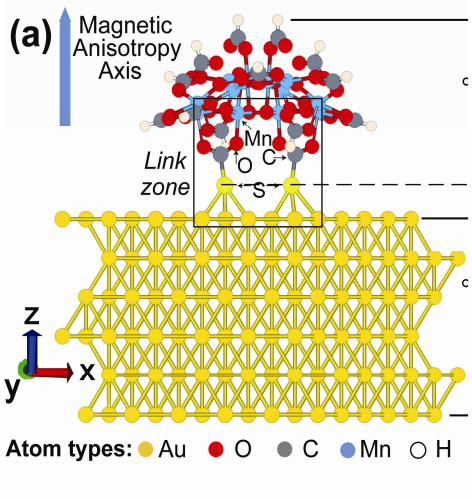
Mn(III): outer, 3.543 μ_B

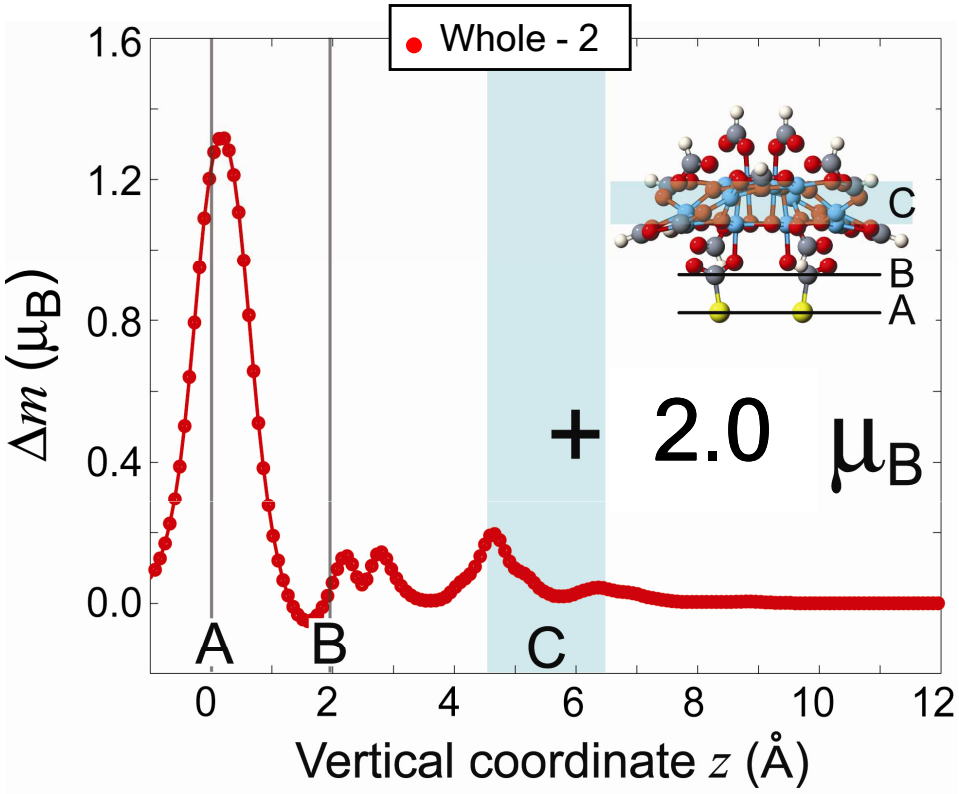
monoclinic unit cell 17.7 x 17.7 x 34.0 $Å^3$

Spatial change of magnetic moments

- From the plane-averaged magnetic moments along the z-direction, we find an increase of 2 μ_B between the S-terminated Mn_{12} and the whole structure

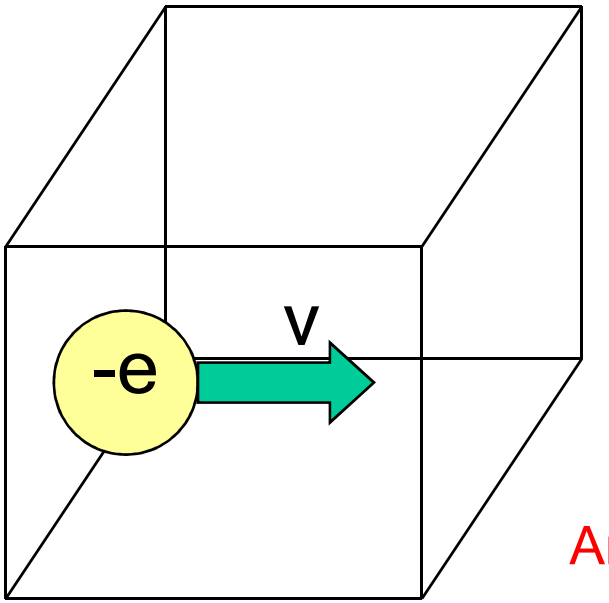
- **The whole structure has a magnetic moment of 20 μ_B.**

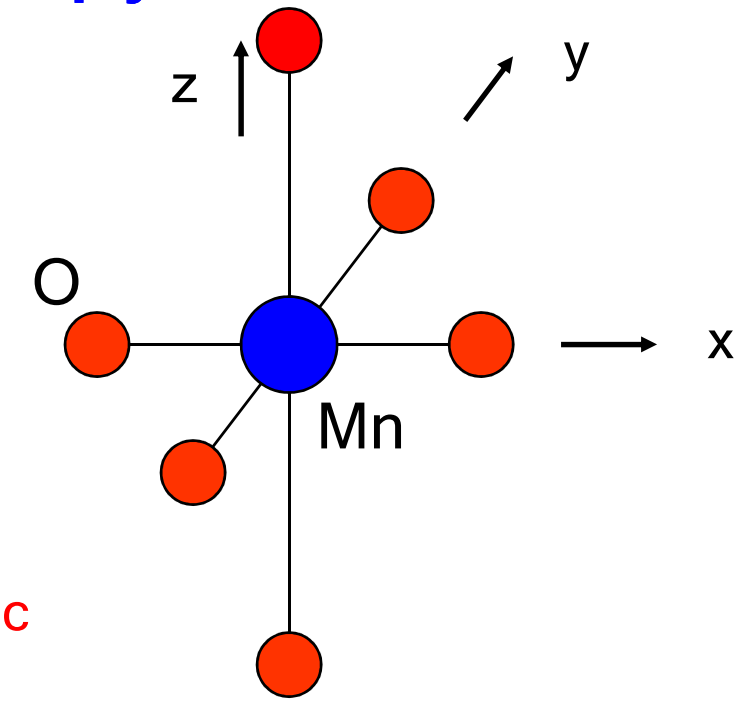




Barraza-Lopez, Avery and Park: *PRB* **76** 224413 (2007)

Magnetic Anisotropy in SMMs





Anisotropic

$$\vec{B} = \vec{v} \times \vec{E} = \vec{v} \times (-\vec{\nabla}\Phi)$$

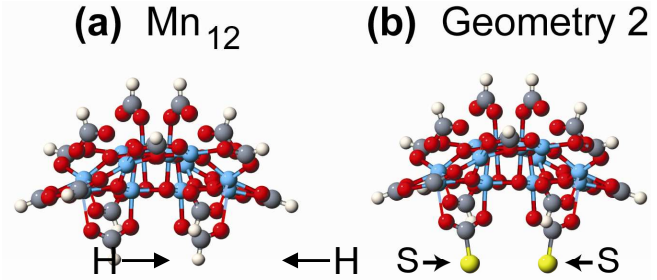
Φ: Coulomb potential due to atomic nuclei and electrons

Spin-orbit coupling

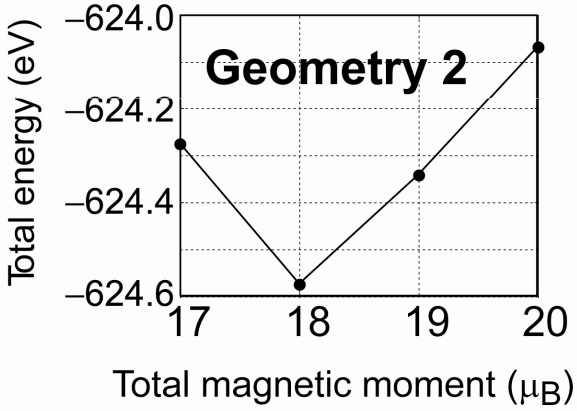
$$V_{LS} = \frac{e}{mc}\vec{S}\cdot\vec{B} = -\frac{1}{2m^2c^2}\vec{S}\cdot(\vec{p}\times\vec{\nabla}\Phi)$$

Magnetic anisotropy barrier for S-terminated Mn_{12}

- To compute magnetic anisotropy barrier, we consider spin-orbit coupling in DFT self-consistently.
- Although total magnetic moment differs for Mn12 and Geo.2 (S-terminated Mn12), the MAB of ordinary Mn12 is the same as that of Geo. 2
- Magnetic anisotropy barrier for Geo. 3 gets reduced by about 9%

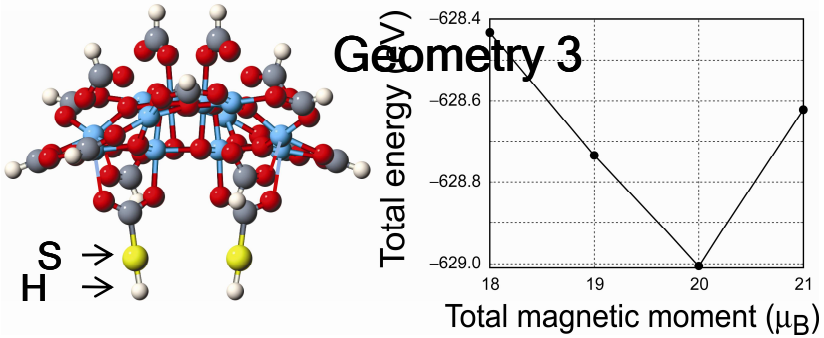


(c) Ground-state magnetic moment



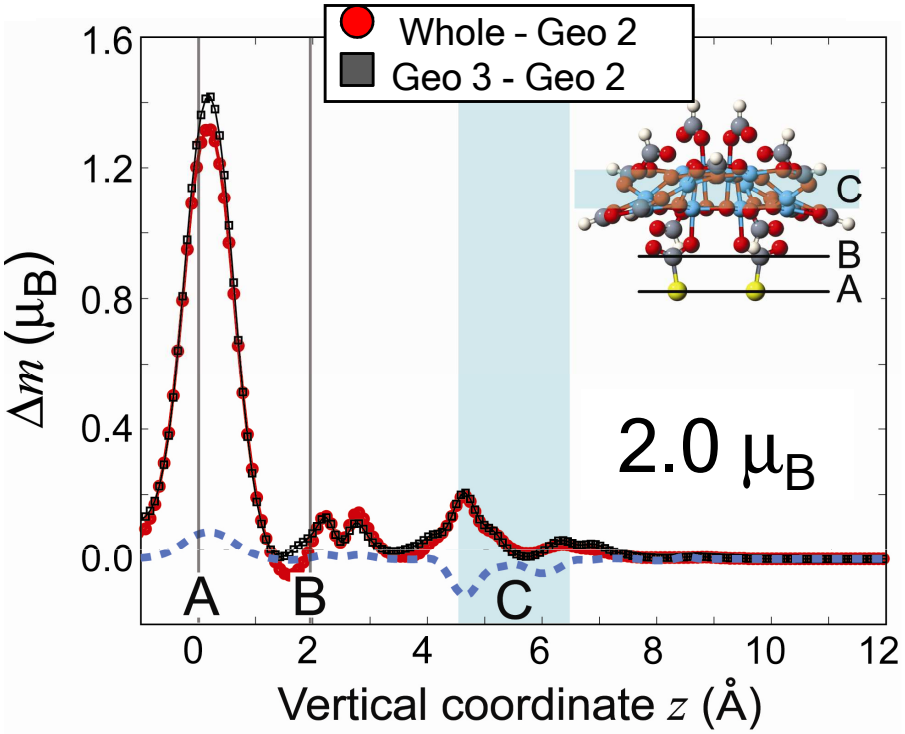
MAGNETIC ANISOTROPY BARRIER (K)

Mn_{12}	Geo 2	Geo 3
66.7	66.9	60.7

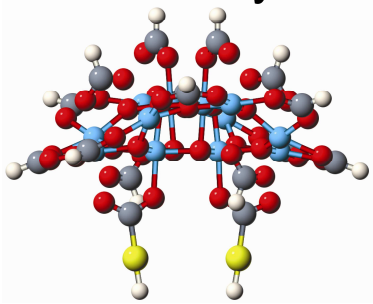


Magnetic anisotropy barrier for whole structure

- The spatial charge and magnetic moment distributes in a similar way for whole structure and Geo. 3.
- So [magneitc ansiotropy barrier (MAB) of Geo 3] = [MAB of whole structure]
- The magnetic anisotropy barrier for the whole structure is *reduced by 9%* of that for the isolated Mn_{12}.



Geometry 3



MAGNETIC ANISOTROPY BARRIER (K)

Mn_{12}	Geo 2	Geo 3	Whole
66.7	66.9	60.7	60.7

Additional inclusion of electron-electron correlations: LSDA+U method

- Takes into account the orbital dependence of strong on-site correlations (in LSDA or in GGA), which is absent in standard DFT.
- Hubbard-like U term plays important role for localized d- or f-electrons.
- d- or f-orbitals are more localized and energy gap increases.
- Value of U term: depends on local environments, determined by experiment or standard DFT calculations by varying the occupancy of d- or f-orbitals.

V. I. Anisimov et al., PRB **44**, 943 (1991)
V. I. Anisimov et al., J. Phys.: Condens. Matter **9**, 767 (1997)

Effect of correlation: GGA+U

- On-site U=6 eV is considered for Mn d-orbitals
- Ordinary Mn_{12}: HOMO levels are shifted down. HOMO-LUMO gap greatly increases due to HOMO and LUMO that are from Mn d-orbitals.
- S-terminated Mn_{12} (Geo 2): HOMO, LUMO are from S p-orbitals so the gap does not change much.
- Direction of charge transfer does not change with U

Barraza-Lopez, Avery and Park, *J. Appl. Phys.* (2008)

Electronic level (eV)	U=6* ↑	U=6* ↓	PBE GGA ↑	PBE GGA ↓
Mn_{12} HOMO	-6.13	-7.04	-5.08	-6.45
Mn_{12} LUMO	-4.78	-4.77	-4.84	-4.50
gap	***1.35***		**0.24**	
Geo 2 HOMO	-6.37	-6.66	-5.37	-6.07
Geo 2 LUMO	-6.05	-5.51	-5.22	-4.84
gap	**0.32**		**0.15**	

(*) Boukhvalov et al, *PRB* **75**, 014419 (2007)

Summary

- Modeled a monolayer of Mn_{12} adsorbed on a Au surface via a thiol group using DFT
- Electronic structure: broadening of molecular orbitals was small, weak coupling between Mn_{12} and a Au surface even with the short link
- Charge transfer from Au to Mn_{12}
- Total moment for whole structure back to 20 μ_B
- Magnetic anisotropy barrier for whole structure is reduced by 9% compared to that for isolated Mn_{12} molecule
- Effect of on-site U on orbitals for isolated molecules

Barraza-Lopez, Avery and Park: *PRB* **76** 224413 (2007), *JAP* **103** 07B907 (2008)

Bulk gold & Au(111) slab

•Bulk gold:

Equilibrium lattice constant = 4.175 Å

Exp: 4.078 Å, difference: 2.8%

•Check convergence with # of k points and energy cutoff for plane waves

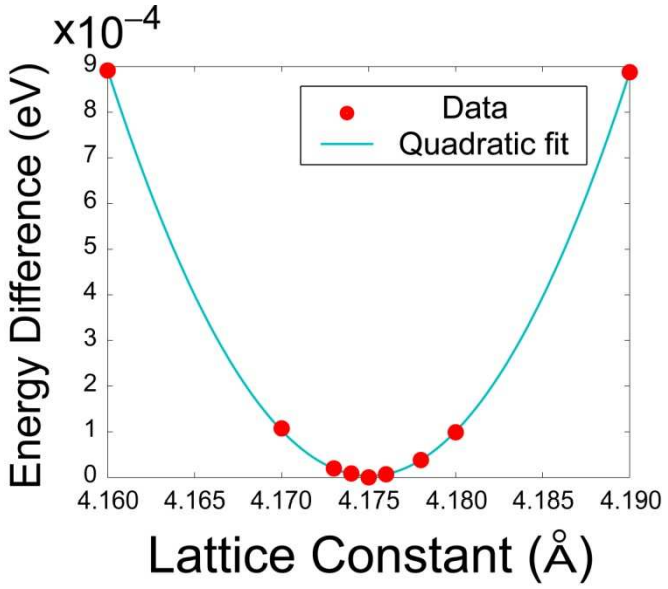
•With calculated lattice constant, we vary # of Au layers and # of vertical vacuum layers

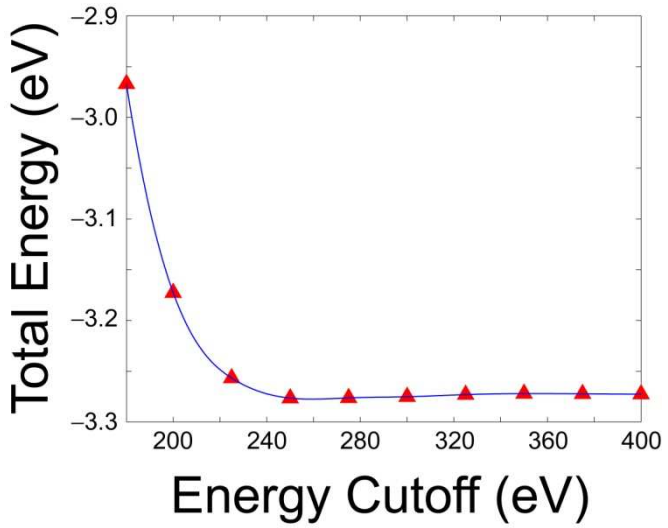
•Au surface energy saturates with 8 Au monolayers and 7 vacuum layers

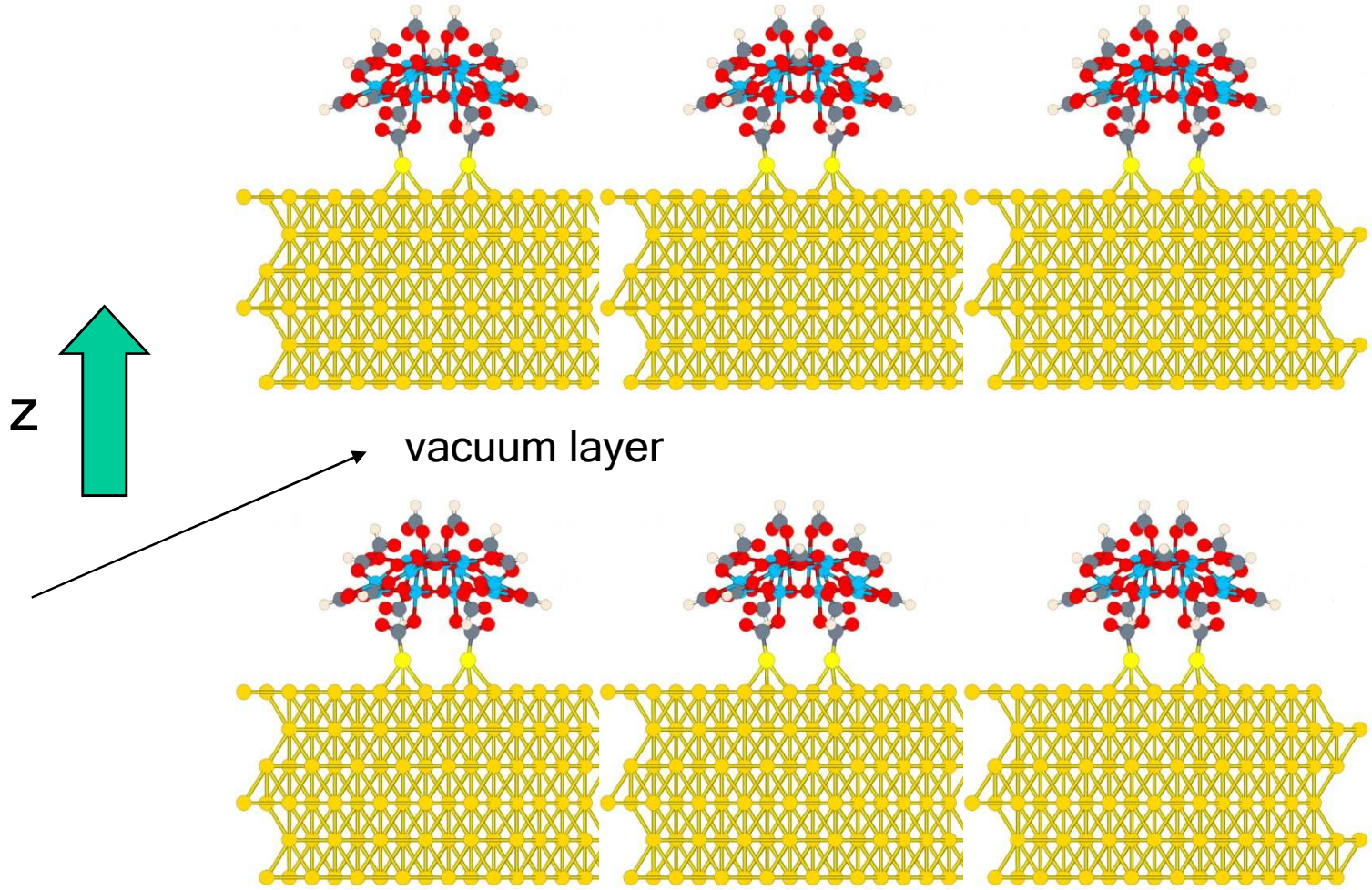
•To cover Mn_{12}, at least 36 surface gold atoms per monolayer are needed

•Use six gold monolayers (36 x 6 = 216 gold atoms)

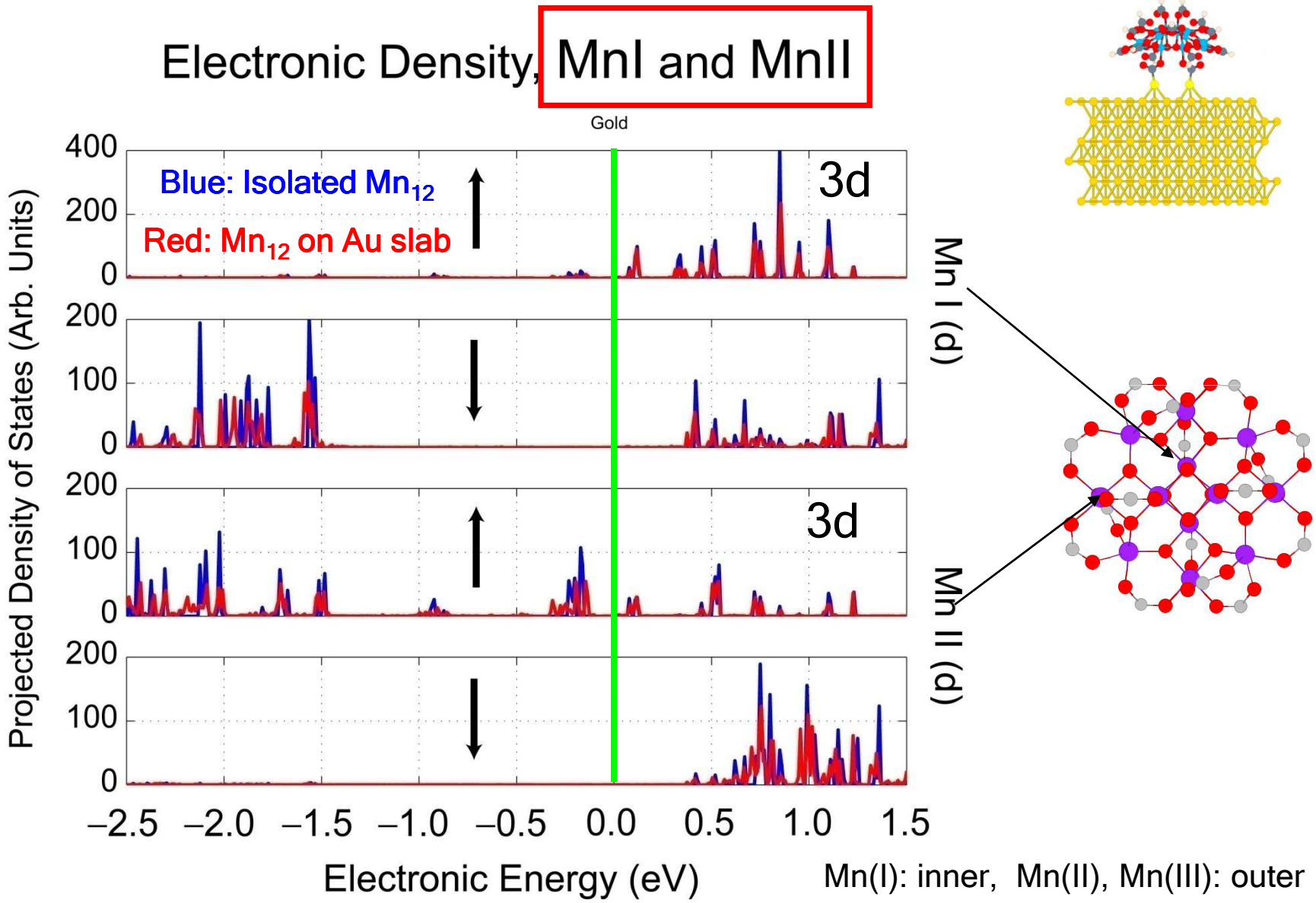
•Relax gold slab (w/o molecule) until max forces are less than 0.01 eV/Å





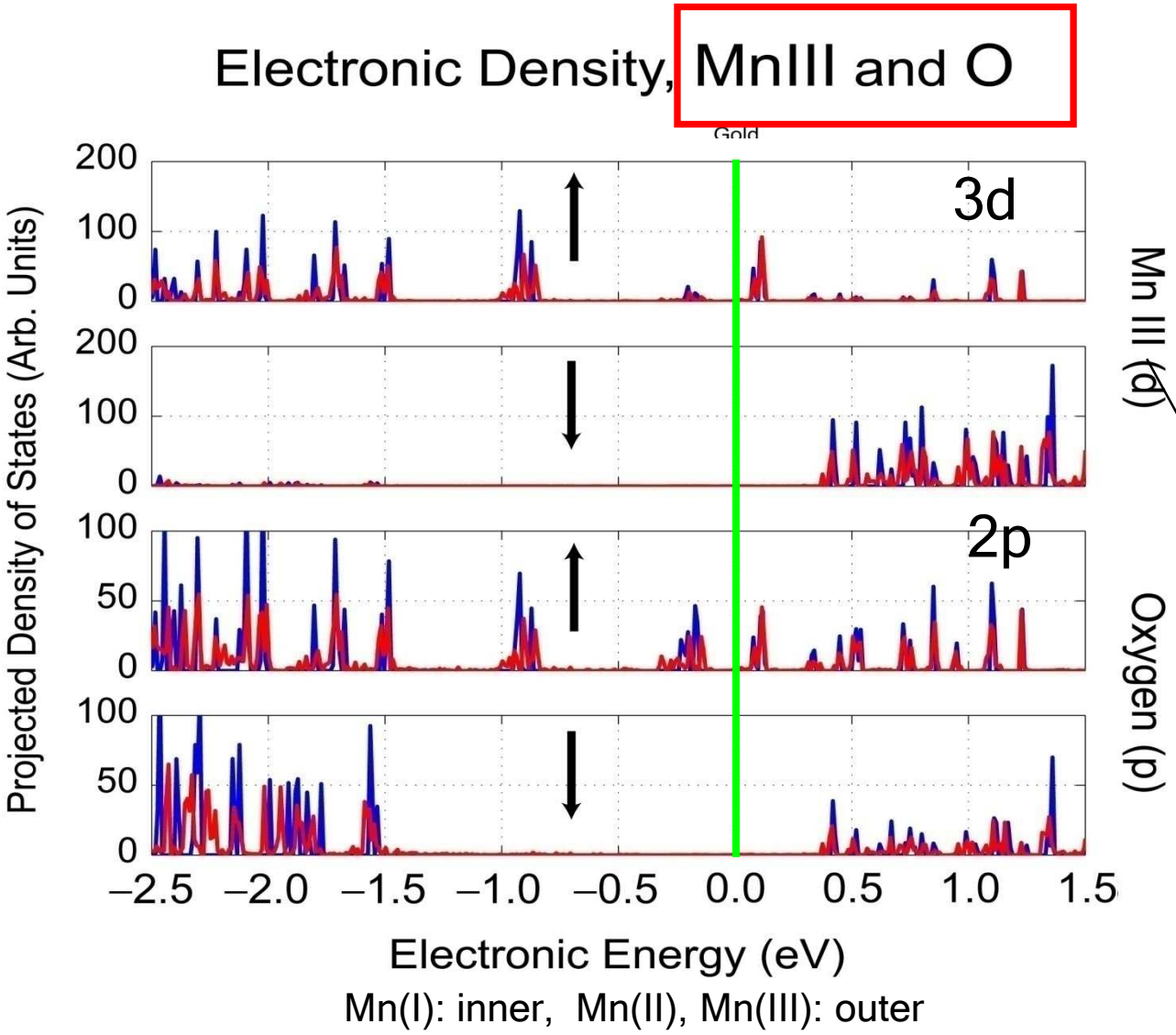

z
vacuum layer

Projected density of states for Mn_{12} on Au slab

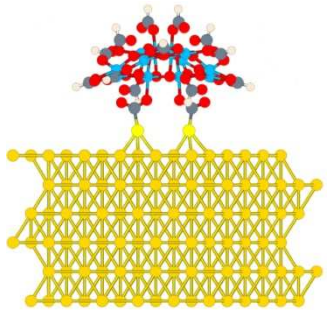


Mn(I): inner, Mn(II), Mn(III): outer

Projected density of states for Mn_{12} on Au slab

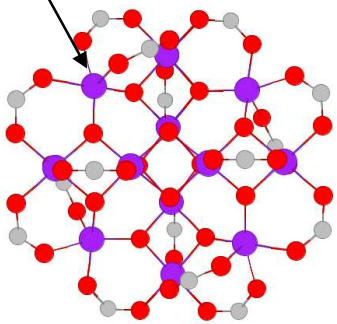


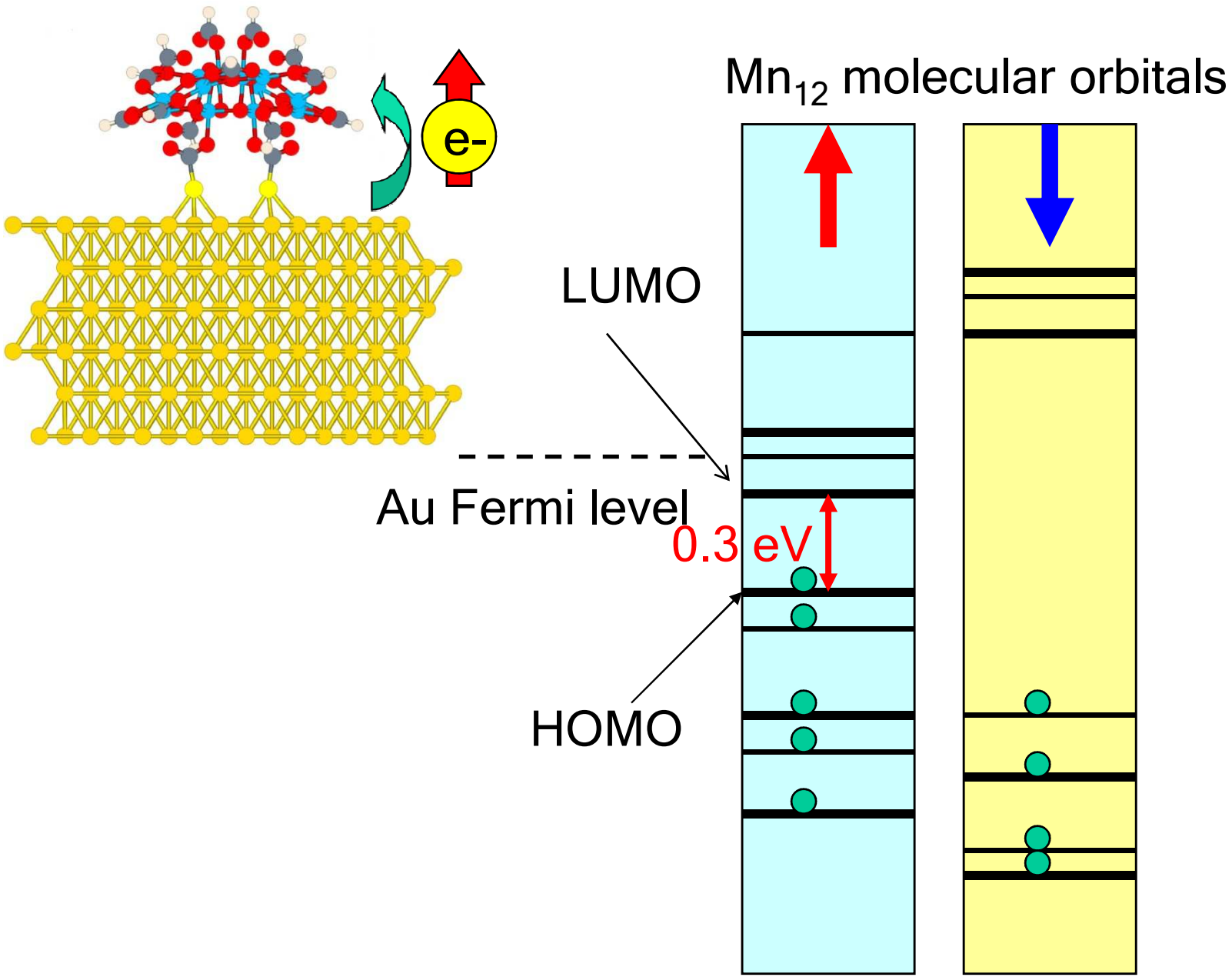
Mn(I): inner, Mn(II), Mn(III): outer

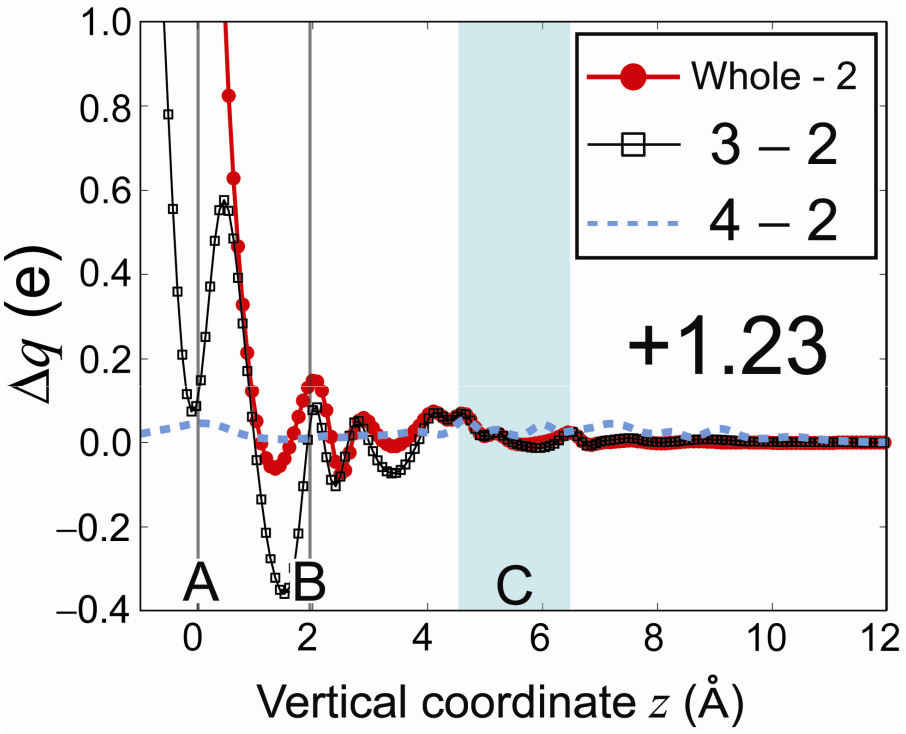


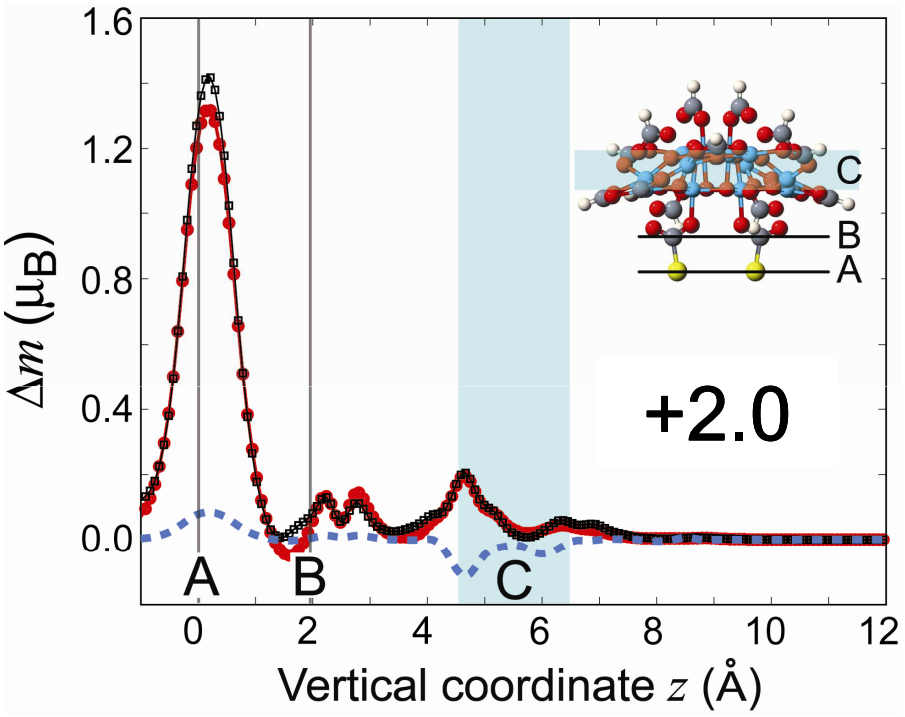
Broadening of orbitals is much less than Coulomb charging energy:

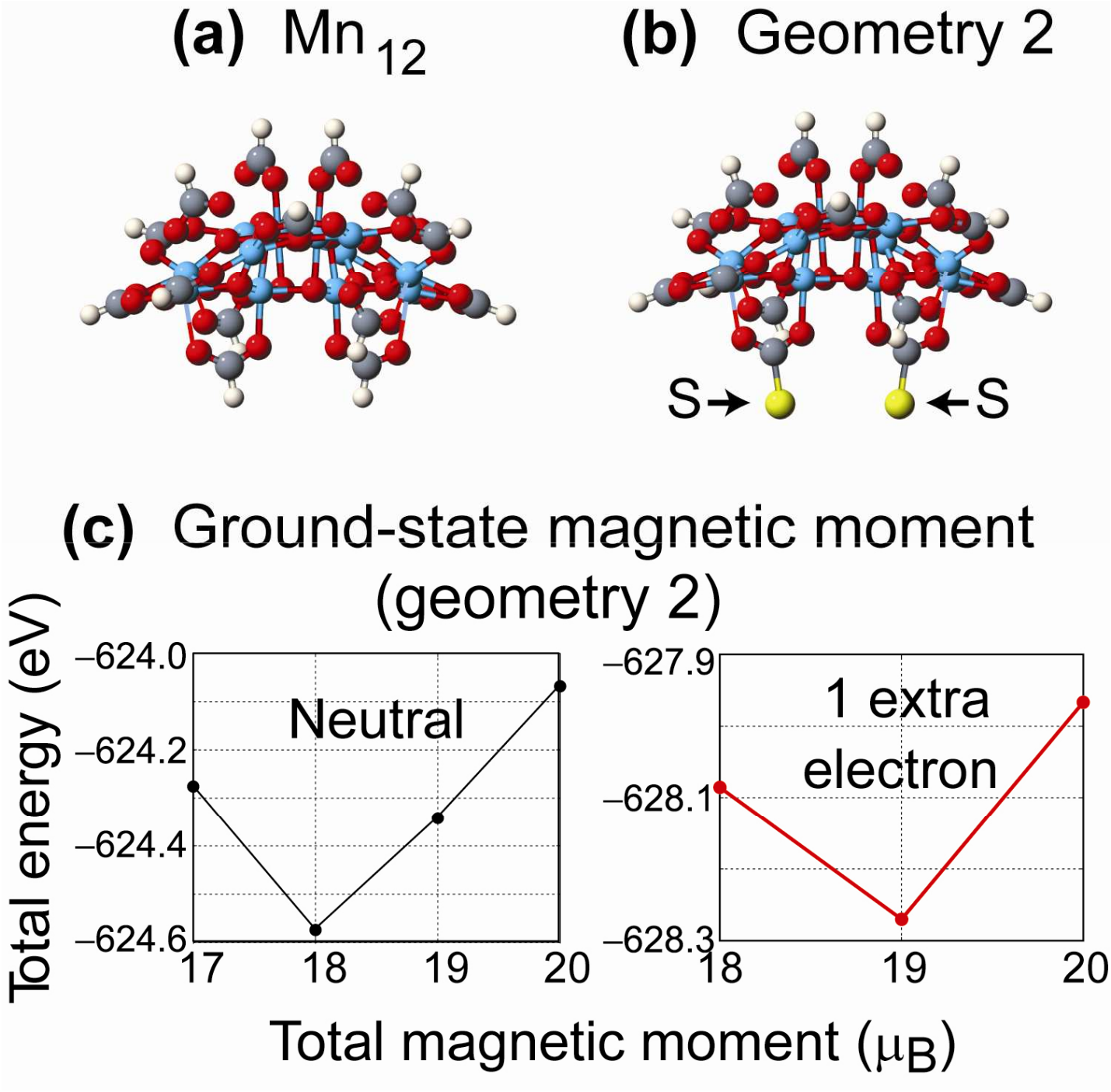
Weak coupling




e-
Mn12 molecular orbitals
LUMO
Au Fermi level
0.3 eV
HOMO


Whole - 2
3 – 2
4 – 2
+1.23
A
B
C
Δq (e)
Vertical coordinate z (Å)


+2.0
A
B
C
Δm (μB)
Vertical coordinate z (Å)


(a) Mn12
(b) Geometry 2
S
S
(c) Ground-state magnetic moment (geometry 2)
Total energy (eV)
–624.0
–624.2
–624.4
–624.6
Neutral
17
18
19
20
–627.9
–628.1
–628.3
1 extra electron
18
19
20
Total magnetic moment (μB)