First-principles study of electronic transport through the single-molecule magnet Mn_{12}

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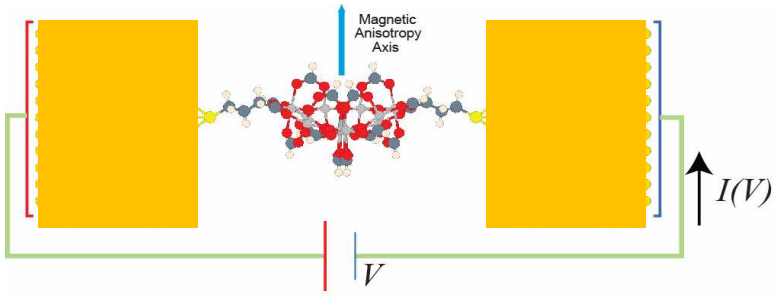


Salvador Barraza-Lopez (former postdoc, now at Georgia Tech)

Jaime Ferrer (Oviedo, Spain)

Victor Garcia-Suarez (Lancaster, UK)

Supported by NSF and Jeffress Memorial Trust Fund

NCSA clusters, Virginia Tech clusters

NCSA

VirginiaTech
Invent the Future

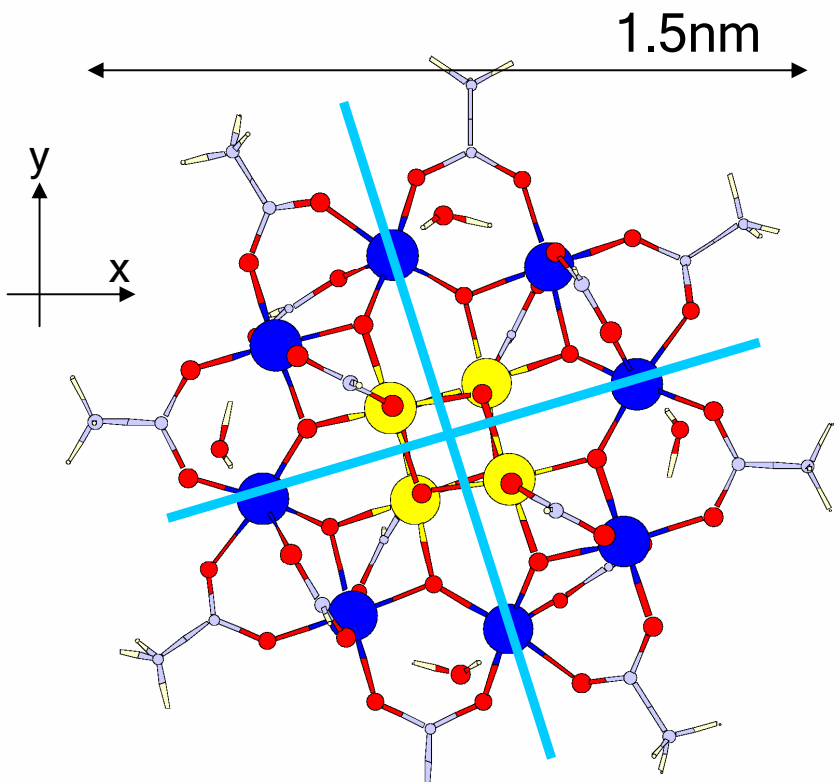
Outline

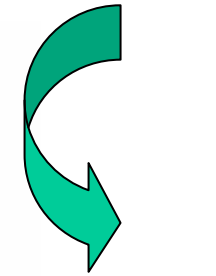
- Structure and properties of single-molecule magnet (SMM) Mn_{12}
- Motivation
- Model and method for transport calculations
- Spin filtering effect
- Dependence of charge distribution and magnetic anisotropy on local environments
- Locally charged vs free-electron added Mn_{12}
- Conclusion

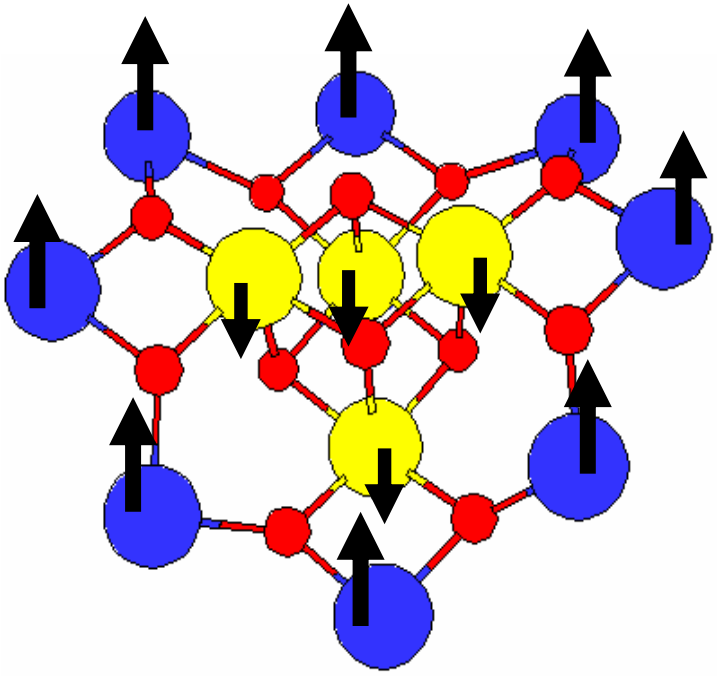
Mn12-acetate

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

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







Mn^{4+}

Mn^{3+}

O

- 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: $S = 8 \times 2 - 4 \times 3/2 = 10$

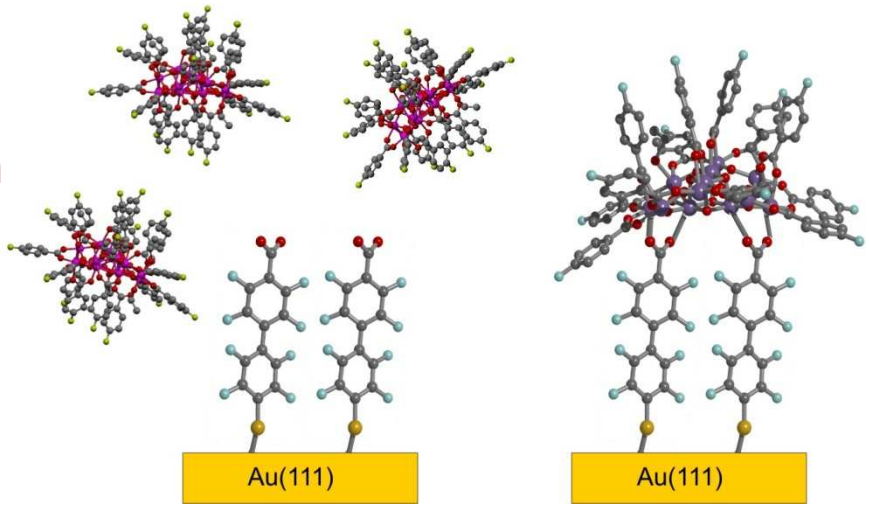
- Magnetic anisotropy barrier = 65 K [A.L. Barra et al., PRB 56, 8192 (1997); S. Hill et al., PRL 80, 2453 (1998)]

Motivation: device applications

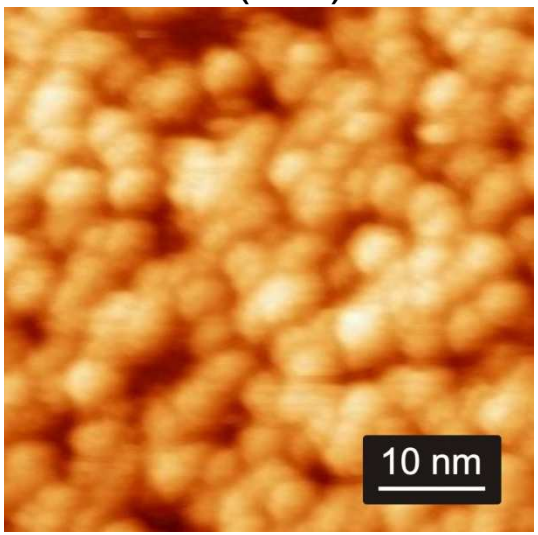
•Deposition of SMMs on surfaces

Zobbi et al, Chem. Comm. (2005); Mannini et al., Nature materials (2009)

•Voss, Fonin, Rudiger, Bergert, Groth (Univ. of Konstanz, Germany): Deposition via ligand exchange reaction allows the reliable and fully reproducible formation of Mn_{12} monolayers.



STM image of intact Mn_{12}-th molecules on functionalized Au(111): S. Voss et al.



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

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

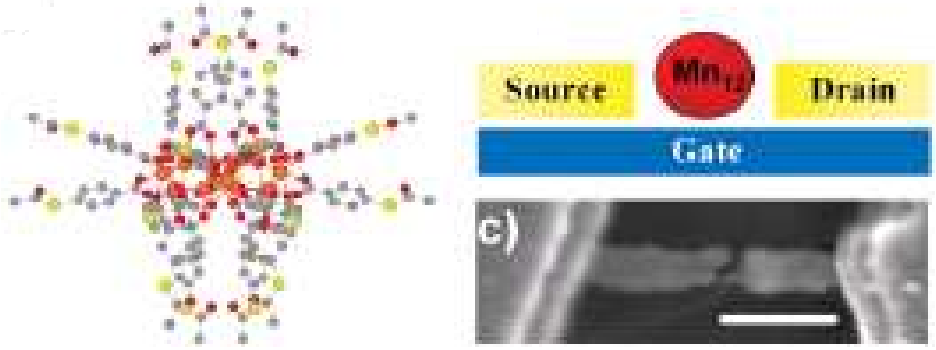
Salman et al., Nano Lett. (2007)

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

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

Motivation: device applications

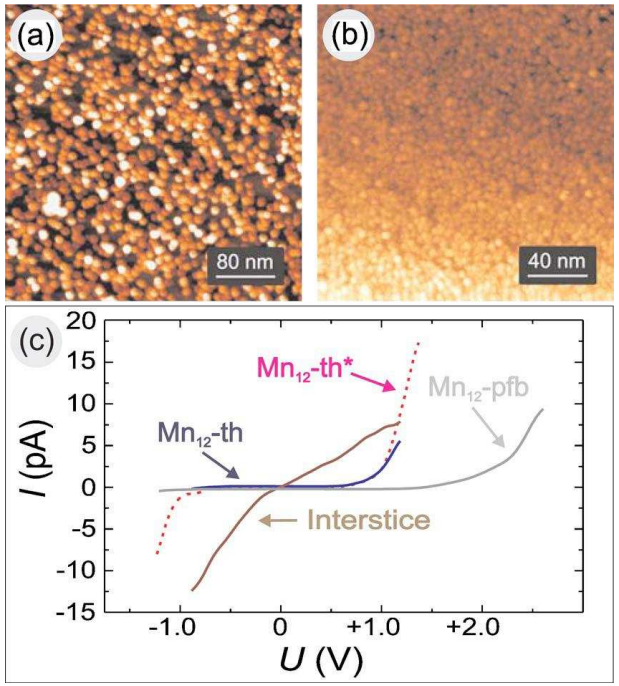
•Electronic transport measurements through SMM Mn_{12}



H. B. Heersche et al., PRL 96, 206801 (2006)

-M. H. Jo et al., Nano Lett 6, 2014 (2006)

-J. J. Henderson et al., J. Appl. Phys. (2007)



S. Voss et al, Appl. Phys. Lett. (2007)

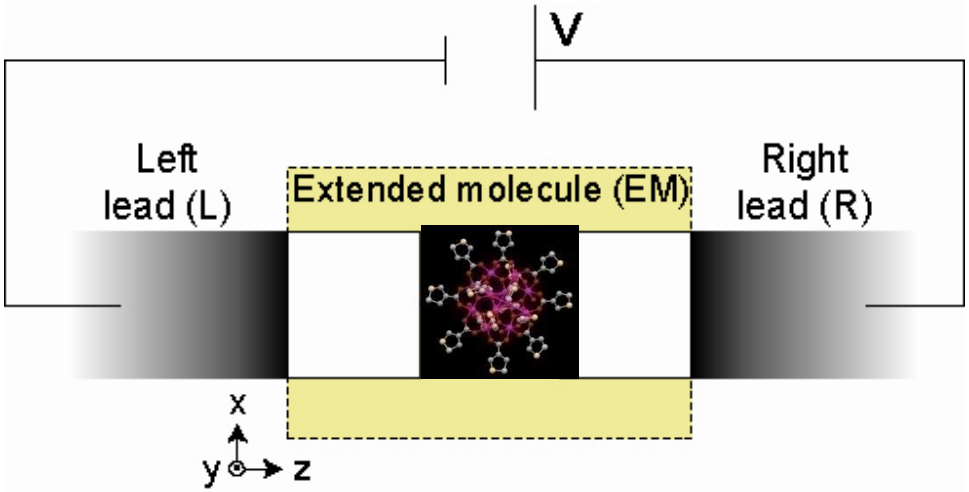
•Theories on transport through SMM:

- G.H. Kim and T.S. Kim, PRL 92, 137203 (2004).
- C. Romeike et al. PRL 96, 196805 (2006)
- Elste and Timm, PRB (2005), PRB (2006)
- Leuenberger and Mucciolo, PRL 97, 126601 (2006).
- L. Michalak et al., arXiv:0812.1058 (2008).

No first-principles calculations on SMMs bridged between electrodes

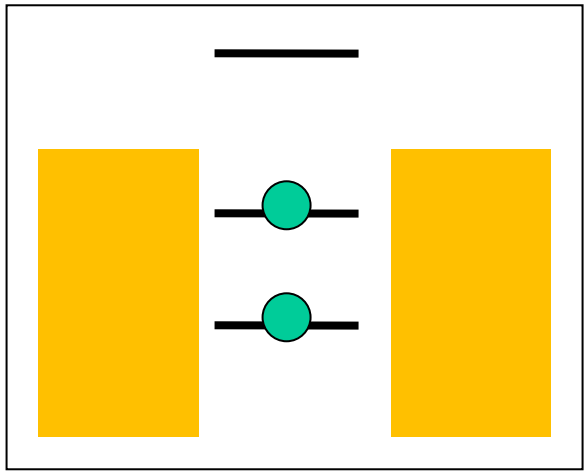
Why electronic transport through Mn12?

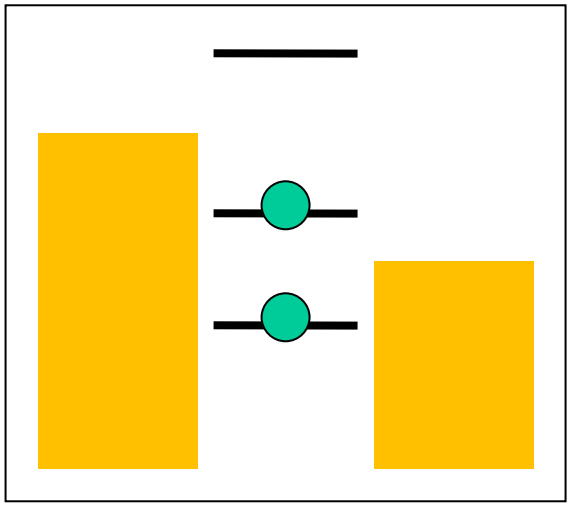
In comparison to other organic molecules



- Magnetic anisotropy barrier substantially changes with extra electrons [KP & M. Pederson, PRB 70, 054414 (2004)]
- Spin filtering effect with low bias [S. Barraza-Lopez, KP, Garcia-Suarez, J. Ferrer, JAP 105, 07E309 (2009).]
- Strong dependence of charge distribution and magnetic anisotropy on molecular geometries and interfaces
- Magnetic quantum tunneling may affect transport

Model & Method: Electron transport





•Model: steady-state algorithms [Rocha et al., PRB 73, 085414 (2006)]

•Assumptions:

(1)Despite a possible transient state, a steady state is eventually achieved.

(2)In non-zero bias voltage, a current can be obtained from the methodology used in ground-state density-functional theory.

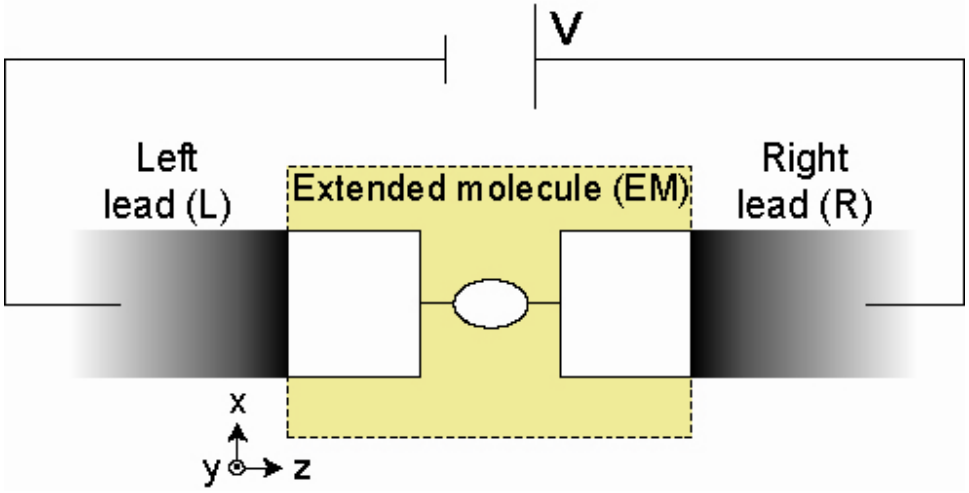
(3)No interactions with phonons

(4)No additional electron correlation effect such as Hubbard-like U term.

•Method: Non-equilibrium Green's function method + Spin polarized density-functional theory

Model & Method: Electron transport

•Semi-infinite leads + scattering region (part of the leads and the molecule, called extended molecule)



•Leads are treated as semi-infinite systems

$$[\varepsilon \boldsymbol{S} - \boldsymbol{H}]\boldsymbol{G}(E) = \boldsymbol{I}$$

Green's function of EM: $G_M(E)=[\varepsilon S_M - H_M - \Sigma_L(E) - \Sigma_R(E)]^{-1}$

Transmission coefficient: $T(E, V)=\Gamma_L(E,V)\, G_M^{\dagger}(E,V)\, \Gamma_R(E,V)\, G_M(E,V)$

$$\text{Current} = (e/h) \int T(E,V) [\, f(E-\mu_L) - f(E-\mu_R)\,]$$

We solve Green's function of EM self-consistently using DFT

Q1: Can NEGF+DFT correctly describe electronic transport of many-body systems?

Q2: If so, then to what extent?

(1) When molecules are strongly coupled to leads:
- Charging energy is smaller than orbital level broadening
- Orbital levels are greatly broadened due to interaction with the leads
- DFT describes the transport quite well (overestimated currents).
- e.g. Au-benzene-Au , Quantum point contact

(2) When molecules are weakly coupled to leads:
- Charging energy is greater than orbital level broadening.
- Coulomb blockade effect
- DFT does not quite work.
- Use many-body model Hamiltonian
- e.g. Au-SMM Mn12-Au

This is not the end of the story!!

- Orbital level broadening
- Transmission coefficient peak positions (with inclusion of U)
- Effect of environmental factors
- Spin filtering effect
- Effect of spin-orbit coupling

Complementary to many-body model Hamiltonian approach even in the weak coupling regime

Focus on zero-bias, without spin-orbit coupling in this talk

Method: Electron transport

•Method: Nonequilibrium Green's function method + DFT

•SIESTA-based quantum transport code, **SMEAGOL** (spin-orbit interaction included) developed by Ferrer and Garcia-Suarez [A. R. Rocha et al., PRB (2006); L. Fernandez-Seivane et al., J. Phys.: Condens. Matt. (2006)] http://www.smeagol.tcd.ie

•PBE GGA for exchange-correlation potential

•Generated pseudopotentials and basis sets for Au, Mn, S, O, C, H.

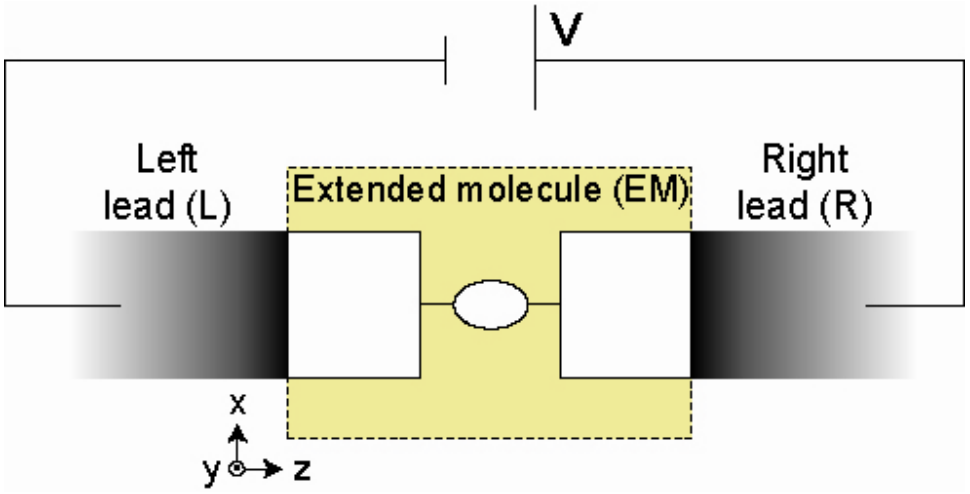
•Tested pseudopotentials and basis sets on bulk Au and isolated Mn_{12} molecules.

•Bulk Au: checked band structure

•Isolated Mn_{12} molecule: obtained 65.3 K for magnetic anisotropy barrier of Mn_{12} using our generated basis sets and pseudopotentials. (c.f. VASP result: 66.7 K) Self-consistent calculations including all orders

Method: Electron transport

•First, compute self-energies of bulk Au leads.



•Leads are treated as semi-infinite systems

Green's function of EM: $G_M(E)=[\varepsilon S_M - H_M - \Sigma_L(E) - \Sigma_R(E)]^{-1}$

Transmission coefficient: $T(E, V)=\Gamma_L(E,V)\, G_M^{\dagger}(E,V)\, \Gamma_R(E,V)\, G_M(E,V)$

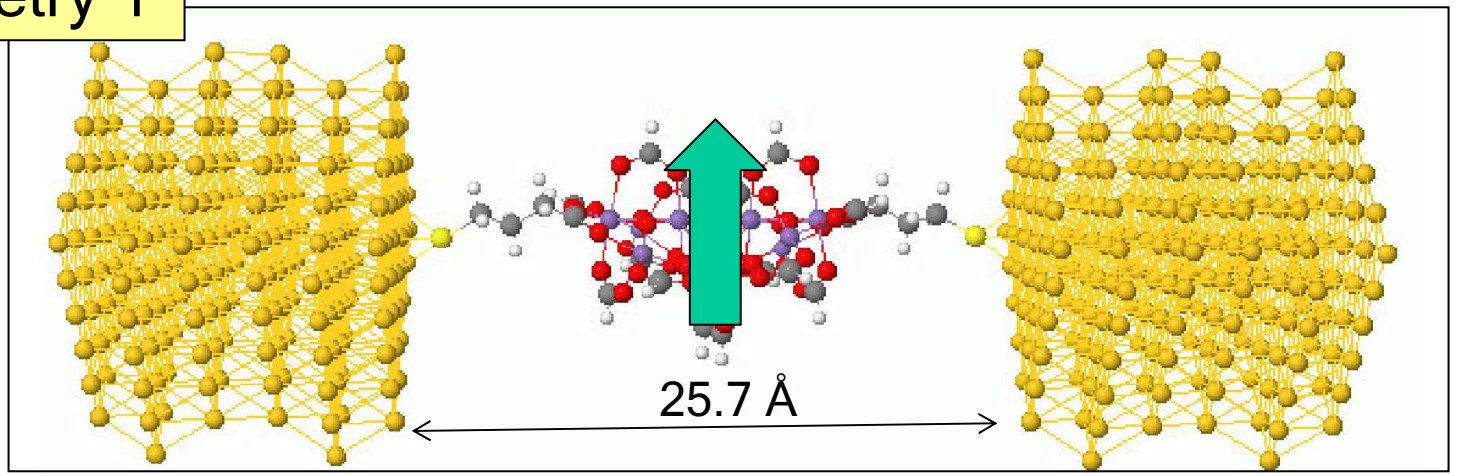
$$\text{Current} = (e/h) \int T(E,V) [\, f(E-\mu_L) - f(E-\mu_R)\,]$$

Extended molecule (EM) geometry

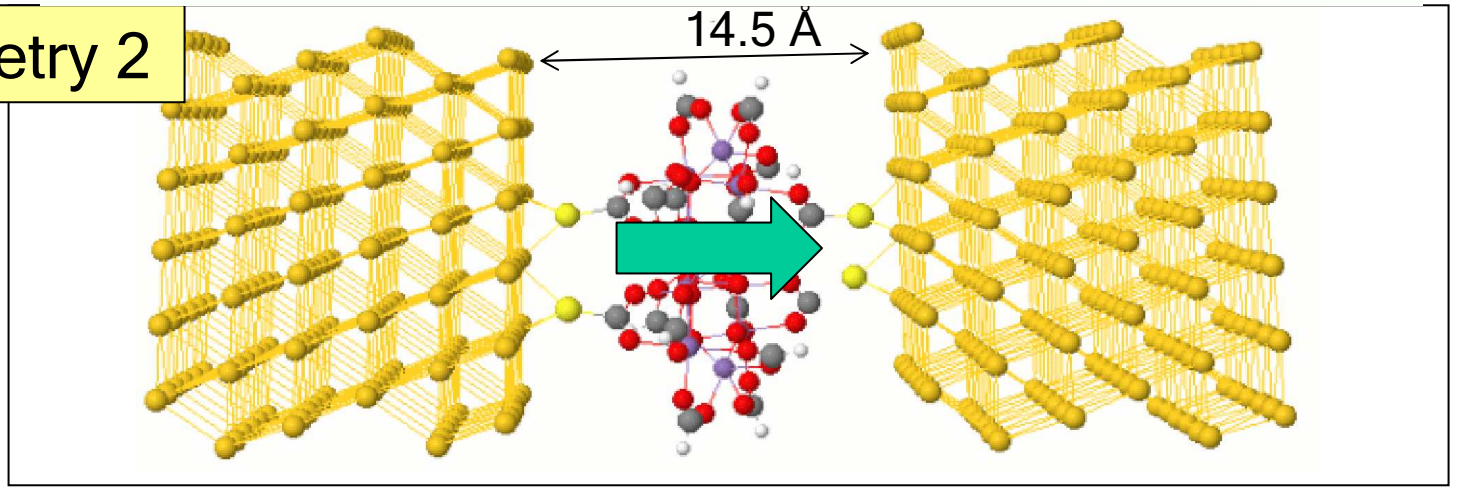
Scattering region

- Two geometries relative to electrodes

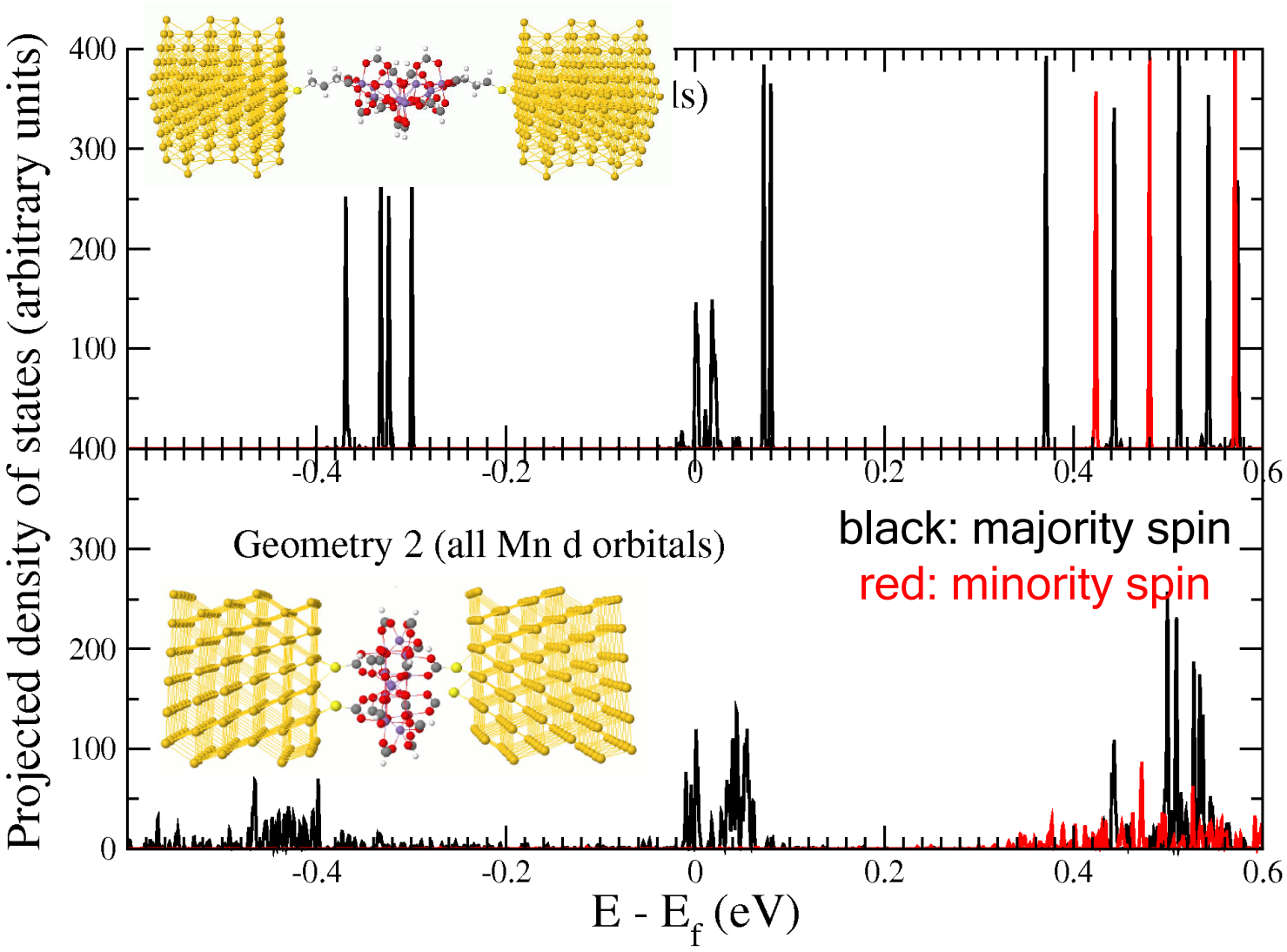
Geometry 1



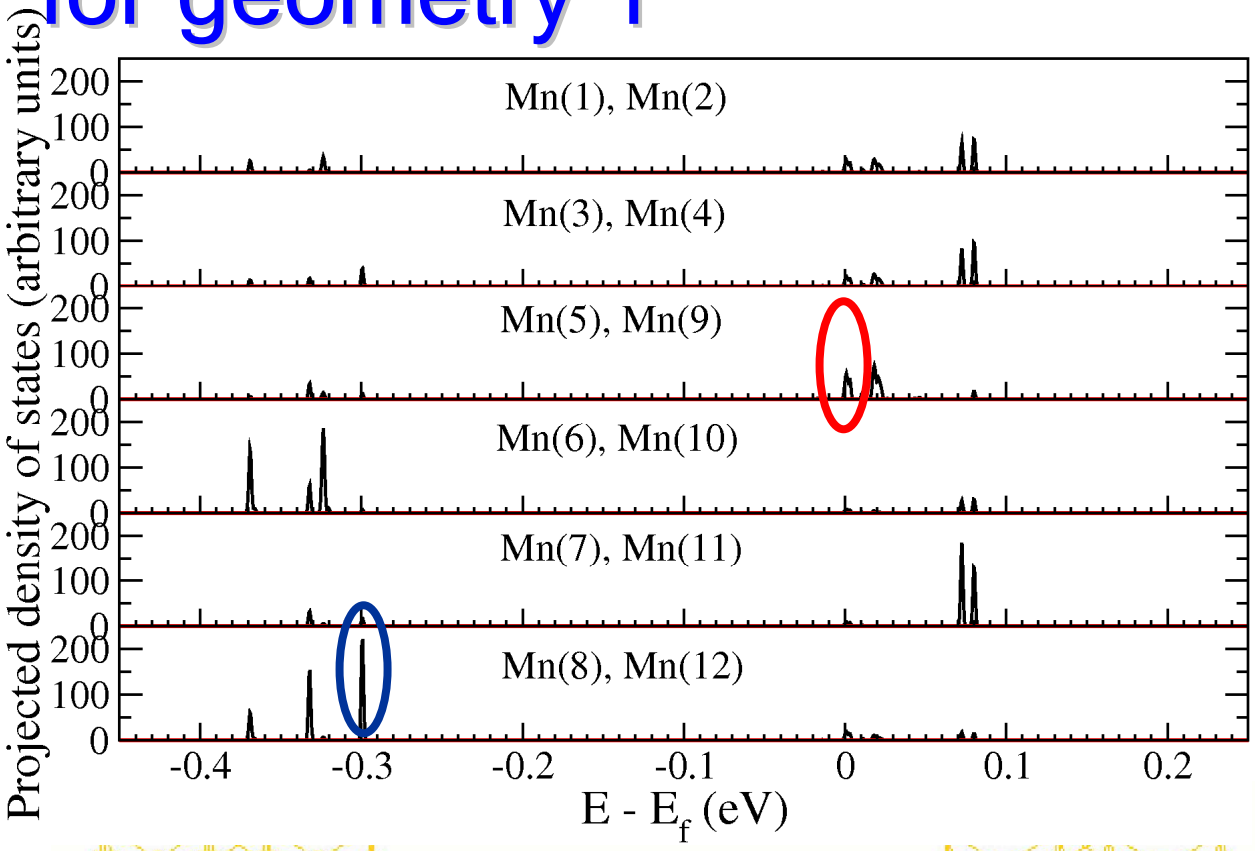
Geometry 2



Density of states projected on Mn d orbitals



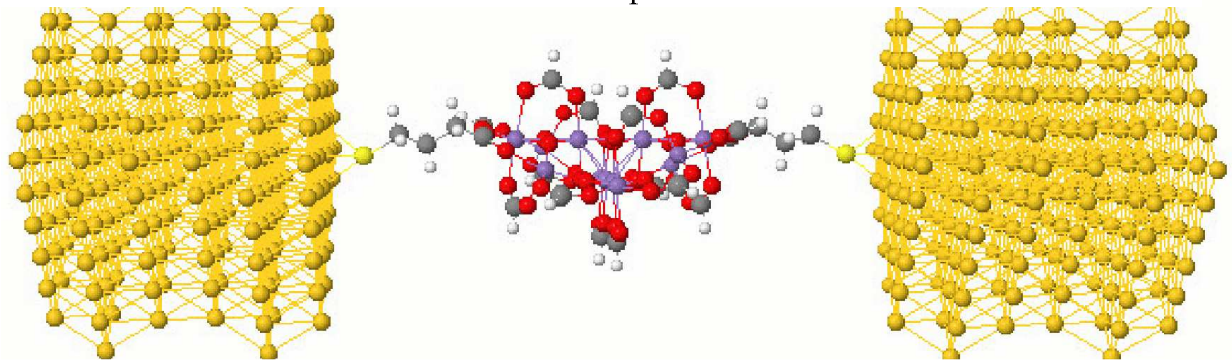
Density of states projected on Mn d orbitals for geometry 1

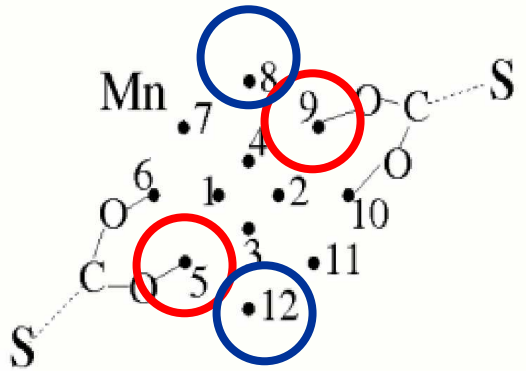


- Minority-spin DOS is zero near Fermi level
- **Charge distribution is mostly over Mn(5) and Mn(9).**

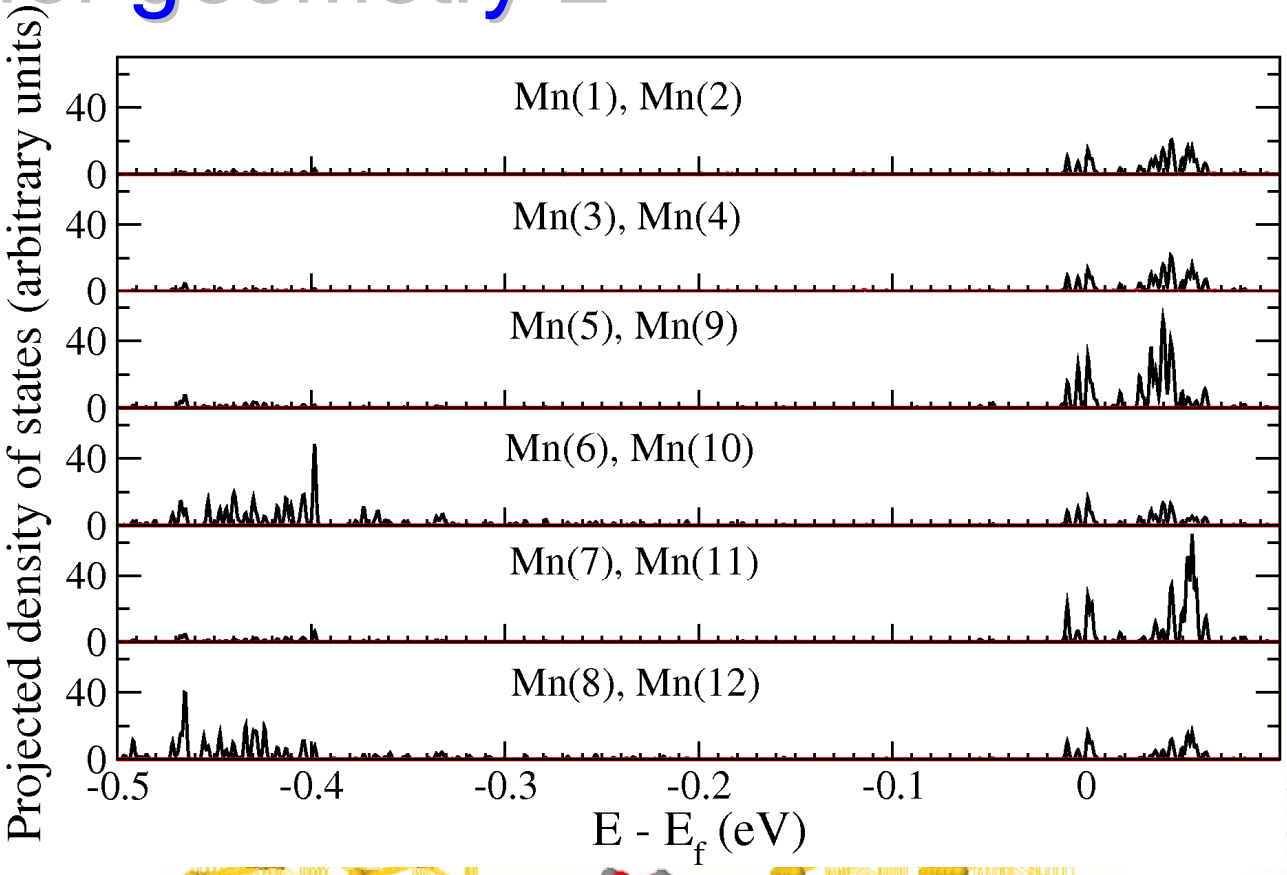
LUMO

HOMO

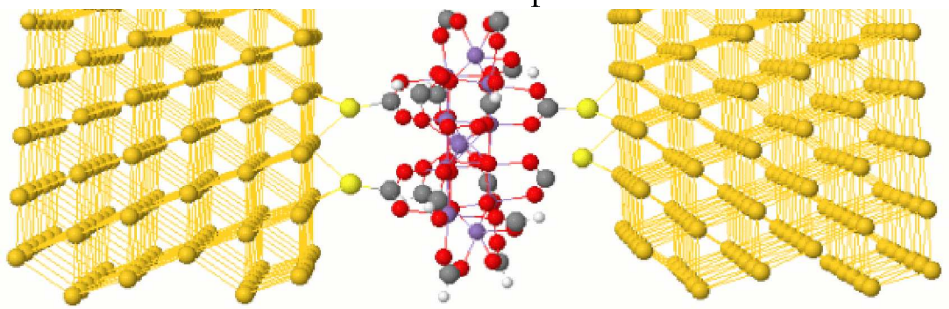


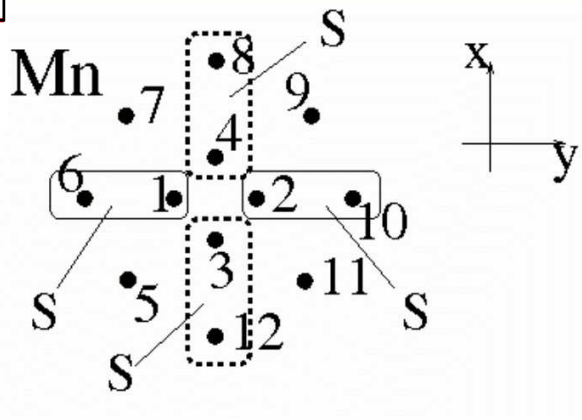


Density of states projected on Mn d orbitals for geometry 2



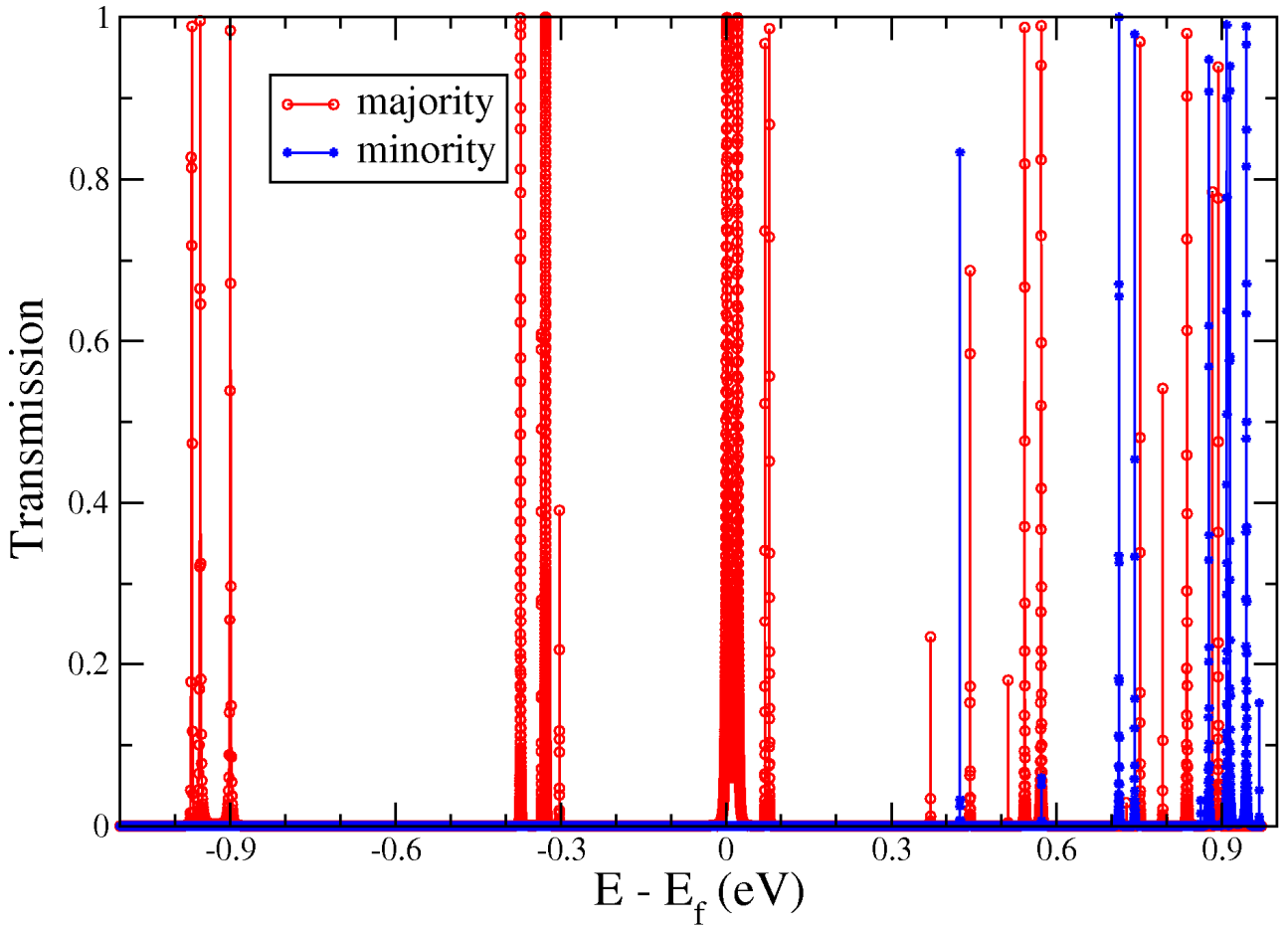
- Minority-spin contribution near Fermi level is zero
- **Charge distribution is over all Mn ions**
- Broadening of orbitals: ~ 0.01 eV



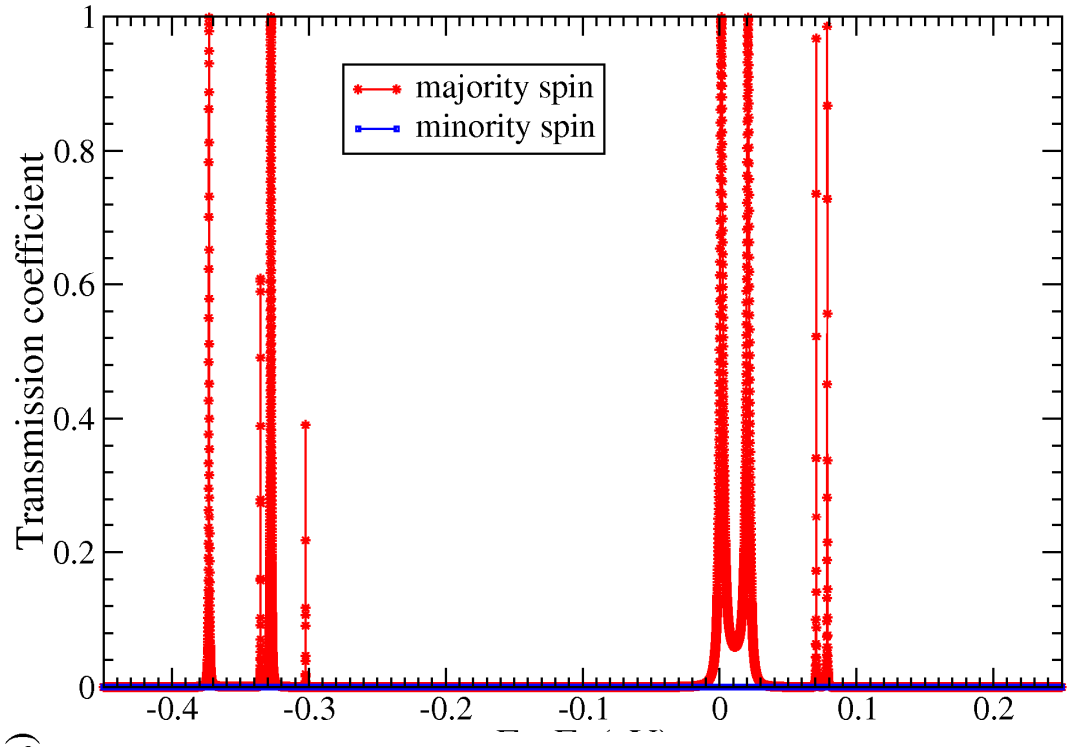


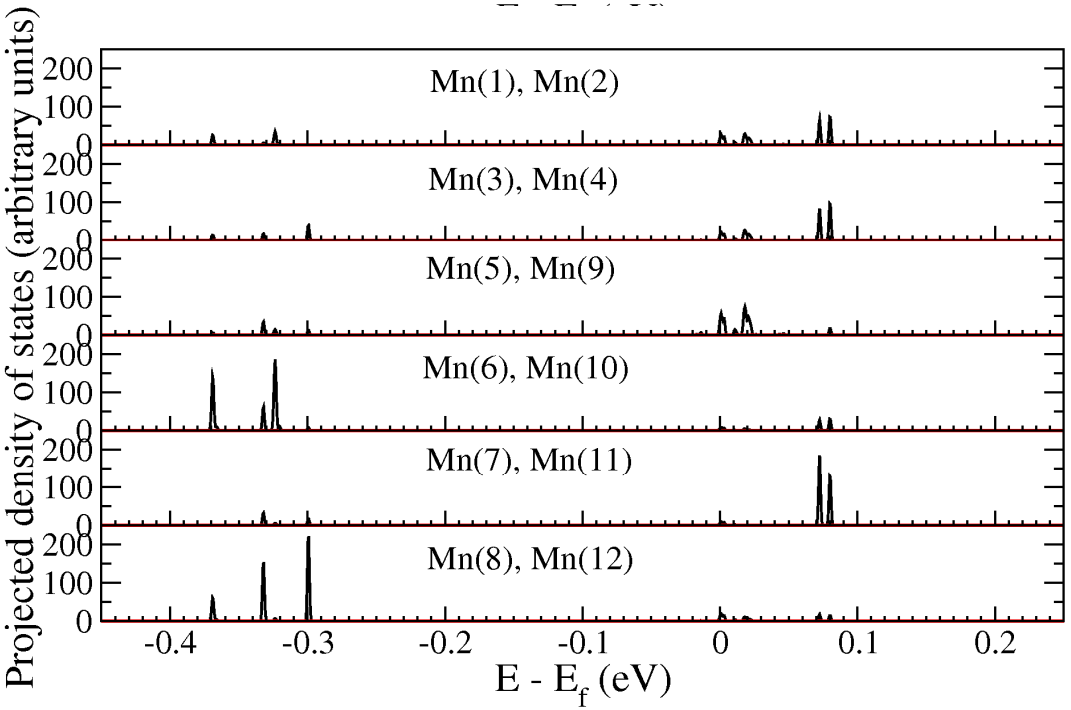
Strong dependence of charge distribution on molecular geometries and interfaces

Transmission coefficient for geometry 1



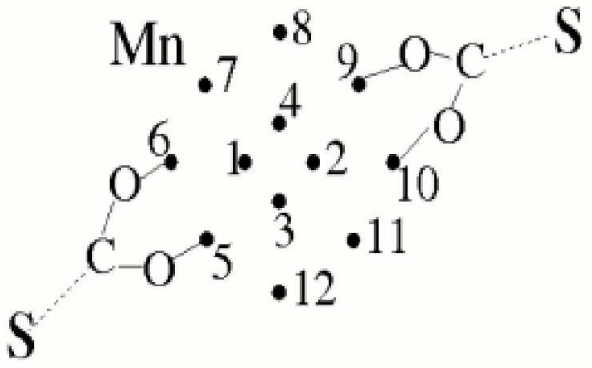
- Very sharp peaks due to weak coupling
- Only majority-spin TC near Fermi level: **spin filtering**
- LUMO is responsible for tunneling near Fermi level



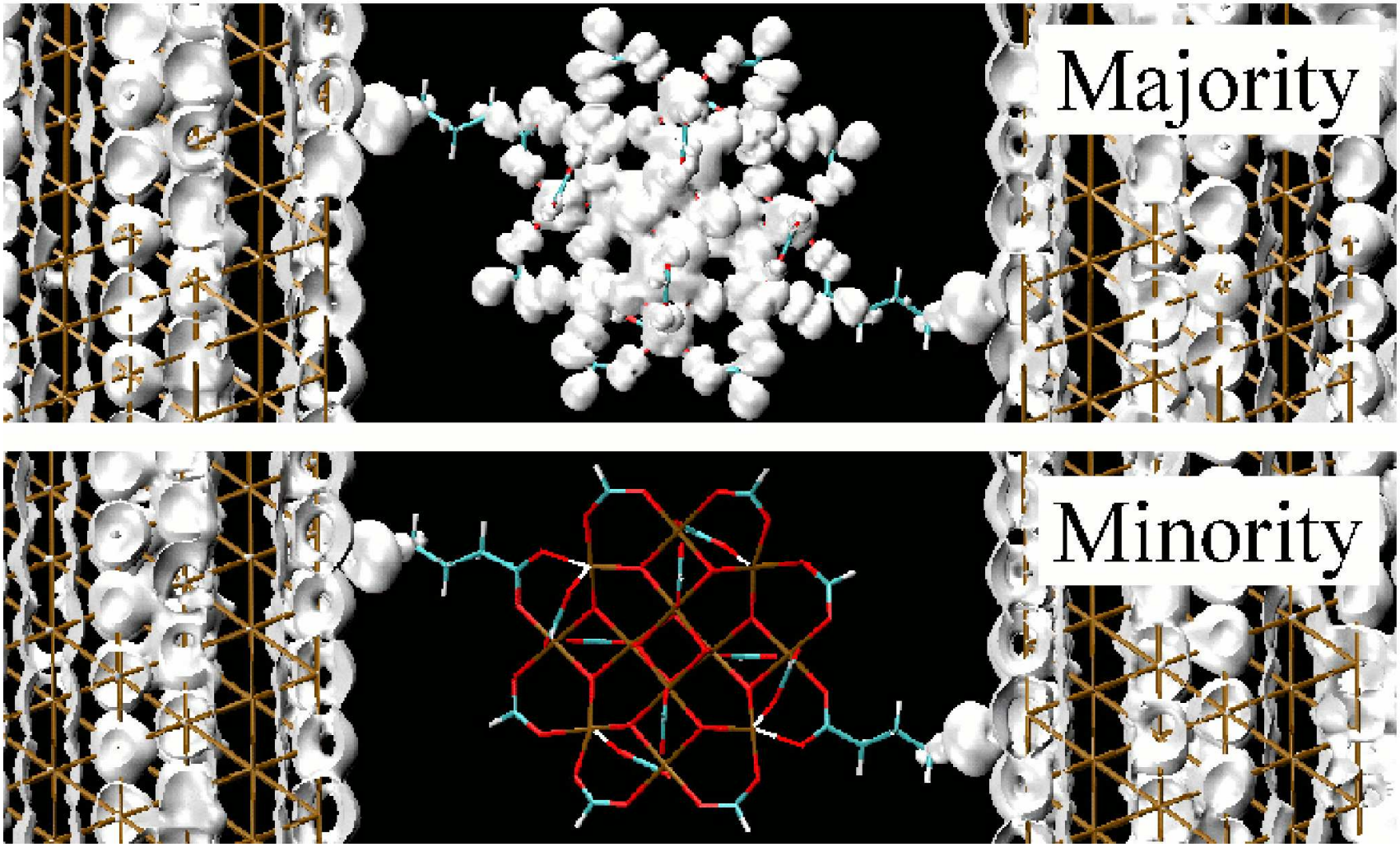


Transmission coefficient & PDOS for geometry 1

- One-to-one mapping between transmission peaks and Mn d orbital levels



Spatially resolved DOS for geometry 1



Integrated over (-0.23, 0.16 eV)

Additional inclusion of electron-electron correlations: DFT+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 correlations: GGA+U on Mn_{12}

- Isolated Mn_{12}: HOMO levels are shifted down. HOMO-LUMO gap greatly increases due to HOMO and LUMO that are from Mn d-orbitals.
- When an extra electron is added, majority-spin orbitals are still well separated from minority-spin orbitals.
- Spin-filtering effect persists with inclusion of additional electron correlations

Electronic level (eV)	U=4 eV * ↑	U=4 eV * ↓	PBE GGA ↑	PBE GGA ↓
Mn_{12} HOMO	-5.80	-7.04	-5.08	-6.45
Mn_{12} LUMO	-4.72	-4.57	-4.84	-4.50
gap	***1.08***		**0.24**	

S. Barraza-Lopez, M. C. Avery, KP, *JAP* 103, 07B907 (2008)

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

Spin-filtering effect in Mn_{12} transport remains robust with different molecular geometries, interfaces, and strong electron correlations.

Magnetic anisotropy change

- Compute magnetic anisotropy barrier (MAB) by including spin-orbit coupling self-consistently
- MAB for neutral Mn_{12}: 66.4 K (VASP), 65.3 K (SIESTA)
- MAB when a free electron is added to Mn_{12}: 56.4 K (VASP), 53 K (SIESTA)
- MAB when a free electron is added to HS-alkane-Mn_{12}-alkane-SH: 38 K (SIESTA)
- MAB significantly depends on local environments.

(Broken symmetry due to the link molecules caused the decrease.)

Locally charged Mn_{12} (by adding electron donors) vs when an extra free electron is added to Mn_{12}

Locally charged Mn_{12}: $[Mn_{12}]^{1-}$

•Experimental realization: $[PPh_4][Mn_{12}]$.

- Eppley et al., JACS 117, 301 (1995) (magnetization); Basler et al., Inorg. Chem. 44, 649 (2005) (inelastic neutron scattering)
- Valence bond sum analysis:

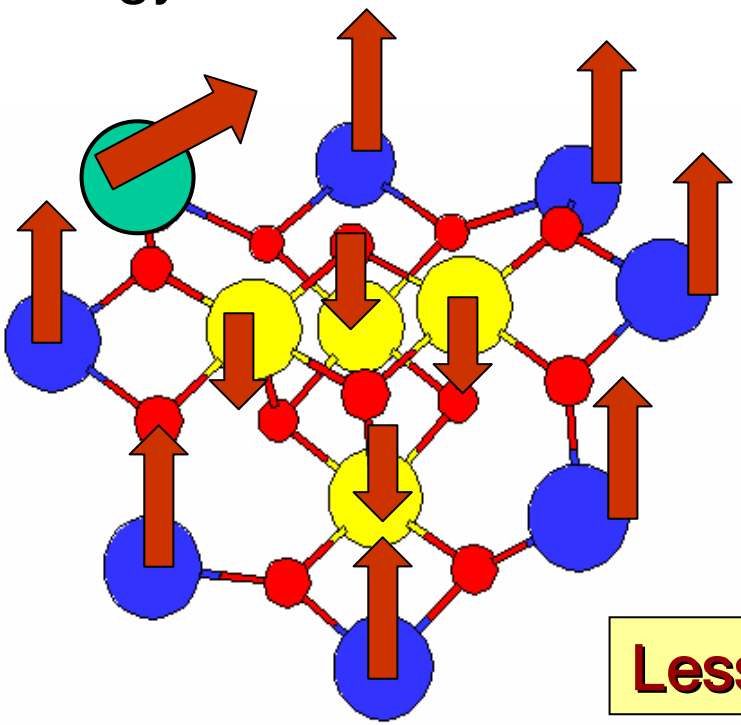
  Only one Mn^{3+} (S=2) → Mn^{2+} (S=5/2)

  [In this sense, locally charged]
- Ground-state spin: S=19/2
- Frequently referred by theoretical transport studies based on model Hamiltonians as S = 10 - 1/2 = 19/2

This looks contradictory to spin-filtering effect.

Locally charged Mn_{12}: $[Mn_{12}]^{1-}$

- Consider neutral $Mn_{11}Fe$ and noncollinear DFT calculations using GGA+U
- Collinear state of 2S=19 [Fe^{3+}(S=5/2)] has 0.1 eV higher energy than collinear state of 2S=21



- Collinear state of 2S=21 has 5.8 meV higher energy than noncollinear state of 2S=18.71 with magnetic moment vector of Fe^{3+}(S=5/2) tilted from z axis

Lesson 1: S=19/2 is not from S= 10 – 1/2

When a free electron is added to Mn_{12}

- The extra free electron will be distributed over several Mn ions instead of being localized at one Mn site
- The distribution depends on the way that the Mn_{12} is attached to the electrodes (geometry 1 vs geometry 2)
- Noncollinear calculations show that collinear state of S=21/2 is the ground state

Lesson 2: Locally charged Mn_{12} does not simulate Mn_{12} in transport.

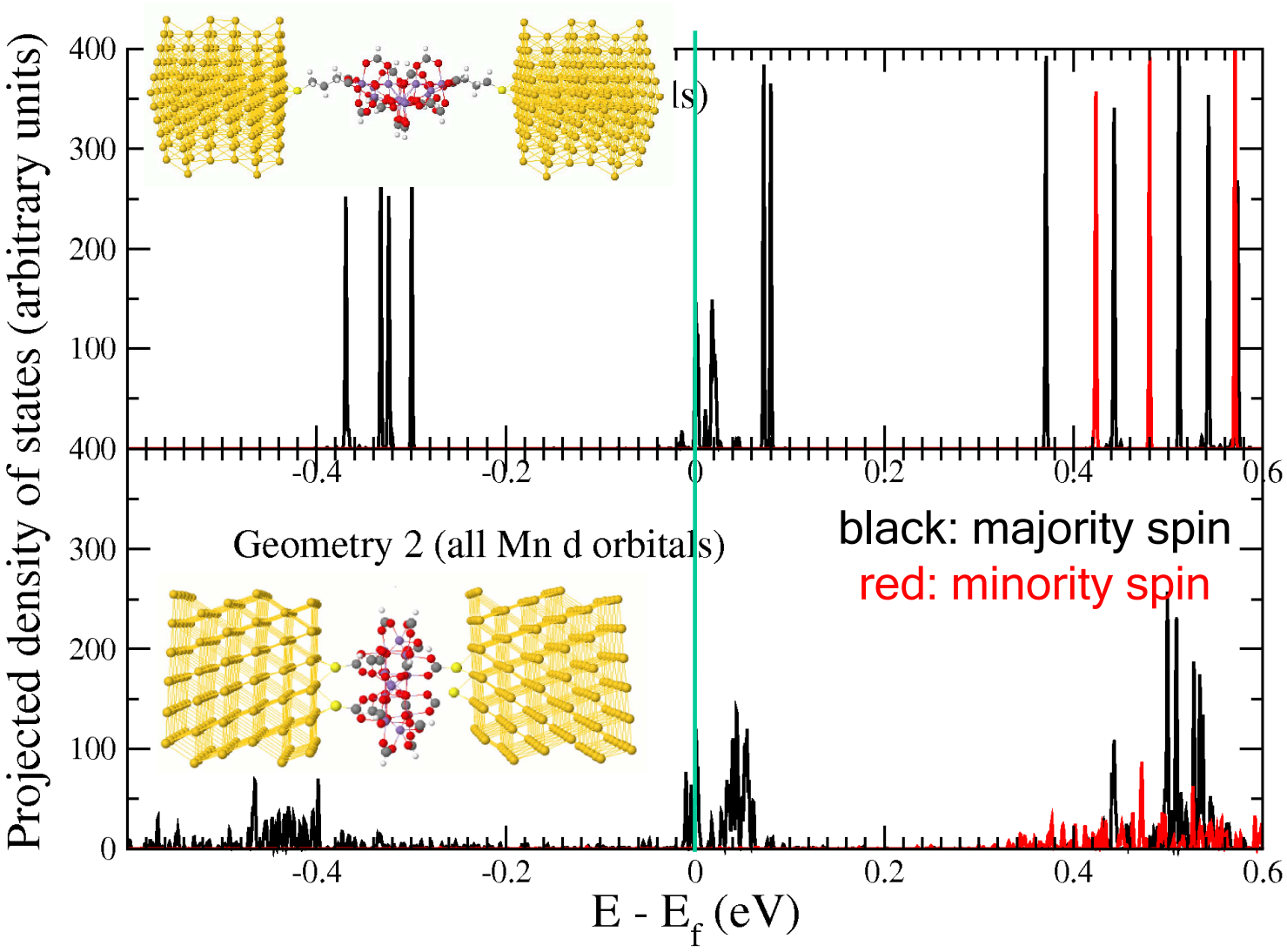
- Spin-filtering effect is compatible with experimental observation of S=19/2.

Summary

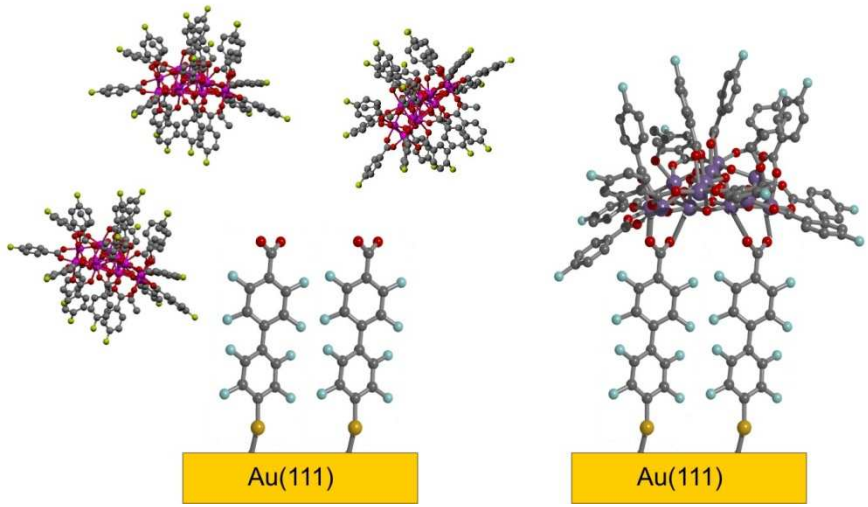
- Modeled electron transport through a Mn_{12} molecule bridged between Au electrodes using NEGF and DFT
- Sharp transmission coefficient peaks due to weak coupling
- LUMO is responsible for the transport near the Fermi level.
- Spin-filtering effect remains robust with molecular geometries, interfaces, and additional electron correlations
- Strong dependence of charge distribution and magnetic anisotropy on molecular geometries and interfaces
- Qualitative difference between locally charged Mn_{12} and Mn_{12} in transport.

Happy 60th Birthday, Eugene!!!!

Density of states projected on Mn d orbitals



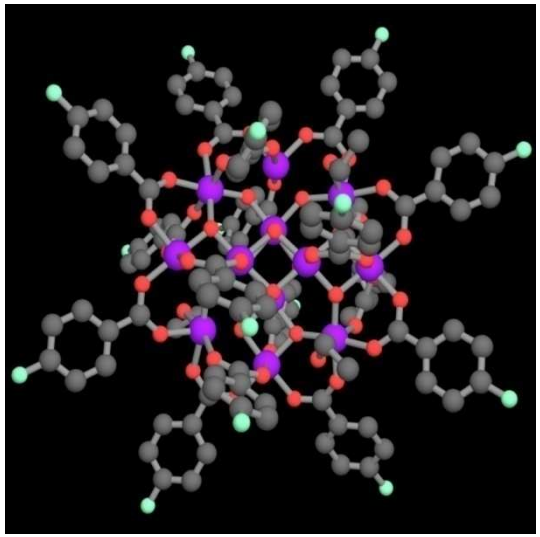
From S. Voss, M. Fonin, U. Rudiger, M. Burgert, and U. Groth



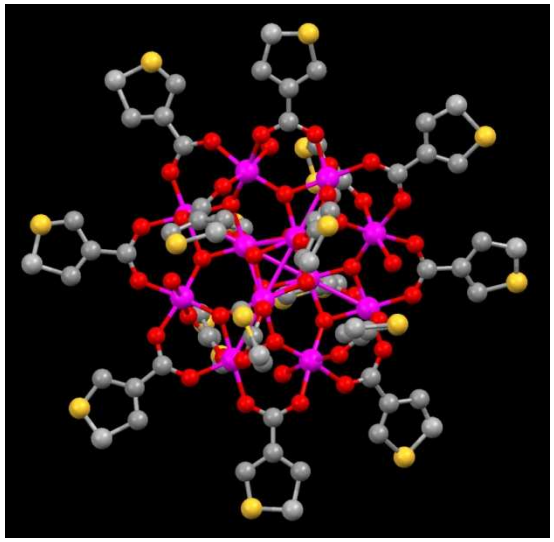
Concept of the ligand exchange reaction:

We found that only the deposition via ligand exchange reaction allows the reliable and fully reproducible formation of Mn12 monolayers.

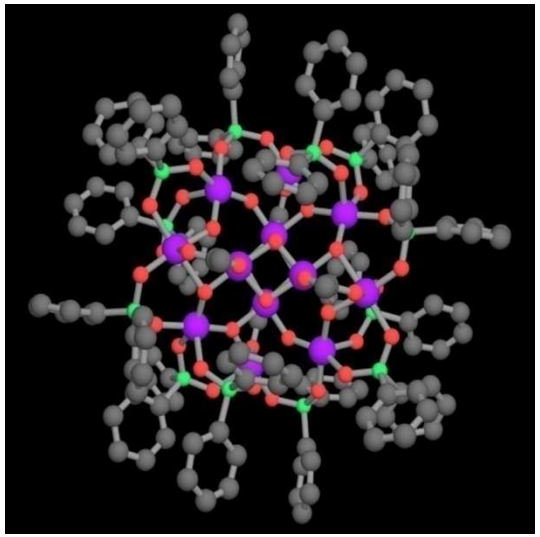
Molecules successfully deposited on functionalized Au(111):



$Mn_{12}O_{12}(O_2CC_6H_4F)_{16}(EtOH)_4$
(Mn12-parafluorobenzoate; Mn12-pfb)



$Mn_{12}O_{12}(O_2CC_4H_3S)_{16}(H_2O)_4$
Mn12-thiophene-carboxylate; Mn12-th



$Mn_{12}O_{12}(O_2PC_{12}H_{10})_{12}(O_2CCH_3)_4(H_2O)_4$
Mn12-phosphinate; Mn12-phn