Advances of Charge transfer mechanism on self-assembled systems

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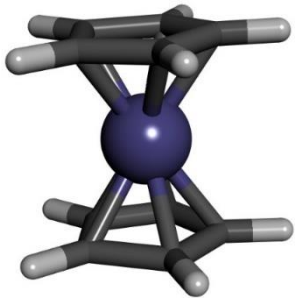
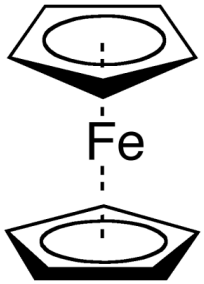
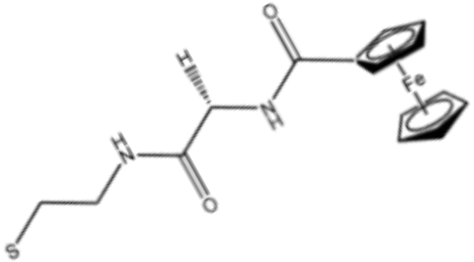
Scientia Vinces

Motivation

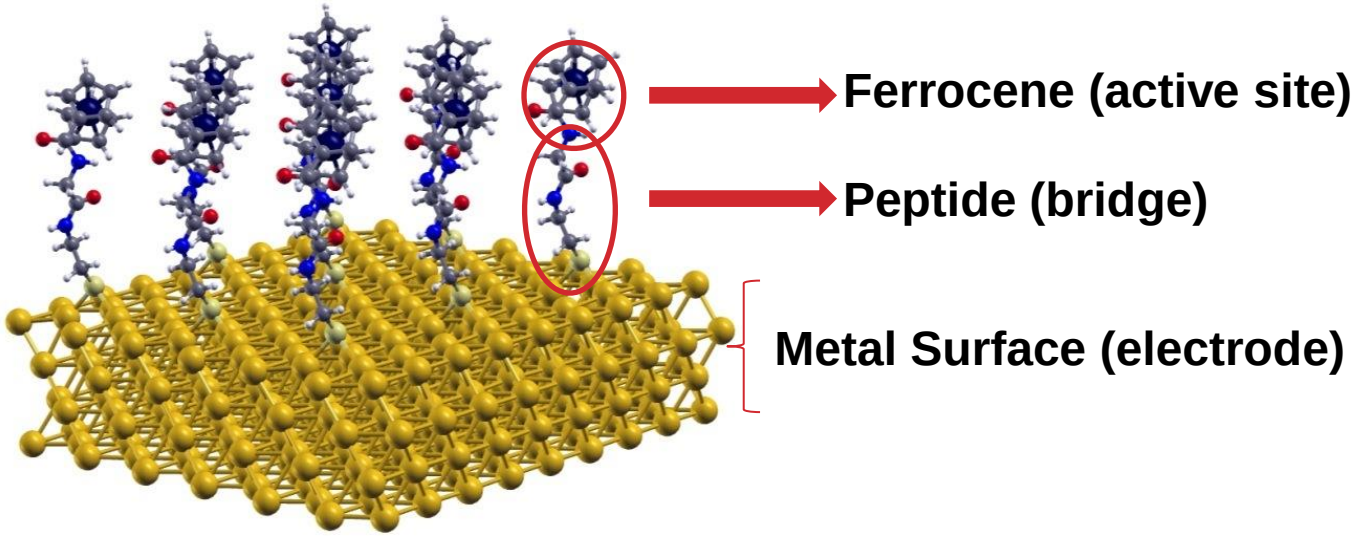
Ferrocene: interesting characteristics per se, but mostly







Ferrocene-terminated self-assembled monolayers (SAMs) offer opportunities to study redox-active processes on metal surfaces



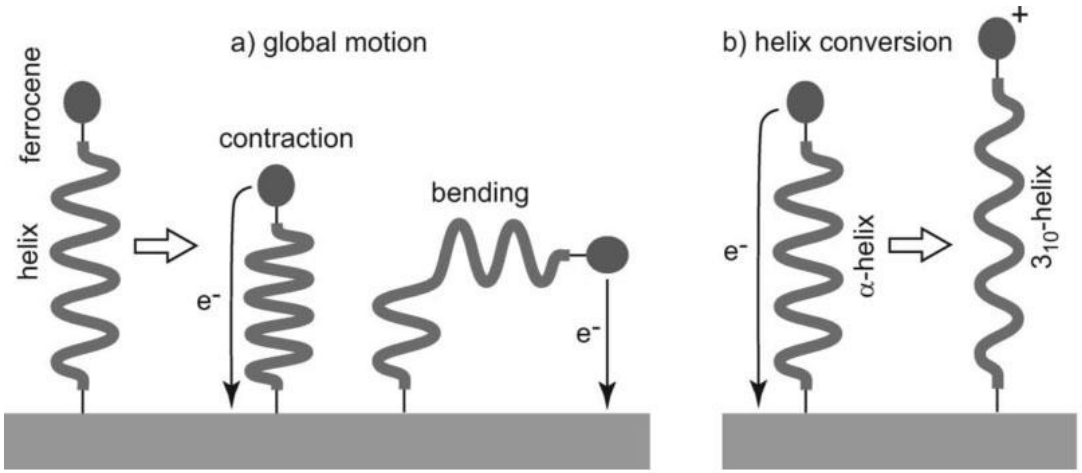
Eckermann, Feld, Shaw,. Meade, *Coord. Chem. Rev.* 254, 1769 (2010).

Charge Transfer Mechanism

Tunneling (Marcus theory), which can involve different mechanisms

vs

Hopping, which directly involves the electronic orbitals of the bridge



Takeda, Morita, Kimura *J. Phys. Chem. B* 112, 12840 (2008). .

Chem Soc Rev

REVIEW ARTICLE

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Electron transfer in peptides

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Afzal Shah,*[abc] Bimalendu Adhikari,[ab] Sanela Martic,[d] Azeema Munir,[c] Suniya Shahzad,[c] Khurshid Ahmad[c] and Heinz-Bernhard Kraatz*[ab]

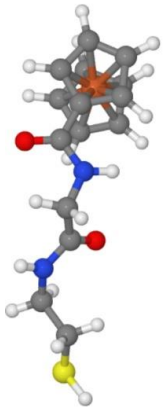
*"**Tunneling** is a coherent ET process as the bridge levels are not occupied due to the high excitation gap between the donor states and bridge states…"*

*"In a **hopping** mechanism, the peptide bridge not only electronically links the electron donor and acceptor but also involves its amino acids in oxidation and reduction thus offering relay stations/ stepping stones for the transport of electrons."*

Here: theoretical study Fc-Gly-CSA/Au

increasing model complexity

Fc-Gly-CSA



thick SAM **solvent effects**

THEORETICAL DETAILS

- Quantum ESPRESSO suit of codes[1].
- KS-DFT[2].
- GGA-PBE[3] exchange correlation functional.
- Vanderbilt ultrasoft pseudopotentials[4].
  - (we considered 5d electrons as “valence” electrons for Au).
- K points grid (4 x 4 x 1)
- Plane wave kinetic energy cutoff: 28 Ry (280 Ry).
- Atomic relaxation, forces smaller than 0.02 eV/Å.
- Slab approach:
  - 4 layers of gold atoms.
  - 12 atoms per layer, (3 x $2\sqrt{3}$) 2D structure.
  - Supercell: (10.2 x 8.8 x 40.6) $Å^3$.

1: http://www.quantum-espresso.org/
2:W. Kohn and L. Sham, Phys. Rev. 140, 1133 (1965).
3:J. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. 78, 1396 (1997).
4:D. Vanderbilt, Phys. Rev. B, 41, R7892 (1990).

Electronic Structure: Fc-Gly-CSA on Au

DOS : Solid
PDOS Au : shaded
PDOS Molecule (red)

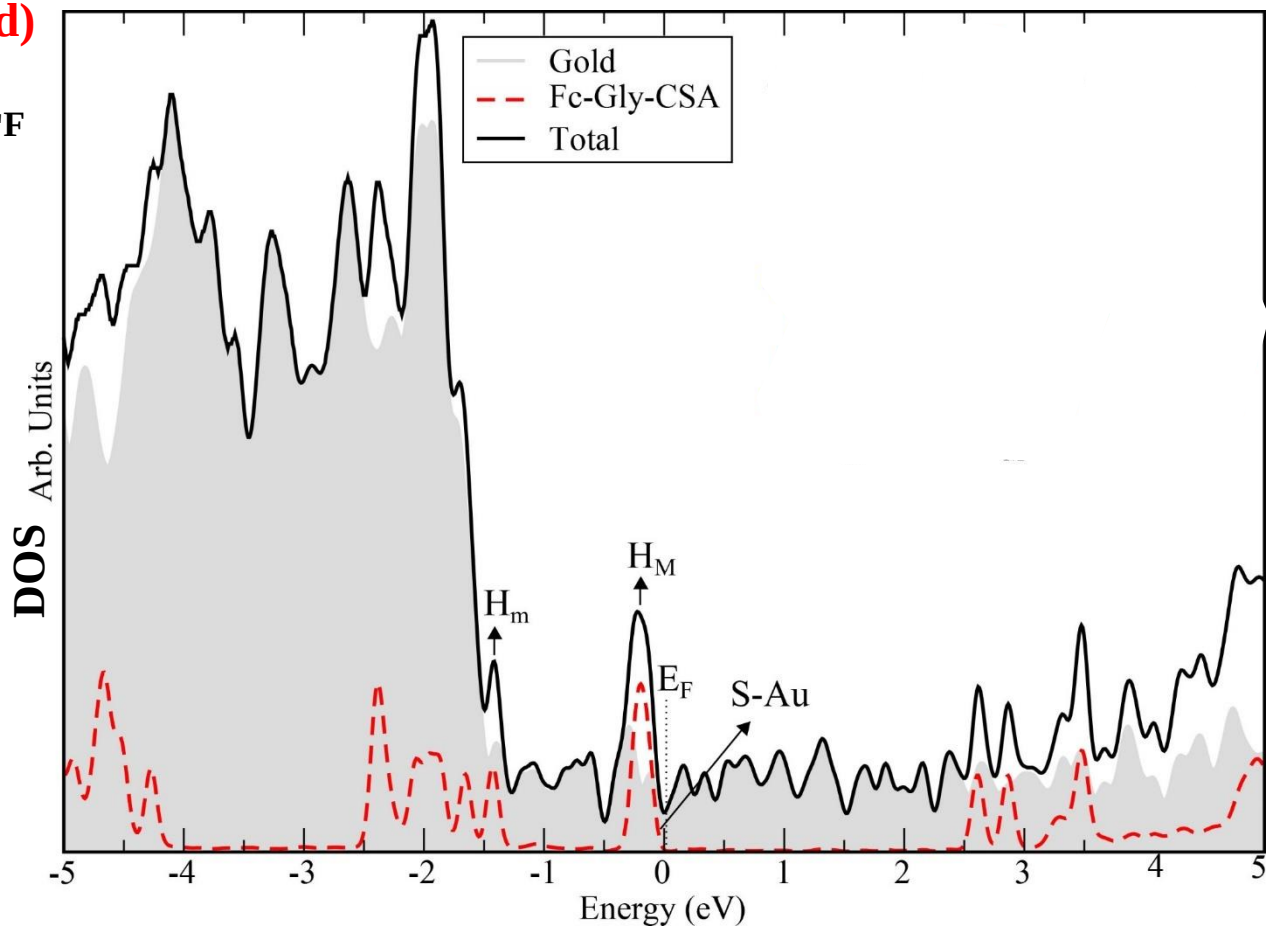
H_m ~1.5 eV below E_F

(bridge)

S-Au closer to E_F

H_M below E_F

(pinned to S-Au)

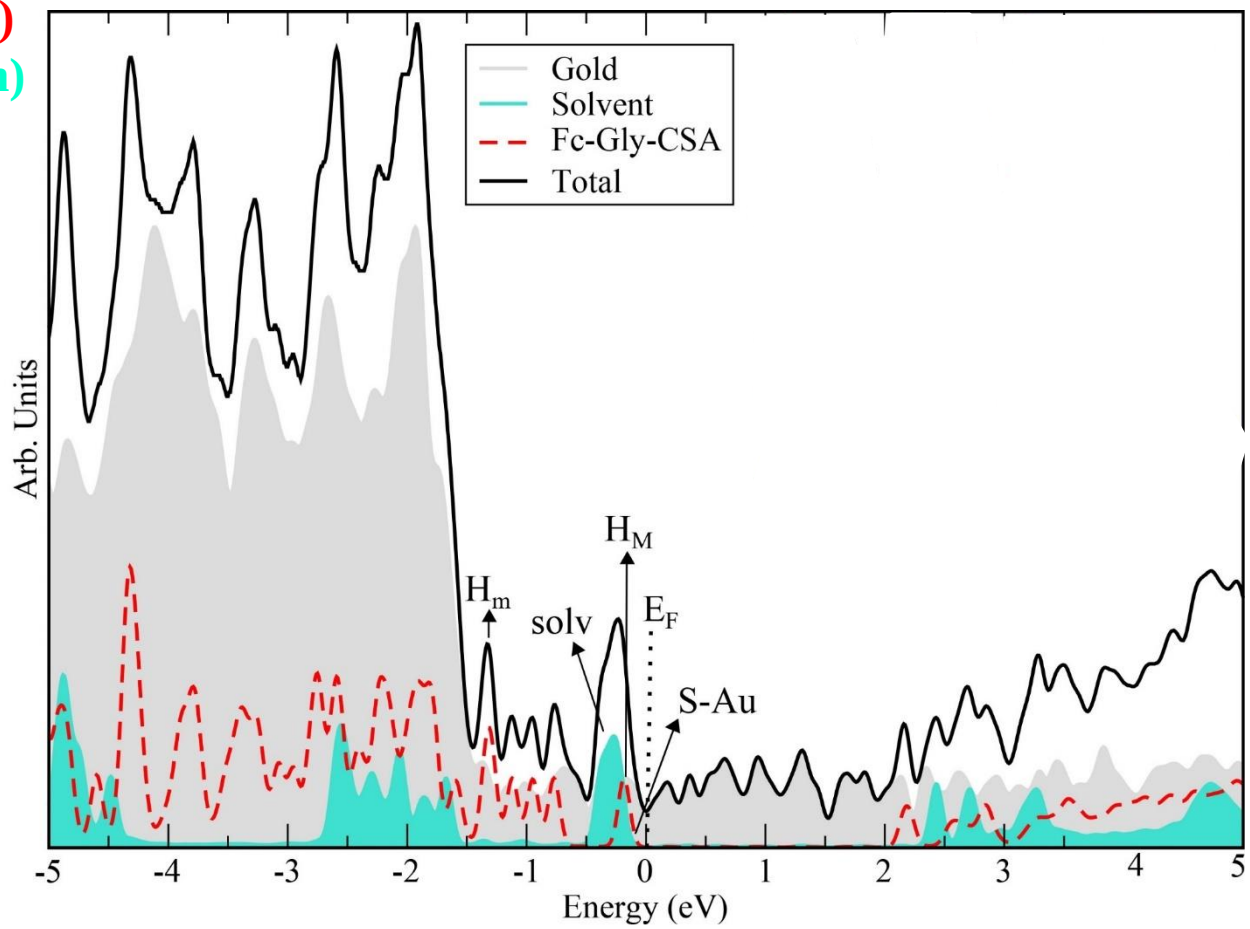


Electronic Structure: Fc-Gly-CSA on Au Solvent

DOS : Solid
PDOS Au : shaded
PDOS Molecule (red)
PDOS Solvent (green)

Molecular levels mostly untouched

Solvent does not couple at relevant energies



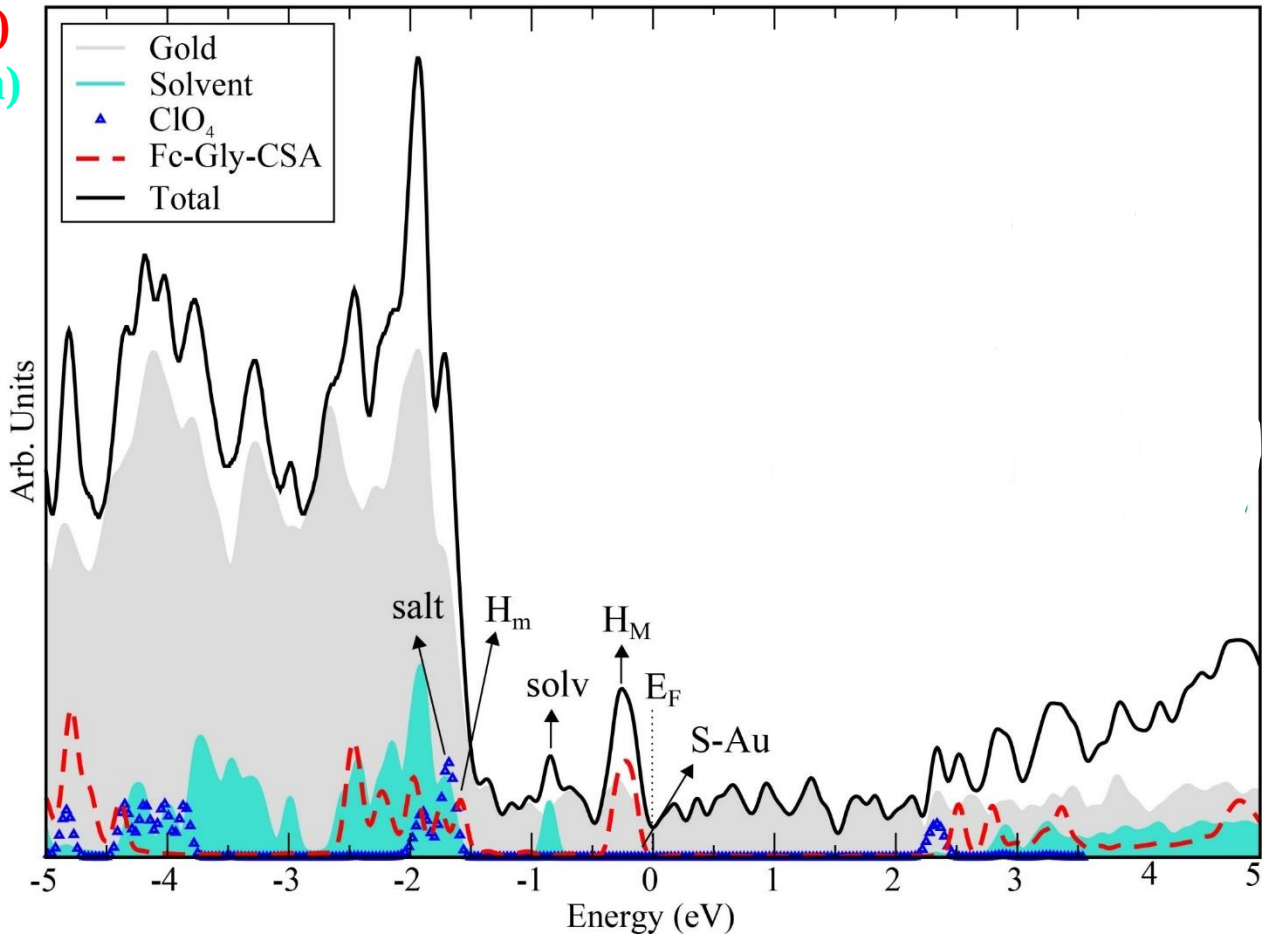
Electronic Structure: Fc-Gly-CSA on Au Solvent+Salt

DOS : Solid
PDOS Au : shaded
PDOS Molecule (red)
PDOS Solvent (green)
PDOS Salt (blue)

Molecular levels mostly untouched

Interaction Solvent+Salt

(detach from E_F)



THE JOURNAL OF PHYSICAL CHEMISTRY C

Article

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Electronic Structure of Self-Assembled Monolayers Modified with Ferrocene on a Gold Surface: Evidence of Electron Tunneling

Filipe C. D. A. Lima,[†] Arrigo Calzolari,[‡] Marília J. Caldas,[†] Rodrigo M. Iost,[§] Frank N. Crespilho,[§] and Helena M. Petrilli*[,†]

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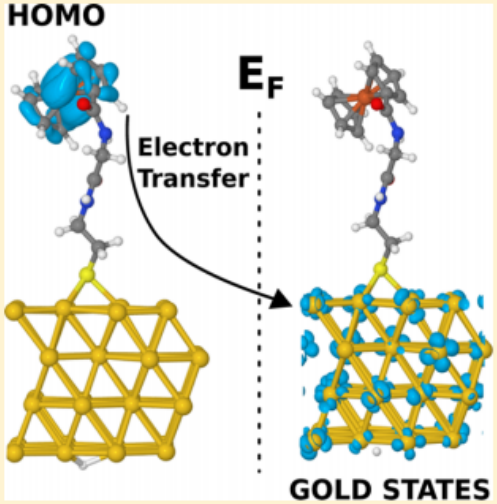
Supporting Information

ABSTRACT: The electron transfer mechanism for the prototypical system ferrocenoyl-glycylcystamine (Fc-Gly-CSA) on Au(111) is investigated within the framework of density functional theory. Different Fc-Gly-CSA/Au systems, including the explicit methanol solvent and sodium perchlorate counterion, are studied. As seen from the partial density of states, electronic contributions close to the Fermi energy are found to derive only from the ferrocene units and gold atoms, while the contributions from electronic states located on the molecular spacers (Gly-CSA) are detected at lower energies, with or without the effects of the environment. These results strongly indicate a direct ferrocene-to-gold tunneling as the electron transfer mechanism across the interface.



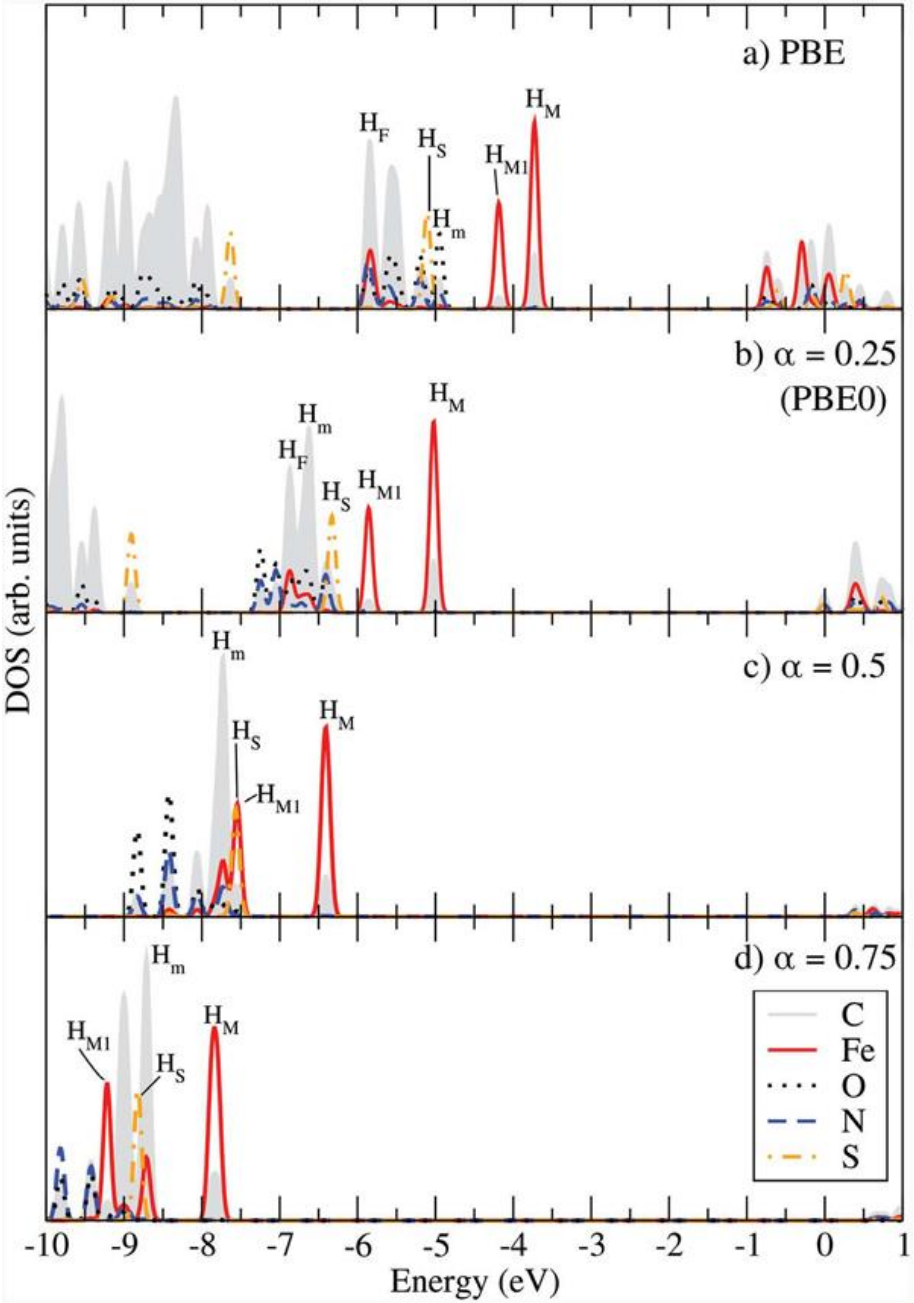
Does this observation is a limitation of the theory level employed?

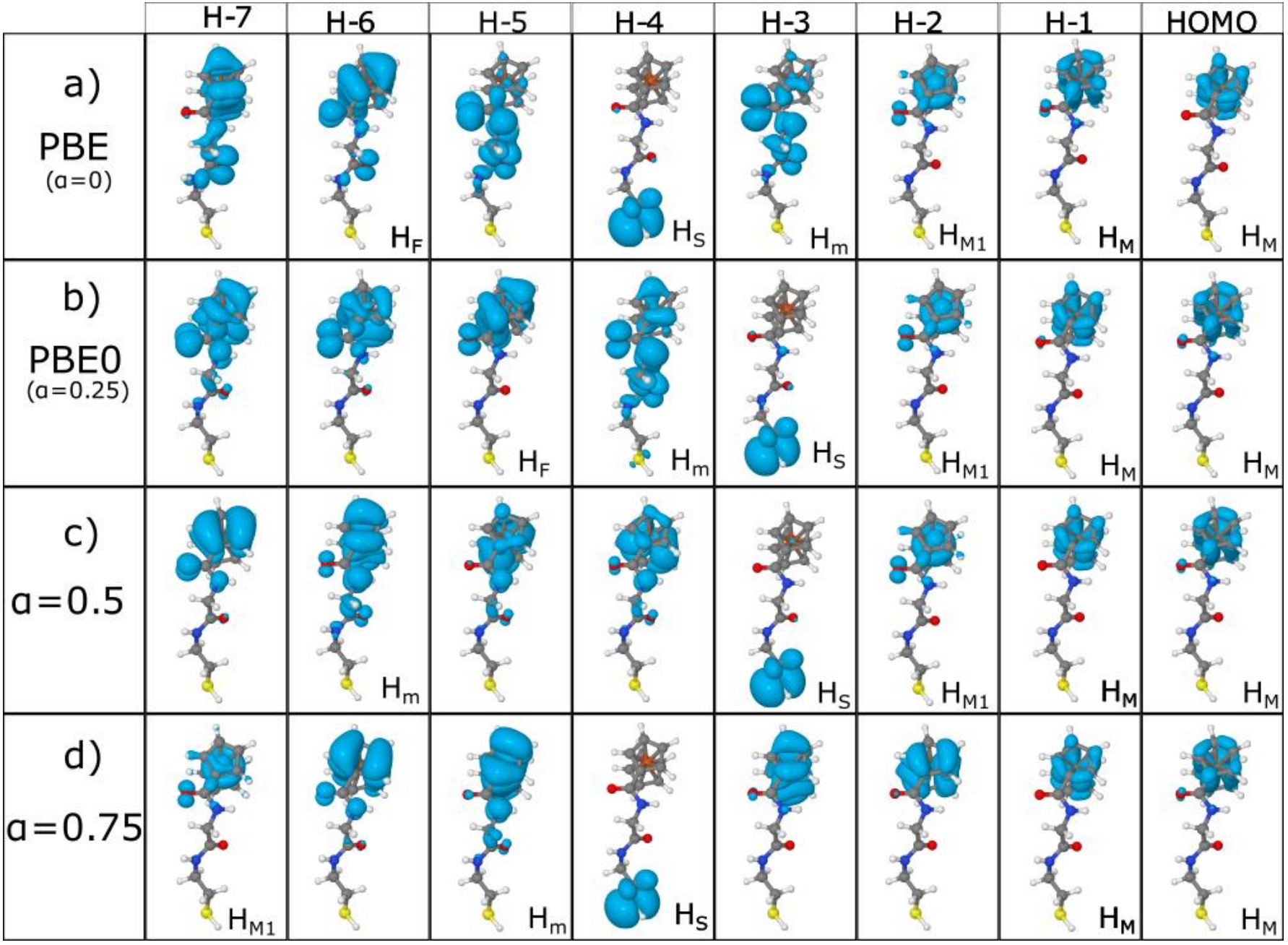
Pure PBE

PBE + 25% of HF

PBE + 50% of HF

PBE + 75% of HF




H-7
H-6
H-5
H-4
H-3
H-2
H-1
HOMO
a)
PBE
(α=0)
b)
PBE0
(α=0.25)
c)
α=0.5
d)
α=0.75
H_F
H_S
H_m
H_M1
H_M

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Robustness of DFT Predictions of the Charge Transfer Mechanism for Self-Assembled Monolayers Modified with Ferrocene on Au(111)

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COMPUTATIONAL DETAILS

- Quantum ESPRESSO suit of codes[1].
- KS-DFT[2].
- GGA-PBE[3] exchange correlation functional.
- GGA-PBE0[3] **exact exchange** !!!!
  - (N-> N^3)

– **Bluegene P:** Plane wave kinetic energy cutoff: 28 Ry (280 Ry).

- 1,939,571 plane waves
- 900 electrons
- Supercell: (10.2 x 8.8 x 40.6) $Å^3$.
- (4x4x1) K-point grid (8 calculations!)

– **Bluegene Q:** Plane wave kinetic energy cutoff: 28 Ry (280 Ry).

- 3,806,893 plane waves
- 1022 electrons
- Supercell: (11 x 10 x 60) $Å^3$.
- (4x4x1) K-point grid (8 calculations!)

1: http://www.quantum-espresso.org/
2:W. Kohn and L. Sham, Phys. Rev. 140, 1133 (1965).
3:J. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. 78, 1396 (1997).
4:D. Vanderbilt, Phys. Rev. B, 41, R7892 (1990).

Conclusions

Clear bonding through S-Au (extended state)

Sizeable energy difference peptide bridge ↔ E_F

State close to E_F always on Ferrocene

For this specific length, we can exclude hopping

Evidences of electronic tunneling with an applied electric field

Lima, Calzolari, Caldas, Iost, Crespilho, Petrilli, *J. Phys. Chem. C* 118, 23111 (**2014**)

Thank you

Grupo Nanomol