2.1 Crystal field symmetries

Consider the three structures shown below. The CF symmetry is indicated.
Sketch qualitatively the energy splitting for the d orbitals.

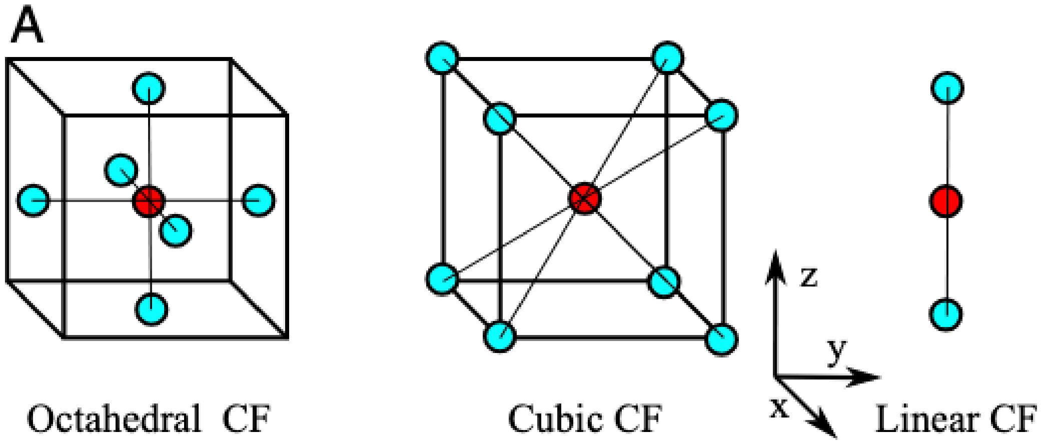


Figure adapted from
https://www.pnas.org/cgi/doi/10.1073/pnas.1922556117

2.1 Crystal field symmetries - Solution

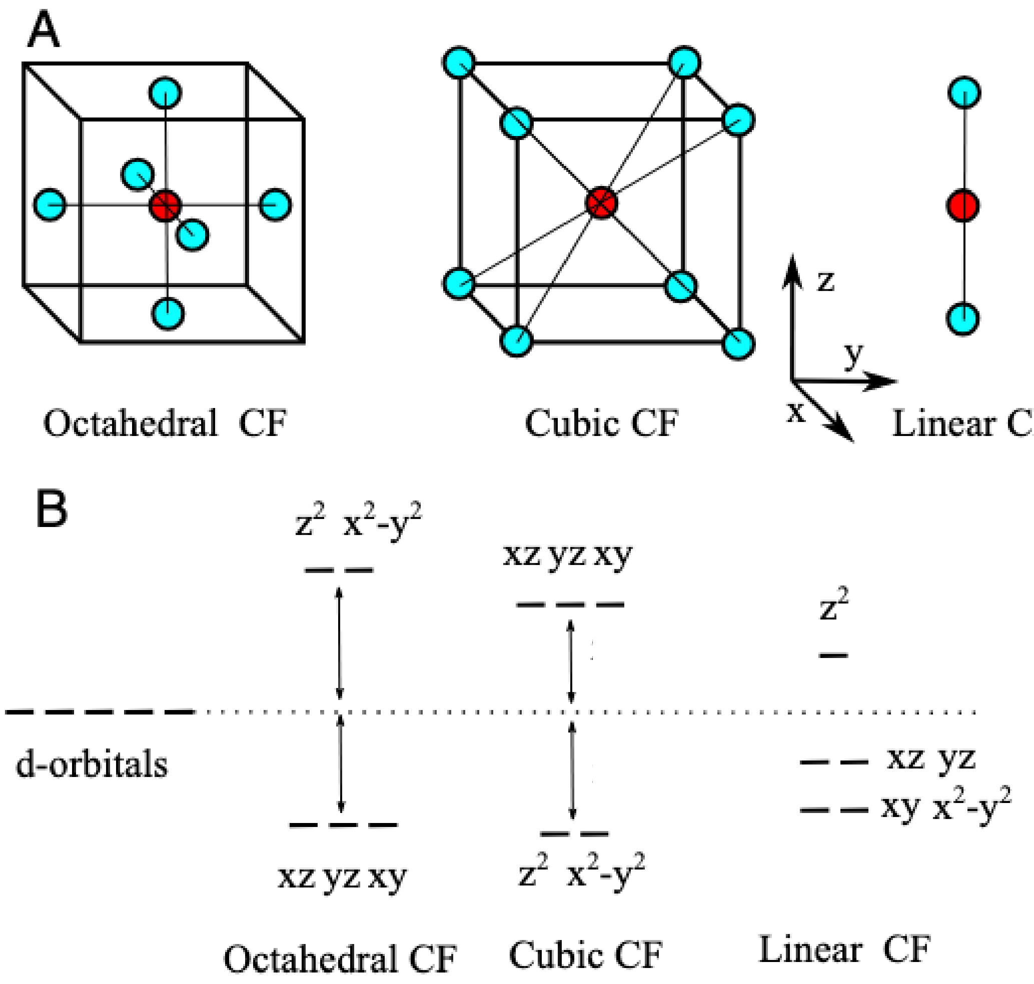
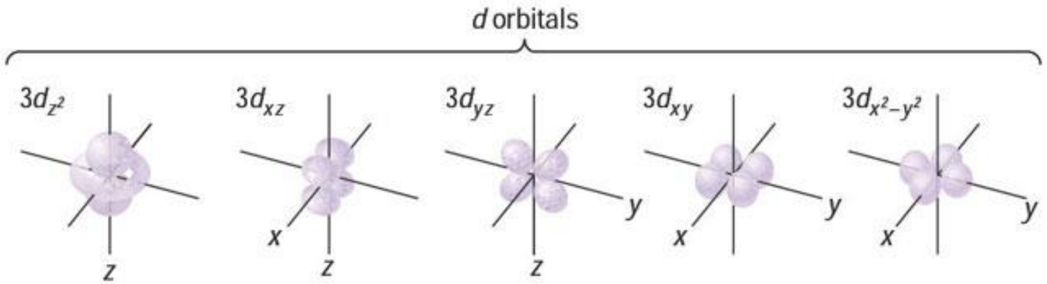


Figure adapted from
https://www.pnas.org/cgi/doi/10.1073/pnas.1922556117



Octahedral CF:
the xy, xz, yz orbitals point in between the ligands;
the $x^2 - y^2$ points towards the ligands in the xy plane and the z^2 points towards the ligands along the z axis →
xy, xz, yz lower, $x^2 - y^2$, z^2 higher

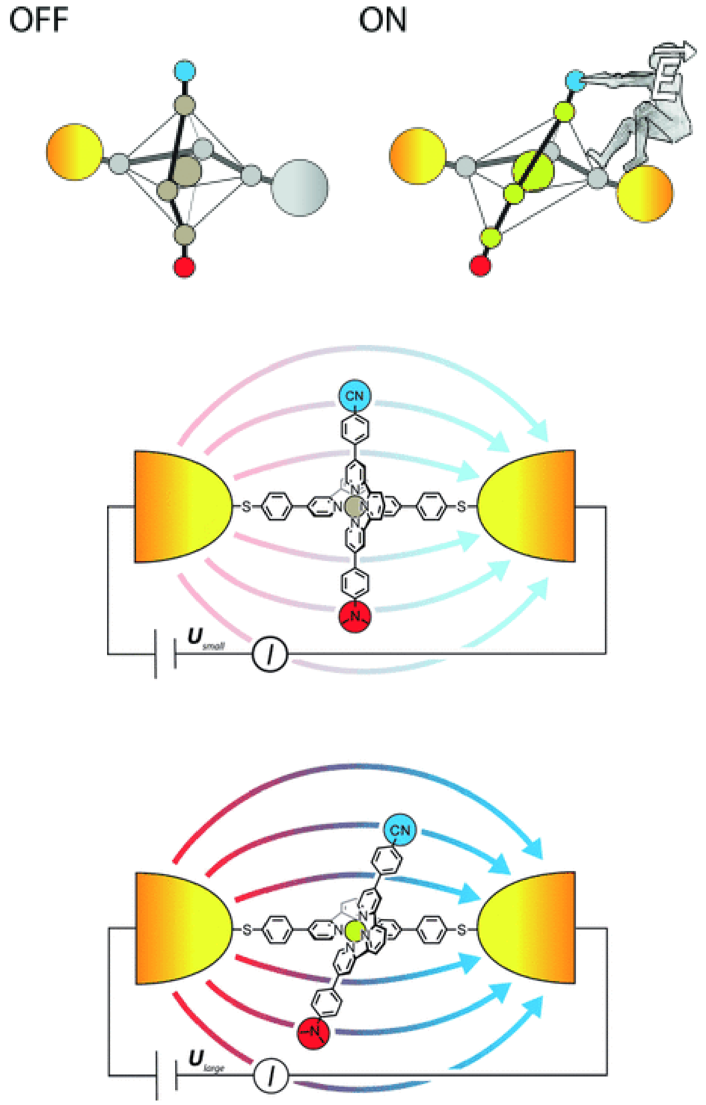
Cubic CF:
none of the orbitals points really towards the ligands, however the xy, xz, yz orbitals point in directions that are closer to the ligands with respect to the directions of the $x^2 - y^2$ and z^2
→ $x^2 - y^2$, z^2 lower, xy, xz, yz higher

Linear CF:
the orbitals without z components are the lowest in energy, the xz and yz are a bit higher, and the z^2, the only one pointing towards the ligands, is the highest in energy

2.2 Spin-crossover molecule for spintronics

Molecules having a single atom metal center are potential candidates for spintronics applications. The basic principle is sketched in the figure. An electric field can be used to deform the molecule, inducing a change in the spin state that can be read by a change in the current flowing in the circuit. This is the case of [$Fe^{2+}(tpy)_2$]. In its normal state, the Fe center feels a very strong octahedral CF (O_h symmetry); the external electric field deforms the structure resulting in a CF weak with respect to Coulomb repulsion and having D_{4h} symmetry.

1) Sketch the d-orbitals energy scheme expected for the unperturbed molecule and for the case where the electric field is applied.
2) Give the value of *S* and *L* in the two cases
3) We replace Fe^{2+} with Co^{2+}; give the value of *S* and *L* in the two cases



Adapted from: https://doi.org/10.1002/anie.201505447

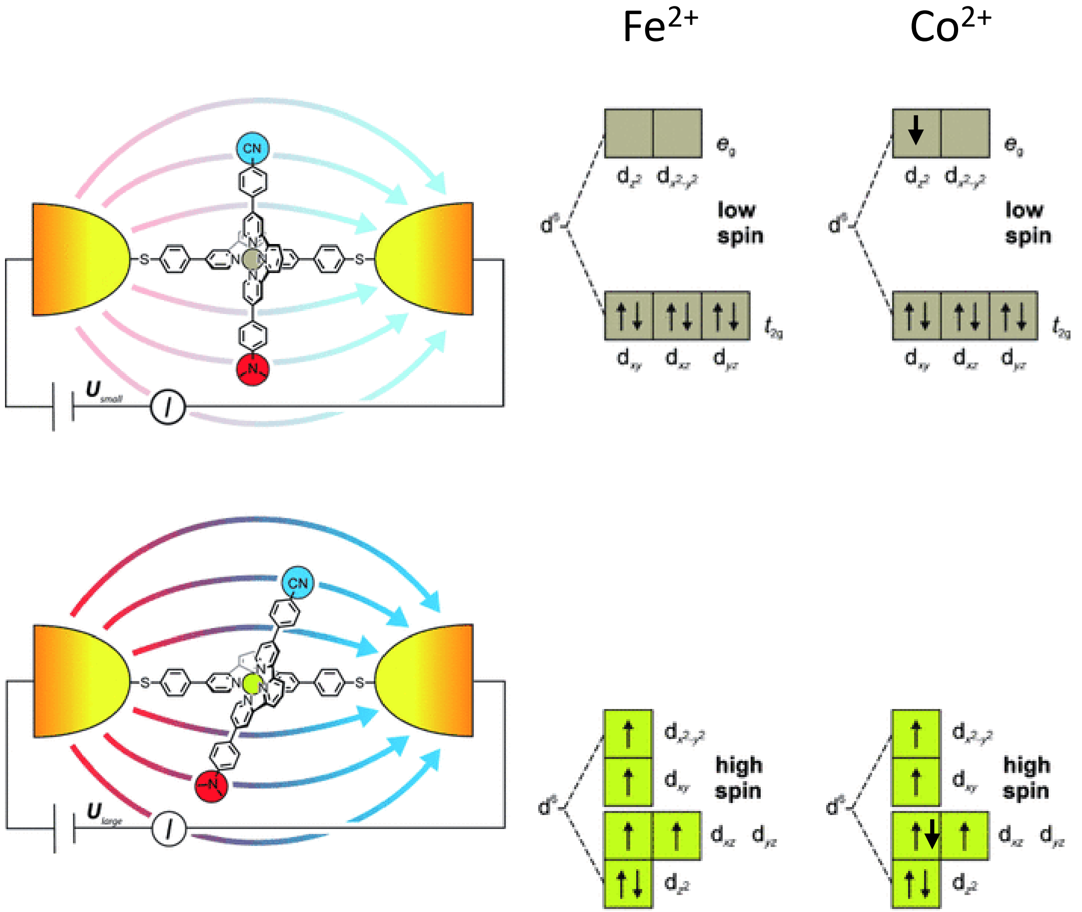
2.2 Spin-crossover molecule for spintronics - Solution

The central Fe atom in Fe^{2+}(tpy)$_2$ is in a Fe^{2+} ion state corresponding to an electronic configuration [Ar] 3d^6 4s^0

The Fe^{2+} ion results in five spin-degenerate d-orbitals. In an almost perfect octahedral coordination, the $10D_q$ crystal field interaction is strong enough to split them in e$_g$ and t$_{2g}$ groups as in figure. The splitting is larger than the Coulomb repulsion; therefore the 6 electrons fill the orbitals according to the figure, giving the low-spin (LS) ground state with zero net spin (S=0, L=0).

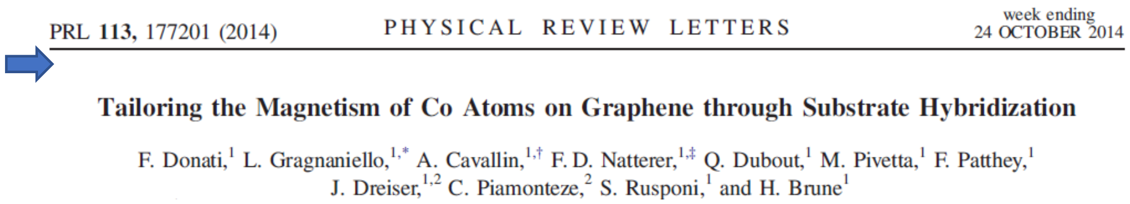
By reduction of the crystal field interaction, for example, by increasing the metal–ligand distance through mechanical distortion, the crystal field splitting parameter $10D_q$ decreases and the e_g states become accessible. Filling the levels according to Hund's rule leads to a maximization of the total net spin (S=2, L=0), the so-called high-spin (HS) state. The exact energy splitting of the 5 d-orbitals depends on the detail of the distortion.

In the case of Co^{2+}, the electronic configuration is [Ar] 3d^7 4s^0.
In O$_h$ symmetry, S=1/2 and L=0 (the two e$_g$ orbitals are degenerate but it is not possible to transform one into the other by a rotation)
In D$_{4h}$ symmetry, S=3/2 and L=1 (the d$_{xz}$ d$_{yz}$ orbitals are degenerate and it is possible to transform one into the other by a rotation $|\langle d_{yz}|L_z|d_{xz}\rangle|$=1)



2.3 Co adatoms on Gr/Ru(0001) and Gr/Ir(111)

Graphene is a 2D material with potential applications in spintronics. In this work we demonstrate that the magnetic properties of Co adatoms adsorbed on graphene can be tuned by choosing the appropriate support for graphene.



PRL 113, 177201 (2014) PHYSICAL REVIEW LETTERS week ending 24 OCTOBER 2014

Tailoring the Magnetism of Co Atoms on Graphene through Substrate Hybridization

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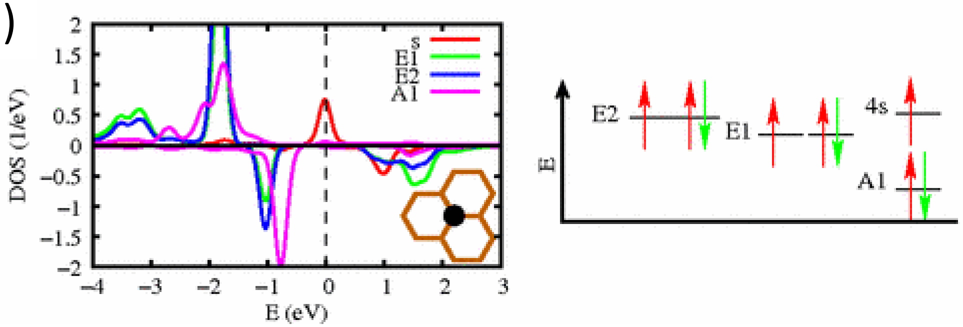
Adapted from: 10.1103/PhysRevLett.113.177201

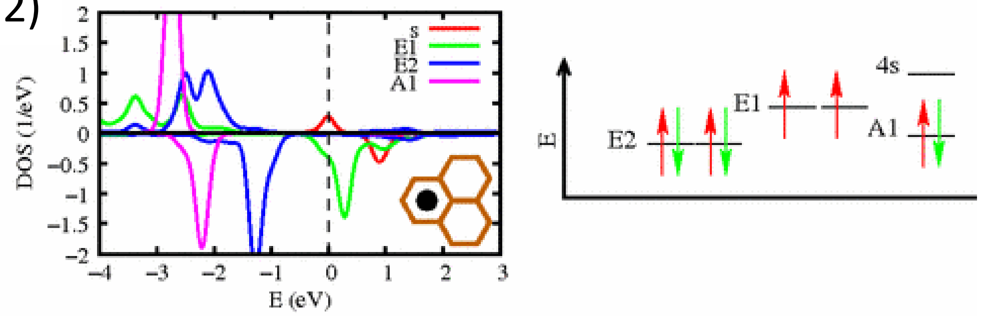
From combined XAS-XMCD and STM measurement we find that Co adatoms adsorb on top of C atom on Gr/Ru(0001) and on the graphene hollow site (center of the honeycomb graphene unitary cell) on Gr/Ir(111).
Fitting the XAS-XMCD data we find that the CF parameters describing the two systems are:
10Dq = 0, Ds = 0.4 eV and Dt = 0.23 eV for on Co/Gr/Ru(0001),
10Dq = 0, Ds = -0.17 eV and Dt = 0.12 eV for on Co/Gr/Ir(111).

1) Calculate the energy splitting of the d-orbitals for the two systems;
2) For Co/Gr/Ru(0001), the Coulomb repulsion redistributes the electron between the 4s and 3d shells resulting in a mixed electronic configuration with 50% d^7 and 50% d^8 ; the d^7 situation is represented in sketch (1), the d^8 configuration is obtained adding one electron to the first free orbital. The following nomenclature is used: A_1 (d_{z2}), E_1 (d_{xz} ; d_{yz}), E_2 (d_{x2-y2} ; d_{xy}).
Calculate L_z
3) For Co/Gr/Ir(111), the Coulomb repulsion redistributes the electron between the 4s and 3d shells resulting in a mixed electronic configuration with about 85% d^8 and 15% d^9; the d^8 situation is represented in sketch (2), the d^9 configuration is obtained adding one electron to the first free orbital.
Calculate L_z

(1)



(2)



https://doi.org/10.1103/PhysRevB.81.115427

2.3 Co adatoms on Gr/Ru(0001) and Gr/Ir(111) - Solution

1) Co/Gr/Ru(0001) the energies are:

-2.18 eV	A_1
0.52 eV	E_1
0.57 eV	E_2

Co/Gr/Ir(111) the energies are:

-0.38 eV	A_1
0.65 eV	E_1
-0.46 eV	E_2

The 4s shell (L = 0) does not contribute to the orbital moment and thus will not be considered in the following.
The A_1 singlet also does not produce orbital moment and then it is not discussed in the following.

2) Co/Gr/Ru(0001):
In the d^7 configuration the E_1 doublet produces L_z=1 (full spin up, one spin down), the E_2 doublet produces L_z = 0 (full spin up, no spin down), thus total L_z = 1
In the d^8 configuration the E_1 doublet produces L_z=1 (full spin up, one spin down), the E_2 doublet produces L_z = 2 (full spin up, one spin down), thus total L_z =3
Since the total electronic configuration is 50% d^7 + 50% d^8 , one finds total L_z = 2.0.
Experimentally, taking into account all the small corrections, one finds total L_z = 2.15

3) Co/Gr/Ir(111):
In the d^8 configuration the E_1 doublet produces L_z= 0 (full spin up), the E_2 doublet (full) produces L_z = 0, thus total L_z = 0
In the d^9 configuration the E_1 doublet (full spin up, one spin down) produces L_z= 1, the E_2 doublet (full) produces L_z = 0, thus total L_z = 1
Since the total electronic configuration is 85% d^8 + 15% d^9 , one finds total L_z = 0 + 0.15*1 =0.15.
Experimentally, taking into account all the small corrections, one finds total L_z = 0.09

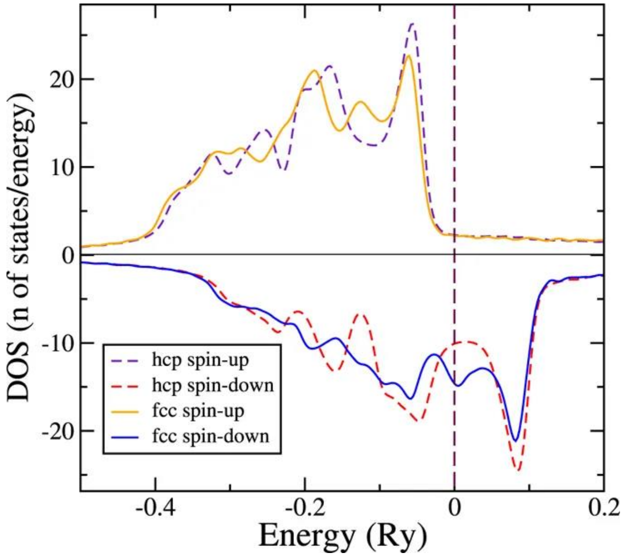
2.4 Co magnetic moment

For spintronics applications, systems having the magnetization pointing out-of-plane have several advantages. We studied the magnetic properties of a monolayer of Co grown on Pt(111) (Co/Pt(111)) as possible candidate. Let's see from a theoretical point of view if this system is promising. This information can be qualitatively inferred by looking at the energy spread of the Density of States (DOS) of Co in three cases, namely in a) bulk, b) free standing monolayer and c) monolayer grown on Pt(111), shown below.

1) Focus on case a). What is the energy range of the d-orbitals?
2) Consider the spin S. Classify the three cases
3) Consider now the orbital moment L. Focus on the monolayer cases (free and supported). Is L the same? Can we say something about the L direction?

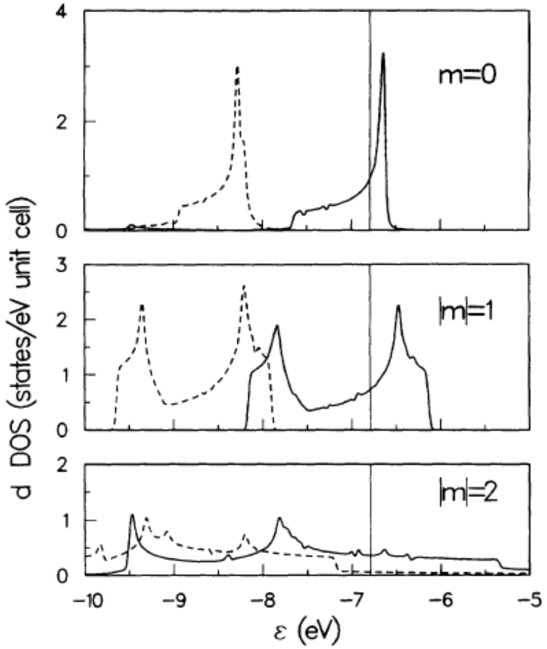
a) Co bulk

1 Ryd=13.6 eV



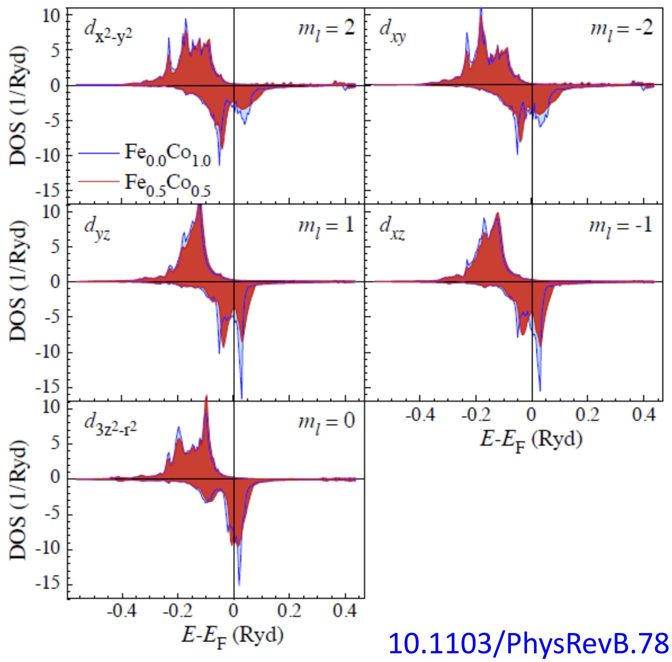
R. Lizarraga et al., Sci. Rep. **7**, 3778 (2017).

b) Free-standing ML



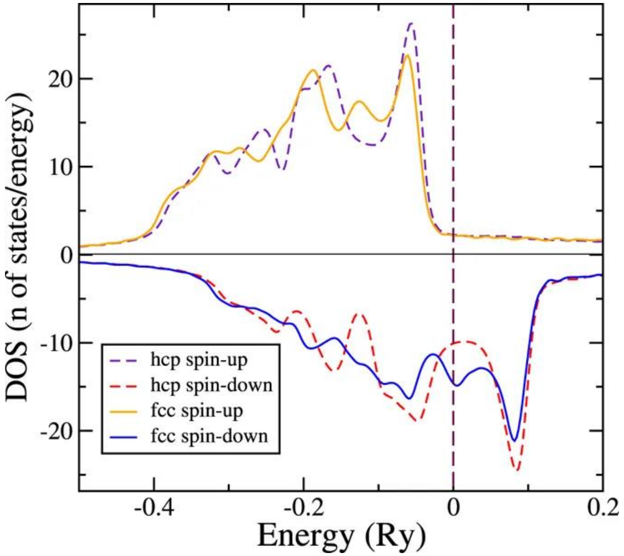
G.H.O. Daalderop *et al.*, Phys. Rev. B **50**, 9989 (1994);

c) Co/Pt(111)



10.1103/PhysRevB.78.214424

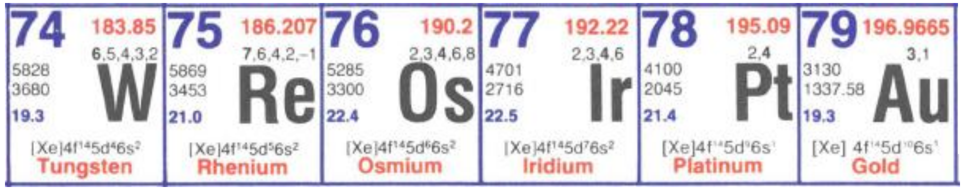
2.4 Co magnetic moment - Solution

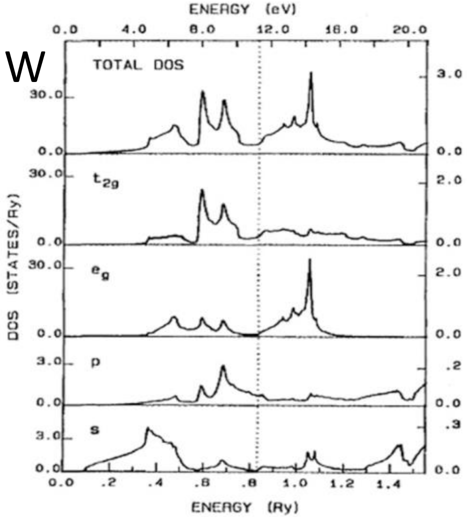


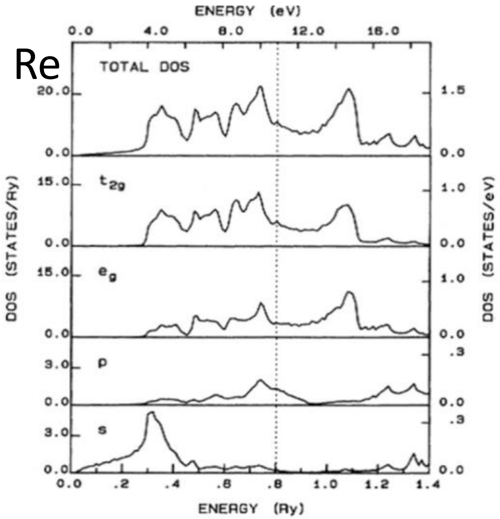
1) The d-orbitals in the bulk case go from about -0.4 Ry (minimum of spin-up) to about 0.12 Ry (maximum of spin-down)
2) The spin moment depends on the unbalance between spin up and down. In all cases the majority states are full. Then, we need to look at the minority states. In the bulk case the minority states extend from -0.3 Ry to 0.12 Ry (i.e. dE = 0.42 Ry); in b) case the minority states extend from -0.2 Ry to 0.12 Ry (i.e. dE = 0.32 Ry). ; in c) case the minority states extend from -0.22 Ry to 0.08 Ry (i.e. dE = 0.32 Ry). Then, S is smaller in the bulk case and almost identical in the other two cases
3) In b) case, the d-orbitals with $m = \pm 2$ are the ones with larger DOS energy spread, i.e. the ones that have larger dispersion, meaning that are the ones that interact more strongly. Since these two orbitals are the ones corresponding to an in-plane orbital precession, the out-of-plane component of L will be quenched. On the contrary d-orbitals with $m = \pm 1{,}0$ are quite narrow in energy, meaning that preserve L values close to the atomic case. Then, in case b) L is pointing in the in-plane direction.
4) In c) case, the DOS energy spread is almost the same for all the d-orbitals, corresponding to an similar reduction factor of L in both in-plane and out-of-plane direction

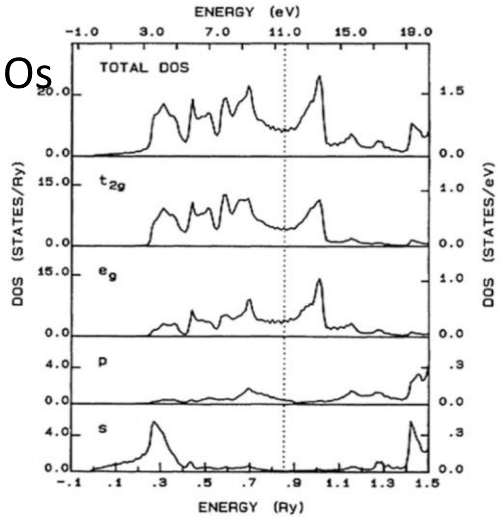
2.5 Interaction at 3d-5d interfaces

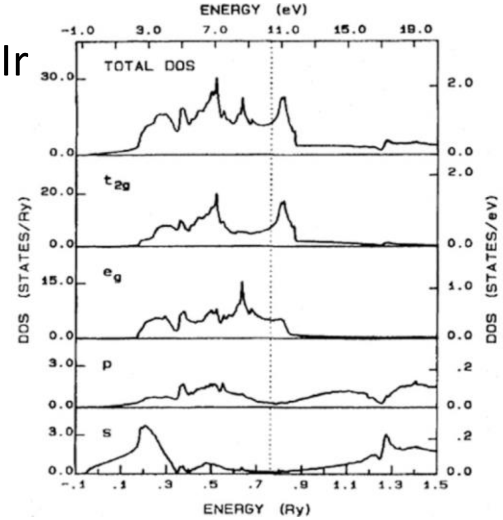
Interfaces composed by 3d thin films grown on a 5d substrate have applications in spintronics due to the high SOC of the 5d substrate. This SOC can be transferred to the 3d element via hybridization. The DOS of 5d metals is shown here below.
Order them from the worse to the best choice in expected strength of the interface hybridization, i.e. in magnetic moment induced in the 5d substrate

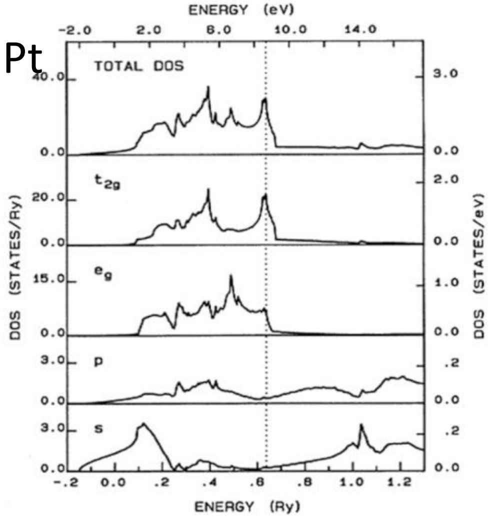


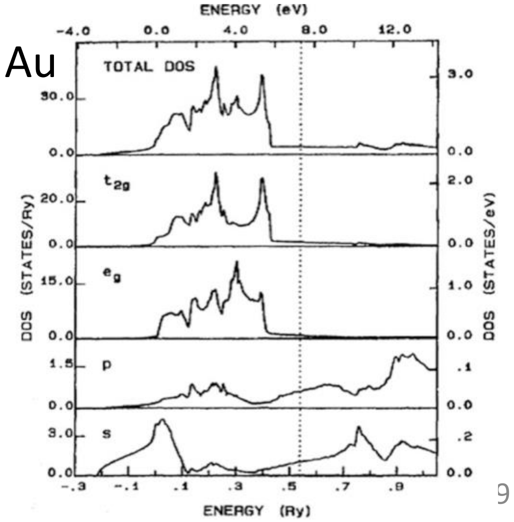








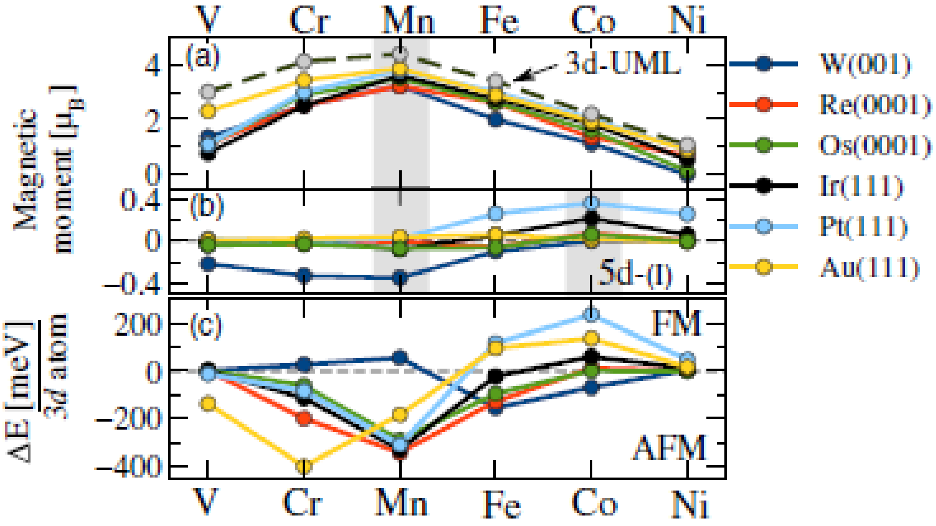




2.5 Interaction at 3d-5d interfaces - Solution

- Au is the worse since it has a negligible d-DOS at Fermi level
- W is next
- Then Re, Os and Ir are mostly equivalent
- Pt is the best choice

You can compare with calculations as shown in the figure on the side.
The trend is mostly respected except for W which also show a large induced moment.
The calculations take into account the lattice size of the different substrate and thus the precise CF and d-orbital splitting



https://doi.org/10.1103/PhysRevLett.117.247202