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# A magnetic tight-binding model : surface effects in transition metals and nanoparticles

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The magnetic and the physical properties of some transition metals from the bulk state to the nanoparticles has been investigated in an accurate tight-binding +  $U$  model which includes the exact Coulomb correlations. With a chemical rule of  $d$  charge neutrality, this new formalism gives the local magnetic moment, explains the relaxation without requiring to the total energy. The model also computes the work function and the free electron states at the surface depending on the coordination in agreement with a Linear Muffin Tin Orbital (LMTO) calculation. Our investigation focuses on the Cobalt FCC with some explorations of the iron BCC, Nickel FCC and the Platinum.

## I. INTRODUCTION

The electronic structure of a transition metal can be seen as a cloud of delocalized electrons which gives the conductivity and the correct cohesive energy. This material can be assimilated as a density of fermions in a mean field approximation. Hence, the Kohn-Sham's approach [1] succeeded in the description of the transition metals behaviors. In the reference [2] it is shown that the delocalization of the  $d$  electrons is a screening effect of a  $s$  state creating the exchange-correlation hole and correcting the Hartree-Fock picture. The Kohn-Sham quasiparticle density becomes then the exact electron density. If the electronic structure of a transition metal is the result of a screening effect of a single electron, the surface properties also derive from the effect of this delocalized electron. In fact on the surface (S), there are free electrons which are spilling out in the vacuum (S+1) showing that at the surface of a transition metal not all the electrons are bonded [3]. It is proved by the mean of a LMTO calculation [4] that the contribution of these free states are essentially  $sp$  state. On the one hand the partially delocalized  $d$  electrons participate to the cohesion. On the second hand, the  $sp$  electron visit all the possible states including the vacuum leading to an oscillation of the charge density. As the charge fluctuate at the surface it is difficult to describe the surface proprieties by a charge neutrality per orbital. In this paper we will present another formalism to understand the charge distribution at the surface of the transition metals. As demonstrated in many references, the total charge is conserved at the surface for the transition metals and transition metal alloys [5]. As the  $sp$  state is a free state, in this paper, we will assume that there is no neutrality of charge of these orbitals ( $s,p$ ) at the surface. This assumption leads to a rule of a partial  $d$  charge neutrality: only the electrons which participated to the cohesion ( $d$  electrons) are subjected to the charge neutrality. This argument is the main point of this paper given the more accurate semi-empirical model for studying the magnetic properties of big size nanoparticles. We will study then

the Stoner magnetism, making a semi-empirical expression to deduce the surface energies, work functions and the magnetism in a Cobalt nanoparticle.

## II. METHODOLOGY

In transition metals, there is no hybridization of orbitals but a screening effect which leads to the metallic bounds. Due to the overlap with the neighboring atoms, an extra Coulomb potential  $\Delta U(r)$  appears and the atomic levels shift by an integral  $\alpha_m$  in the first order in the perturbation theory.

$$\epsilon_d = \underbrace{\int \psi_m^*(r) H^{at} \psi_m(r) d^3r}_{\text{local}} + \underbrace{\int \psi_m^*(r) \Delta U(r) \psi_m(r) d^3r}_{\alpha_m : \text{non local term}} \quad (1)$$

The strength of this perturbation integral depends directly of the overlap between two  $d$  orbitals from one atom to his neighbor. This integral quantifies then the energy of the system depending of the interatomic distance. We can then in a first approximation deduce the interatomic potential by setting the correct  $\alpha_m$  depending of the distance. Normally at the equilibrium for the  $3d$  metals this integral is small and can be neglected. But in  $5d$  metals the impact of this integral starts to be important. We will use this parameter to simulate the relaxation (contraction or reduction of the interatomic distances) and getting the relaxed electronic structure at the surface without trying to compute the total energy. But first we will study the local magnetism by the means of the Hubbard model applying on the  $d$  orbitals.

$$H = -t \sum_{i,j,\sigma} \left( c_{i\sigma}^\dagger c_{j\sigma} + h.c. \right) + U_d \sum_{\lambda}^{n_0} n_{\lambda\uparrow} n_{\lambda\downarrow} \quad (2)$$

As seen in the reference [2], for a transition metal,  $U_d$  contains the Hartree term  $U_H$ , the exchange  $J_{d-d}$  and the correlations on  $n_0 = 5$   $d$  orbitals noted  $\lambda$ . We will derive the Stoner Criterion in the mean field approximation.

### A. The Stoner local magnetism

The magnetism is a local effect, which comes from the occupation per spin ( $\sigma$ ) on a atomic site. The spin magnetic moment  $\mu$  and the total number of electrons in the  $d$  band can be written by the charge fluctuation [6] :

$$\mu = n_0 \langle n_{\lambda\uparrow} - n_{\lambda\downarrow} \rangle \quad \text{and} \quad n = n_0 \langle n_{\lambda\uparrow} + n_{\lambda\downarrow} \rangle \quad (3)$$

The population of one orbital by spin ( $\sigma$ ) :

$$\langle n_{\lambda\uparrow} \rangle = \frac{1}{2n_0}(n - \mu) \quad \text{et} \quad \langle n_{\lambda\downarrow} \rangle = \frac{1}{2n_0}(n + \mu)$$

The Coulomb term can be decomposed in the mean field approximation to (inspired from the reference [6]) :

$$\begin{aligned} U_d \sum_{\lambda} n_{\lambda\uparrow} n_{\lambda\downarrow} &\approx \sum_i n_{\lambda\uparrow} \langle n_{\lambda\downarrow} \rangle + n_{\lambda\downarrow} \langle n_{\lambda\uparrow} \rangle - \langle n_{\lambda\uparrow} \rangle \langle n_{\lambda\downarrow} \rangle \\ &= \sum_{k,\sigma} n_{k\sigma} \langle n_{-\sigma} \rangle - n_0 U_d \langle n_{\lambda\uparrow} \rangle \langle n_{\lambda\downarrow} \rangle \\ &= \frac{U_d}{2n_0} \sum_{k\sigma} (n - \sigma\mu) c_{k\sigma}^\dagger c_{k\sigma} \\ &\quad - n_0 U_d \frac{1}{4n_0^2} (n - \mu)(n + \mu) \\ &= \frac{U_d}{n_0} \sum_{k\sigma} \left( \frac{n}{2} - \frac{\sigma}{2}\mu \right) c_{k\sigma}^\dagger c_{k\sigma} - \frac{U_d}{n_0} \left( \frac{n^2}{4} - \frac{\mu^2}{4} \right) \end{aligned}$$

The Hubbard hamiltonian becomes finally :

$$H = \sum_{k\sigma} \left( \epsilon_k + \frac{nU_d}{2n_0} - \frac{\sigma U_d\mu}{2n_0} \right) c_{k\sigma}^\dagger c_{k\sigma} - \frac{U_d}{n_0} \left( \frac{n^2}{4} - \frac{\mu^2}{4} \right) \quad (4)$$

The band structure  $\epsilon_{k\sigma} = \epsilon_k + \frac{nU_d}{2n_0} - \frac{\sigma U_d\mu}{2n_0}$  is then dependent of the spin  $\sigma$  and the bands are then shifted by an exchange energy  $\Delta\epsilon$ . We have the Stoner relation :

$$\Delta\epsilon = \frac{U_d\mu}{n_0} = I\mu \quad \text{and} \quad \mu = \frac{n_0}{\mu} \Delta\epsilon \quad (5)$$

And the Stoner parameter  $I$ , defined as  $I = U_d/n_0$ .  $I$  and  $U$  are self-consistency parameters to obtain a good magnetic moment. The equation (4) gives a form of the electronic on-site total energy in the tight-binding approximation. We can then obtain the total energy of a magnetic system by making the summation in the expression (4) depending of the spin :

$$E_{tot} = \left\{ \begin{array}{l} \sum_{k\uparrow} \epsilon_k^\uparrow + \frac{nU_d}{2n_0} - \frac{1}{2} \frac{U_d\mu}{n_0} \\ \sum_{k\downarrow} \epsilon_k^\downarrow + \frac{nU_d}{2n_0} + \frac{1}{2} \frac{U_d\mu}{n_0} \end{array} - \frac{U_d}{n_0} \left( \frac{n^2}{4} - \frac{\mu^2}{4} \right) \right. \quad (6)$$

By making this summation of the band energy *spin up* and *spin down* containing respectively  $n_\uparrow$  et  $n_\downarrow$  electrons, we obtain :

$$E_{tot} = \left\{ \begin{array}{l} \epsilon_{band}^\uparrow + \frac{nU_d}{2n_0} N_\uparrow - \frac{1}{2} \frac{U_d\mu}{n_0} N_\uparrow \\ \epsilon_{band}^\downarrow + \frac{nU_d}{2n_0} N_\downarrow + \frac{1}{2} \frac{U_d\mu}{n_0} N_\downarrow \end{array} - \frac{U_d}{n_0} \left( \frac{n^2}{4} - \frac{\mu^2}{4} \right) \right. \quad (7)$$

Or linearly :

$$\begin{aligned} E_{tot} &= \epsilon_{band}^\uparrow + \epsilon_{band}^\downarrow + \frac{nU_d}{2n_0} (N_\uparrow + N_\downarrow) \\ &\quad - \frac{1}{2} \frac{U_d\mu}{n_0} (N_\uparrow - N_\downarrow) - \frac{U_d}{n_0} \left( \frac{n^2}{4} - \frac{\mu^2}{4} \right) \\ &= \epsilon_{band}^\uparrow + \epsilon_{band}^\downarrow + \frac{nU_d}{2n_0} n - \frac{1}{2} \frac{U_d\mu}{n_0} n - \frac{U_d}{n_0} \left( \frac{n^2}{4} - \frac{\mu^2}{4} \right) \\ E_{tot} &= \epsilon_{band}^\uparrow + \epsilon_{band}^\downarrow + \frac{1}{4n_0} U_d n^2 - \frac{1}{4n_0} U_d \mu^2 \end{aligned}$$

The variation of the energy when we make the transition from a non magnetic state to a magnetic state is then given by :

$$\Delta E_{mag} = E_{tot}^{mag} - E_{tot}^{non.mag} \quad (8)$$

$$= \epsilon_{band}^\uparrow + \epsilon_{band}^\downarrow - \epsilon_{band}^{non.mag} - \frac{1}{4n_0} U_d \mu^2 \quad (9)$$

$$\Delta E_{mag} = \Delta E_{coh} - \frac{1}{4n_0} U_d \mu^2 \quad (10)$$

If our tight-binding parameters are extracted from the DFT band structure then the effective coulomb repulsion contains the correlations [2].

### B. A surface effect : the relaxation

At the surface, the coordination is lower, so that the bandwidth decreased. The surface will then undergo a relaxation to get the same bandwidth than in the bulk and conserve the Coulomb correlations. This relaxation can be simulated by two methods : the displacement of atoms at the surface inward, increasing the overlap and the  $d$  bandwidth or by using the perturbation theory by shifting the  $d$  atomic levels then increasing the bandwidth as well. For the sake of simplicity, the relaxation should be simulated by shifting the  $d$  atomic levels and then avoid to calculate the interatomic potential. As the  $sp$  state are free electrons they cannot be constrained to shift their atomic levels, only the  $d$  electrons which participated to the cohesion are shifted. The atomic levels of the  $d$  electrons are shifted by a quantity  $\delta\epsilon_{i\lambda}$  ( $\alpha_m$ ) to get the charge of the bulk material at the Fermi level (which is defined by the bulk in big size material or by an average in a small nanoparticles) : this procedure is physically and energetically the same as a dynamic relaxation. As the  $sp$  levels are fixed, there are free  $sp$  states at the vicinity of the Fermi level : a level above the surface (S+1) as in a LMTO calculation. The partial  $d$  charge neutrality leads then to the inclusion of the

free electrons states at the surface in the Slater-Koster tight-binding model. After this  $d$  charge neutrality (or relaxation) the surface proprieties can be calculated as the surface energy, the work function and the magnetic proprieties. As the surface energy is a variation of the Coulomb potential due principally to the breaking of the symmetry of bonds, we can deduce the surface energy by the difference in the band energy after the  $d$  charge neutrality (inspired by the reference [7]).

$$\gamma_i = \frac{1}{3} \left[ \sum_{\lambda} \left( \int_{-\infty}^{E_f} E n_i(E, \delta\epsilon_{i\lambda}) dE - N_e(\lambda) \delta\epsilon_{i\lambda} \right) - E_{band}^{bulk} \right] \quad (11)$$

This equation is the mean value of the contribution of all the orbitals  $s$ ,  $p$  and  $d$ . This expression contains the term  $N_e(\lambda) \delta\epsilon_{i\lambda}$  which takes into account the energy for shifting the atomic levels of the  $d$  orbitals by a quantity  $\delta\epsilon_{i\lambda}$  ( $\alpha_m$ ). In this model, if the  $d$  charge neutrality self-consistency procedure is accurate, then the surface energies are then also accurate. After doing this simulation of the relaxation by the conservation of the  $d$  charge, we can deduce the magnetism at the surface. From the non magnetic relaxed DOS, we create two DOS spin up and spin down and we shift these DOS by different values of the exchange energy  $\Delta\epsilon$  (as in the reference [8]). And calculate the work function by [9] :

$$W = E_{vacuum} - E_f \quad (12)$$

Where  $E_{vacuum}$  is the energy to extract an electron from the surface to the vacuum without an additional kinetic energy. This vacuum energy depends on the surface properties and the mean value of the band energy after the  $d$  charge neutrality (relaxed electronic structure).

$$E_{vacuum} = \frac{1}{3} \left[ \sum_{\lambda} \frac{1}{N_e(\lambda)} \left( \int_{-\infty}^{E_f} E n_{i\lambda}(E, \delta\epsilon_{id}) dE \right) \right] - 3\gamma_i \quad (+\Delta E_{mag.})$$

We add the variation of the magnetic contribution to get the magnetic work function.

### III. RESULTS

Our calculations are based on the Slater-Koster parameters to build the hopping integrals and the tight-binding hamiltonian with the atomic levels. These parameters  $ss\sigma$ ,  $sp\sigma$ ,  $sd\sigma$ ,  $pp\sigma$ ,  $pp\pi$ ,  $pd\sigma$ ,  $pd\pi$ ,  $dd\sigma$ ,  $dd\pi$ ,  $ddd$  along with the atomic levels  $\epsilon_s$ ,  $\epsilon_p$  and  $\epsilon_d$  are obtained by fitting the tight-binding band structure after diagonalizing the hamiltonian with a Density Functional Theory (DFT) code SIESTA [10] using GGA-PBE as the exchange-correlation functional. This fitting (using a non linear regression) and our tight-binding hamiltonian is restricted to the first neighbors approximation, this

approximation seemed enough to have a good accuracy (more than 90% of agreement) in band energy calculated with SIESTA. However for the Iron BCC our parameters are taken from the reference [11] .

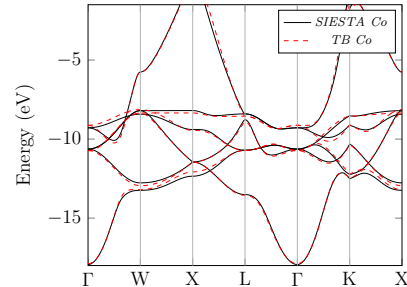


FIG. 1. Band fitting of non magnetic the FCC Cobalt.

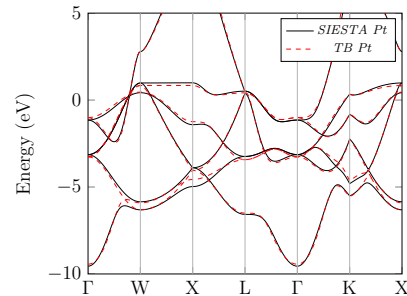


FIG. 2. Band fitting of the FCC Platinum .

#### A. Results in the bulk material

The magnetic properties of the bulk material have been studied in the reference [2] we got respectively 6.1 eV, 6.1 eV and 6.3 eV (with some uncertainties due to the fitting) for the Iron BCC, Cobalt FCC and Nickel FCC. In general, the Coulomb effective repulsion term for the  $3d$  material is around 6 eV. It means that adding one electron on a  $3d$  orbitals, this electron is subjected to an effective coulomb repulsion close to 6 eV. If the Stoner criterion is  $Un(E_f)/5 > 1$  [8] and if  $U$  is almost the same for all  $3d$  transition elements then, the Stoner criterion is applied depending chiefly on the density of state at the Fermi level, which should be  $n(E_f) > 0.9$  electrons and this condition is satisfied for the end of series  $3d$  transition metals. In the case of the Cobalt FCC we can see in the Fig (3) the fitting of the magnetic moment defined by the relations (5) and  $\mu = N_{\uparrow} - N_{\downarrow}$  (shift of rigid DOS) to get the correct Coulomb correlations ( $U = 6.09$  eV) and the exact magnetic moment ( $\mu = 1.61 \mu_B$ ). We can deduce that the variation of the total energy by magnetizing the system is -0.17 eV which is in consistent with DFT calculations using SIESTA. In the same manner, we can deduce the Coulomb correlations and the magnetic moment for the Nickel and the iron BCC.

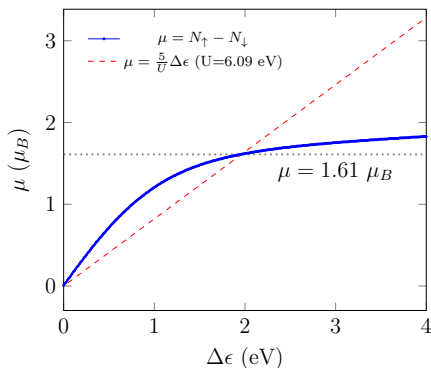


FIG. 3. Calculating the magnetic moment in Co FCC .

TABLE I. Coulomb parameters calculated to get the exact magnetic moment

	Fe	Co	Ni
$U_d$ [eV]	6.1	6.1	6.3
$\Delta\epsilon$ [eV]	2.76	1.87	0.81
$\mu$ [ $\mu_B$ /atom]	2.22	1.61	0.61
$\Delta E_{mag}^{bulk}$ [eV]	-0.45	-0.17	-0.04

## B. Results at the surface

### 1. Non magnetism surface

By applying a self-consistent loop on the  $d$  band to get a neutrality of charge at the surface (S), the relaxed electronic structure and the conservation of the correlations, the  $d$  atomic levels are then shifted by  $\delta\epsilon_{id}$  ( $\alpha_m$ ) depending of the crystallography direction. This surface self-consistency  $d$  charge neutrality as stated previously will create an extra free charge on the  $sp$  band in the vacuum (S+1).

TABLE II. Shifting of the  $d$  atomic level to obtain the  $d$  charge neutrality in Co, Ni, Fe and Pt compared to the bulk

	Fe	Co	Ni	Pt
$\delta\epsilon_{id}(111)$ [eV]	-	0.32	0.30	0.54
$\delta\epsilon_{id}(110)$ [eV]	0.18	-	-	-
$\delta\epsilon_{id}(100)$ [eV]	0.31	0.41	0.44	0.77

We can see that the relaxation depends on the crystallographic direction of the surface. We obtain exactly the same contribution to the free electrons state at the level (S+1) in the Nickel FCC, not enough to generalize that the occupation of this level depends on the crystalline structure. However in the iron BCC, the total contribution to S+1(100) and S+1(110) are respectively 0.65 and 0.26 electrons which is larger than in the FCC structure. So the number of free electrons spilling out in the vacuum depends of the packing of the atoms and the crystalline structure. After this selfconsistency procedure we can

deduce the non magnetic surface energies by the relation (11).

TABLE III. Occupation by orbitals at the surface (S) and in the vacuum (S+1) for the non magnetic Co FCC

	s	p	d	Total
$N_e(100)(S)$	0.28	0.46	7.93	8.67
$N_e(100)(S+1)$	0.26	0.11	-0.03	0.34
$N_e(111)(S)$	0.36	0.51	7.92	8.79
$N_e(111)(S+1)$	0.18	0.05	-0.02	0.23

TABLE IV. Contribution to the non magnetic surface energies of the Co, Ni, Fe and Pt

	Fe	Co	Ni	Pt
$\gamma(111)$ [eV]	-	0.90	0.78	1.05
$\gamma(110)$ [eV]	1.02	-	-	-
$\gamma(100)$ [eV]	2.1	1.21	1.06	1.45

The value of the surface energies  $\gamma_{Fe}(100)$  is overestimated compared to the experimental value of 1.26 eV [12], even if the surface the magnetism will decrease this value, the facet Fe(100) non magnetic will certainly be a reconstructed surface for reducing surface energy. Likewise the value of the surface energy of the Pt(100) is also overestimated, since the fitting is quite accurate the explanation of this value is the fact that this direction is reconstructed [13]. The relaxation is not enough to reduce the surface energy of the facet Pt(100), the reconstruction of this surface give an hexagonal structure [14] which has a smaller surface energy than the non reconstructed surface. But the value of facet Pt(111) is consistent with the experimental value of 1.09 eV [15].

### 2. surface magnetism

For getting the magnetic proprieties at the surface as the magnetic moment and the variation of the energy, we shift the non magnetic rigid DOS after the  $d$  charge neutrality and we fit the magnetic moment defined by  $\mu = N_{\uparrow} - N_{\downarrow}$  with the relation (5) using the same  $U$  as in the bulk : 6.09 eV as the Coulomb correlations are conserved after the  $d$  charge neutrality. We found 1.72  $\mu_B$  and 1.80  $\mu_B$  respectively for the surfaces Co(111) and Co(100) which are comparable to another calculation using LMTO [16]. By applying the same procedure with the other ferromagnetic elements we obtain the Table (V). The values of the magnetic moment in the surface are comparable to the references [16, 17] and we can deduce the magnetic surface energy by applying the simple formula :

$$\gamma^{mag} = \gamma + \delta\Delta E_{mag}. \quad (13)$$

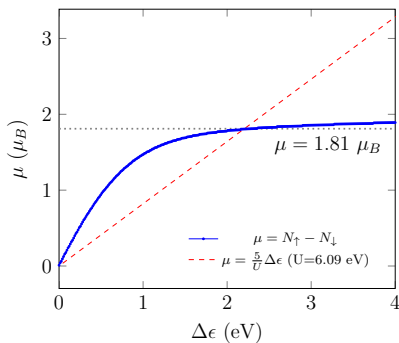


FIG. 4. Magnetic moment on the surface Co(100).

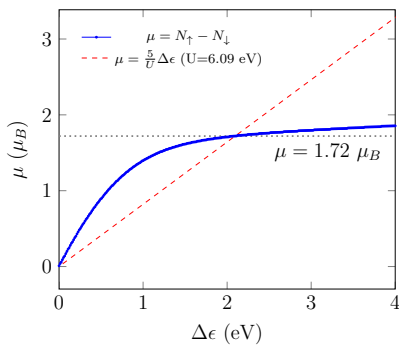


FIG. 5. Magnetic moment on the surface Co(111)

TABLE V. Magnetic moment on the surface of the Cobalt, Ni and Fe along with the variation of the energy

	Fe	Co	Ni
$\mu(111)$ [ $\mu_B$ ]	-	0.90	0.78
$\mu(110)$ [ $\mu_B$ ]	1.02	-	-
$\mu(100)$ [ $\mu_B$ ]	2.10	1.21	1.06
$\Delta E_{mag}(111)$ [eV]	-	-0.27	-0.01
$\Delta E_{mag}(110)$ [eV]	-0.60	-	-
$\Delta E_{mag}(100)$ [eV]	-1.60	-0.48	-0.07

Where  $\delta\Delta E_{tot}^{mag} = \Delta E_{mag}(100/111/110) - \Delta E_{mag}^{bulk}$ . The magnetic surface energies are then :  $\gamma_{Fe}^{mag}(100) = 1.23$  eV,  $\gamma_{Fe}^{mag}(110) = 0.96$  eV which is not so far from the experimental value : 1.26 eV [12]. For the Cobalt  $\gamma_{Co}^{mag}(100) = 0.97$  eV,  $\gamma_{Co}^{mag}(111) = 0.88$  eV in consistent with the experimental value : 0.87 eV [12] and finally the surface energy of the ferromagnetic Nickel is  $\gamma_{Ni}^{mag}(100) = 0.99$  eV,  $\gamma_{Ni}^{mag}(111) = 0.78$  eV. As the description of the surface in our formalism is accurate with reasonable magnetic moment and surface energies, we can deduce the work function by applying the expression (12) :

The work function calculated are close to the experimental values then validating the model. As we know that we can obtain the magnetic proprieties of the bulk, and the surface with a good accuracy, we can extent finally the model to the study of nanoparticles. In

this paper we will limit our study to the Cobalt FCC Nanoparticles (Cuboctahedron) but the formalism can be applying on any magnetic nanoparticle.

### C. Nanoparticles

To extract the proprieties of a nanoparticle we should make an approximation that all the atomic sites with the same coordination in a first neighbor approximation have the same proprieties called classes of sites. In a Cuboctahedron there are five classes of sites : The bulk (coordination : 12), the edges (coordination : 7), the vertex (coordination : 5), the facet (100) (coordination : 8) and the facet (111) with the coordination : 9. We studied the Cobalt nanoparticles with the size going from 55 atoms to 1415 atoms. The selfconsistency procedure is the same, we fix a general Fermi level and we shift the  $d$  atomic levels of all sites of all classes until at this Fermi level the charge is respected in all the classes of site. This process relaxes also directly the nanoparticle and give the correct electronic structure on all the nanoparticle. After we shift each class non magnetic DOS with different values of the exchange energy (so we have five curve defined by  $\mu = N_{\uparrow} - N_{\downarrow}$ ), this curves are intercepting this curve with the relation (5) with the same Coulomb parameter  $U = 6.09$  eV which gives a correct magnetic moment which depends on the coordination on the Fig (6) and summarize in the Tables (VII) and (VIII).

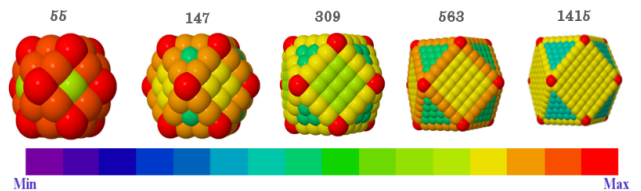


FIG. 6. Magnetic moment dependent of the coordination and the size in a Co FCC cuboctaedron calculated in TB + U = 6.09 eV

We can conclude that this model is quite accurate for deducing the properties in an atomic site like the local magnetic moment, the work function and the surface energy. There is an oscillation of the magnetic moment depending of the size (like in the reference [20] in Co clusters). This is a size effect which can appear in our simple model. This oscillation can also been observe in the variation of the work function depending of the size of the particle. However the surface energy decreased with the size without a significant oscillation.

### IV. CONCLUSION

Nowadays, the nanoparticles occurs in many applications. The understanding of their proprieties is

TABLE VI. Work function [eV] for the Fe, Co and the Nickel

	Fe (100)	Fe (110)	Co (100)	Co (111)	Ni (100)	Ni (111)	Pt(111)
$W$ (Non mag.)	8.91	5.84	6.49	5.47	5.99	5.03	6.36
$W$ (Ferro)	5.94	5.26	5.58	5.09	5.92	5.02	
$W$ (Expt)	4.17 <sup>a</sup>			5.00 <sup>b</sup>		5.35 <sup>c</sup>	5.7/6.35 <sup>d</sup>

<sup>a</sup> From the reference [18]<sup>b</sup> From the reference [19]<sup>c</sup> From the reference [19]<sup>d</sup> From the reference [19]

TABLE VII. Magnetic moment, work function, surface tension for a nanoparticle of 1415 atoms

	Bulk	Vertex	Edges	(100)	(111)
$\mu$ [ $\mu_B$ ]	1.62	1.91	1.85	1.84	1.74
$W$ [eV]	-	7.84	6.48	6.03	5.23
$\gamma$ [eV]	-	1.64	1.22	1.02	0.81

TABLE VIII. Magnetic moment, work function, surface tension for a nanoparticle of 309 atoms

	Bulk	Vertex	Edges	(100)	(111)
$\mu$ [ $\mu_B$ ]	1.64	1.88	1.79	1.87	1.79
$W$ [eV]	-	7.41	6.14	5.73	4.96
$\gamma$ [eV]	-	1.63	1.23	1.01	0.75

crucial and was limited since the calculations using an *abinitio* code was limited to about hundreds of atoms. We develop this new formalism which encompasses the exact correlations and which allows to determine several proprieties by just applying a rule of  $d$  charge neutrality. This method shows its efficiency by computing values very close to the experimental data. The relaxation process is then describe just as a conservation of the  $d$  bandwidth by shifting the atomic level and conserving the Coulomb correlations. This method should extend to the study of the reconstruction, study of the alloys which are a bit more complicated and the process of segregation at the surface of alloys. The advantages of this formalism is the accuracy and the gain in speed of the calculation and its extension to non crystalline materials or structures with defects and distortions.

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