A magnetic tight-binding model: correlations in ferromagnetic transition metals.

Jacques R. Eone II

Department of Physics, University of Strasbourg, Strasbourg, France
(Dated: December 10, 2018)

The estimation of correlations through approximations in an electronic many-body calculation often leads to overestimated or underestimated physical properties. But it is possible to better evaluate and understand the effect of correlations from the charge distribution and a screening effect due to a delocalized s state. This provides an accurate description of the d-band magnetism, unifying a localized and delocalized approach and giving approximate values of the band gap in the monoxides of ferromagnetic transition metals. From a tight-binding calculation, 1.3 eV for bcc iron, 1.5 eV for fcc cobalt and 2.1 eV for fcc nickel are found as Coulomb correlations correcting the magnetic energies of a localized d-band approximation.

I. INTRODUCTION

The Kohn-Sham equation gives an efficient method to calculate the electronic structure of a solid. But this approach remains approximate as long as we do not know how to express an exact exchange-correlation functional. Thus, we obtain underestimated or overestimated physical properties depending on the choice of this functional and an incorrect estimation of the gap of semiconductors or insulators. Many tools such as the GW approximation and Hubbard corrections are well known to tackle these limitations. The purpose of this work is to make a study of these corrections, but the physical process induced by the Coulomb correlations and its relationship to the local magnetism in a semi-empirical model using the tight-binding approximation. The magnetism can be integrated in the tight-binding approximation limited to the d-band using the Stoner model from a local Hubbard Hamiltonian. This integration of magnetism often leads to a Coulomb parameter $U$ which seems to be overestimated but describes accurately of the energies. This calculation uses a delocalized d-band from the spd orbitals basis. Another calculation gives a model of magnetism in agreement with photoemission experiments but a description of energies in disagreement with an ab initio calculation. This calculation is made with a localized d-band without any effect of the s and p orbitals in the basis. These examples based on the d-band show here a problem related to the misrepresentation of correlations. Generally, all the interactions in a solid are a competition to reduce the energy. From a chemical point of view, the d-band is formed by pairing all the electrons of the d-orbitals reducing the kinetic energy and giving a cohesion. This process describes covalent bonds which are directional and do not describe the delocalized electrons of a transition metal where the effects of correlations occur to decrease the energy. These correlation effects come from the action of the sp-band occupied by about one electron on the d-band for our three ferromagnetic transition metals. This electron coming from the s orbital has a dramatic effect on the electronic structure. Being a nearly free electron, it forms the sp-band by visiting the s, p and d states. By its presence, the Coulomb potential felt by the d electrons is then screened, modifying the occupation and giving an increase of the Coulomb interactions undergone by these electrons. The electrons in the d-band are then delocalized, the bonds become non directional and the cohesive energy decreases. We will describe this process in a simple tight-binding approximation with and without the contribution of the sp-band.

II. METHODOLOGY

In a mean field approximation, the local form of the Hubbard Hamiltonian for the d-band can be written as:

$$H = -t \sum_{i,j,\sigma} \left( \epsilon_{i\sigma} c_{j\sigma}^\dagger + h.c. \right) + U_d \sum_{\lambda} n_{\lambda\uparrow} n_{\lambda\downarrow}$$  \hspace{1cm} (1)

This Hamiltonian has nothing to do with the form of the Hubbard model in a crystal lattice. This Hubbard Hamiltonian is applied on $n_\lambda = 5$ d orbitals noted $\lambda$ in a one atom basis. $U_d$ is the effective Coulomb repulsion on one d orbital $\lambda$. This Hamiltonian consists of $t$ the hopping integral. This parameter is associated with the atomic energies $\epsilon_\lambda$ of the d electrons which can be decomposed into the atomic basis $\psi_\lambda$ with the atomic Hamiltonian $H^\text{at}$ as a local term and a perturbation $\alpha$.

$$\epsilon_d = \int_{\text{local}} \psi_\lambda^\ast(r) H^\text{at} \psi_\lambda(r) d^3r + \int_{\alpha : \text{perturbation}} \psi_\lambda^\ast(r) \Delta U(r) \psi_\lambda(r) d^3r$$  \hspace{1cm} (2)

$\alpha$ comes from the first order in perturbation where the atomic potential $V^\text{at}_i(r)$ is perturbed by a weak perturbation $\Delta U(r)$ due to the interaction with the neighboring atoms. This perturbation contains the interatomic interactions. As the overlap of the d electrons is weak, the non-local term is often neglected giving a tight binding model without interatomic correlations. But this non-local contribution means that every variation of the atomic potential by a perturbation leads to a shift of the atomic levels by a quantity $\alpha$ so that the band energy is modified. Reciprocally, every shift of the atomic energies is due to the apparition of a potential $\Delta U(r)$ as a
perturbation. This argument can be used to create a self-consistency correction for example when the bounds are broken on the surface. The interaction with the neighbors opens a band with a width $W$ defined as the allowed energies for the $d$ electrons in the solid. The bandwidth $W$ is proportional to the hopping integral from an $\Lambda$ atomic orbital to another $\nu$ atomic orbital of the neighboring atom.

$$W \propto -\int \psi^*_{\Lambda}(r) \Delta U(r) \psi_{\nu}(r - R_n) d^3r$$  \hspace{1cm} (3)

The local Hubbard Hamiltonian Eq. 4 in the Hartree-Fock (HF) approximation gives the effective Coulomb repulsion $U_d$ limited to the exchange interaction. We can add another Coulomb repulsion due to the screening effect induced by the s charge on the $d$-band as representing the correlations.

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

$$+ U_{xc} \sum_{\lambda} n_{\lambda\uparrow} n_{\lambda\downarrow}$$

The eigenvalues of this Hamiltonian simulate a delocalized state as representing the solutions to the Kohn-Sham equation compared to a very localized $d$-band from the Hartree-Fock approximation. The Coulomb repulsion parameter $U_d$ containing the correlations can be related to the $d$-band magnetism.

From the Eq. 4 by considering $n_0 = 5$ $d$ orbitals containing $n_d$ electrons, the local spin magnetic moment $\mu$ and the number of electrons $n_d$ in the $d$-band are given by : $\mu = n_0 \langle n_{\uparrow} - n_{\downarrow} \rangle$ and $n_d = n_0 \langle n_{\uparrow} + n_{\downarrow} \rangle$. The Coulomb part of the Hamiltonian can be written as (inspired by a formulation[3] in a lattice description) :

$$U_d \sum_{\lambda} n_{\lambda\uparrow} n_{\lambda\downarrow} \approx U_d \sum_{\lambda} n_{\lambda\uparrow} \langle n_{\lambda\uparrow} \rangle + n_{\lambda\downarrow} \langle n_{\lambda\downarrow} \rangle - \langle n_{\uparrow} \rangle \langle n_{\downarrow} \rangle$$

$$= U_d \sum_{k,\sigma} n_{k\sigma} \langle n_{-\sigma} \rangle - n_0 U_d \langle n_{\uparrow} \rangle \langle n_{\downarrow} \rangle$$

$$= \frac{U_d}{2n_0} \sum_{k\sigma} \left( n_d - \sigma \mu \right) c^\dagger_{k\sigma} c_{k\sigma} - n_0 U_d \frac{1}{4n_0^2} (n_d - \mu)(n_d + \mu)$$

$$= \frac{U_d}{n_0} \sum_{k\sigma} \left( \frac{n_d}{2} - \frac{\sigma}{2} \mu \right) c^\dagger_{k\sigma} c_{k\sigma} - \frac{U_d}{n_0} \left( \frac{n_d^2}{4} - \frac{\mu^2}{4} \right)$$

If the Stoner criterion is fulfilled, the band structure $\epsilon_{k\sigma} = \epsilon_k + \frac{n_d U_d}{2n_0} - \frac{\sigma}{2} \frac{U_d}{n_0} \mu$ is therefore dependent on the spin $\sigma$ and the bands per spin are shifted by the exchange splitting :

$$\Delta \epsilon = \frac{U_d \mu}{n_0} = I_d \mu$$  \hspace{1cm} (4)

Where $I_d$ is the Stoner parameter. The local Hamiltonian Eq. 4 can be written as :

$$H = \sum_{k\sigma} \left( \epsilon_k + \frac{n_d U_d}{2n_0} - \frac{\sigma}{2} \frac{U_d}{n_0} \mu \right) c^\dagger_{k\sigma} c_{k\sigma} - \frac{U_d}{n_0} \left( \frac{n_d^2}{4} - \frac{\mu^2}{4} \right)$$  \hspace{1cm} (5)

We can deduce the Stoner relation Eq. 4 intuitively by assuming that the exchange splitting $\Delta \epsilon$ as a perturbation on the atomic levels is due to the reduction of the Coulomb repulsion $U_d$ of $\mu$ unpaired electrons for the $n_0 d$-bands. From the Hamiltonian Eq. 5 we can deduce the variation of the cohesive energy $E_{coh}$ from a non-magnetic state to a ferromagnetic state.

$$\Delta E_{mag} = E_{coh}^{ferro} - E_{coh}^{non \ mag}.$$  \hspace{1cm} (6)

$$= \Delta E_{coh} - \frac{1}{4n_0} U_{d\mu}^2 (\text{delocalized})$$

$$= \Delta E_{coh} - \frac{1}{4n_0} U_{d\mu}^2 + \frac{1}{4n_0} U_{xc d\mu}^2 (\text{localized})$$

Where $\Delta E_{coh} = E_{coh}^{\uparrow} + E_{coh}^{\downarrow} - E_{coh}^{\text{non \ mag}}$. As the magnetic state is stable for a ferromagnetic metal, $\Delta E_{mag}$ will always have a negative value. The correlations $U_{xc d \mu}$ in this case allows us to find in energy a delocalized behavior from a localized approximation. In the delocalized case, the effective Coulomb repulsion $U_d$ already contains all the correlations. It is possible to obtain the contribution of the correlations $U_{xc \mu}$ by using more or less complex methods. But in this work we will simply use the local density of states (LDOS) $n(E)$ obtained from a simple tight-binding calculation.

The tight-binding approximation gives the possibility to calculate a localized $d$-LDOS $n_d^{loc}(E)$ by diagonalizing a $5 \times 5$ Hamiltonian matrix constituted of the three $d$ hopping parameters $(dd, dd\sigma, dd\bar{\sigma})$ and where the parameters of the $s$ and $p$ orbitals are neglected. The delocalized $d$-LDOS $n_d^{deloc}(E)$ is obtained by diagonalizing a $9 \times 9$ matrix containing all the orbitals and restricting to the $d$-band by projection. We can define the contribution in energy due to the correlations $U_{d\mu}^{xc}$ or the transition energy from a localized state (loc.) to a delocalized state (deloc.) as a difference of cohesive or band energy :

$$U_{d\mu}^{xc} = \int_{-\infty}^{E_F} E n_d^{loc}(E) dE - \int_{-\infty}^{E_F} E n_d^{deloc}(E) dE$$  \hspace{1cm} (6)

$U_{d\mu}^{xc}$ is always positive since the localized state is always higher in energy than the delocalized state. This parameter $U_{d\mu}^{xc}$ therefore includes the screening effects or the impact of the $sp$-band on the $d$-band. If this parameter is large, then the localized approach can no longer describe energetically the considered transition metal. From the expression $U_{d\mu}^{xc}$, $U_{d\mu}^{xc}$ is highly dependent on the charge in the $d$-band. For this reason, we have calculated the values of $U_{d\mu}^{xc}$ correcting $\Delta E_{mag}$ from the localized approximation. This calculation gives the following values of $U_{d\mu}^{xc} : 1.3$ eV for bcc Fe, 1.5 eV for fcc Co and 2.1 eV for fcc Ni. These values are similar to those obtained to correct the band structures in another paper[13].

The value of the Coulomb parameter $U_d$ has already been studied in several references[11] Normally its value is given by the relation[22][13] :

$$U_d = E(n_d + 1) + E(n_d - 1) - 2E(n_d)$$  \hspace{1cm} (7)
\(E\) denotes a total energy which unfortunately cannot be calculated with the local density of states from a tight-binding calculation. Such a calculation leads to underestimated values of \(U_d\). On the other hand, we can deduce the value of \(U_d\) directly from the magnetism.

**III. RESULTS**

\[n_d(E) \text{ localized}
\]
\[n_d(E) \text{ delocalized}
\]

**FIG. 1.** Comparison of the LDOS of a localized \(d\)-band and a delocalized \(d\)-band.

Using the hopping parameters from the book of D. A. Papaconstantopoulos\[14\] with our own parameters by fitting the band structures, we have calculated the localized and delocalized local density of states. Fig. 1 shows that the localized \(d\)-LDOS has a small bandwidth and a higher density of states compared to the delocalized \(d\)-LDOS. A small bandwidth means that the electrons are very localized and describe a system in disagreement with the metallic nature of transition metals. This localized state is typically a situation where the \(s\) and \(p\) electrons are involved in covalent bonds and do not interact with the \(d\)-band. Such a situation defines much more the ground state of a transition metal oxide. The description of a transition metal using a localized \(d\)-LDOS leads to improper values of the cohesive or surface energies implying to apply corrections. The delocalized \(d\)-LDOS gives energetically the effects of the \(sp\)-band on the \(d\)-band and is the ground state of a transition metal.

The value of the constant \(U_d\) is found by fitting two curves to obtain the optimal value of the magnetic moment\[5\]. The first curve is the result of shifting the rigid LDOS by different values of \(\Delta \epsilon\) while keeping the charge in the \(d\)-band.

\[\mu(\Delta \epsilon) = n_{d\uparrow}(E) - n_{d\downarrow}(E) = n_d(E - \frac{\Delta \epsilon}{2}) + n_d(E + \frac{\Delta \epsilon}{2}) \]

(8)

The second curve is derived from the Stoner model Eq. 4.

\[\mu(\Delta \epsilon) = \frac{5}{U_d} \Delta \epsilon \]

(9)

Our calculation using a localized \(d\)-LDOS gives \(U_d = 3.04\) eV for fcc Co. This value is found by shifting the LDOS by an exchange splitting of \(\Delta \epsilon = 0.98\) eV to obtain a magnetic moment of about \(\mu = 1.61\) \(\mu_B\). This value is in agreement with photoemission results about \(\Delta \epsilon = 1.0\) eV\[15\]. In the same way, we obtain for bcc Fe and fcc Ni respectively \(U_d = 2.93\) eV and \(U_d = 2.21\) eV by shifting the \(d\)-LDOS with \(\Delta \epsilon = 1.29\) eV and \(\Delta \epsilon = 0.27\) eV. Values that are also in agreement with photoemission experience\[16\] for a coherent magnetic moment of 2.2 \(\mu_B\) in bcc Fe and 0.61 \(\mu_B\) in fcc Ni. These results are summarized in the table II where \(\Delta E_{mag} = \Delta E_{coh} - \frac{1}{4}U_{loc} \mu^2\) is calculated without a correction.

**TABLE I.** Calculated values of \(U_d\), \(\Delta \epsilon\) and \(\Delta E_{mag}\) of a localized \(d\) band.

|          | BCC Fe | FCC Co | FCC Ni |
|----------|--------|--------|--------|
| \(U_d^{loc.}\) [eV] | 2.93   | 3.04   | 2.21   |
| \(\mu\) [eV]      | 2.20   | 1.61   | 0.61   |
| \(\Delta \epsilon\) [eV] | 1.29   | 0.98   | 0.27   |
| \(I_s\) [eV]     | 0.98   | 0.61   | 0.44   |
| \(\Delta E_{mag}\) [eV] | -0.13  | 0.02   | -0.004 |

Not surprisingly, the localized approach does not correctly describe the \(d\)-band magnetism giving without any correction underestimated values and energies in disagreement with the stability of the ferromagnetic state despite its agreement with photoemission results. We can also notice that the value of the Coulomb parameter \(U_d^{loc.}\) must increase with the filling of the \(d\)-band\[11\] which is not the case here. A total energy calculated with this localized approximation is know to lead to surface energies half the value obtained by an \textit{ab initio} calculation.

In the case of a delocalized \(d\)-band, the exchange splitting \(\Delta \epsilon\) for bcc Fe, fcc Co and fcc Ni is respectively: 2.23 eV, 1.94 eV and 0.82 eV (comparable to another calculations\[20\]). As well as the respective values of \(U_d\): 4.98 eV, 6.02 eV and 6.72 eV to obtain an accurate magnetic moment. The results are summarized in the table II.

These values are in agreement with a ferromagnetic state where \(\Delta E_{mag}\) is always negative the three ferromagnetic materials. Unlike the localized approximation, we obtain a reasonable values of \(\Delta E_{mag}\) in agreement with an \textit{ab initio} calculation. Although the Coulomb parameter seems to be overestimated. This is due to the fact that it contains all the correlations.

This delocalized approximation on the other hand does not correctly describe the case where the \(d\)-band is loca-
The interactions between electrons in a solid are fundamental in solid state physics. The means to describe them remain approximate until we know how to better express the electronic correlations. We have seen in this work that the correlations allow to link two approaches that describe the $d$-band of a transition metal. These two approaches, called localized and delocalized, which seem quite different, are however well related. If the localized model seems to be a simple way to describe the $d$-band of a transition metal, it cannot completely describe the energies of these materials. When the impact of the $sp$-band on the $d$-band is important, the localized model cannot be used, it is then necessary to turn to a delocalized approach which correctly describes the metallic behavior. Although there are corrections like the one made on the magnetic energy for the localized model, these corrections are difficult to apply for all physical situations. The $d$-band called delocalized in this work means simply less localized. The $d$-band always remains more localized than the $s$- and $p$-bands. The tight-binding approximation in general remain the simplest and fastest tool to deduce the properties of complex materials by parameterizing the effects of electronic correlations. The semi-empirical magnetism as presented here can be extended to the study of magnetic surfaces and nanoparticles as well as to determine the properties of transition metal alloys.

### IV. CONCLUSION

TABLE II. Calculated values of $U_d$, $\Delta \epsilon$ and $\Delta E^{mag}$ of a delocalized $d$ band.

|          | BCC Fe | FCC Co | FCC Ni |
|----------|--------|--------|--------|
| $U_d^{deloc.}$ [eV] | 4.98   | 6.02   | 6.72   |
| $\mu$ [eV]   | 2.24   | 1.61   | 0.61   |
| $\Delta \epsilon$ [eV] | 2.23   | 1.94   | 0.82   |
| $I_d$ [eV]     | 0.99   | 1.20   | 1.34   |
| $\Delta E^{mag}$ [eV] | -0.40  | -0.22  | -0.035 |

This relation used simply in our case can not be generalized to all transition metals. The calculated gaps $E_g$ for the NiO, FeO et CoO are respectively 2.05 eV, 2.98 eV et 4.51 eV (in agreement with values obtained in the work of Anisimov et al.\textsuperscript{23} and Ashraf et al.\textsuperscript{23}).