Tight-binding : the correction of the simple d-band inconsistencies

Jacques R. Eone II

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The physical properties of the transitional metals from the bulk to the nanoparticles cannot be calculated accurately using a tight-binding approximation restricted to a simple d-band. The investigations on this approximation show the limitations, leading to a wrong cohesive energy compared to an all-electron tight-binding basis calculation. These investigations through the second moment approximation, the charge neutrality and the Stoner model allow us to derive the appropriate corrections to these inconsistencies.

I. INTRODUCTION

Within several years the tight-binding approximation theory has been split in two groups: the first group is the simple d-band approximation [1, 2], where the sp-band restricted to the transport is neglected for a sake of simplicity. The d-band is then localized and the cohesive and surface energies are not in agreement with an ab-initio calculation. The second approximation is the classic tight-binding model with all the orbitals in the basis [3], the d-band is partially delocalized giving a coherent cohesive and surface energies.

The cause of the split of the tight-binding approximation is the fact that the correlation between these two ways of description were unknown. These correlations of these two approaches were added recently [4]. A process is described where the localized d-band is partially delocalized due to a screening effect when the sp-band overlaps the d-band. As a consequence of this effect, we obtain a wider and delocalized d-band comparable to the results of a first principle calculation (density functional theory: DFT). This delocalized d-band is lower in cohesive and band energy compared to a localized d-band where the sp-band effects are neglected.

The correlations due to the sp-band are dependents on the distance, an interactomic potential without the sp-band cannot encompass the electronic structure and derive the correct physical properties. The second moment approximation (SMA) [5] limited to the d hopping integrals is not adapted for the study of the transitional metals. An atomic potential can be derived from the all-electron basis called the NRL-tight-binding model [6] compared to the second moment in the localized case. In the delocalized case, the surface energies can be derived easily respecting a so called partial charge neutrality: where the charge neutrality is only for the electron participating to the cohesive energy (d electron). The sp-band is not subjected to the charge neutrality. The partial charge neutrality leads to a linear muffin-tin orbitals charge distribution. The Stoner model gives the correct magnetic surface energy [4]. We will explore the correction of the SMA, a correct representation of an interactomic potential and finally the charge transfers and the magnetic properties.

II. SECOND MOMENT APPROXIMATION (SMA) : INCONSISTENCIES

A. Expression of the second moment approximation

The second moment approximation (SMA) describes a semi-classical interatomic potential. This interatomic potential is used until now despite the fact that the number of users do not fit the accuracy of this approximation. The SMA uses a linear expression which is derived from a rectangular density of states and then gives a direct expression of the total energy as:

\[ E_{tot}(r) = E_r(r) + E_b(r) \]

Where the attractive part \( E_b(r) \) is related to the band energy and the cohesion:

\[ E_b(r) = -\left\{ \sum \zeta^2 \exp \left[ -2q \frac{r_{ij}}{r_o} (1 - 1) \right] \right\}^{1/2} \]

And the repulsive part \( E_r(r) \) related to the ions is defined by:

\[ E_r(r) = \sum A \exp \left[ \frac{r_{ij}}{r_o} (1 - 1) \right] \]

Where \( q, \zeta, A \) are parameters to fit the total energy to an abinitio total energy at the equilibrium distance \( r_o \). In the nth moment theory, the \( \zeta \) is simply related to the hopping integral \( \beta \) in the localized d-band. This approximation is often restricted to the localized d-band, giving always the surface energie as the half of surface energy obtained by an abinitio calculation.

B. Correction of the simple d-band

In another calculation the sp-band added to the SMA gives a correction [7] without mentioning the origin of the divergence due to the sp-band. The absolute value of the surface energy are easy to obtain if we take into account the sp-band as the origin of the delocalized d-band in the reference [4].
We see on the figure [3] that without the sp effect in the d-LDOS (Local Density of States), the bandwidth is thin, the d electrons are then localized compared to the d-band with the sp effects. We deduce that the sp-band delocalizes the d-band by an impact in energy that we call correlation : $U_{xc}^d$ as the correlation energy between the localized d-band and the delocalized d-band. This correlation in the band structure can be quantized as the difference between the band energies in the localized and delocalized states.

$$U_{xc}^d = \int_{E_f}^{E} n_d(E)_{\text{localized}} EdE - \int_{E_f}^{E} n_d(E)_{\text{delocalized}} EdE$$

Where $n_d(E)$ is the density of states of the d-band. As the atomic energy is in the center on the two bands, this $U_{xc}^d$ is also a difference of the cohesive energy. This $U_{xc}^d$ is always positive whatever the element, so the delocalized state of the d-band is always lower in energy than the localized state. The delocalized state is then the ground state of a transitional metal. The process of reaching to the ground state is described in this document [8] as a screening effect of the d electrons by the sp-band. As the sp-band is dependent on the distance, therefore, $U_{xc}^d$ is Coulomb interaction dependent on the distance :

The delocalized d-band is always lower in energy than the localized d-band on the figure [2]. $U_{xc}^d$ is a curve decreasing with the distance to zero when $r \to \infty$, as the overlap of the delocalized sp electrons decreases with the distance. We reach the limit of the localized d-band when the interatomic distance is high $r >>$. The simple and localized d-band is then not suited to described correctly the electronic of the transitional metals near to the equilibrium. A correction of the localized d-band potential is simply :

$$E_{tot}(r) = E_r(r) + E_b(r) - U_{xc}^d(r)$$

But the dependency of $U_{xc}^d(r)$ on the distance is not a trivial function.

C. Case of the noble metals

Even if the SMA includes the sp-band or the correlations, the description of the noble metal will not be correct since the band energy of the noble metals as the platinum is not exponentially dependent.

In the figure [4], the band energy and the repulsive energy ($E_{tot} - E_{band}$) have a bell-shape and nodes. This
shape cannot be represented by an exponential function even if we fit in a small interval near to the equilibrium ($r_0 = 1.92$ nm for the Platinum). It is therefore not possible to have a fit of the total energy from the abinitio using the second or nth moment restricted in the d-band, because all the hopping parameters depends on distance (Figure 3).

Even if the hopping parameters depends on the distance, the complete description of the atomic energies is only possible with a dependency on the distance as shown in the figure 6.

The second moment do not encompass the variation of the atomic energies with the distance, this leads to an incorrect description of the atomic behaviors. We define the atomic energies $\epsilon_s$, $\epsilon_p$, and $\epsilon_d$, as:

$$\epsilon_d = a_1 \cdot \exp(b_1 \frac{r}{r_0}) + a_2 \cdot \exp(b_2 \frac{r}{r_0})$$

$$\epsilon_p = a_1 \cdot \exp(b_1 \frac{r}{r_0}) + a_3 \cdot \exp(a_4 \frac{r}{r_0})$$

The variation of $\epsilon_s$ is almost negligible. We obtain a potential quite similar to the one obtained by making an abinitio calculation. The interatomic semi-empirical potential is obtained by adding a repulsive contribution as a polynomial function. We have an accurate long range fit between the semi-empirical tight-binding and the abinitio interatomic potential encompassing the correct bandstructure in the Figure 7.

### III. Charge Neutrality Rules at the Surfaces and the Alloys

According to a density functional theory (DFT) calculation in a linear combination of atomic orbital (LCAO),
the charge is neutral in a transition metals and alloys per atom, par orbital and per chemical species [9] in the bulk and at the surface. This global charge neutrality derived from the Mulliken population is not consistent with a Bader charge analysis and some experimental results [10].

A. Charge transfer in the alloys

In the alloy CoPt L1₀ (stable phase) from a plane wave basis calculation, there is a charge transfer of 0.25e from the Cobalt to the Platinium using a Bader charge analysis. A further calculation on the other phases of CoPt gives also a charge transfer decreasing with the concentration of the Co. Of course restricted to the localized d-band, there is a conservation of the charge. But we cannot generalize the charge neutrality to a global charge neutrality in the delocalized case as this approximation simplified the difficulty using an all-orbitals spd tight-binding calculation. To handle this difficulty, the LDOS are filled simultaneous to obtain the sum of the valence electrons of the two species Co and Pt (9+10 electrons) as the Fermi level.

\[ N_e = \int_{-\infty}^{E_f} \left[ n_{Co}^{spd}(e) + n_{Pt}^{spd}(e) \right] de \]

As \( N_e \) is equal to 19 electrons, then we reach the Fermi level :

From the hopping parameters derived from an all-electron DFT calculation [11], by computing the partial charge in the d-band, we obtain a charge transfer from Co to Pt around 0.20 e consistent to the Bader charge analysis and the experimental results [10].

B. Charge transfer at the surface

At the surface, it was consider that there is a charge neutrality compared to the bulk. By applying this charge neutrality per orbitals, we obtain always the surface energies far from the result of an abinitio calculation. Although there is a charge neutrality, the electron distribution is an important factor. For this reason we use this assumption : there is charge neutrality at the surface, only for the electrons in the d-band.

The charge neutrality rule is applied this way : as the atoms at the surface are constrained to a charge neutrality, the atomic level of the d-electrons is shifted [12] modifying the local density of states like a relaxation and giving a fermi level (normaly defined from the bulk) respecting the charge at the surface compared to the bulk.

We introduce the shift on the atomic d energy \( \delta \epsilon_D \) and the selfconsitency treatment will be \( \epsilon_D = \epsilon_D + \delta \epsilon_D \) until the d charge neutrality is achieved [13]. Obviously, the atomic s and p energies (\( \delta \epsilon_s = 0 \) and \( \delta \epsilon_p = 0 \)) are not shifted. After the Fermi level defined by the d-band there is always an extra sp charge noted \( (S+1) \) as the free electrons (about 0.1e ) [11] in consistent with the charge distribution obtained by the spheres in a linear muffin tin orbitals (LMTO).

IV. STONER MAGNETISM

The Hubbard hamiltonian restricted in d-band in the mean field approximation gives the spin magnetic moment as (from [8] [14]):

\[ \mu = \frac{5}{U_d} \Delta E = \frac{\Delta E}{I} \]

Where \( U \) is the Hubbard parameter, \( I \) the Stoner parameter, \( \Delta E \) the exchange energy. The variation of energy due to the magnetization always negative for ferromagnetic elements can be write as :

\[ \Delta E_{mag} = \Delta E_{coh} - \frac{1}{20} U_d \mu^2 \]

\[ n_\uparrow(E) = n(E - \frac{\Delta E}{2}) \]

\[ n_\downarrow(E) = n(E + \frac{\Delta E}{2}) \]

and the magnetic moment is given by :

\[ \mu = \int_{-\infty}^{E_f} \left[ n(E - \frac{\Delta E}{2}) - n(E + \frac{\Delta E}{2}) \right] dE \]

This expression is fitted with the expression coming from the Stoner model \( \mu = 5 \cdot \Delta E/U \) to obtain the corresponding magnetic moment and the \( U \) [13]. For the Cobalt
CFC, in a simple d-band, we have $\Delta E_{mag} > 0$, where $U = 3\text{eV}$ as in the reference [8]. We observe that $U$ for the localized d-band is widely dependent on the distance in the Figure [8] to get the correct magnetic moment. The variation of the corrected localized $U$ is like the variation of the $U_d^{xc}$. We can conclude that the corrected localized $U$ with the distance contains the correlations $U_d^{xc}$).

![Image](image.png)

**FIG. 8:** Variation of $U$ with the distance with the localized d-band

The correction of the wrong energy is to use an all-orbital tight-binding calculation with a delocalized d-band for a $U = 6$ eV containing the correlations. Another correction, is to add directly the correlations $U_d^{xc}$ to the energy [8] representing the mathematical correction of the localized $U$.

$$\Delta E_{mag} = \Delta E_{coh} - \frac{1}{20} U_d \mu^2 - \frac{1}{20} U_d^{xc} \mu^2$$

V. CONCLUSION

The simple d-band approximation is limited in energy when we explore the physical properties of the transitional metals: the wrong cohesive and band energies can be corrected if we make a spd tight-binding calculation or if we add a correction by a correlation contribution. This correlation function gives a coherence from the SMA-interatomic potential to a magnetic calculation even if this function has not an analytic expression and differs from one transitional metal to another. Even if this local correction catch up with the first principle, the sp band contribution to the charge distribution is important for the charge transfer and the charge at the surface. A d-band limitation cannot describe the properties of the alloys as they combine a charge transfer and a small size where the surface properties are important. The localized electronic structure of the simple d-band gives a similitude to the electronic structure of a transitional metal oxides where the delocalized sp-band is bonded. The delocalized d-band is suited for the study of the transitional metal, unless the corrections are tedious. This study should be extended to the oxides and alloys of transitional metals.

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