Probabilities of Diagonal and Non-Diagonal Couplings between $d$ Electrons in Transition Metal

I. The $d$-Band Energy

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Abstract

It is shown that the full account of the non-diagonal couplings between $d$ electrons sited on different atoms in a transition metal implemented within the framework of the Wills-Harrison model leads to vanishing the $d$-band contribution to the internal energy.

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In the Wills-Harrison (WH) model [1] for the transition-metal internal energy, the $d$-band energy, $E_b$, is represented as follows (hereafter, per atom):

$$E_b = -\frac{1}{2} z_d \left(\frac{10 - z_d}{10}\right) W ,$$

where $z_d$ is the effective $d$-electron valence, $W$ - $d$-band width:

$$W = \left(\frac{12}{N} \sum_{m=1}^{N} \sum_{l=1}^{N} V_{d}^2(r_{ml})\right)^{1/2} ,$$

where $N$ is the number of atoms, $V_{d}(r)$ - effective potential of the $d$-$d$ interaction (hereafter, in atomic units):

$$V_{d}(r) = \frac{r_d^2}{r^3} K_b .$$
Here, $r_d$ is the $d$-state radius, $K_b$ - combinatoric coefficient, which in the WH approximation depends on diagonal only couplings between $d$ electrons sited on different atoms:

$$K_b^\text{WH} = \left( \sum_{m=-2}^{2} \frac{y_m^2}{5} \right)^{1/2},$$  

(4)

where $m$ is the magnet quantum number,

$$y_m = y_{|m|} = -\frac{(-1)^{|m|} 180}{\pi (2 + |m|)! (2 - |m|)!}.$$

(5)

From (4), (5)

$$K_b^\text{WH} = 28.06/\pi.$$  

(6)

In [2] was introduced the probability $p$ that all 25 $d-d$ couplings between two different atoms in a metal are equiprobable. Then, the probability of the WH limit case that only 5 equiprobable diagonal couplings are possible is $(1 - p)$. From this assumption, the probability of a non-diagonal coupling is $0.8p$, probability of a diagonal coupling is $(1 - 0.8p)$ and

$$K_b = \left[ \frac{1}{5} \left( \left(1 - \frac{4p}{5}\right)y_0^2 + \left(2 - \frac{6p}{5}\right)(y_i^2 + y_j^2) + \frac{4p}{5}y_0(y_i + y_j) + \frac{8p}{5}y_i y_j \right) \right]^{1/2}. $$

(7)

Now, allow us to apply (5) to (7). As a result,

$$K_b = K_b^\text{WH} / \sqrt{1 - p}.$$  

(8)

This surprising result denotes that at full account of the non-diagonal couplings between $d$ electrons sited on different atoms $(p = 1)$, the $d$-band energy in a transition metal is being become equal to zero.

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References


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