

New Results on the Density of Electronic States, Superexchange Interaction, and Electrical Conduction in Transition-Metal Salts

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(Received May 7, 2015)

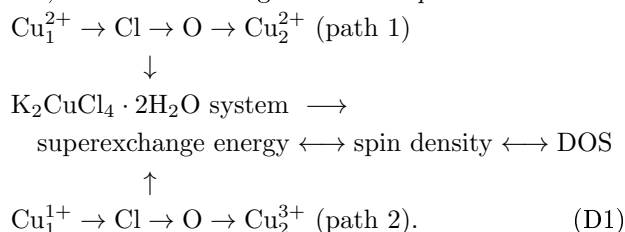
We investigate several issues related to the electronic states in the ligand orbital of a given transition-metal salt as, for example, a $\text{K}_2\text{CuCl}_4 \cdot 2\text{H}_2\text{O}$ -type compound. In fact, to get our calculation, we start from an expression for the electronic density of states in a compound of the above type. In addition, various aspects related to superexchange interaction in both the paramagnetic and ferromagnetic cases are discussed and the electronic conduction process in the ligand orbital is studied.

DOI: [10.12693/APhysPolA.128.394](https://doi.org/10.12693/APhysPolA.128.394)

PACS: 75.20.-g; 75.20.En; 75.50.-y; 75.76.+j

1. Introduction

As significant salts in the context of chemical physics, transition-metal salts (consider, for instance, $\text{K}_2\text{CuCl}_4 \cdot 2\text{H}_2\text{O}$ -type crystals) are interesting compounds from the point of view of magnetism in solids. In particular, the importance of these salts is manifested when one examines superexchange interaction. As a matter of fact, the superexchange interaction of the involved magnetic ions is strongly linked to the spin transfer to a non-magnetic ligand so a superexchange path is created. Considering the compound $\text{K}_2\text{CuCl}_4 \cdot 2\text{H}_2\text{O}$, we should remark the relevance of the superexchange path between the nearest neighbour copper ions. In this context, the p orbital of oxygen has an $1s$ unpaired electron of the hydrogen atom. All the p orbitals of Cl and O, assuming that they are a ligand, are filled with two mutually opposite spins. By regarding that these orbitals are equivalent and that the ligand between the Cu^{2+} ions is formed by these two anions, then one has a ligand with all p filled orbitals:



The Cu^{2+} magnetic ion of the above compound is surrounded by a distorted octahedron with two O^{2-} and four Cl^- ions that are bonded to the hydrogen atoms. One would notice that, apart from $3d_{x^2-y^2}$ (which contains one unpaired electron), all $3d$ shells of the Cu^{2+} ion are filled. On the other hand, we wish to note that path 1

in the diagram D1 has two electrons of mutually opposite spins in the same p orbital of the ligand, joining Cu_1^{2+} ($d_{x^2-y^2}$) and Cu_2^{2+} ($d_{x^2-y^2}$). This will be the key point in our formulation (Sect. 2) relative to density of states and electronic conduction in the ligand orbital. As a matter of fact, we will regard a two-electron approach to certainly discover new physics in transition-metal salts.

Unfortunately, investigating theoretically the magnetic properties of the compounds in question has received very little attention so only a few of theoretical papers on the subject have been published (see, for example, Refs. [1, 2]). The above properties can be investigated by starting from the concept of electronic density of states [1–3]. In fact, the theoretical-analytical approach presented here starts from the aforementioned concept. On the experimental side, also little work has been done. On the other hand, we wish to remark the relevance of the concept of superexchange interaction in magnetism of solids [4, 5] so important research efforts on the above subject are needed.

In transition-metal salts, on the one hand, the spin transfer to a non-magnetic ligand is directly related to regard the corresponding free-spin density and, on the other hand, we have said before that there is a clear dependence between the spin transfer and the superexchange interaction of the involved magnetic ions. Indeed, the free-spin density may be viewed as a key physical quantity with some interesting implications. In fact, the electronic density of states in the ligand orbital relative to a transition-metal salt relies (weakly) upon the free-spin density. Of course, this dependence will be expressed in the following by means of a significant relationship [1–3] from which determination of the total number of electronic states will be carried out. As a result, the total number of electronic states in the ligand orbital of a transition-metal salt does not (approximately) depend on the free-spin density. The main aspects related to our calculation will be discussed as well as some aspects of the superexchange interaction. On the other hand, we

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shall study the electronic conduction process in the ligand orbital. We want to notice that, surprisingly, nor experimental neither theoretical work on the subject has been published. Consequently, it is clear that our approach may be regarded as a substantial improvement of the state of the art. The paper is organized as follows: Sect. 2 is devoted to the electronic density of states in the ligand orbital, superexchange interaction in the paramagnetic case, and electrical conduction in the ligand orbital; Sect. 3 deals with superexchange interaction in the ferromagnetic case; Sect. 4 is a discussion of results; concluding remarks are given in Sect. 5.

2. Theoretical formulation: the paramagnetic case

Let us consider a transition-metal salt as, for instance, the compound mentioned in Sect. 1. As in the aforementioned example, by considering d (magnetic) and p (ligand, non-magnetic) orbitals, the corresponding total density of electronic states in the non-magnetic orbital as a function of the electronic energy, reads [1-3]:

$$g(E) \approx 2kV \{ \delta(E - E_p) + \rho_s [\delta(E - E_{d1}) + \delta(E - E_{d2})] \}, \quad (1)$$

where k is a non-negative real constant, V is the volume of the ligand (non-magnetic) orbital which, as we have said before, is assumed to be the p orbital, δ stands for (truncated to unity) Dirac delta function, $d1$ and $d2$ are the magnetic orbitals, and ρ_s stands for free-spin density. This density depends on temperature but, for convenience, this dependence will be not considered explicitly here. On the other hand, we wish to remark that formula (1) is so accurate from the mathematical-physics point of view and is also consistent with previous published work either experimental or theoretical [1-9]. In fact, expression (1) has been tested satisfactorily. In other words, the formula in question is a manifestly sound starting point to elaborate the following formulation.

Taking into account that $\rho_s \ll 1$, by integrating both sides of (1) over a finite energy interval denoted by ε , we get the total number of electronic states as follows:

$$N \approx 2kV. \quad (2)$$

From expression (2), it follows clearly that, in a first approximation, the total number of electronic states does not depend upon the free-spin density.

By assuming realistically that $E_{d1} \approx E_{d2}(= E_d)$ (see, for instance, Ref. [1]), then from relationship (1) one has that $g(E_p) \approx 2kV$ as well as

$$g(E_d) \approx 4kV\rho_s. \quad (3)$$

We note that $0 < E_p < E_d \leq \varepsilon$. On the other hand, from relation (2) it follows that $k \approx N/(2V)$ which, replaced into (1) with the approximation namely $E_{d1} \approx E_{d2}(= E_d)$ and taking into account that $\rho_s \ll 1$ (notice that the Dirac delta function used here is truncated to unity), then gives

$$g(E) \approx N\delta(E - E_p), \quad (4)$$

which, of course, may be obtained by neglecting ρ_s in formula (1) and integrating directly both sides of (1) for $0 \leq E \leq \varepsilon$.

Eliminating now ρ_s from expression (3) and the following relationship obtained from second-order perturbation theory [1]:

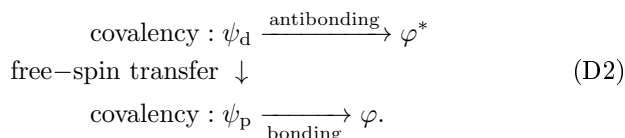
$$JW \approx 4(E_d - E_p)^2 \rho_s^2, \quad (5)$$

where J denotes superexchange interaction energy and W is the difference between the ground-state and excited-state energies of the system, then one finds

$$g(E_d) \approx \frac{2kV\sqrt{JW}}{E_d - E_p}. \quad (6)$$

On the other side, from expression (4) it follows that $g(E_d) \approx 0$ which is consistent with formula (6) because, by relationship (5), J is significantly small due to the fact that $\rho_s^2 \lll 1$. At this point, let us remember that $\rho_s \ll 1$ ($\rho_s \approx 0.003$ is a typical value) so $\rho_s^2 \lll 1$. Definitively, one may say that $g(E_d)$ is extremely small.

Now we wish to discuss some issues concerning the p orbital. First, notice that, by virtue of the covalent bonding involved in our transition-metal salt, the d orbital becomes the corresponding antibonding molecular orbital whereas the p orbital becomes the bonding molecular orbital:



Before and after bonding, the d orbital is singly occupied while the p orbital is doubly occupied so it contains two electrons of mutually opposite spins, that is, the quantum state of these two electrons is the same (consider the exclusion principle; see Sect. 1). Therefore, one has that $N = 1$ which, inserted into (4), yields $g(E) \approx \delta(E - E_p)$. From the fact that $N = 1$ with formulae (2) and (6), it follows:

$$g(E_d) \approx \frac{\sqrt{JW}}{E_d - E_p}. \quad (7)$$

Next we will consider the paramagnetic phase of a transition-metal salt. On the other hand, note that the spatial electron density in the ligand orbital is $2/V$ so the Fermi level of the ligand orbital at zero absolute temperature reads

$$E_F = \frac{\hbar^2}{2m} \left(\frac{6\pi^2}{V} \right)^{2/3}. \quad (8)$$

Equating (8) with mv_F^2 (notice that the involved mass is $2m$), where v_F is the magnitude of the Fermi velocity at zero absolute temperature, then one gets

$$v_F = \frac{\hbar}{\sqrt{2m}} \left(\frac{6\pi^2}{V} \right)^{1/3}, \quad (9)$$

which gives rise to a current density of magnitude $j = 2ev_F/V$, that is

$$j = \frac{\sqrt{2}e\hbar}{m} \left(\frac{6\pi^2}{V^4} \right)^{1/3}, \quad (10)$$

where e is the absolute value of the electron charge.

One has that $g(E_F) \approx \alpha j$ where α is a non-negative constant (see, for instance, Refs. [10–13]). From this fact together with that $N = 1$, with relationship (4) when the electronic conduction occurs, i.e., $E_F = E_P$, and with Eq. (10) in atomic units, then it follows:

$$\alpha \approx \frac{1}{\sqrt{2}} \left(\frac{V^4}{6\pi^2} \right)^{1/3}. \quad (11)$$

We emphasize that the electron conduction takes place in the ligand orbital when the energy of this orbital equals the corresponding Fermi level. On the other hand, since $E_d > E_p$, from Eq. (8) it follows in atomic units:

$$E_d > \frac{1}{2} \left(\frac{6\pi^2}{V} \right)^{2/3}. \quad (12)$$

Inequality (12) provides an inaccessible lower bound for the energy of the d orbital.

This bound depends significantly upon the volume of the ligand orbital.

3. The ferromagnetic case

As a, say, typical example, the $K_2CuCl_4 \cdot 2H_2O$ -type solids can exhibit ferromagnetic behaviour; a solid of this type can behave as insulating Heisenberg ferromagnet. So, in the following, we shall tackle the above crystals in the ferromagnetic case. As a matter of fact, we will focus on the insulating Heisenberg ferromagnet which, for obvious reasons, will not be treated from the standpoint of electron conduction. In this framework, the electron energy in the ligand orbital reads $E = -Js_1s_2$ where $s_1 = s_2 = 1/2$ are the spin values relative to the two electrons which occupy the above orbital. From the conjunction of this fact with formula (5), it follows:

$$E \approx -\frac{(E_d - E_p)^2 \rho_s^2}{W}. \quad (13)$$

Note that $t = (E_d - E_p) \rho_s$ is the corresponding hopping matrix element so, by relation (13), one has briefly that $E \approx -t^2/W$.

Moreover, we have (see, for instance, Ref. [1]) the following expression, which holds for the paramagnetic case

$$J = \frac{\langle \psi_d | \hat{H} | \psi_p \rangle^2}{E_d - E_p}, \quad (14)$$

where \hat{H} is the interaction Hamiltonian operator of perturbation. In antibonding, the p orbital of the ligand is viewed as a perturbation to the d orbital of the copper ion while in bonding, the d orbital is a perturbation of the p orbital.

Concerning, in particular, the $K_2CuCl_4 \cdot 2H_2O$ system, the d orbital of the Cu^{2+} ion overlaps with the p orbital of the ligand (the main bond between a copper ion and the ligand is created with the d orbital of the Cu^{2+} ion). Then, the aforementioned overlapping involves the matrix element namely $\gamma_{dp} = \langle \psi_d | \hat{H} | \psi \rangle$. Consequently,

from formula (5) with expression (14), one gets

$$\left(\frac{\gamma_{dp}}{t} \right)^2 \approx 2 \left(\frac{E_d - E_p}{W} \right). \quad (15)$$

In practice, we have that $E_d - E_p \approx 1$ eV and $W \approx 2$ eV (see, for example, Ref. [14]) so, from relation (15) it follows that $\gamma_{dp} \approx t$. Of course, relation (15) holds in the paramagnetic case. After formula (13), we have written $E \approx -t^2/W$ so, in practice, we have that $E \approx -\gamma_{dp}^2/W$.

4. Discussion

For the first time, we have proposed a theoretical model relative to the electronic density of states in the ligand orbital of transition-metal salts, the total number of these states, superexchange interaction, and electron conductance by considering the paramagnetic state. In particular, the total electronic density of states (in the ligand orbital) at the Fermi level (at zero absolute temperature) has been determined. Of course, the Sommerfeld expansion should be employed to extrapolate the Fermi level at any temperature. The current density in the ligand orbital has been also determined so the main aspects of the electronic conduction process in the ligand orbital have been discussed. The ferromagnetic case has been also treated. In fact, we have concentrated on the insulating Heisenberg ferromagnet (see relations (13), (14) and (15)), which, to date, has not still been tackled theoretically in relation to transition-metal salts.

On the other hand, we want to remark the relevance of our study within the framework of the concept of covalent bond related to magnetism in solids (see Sect. 2 and Sect. 3, expression (14)). In this context, by virtue of perturbation theory, we can write (see diagram D2 and, for instance, Ref. [1]):

$$\varphi = \psi_p + \gamma_1 \psi_d, \quad (16)$$

$$\varphi^* = \psi_d - \gamma_2 \psi_p, \quad (17)$$

where φ and φ^* denote bonding and antibonding molecular orbitals respectively whereas γ_1 and γ_2 are coefficients to be determined by considering

$$\varphi^* = \psi_d^{(0)} + \psi_d^{(n)} = \psi_d + \frac{\gamma_{dp} \psi_p}{E_d - E_p}, \quad (18)$$

$$\varphi = \psi_p^{(0)} + \psi_p^{(n)} = \psi_p - \frac{\gamma_{dp} \psi_d}{E_d - E_p}, \quad (19)$$

where $\psi_d^{(n)}$ and $\psi_p^{(n)}$ are the respective n -th perturbed terms.

Equating, on the one hand, formulae (16) and (19) and, on the other hand, (17) and (18), then it follows:

$$\gamma_1 = \gamma_2 = -\frac{\gamma_{dp}}{E_d - E_p}. \quad (20)$$

We have said that, in practice (see, for instance, Ref. [14]), one has $\gamma_{dp} \approx t$ so expression (20) can be rewritten as $\gamma_1 = \gamma_2 \approx -t/(E_d - E_p)$.

Our formulation should be certainly useful to study the magnetic properties of amorphous salts of the above type. In addition, optical absorption (particularly far-infrared absorption) in these compounds could be calculated [2].

Within this context, by using a formula involving $g(E)$ given by expression (1), the coefficient of optical absorption can be computed [2].

5. Concluding remarks

Formulae (8) to (12) are the core to do future studies on electron transport through certain nanostructures. From the previous considerations upon electron conduction through transition-metal salts in the paramagnetic state, one may establish a two-electron model suitable to investigate crucial problems relative to electron transport in, for example, quantum dots. At this point, we recall the atom-like nature of a quantum dot. This nature resembles the physics of the ligand orbital in a metal-transition salt. Therefore, key aspects of the above physics should be extrapolated to study electron transport in quantum dots. These studies would be analytical (in the spirit of, for instance, Refs. [15–19]) in order to elaborate new well-grounded theories.

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