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Origin of the magnetic exchange in insulators: Localized vs. delocalized electrons

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Abstract. The present study focuses on the fundamental physical principles underlying the exchange interactions between two metallic centers in magnetic insulators. Using the variational method in conjunction with the Heisenberg model, we demonstrate that the exchange symmetry is tightly related to the magnetism of the considered system and that the electrons' distributions affect the corresponding exchange interactions.

1. Introduction

Exchange interaction theory have played a crucial role in the advancement of the quantum theory of solids and it has been an extensive subject of studies in many areas of physics, such as atomic physics and magnetism [1–6]. Exchange interactions have no classical analog and are invaluable source of insight in microscopic effects. They can be used to address the magnetism of molecular magnets [7–9], low-dimensional systems [10–12] and other magneto-related effects [13–15], including magnetic resonances at visible light frequencies [16, 17].

Owing to the chemical composition of magnetic compounds and thus the associated interatomic bonds, the exchange mechanism may be either direct or indirect. Direct exchange is encountered in the absence of intermediate bonding atoms, with H_2 and O_2 being typical examples [18, 19]. Apart from the metallic bonding, the indirect exchange takes place solely mediated by non-magnetic atoms, like in Mn based complexes [20, 21]. It includes the subgroup of superexchange and double exchange mechanisms [22]. Those refer to compounds consisting of metallic centers characterized by the same and different valence, respectively. In other words, the superexchange mechanism applies to insulators (such as $Pb_3Cu_3(PO_4)_4$ illustrated in figure 1) and the double-exchange one to semiconductors. In metallic compounds both direct and indirect mechanisms are present.

The present paper discusses the basic physical principles underlying the magnetic exchange effect in insulators and demonstrates how exchange interactions are affected by valence electrons distributions. To this end, we use a spin-half dimer unit with identical metal centers, where on one hand the electrons are taken as localized to a large extent occupying atomic states and on the other as delocalized occupying molecular orbitals. In both cases, we use the Heisenberg Hamiltonian to derive the explicit representation of the corresponding exchange coupling and discuss of the resulting expressions.

2. Two-electron approximation

In order to demonstrate the relation of exchange symmetry to magnetism, we consider a magnetic unit that may be described by a two-electron system. Prominent candidates are compounds consisting of



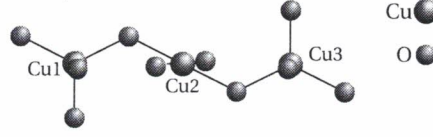


Figure 1. Structural fragment of the magnetic insulator $\text{Pb}_3\text{Cu}_3(\text{PO}_4)_4$. The magnetic properties are governed by the superexchange via the oxygen atoms. For brevity the Pb atoms are not illustrated.

isolated pairs of indistinguishable spin-half metallic centers or represent a dimeric single molecular magnets. Such units exhibit a single magnetic excitation and a plateau in the magnetization, see for example copper based materials [23–26]. Their magnetic properties are studied within the adiabatic approximation and negligible hyperfine magnetic interactions. Thus, they are viewed as non-relativistic multi-electron systems composed of N valence electrons, with $N-2$ distributed over $(N-2)/2$ singlet pairs without affecting the correlations between the remaining two electrons. Moreover, in the zero-field case the contribution of all $N-2$ electrons' dipole magnetic moments to the system's magnetic properties may be ruled out. As a result, the spins of $(N-1)$ -th and N -th electrons are thought to govern the corresponding low-temperature and zero-field magnetic properties.

2.1. The semi-classical Hamiltonian

In the system under consideration all bonding processes are governed by the electron-electron and electron-nuclei Coulomb interactions. All fine and hyperfine magnetic interactions are negligible and hence in the two electrons' approximation the canonical Hamiltonian reads

$$\hat{H} = \frac{\hat{\mathbf{p}}_{N-1}^2}{2m_e} + \frac{\hat{\mathbf{p}}_N^2}{2m_e} + \hat{K}_o + \hat{R}(r_{N-1,N}) + \hat{V}(r_{N-1}, r_N) + \sum_{\eta} \hat{U}(r_{\eta,N-1}, r_{\eta,N}) + \sum_{\eta} \hat{U}(r_{\eta}), \quad (1)$$

where for $i = N-1, N$, $\hat{\mathbf{p}}_i$ is the i -th electron's momentum operator, m_e is the electron's rest mass, $\hat{K}_o \equiv K_o$ is the average kinetic energy of all $N-2$ electrons, $\hat{R}(r_{N-1,N})$ accounts for the repulsion between $(N-1)$ -th and N -th electrons, $\hat{V}(r_{N-1}, r_N)$ takes into account the interaction of $(N-1)$ -th and N -th electrons in the averaged field induced by the remaining $N-2$ electrons, $\hat{U}(r_{\eta,N-1}, r_{\eta,N})$ is the potential energy operator accounting for the interaction of both electrons with the η nucleus and $\hat{U}(r_{\eta}) \equiv U(r_{\eta})$ is the averaged energy of the interaction between the η nucleus and all remaining $N-2$ electrons. Here, $r_{N-1,N} = |\mathbf{r}_{N-1} - \mathbf{r}_N|$ and $r_{\eta,i} = |\mathbf{r}_i - \mathbf{r}_{\eta}|$, where for $i = N-1, N$, $\mathbf{r}_i = (x_i, y_i, z_i)$ is the position vector of the i -th electron, with $r_i = |\mathbf{r}_i|$ and \mathbf{r}_{η} is the position vector of the η nucleus. Notice that, since we work in the adiabatic approximation, all nucleus-nucleus interactions are excluded from (1).

To compute the energy spectrum of Hamiltonian (1) we apply the variational approach with state functions depending on the total spin $s_{N-1,N}$ and magnetic $m_{N-1,N}$ quantum numbers of the electron pair formed by $(N-1)$ -th and N -th electrons.

2.2. The effective spin Hamiltonian

The considered system is fully isotropic. Therefore, to reproduce the variational energy spectrum obtained via (1) and describe the relevant magnetic features, we employ the Heisenberg model

$$\hat{\mathcal{H}} = cJ\hat{\mathbf{s}}_1 \cdot \hat{\mathbf{s}}_2, \quad (2)$$

where $c = \pm 1$, J is the corresponding effective exchange coupling and $\hat{\mathbf{s}}_i = (\hat{s}_i^{\alpha})_{\alpha \in \mathbb{K}}$, with $i = 1, 2$ and $\mathbb{K} = \{x, y, z\}$, is the spin operator of the i -th effective spin-half metal center.

The total spin $s = 1$ and magnetic $-s \leq m \leq s$ quantum numbers are good quantum numbers, with $s \equiv s_{N-1,N}$ and $m \equiv m_{N-1,N}$. Hence, Hamiltonian (2) satisfies

$$\hat{\mathcal{H}}|s, m\rangle = \mathcal{E}_{s,m}|s, m\rangle, \quad \mathcal{E}_{s,m} = cJ \frac{2s(s+1)-3}{4}, \quad \forall m. \quad (3)$$

In the case of triplet ground state $c = -1$ and for singlet one $c = 1$.

3. Atomic and molecular states

To study the mechanisms of electron exchange one has to account for the peculiar features of the considered compound, such as type and number of bonded atoms, their arrangements and other properties. Accordingly, the electrons may be considered as localized or delocalized. Localized to a large extent electrons can be approximately described by atomic-like states. Delocalized electrons occupy molecular orbitals.

3.1. Atomic-like states

An atomic-like state of the i -th electron, with $i = N - 1, N$, is given by

$$\psi_{\tau_{i,\eta},m_i}^\eta(\mathbf{r}_i) \equiv \prod_{\alpha \in \mathbb{K}} \psi_{\tau_{i,\eta}}^\eta(\alpha_i) |m_i\rangle, \quad (4)$$

where $m_i = \pm \frac{1}{2}$ is the corresponding spin-magnetic quantum number and $\tau_{i,\eta}$ labels the principal atomic shell and subshell the i -th electron occupies. Therefore, if the N -th electron occupy the $2p_z$ orbital on the 2-nd metal center, then its distribution around the associated nucleus is described by the state $\psi_{2p_z,m_N}^{(2)}(\mathbf{r}_N)$, where $\tau_{N,2} \rightarrow 2p_z$. With respect to a particular value of η , the state functions (4) are orthonormal. On the other hand, for different atomic centers they overlap. The overlap integral between two atomic states of the same orbital symmetry reads

$$\varrho_{\tau_{i,\eta}\tau_{i,\eta'}} = \int \tilde{\psi}_{\tau_{i,\eta},m_i}^\eta(\mathbf{r}_i) \psi_{\tau_{i,\eta'},m_i}^{\eta'}(\mathbf{r}_i) d\mathbf{r}_i, \quad 0 \leq \varrho_{\tau_{i,\eta}\tau_{i,\eta'}} < 1. \quad (5)$$

3.2. Molecular orbitals

Molecular orbitals are constructed as linear combinations of the atomic states (4). By analogy to atomic orbitals, molecular orbitals are distinct by energy, symmetry and describe the electrons' distribution within the considered molecule or chemical complex.

Let $n \in \mathbb{N}$ indicates the number of each molecular orbital with respect to its energy, such that the lowest value of n corresponds to the most energetically favorable one. Therefore, we represent the n -th molecular orbital occupied by the i -th electron by

$$\phi_{n,m_i}(\mathbf{r}_i) = \sum_{\eta} c_n^\eta \psi_{\tau_{i,\eta},m_i}^\eta(\mathbf{r}_i), \quad (6)$$

where the coefficients c_n^η are functions of the overlap integrals between the atomic-like states, see (5). Hence, in contrast to (4), the states in (6) form an orthonormal basis set.

4. Localized electrons

4.1. State functions

The metal centers are indistinguishable, thus $\tau_{N-1,1} \equiv \tau_{N,2} \rightarrow \lambda$, where λ indicate the occupied atomic shell and subshell. Further, in constructing the total state we exclude the case when the $(N - 1)$ -th and N -th electrons reside on the same metal center, since according to the Pauli exclusion principle the electrons would be paired in singlet and the probability of observing a singlet-triplet transition equals zero. Therefore, accounting for all four Slater determinants and considering the constructive and destructive superpositions between the determinants with $m_{N-1} = \frac{1}{2}$, $m_N = -\frac{1}{2}$ and $m_{N-1} = -\frac{1}{2}$, $m_N = \frac{1}{2}$, as a general expression for the total state we get

$$\Psi_{s,m}(\mathbf{r}_{N-1}, \mathbf{r}_N) \equiv \frac{1}{\sqrt{2f_s}} (\psi_\lambda^{(1)}(\mathbf{r}_{N-1}) \psi_\lambda^{(2)}(\mathbf{r}_N) + (-1)^s \psi_\lambda^{(2)}(\mathbf{r}_{N-1}) \psi_\lambda^{(1)}(\mathbf{r}_N)) |s, m\rangle, \quad (7)$$

where we use the bra-ket notation (4) and $f_s = (1 + (-1)^s \varrho^2)$, with $\varrho_{\lambda\lambda} \rightarrow \varrho$ since in the considered system the λ orbitals are unique. The spin component of the state function (7) is symmetric for $s = 1$ and antisymmetric for $s = 0$.

4.2. Key integrals

Let us present the four expectation values of (1) that describes the long-distance physics of the effective spin model (2). These are: The energy of the system when both electrons reside on the same metal center

$$u = \iint \bar{\psi}_\lambda^\eta(\mathbf{r}_{N-1}) \bar{\psi}_\lambda^\eta(\mathbf{r}_N) \hat{H} \psi_\lambda^\eta(\mathbf{r}_{N-1}) \psi_\lambda^\eta(\mathbf{r}_N) d\mathbf{r}_{N-1} d\mathbf{r}_N \quad (8a)$$

and the energy associated to the case when the N -th electron hops between both ions,

$$t = \iint \bar{\psi}_\lambda^{(1)}(\mathbf{r}_{N-1}) \bar{\psi}_\lambda^{(1)}(\mathbf{r}_N) \hat{H} \psi_\lambda^{(1)}(\mathbf{r}_{N-1}) \psi_\lambda^{(2)}(\mathbf{r}_N) d\mathbf{r}_{N-1} d\mathbf{r}_N. \quad (8b)$$

Further, we have the energy in the case the $(N-1)$ -th electron reside on the 1st metal center and the N -th one on the 2nd metal center, or vice versa,

$$v = \iint \bar{\psi}_\lambda^{(1)}(\mathbf{r}_{N-1}) \bar{\psi}_\lambda^{(2)}(\mathbf{r}_N) \hat{H} \psi_\lambda^{(1)}(\mathbf{r}_{N-1}) \psi_\lambda^{(2)}(\mathbf{r}_N) d\mathbf{r}_{N-1} d\mathbf{r}_N \quad (8c)$$

and the energy of the direct exchange between both electrons

$$d = \iint \bar{\psi}_\lambda^{(1)}(\mathbf{r}_{N-1}) \bar{\psi}_\lambda^{(2)}(\mathbf{r}_N) \hat{H} \psi_\lambda^{(2)}(\mathbf{r}_{N-1}) \psi_\lambda^{(1)}(\mathbf{r}_N) d\mathbf{r}_{N-1} d\mathbf{r}_N. \quad (8d)$$

As we have discussed above, within the atomic state approximation, the probability of observing magnetic transition when both electrons reside on the same metal center is zero. Therefore, the probability of measuring the energy values (8a) and (8b) is also zero. It is then clear that the exchange coupling in (2) will depend only on the expectation values (8c) and (8d).

4.3. Exchange coupling

The energy of triplet and singlet spin levels are calculated as expectation values of the Hamiltonian (1) with respect to the triplet and singlet functions (7). We have,

$$E_{s,m} = \iint \bar{\Psi}_{s,m}(\mathbf{r}_{N-1}, \mathbf{r}_N) \hat{H} \Psi_{s,m}(\mathbf{r}_{N-1}, \mathbf{r}_N) d\mathbf{r}_{N-1} d\mathbf{r}_N, \quad (9)$$

where $\langle m, s | s', m' \rangle = \delta_{ss'} \delta_{mm'}$. Since Hamiltonian (1) is spin independent, over the expectation values (9) we construct an effective Hamiltonian which is diagonal in the spin space, satisfying

$$\hat{H}_{\text{eff}} |s, m\rangle = E_{s,m} |s, m\rangle, \quad E_{s,m} = \frac{v + (-1)^s d}{1 + (-1)^s \rho^2}, \quad \forall m. \quad (10)$$

The overlap integral is usually small and the system's ground state depends mostly on the sign of v and d . Thus, when $v > 0$ and $d > 0$, the kinetic and repulsion terms in (1) outweigh the attraction terms and hence the ground state is triplet. As a result, in the Heisenberg model (1), we have $c = -1$.

Henceforth, we assume that the Coulomb attraction potentials dominate. In other words, we have $v < 0$ and $d < 0$ which in turn leads to a singlet ground state. Therefore, as the Heisenberg spectrum (3) and the variational one (10) describe the same energy transition, we have $\mathcal{E}_{1,m} - \mathcal{E}_{0,0} = E_{1,m} - E_{0,0}$, where within the considered ground state $c = 1$. Consequently, for the exchange coupling we obtain

$$J = 2 \frac{|d| - |v| \rho^2}{1 - \rho^4}. \quad (11)$$

The last relation demonstrates how the magnetic exchange effect depends on the direct overlap between atomic-like states of both electrons. When the metal centers are indirectly coupled the overlap integral $\rho \rightarrow 0$, the integral (8d) vanish and so does the exchange coupling (11). Therefore, the atomic state approximation is not consistent with the concept of indirect interactions between metal centers. The adequate approach is to consider the electrons as delocalized.

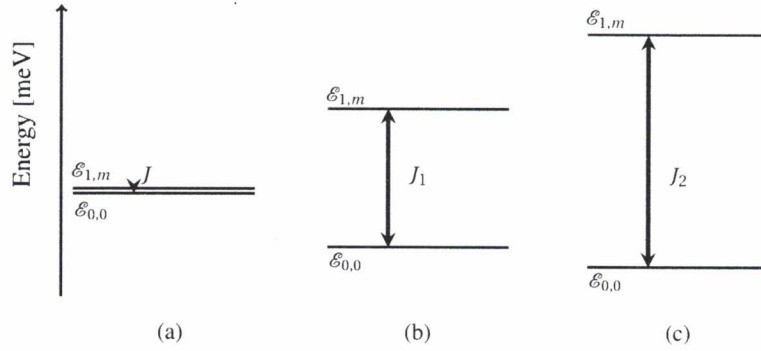


Figure 2. Heisenberg energy spectrum (3) in case of: (a) localized electrons with exchange coupling (11); (b) delocalized electrons with dominated kinetic terms with J_1 given by (20); (c) delocalized electrons with superexchange coupling J_2 given by (19).

5. Delocalized electrons

5.1. State functions

Assuming that the electrons in the considered system occupy the molecular orbitals (6), we get $(N-2)/2$ core and 2 active orbitals. The core molecular orbitals represent all $N-2$ singlet pairs. Both active molecular orbitals, accordingly $(n-1)$ -th and n -th, are the highest in energy and may be occupied by the $(N-1)$ -th and N -th electrons. As an additional approximation, we assume that both active orbitals have the same energy.

To obtain a general expression for the two-electron state functions we consider two cases. First, at singlet and triplet states the $(N-1)$ -th and N -th electrons occupy distinct molecular orbitals. Second, both electrons occupy the same molecular orbital. In the first case, the state is build up from four Slater determinants such that the non-magnetic triplet and singlet states are given as a superposition of determinants with $m_{N-1} = \frac{1}{2}$, $m_N = -\frac{1}{2}$ and $m_{N-1} = -\frac{1}{2}$, $m_N = \frac{1}{2}$. Thus, with respect to (6) and the bra-ket notation (4), by analogy to (7) we have

$$\Psi_{s,m}(\mathbf{r}_{N-1}, \mathbf{r}_N) \equiv \frac{1}{\sqrt{2}} (\phi_{n-1}(\mathbf{r}_{N-1})\phi_n(\mathbf{r}_N) + (-1)^s \phi_n(\mathbf{r}_{N-1})\phi_{n-1}(\mathbf{r}_N)) |s, m\rangle. \quad (12)$$

For the second case, due to the Pauli exclusion principle, the determinants associated to the triplet states vanish. Then, we end up with the constructive and destructive superpositions of singlet states of the $(n-1)$ -th and n -th orbitals

$$\Psi_{s,m}^{\pm}(\mathbf{r}_{N-1}, \mathbf{r}_N) = \frac{\delta_{0s}}{\sqrt{2}} (\phi_{n-1}(\mathbf{r}_{N-1})\phi_{n-1}(\mathbf{r}_N) \pm \phi_n(\mathbf{r}_{N-1})\phi_n(\mathbf{r}_N)) |s, m\rangle, \quad (13)$$

The functions (12) and (13) form an orthonormal basis set that accounts for all spin-orbital configurations.

5.2. Key integrals

Writing down the four integrals analogous to (8), we have to bear in mind that $(n-1)$ -th and n -th molecular orbitals are of the same energy. Therefore, we have two integrals favoring exclusively the singlet ground state. The single orbital integral

$$U = \iint \bar{\phi}_n(\mathbf{r}_{N-1})\bar{\phi}_n(\mathbf{r}_N) \hat{H} \phi_n(\mathbf{r}_{N-1})\phi_n(\mathbf{r}_N) d\mathbf{r}_{N-1} d\mathbf{r}_N, \quad (14a)$$

and

$$T = \iint \bar{\phi}_n(\mathbf{r}_{N-1})\bar{\phi}_n(\mathbf{r}_N) \hat{H} \phi_n(\mathbf{r}_{N-1})\phi_{n-1}(\mathbf{r}_N) d\mathbf{r}_{N-1} d\mathbf{r}_N, \quad (14b)$$

describing the case when the N -th electron hops between n -th and $(n-1)$ -th molecular orbitals. The other two integrals are

$$V = \iint \bar{\phi}_{n-1}(\mathbf{r}_{N-1}) \bar{\phi}_n(\mathbf{r}_N) \hat{H} \phi_{n-1}(\mathbf{r}_{N-1}) \phi_n(\mathbf{r}_N) d\mathbf{r}_{N-1} d\mathbf{r}_N, \quad (14c)$$

corresponding to the case with both electrons occupy different molecular orbitals and

$$D = \iint \bar{\phi}_{n-1}(\mathbf{r}_{N-1}) \bar{\phi}_n(\mathbf{r}_N) \hat{H} \phi_n(\mathbf{r}_{N-1}) \phi_{n-1}(\mathbf{r}_N) d\mathbf{r}_{N-1} d\mathbf{r}_N, \quad (14d)$$

associated with the direct exchange of the electrons.

Integrals (14a) and (14b) are not zero only when the electrons' spins are antiparallel, see (13). Hence, they favor singlet ground state where the dimer resemble a closed shell system. The other two integrals, (14c) and (14d), conserve the number of active orbitals at singlet state, see also (12). Accordingly, they may favor either a parallel and antiparallel ground state spin configuration.

5.3. Exchange coupling

In constructing the variational energy spectrum of Hamiltonian (1) under the functions (12) and (13), we obtain the following expectation values

$$\iint \bar{\Psi}_{s,m}(\mathbf{r}_{N-1}, \mathbf{r}_N) \hat{H} \Psi_{s,m}(\mathbf{r}_{N-1}, \mathbf{r}_N) d\mathbf{r}_{N-1} d\mathbf{r}_N = V + (-1)^s D, \quad (15a)$$

$$\iint \bar{\Psi}_{s,m}^{\pm}(\mathbf{r}_{N-1}, \mathbf{r}_N) \hat{H} \Psi_{s,m}^{\pm}(\mathbf{r}_{N-1}, \mathbf{r}_N) d\mathbf{r}_{N-1} d\mathbf{r}_N = \delta_{0s} (U \pm D), \quad (15b)$$

$$\iint \bar{\Psi}_{s,m}(\mathbf{r}_{N-1}, \mathbf{r}_N) \hat{H} \Psi_{s,m}^{+}(\mathbf{r}_{N-1}, \mathbf{r}_N) d\mathbf{r}_{N-1} d\mathbf{r}_N = 2\delta_{0s} T, \quad (15c)$$

$$\iint \bar{\Psi}_{s,m}(\mathbf{r}_{N-1}, \mathbf{r}_N) \hat{H} \Psi_{s,m}^{-}(\mathbf{r}_{N-1}, \mathbf{r}_N) d\mathbf{r}_{N-1} d\mathbf{r}_N = 0, \quad (15d)$$

$$\iint \bar{\Psi}_{s,m}^{+}(\mathbf{r}_{N-1}, \mathbf{r}_N) \hat{H} \Psi_{s,m}^{-}(\mathbf{r}_{N-1}, \mathbf{r}_N) d\mathbf{r}_{N-1} d\mathbf{r}_N = 0. \quad (15e)$$

Due to the existence of multiple spin-orbital configurations the singlet states $\Psi_{0,0}(\mathbf{r}_{N-1}, \mathbf{r}_N)$ and $\Psi_{0,0}^{+}(\mathbf{r}_{N-1}, \mathbf{r}_N)$ mix, see (15c), yielding to a non-diagonal matrix representation of the corresponding effective Hamiltonian \hat{H}_{eff} .

Now, working with the diagonal effective basis, we get

$$\hat{H}_{\text{eff}} |\Omega_{s,m}^{n_s}\rangle = E_{s,m}^{(n_s)} |\Omega_{s,m}^{n_s}\rangle,$$

where n_s indicates the zero field degeneracy of the spin levels and

$$E_{1,m}^{(1)} = V - D, \quad m = 0, \pm 1, \quad (16a)$$

$$E_{0,0}^{(1)} = D + \frac{U+V}{2} - \sqrt{4T^2 + \frac{(U-V)^2}{4}}, \quad (16b)$$

$$E_{0,0}^{(2)} = D + \frac{U+V}{2} + \sqrt{4T^2 + \frac{(U-V)^2}{4}}, \quad E_{0,0}^{(3)} = U - D. \quad (16c)$$

Hence, the states $|\Omega_{0,0}^1\rangle, |\Omega_{0,0}^2\rangle$ can be represented as a linear combination of the singlets $|\Psi_{0,0}\rangle$ and $|\Psi_{0,0}^{+}\rangle$.

The energy spectrum (16) is not compatible with the Heisenberg one (3), since the latter has a unique singlet level. In order to obtain the exchange coupling as a function of (14) we have to exclude two singlet energy values from (16). These are (16c) since for either positive or negative integrals (14) the singlet

energy (16b) always takes minimal values. Therefore, the final variational energy spectrum is build up from the energy values (16a) and (16b) such that the corresponding effective Hamiltonian, denoted by \hat{H}_{eff} , satisfies

$$\hat{H}_{\text{eff}}|s, m\rangle = E_{s,m}|s, m\rangle, \quad E_{s,m} = \delta_{0s} \left(D + \frac{U+V}{2} - \sqrt{4T^2 + \frac{(U-V)^2}{4}} \right) + \delta_{1s}(V-D), \quad \forall m. \quad (17)$$

Within our approximations, the energy spectrum (3) and (17) have to describe the same energy transition and thus magnetic excitation. Since independently of the sign of (14) the ground state is singlet, we consider two cases:

(1) Integrals (14) take negative values. As a consequence, for the exchange coupling in (2), we obtain

$$J = 2|D| + \frac{|U|-|V|}{2} + 2\sqrt{|T|^2 + \frac{(|V|-|U|)^2}{16}}, \quad (18)$$

where $c = 1$ and for example $D = -|D|$.

As it was pointed out at the end of section 5.2, the integrals U , T and V , D refer to different spin-orbital configurations and hence electrons' distributions. Within (18) the quantities U , T are related to the state $|\Psi_{0,0}^+\rangle$. The other singlet state $|\Psi_{0,0}\rangle$ corresponds to the functions D and V . When the sates $|\Psi_{0,0}\rangle$ and $|\Psi_{0,0}^+\rangle$ are not superposed and the spatial distribution of $(N-1)$ -th and N -th electrons is such that $|U| \gg |D|, |V|$ and $|U| > |T|$, expression (18) can be simplified by perturbing over the value of $|T|/|U|$. Taking into account only the first two terms in the series, we get

$$J = |U| + 4|T|^2|U|^{-1}. \quad (19)$$

Therefore, the effective spin-spin interaction is strong since at the singlet level both electrons may have the same spatial distribution.

When both electrons do not occupy the same molecular orbital, there is no superposition and the integrals (14a), (14b) vanish. In this case (18) is twice the direct exchange integral's absolute value $J = 2|D|$. Here both electrons do not occupy the same region of the three-dimensional space and the effective spin-spin interaction is weaker.

(2) Integrals (14) take positive values. In other words the kinetic and repulsion terms in (2) dominate. Here, only the sign before first two terms in (18) changes and similarly to (19) the inequalities $U \gg D, V$ and $U > T$ hold. Thus, perturbing over the ratio T/U , we get

$$J = 4T^2U^{-1}. \quad (20)$$

In this case, the effective interaction between both spins is less stronger than that defined by (19), since the electrons have greater kinetic energy, see figure 2. Accordingly, the bond lengths between constituent atoms and bond angles would be different, see for example the Goodenough-Kanamori-Anderson rules [27–30].

6. Conclusion

We discuss the origin of magnetic exchange between two metal centers in insulators and demonstrate how it depends on the distribution of the valence electrons. To this end we apply the variational approach in conjunction with the Heisenberg Hamiltonian. In the case of localized electrons (4), the direct overlap and thus the exchange coupling vanish, see (11) and figure 2. As a result, the magnetic properties may be governed by the individual spin magnetic moments and depending on the local orbital contribution the single-ion anisotropy may rise as a dominant effect. Therefore, except the cases of covalent bonds or those of isolated coordination complexes, the application of atomic states in studying the exchange interactions is inappropriate.

In order for the exchange interactions to contribute to the properties of magnetic insulators all electrons have to be delocalized, occupying molecular orbitals (6). According to the value of overlap integrals (5) that the coefficients in (6) are defined the electrons can be viewed as delocalized to a large extent or only around a particular cluster of atoms and intermediate bridge, but not itinerant. In both cases the exchange mechanism is indirect and the associated effective spin couplings given by (18)-(20) are superexchange coupling constants. In particular, relations (19) and (20) represent a particular case of, so to speak, superexchange coupling when the one-orbital integrals (14a) and (14b) dominate over the two-orbital ones (14c) and (14d). Therefore, the electrons are delocalized along the intermediate bridge connecting both metal centers, occupying molecular orbitals.

To conclude, it is worth mentioning that effective spin Hamiltonians, such as (2), are an ideal microscopic models for describing the magnetic properties of insulators. However, for insulators with non-trivial exchange bridging structure connecting the metal centers the Heisenberg Hamiltonian may not be an adequate model.

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References

- [1] Dirac P A M 1926 *Proc. R. Soc. London, Ser. A* **112** 661
- [2] Heisenberg W 1926 *Z. Phys.* **38** 411
- [3] Lennard-Jones J E 1929 *Trans. Faraday Soc.* **25** 668
- [4] Slater J C 1930 *Phys. Rev.* **35** 210
- [5] Goodenough J B, Wold A, Arnott R J and Menyuk N 1961 *Phys. Rev.* **124** 373
- [6] Anderson P W 1963 *Solid State Phys.* **14** 99
- [7] Rüegg C 2012 *Nat. Phys.* **8** 859
- [8] Aravena D, Venegas-Yazigi D and Ruiz E 2016 *Sci. Rep.* **6** 23847
- [9] Coronado E 2020 *Nat. Rev. Mater.* **55** 87
- [10] Weihong Z, Kotov V and Oitmaa J 1998 *Phys. Rev. B* **57** 11439
- [11] Deng G, Yu D, Mole R, Pomjakushina E, Conder K, Kenzelmann M, Yano S i, Wang C W, Rule K C, Gardner J S, Luo H, Li S, Ulrich C, Imperia P, Ren W, Cao S and McIntyre G J 2018 *Phys. Rev. B* **98** 184411
- [12] Georgiev M and Chamati H 2019 *C.R. Acad. Bulg. Sci.* **72** 29
- [13] Dagotto E 2003 *Nanoscale phase separation and colossal magnetoresistance : The physics of manganites and related compounds* (Berlin: Springer)
- [14] Fitta M, Peřka R, Konieczny P and Bařanda M 2018 *Crystals* **9** 9
- [15] Abeed M A, Atulasimha J and Bandyopadhyay S 2018 *J. Phys. Condens. Matter* **30** 394001
- [16] Zhang G P, Latta T, Babyak Z, Bai Y H and George T F 2016 *Modern Phys. Lett. B* **30** 16300052
- [17] Varbev S, Boradjiev I, Tonchev H and Chamati H 2020 *Eur. Phys. J. B* **93** 131
- [18] Masuda T, Takamizawa S, Hirota K, Ohba M and Kitagawa S 2008 *J. Phys. Soc. Jpn* **77** 083703
- [19] D D Stancil and A Prabhakar 2009 *Spin Waves* (Boston: Springer)
- [20] Law N A, Kampf J W and Pecoraro V L 2000 *Inorg. Chim. Acta* **297** 252
- [21] Chiesa A, Guidi T, Carretta S, Anbro S, Timco G, Vitorica-Yrezabal I, Garlatti E, Amoretti G, Winpenny R and Santini P 2017 *Phys. Rev. Lett.* **119** 217202
- [22] Blundell S 2001 *Magnetism in condensed matter* Oxford master series in condensed matter physics (New York: OUP)
- [23] Felthouse T R, Laskowski E J and Hendrickson D N 1977 *Inorg. Chem.* **16** 1077
- [24] Kitaura R, Kitagawa S, Kubota Y, Kobayashi T C, Kindo K, Mita Y, Matsuo A, Kobayashi M, Chang H C, Ozawa T C, Suzuki M, Sakata M and Takata M 2002 *Sci.* **298** 2358
- [25] Furrer A 2010 *Int. J. Mod. Phys. B* **24** 3653
- [26] Sadhu M H, Mathoniere C, Patil Y P and Kumar S B 2017 *Polyhedron* **122** 210
- [27] Anderson P W 1950 *Phys. Rev.* **79** 350
- [28] Goodenough J B 1955 *Phys. Rev.* **100** 564
- [29] Kanamori J 1959 *J. Phys. Chem. Solids* **10** 87
- [30] Anderson P W 1959 *Phys. Rev.* **115** 2