FIP10604 – Text 05 – EXCHANGE INTERACTIONS

Effect of interactions

We have seen that **independent** atoms show **paramagnetic** behavior, obeying Curie's law. The examples presented involved certain salts of transition-metal or rare-earth ions. However, there are many other compounds with this kind of ions, and the behavior observed experimentally is **not** in general paramagnetism.

For the moment, we restrict our analysis to insulating solids, that is, only atomic (localized) magnetic moments. Later on, we will study magnetic properties associated to the spin of conduction electrons (itinerant moments) in metallic solids. From the viewpoint of comparison with Curie's law, i.e., **focusing on the susceptibility as a function of temperature**, the main types of magnetic behavior observed in insulating solids (succinctly described in Text 01) are summarized in the following list.

- **Diamagnetism -** The magnetic susceptibility as a function of temperature is essentially a straight line parallel to the T axis and below it. That is, χ is negative and independent of temperature. As we have seen, this occurs when atoms have closed shells, not presenting an intrinsic magnetic moment.

- **Paramagnetism -** This was the case studied in Text 03 (and complemented in Text 04). The plot of χ^{-1} *vs* T is a straight line passing through the origin and with positive slope (Curie's law).

- **Ferromagnetism -** The plot of χ^{-1} *vs* T in the high-temperature region is still a straight line. This straight line, extrapolated to low temperatures, intercepts the T axis at a **nonzero** temperature θ. The behavior for $T \gg \theta$ is of type $\chi = C/(T - \theta)$, which is known as the *Curie-Weiss law* . As the temperature decreases, approaching θ, the curve χ^{-1} deviates from a straight line, intercepting the T axis at a temperature $T_C < \theta$, which is called *Curie temperature.* The susceptibility *diverges* (experimentally, shows a sharp increase) at this temperature, indicating the establishment of *ferromagnetic order* for $T < T_C$, which is characterized by a **spontaneous magnetization** (non-null at zero field) .

- **Antiferromagnetism -** The high-temperature susceptibility satisfies a Curie-Weiss law with $\theta < 0$, and can be written as $\chi = C/(T + |\theta|)$. Therefore, its extrapolation reaches the T axis at a **negative** temperature. However, in the vicinity of a positive temperature T_N (Néel temperature), χ^{-1} deviates from the straight line and rises again (i.e., χ decreases). Below T_N, an *antiferromagnetic order* is observed: no global spontaneous magnetization, but locally the magnetic moments have a nonzero average value. In the simplest case, the array of magnetic moments can be divided into two interpenetrating sublattices, with moments oriented in opposite directions.

- **Ferrimagnetism -** The high temperature susceptibility follows a Curie-Weiss law, but θ can be negative or positive, depending on details of the specific system. In both cases, deviation from a straight line occurs as a reduction of χ^{-1}, which intercepts the T axis at a positive T_C. This is consistent with the picture of two sublattices, with opposite ($\theta < 0$) or aligned ($\theta > 0$) moments, but of different magnitudes, which results in a nonzero spontaneous magnetization.

The first two cases of magnetic behavior listed above (diamagnetism and paramagnetism) can be understood, as we have seen, as the response of **independent** atoms or ions to an applied magnetic field. The **spontaneous magnetic order** present in the other cases can only be understood as resulting from **interaction** between the microscopic magnetic moments, since they present a collective behavior.

Then, the relevant question is: What is the nature of these interactions?

1st hypothesis: dipolar interaction

Although the existence of permanent atomic magnetic moments has been understood via Quantum Mechanics, we can, as a first hypothesis, start from the classical form of interaction between magnetic dipoles.

In classical electromagnetism, the interaction between two magnetic dipoles may be viewed as the interaction of either one with the magnetic field generated by the other. As can be found in any textbook of electromagnetism, placing a dipole $\boldsymbol{\mu}_1$ at the origin of the coordinate system (arbitrary point) and a dipole $\boldsymbol{\mu}_2$ at a position $\mathbf{r}$ with respect to this origin, the interaction energy between them is

$$E_{\text{dip}} = \frac{1}{r^3}\left[\boldsymbol{\mu}_1 \cdot \boldsymbol{\mu}_2 - 3(\boldsymbol{\mu}_1 \cdot \hat{\mathbf{r}})(\boldsymbol{\mu}_2 \cdot \hat{\mathbf{r}})\right] , \tag{1}$$

where $\hat{\mathbf{r}} \equiv \mathbf{r}/|\mathbf{r}|$. Note that when the two dipoles align along a straight line joining them the second term dominates and favors parallel orientation. On the other hand, if the dipoles are oriented perpendicularly to the line joining them the second term is null and the first one favors antiparallel alignment. In a system with a large number of dipoles, the competition between these two terms, and the combined effects of many magnetic moments (due to the long range of this interaction) often lead to complex configurations.

It is important to estimate the order of magnitude of the dipolar interaction between two magnetic moments of module $\sim \mu_B$, separated by a distance d approximately equal to the typical interatomic spacing in crystalline solids. In this case, we have (not worrying about the sign)

$$E_{\text{dip}} \sim \frac{\mu_B^2}{d^3} . \tag{2}$$

Assuming that $d \sim 3$–4 Å, we obtain $E_{\text{dip}} \sim 10^{-18}$ erg, or

$$E_{\text{dip}}/k_B \sim 0.01 \text{ K} . \tag{3}$$

This should be the order of magnitude of T_C, the critical temperature below which interactions dominate and the system becomes magnetically ordered. However, experimental results in magnetic insulators indicate typical temperatures of 10–10^2 K, that is, **two to three orders of magnitude higher**!

The only possible conclusion is that dipolar interactions are **not** the source of magnetic ordering in solids.

Exchange interaction

Our discussion of Hund's rules in many-electron atoms made clear that the atomic spin is maximized by a combined effect of **Coulomb interaction** between electrons and the **exchange antisymmetry** of their wave function. We may suppose, as an alternative hypothesis to dipolar interactions, that the same mechanism might work between **electrons of neighboring atoms**, in which case it would be the origin of magnetic ordering.

The simplest case is the problem of two electrons interacting with each other and subject to an external potential, which can be due to a single nucleus or two (fixed) nuclei. This system's Hamiltonian can be written schematically as

$$\mathcal{H} = \mathcal{H}_1 + \mathcal{H}_2 + V(1,2) , \tag{4}$$

where $\mathcal{H}_1$ and $\mathcal{H}_2$ contain only the coordinates of each electron (here identified by the numbers 1 and 2), and $V(1,2)$ contains the coordinates of both electrons, necessarily including the Coulomb repulsion between them.

Due to the absence of spin-dependent interaction, the wavefunctions (or state vectors) of this two-electron system is separable in spin and orbital parts. Seeking states with definite eigenvalues of the total spin and one of its components (z), the possibilities for the spin part (in obvious notation) are

$$\chi_S^\alpha(1,2) \longrightarrow |\chi_S^\alpha\rangle = \begin{cases} |\uparrow\uparrow\rangle \\ \frac{1}{\sqrt{2}} (|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle) \\ |\downarrow\downarrow\rangle \end{cases}$$

$$\chi_A(1,2) \longrightarrow |\chi_A\rangle = \frac{1}{\sqrt{2}} (|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle) , \tag{5}$$

where S and A indicate symmetry and antisymmetry under particle exchange ($1 \leftrightarrow 2$), and different values of α identify each of the three symmetric states. The *triplet* (χ_S^α) corresponds to a total spin $S_{\text{tot}} = 1$, and the *singlet* (χ_A) to $S_{\text{tot}} = 0$.

Including an orbital part, the complete wave functions are

$$\begin{aligned} \Psi_t^\alpha(1,2) &= \Phi_A(1,2)\chi_S^\alpha(1,2) , \\ \Psi_s(1,2) &= \Phi_S(1,2)\chi_A(1,2) , \end{aligned} \tag{6}$$

where the subscripts s and t refer to singlet and triplet. Since both Ψ's must be antisymmetric under particle exchange, the orbital functions Φ_A and Φ_S must be, respectively, antisymmetric and symmetric.

The simplest approximation, which corresponds to treating $V(1,2)$ in first order of perturbation, consists in choosing

$$
\begin{aligned}
\Phi_S(1,2) &= \frac{1}{\sqrt{2}} \left[\varphi_\mu(1)\varphi_\nu(2) + \varphi_\mu(2)\varphi_\nu(1) \right] , \\
\Phi_A(1,2) &= \frac{1}{\sqrt{2}} \left[\varphi_\mu(1)\varphi_\nu(2) - \varphi_\mu(2)\varphi_\nu(1) \right] ,
\end{aligned} \tag{7}
$$

where φ_μ and φ_ν are eigenfunctions of $\mathcal{H}_1$ and/or $\mathcal{H}_2$.

Once the wave functions are known, we can evaluate the energies of singlet and triplet states as

$$
\begin{aligned}
E_s &= \frac{\langle \Phi_S | \mathcal{H} | \Phi_S \rangle}{\langle \Phi_S | \Phi_S \rangle} , \\
E_t &= \frac{\langle \Phi_A | \mathcal{H} | \Phi_A \rangle}{\langle \Phi_A | \Phi_A \rangle} ,
\end{aligned} \tag{8}
$$

the latter with degeneracy 3 due to the spin part.

The energy difference between the singlet and triplet states defines the *exchange constant*

$$
J \equiv \tfrac{1}{2} \left(E_s - E_t \right) . \tag{9}
$$

Note that $J > 0$ if the triplet (parallel spins) has lower energy, and $J < 0$ if the lowest energy corresponds to the singlet (antiparallel spins).

Next we study some cases arising from different choices of the zeroth-order problem, i.e., $\mathcal{H}_1$ and $\mathcal{H}_2$.

Two electrons of the same atom

This is the situation already qualitatively analyzed for an atomic subshell. Here, $\mathcal{H}_1$ and $\mathcal{H}_2$ are identical, being the atomic Hamiltonian of a single electron, and $V(1,2)$ is the Coulomb repulsion between the two electrons. In this case, φ_μ and φ_ν belong to the same set of orthonormal eigenfunctions.

If the subshell does not have orbital degeneracy, we can only have $\varphi_\mu = \varphi_\nu \equiv \varphi$, which restricts us to the singlet state, with total energy $2\varepsilon + K$ (to first order in $V(1,2)$), where ε is the atomic energy of the one-electron problem, and

$$
K = \int d\mathbf{r}_1 \int d\mathbf{r}_2 \, |\varphi(1)|^2 \, |\varphi(2)|^2 \, \frac{e^2}{r_{12}} . \tag{10}
$$

This would be, for instance, the only possibility as an approximation for the He atom's ground-state. But we can also apply this procedure as a correction to the Hartree approximation for a many-electron atom, dealing with the last (partially occupied) subshell. Then, if the subshell is orbitally degenerate, we may choose $\varphi_\mu \neq \varphi_\nu$. Now, the energies of the singlet and triplet states are

$$
\begin{aligned}
E_s &= \varepsilon_\mu + \varepsilon_\nu + K_{\mu\nu} + J_{\mu\nu} \;, \\
E_t &= \varepsilon_\mu + \varepsilon_\nu + K_{\mu\nu} - J_{\mu\nu} \;,
\end{aligned}
\tag{11}
$$

where

$$
K_{\mu\nu} = \int \mathrm{d}\mathbf{r}_1 \int \mathrm{d}\mathbf{r}_2 \, |\varphi_\mu(1)|^2 \, |\varphi_\nu(2)|^2 \, V(1,2)
\tag{12}
$$

and

$$
J_{\mu\nu} = \int \mathrm{d}\mathbf{r}_1 \int \mathrm{d}\mathbf{r}_2 \, \varphi_\mu^*(1) \, \varphi_\nu^*(2) \, V(1,2) \, \varphi_\mu(2) \, \varphi_\nu(1) \;.
\tag{13}
$$

The usual denomination for $J_{\mu\nu}$ is *exchange integral*, for obvious reasons. In the present case it determines the *exchange constant*, defined by Eq. (9). It can be verified that $J_{\mu\nu} \geq 0$, which implies $E_t < E_s$. This is essentially the first Hund's rule!

Diatomic molecule - molecular orbitals

Now, $\mathcal{H}_1$ and $\mathcal{H}_2$ remain identical, but correspond to **one** electron in the presence of **two** nuclei. $V(1,2)$ is still the Coulomb repulsion between the electrons. Although it is a one-electron problem, determining the individual eigenfunctions (φ_μ and φ_ν) is not trivial due to the two centers. The most common procedure is to build up these functions as **linear combinations of atomic orbitals** (LCAO). Taking, for example, the hydrogen molecule, the molecular orbitals of lowest energies are combinations of 1s atomic orbitals centered on each atom:

$$
\begin{aligned}
\varphi_\mu(\mathbf{r}) &= \frac{1}{\sqrt{2}} \left[\psi_{1s}(\mathbf{r} - \mathbf{R}_1) + \psi_{1s}(\mathbf{r} - \mathbf{R}_2) \right] \;, \\
\varphi_\nu(\mathbf{r}) &= \frac{1}{\sqrt{2}} \left[\psi_{1s}(\mathbf{r} - \mathbf{R}_1) - \psi_{1s}(\mathbf{r} - \mathbf{R}_2) \right] \;,
\end{aligned}
\tag{14}
$$

where $\mathbf{R}_1$ and $\mathbf{R}_2$ identify the positions of the nuclei. The state φ_μ is called *binding*, because the corresponding energy (including repulsion between the nuclei) has a minimum value for a finite interatomic distance. The state φ_ν is called *antibonding* because the energy is reduced asymptotically to zero with increasing separation between the nuclei.

From here on, the problem is similar to the single-atom case. The energies and Coulomb integrals are still given by Eqs. (11)–(13), only reinterpreting the single-particle functions. Strictly for a hydrogen molecule (non-degenerate combinations of 1s atomic orbitals), the ground state is a singlet, with both electrons occupying the molecular orbital φ_μ and the first excited state is a spin triplet with an electron in the orbital φ_μ and the other in φ_ν.

For the O_2 molecule, however, successive occupation of the molecular orbitals leads to a ground state in which two electrons have parallel spins (occupying different 2p orbitals).

The above situations, if applicable to a solid, seem to describe both ferromagnetism and antiferromagnetism. However, in this formulation the electrons are **shared** by the nuclei, so that it is impossible to associate a (localized) magnetic moment to each atom.

Diatomic molecule - Heitler-London formulation

In the treatment of a diatomic molecule proposed by Heitler and London,[1] both $\mathcal{H}_1$ and $\mathcal{H}_2$ correspond to a **one-electron atom**. In this case, the zeroth-order ground state has each electron occupying an **atomic** orbital, with these orbitals centered on separate nuclei. $V(1,2)$ contains, in addition to the Coulomb repulsion between the two electrons, attractive interactions of each one by **the other nucleus**.

For the hydrogen molecule, we can choose

$$
\begin{aligned}
\varphi_\mu(\mathbf{r}) &= \psi_{1s}(\mathbf{r} - \mathbf{R}_1) \,, \\
\varphi_\nu(\mathbf{r}) &= \psi_{1s}(\mathbf{r} - \mathbf{R}_2) \,.
\end{aligned}
\tag{15}
$$

Note that in this formulation, by construction, the electrons tend to "avoid" each other, since their unperturbed wavefunctions are centered in different atoms. However, these functions are **not** orthogonal. Defining the *overlap integral*

$$
\mathcal{L} \equiv \int d\mathbf{r}\, \varphi_\mu^*(\mathbf{r})\varphi_\nu(\mathbf{r}) = \int d\mathbf{r}\, \varphi_\nu^*(\mathbf{r})\varphi_\mu(\mathbf{r}) \,,
\tag{16}
$$

and using the definitions (7), we have that

$$
\begin{aligned}
\langle \Phi_S | \Phi_S \rangle &= 1 + \mathcal{L}^2 \,, \\
\langle \Phi_A | \Phi_A \rangle &= 1 - \mathcal{L}^2 \,.
\end{aligned}
\tag{17}
$$

Consequently, Eqs. (8) result in

$$
\begin{aligned}
E_s &= \varepsilon_\mu + \varepsilon_\nu + \frac{K_{\mu\nu} + J_{\mu\nu}}{1 + \mathcal{L}^2} \\
E_t &= \varepsilon_\mu + \varepsilon_\nu + \frac{K_{\mu\nu} - J_{\mu\nu}}{1 - \mathcal{L}^2} \,.
\end{aligned}
\tag{18}
$$

The corresponding exchange constant, according to Eq. (9), is given by

$$
J = \frac{J_{\mu\nu} - \mathcal{L}^2\, K_{\mu\nu}}{1 - \mathcal{L}^4} \,.
\tag{19}
$$

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[1] Original article: W. Heitler and F. London, Z. Physik **44**, 455 (1927).

In the previous cases we had $\mathcal{L} = 0$, and therefore $J = J_{\mu\nu} > 0$. Here, Eq. (19) can lead to negative values of J, depending on the relative values of K_{ab}, $J_{\mu\nu}$ and $\mathcal{L}$. In the original calculation of Heitler and London, explicitly for the H_2 molecule, $J < 0$ was obtained, in agreement with the treatment involving molecular orbitals.

It should be noticed that the method of Heitler and London has some inconsistencies. The employed wave functions force the electrons to be in separate atoms, but the possibility of exchange between them is not included in the kinetic-energy term, although taken into account in the Coulomb interaction. Localizing the electrons is in principle more suitable to treat atomic magnetic moments. However, the possibility of obtaining $J < 0$ depends on the existence of a nonzero overlap between the individual wave functions, which should also favor the passage of each electron from one atom to the other.

We will see below how the kinetic-energy term can be included in a description of exchange integrals that is applicable to crystalline solids with localized moments.

Exchange interactions in a solid

For simplicity, we will focus on a crystal composed of identical atoms, each with a single electron in the outermost non-degenerate energy level. This simplification is not unrealistic as it might seem at first sight, in view of our discussion about crystal-field splitting. This is the starting point to describe a *tight-binding* band if we allow the electrons to move and neglect their Coulomb interaction. The most convenient way is to use a basis of Wannier functions $w(\mathbf{r} - \mathbf{R}_i)$, obtained from the Bloch functions $\psi_{\mathbf{k}}(\mathbf{r})$ by a discrete Fourier transform relating wavevectors $\mathbf{k}$ to lattice vectors $\mathbf{R}_i$.

At this non-interacting level, the Hamiltonian in the Wannier representation can be written as

$$\mathcal{H}_0 = \varepsilon_0 \sum_{i\sigma} |i\sigma\rangle\langle i\sigma| - \sum_{ij\sigma} |i\sigma\rangle t_{ij}\langle j\sigma| , \tag{20}$$

where $\varepsilon_0 = \langle i|\mathcal{H}_0|i\rangle$ is the local (atomic) energy, in general chosen as $\varepsilon_0 = 0$, and the kinetic-energy part contributes to the hopping integral $t_{ij} = -\langle i|\mathcal{H}_0|j\rangle$. Including the interaction between electrons, the Hamiltonian becomes

$$\mathcal{H} = \mathcal{H}_0 + V , \tag{21}$$

where

$$V = \frac{1}{2} \sum_{\substack{ii'\sigma \\ jj'\sigma'}} |i'\sigma\rangle|j'\sigma'\rangle V_{ii',jj'}\langle j\sigma'|\langle i\sigma| , \tag{22}$$

and $V_{ii',jj'}$ can be evaluated using Wannier **functions** (coordinate representation):

$$V_{ii',jj'} = \int d\mathbf{r} \int d\mathbf{r}'\, w^*(\mathbf{r} - \mathbf{R}_{i'})w^*(\mathbf{r}' - \mathbf{R}_{j'})\frac{e^2}{|\mathbf{r} - \mathbf{r}'|}w(\mathbf{r}' - \mathbf{R}_j)w(\mathbf{r} - \mathbf{R}_i) . \tag{23}$$

Supposing small overlap between different Wannier orbitals (tight-binding limit), the most important interaction term is $V_{ii,ii} \equiv U$. We can identify, among other possible terms, the direct and exchange Coulomb integrals that we saw previously: $K = V_{ii,jj}$ and $J = V_{ij,ji}$.

Turning to the language of *second quantization*, and keeping only the local term in the electron-electron interaction, we have the *Hubbard model*, described by the Hamiltonian

$$\mathcal{H} = \varepsilon_0 \sum_{i\sigma} n_{i\sigma} - \sum_{ij\sigma} t_{ij} c_{i\sigma}^\dagger c_{j\sigma} + U \sum_i n_{i\uparrow} n_{i\downarrow} \; . \tag{24}$$

At this point, it is not obvious that such a model, in principle aimed to describe interacting conduction electrons, would be relevant to the magnetism of insulators. But an insulating state is obtained in the limit $t_{ij} \ll U$. In this case, starting from a global state with one electron per site, hopping is strongly inhibited because of the energy price payed to have two electrons at the same site.

To understand the basic mechanism, let us consider initially only two sites (that would be neighbors in a crystal lattice). The Hamiltonian of this system (choosing $\varepsilon_0 = 0$) is

$$H = -t \sum_\sigma (c_{1\sigma}^\dagger c_{2\sigma} + c_{2\sigma}^\dagger c_{1\sigma}) + U(n_{1\uparrow} n_{1\downarrow} + n_{2\uparrow} n_{2\downarrow}) \; , \tag{25}$$

For two electrons, if we choose both with spin up or both with spin down, we must have one in each site, and hopping is impossible. These states are degenerate, with energy $E_0 = 0$, and eigenvalues of S_{tot}^z equal to $+1$ and -1, respectively.

There are four possible states with $S_{\text{tot}}^z = 0$, which are $|2\,0\rangle, |0\,2\rangle, |\uparrow\downarrow\rangle, |\downarrow\uparrow\rangle$, where the two places in the ket refer to the two sites. The Hamiltonian matrix in this subspace (with the order of basis vectors just shown) is

$$\mathcal{H}_{\uparrow\downarrow} = \begin{pmatrix} U & 0 & -t & -t \\ 0 & U & -t & -t \\ -t & -t & 0 & 0 \\ -t & -t & 0 & 0 \end{pmatrix} \; . \tag{26}$$

Diagonalizing this matrix (**EXERCISE**), we obtain the following four eigenvalues:

$$\begin{aligned} E_0 &= 0 \; , \\ E_U &= U \; , \\ E_\pm &= \frac{U}{2} \left[1 \pm \sqrt{1 + \left(\frac{4t}{U}\right)^2} \right] \; . \end{aligned} \tag{27}$$

The state with energy E_0 corresponds to the symmetric combination of one-electron states at each site. It completes the triplet with the two equal-spin states (($|\uparrow\uparrow\rangle$ and $|\downarrow\downarrow\rangle$). The states with energies E_U and $E_\pm$ are all singlets.

Note that $E_- < E_0 < E_U < E_+$. If U is significantly larger than t, we have two high-energy singlets, with energies E_U and E_+ (both of order U), while the low-energy sector comprises the singlet with energy E_- and the triplet with energy E_0. Changing the notation of these last two energies respectively to E_s and E_t, the electron Hamiltonian projected onto this low-energy subspace is equivalent to a Hamiltonian containing only spin operators, in the form

$$\mathcal{H} = \tfrac{1}{4}(E_s + 3E_t) - (E_s - E_t)\, \mathbf{S}_1 \cdot \mathbf{S}_2 \ . \tag{28}$$

To prove this equivalence it is sufficient to check that the set of states χ_S and χ_A, as defined in Eq. (5), are eigenstates of the Hamiltonian (28) with eigenvalues E_t and E_s, respectively. Keeping the definition of J as half the energy difference between these two states, we have $J = E_s < 0$ and the ground state is a singlet (zero total spin). Expanding the square root for E_- ($= E_s$) in Eq. (27) to second order in t/U, we obtain

$$J = -\frac{2t^2}{U} \ . \tag{29}$$

From perturbation theory, we can interpret this result as the energy correction of second order in the hopping to a zeroth-order ground state having one electron per site with opposite spins. It involves two virtual hoppings (t^2) and an intermediate state with both electrons at the same site (energy U).

Suppressing the constant term, and using Eq. (29), the Hamiltonian (28) can be written as

$$\mathcal{H} = -2J\, \mathbf{S}_1 \cdot \mathbf{S}_2 \ . \tag{30}$$

In this form, it describes two localized spins with an *exchange interaction J*.

By construction, the spin operators in the above equation can be identified with the spins of each atom. In this simple case the atomic spin is $1/2$ because there is a single electron per atom. But the mechanism can be generalized to more complex cases, as in the following example.

Suppose that a certain transition metal ion, in addition to the closed shells of the ionic core, has three electrons occupying the (degenerate) 3d-t_{2g} states in cubic symmetry. Furthermore, suppose that the e_g states have significantly higher energy. The intra-atomic exchange interaction (Hund's rule) ensures an atomic spin $S = 3/2$. Considering a pair of these ions, any of the three electrons from one ion can make a virtual hopping to the other, provided that the specific state to which it jumps is available, that is, if the electrons of the other ion are occupying states with **opposite** spin with respect to the jumping electron. Therefore, a Hamiltonian of the form (30) remains applicable for an $S > 1/2$.

Up to this point, we only generated antiferromagnetic interactions ($J < 0$). However, a multi-orbital case may favor hopping with parallel spins due to the on-site Hund's rule effect if there are empty orbitals that are close in energy (or degenerate).

Superexchange

Another typical situation is to have a closed-shell ion (e.g., O^{2-}) positioned between two magnetic ions (e.g., transition-metal ions such as Fe^{2+}, Co^{2+}, etc.). A simplified model for this situation has a single d orbital in each magnetic ion, as in the previous case, plus a s orbital on the intermediate site. The s orbital has a local energy $\Delta > 0$ relative to the d orbitals, and the extent of the local orbitals do not allow for direct hopping between the d orbitals, but only between them and the intermediate s orbital.

The state of lowest energy for two electrons corresponds to each one occupying one of the d states, with the s state empty. The degeneracy of spin configurations is lifted by virtual hoppings to the s state.

The relevant Hamiltonian, choosing $U_s = 0$ and $U_d \gg \Delta > t$, is

$$H = \Delta \sum_\sigma n_{s\sigma} - t \sum_{i=1,2} \sum_\sigma \left(d_{i\sigma}^\dagger c_\sigma + c_\sigma^\dagger d_{i\sigma} \right) \ , \tag{31}$$

without taking explicitly into account the interaction U_d, but **imposing** the condition of no double occupancy on d states, i.e., leaving out doubly occupied d states.

Solving as in the two-site example above, the case of opposite spins now involves a 7×7 determinant. Without developing the details, we can say that once more the ground state is a singlet, the first excited state is a triplet, and the energy difference between them, expanded in powers of the hopping, yields an **antiferromagnetic** exchange constant of the order of t^4/Δ^3. An equivalent result is obtained if we consider the fully occupied p subshell of the mediating atom (presumably oxygen) instead of the next empty s state, but this would involve double occupancy of the d level in the intermediate state (U_d not very strong). Which of these is the physical situation depends on the relative energies of the involved orbitals in a particular solid.

Our previous comment about the possibility of ferromagnetic exchange remains valid for superexchange, under the same conditions. Actually, it should be easier to have it in this case, since the geometry of the intermediate orbitals may favor non-straight-line connections, thus involving different orbitals on the magnetic sites.

Magnitude of the exchange interactions

From the calculations developed here, the exchange constant is of order t^2/U or t^4/Δ^3. The orders of magnitude of the relevant parameters are typically $U \sim 1$–10 eV, Δ and $t \sim 1$ eV or fractions of eV (with $t < \Delta$). With this, we obtain $J \sim 10^{-3}$–10^{-2} eV, which means that $J/k_B \sim 10$–100 K. This is comparable to the critical temperatures of magnetic order observed in insulators (in contrast to what we obtained with magnetic dipolar interactions). Thus, we can then say that the relevant *magnetic* interactions in solids are exchange interactions. In other words, the interactions responsible for magnetic

order are actually *electric* (Coulomb) interactions in association with the Pauli Principle (antisymmetry of the wave functions). This was seen here for localized (atomic) magnetic moments, but also applies in the case of metals, although involving more directly the Coulomb interaction and Pauli Principle, as we will see later.