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where $\vec{r}$ is the separation between the dipoles. Since the dipoles point along the x-axis and are of the same magnitude we can write

$$E = \frac{\mu_o}{4\pi r^3}\left[\mu_B^2 - \frac{3}{r^2}\mu_B^2 r^2\right], \tag{11.122}$$

$$E = -2\frac{\mu_o}{4\pi r^3}\mu_B^2.$$

Inserting numbers, $\mu_B = 9.274\times 10^{-24} A\cdot m^2$ and $r = 1$ Å, we have $|E| = 1.7\times 10^{-23}$ J. Dividing by the Boltzmann constant the temperature scale is given by 1.25 K. This energy scale is low compared to the Curie transition temperatures of ferromagnets such as Fe, Ni, and Co!

(b) The Coulomb interaction energy of a pair of electrons is given by

$$U = \frac{1}{4\pi\varepsilon_o}\frac{q^2}{r}, \tag{11.123}$$

$$U = \frac{1}{4\pi(8.85\times 10^{-12})}\frac{(1.6\times 10^{-19})^2}{1\times 10^{-10}},$$

$$U = 2.3\times 10^{-18}\text{J}.$$

The temperature scale corresponding to this energy is 1.67×10^5K!

So what does the above example teach us? It clearly demonstrates that magnetic dipole–dipole interactions cannot explain the very high Curie-Weiss temperatures of Fe, Ni, and Co of 1043 K, 1400 K, and 627 K. Rather, consider the following scenario where two atoms with unpaired electrons interact with each other. If the spins of these two electrons are antiparallel to each other, the electrons can approach each other as close as possible, thereby raising the Coulomb interaction energy. However, if the states are parallel, the Pauli exclusion principle causes the electrons to stay as far away as possible leading to a reduction of the Coulomb interaction energy. The order of magnitude of this Coulomb interaction was estimated to be at 10^5 K in the above example. So even for a small change of 1%, the cost associated with the process would be of the order of 1000 K, an order of magnitude similar to the Curie-Weiss temperature of the aforementioned ferromagnetic materials. Thus, the key to explaining magnetism is the combined effect of Coulomb interaction energy and Pauli exclusion principle. These two basic ideas give rise to what is known as the **exchange interaction**. The exchange interaction was introduced by the german theoretical physicist Werner Heisenberg in 1926 to interpret the origin of the large Curie-Weiss transition temperature.

To derive a quantum mechanical expression for the exchange interaction energy, consider two electrons, for example, in the $3d^2$ state. The state of each electron is specified by the product of the orbital wavefunction $\psi(\vec{r})$ and spin wavefunction (spinor, $\chi(\vec{s})$). It will be assumed that the one-electron problem has been solved and the orbital wavefunctions of the two electrons are given by the two orthonormal eigenstates $\psi_a(\vec{r})$) and $\psi_b(\vec{r})$). For the ↑ (↓) spin electron state, we choose the normalized spinor wavefunctions as $\alpha(s)(\beta(s))$. The Hamiltonian for the two-electron problem is given by

$$\mathscr{H}_{el} = \mathscr{H}_0(\vec{r}_1) + \mathscr{H}_0(\vec{r}_2) + \frac{e^2}{|\vec{r}_1 - \vec{r}_2|}, \tag{11.124}$$

consisting of two spin independent one-electron Hamiltonian $\mathscr{H}_0(\vec{r})$ and the Coulomb interaction. The one-electron eigenenergies E_a and E_b are given by

$$\mathscr{H}_0\psi_a(\vec{r}) = E_a\psi_a(\vec{r}), \tag{11.125}$$

$$\mathscr{H}_0\psi_b(\vec{r}) = E_b\psi_b(\vec{r}). \tag{11.126}$$

To proceed further we will diagonalize the two-electron Hamiltonian $\mathscr{H}_{el}$ in the subspace of the $3d^2$ state where orbital character is fixed to d-orbitals, but the spins can vary. We then have four possible wavefunction combinations. Two with parallel spins and two with antiparallel spins. Now, quantum mechanics informs us that for electrons, which are fermions, the overall wavefunction must be antisymmetric in order to satisfy the Pauli principle. The easiest way to ensure this condition is to construct the **Slater determinant**. When both spins point up, we can write

$\alpha(s_1) = \chi_{+1/2}(s_1) = |\uparrow\rangle_1 = |\tfrac{1}{2}, +\tfrac{1}{2}\rangle_1$ / $\beta(s_1) = \chi_{-1/2}(s_1) = |\tfrac{1}{2}, -\tfrac{1}{2}\rangle_1 = |\downarrow\rangle_1$

Ψ_1

$$\Psi_{\uparrow\uparrow} = \frac{1}{\sqrt{2}}\begin{vmatrix}\psi_a(\vec{r}_1)\alpha(s_1) & \psi_a(\vec{r}_2)\alpha(s_2)\\ \psi_b(\vec{r}_1)\alpha(s_1) & \psi_b(\vec{r}_2)\alpha(s_2)\end{vmatrix}, \quad \rightarrow \{S_{1z}, S_{2z}\} \text{ basis} \tag{11.127}$$

$$\Psi_{\uparrow\uparrow} = \frac{1}{\sqrt{2}}\alpha(s_1)\alpha(s_2)\left[\psi_a(\vec{r}_1)\psi_b(\vec{r}_2) - \psi_a(\vec{r}_2)\psi_b(\vec{r}_1)\right]. \tag{11.128}$$

With both spins pointing down, we can write

Ψ_4

$$\Psi_{\downarrow\downarrow} = \frac{1}{\sqrt{2}}\begin{vmatrix}\psi_a(\vec{r}_1)\beta(s_1) & \psi_a(\vec{r}_2)\beta(s_2)\\ \psi_b(\vec{r}_1)\beta(s_1) & \psi_b(\vec{r}_2)\beta(s_2)\end{vmatrix}, \tag{11.129}$$

$$\Psi_{\downarrow\downarrow} = \frac{1}{\sqrt{2}}\beta(s_1)\beta(s_2)\left[\psi_a(\vec{r}_1)\psi_b(\vec{r}_2) - \psi_a(\vec{r}_2)\psi_b(\vec{r}_1)\right]. \tag{11.130}$$

For the antiparallel combinations we have

Ψ_2

$$\Psi_{\downarrow\uparrow} = \frac{1}{\sqrt{2}}\begin{vmatrix}\psi_a(\vec{r}_1)\beta(s_1) & \psi_a(\vec{r}_2)\beta(s_2)\\ \psi_b(\vec{r}_1)\alpha(s_1) & \psi_b(\vec{r}_2)\alpha(s_2)\end{vmatrix}, \tag{11.131}$$

$$\Psi_{\downarrow\uparrow} = \frac{1}{\sqrt{2}}\left[\psi_a(\vec{r}_1)\psi_b(\vec{r}_2)\beta(s_1)\alpha(s_2) - \psi_b(\vec{r}_1)\psi_a(\vec{r}_2)\alpha(s_1)\beta(s_2)\right], \tag{11.132}$$

and

Ψ_3

$$\Psi_{\uparrow\downarrow} = \frac{1}{\sqrt{2}}\begin{vmatrix}\psi_a(\vec{r}_1)\alpha(s_1) & \psi_a(\vec{r}_2)\alpha(s_2)\\ \psi_b(\vec{r}_1)\beta(s_1) & \psi_b(\vec{r}_2)\beta(s_2)\end{vmatrix}, \tag{11.133}$$

$$\Psi_{\uparrow\downarrow} = \frac{1}{\sqrt{2}}\left[\psi_a(\vec{r}_1)\psi_b(\vec{r}_2)\alpha(s_1)\beta(s_2) - \psi_b(\vec{r}_1)\psi_a(\vec{r}_2)\beta(s_1)\alpha(s_2)\right], \tag{11.134}$$

We now diagonalize the $\mathscr{H}_{el}$ in the subspace of

$$|\Psi\rangle = |\Psi_{\uparrow\uparrow}, \Psi_{\downarrow\uparrow}, \Psi_{\uparrow\downarrow}, \Psi_{\downarrow\downarrow}\rangle \tag{11.135}$$

Using the above definition we construct the 4 × 4 matrix obtained by taking the expectation value of the two-electron Hamiltonian, $\mathscr{H}_{el}$

$$E_{el} = \langle\Psi_{\uparrow\uparrow}, \Psi_{\downarrow\uparrow}, \Psi_{\uparrow\downarrow}, \Psi_{\downarrow\downarrow}|\mathscr{H}_{el}|\Psi_{\uparrow\uparrow}, \Psi_{\downarrow\uparrow}, \Psi_{\uparrow\downarrow}, \Psi_{\downarrow\downarrow}\rangle \tag{11.136}$$

We now need to compute each and every possible combination of matrix element. Since it is a 4 × 4 matrix, we have sixteen possible choices. In Exercise 11.11.19 you will derive Equation (11.137) and the solutions for the singlet (E_s) and triplet (E_{tr}) eigenenergy states. The singlet state is characterized by a state with only one eigenenergy (since total $S = 0$, m_S can take only one value) and the triplet state by three (since total $S = 1$, m_S can take three values 0, ±1), hence their names. For the moment we will simply state the solution of the two-electron energy matrix and focus on the physical interpretation of the solution. The solution is given by the expression

$$E_{el} = (E_a + E_b)\begin{pmatrix}1 & 0 & 0 & 0\\ 0 & 1 & 0 & 0\\ 0 & 0 & 1 & 0\\ 0 & 0 & 0 & 1\end{pmatrix} + \begin{pmatrix}K_{ab} - J_{ab} & 0 & 0 & 0\\ 0 & K_{ab} & -J_{ab} & 0\\ 0 & -J_{ab} & K_{ab} & 0\\ 0 & 0 & 0 & K_{ab} - J_{ab}\end{pmatrix}, \tag{11.137}$$

with E_s and E_{tr} given by

$$E_s = E_a + E_b + K_{ab} + J_{ab}, \tag{11.138}$$

$$E_{tr} = E_a + E_b + K_{ab} - J_{ab}. \tag{11.139}$$

↓ Matrix is not diagonal in $\{S_{1z}, S_{2z}\}$ basis but is diagonal in $\{S^2, S_z\}$ basis

In the above equations, we have introduced the definitions

$$E_a = \langle \Psi | \mathscr{H}_0(\vec{r}_1) | \Psi \rangle = \langle \Psi_{\uparrow\uparrow}, \Psi_{\downarrow\uparrow}, \Psi_{\uparrow\downarrow}, \Psi_{\downarrow\downarrow} | \mathscr{H}_0(\vec{r}_1) | \Psi_{\uparrow\uparrow}, \Psi_{\downarrow\uparrow}, \Psi_{\uparrow\downarrow}, \Psi_{\downarrow\downarrow} \rangle, \tag{11.140}$$

$$E_b = \langle \Psi | \mathscr{H}_0(\vec{r}_2) | \Psi \rangle = \langle \Psi_{\uparrow\uparrow}, \Psi_{\downarrow\uparrow}, \Psi_{\uparrow\downarrow}, \Psi_{\downarrow\downarrow} | \mathscr{H}_0(\vec{r}_2) | \Psi_{\uparrow\uparrow}, \Psi_{\downarrow\uparrow}, \Psi_{\uparrow\downarrow}, \Psi_{\downarrow\downarrow} \rangle, \tag{11.141}$$

$$K_{ab} = \int\int d\vec{r}_1 d\vec{r}_2 |\psi_a(\vec{r}_1)|^2 \frac{e^2}{|\vec{r}_1 - \vec{r}_2|} |\psi_b(\vec{r}_2)|^2, \text{ (Coulomb integral)} \tag{11.142}$$

and

$$J_{ab} = \int\int d\vec{r}_1 d\vec{r}_2 \psi_a^*(\vec{r}_1) \psi_b^*(\vec{r}_2) \frac{e^2}{|\vec{r}_1 - \vec{r}_2|} \psi_b(\vec{r}_1) \psi_a(\vec{r}_2). \text{ (Exchange integral)} \tag{11.143}$$

Example 11.8.0.2
Show that the energy for the singlet and triplet state can be combined into a single expression as

$$E = \frac{E_s + E_{tr}}{2} \pm \frac{E_s - E_{tr}}{2}. \tag{11.144}$$

Solution
Adding the two eigenenergy expressions we get

$$E_a + E_b + K_{ab} = \frac{E_s + E_{tr}}{2}, \tag{11.145}$$

and subtracting the two eigenenergies we have

$$J_{ab} = \frac{E_s - E_{tr}}{2}. \tag{11.146}$$

Thus we can write

$$E = E_a + E_b + K_{ab} \pm J_{ab} = \frac{E_s + E_{tr}}{2} \pm \frac{E_s - E_{tr}}{2}. \tag{11.147}$$

Inspecting the singlet and triplet energies we observe that since $J_{ab} > 0$, the energy of the triplet energy state will always be lower than the singlet. For orthogonal orbitals participating in a direct exchange process, we find that a $S = 1$ state is favored over $S = 0$. Direct exchange operates between spins which are close enough to have sufficient overlap of their wavefunctions. It gives a strong but short range coupling which decreases rapidly as the ions are separated. What does this mean? It implies that ferromagnetism is always the choice of ground state. Intuitively, this makes sense if we keep in mind that two parallel electrons because of the Pauli exclusion principle will try to avoid each other as much as possible to try and reduce the Coulomb repulsion between them. However, with antiparallel spins, such as in the singlet state, quantum mechanics does not forbid the electron spins to get closer to each other thereby raising the Coulomb repulsion energy. There is a technical name for this – it is called the **exchange hole effect**. Note, that with non-orthogonal orbitals either the singlet or the triplet state can be favored based on the degree of overlap. In fact, in nature antiferromagnetism (anti-aligned spin configuration) is seen more often than the ferromagnetic arrangement we just discussed.

Example 11.8.0.3
Show that for two electron spin operators $\vec{S}_1$ and $\vec{S}_2$ we have

$$2\vec{S}_1 \cdot \vec{S}_2 + \frac{1}{2} = \left(\vec{S}_1 + \vec{S}_2\right)^2 - 1. \tag{11.148}$$

Evaluate the above expression for the case of (i) a singlet and (ii) a triplet state.
Solution
We start off by noting that S = 1/2 for an electron. For two electrons the total spin is given by $\vec{S} = \vec{S}_1 + \vec{S}_2$. Squaring both sides gives

$$\vec{S}_1^2 + \vec{S}_2^2 + 2\vec{S}_1 \cdot \vec{S}_2 = \left(\vec{S}_1 + \vec{S}_2\right)^2. \tag{11.149}$$

Now, using Equation (11.9) for both the spin 1/2 operators we have

$$\begin{aligned} 2S(S+1) + 2\vec{S}_1 \cdot \vec{S}_2 &= \left(\vec{S}_1 + \vec{S}_2\right)^2, \\ 2\frac{1}{2}\left(\frac{1}{2} + 1\right) + 2\vec{S}_1 \cdot \vec{S}_2 &= \left(\vec{S}_1 + \vec{S}_2\right)^2, \\ \Rightarrow 2\vec{S}_1 \cdot \vec{S}_2 + \frac{1}{2} &= \left(\vec{S}_1 + \vec{S}_2\right)^2 - 1. \end{aligned} \tag{11.150}$$

For a singlet the total S = 0. Thus we have

$$2\vec{S}_1 \cdot \vec{S}_2 + \frac{1}{2} = \left(\vec{S}_1 + \vec{S}_2\right)^2 - 1 = -1. \tag{11.151}$$

For a triplet state $S = 1$. Thus

$$\begin{aligned} 2\vec{S}_1 \cdot \vec{S}_2 + \frac{1}{2} &= \left(\vec{S}_1 + \vec{S}_2\right)^2 - 1 \\ &= S^2 - 1 = S(S+1) - 1 = 1(1+1) - 1 = 1. \end{aligned} \tag{11.152}$$

Let us pause here for a moment and make the following observations. From Example 11.8.0.2 we know that the two-electron energy can be combined into a single expression involving the total singlet and triplet energies and the relative singlet and triplet energies, with a ±1 factor in between. But note from Example 11.8.0.3 we learned we could generate a ± simply out of the space of two spins interacting with each other. Thus we could in principle mimic the energy expression simply out of a set of spin operators and not worry about the space components. This remarkable connection was put forward by Paul A. M. Dirac (1902–1984). His brilliant insight allows us to combine all these facts into a single Hamiltonian expression dependent only on spin operators and now popularly known in the magnetism community as the **Heisenberg exchange Hamiltonian** $\mathscr{H}_{\text{ex}}$. The explicit expression for a pair of electron spins is given by

$$\mathscr{H}_{12} = \frac{E_s + E_{tr}}{2} - \frac{E_s - E_{tr}}{2}\left(2\vec{S}_1 \cdot \vec{S}_2 + \frac{1}{2}\right), \tag{11.153}$$

→ eqn 3 in HW 8

$$= \text{const.} - 2J_{12}\vec{S}_1 \cdot \vec{S}_2. \tag{11.154}$$

Finally, dropping the constant energy term, absorbing the factor of two in the definition of the exchange constant, and generalizing the interaction to act between any two electron pairs in the magnetic solid we have

$$\mathscr{H}_{\text{ex}} = -\sum_{i,j} J_{ij}\vec{S}_i \cdot \vec{S}_j, \tag{11.155}$$