

Magnetic properties of a two-electron system

consider a two-electron system with spin-independent Hamiltonian.

The general stationary state Φ will be product of a purely orbital stationary states $\phi(\vec{r}_1, \vec{r}_2)$ and the spin state $\chi(\sigma_1, \sigma_2)$.

(Note that we can write $\Phi = \phi \chi$ because the Hamiltonian is independent of spin (does not depend on spin).

$\phi(\vec{r}_1, \vec{r}_2)$, the orbital part, satisfies the orbital Schrödinger eqn.

$$H\phi = -\left(\frac{\hbar^2}{2m}\nabla_1^2 + \frac{\hbar^2}{2m}\nabla_2^2\right)\phi + V(\vec{r}_1, \vec{r}_2)\phi = E\phi.$$

Let us focus on the spin part.

There are four spin states if we are given two electrons

$$|1: \sigma_2 = \frac{1}{2}; 2: \sigma_2 = -\frac{1}{2}\rangle \equiv |\uparrow\downarrow\rangle$$

$$|1: \sigma_2 = -\frac{1}{2}; 2: \sigma_2 = \frac{1}{2}\rangle \equiv |\downarrow\uparrow\rangle$$

$$|1: \sigma_2 = \frac{1}{2}; 2: \sigma_2 = \frac{1}{2}\rangle \equiv |\uparrow\uparrow\rangle$$

$$|1: \sigma_2 = -\frac{1}{2}; 2: \sigma_2 = -\frac{1}{2}\rangle \equiv |\downarrow\downarrow\rangle$$

We must construct appropriate linear combinations of these states in order to get states with a definite value of total spin S and its component along an axis.

There are:

$$\frac{1}{\sqrt{2}} (|1\uparrow\downarrow\rangle - |1\downarrow\uparrow\rangle) \equiv \frac{1}{\sqrt{2}} \left(\chi_{\uparrow}^{(\sigma_1)} \chi_{\downarrow}^{(\sigma_2)} - \chi_{\downarrow}^{(\sigma_1)} \chi_{\uparrow}^{(\sigma_2)} \right)$$

$$|1\uparrow\uparrow\rangle \equiv \chi_{\uparrow}^{(\sigma_1)} \chi_{\uparrow}^{(\sigma_2)}$$

$$\frac{1}{\sqrt{2}} (|1\uparrow\downarrow\rangle + |1\downarrow\uparrow\rangle) \equiv \frac{1}{\sqrt{2}} \left(\chi_{\uparrow}^{(\sigma_1)} \chi_{\downarrow}^{(\sigma_2)} + \chi_{\downarrow}^{(\sigma_1)} \chi_{\uparrow}^{(\sigma_2)} \right)$$

$$|1\downarrow\downarrow\rangle \equiv \chi_{\downarrow}^{(\sigma_1)} \chi_{\downarrow}^{(\sigma_2)}$$

$S \uparrow S_z$

$S=0, S_z=0$

$S=1, S_z=1$

$S=1, S_z=0$

$S=1, S_z=-1$

Singlet state, $S=0$: This state changes sign when the spins of the two electrons are interchanged.

$$(|1\uparrow\downarrow\rangle - |1\downarrow\uparrow\rangle) \xleftrightarrow{(-1)} (|1\uparrow\rangle - |1\downarrow\rangle).$$

Triplet state, $S=1$: The remaining three states do not change sign when the spins of the two electrons are interchanged.

The Pauli exclusion principle requires that the total wave function Ψ change sign under the simultaneous interchange of both space and spin coordinates.

$$\Psi = \phi \chi$$

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Spatial part

The above statement imposes a strict correlation between the spatial symmetry of the solution to the spin-independent orbital Schrödinger equation and the total spin.

\Rightarrow The symmetric spatial solutions $\phi(\vec{r}_1, \vec{r}_2) = \phi(\vec{r}_2, \vec{r}_1)$ cannot under the interchange of \vec{r}_1 and \vec{r}_2 must be associated with the singlet state with $S=0$.

And, the anti-symmetric spatial solutions $\phi(\vec{r}_1, \vec{r}_2) = -\phi(\vec{r}_2, \vec{r}_1)$ combine with triplet states having $S=1$.

If E_s and E_t are the lowest eigenvalues of the orbital Schrödinger equation associated with the singlet (symmetric spatial part) and triplet (antisymmetric) solutions, the ground state will have zero spin zero or one, depending on whether E_s is less than or greater than E_t .

[Note that this is completely determined by the analysis of the spin-independent Schrödinger equation.]

Exercise (Problem 2 in Ashcroft & Mermin)

For two-electron systems the ground state wave function for the orbital Schrödinger equation must be symmetric. Prove the above statement.

However, the above statement holds only for two-electron systems. We must find a general way to estimate

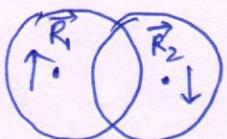
$$\Delta E = E_S - E_T \text{ for an } N\text{-atom atom.}$$

Observe that the singlet-triplet energy splitting ΔE provides a measure of the extent to which the anti-parallel ($S=0$) spin alignment of two electrons is more favorable than the parallel ($S=1$).

Emergence of interactions between spins from Coulomb forces

Now we will take up a calculation that was originally done by Heitler and London (1927) which illustrates the emergence of interactions between spins from coulomb forces.

Let us consider two adjacent atoms separated by a distance $\vec{R}_{12} = \vec{R}_1 - \vec{R}_2$.



Two electrons, possibly of different spin, surround nuclei at locations \vec{R}_1 and \vec{R}_2 . Correlations between the spins are induced by the overlap of the wavefunctions.

Let $\phi_1(\vec{r})$ and $\phi_2(\vec{r})$ be spatial wave functions of the outermost electrons on atoms 1 and 2, respectively,

These wave functions are determined when the atoms are infinitely far apart, not interacting; the coulomb force between the two atoms will be treated as a perturbation.

The wavefunctions ϕ_1 and ϕ_2 will not be orthogonal when the atoms are brought close together, as these were determined when the atoms were far separated.

The overlap integral $R \equiv \int d\vec{r} \phi_1^*(\vec{r}) \phi_2(\vec{r})$
is not zero.

In what follows we will assume that the excited states of the two atoms remain irrelevant.

Also, we know that the Hamiltonian does not depend upon spin explicitly, so all spin operators commute with the Hamiltonian, and the eigenfunctions can be chosen as the eigenfunctions of the commuting operators S^2 and S_z .

From the two functions ϕ_1 and ϕ_2 , only one even (symmetric) and one odd (anti-symmetric spatially) can be constructed.

Taking into account the overlap integral, the normalized spatial wave functions are given by

$$\phi_s(\vec{r}_1, \vec{r}_2) = \frac{1}{\sqrt{2+2\ell^2}} \left\{ \phi_1(\vec{r}_1) \phi_2(\vec{r}_2) + \phi_1(\vec{r}_2) \phi_2(\vec{r}_1) \right\}$$

$$\phi_t(\vec{r}_1, \vec{r}_2) = \frac{1}{\sqrt{2-2\ell^2}} \left\{ \phi_1(\vec{r}_1) \phi_2(\vec{r}_2) - \phi_1(\vec{r}_2) \phi_2(\vec{r}_1) \right\}.$$

The Hamiltonian is diagonal in the space spanned by the four wave functions $\{\chi_{\text{singlet}} \phi_s, \chi_{\text{triplet}} \phi_t\}$. produced by

the products of the above spin and spatial wave functions, because the Hamiltonian is independent of spin.
(Note that χ 's are orthogonal.)

These ^{four} wave functions must be eigenfunctions of the subspace, although not necessarily of the full Hamiltonian.

Next we should compute the expectation value of the Hamiltonian in each of them, and find an approximation for the wave function of the ground state.

Evaluation of Energies

Let ϵ_0 be the energies of each atom when the two atoms are infinitely separated, so that

$$\left\{ -\frac{\hbar^2}{2m} \nabla_1^2 - \frac{1}{4\pi\epsilon_0} \frac{e^2}{|\vec{r}_1 - \vec{R}_1|} \right\} \phi_1(\vec{r}_1) = \epsilon_0 \phi_1(\vec{r}_1).$$

When the two atoms are brought together, the full Hamiltonian is

$$\hat{H} = \frac{\hat{p}_1^2}{2m} - \frac{1}{4\pi\epsilon_0} \frac{e^2}{|\vec{r}_1 - \vec{R}_1|} + \frac{\hat{p}_2^2}{2m} - \frac{1}{4\pi\epsilon_0} \frac{e^2}{|\vec{r}_2 - \vec{R}_2|} \\ + \frac{1}{4\pi\epsilon_0} \frac{e^2}{|\vec{r}_1 - \vec{r}_2|} + \frac{1}{4\pi\epsilon_0} \frac{e^2}{|\vec{R}_1 - \vec{R}_2|} - \frac{1}{4\pi\epsilon_0} \frac{e^2}{|\vec{r}_1 - \vec{R}_1|} - \frac{1}{4\pi\epsilon_0} \frac{e^2}{|\vec{r}_2 - \vec{R}_1|}$$

We can easily show the following:

$$\int d\vec{r}_1 d\vec{r}_2 \phi_1^*(\vec{r}_1) \phi_2^*(\vec{r}_2) \hat{H} \phi_1(\vec{r}_1) \phi_2(\vec{r}_2) \\ = \int d\vec{r}_1 d\vec{r}_2 \phi_2^*(\vec{r}_1) \phi_1^*(\vec{r}_2) \hat{H} \phi_2(\vec{r}_1) \phi_1(\vec{r}_2) \\ = 2\epsilon_0 + U,$$

where $U = \int d\vec{r}_1 d\vec{r}_2 |\phi_1(\vec{r}_1)|^2 |\phi_2(\vec{r}_2)|^2 \left\{ \frac{e^2}{4\pi\epsilon_0} \left[\frac{1}{|\vec{r}_1 - \vec{r}_2|} + \frac{1}{|\vec{R}_1 - \vec{R}_2|} \right] \right. \\ \left. - \frac{1}{|\vec{r}_1 - \vec{R}_1|} - \frac{1}{|\vec{r}_2 - \vec{R}_1|} \right\},$

Also,

$$\begin{aligned} & \int d\vec{r}_1 d\vec{r}_2 \phi_2^*(\vec{r}_1) \hat{H} \phi_1(\vec{r}_2) \hat{H} \phi_1(\vec{r}_1) \phi_2(\vec{r}_2) \\ &= \int d\vec{r}_1 d\vec{r}_2 \hat{H} \phi_1(\vec{r}_1) \phi_2^*(\vec{r}_2) \hat{H} \phi_2(\vec{r}_1) \phi_1(\vec{r}_2) \\ &= 2\varepsilon_0 l^2 + V, \end{aligned}$$

where

$$V = \int d\vec{r}_1 d\vec{r}_2 \phi_1^*(\vec{r}_1) \phi_2^*(\vec{r}_2) \phi_2(\vec{r}_1) \phi_1(\vec{r}_2) \left\{ \frac{e^2}{4\pi\epsilon_0} \left[\frac{e^2}{|\vec{r}_1 - \vec{r}_2|} \right. \right. \\ \left. \left. + \frac{e^2}{|\vec{R}_1 - \vec{R}_2|} - \frac{e^2}{|\vec{r}_1 - \vec{R}_1|} - \frac{e^2}{|\vec{r}_2 - \vec{R}_2|} \right] \right\}.$$

Thus,

$$\begin{aligned} \varepsilon_s &= \langle \phi_s | \hat{H} | \phi_s \rangle = \left[\underbrace{\langle \phi_{11}^* \phi_{22}^* | H | \phi_{11} \phi_{22} \rangle}_{2\varepsilon_0 + V} + \underbrace{\langle \phi_{21}^* \phi_{12}^* | H | \phi_{12} \phi_{21} \rangle}_{2\varepsilon_0 l^2 + V} \right. \\ &\quad \left. + \underbrace{\langle \phi_{12}^* \phi_{21}^* | H | \phi_{12} \phi_{21} \rangle}_{2\varepsilon_0 l^2 + V} + \underbrace{\langle \phi_{21}^* \phi_{12}^* | H | \phi_{21} \phi_{12} \rangle}_{2\varepsilon_0 + V} \right] \\ &\quad \times \frac{1}{2+2l^2}, \end{aligned}$$

where we have used the notation $\phi_{11} = \phi_1(\vec{r}_1)$; $\phi_{12} = \phi_1(\vec{r}_2)$, etc.

$$\varepsilon_s = 2 \frac{2\varepsilon_0 + V + 2\varepsilon_0 l^2 + V}{2+2l^2} = 2\varepsilon_0 + \frac{V+V}{1+l^2},$$

Similarly,

$$\begin{aligned} \varepsilon_t &= \langle \phi_t | \hat{H} | \phi_t \rangle = \frac{2\varepsilon_0 + V - (2\varepsilon_0 l^2 + V) - (2\varepsilon_0 l^2 + V) + (2\varepsilon_0 + V)}{2-2l^2} \\ &= 2\varepsilon_0 + \frac{V-V}{1-l^2}. \end{aligned}$$

The difference between triplet and singlet energies is

$$\Delta E = \varepsilon_s - \varepsilon_t = - \frac{(U-V)(1+\ell^2) - (U+V)(1-\ell^2)}{1-\ell^4}$$

$$= - \frac{[U-V - U-V + V\ell^2 - V\ell^2 + U\ell^2 + V\ell^2]}{1-\ell^4}$$

$$= \frac{2V - 2V\ell^2}{1-\ell^2} = J$$

$$\boxed{\Delta E = \varepsilon_s - \varepsilon_t = J} .$$

The sign of the singlet-triplet energy splitting can vary according to the magnitudes of the three integrals ℓ , U and V .

The effective spin hamiltonian and the Heisenberg model

We know that there is a strict correlation between the spatial symmetry of the solution to the spin-independent orbital Schrödinger equation for a system of two electrons and the total spin.

It has been shown (Dirac 1926 & Heisenberg 1928) that the original Hamiltonian, which acts only on spatial degrees of freedom, can be replaced by a new Hamiltonian which acts only on the spin degrees of freedom.

This new effective Hamiltonian is so constructed that it gives results identical to the original (spatial) Hamiltonian within the subspace of states spanned by the wave functions for the sphere obtained by combining the spin and spatial wfs. ($\chi_{\text{singlet}} \phi_s, \chi_{\text{triplet}} \phi_t$).

Let \vec{s}_1 and \vec{s}_2 be the spin operators for the two spin- $1/2$ particles (electrons in our case).

When taken together as a joint entity, the total spin can be represented by an operator

$$S = \vec{s}_{\text{tot}} = \vec{s}_1 + \vec{s}_2,$$

$$\text{so that } \vec{s}_{\text{tot}}^2 = \vec{s}^2 = (\vec{s}_1 + \vec{s}_2)^2 = (\vec{s}_1)^2 + (\vec{s}_2)^2 + 2\vec{s}_1 \cdot \vec{s}_2$$

Also note that the individual electron spin operator satisfies

$$\vec{S}_i^2 = \mathcal{L}(\mathcal{L}+1) = \frac{1}{2}(\frac{1}{2}+1) = \frac{3}{4}.$$

Therefore, the total spin satisfies

$$\vec{S}^2 = (\vec{S}_1 + \vec{S}_2)^2 = \frac{3}{4} + \frac{3}{4} + 2\vec{S}_1 \cdot \vec{S}_2.$$

\vec{S}^2 has eigenvalues $s(s+1)$ in the states of spin S .

Thus, we can determine the eigenvalues of the operator $\vec{S}_1 \cdot \vec{S}_2$ in the singlet ($s=0$) and the triplet state ($s=1$).

Singlet state: $s(s+1) = 0(0+1) = \frac{3}{2} + 2\vec{S}_1 \cdot \vec{S}_2$
 $\Rightarrow \vec{S}_1 \cdot \vec{S}_2$ has an eigenvalue
of $-3/4$.

Triplet state: $1(1+1) = 2 = \frac{3}{2} + 2\vec{S}_1 \cdot \vec{S}_2$
 $\Rightarrow \vec{S}_1 \cdot \vec{S}_2$ has an eigenvalue
of $+1/4$.

Let us now consider an operator of the following form

$$\mathcal{H}^{\text{spin}} = a + b\vec{S}_1 \cdot \vec{S}_2,$$

where a and b are constants.

We wish this to be actually our new Hamiltonian that acts only on the spin degrees of freedom.

Therefore, it has an eigenvalue E_s in the singlet state and E_t in each of the three triplet states.

So, we have

$$E_s = a - \frac{3b}{4} \quad (\text{singlet state})$$

$$E_t = a + \frac{b}{4} \quad (\text{triplet state}) .$$

$$\Rightarrow b = -(E_s - E_t) \quad \text{and} \quad a = E_s + \frac{3b}{4} = \frac{(E_s + 3E_t)}{4}$$

Thus,

$$\mathcal{H}^{\text{Spin}} = \frac{(E_s + 3E_t)}{4} - (E_s - E_t) \vec{S}_1 \cdot \vec{S}_2 .$$

Now we can redefine the zero of the energy in order to omit writing the constant $(E_s + 3E_t)/4$ that is common to all four states. Also, recall that $J = E_s - E_t$. To write the Hamiltonian as

$$\boxed{\mathcal{H}^{\text{Spin}} = -J \vec{S}_1 \cdot \vec{S}_2 .}$$



Direct exchange

It arises from the direct Coulomb interaction among electrons from the ions.

Super exchange

It often happens that the two magnetic ions are separated by a non-magnetic ion (i.e. one with all electronic shells closed). It is then possible for the magnetic ions to have a magnetic interaction mediated by the electrons in their common non-magnetic neighbours, which is more important than their direct exchange interaction.

Indirect exchange

Such a magnetic interaction can occur between electrons in the partially filled f-shells in the rare earth metals.

In addition to their direct exchange coupling, the f-electrons are coupled through their interactions with the conduction electrons. This mechanism (in a sense the metallic analogue of superexchange in insulators) is known as indirect exchange. It can be stronger than the direct exchange coupling since the f-shells generally overlap very little.

Itinerant exchange

There are also important exchange interactions in metals among the conduction electrons themselves, often referred to as itinerant exchange.