2 Coupled magnetic moments

- Coupling between individual magnetic moments allows for a magnetically ordered state:

    - Ferromagnetism

- In these cases there is the presence of a collective long range order of the permanent magnetic moments in a solid-state body.

- Characteristics:
  - Spontaneous orientation of the moments, so breaking of the rotational invariance symmetry.
  - The susceptibility $\chi = \mu_0 \cdot M/B$ is divergent for $B \to 0$, because $M \neq 0$ in the ordered state (ferromagnet).
  - The relation between the magnetic induction $\mathbf{B} = B_0 + \mu_0 \mathbf{M}(\mathbf{B}_0)$ and the external field $\mathbf{B}_0$ is nonlinear.
  - The temperature dependence of the magnetic order is given by the competing behavior of the order due to coupling and disorder due to thermal energy.
  - Dirac[19] and Heisenberg[20]: the quantum mechanical exchange interaction is the origin of collective magnetic order.

[12] Paul DIRAC (1902-1984), English physicist
[13] Werner HEISENBERG (1901-1976), German physicist

2.1 Dipole-dipole interaction

- The dipole-dipole interaction is the interaction of two magnetic dipole moments $\boldsymbol{\mu}_k$ and $\boldsymbol{\mu}_l$ at distance $\mathbf{r}_{kl}$.
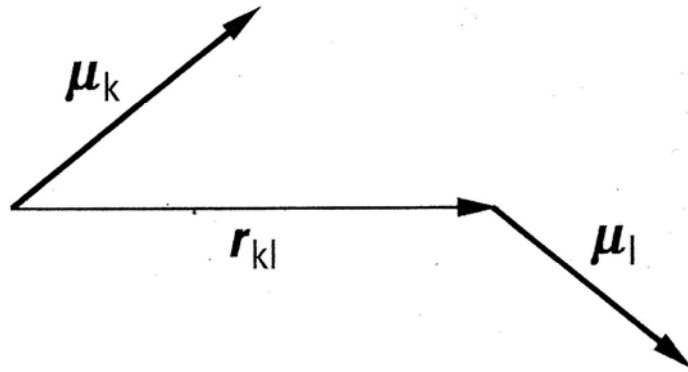
Figure: Dipole-dipole interaction

- The magnetostatic interaction energy is:

- In comparison to the quantum mechanical exchange interaction which will be dealt with in the following chapter, the magnetic dipole-dipole interaction is very small.

  ➜   See exercise

2.2 Direct exchange interaction

- To cause a long range magnetic order, the individual magnetic moments in a solid-state body need to couple. The coupling is mediated by the electrons themselves.

- Since the electrons are Fermions the many body wave function obeys the antisymmetry principle, so if two electrons are swapped the wave function changes sign.

- If the wave function is represented as a product of the spatial and spin wave functions, then only combinations of…

  … symmetric spatial function with an antisymmetric spin function
  … antisymmetric spatial function with a symmetric spin function

  is allowed.

2.2.1 Quantum mechanical interlude
2.2.1.1 Wave function of N identical particles (for instance electrons)

- The Hamilton operator $\mathcal{H} = \mathcal{H}(1,2,…,N)$ is symmetric in variables 1, 2,…. Here 1 stands for $\mathbf{x}_1$, χ_1, which means the spatial and spin degrees of freedom.

- The wave function is then $\psi = \psi(1,2,…,N)$.

- The permutation operator P_{ij} swaps i and j:

$$P_{ij}\psi(1, …, i, …, j, …, N) = \psi(1, …, j, …, i, …, N)$$

- With $P_{ij}^2 = 1$, so from this the eigenvalues of ± 1 follow.

- Since identical particles are influenced identically by any external influence, all physical operators are symmetric: ψ(1,2,…,N) and Pψ(1,2,…,N) cannot be distinguished.

- One asks oneself if all states in nature are realized. For this we consider completely symmetric and completely antisymmetric states:

- For two particles:

- In the case of N identical non-interacting particles, the Hamilton operator $\mathcal{H}$ can be written as the sum of N identical single particle Hamilton operators $\mathcal{H}(i)$:

- From the solution of the single particle Schrödinger equation:

- The product states:

- Are formed as eigenstates of $\mathcal{H}$ with energy eigenvalues:

- But the states are neither symmetric nor antisymmetric.

- The antisymmetric wave function for two fermions is:

- Respectively for N particles:

- The determinant of single particle states is called the Slater[21] determinant.

- It follows the Pauli principle; the prefactor guarantees the normalization of the wave function.

- Antisymmetry is given since the swapping of two columns yields a change in the determinant by a factor of -1.

[21] John Clarke SLATER (1900-1976), American physicist

2.2.1.2 Pauli matrices and spinors

- The description of the electron spins is based on the three Pauli matrices:

- The definition of the spin moment operator:

$$(\textit{with} \quad \hat{S}_x = \frac{1}{2}\hat{\sigma}_x, \ \hat{S}_y = \frac{1}{2}\hat{\sigma}_y, \ \textit{and} \quad \hat{S}_z = \frac{1}{2}\hat{\sigma}_z)$$

- Convention: presentation in units of ℏ (multiplying).

- Only $\hat{S}_z$ is diagonal. (The description is simple, if the spin is oriented along the z direction.)

- The eigenvalues of $\hat{S}_z$ are $m_s = \pm \frac{1}{2}$. The accompanying eigenstates are:

- The spin of the electrons is therefore oriented parallel or antiparallel to the z-axis:

- The eigenstates for spin orientation parallel or antiparallel to the x- and y-axes are:

- The two component description of the spin wave function is called spinor representation, and the respective eigenstates are called spinors.

- The general state is given by:

$$(\text{with } |a|^2 + |b|^2 = 1 \text{ and } a, b \text{ complex})$$

- We define the total spin operator $\hat{\mathbf{S}}$:

- Here **i**, **j** and **k** are the Cartesian unit vectors.

- For the $\hat{\mathbf{S}}^2$ operator $\hat{\mathbf{S}}^2 = \hat{S}_x^2 + \hat{S}_y^2 + \hat{S}_z^2$.

- The eigenvalues of $\hat{S}_x^2, \hat{S}_y^2$ and $\hat{S}_z^2$ are:

- For every spin state $|\psi\rangle$:

- Generalizing this for spin quantum numbers larger than ½ one obtains as the eigenvalues for $\hat{\mathbf{S}}^2$:

- And the commutator relation is given by:

- More than one component of $\hat{\mathbf{S}}$ is not measurable simultaneously. But every one of the operators $\hat{S}_x, \hat{S}_y$ and $\hat{S}_z$ commutes with $\hat{\mathbf{S}}^2$, so:

- The total spin as well as one component can be determined simultaneously.

2.2.1.3 Coupling of two spins (singlet and triplet state)

- The Hamilton operator of two coupled spin ½ particles (type of coupling is arbitrary) is:

- Here $\hat{\mathbf{S}}^a$ and $\hat{\mathbf{S}}^b$ are spin operators.

- The total spin operator has the form:

- The spin quantum numbers of two coupled spin ½ particles are S = 0 and S = 1.

- The eigenvalues of $(\hat{\mathbf{S}}^{tot})^2$ correspond to S(S + 1), so 0 for S = 0 and 2 for S = 1; the eigenvalues of $(\hat{\mathbf{S}}^{a})^2$ and $(\hat{\mathbf{S}}^{b})^2$ are ¾.

- So with this we obtain:

- From the previously defined Hamilton operator for two interacting spin ½ particles one obtains for the energy eigenvalues for S = 0 and S = 1:
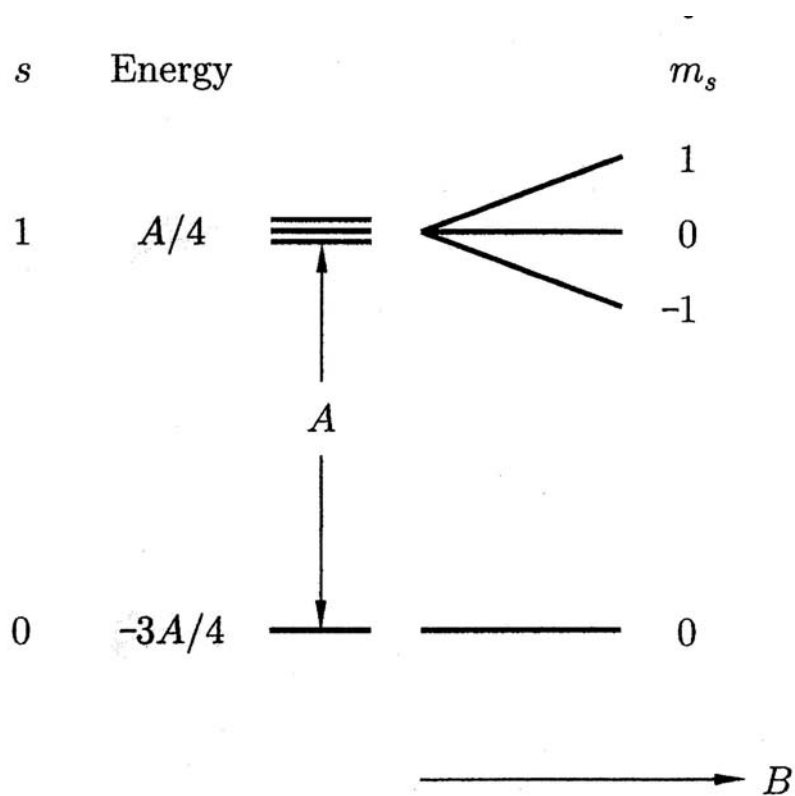
Figure: Energy eigenvalues for S = 0 and 1

- The states are (2S + 1) times degenerate:

  S = 0 corresponds to singlet state
  S = 1 corresponds to triplet state

- The z components of the triplet states are:

- And the z component of the singlet states are:

- In addition to the eigenvalues of $\hat{S}^a \cdot \hat{S}^b$ the eigenstates are of course important. Its basis given by:

$$| \uparrow\uparrow \rangle, | \uparrow\downarrow \rangle, | \downarrow\uparrow \rangle, | \downarrow\downarrow \rangle$$

- ↑ designates the z component of the spin.

- The eigenstates of $\hat{S}^a \cdot \hat{S}^b$ are linear combinations of the above mentioned basis states.

Eigenstate	m_s	s	$\hat{S}^a \cdot \hat{S}^b$
$\| \uparrow\uparrow \rangle$	1	1	$\frac{1}{4}$
$\dfrac{\| \uparrow\downarrow \rangle + \| \downarrow\uparrow \rangle}{\sqrt{2}}$	0	1	$\frac{1}{4}$
$\| \downarrow\downarrow \rangle$	−1	1	$\frac{1}{4}$
$\dfrac{\| \uparrow\downarrow \rangle - \| \downarrow\uparrow \rangle}{\sqrt{2}}$	0	0	$-\frac{3}{4}$

Figure: Eingenstates of $\hat{S}^a \cdot \hat{S}^b$ and the associated eigenvalues of m_s, s as well as the eigenvalues of $\hat{S}^a \cdot \hat{S}^b$

- The basis states do not obey the requirement for antisymmetry for the exchange of two electrons.

- The total wave function is a product of the spatial wave function $\psi(\mathbf{r}_1,\mathbf{r}_2)$ and the spin wave function χ.

- χ is a linear combination of the above mentioned basis states.

- The spatial wave function (of two spin ½ particles) is:

- Here + is the symmetric and − the antisymmetric spatial wave function; $\varphi(\mathbf{r}_i)$ and $\Phi(\mathbf{r}_i)$ are the single particle wave functions of the ith electron.

- The symmetry of the spin function χ has to be chosen so that the total wave function becomes antisymmetric:

$$|\uparrow\uparrow\rangle \text{ and } |\downarrow\downarrow\rangle: \text{ symmetric}$$

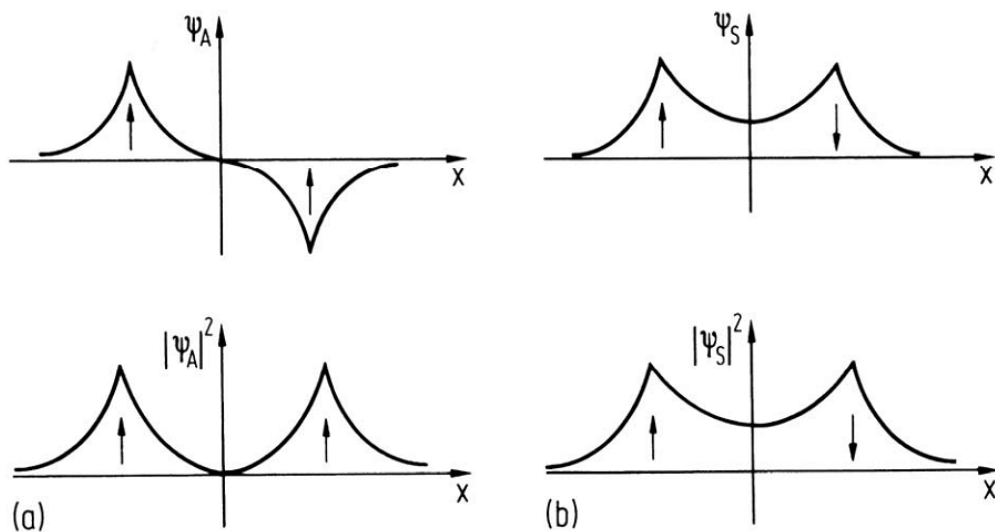$$|\downarrow\uparrow\rangle \text{ and } |\uparrow\downarrow\rangle: \text{ neither symmetric nor antisymmetric}$$

Figure: Wave function and the associated square of the amplitude; triplet state (left) and singlet state (right); in the triplet state the spin ½ particles are strongly localized at the nuclei

Note: swapping the electrons for the state $|\uparrow\downarrow\rangle$ yields $|\downarrow\uparrow\rangle$, which is not a multiple of $|\uparrow\downarrow\rangle$.

- With this we have:

- Now we investigate the **Pauli principle**. For two electrons with identical spatial and spin wave functions (for example both spin up) the spatial wave function has to be antisymmetric since the spin wave function is symmetric:

2.3 Continuation: the exchange interaction

- The exchange interaction is nothing but the combination of the Coulomb interaction and the Pauli principle.

- We stay with the model systems, two electrons with positions $\mathbf{r}_1$ and $\mathbf{r}_2$. The total wave function, as shown in the quantum mechanical interlude is given by:

for the singlet state S = 0
and:

for the triplet state S = 1. The total wave function is antisymmetric!

- We consider the energy of the possible states. For the singlet state we find:

- And for the multiplet state we find:

Note: the spin wave functions are normalized.

- The energy difference between a singlet and triplet state is given by:

- This energy difference can be parameterized using $\mathbf{S}_1 \cdot \mathbf{S}_2$. In the quantum mechanical interlude we found that:

- The Hamilton operator can then be rewritten as:

1$^{\text{st}}$ part: constant, can be included in other energy terms.
2$^{\text{nd}}$ part: depends on the spin orientation.

- We test these by entering for $\mathbf{S}_1 \cdot \mathbf{S}_2$ the value -¾, so:

- Similarly we enter for $\mathbf{S}_1 \cdot \mathbf{S}_2$ the value ¼ and we obtain:

- A comparison of the energy difference between triplet and singlet states and the parameterized Hamilton operator $\hat{\mathcal{H}}$ yields the exchange constant, respectively the exchange integral J:

- From this the spin dependent term and effective Hamiltonian follow:

- In the case of $J > 0$ one finds $E_S > E_T$, so $S = 1$, so triplet state energetically favourable (ferromagnetism).

- In the case of $J < 0$ one finds $E_S < E_T$, so $S = 0$, so singlet state energetically favourable (antiferromagnetism).

- This is relatively simple for a two particle system, but very difficult for a generalized multiparticle system.

- The limitation to nearest neighbor interaction yields as the Hamilton operator in the Heisenberg model (localized spin system):

- J_{ij} is now the exchange integral between the ith and the jth spin. The factor 2 is removed to avoid double counting.

- Alternatively, one could write:

Note 1: both electrons are of the same atom, so the exchange integral is typically positive and the triplet state is energetically favourable. The spatial wave function is then antisymmetric, so that the Coulomb energy is minimized by spatially separating the electrons (compare with 1st Hund rule).

Note 2: if the electrons considered belong to neighbouring atoms, the total wave function is a combination of the appropriate single state wave functions. The localized states are localized at the atoms considered.

- We consider the energy situation with an electron in a one dimensional box: the energy is proportional to $\frac{1}{L^2}$ and can be considered as kinetic energy.

- The presence in a very small box (with small L) costs a large contribution to kinetic energy.

- By forming bonds which allow the electrons to move beyond the lateral extent of a single system, the kinetic energy is reduced.

- The associated molecular orbitals are the bonding (spatially symmetric) and antibonding (spatially antisymmetric) orbitals: the antibonding orbitals are localized more strongly at single atoms, which means they cost most kinetic energy.

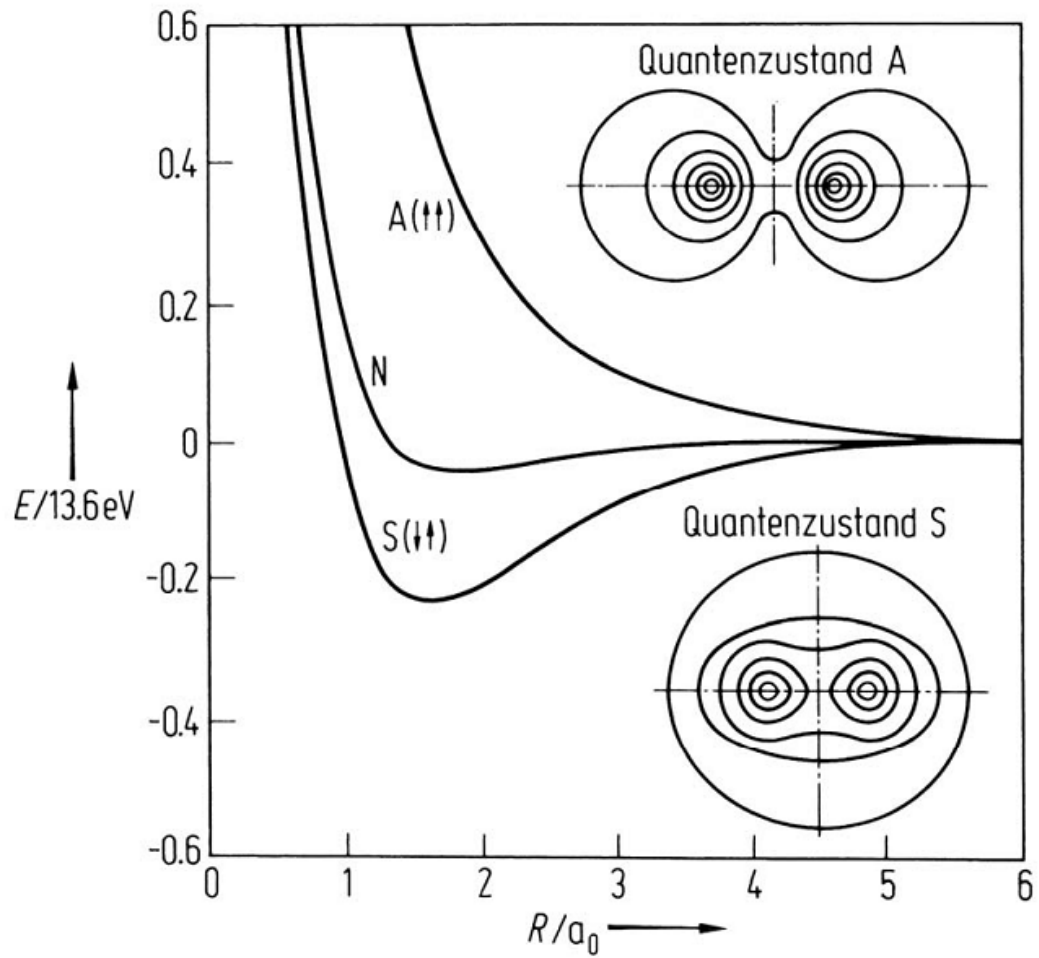- So a symmetric spatial wave function and an antisymmetric spin function (singlet state) are favoured.

Figure: Binding energy as a function of the distance;
binding singlet state (S) and antibinding triplet state (A)