5. Exchange interaction

The dipole interaction between the magnetic moments of the electrons is much too weak for supporting magnetic order of materials at high temperatures. For explaining the observed magnetism, we need to find a strong interaction between the electrons. We might think that an interaction depending explicitly on the spin (the magnetic moments) of the electrons is needed; no such interaction is known though. In 1928, Werner Heisenberg realized that the responsible interaction is the Coulomb repulsion between electrons; this is a strong interaction but does not explicitly depend on the spin. Spin selectivity is due to quantum mechanics, in particular the Pauli principle: Two electrons with parallel or antiparallel spin behave differently even though the fundamental interaction is the same; the spatial wave function $\psi(\vec{r}_1, \vec{r}_2)$ has to be antisymmetric and symmetric, respectively. One consequence is that two electrons with parallel spin cannot be in the same place. In order to discuss how the Coulomb interaction term leads to an exchange interaction of the spins, we first write this interaction in second quantization; we will introduce this very useful representation first.

5.1 Occupation number representation for fermions

So far, we have discussed the Hamiltonian in so-called first quantization:

$$H = H_0 + H_1 \, , H_0 = \sum_{i=1}^{N_e} h_i = \sum_{i=1}^{N_e} \frac{\vec{P}_i^2}{2m} + \sum_{i=1}^{N_e} V(\vec{r}_i) \, , H_1 = \sum_{i<j} u(\vec{r}_i - \vec{r}_j) \tag{5.1}$$

where $u(\vec{r}_i - \vec{r}_j)$ is either the bare Coulomb potential

$$u(\vec{r}_i - \vec{r}_j) = \frac{e^2}{|\vec{r}_i - \vec{r}_j|} \tag{5.2}$$

or an effective, screened interaction. First quantization implies that the antisymmetry of the wave function has to be taken into account by working

with Slater determinants which is rather cumbersome. Therefore, many-body calculations in solid state theory are usually performed in so-called second quantization, using the occupation number representation.

Slater determinant

Let's assume that we can solve the single particle problem exactly, *i.e.* for electron i we have

$$h_i|k_\alpha\rangle^{(i)} = \varepsilon_{k_\alpha}|k_\alpha\rangle^{(i)} \tag{5.3}$$

or in position representation

$$h_i\varphi_{k_\alpha}(\vec{r}_i) = \left(\frac{\vec{p}_i^{\,2}}{2m} + V(\vec{r}_i)\right)\varphi_{k_\alpha}(\vec{r}_i) = \varepsilon_{k_\alpha}\varphi_{k_\alpha}(\vec{r}_i) \tag{5.4}$$

with a complete set of single particle quantum numbers $k_\alpha = (l, \vec{k}, \sigma)$ of Bloch states. The Pauli principle now implies that only the part of the product space of N_e single particle Hilbert spaces is realized which consists of the particle indices of totally antisymmetric wave functions. A basis of the N_e particle Hilbert space are the Slater determinants which we can compose of single particle states as follows:

$$\begin{aligned}|\psi_{k_1,\cdots,k_{N_e}}(1\cdots N_e)\rangle &= \frac{1}{\sqrt{N_e!}}\sum_{P\in S_{N_e}}(-1)^{\chi_P}|k_{P(1)}\rangle^{(1)}\cdots|k_{P(N_e)}\rangle^{(N_e)} \\ &= \frac{1}{\sqrt{N_e!}}\det\begin{pmatrix}|k_1\rangle^{(1)} & \cdots & |k_1\rangle^{(N_e)} \\ \vdots & & \vdots \\ |k_{N_e}\rangle^{(1)} & \cdots & |k_{N_e}\rangle^{(N_e)}\end{pmatrix} = \frac{1}{\sqrt{N_e!}}\det\left(|k_\alpha\rangle^{(i)}\right)\end{aligned} \tag{5.5}$$

where P are the elements of the permutation group S_{N_e} of N_e elements, and χ_P is the character of the permutation (number of transpositions, which lead to the permutation). The product state

$$|k_1\rangle^{(1)}|k_2\rangle^{(2)}\cdots|k_{N_e}\rangle^{(N_e)}$$

means that particle 1 is in state k_1, particle 2 in state k_2 and so on; but as the particles are not distinguishable, it has to be irrelevant which particle is in state k_1, k_2 etc. Therefore, we have to sum over all possible permutations. The Slater determinants are a suitable basis for the N_e particle Hilbert space $\mathcal{H}_A(N_e)$, even if not all states of this Hilbert space correspond to a single Slater determinant.

Fock space

The basis of $\mathcal{H}_A(N_e)$ which is described by Slater determinants can also be written down in occupation number representation by writing down how many of the indistinguishable N_e particles are in state k_α; however, the sum over all occupation numbers has to be N_e. We can get rid of this restriction if we do not work in the N_e particle Hilbert space but instead in Fock space

$$\mathcal{H}_{A,\mathrm{Fock}} = \mathcal{H}_A(0) \oplus \mathcal{H}_A(1) \oplus \cdots \oplus \mathcal{H}_A(N_e) \oplus \cdots \tag{5.6}$$

which is defined as direct sum over the Hilbert spaces for all possible particle numbers. If we allow an arbitrary number of (identical) particles in the Hilbert space, then this product space is called Fock space. We can now define operators that "ascend" and "descend" between segments of Fock space with different particle numbers. These operators create and annihilate particles; therefore, they are called creation and annihilation operators. They play a central role in many serious calculations within quantum mechanics. Fock space is always explicitly or implicitly used for grand canonical treatments. In the following, we note the most important relations for fermions and bosons; therefore, we use N for the number of particles.

Starting point is the representation of N particle states. Let's assume a discrete, ordered single particle basis is given: $|1\rangle$, $|2\rangle$, ..., where i in $|i\rangle$ stands for a set of single particle quantum numbers $(lk\sigma)_i$. The normalization is $\langle i|j\rangle = \delta_{ij}$. All N particle states can be represented by superposition of

$$P_\pm\big(|r_1\rangle|r_2\rangle \ldots |r_N\rangle\big) \tag{5.7}$$

where P_+ symmetrizes for bosons and P_- antisymmetrizes for fermions. Explicitly, we have

$$P_-\big(|r_1\rangle|r_2\rangle \ldots |r_N\rangle\big) = \frac{1}{\sqrt{N!}} \sum_{P \in S_N} (-1)^P |r_{P(1)}\rangle|r_{P(2)}\rangle \ldots |r_{P(N)}\rangle \tag{5.8}$$

and

$$P_+\big(|r_1\rangle|r_2\rangle \ldots |r_N\rangle\big) = \frac{1}{\sqrt{N! n_1! n_2! \ldots}} \sum_{P \in S_N} |r_{P(1)}\rangle|r_{P(2)}\rangle \ldots |r_{P(N)}\rangle \tag{5.9}$$

where P runs over all permutations and n_i is the number of single particle states $|i\rangle$ in the product.

An equivalent characterization of the (basis) states is possible in occupation number representation:

$$\big|\{n\}\big\rangle \equiv |n_1, n_2, \dots\rangle := P_{\pm}\big(\underbrace{|1\rangle \dots |1\rangle}_{n_1 \text{ times}}\underbrace{|2\rangle \dots |2\rangle}_{n_2 \text{ times}} \dots\big) \tag{5.10}$$

(Obviously, for fermions we have $n_i \in \{0, 1\}$). $\big|\{n\}\big\rangle$ thus stands for a complete set of occupation numbers for all single particle states.
A further step for the efficient representation is the introduction of particle creation and annihilation operators: $c_i^\dagger$, c_i. We do this for fermions here and cite the result for bosons below. We define c_i and $c_i^\dagger$ by their effect on the basis states as follows:

$$\begin{aligned} c_i\big|\{n\}\big\rangle = c_i|\dots n_i \dots\rangle &= (-1)^{\sum_{j=1}^{i-1} n_j}|\dots (n_i - 1)\dots\rangle \\ c_i^\dagger\big|\{n\}\big\rangle = c_i^\dagger|\dots n_i \dots\rangle &= (-1)^{\sum_{j=1}^{i-1} n_j}|\dots (n_i + 1)\dots\rangle \end{aligned} \tag{5.11}$$

Concerning the notation, $c_i^\dagger$ is indeed the adjunct operator for c_i:

$$\begin{aligned} \big\langle\{m\}\big|c_i\big|\{n\}\big\rangle &= \begin{cases} (-1)^{\sum_{j<i} n_j}, & \text{if } m_i = n_i - 1\,,\, m_j = n_j \text{ for } j \neq i\,, \\ 0, & \text{otherwise} \end{cases} \\ \big\langle\{n\}\big|c_i^\dagger\big|\{m\}\big\rangle &= \begin{cases} (-1)^{\sum_{j<i} m_j}, & \text{if } n_i = m_i + 1\,,\, n_j = m_j \text{ for } j \neq i\,, \\ 0, & \text{otherwise} \end{cases} \end{aligned} \tag{5.12}$$

Remark: c_i maps totally antisymmetric N particle states to totally antisymmetric $(N-1)$ particle states; $c_i^\dagger$ acts "in the opposite way": Creation and annihilation, respectively.
For the particle operators the important anticommutation relations are valid:

$$[c_i, c_j]_+ = c_i c_j + c_j c_i = 0 \tag{5.13}$$

and also

$$[c_i^\dagger, c_j^\dagger]_+ = c_i^\dagger c_j^\dagger + c_j^\dagger c_i^\dagger = 0 \tag{5.14}$$

Verification: we assume $i < j$ (otherwise, the labels can be exchanged, $i = j$ is obvious):

$$\begin{aligned} c_i c_j\big|\{n\}\big\rangle &= c_i(-1)^{\nu_j}|\dots (n_j - 1)\dots\rangle \\ &= (-1)^{\nu_i + \nu_j}|\dots (n_i - 1)\dots (n_j - 1)\dots\rangle \\ c_j c_i\big|\{n\}\big\rangle &= c_j(-1)^{\nu_i}|\dots (n_i - 1)\dots\rangle \end{aligned}$$

$$= (-1)^{\nu_j - 1 + \nu_i} |\ldots (n_i - 1) \ldots (n_j - 1) \ldots \rangle \tag{5.15}$$

Here we abbreviated $\nu_i = \sum_{j=1}^{i-1} n_j$. Thus, the second equation of (5.15) has an extra minus sign, and if we add both equations, we find $c_i c_j + c_j c_i = 0$. Furthermore,

$$[c_i, c_j^\dagger]_+ = \delta_{ij} \tag{5.16}$$

Justification: We assume $i < j$ (otherwise, we again relabel); as before, we find

$$\begin{aligned} c_i c_j^\dagger \big|\{n\}\big\rangle &= (-1)^{\nu_i + \nu_j} |\ldots (n_i - 1) \ldots (n_j + 1) \ldots \rangle \\ c_j^\dagger c_i \big|\{n\}\big\rangle &= (-1)^{\nu_j - 1 + \nu_i} |\ldots (n_i - 1) \ldots (n_j + 1) \ldots \rangle \end{aligned} \tag{5.17}$$

i.e. for $i \neq j$ c_i and $c_j^\dagger$ anticommute. Now let $i = j$:

$$\begin{aligned} c_i c_i^\dagger \big|\{n\}\big\rangle &= \begin{cases} \big|\{n\}\big\rangle, & \text{if } n_i = 0\,, \\ 0, & \text{if } n_i = 1\,, \end{cases} \\ c_i^\dagger c_i \big|\{n\}\big\rangle &= \begin{cases} 0, & \text{if } n_i = 0\,, \\ \big|\{n\}\big\rangle, & \text{if } n_i = 1\,, \end{cases} \end{aligned} \tag{5.18}$$

From the sum of these two equations, we obtain

$$(c_i c_i^\dagger + c_i^\dagger c_i) |\{n\}\rangle = \big|\{n\}\big\rangle \curvearrowright [c_i, c_i^\dagger]_+ = 1\,.$$

If we now define the vacuum as

$$|0\rangle := |00 \ldots 0 \ldots \rangle \tag{5.19}$$

then we have

$$\big|\{n\}\big\rangle = (c_1^\dagger)^{n_1} (c_2^\dagger)^{n_2} \ldots |0\rangle, \tag{5.20}$$

so that for N particle states, we obtain

$$c_{r_1}^\dagger c_{r_2}^\dagger \ldots c_{r_N}^\dagger |0\rangle, \tag{5.21}$$

Therefore, we have the correspondence, for example for two particles

$$\big|\psi_{k_1 k_2}(12)\big\rangle = \frac{1}{\sqrt{2}} \begin{vmatrix} |k_1\rangle^{(1)} & |k_1\rangle^{(2)} \\ |k_2\rangle^{(1)} & |k_2\rangle^{(2)} \end{vmatrix} \;\leftrightarrow\; c_1^\dagger c_2^\dagger |0\rangle \tag{5.22}$$

$$\big|\psi_{k_1 k_2}(12)\big\rangle = -\big|\psi_{k_2 k_1}(12)\big\rangle \;\leftrightarrow\; c_2^\dagger c_1^\dagger |0\rangle = -c_1^\dagger c_2^\dagger |0\rangle \tag{5.23}$$

Both for the Slater determinant in first quantization and in second quantization, the antisymmetry of the wave function is guaranteed.
In particular for fermions, this has the consequence

$$c_1^\dagger c_1^\dagger |0\rangle = -c_1^\dagger c_1^\dagger |0\rangle = 0\,,$$

two fermions cannot have the same quantum numbers.
For bosons, we briefly note the definitions

$$\begin{aligned} c_i|\dots n_i \dots\rangle &= \sqrt{n_i}|\dots (n_i-1)\dots\rangle \\ c_i^\dagger|\dots n_i \dots\rangle &= \sqrt{n_i+1}|\dots (n_i+1)\dots\rangle \end{aligned} \tag{5.24}$$

as well as the commutation relations

$$\begin{aligned} &[c_i, c_j] = [c_i^\dagger, c_j^\dagger] = 0 \\ &[c_i, c_j^\dagger] = \delta_{ij} \end{aligned} \tag{5.25}$$

Particle number operator

From the anticommutation (commutation) relations, we can also conclude that the operator $n_i = c_i^\dagger c_i$ (for bosons: $n_i = b_i^\dagger b_i$) is the particle number operator. For fermions, we have

$$\begin{aligned} n_i|\dots (n_i=0)\dots\rangle &= c_i^\dagger c_i|\dots (n_i=0)\dots\rangle = 0 \\ n_i|\dots (n_i=1)\dots\rangle &= c_i^\dagger c_i c_i^\dagger|\dots (n_i=0)\dots\rangle \\ &= c_i^\dagger\big(1-c_i^\dagger c_i\big)|\dots (n_i=0)\dots\rangle = |\dots (n_i=1)\dots\rangle\,. \end{aligned} \tag{5.26}$$

For bosons,

$$n_i\big(b_i^\dagger\big)^N|0\rangle = N\left(b_i^\dagger\right)^N|0\rangle\,,$$

as can easily been shown recursively.

Change of basis

If we change from one single particle basis $|i\rangle$ to another, $|\tilde{i}\rangle$, by inserting a unit operator

$$\tilde{c}_j^\dagger\,|0\rangle \;\equiv\; |\tilde{j}\rangle \;=\; \sum_i |i\rangle\langle i|\tilde{j}\rangle = \sum_i \langle i|\tilde{j}\rangle\, c_i^\dagger\,|0\rangle\,, \tag{5.27}$$

the operators c_i turn into operators $\tilde{c}_j$ according to

$$\boxed{\tilde{c}_j^\dagger \;=\; \sum_i \langle i|\tilde{j}\rangle\, c_i^\dagger\,, \qquad \tilde{c}_j \;=\; \sum_i \langle \tilde{j}|i\rangle\, c_i} \,. \tag{5.28}$$

Operators in second quantization

So far, we have only considered a discrete single particle basis $|i\rangle$. We will now define field operators $\hat{\Phi}(\vec{x})$ over the single particle states corresponding to the position operator, and analogously field operators $c_{\vec{k}}$ that correspond to the momentum operator:

$$\begin{aligned}\hat{\Phi}(\vec{x}) &= \sum_i \langle\vec{x}|i\rangle c_i \\ c_{\vec{k}} &= \sum_i \langle\vec{k}|i\rangle c_i = \int d^3x \langle\vec{k}|\vec{x}\rangle \sum_i \langle\vec{x}|i\rangle c_i = \frac{1}{(2\pi)^{3/2}} \int d^3x\, e^{-i\vec{k}\cdot\vec{x}} \hat{\Phi}(\vec{x})\end{aligned} \tag{5.29}$$

Here, the unit operator $\mathbb{1} = \int d^3x\, |\vec{x}\rangle\langle\vec{x}|$ was introduced. Furthermore,

$$\hat{\Phi}(\vec{x}) = \int d^3k \sum_i \langle\vec{x}|\vec{k}\rangle\langle\vec{k}|i\rangle c_i = \int d^3k \langle\vec{x}|\vec{k}\rangle c_{\vec{k}} = \frac{1}{(2\pi)^{3/2}} \int d^3k\, e^{i\vec{k}\cdot\vec{x}} c_{\vec{k}} \tag{5.30}$$

Field operators corresponding to the position operator $\hat{\Phi}(\vec{x})$ ($\hat{\Phi}^\dagger(\vec{x})$) annihilate (create) a particle at position $\vec{x}$ (while annihilation/creation operators c_i, $c_i^\dagger$ do this for particles in a certain single particle state). The anticommutation relations

$$\begin{aligned}\left[\hat{\Phi}(\vec{x}), \hat{\Phi}(\vec{y})\right]_+ &= \left[\hat{\Phi}^\dagger(\vec{x}), \hat{\Phi}^\dagger(\vec{y})\right]_+ = 0, \\ \left[\hat{\Phi}(\vec{x}), \hat{\Phi}^\dagger(\vec{y})\right]_+ &= \sum_{i,j} \langle\vec{x}|i\rangle\langle j|\vec{y}\rangle \left[c_i, c_j^\dagger\right]_+ \\ &= \sum_i \langle\vec{x}|i\rangle\langle i|\vec{y}\rangle = \langle\vec{x}|\vec{y}\rangle = \delta^3(\vec{x}-\vec{y})\end{aligned} \tag{5.31}$$

and analogously for $c_{\vec{k}}$ are valid.

Remark. For systems with a finite volume V one defines $\hat{\Phi}(\vec{x})$ and $c_{\vec{k}}$ as above; $\vec{x}$ then varies continuously over V and $\vec{k}$ is quantized with corresponding volume $d^3k = \frac{(2\pi)^3}{V}$. Transformation from $\hat{\Phi}(\vec{x})$ to $c_{\vec{k}}$ is done using $\langle x|k\rangle = \frac{1}{\sqrt{V}} e^{i\vec{k}\vec{x}}$. The (anti-) commutation relations are valid as noted above, and the δ symbol for operators $c_{\vec{k}}$, $c_{\vec{k}}^\dagger$ becomes a Kronecker delta.

Representation of states

Let $|\psi\rangle$ be an N particle state; then we can write $|\psi\rangle$ as

$$|\psi\rangle = \frac{1}{N!}\int d^3x_1 \dots d^3x_N \psi(\vec{x}_1, \vec{x}_2, \dots, \vec{x}_N)\hat{\Phi}^\dagger(\vec{x}_1)\dots\hat{\Phi}^\dagger(\vec{x}_N)|0\rangle \quad (5.32)$$

with a function $\psi(\vec{x}_1, \vec{x}_2, \dots, \vec{x}_N)$ which is chosen totally (anti-)symmetric without loss of generality. We remember that

$$P_-\big(|\vec{x}_1\rangle|\vec{x}_2\rangle\dots|\vec{x}_N\rangle\big) =: |\vec{x}_1\vec{x}_2\dots\vec{x}_N\rangle = \hat{\Phi}^\dagger(\vec{x}_1)\hat{\Phi}^\dagger(\vec{x}_2)\dots\hat{\Phi}^\dagger(\vec{x}_N)|0\rangle \quad (5.33)$$

Apparently, the function $\psi(\vec{x}_1, \vec{x}_2, \dots, \vec{x}_N)$ is the wave function in second quantization.
We can also see by applying (anti-) commutation rules, that $\langle\vec{y}_1\vec{y}_2\dots\vec{y}_N|\psi\rangle = \psi(\vec{y}_1, \vec{y}_2, \dots, \vec{y}_N)$:

$$\begin{aligned}\langle\vec{y}_1\vec{y}_2\dots\vec{y}_N|\psi\rangle &= \frac{1}{N!}\int d^3x_1\dots d^3x_N\psi(\vec{x}_1,\vec{x}_2,\dots,\vec{x}_N)\times \\ &\qquad \times\langle 0|\hat{\Phi}(\vec{y}_N)\dots\hat{\Phi}(\vec{y}_1)\hat{\Phi}^\dagger(\vec{x}_1)\dots\hat{\Phi}^\dagger(\vec{x}_N)|0\rangle \\ &= \psi(\vec{y}_1,\vec{y}_2,\dots,\vec{y}_N) \end{aligned} \quad (5.34)$$

This presents the explicit relationship between first and second quantization.

So far, we have only considered one species of particles. We will for example consider interactions between electrons (fermions) and phonons (bosons). The corresponding states will then be created by products of fermionic and bosonic creation operators, for example

$$c^\dagger_{\vec{k}_1} c^\dagger_{\vec{k}_2} b^\dagger_{\vec{q}_1} b^\dagger_{\vec{q}_2} b^\dagger_{\vec{q}_3}|0\rangle \quad (5.35)$$

as a state of two fermions and three bosons with momenta $\vec{k}_1$, $\vec{k}_2$, and $\vec{q}_1$, $\vec{q}_2$, $\vec{q}_3$. Here, different fermions anticommute, and bosons among each other as well as bosons and fermions commute.

Operators in occupation number representation

In the description of many particle systems, so-called one particle and two particle operators appear. In first quantization, we can write a one particle operator for an N_e particle system as

$$A^{(1)} = \sum_{i=1}^{N_e} A^{(1)}(\vec{r}_i)\,. \quad (5.36)$$

It is added up from contributions, each of which is only acting on one of the N_e particles. Examples are the kinetic energy and the external potential of the single particle Hamiltonian, the current operator or the particle density operator. Two particle operators in first quantization are of the form

$$A^{(2)} = \frac{1}{2} \sum_{i \neq j} A^{(2)}(\vec{r}_i, \vec{r}_j) \,. \tag{5.37}$$

All addends simultaneously act on two different particles. An example is the Coulomb interaction. Now, we express the one particle operator by creation and annihilation operators by introducing the unit operators $\mathbb{1} = \sum_\alpha |k_\alpha\rangle^{(i)\ (i)}\langle k_\alpha|$:

$$\begin{aligned} A^{(2)} &= \sum_{i=1}^{N_e} \sum_{\alpha=1}^{\infty} |k_\alpha\rangle^{(i)\ (i)}\langle k_\alpha| A^{(1)}(\vec{r}_i) \sum_{\beta=1}^{\infty} |k_\beta\rangle^{(i)\ (i)}\langle k_\beta| \\ &= \sum_{\alpha,\beta=1}^{\infty} \langle k_\alpha| A^{(1)}(\vec{r})|k_\beta\rangle \sum_{i=1}^{N_e} |k_\alpha\rangle^{(i)\ (i)}\langle k_\beta| \end{aligned} \tag{5.38}$$

Here we used that the matrix element of $A^{(1)}$ with respect to the single particle states is not anymore dependent on the particle index:

$${}^{(i)}\langle k_\alpha| A^{(1)}(\vec{r}_i)|k_\beta\rangle^{(i)} = \int d^3 r_i \, \varphi^*_{k_\alpha}(\vec{r}_i) A^{(1)}(\vec{r}_i) \varphi_{k_\beta}(\vec{r}_i) = \langle k_\alpha| A^{(1)}(\vec{r})|k_\beta\rangle \tag{5.39}$$

We have

$$\sum_{i=1}^{N_e} |k_\alpha\rangle^{(i)\ (i)}\langle k_\beta| = c^+_{k_\alpha} c_{k_\beta} \tag{5.40}$$

because the operator $|k_\alpha\rangle^{(i)\ (i)}\langle k_\beta|$, applied to an N_e particle state only gives a non-zero result if the one particle state k_β is contained in the manyparticle state; in this case, the state $|k_\beta\rangle$ in this manyparticle state is replaced by $|k_\alpha\rangle$; this corresponds to the annihilation of a particle in the state k_β and the creation of a particle in the state k_α.
Thus, the single particle operator in occupation number representation is

$$A^{(1)} = \sum_{\alpha,\beta=1}^{\infty} A^{(1)}_{k_\alpha,k_\beta} c^\dagger_{k_\alpha} c_{k_\beta} \quad \text{with } A^{(1)}_{k_\alpha,k_\beta} = \langle k_\alpha| A^{(1)}(\vec{r})|k_\beta\rangle \tag{5.41}$$

The one particle operator is expressed as a linear combination over all possible pairs of creation and annihilation operators, with matrix elements of the single particle operator with respect to the single particle states as coefficients. Correspondingly, we have for the two particle operator, if we insert unit operators:

$$\begin{aligned} A^{(2)} &= \frac{1}{2} \sum_{i \neq j} \sum_{\alpha,\beta,\gamma,\delta} |k_\alpha\rangle^{(i)} |k_\beta\rangle^{(j)\ (i)} \langle k_\alpha|^{\ (j)} \langle k_\beta| A^{(2)}(\vec{r}_i, \vec{r}_j) |k_\gamma\rangle^{(j)} |k_\delta\rangle^{(i)\ (j)} \langle k_\gamma|^{\ (i)} \langle k_\delta| \\ &= \frac{1}{2} \sum_{\alpha,\beta,\gamma,\delta} A^{(2)}_{k_\alpha k_\beta, k_\gamma k_\delta} \sum_{i \neq j} |k_\alpha\rangle^{(i)} |k_\beta\rangle^{(j)\ (j)} \langle k_\gamma|^{\ (i)} \langle k_\delta| \end{aligned} \tag{5.42}$$

with the two particle matrix element

$$\begin{aligned} A^{(2)}_{k_\alpha k_\beta, k_\gamma k_\delta} &= {}^{(i)}\langle k_\alpha|^{\ (j)} \langle k_\beta| A^{(2)}(\vec{r}_i, \vec{r}_j) |k_\gamma\rangle^{(j)} |k_\delta\rangle^{(i)} \\ &= \int d^3 r_i d^3 r_j\ \varphi^*_{k_\alpha}(\vec{r}_i) \varphi^*_{k_\beta}(\vec{r}_j) A^{(2)}(\vec{r}_i, \vec{r}_j) \varphi_{k_\gamma}(\vec{r}_j) \varphi_{k_\delta}(\vec{r}_i) \end{aligned} \tag{5.43}$$

which is again independent of the particle indices because in the calculation of the matrix element in position representation, there is an integral over these indices. If we apply the operator $\sum_{i \neq j} |k_\alpha\rangle^{(i)} |k_\beta\rangle^{(j)\ (j)} \langle k_\gamma|^{\ (i)} \langle k_\delta|$ on a manybody state we only obtain something nonzero if in this many body state, the single particle states k_γ and k_δ are occupied. In this case the operator replaces these states by k_α and k_β; then, in the manybody state k_γ, k_δ are unoccupied and k_α, k_β are occupied; this corresponds to

$$\sum_{i \neq j} |k_\alpha\rangle^{(i)} |k_\beta\rangle^{(j)\ (j)} \langle k_\gamma|^{\ (i)} \langle k_\delta| = c^\dagger_{k_\alpha} c^\dagger_{k_\beta} c_{k_\gamma} c_{k_\delta} \tag{5.44}$$

Thus, the two particle operator $A^{(2)}$ is in occupation number representation

$$\begin{aligned} A^{(2)} &= \frac{1}{2} \sum_{\alpha,\beta,\gamma,\delta} A^{(2)}_{k_\alpha k_\beta, k_\gamma k_\delta} c^\dagger_{k_\alpha} c^\dagger_{k_\beta} c_{k_\gamma} c_{k_\delta} \\ A^{(2)}_{k_\alpha k_\beta, k_\gamma k_\delta} &= \int d^3 r_i d^3 r_j\ \varphi^*_{k_\alpha}(\vec{r}_i) \varphi^*_{k_\beta}(\vec{r}_j) A^{(2)}(\vec{r}_i, \vec{r}_j) \varphi_{k_\gamma}(\vec{r}_j) \varphi_{k_\delta}(\vec{r}_i) \end{aligned} \tag{5.45}$$

All operators become linear combinations of creation and annihilation operators with coefficients which are given by the matrix element of the corresponding operator with respect to the single particle states.

The operators can also be expressed using the representation of free field operators:

$$A^{(1)} = \int d^3r\, \hat{\Phi}^\dagger(\vec{r}) A^{(1)}(\vec{r}) \hat{\Phi}(\vec{r})$$
$$A^{(2)} = \frac{1}{2} \int d^3r d^3r'\, \hat{\Phi}^\dagger(\vec{r}) \hat{\Phi}^\dagger(\vec{r}') A^{(2)}(\vec{r}, \vec{r}') \hat{\Phi}(\vec{r}') \hat{\Phi}(\vec{r}) \tag{5.46}$$

This can be checked by introducing the expansion of the field operators in a single particle basis. The name second quantization is now due to the fact that in these relationships, also the wave functions are replaced by operators.
Especially the Hamiltonian (5.1) can now be written in occupation number representation:

$$H = H_0 + H_1 = \sum_\alpha \varepsilon_{k_\alpha} c^\dagger_{k_\alpha} c_{k_\alpha} + \frac{1}{2} \sum_{\alpha,\beta,\gamma,\delta} u_{k_\alpha k_\beta, k_\gamma k_\delta} c^\dagger_{k_\alpha} c^\dagger_{k_\beta} c_{k_\gamma} c_{k_\delta} \tag{5.47}$$

where the single particle basis of the single particle Hamiltonian was used. We have

$$u_{k_\alpha k_\beta, k_\gamma k_\delta} = \int d^3r d^3r'\, \varphi^*_{k_\alpha}(\vec{r}) \varphi^*_{k_\beta}(\vec{r}') u(\vec{r} - \vec{r}') \varphi_{k_\gamma}(\vec{r}') \varphi_{k_\delta}(\vec{r}) \tag{5.48}$$

The use of a different single particle basis is also possible; however, the single particle component of H is then not diagonal anymore.

5.2 Direct ferromagnetic exchange interaction

The Coulomb interaction is

$$H_{\text{Coulomb}} = \frac{1}{2} \frac{1}{4\pi\epsilon_0} \int d^3r_1 d^3r_2 \frac{\rho(\vec{r}_1)\rho(\vec{r}_2)}{|\vec{r}_1 - \vec{r}_2|} \tag{5.49}$$

In second quantized notation, $\rho(\vec{r})$ is the operator of the charge density

$$\rho(\vec{r}) = -e \sum_\sigma \psi^\dagger_\sigma(\vec{r}) \psi_\sigma(\vec{r})$$

with spin orientation $\sigma = \uparrow, \downarrow$ and the field operator $\psi_\sigma(\vec{r})$. This operator satisfies the anticommutation relations

$$\left[\psi_{\sigma_1}(\vec{r}_1), \psi^+_{\sigma_2}(\vec{r}_2)\right]_+ \equiv \psi_{\sigma_1}(\vec{r}_1)\psi^+_{\sigma_2}(\vec{r}_2) + \psi^+_{\sigma_2}(\vec{r}_2)\psi_{\sigma_1}(\vec{r}_1) = \delta_{\sigma_1\sigma_2}\delta(\vec{r}_1 - \vec{r}_2)$$
$$\left[\psi_{\sigma_1}(\vec{r}_1), \psi_{\sigma_2}(\vec{r}_2)\right]_+ = 0 \qquad \left[\psi^+_{\sigma_1}(\vec{r}_1), \psi^+_{\sigma_2}(\vec{r}_2)\right]_+ = 0$$

(5.50)

as it is a Fermionic field. We find

$$\begin{aligned} H_{\text{Coulomb}} &= \frac{1}{2}\frac{1}{4\pi\epsilon_0}\int d^3r_1 d^3r_2 \sum_{\sigma_1\sigma_2} \psi^\dagger_{\sigma_1}(\vec{r}_1)\psi_{\sigma_1}(\vec{r}_1)\frac{e^2}{|\vec{r}_1-\vec{r}_2|}\psi^\dagger_{\sigma_2}(\vec{r}_2)\psi_{\sigma_2}(\vec{r}_2) \\ &= \frac{1}{2}\frac{1}{4\pi\epsilon_0}\int d^3r_1 d^3r_2 \sum_{\sigma_1\sigma_2} \psi^\dagger_{\sigma_1}(\vec{r}_1)\psi^\dagger_{\sigma_2}(\vec{r}_2)\frac{e^2}{|\vec{r}_1-\vec{r}_2|}\psi_{\sigma_2}(\vec{r}_2)\psi_{\sigma_1}(\vec{r}_1) \\ &\quad + \frac{1}{2}\frac{1}{4\pi\epsilon_0}\int d^3r_1 \sum_{\sigma_1} \frac{e^2}{|\vec{r}_1-\vec{r}_1|}\psi^\dagger_{\sigma_1}(\vec{r}_1)\psi_{\sigma_1}(\vec{r}_1) \end{aligned} \tag{5.51}$$

The last singular term is unphysical; in fact, the field operators should be written in normal order ($\psi^\dagger\psi^\dagger\psi\psi$) from the start. ψ can be expanded into any orthonormal set of single particle wave functions. A set of Wannier functions, *i.e.* orthonormal functions $\phi_{\vec{R}m}(\vec{r})$ localized at the ion position $\vec{R}$ is advantageous; m includes all orbital quantum numbers except for the spin σ. We also introduce spinors

$$\chi_\uparrow = \begin{pmatrix}1\\0\end{pmatrix}, \chi_\downarrow = \begin{pmatrix}0\\1\end{pmatrix}$$

which are eigenvectors of

$$s^z = \frac{1}{2}\sigma^z = \frac{1}{2}\begin{pmatrix}1 & 0\\ 0 & -1\end{pmatrix}$$

with eigenvalues $\pm\frac{1}{2}$. Then the field operator is

$$\psi_\sigma(\vec{r}) = \sum_{\vec{R}m} a_{\vec{R}m\sigma}\phi_{\vec{R}m}\chi_\sigma \tag{5.52}$$

with Fermionic annihilation operators $a_{\vec{R}m\sigma}$ which satisfy $[a_{\vec{R}m\sigma}, a^\dagger_{\vec{R}m\sigma}]_+ = \delta_{\vec{R}\vec{R}'}\delta_{mm'}\delta_{\sigma\sigma'}$ etc. The Coulomb interaction becomes

$$\begin{aligned} H_{\text{Coulomb}} = \frac{1}{2}\sum_{\vec{R}_1 m_1}\cdots\sum_{\vec{R}_4 m_4}\int d^3r_1 d^3r_2 \phi^*_{\vec{R}_1 m_1}(\vec{r}_1)\phi^*_{\vec{R}_2 m_2}(\vec{r}_2)\frac{e^2}{4\pi\epsilon_0|\vec{r}_1-\vec{r}_2|}\times \\ \times\,\phi_{\vec{R}_3 m_3}(\vec{r}_2)\phi_{\vec{R}_4 m_4}(\vec{r}_1)\sum_{\sigma_1\sigma_2}\chi^\dagger_{\sigma_1}\chi^\dagger_{\sigma_2}\chi_{\sigma_2}\chi_{\sigma_1}a^\dagger_{\vec{R}_1 m_1\sigma_1}a^\dagger_{\vec{R}_2 m_2\sigma_2}a_{\vec{R}_3 m_3\sigma_2}a_{\vec{R}_4 m_4\sigma_1} \end{aligned}$$

(5.53)

The scalar product of the spinors are simply $\chi^\dagger_{\sigma_1}\chi_{\sigma_1} = \chi^\dagger_{\sigma_2}\chi_{\sigma_2} = 1$. We define the integral

$$\left\langle \vec{R}_1 m_1, \vec{R}_2 m_2 \middle| \frac{e^2}{4\pi\epsilon_0|\vec{r}_1 - \vec{r}_2|} \middle| \vec{R}_3 m_4, \vec{R}_4 m_4 \right\rangle :=$$
$$\int d^3r_1 d^3r_2 \phi^*_{\vec{R}_1 m_1}(\vec{r}_1)\phi^*_{\vec{R}_2 m_2}(\vec{r}_2)\frac{e^2}{4\pi\epsilon_0|\vec{r}_1 - \vec{r}_2|}\phi_{\vec{R}_3 m_3}(\vec{r}_2)\phi_{\vec{R}_4 m_4}(\vec{r}_1) \quad (5.54)$$

and obtain

$$H_{\text{Coulomb}} = \frac{1}{2}\sum_{\vec{R}_1 m_1} \cdots \sum_{\vec{R}_4 m_4} \left\langle \vec{R}_1 m_1, \vec{R}_2 m_2 \middle| \frac{e^2}{4\pi\epsilon_0|\vec{r}_1 - \vec{r}_2|} \middle| \vec{R}_3 m_4, \vec{R}_4 m_4 \right\rangle \times$$
$$\times \sum_{\sigma_1\sigma_2} a^\dagger_{\vec{R}_1 m_1 \sigma_1} a^\dagger_{\vec{R}_2 m_2 \sigma_2} a_{\vec{R}_3 m_3 \sigma_2} a_{\vec{R}_4 m_4 \sigma_1} \quad (5.55)$$

5.2.1 On-site Coulomb interaction

We first consider the contribution of $\vec{R}_1 = \vec{R}_2 = \vec{R}_3 = \vec{R}_4 \equiv \vec{R}$ and drop the index $\vec{R}$ where it doesn't create confusion. In general, the quantum numbers $m_1, \ldots, m_4$ in the integral $\left\langle m_1, m_2 \middle| \frac{e^2}{4\pi\epsilon_0|\vec{r}_1 - \vec{r}_2|} \middle| m_3, m_4 \right\rangle$ can all be different and still lead to a nonzero integral. However, in treating H_{Coulomb} as a perturbation, a nonzero first-order contribution requires a pairing of creation and annihilation operators $a^\dagger$, a for each orbital. This requires $m_1 = m_4$ and $m_2 = m_3$ or $m_1 = m_3$, $m_2 = m_4$. This leads to the direct Coulomb integrals

$$K_{m_1 m_2} := \left\langle m_1, m_2 \middle| \frac{e^2}{4\pi\epsilon_0|\vec{r}_1 - \vec{r}_2|} \middle| m_2, m_1 \right\rangle$$
$$= \int d^3r_1 d^3r_2 |\phi_{m_1}(\vec{r}_1)|^2 \frac{e^2}{4\pi\epsilon_0|\vec{r}_1 - \vec{r}_2|} |\phi_{m_2}(\vec{r}_2)|^2 \quad (5.56)$$

and the exchange integrals

$$J_{m_1 m_2} := \left\langle m_1, m_2 \middle| \frac{e^2}{4\pi\epsilon_0|\vec{r}_1 - \vec{r}_2} \middle| m_1, m_2 \right\rangle$$
$$= \int d^3r_1 d^3r_2 \phi^*_{m_1}(\vec{r}_1)\phi^*_{m_2}(\vec{r}_2)\frac{e^2}{4\pi\epsilon_0|\vec{r}_1 - \vec{r}_2|}\phi_{m_1}(\vec{r}_2)\phi_{m_2}(\vec{r}_1)\,, \quad (5.57)$$

so-called because m_1 and m_2 are exchanged in the last factor compared to the direct integrals. To first order we obtain

$$H_{\text{Coulomb}} \approx \frac{1}{2} \sum_{\vec{R}} \sum_{m_1 m_2} \sum_{\sigma_1 \sigma_2} \Big(K_{m_1 m_2} a^\dagger_{\vec{R} m_1 \sigma_1} a^\dagger_{\vec{R} m_2 \sigma_2} a_{\vec{R} m_2 \sigma_2} a_{\vec{R} m_1 \sigma_1} + J_{m_1 m_2} a^\dagger_{\vec{R} m_1 \sigma_1} a^\dagger_{\vec{R} m_2 \sigma_2} a_{\vec{R} m_1 \sigma_2} a_{\vec{R} m_2 \sigma_1} \Big) \quad (5.58)$$

(double counting of contributions from $m_1 = m_2$ and $\sigma_1 = \sigma_2$ is not a problem because the terms contain $a_{\vec{R} m_1 \sigma_1} a_{\vec{R} m_1 \sigma_1} = 0$). Therefore

$$H_{\text{Coulomb}} \approx \frac{1}{2} \sum_{\vec{R}} \sum_{m_1 m_2} \sum_{\sigma_1 \sigma_2} \Big(K_{m_1 m_2} a^\dagger_{\vec{R} m_1 \sigma_1} a_{\vec{R} m_1 \sigma_1} a^\dagger_{\vec{R} m_2 \sigma_2} a_{\vec{R} m_2 \sigma_2} - J_{m_1 m_2} a^\dagger_{\vec{R} m_1 \sigma_1} a_{\vec{R} m_1 \sigma_2} a^\dagger_{\vec{R} m_2 \sigma_2} a_{\vec{R} m_2 \sigma_1} \Big) + \text{irrelevant potential terms} \quad (5.59)$$

We now define the number operators $n_{\vec{R} m} := \sum_\sigma a^\dagger_{\vec{R} m \sigma} a_{\vec{R} m \sigma}$ and the spin operators $s^\alpha_{\vec{R} m} := \sum_{\sigma\sigma'} a^\dagger_{\vec{R} m \sigma} \frac{1}{2} \sigma^\alpha_{\sigma\sigma'} a_{\vec{R} m \sigma'}$ with Pauli matrices σ^α, $\alpha = x, y, z$. After some algebra,

$$\begin{aligned} &\sum_{\sigma_1 \sigma_2} a^\dagger_{\vec{R} m_1 \sigma_1} a_{\vec{R} m_1 \sigma_2} a^\dagger_{\vec{R} m_2 \sigma_2} a_{\vec{R} m_2 \sigma_1} \\ &\quad = \frac{1}{2} n_{\vec{R} m_1} n_{\vec{R} m_2} + 2 s^z_{\vec{R} m_1} s^z_{\vec{R} m_2} + s^+_{\vec{R} m_1} s^-_{\vec{R} m_2} + s^-_{\vec{R} m_1} s^+_{\vec{R} m_2} \\ &\quad = \frac{1}{2} n_{\vec{R} m_1} n_{\vec{R} m_2} + 2 \vec{s}_{\vec{R} m_1} \cdot \vec{s}_{\vec{R} m_2} \end{aligned} \quad (5.60)$$

Therefore, we obtain

$$H_{\text{Coulomb}} \approx \sum_{\vec{R}} \frac{1}{2} \sum_{m_1 m_2} \Big\{ \Big(K_{m_1 m_2} - \frac{1}{2} J_{m_1 m_2} \Big) n_{\vec{R} m_1} n_{\vec{R} m_2} - 2 J_{m_1 m_2} \vec{s}_{\vec{R} m_1} \cdot \vec{s}_{\vec{R} m_2} \Big\} . \quad (5.61)$$

The first term is the m site Coulomb interaction. From the definition (5.56), we can read off immediately that $K_{m_1 m_2} > 0$. To show that $J_{m_1 m_2} \geqslant 0$, we use the Fourier transform

$$\frac{1}{|\vec{r}_1 - \vec{r}_2|} = \int \frac{d^3 k}{(2\pi)^3} e^{i \vec{k} \cdot (\vec{r}_1 - \vec{r}_2)} \frac{4\pi}{k^2} . \quad (5.62)$$

Then,

$$J_{m_1m_2} = \int \frac{d^3k}{(2\pi)^3}\frac{e^2}{\epsilon_0 k^2} \underbrace{\int d^3r_1 \phi^*_{m_1}(\vec{r}_1)\phi_{m_2}(\vec{r}_1)e^{i\vec{k}\cdot\vec{r}_1}}_{=:I(\vec{k})} \underbrace{\int d^3r_2 \phi_{m_1}(\vec{r}_2)\phi^*_{m_2}(\vec{r}_2)e^{-i\vec{k}\cdot\vec{r}_2}}_{=:I^*(\vec{k})}$$
$$= \int \frac{d^3k}{(2\pi)^3}\frac{e^2}{\epsilon_0 k^2}|I(\vec{k})|^2 \geqslant 0\,. \tag{5.63}$$

We also show that $K_{m_1m_2} \geqslant J_{m_1m_2}$:

$$\begin{aligned} K_{m_1m_2} - J_{m_1m_2} &= \frac{1}{2}\big(K_{m_1m_2} + K_{m_2m_1} - J_{m_1m_2} - J_{m_2m_1}\big) \\ &= \frac{1}{2}\int d^3r_1 d^3r_2 \frac{e^2}{4\pi\epsilon_0|\vec{r}_1-\vec{r}_2|} \underbrace{\big[\phi^*_{m_1}(\vec{r}_1)\phi^*_{m_2}(\vec{r}_2) - \phi^*_{m_2}(\vec{r}_1)\phi^*_{m_1}(\vec{r}_2)\big]}_{=:f(\vec{r}_1,\vec{r}_2)} \times \\ &\qquad \times \underbrace{\big[\phi_{m_2}(\vec{r}_2)\phi_{m_1}(\vec{r}_1) - \phi_{m_1}(\vec{r}_2)\phi_{m_2}(\vec{r}_1)\big]}_{=:f^*(\vec{r}_1,\vec{r}_2)} \\ &= \frac{1}{2}\int d^3r_1 d^3r_2 \frac{e^2}{4\pi\epsilon_0|\vec{r}_1-\vec{r}_2|}|f(\vec{r}_1,\vec{r}_2)|^2 \geqslant 0\,. \end{aligned} \tag{5.64}$$

Therefore, the corrected Coulomb term $K_{m_1m_2} - \frac{1}{2}J_{m_1m_2} > 0$ is reduced but still repulsive. The new finding is a spin-spin interaction of the form

$$-J_{m_1m_2}\vec{s}_{\vec{R}m_1}\cdot\vec{s}_{\vec{R}m_2}$$

with $J_{m_1m_2} \geqslant 0$. This interaction prefers parallel alignment of the spins, *i.e.* it is a ferromagnetic interaction. Thus, we have derived the first Hund's rule: The total spin of electrons in a partially filled shell of one ion tends to be maximal.

Note that all terms containing $J_{m_1m_2}$ are quantum mechanical in origin; they appear because we have written the density $\rho = -e\psi^\dagger\psi$ as a bilinear form in the field operator which made unconventional pairings of the orbital indices possible. There is no analogy in classical physics. For a single

relevant orbital $\phi(\vec{r})$, we get

$$\begin{aligned}
H_{\text{Coulomb}} &\approx \frac{1}{2}\sum_{\vec{R}}\int d^3r_1 d^3r_2 \phi^*(\vec{r}_1)\phi^*(\vec{r}_2)\frac{e^2}{4\pi\epsilon_0|\vec{r}_1-\vec{r}_2|}\phi(\vec{r}_2)\phi(\vec{r}_1)\times \\
&\qquad \times \sum_{\sigma_1\sigma_2} a^\dagger_{\vec{R}\sigma_1} a^\dagger_{\vec{R}\sigma_2} a_{\vec{R}\sigma_2} a_{\vec{R}\sigma_1} \\
&= \frac{1}{2}\sum_{\vec{R}}\int d^3r_1 d^3r_2 \phi^*(\vec{r}_1)\phi^*(\vec{r}_2)\frac{e^2}{4\pi\epsilon_0|\vec{r}_1-\vec{r}_2|}\phi(\vec{r}_2)\phi(\vec{r}_1)\times \\
&\qquad \times \left(a^\dagger_{\vec{R}\uparrow} a^\dagger_{\vec{R}\downarrow} a_{\vec{R}\downarrow} a_{\vec{R}\uparrow} + a^\dagger_{\vec{R}\downarrow} a^\dagger_{\vec{R}\uparrow} a_{\vec{R}\uparrow} a_{\vec{R}\downarrow}\right) \\
&= \sum_{\vec{R}} \underbrace{\int d^3r_1 d^3r_2 \phi^*(\vec{r}_1)\phi^*(\vec{r}_2)\frac{e^2}{4\pi\epsilon_0|\vec{r}_1-\vec{r}_2|}}_{=:U} a^\dagger_{\vec{R}\uparrow} a^\dagger_{\vec{R}\downarrow} a_{\vec{R}\downarrow} a_{\vec{R}\uparrow} \\
&= \sum_{\vec{R}} U a^\dagger_{\vec{R}\uparrow} a^\dagger_{\vec{R}\downarrow} a_{\vec{R}\downarrow} a_{\vec{R}\uparrow},
\end{aligned} \tag{5.65}$$

where U is the famous Hubbard U.

5.2.2 Ion-ion exchange interaction

If we allow the ionic sites $\vec{R}_1, \ldots, \vec{R}_4$ to be different, most of the calculation of the previous section remains unchanged; we just have to treat $\vec{R}_i$ as another quantum number besides m_i. Here, we restrict ourselves to a model with a single, non-degenerate (apart from spin) orbital per site. Then, we can drop the orbital quantum numbers m_i. We again assume the orbitals on different sites to have negligible overlap, *i.e.* they are orthogonal. This time, we will have a first order contribution if $\vec{R}_1 = \vec{R}_4$ and $\vec{R}_2 = \vec{R}_3$ or $\vec{R}_1 = \vec{R}_3$ and $\vec{R}_2 = \vec{R}_4$. In complete analogy to the previous section we obtain

$$H_{\text{Coulomb}} \approx \frac{1}{2}\sum_{\vec{R}_1\vec{R}_2}\left\{\left(K_{12}-\frac{1}{2}J_{12}\right)n_1 n_2 - 2J_{12}\vec{s}_1\cdot\vec{s}_2\right\} \tag{5.66}$$

where

$$K_{12} \equiv K_{\vec{R}_1\vec{R}_2} := \int d^3r_1 d^3r_2 \left|\phi_{\vec{R}_1}(\vec{r}_1)\right|^2 \frac{e^2}{4\pi\epsilon_0|\vec{r}_1-\vec{r}_2|}\left|\phi_{\vec{R}_2}(\vec{r}_2)\right|^2$$

$$J_{12} \equiv J_{\vec{R}_1\vec{R}_2} := \int d^3r_1 d^3r_2 \phi^*_{\vec{R}_1}(\vec{r}_1)\phi^*_{\vec{R}_2}(\vec{r}_2)\frac{e^2}{4\pi\epsilon_0|\vec{r}_1-\vec{r}_2|}\phi_{\vec{R}_1}(\vec{r}_2)\phi_{\vec{R}_2}(\vec{r}_1)\,. \tag{5.67}$$

If we make the assumption (to be relaxed later) than in an ionic crystal the charge $-en_i$ does not fluctuate much, we can consider the electron number $n_i = 1$ (otherwise there is no spin) and find for the interaction if we disregard a constant

$$H_{\rm exc} = -\sum_{\vec{R}_1\vec{R}_2} J_{12}\vec{s}_1\cdot\vec{s}_2\,. \tag{5.68}$$

By the argument given above, $J_{12} \geqslant 0$. thus, the Coulomb repulsion between electrons in orthogonal orbitals always leads to a ferromagnetic exchange interaction. The physical interpretation is that electrons with parallel spins cannot occupy the same orbital; therefore, they avoid the strong intra-orbital Coulomb repulsion. Thus, their energy is lower than for antiparallel spins.

5.3 Kinetic antiferromagnetic exchange interaction

Previously, we neglected charge fluctuations but as this is not usually a good approximation even for ionic crystals, we now go one step further. In an independent-electron or band picture, the hybridization between orbitals of different ions leads to charge fluctuations and thus allows electrons to tunnel or hop from one ion to another. While studying the effect of the hybridization, we neglect the non-local (inter-ionic) Coulomb repulsion; we already know that it leads to ferromagnetic exchange. The model describing the competition between the kinetic energy and the on-site Coulomb repulsion for a single relevant orbital is the Hubbard model:

$$H = \sum_{\vec{R}\vec{R}'\sigma} t(\vec{R}-\vec{R}')a^\dagger_{\vec{R}'\sigma}a_{\vec{R}\sigma} + U\sum_{\vec{R}} a^\dagger_{\vec{R}\uparrow}a_{\vec{R}\uparrow}a^\dagger_{\vec{R}\downarrow}a_{\vec{R}\downarrow}\,. \tag{5.69}$$

As a toy model, we consider the case of a dimer:

$$H = -t\sum_\sigma \left(a^\dagger_{1\sigma}a_{2\sigma}+a^\dagger_{2\sigma}a_{1\sigma}\right) - \mu\sum_\sigma\left(a^\dagger_{1\sigma}a_{1\sigma}+a^\dagger_{2\sigma}a_{2\sigma}\right)+U\sum_{i=1}^{2}a^\dagger_{i\uparrow}a_{i\uparrow}a^\dagger_{i\downarrow}a_{i\downarrow}\,.$$

(5.70)

The dimension of the Fock space is $4^2 = 16$ because each site can be in one of four states (empty $|0\rangle$, spin up $|\uparrow\rangle$, spin down $|\downarrow\rangle$, and doubly occupied $|\uparrow\downarrow\rangle$). The sectors with $0, 1, 2, 3, 4$ electrons have $1, 4, 6, 4, 1$ states, respectively. We consider the two electron sector which corresponds to a six dimensional Hilbert space. In this space, the chemical potential is an irrelevant constant. We choose as basis vectors $\Big\{|\uparrow\downarrow, 0\rangle, |0, \uparrow\downarrow\rangle, |\uparrow, \downarrow\rangle, |\downarrow, \uparrow\rangle, |\uparrow, \uparrow\rangle, |\downarrow, \downarrow\rangle\Big\}$. In this basis, the Hamiltonian is a 6×6 matrix

$$\mathsf{H}' = \begin{pmatrix} \mathsf{U} & 0 & \mathsf{t} & -\mathsf{t} & 0 & 0 \\ 0 & \mathsf{U} & \mathsf{t} & -\mathsf{t} & 0 & 0 \\ \mathsf{t} & \mathsf{t} & 0 & 0 & 0 & 0 \\ -\mathsf{t} & -\mathsf{t} & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \end{pmatrix} . \tag{5.71}$$

We can simplify H' by transforming from $|\uparrow, \downarrow\rangle, |\downarrow, \uparrow\rangle$ to $(|\uparrow, \downarrow\rangle - |\downarrow, \uparrow\rangle)/\sqrt{2}$, $(|\uparrow, \downarrow\rangle + |\downarrow, \uparrow\rangle)/\sqrt{2}$ and obtain

$$\mathsf{H}' = \begin{pmatrix} \mathsf{U} & 0 & \sqrt{2}\mathsf{t} & 0 & 0 & 0 \\ 0 & \mathsf{U} & \sqrt{2}\mathsf{t} & 0 & 0 & 0 \\ \sqrt{2}\mathsf{t} & \sqrt{2}\mathsf{t} & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \end{pmatrix} \tag{5.72}$$

with eigenenergies

$$\begin{aligned} &\mathsf{U}, \frac{1}{2}\big(\mathsf{U} \pm \sqrt{\mathsf{U}^2 + 16\mathsf{t}^2}\big) \text{ in the first sector} \\ &0, 0, 0 \text{ in the second sector} \end{aligned} \tag{5.73}$$

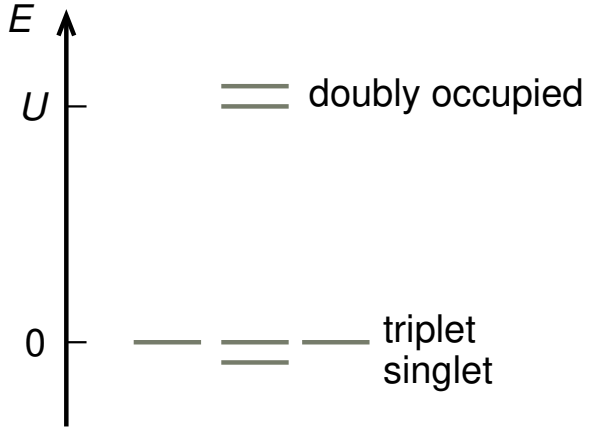
The latter eigenenergies correspond to the spin triplet, the states $(|\uparrow, \downarrow\rangle + |\downarrow, \uparrow\rangle)/\sqrt{2}$, $|\uparrow, \uparrow\rangle$ and $|\downarrow, \downarrow\rangle$.
We are interested in the ionic systems for which t should be small, $\mathsf{t} \ll \mathsf{U}$. Then the first sector contains two very large energies

$$\mathsf{U} \quad \text{and} \quad \frac{1}{2}\big(\mathsf{U} + \sqrt{\mathsf{U}^2 + 16\mathsf{t}^2}\big) \approx \mathsf{U} + \frac{4\mathsf{t}^2}{\mathsf{U}} ,$$

and one small energy

$$\frac{1}{2}\big(U - \sqrt{U^2 + 16t^2}\big) \approx -\frac{4t^2}{U} < 0\,. \tag{5.74}$$

For $\frac{U}{|t|} \to \infty$, the corresponding eigenstate approaches $(|\uparrow,\downarrow\rangle - |\downarrow,\uparrow\rangle)/\sqrt{2}$, *i.e.* the spin singlet. For finite U, it has some admixture of doubly occupied states. The spectrum looks like this:



We find that the singlet ($S = 0$) is lower in energy than the triplet ($S = 1$), *i.e.* there is an antiferromagnetic interaction. This results from the lowering of the kinetic energy for antiparallel spins. For parallel spins, the hopping is blocked by the Pauli principle which is why t does not even appear in the eigenenergies of the triplet. Therefore, this mechanism is called kinetic exchange. An example is the H_2 molecule which has a singlet ground state. To compare this model to an interacting pair of spins $s_1 = s_2 = \frac{1}{2}$, we write

$$\begin{aligned} H_{\text{eff}} &= -J\vec{s}_1 \cdot \vec{s}_2 = -\frac{J}{2}\big[\vec{S}\cdot\vec{S} - \vec{s}_1\cdot\vec{s}_1 - \vec{s}_2\cdot\vec{s}_2\big] \quad \text{with } \vec{S} = \vec{s}_1 + \vec{s}_2 \\ &= -\frac{J}{2}\Big[S\Big(S+\frac{1}{2}\Big)\underbrace{-\frac{3}{4}-\frac{3}{4}}_{\text{const}}\Big] = \text{const} \; - \frac{J}{2}S\Big(S+\frac{1}{2}\Big) \\ &= \text{const} \begin{cases} +0 \text{ for } S = 0 \\ -J \text{ for } S = 1 \end{cases} \end{aligned} \tag{5.75}$$

By comparing this with Eq. (5.74), we read off

$$J = -\frac{4t^2}{U} \quad \text{for } U \gg t\,. \tag{5.76}$$

An analogous result holds for the Hubbard model on a lattice, not only for

a dimer. The result is for a lattice at half filling and in the limit $U \gg t$

$$H_{\text{eff}} = -J \sum_{\langle ij \rangle} \vec{s}_i \cdot \vec{s}_j \quad \text{with } J = -\frac{4t^2}{U} \tag{5.77}$$

where $\sum_{\langle ij \rangle}$ runs over all nearest neighbor bonds, and each bond is counted only once ($\langle ij \rangle$ and $\langle ji \rangle$ are the same bond and enter the sum only once).