

Lecture note on Magnetism (2)

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1.4.4 Spin-orbit interaction

Another important effect stems from the Dirac equation is **spin-orbit interaction** (SOI). We have already seen that the four components in the solution of the Dirac equation correspond to (freedom of particle-antiparticle)×(spin freedom). In the Pauli representation (1.44b), (1.47), within non-relativistic limit of $p \ll mc$, the upper two rows correspond to the solution with positive energy, the lower two correspond to that with negative energy. However with growing p , the shifts from the free particle become large and some mixing appears between the upper two and the lower. For example, we consider a free dirac particle propagating along z -direction with up-spin for quantization axis of z -axis. Let $\tan 2\theta$ be

$$\tan 2\theta = \frac{p}{mc}, \quad (1.65)$$

then the four component wavefunction is

$$\psi_{\uparrow} = e^{i(kz - \omega t)} \begin{pmatrix} \cos \theta \\ 0 \\ \sin \theta \\ 0 \end{pmatrix}, \quad (1.66)$$

which indicates the increase of negative energy component with p . Inclusion of this leakage into the picture of particle with two-component of spin creates the SOI as the correction.

The equation for stationary solution obtained from the treatment in (1.60) is given by

$$(\boldsymbol{\alpha} \cdot \mathbf{p} + \beta mc^2 + V)\varphi = \epsilon\varphi, \quad (1.67)$$

where σ_j are Pauli matrices defined in eq. (1.45), $\boldsymbol{\alpha}$ is a vector of elements α_k defined in eq. (1.47), β is defined in eq. (1.47). We write φ as a two-component vector of φ_A and φ_B as $\varphi = {}^t(\varphi_A \ \varphi_B)$. Then eq. (1.67) is written in a simultaneous equation as follows.

$$\boldsymbol{\sigma} \cdot \mathbf{p}\varphi_B = c^{-1}(\delta - V)\varphi_A, \quad (1.68a)$$

$$\boldsymbol{\sigma} \cdot \mathbf{p}\varphi_A = c^{-1}(\delta - V + 2mc^2)\varphi_B, \quad (1.68b)$$

where $\delta = \epsilon - mc^2$ and $\boldsymbol{\sigma}$ is a vector of Pauli matrices as elements. φ_B can be erased virtually as

$$c^{-2}\boldsymbol{\sigma} \cdot \mathbf{p}(\delta - V + 2mc^2)^{-1}\boldsymbol{\sigma} \cdot \mathbf{p}\varphi_A = (\delta - V)\varphi_A. \quad (1.69)$$

We apply low energy expansion, in which we assume the kinetic energy of electron is sufficiently smaller than the rest energy mc^2 .

$$c^2(\delta - V + 2mc^2)^{-1} \approx \frac{1}{2m} \left[1 - \frac{\delta - V}{2mc^2} + \dots \right]. \quad (1.70)$$

The second term in rhs corresponds to $(v/c)^2$, where v is the electron velocity and we take up to this term. Substituting this to eq. (1.69) leads to the equation of ψ_A . However, the normalization condition is $\langle \varphi | \varphi \rangle = \langle \varphi_A | \varphi_A \rangle + \langle \varphi_B | \varphi_B \rangle = 1$, which should be considered in solving eq. (1.68) for φ_A . The first order perturbative mixing in wavefunction is on the second order in the normalization and in eq. (1.70). Hence in eq. (1.70), we take the first term in rhs. We use the commutation of σ_j and p_i , $\sigma_j^\dagger = \sigma_j$ and the following identity

$$(\boldsymbol{\sigma} \cdot \mathbf{a})(\boldsymbol{\sigma} \cdot \mathbf{b}) = (\mathbf{a} \cdot \mathbf{b}) + i[\boldsymbol{\sigma} \cdot (\mathbf{a} \times \mathbf{b})],$$

In the presence of magnetic field $\mathbf{B} = \nabla \times \mathbf{A}$, we replace \mathbf{p} with $\mathbf{p} + e\mathbf{A}$ to get

$$\langle \varphi_B | \varphi_B \rangle = \langle \varphi_A | \left[\frac{p^2 + e\hbar \boldsymbol{\sigma} \cdot \mathbf{B}}{4m^2 c^2} \right] | \varphi_A \rangle = O\left(\frac{v^2}{c^2}\right).$$

Then as the wavefunction

$$\varphi_a = \left(1 + \frac{p^2 + e\hbar \boldsymbol{\sigma} \cdot \mathbf{B}}{8m^2 c^2} \right) \varphi_A \quad (1.71)$$

is enough for the approximation to order of $(v/c)^2$. From eq. (1.69), we reach the Pauli equation (approximation to order of $(v/c)^2$) as

$$\left[\frac{p^2}{2m} + V + \frac{e\hbar}{2m} \boldsymbol{\sigma} \cdot \mathbf{B} - \frac{e\hbar \boldsymbol{\sigma} \cdot \mathbf{p} \times \mathbf{E}}{4m^2 c^2} - \frac{e\hbar^2}{8m^2 c^2} \nabla \cdot \mathbf{E} - \frac{p^4}{8m^3 c^2} - \frac{e\hbar p^2}{4m^3 c^2} \boldsymbol{\sigma} \cdot \mathbf{B} - \frac{(e\hbar B)^2}{8m^3 c^2} \right] \varphi_a = \delta \varphi_a, \quad (1.72)$$

where $\mathbf{E} = -\nabla V/e$ is the electric field. In the lhs of eq. (1.72), the third term is the Zeeman energy, the fourth is the spin-orbit interaction.

If we write $\mathbf{B}_{so} \equiv \mathbf{p} \times \mathbf{E}/2mc^2$, the fourth SOI term looks like in the same form as the third term. Namely the spin feels an effective magnetic field of \mathbf{B}_{so} , which is sometimes called a spin-orbit effective field.

1.5 Magnetism in quantum theory

In Sec. 1.3.3, we saw that the magnetism cannot be explained within the framework of classical theory. On the other hand in Sec. 1.4, in the Dirac theory, which considers both quantum theory and relativity, an electron, though it is a point charge, has a spin angular momentum and an associated magnetic moment. We will see, throughout this lecture for a semester, how the difficulty in the classical theory is solved. But here we see quickly how this spin angular momentum produces magnetism in a simple model of the classical framework plus spin.

A Hamiltonian with magnetic field \mathbf{B} is given by

$$\mathcal{H} = \sum_n \left[\frac{1}{2m} (\mathbf{p}_n + e\mathbf{A}(\mathbf{r}_n))^2 + U(\mathbf{r}_n) + g\mu_B \mathbf{s}_n \cdot \mathbf{B} \right] + V(\mathbf{r}_1, \mathbf{r}_2, \dots), \quad (1.73)$$

where a nucleus potential is written as $U(\mathbf{r}_n)$. In (1.52), we define \mathbf{s} as to have the dimension of angular momentum and then $(\hbar/2)\boldsymbol{\sigma}$ is \mathbf{s} . But here we redefine \mathbf{s} to fit the ordinary definition:

$$\mathbf{s} : \frac{\hbar \boldsymbol{\sigma}}{2} \rightarrow \frac{\boldsymbol{\sigma}}{2}, \quad (1.74)$$

which has the difference of a factor \hbar . The third term in the summation is the Zeeman term mentioned in Sec. 1.4. g is called **g-factor**, which is just 2 within the approximation of eq. (1.72). In the quantum electrodynamics, this is a bit larger than 2, due to the effect of electromagnetic field. As we will see later, in some cases we need to include orbital angular momentum into the form of g-factor (Landé g-factor). Here we do not include the spin-orbit interaction.

Just as before, we take symmetric gauge $\mathbf{A}(\mathbf{r}_n) = (\mathbf{B} \times \mathbf{r}_n)/2$ to obtain

$$\mathcal{H} = \sum_n \left[\frac{\mathbf{p}_n^2}{2m} + U(\mathbf{r}_n) \right] + V(\mathbf{r}_1, \mathbf{r}_2, \dots) \quad \mathcal{H}_0 \quad (1.75a)$$

$$+ \mu_B \sum_n (\mathbf{l}_n + g\mathbf{s}_n) \cdot \mathbf{B} \quad \mathcal{H}_1 \quad (1.75b)$$

$$+ \frac{e^2}{8m} \sum_n \{r_n^2 B^2 - (\mathbf{B} \cdot \mathbf{r}_n)^2\} \quad \mathcal{H}_2, \quad (1.75c)$$

where we write the orbital angular momentum in unit of \hbar as

$$\hbar \mathbf{l}_n \equiv \mathbf{r}_n \times \mathbf{p}_n. \quad (1.76)$$

And $\mathcal{H}_0, \mathcal{H}_1, \mathcal{H}_2$ are the terms of order zero-th, 1st, 2nd order of B respectively.

There are commutation relations between the coordinate and momentum operators:

$$[r_{n\alpha}, p_{n\beta}] = r_{n\alpha}p_{n\beta} - p_{n\beta}r_{n\alpha} = i\hbar\delta_{\alpha\beta} \quad (\alpha, \beta = x, y, z). \quad (1.77)$$

And from the redefinition of eq. (1.74),

$$[s_{n\alpha}, s_{n\beta}] = is_{n\gamma} \quad (\alpha, \beta, \gamma = x, y, z \text{ (cyclic)}). \quad (1.78)$$

The same for the orbital angular momentum as

$$[l_{n\alpha}, l_{n\beta}] = il_{n\gamma} \quad (\alpha, \beta, \gamma = x, y, z \text{ (cyclic)}). \quad (1.79)$$

The magnetic moment is given as in eq. (1.35) by

$$\begin{aligned} \mu &= -\frac{\partial \mathcal{H}}{\partial \mathbf{B}} = -\mu_B \sum_n (\mathbf{l}_n + g\mathbf{s}_n) - \frac{e^2}{4m} \sum_n \{r_n^2 \mathbf{B} - \mathbf{r}_n (\mathbf{r}_n \cdot \mathbf{B})\} \\ &= -\mu_B \sum_n (\mathbf{l}_n + g\mathbf{s}_n) - \frac{e^2}{4m} \sum_n (\mathbf{r}_n \times (\mathbf{B} \times \mathbf{r}_n)). \end{aligned} \quad (1.80)$$

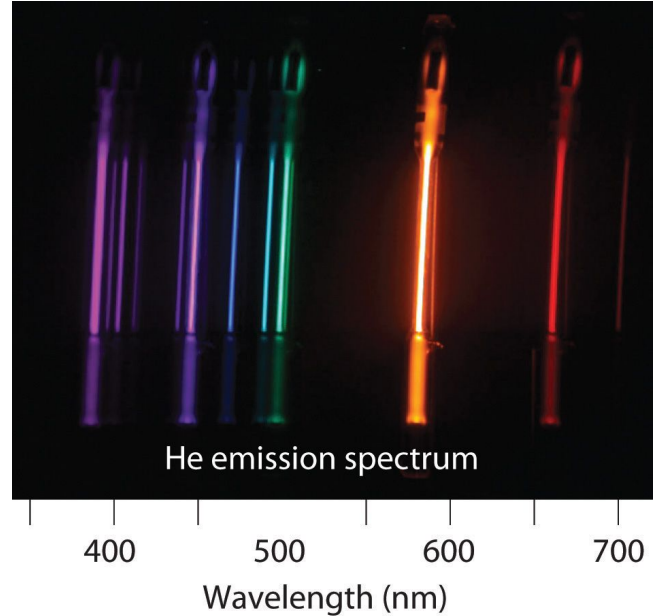
In comparison with (1.35), naturally the term \mathbf{s}_n is the difference in this mathematical form.

In a naive thought, the relativistic quantum mechanics brings in the spin-angular momentum and magnetic moment, and that leads to the explanation of the magnetism. It is true that the spin magnetic moment plays an important role but the above is too naive of course. In quantum theory, the quantization in orbital angular moments, spatial distribution of particles, and also statistics of particles give big differences both in paramagnetic and diamagnetic terms, which lead to the appearance of magnetic moment. What we have seen are the minimum knowledges to consider the magnetism. In the next chapter let us first have a look on the magnetism of atoms and ions, in which the quantization gives crucial effects.

I have a little comment on the spin of particles, that is the **nuclear magnetism**. Representative nucleons are proton and neutron, which both are known to have spin 1/2 (the history of finding these facts is described in Ref. [1]). Though the concept of spin was naturally introduced by the Dirac equation, proton and neutron belong to hadron and are not described by the Dirac equation. Actually the g-factors are very different from 2 that is the value in the Dirac equation. Proton has a charge of $+e$ and the magnetic moment can be naturally understood. On the other hand, neutron does not have total charge and still has a magnetic moment. This is due to the inner structure, that is the inner charge distribution. The spins of nucleons have opened up a huge field of magnetic detection of various phenomena. A representative is magnetic resonance imaging (MRI), which is now an important inspection device for the protection of lives. And the neutron diffraction is widely used to explore magnetic structures taking advantage of electrical neutrality.

Chapter 2

Magnetism of Localized Electrons



The goal of elementary quantum mechanics is the derivation of hydrogen atomic spectrum, that is the quantum confinement by spherical Coulomb potential. But the goal is at the same as the starting point of atomic/molecular spectroscopy as well as magnetism. The problem of localized electrons as the basics of magnetism is, in other words, the many-body problem in localized potentials. The subject of this chapter is how the magnetic moments arise from many-body systems.

2.1 Localized many-body problem

Let us consider the magnetism in localized electron systems like atoms and ions. When they are placed inside crystals, we need to consider the effect of surrounding lattices. Then we write the hamiltonian as

$$\mathcal{H}_L = \mathcal{H}_{L0} + \mathcal{H}_C + \mathcal{H}_{SOI} + \mathcal{H}_{CF}, \quad (2.1)$$

where \mathcal{H}_{L0} is an ordinary spherical potential hamiltonian, \mathcal{H}_C is the Coulomb interaction among electrons, \mathcal{H}_{SOI} is the SOI, and \mathcal{H}_{CF} is the **crystal field** caused by surrounding lattices. The amplitude of \mathcal{H}_{CF} greatly depends on the situation. When it is large, sometimes we need to go back to the single-electron problem in the potential under the effect of ligands[2]. There is no that term in the case of gases.

2.1.1 Problem of spherical potential

\mathcal{H}_{L0} is the sum of kinetic energy and the spherical potential $V_{sp}(r)$ created by nucleus as

$$\mathcal{H}_{L0} = \sum_j \left[\frac{\mathbf{p}_j^2}{2m} + V_{sp}(r_j) \right], \quad (2.2)$$

which has basically the same form as hydrogen atom problem. Then the energy eigenvalue is indexed with (main quantum number, azimuthal quantum number, magnetic quantum number) = (n, l, m) . A specific form of wavefunction in the polar coordinate representation is

$$\psi_{nlm}(\mathbf{r}) = R_{nl}(r)Y_{lm}(\theta, \varphi), \quad (2.3)$$

where $R_{nl}(r)$ is a radial wavefunction, $Y_{lm}(\theta, \varphi)$ is the spherical harmonic function. In the case that $V_{sp}(r)$ is the Coulomb potential, which is proportional to r^{-1} ,

$$R_{nl}(r) = b_{nl}\rho^l e^{-\rho/2} L_{n+l-1}^{2l+1}(\rho), \quad \rho \equiv \frac{2}{n} \frac{r}{a_0}, \quad (2.4)$$

where b_{nl} is the normalization constant, L_{n+l-1}^{2l+1} , an associated Laguerre polynomial, is a polynomial of $n+l-(2l+1) = n-l-1$ -th order, a_0 is a quantity of length dimension, the Bohr radius in the case of Hydrogen atom[3]. The eigenenergies are degenerated for l, m and written as the function of main quantum number n as

$$\epsilon_{nl} = -\frac{R_\infty}{n^2}, \quad R_\infty = \frac{me^4}{8\epsilon_0 h^3 c}. \quad (2.5)$$

In the above, the spin-degree of freedom is dropped. Hence here, as in many non-relativistic approximation, we take the spin degree of freedom σ into account by taking the direct product. \mathcal{H}_{L0} can be written in the form of second quantization as

$$\mathcal{H}_{L0} = \sum_{nl} \epsilon_{nl} \sum_{m\sigma} a_{nlm\sigma}^\dagger a_{nlm\sigma}. \quad (2.6)$$

2.1.2 Larmor precession

To see the effect of quantization on the magnetic moment caused by the orbital angular momentum, we consider the Coulomb potential of atomic number Z ,

$$V_{sp}(r_j) = -\frac{Ze^2}{4\pi\epsilon_0} \frac{1}{r_j}. \quad (2.7)$$

The total orbital angular momentum $\hbar\mathbf{L}$ is written as the sum of each orbital contributions:

$$\hbar\mathbf{L} = \hbar \sum_i \mathbf{l}_i. \quad (2.8)$$

To concentrate ourselves on the effect of orbitals, we tentatively drop the spin (s) term and write the term in (1.75b) as

$$\mathcal{H}_1 = \mu_B \mathbf{L} \cdot \mathbf{B} = \mu_B L_z B. \quad (2.9)$$

\mathbf{B} is taken to be parallel to z -axis. L_z is azimuthally quantized by

$$L_z = M : -L, -L+1, \dots, L-1, L.$$

The electron energy in the magnetic field is

$$E = E_0 + \mu_B M B \equiv E_0 + \hbar\omega_L M, \quad \omega_L \equiv \frac{\mu_B B}{\hbar} = \frac{eB}{2m} \text{ (Larmor frequency)}, \quad (2.10)$$

where E_0 is the value for zero magnetic field.

We will have a look at a motion of angular momentum \mathbf{L} in magnetic field \mathbf{B} along z -axis. Heisenberg equation of motion for \mathbf{L} is given by

$$\frac{d\mathbf{L}}{dt} = \frac{1}{i\hbar} [\mathbf{L}, \mathcal{H}_0 + \mathcal{H}_1 + \mathcal{H}_2], \quad (2.11)$$

with the hamiltonian in eq. (1.75). In the hamiltonian, the term \mathcal{H}_0 in zero-th order of B is \mathcal{H}_{L0} in eq. (2.2) in this problem. The terms of higher order in B than 2 are ignored here and we drop \mathcal{H}_2 .

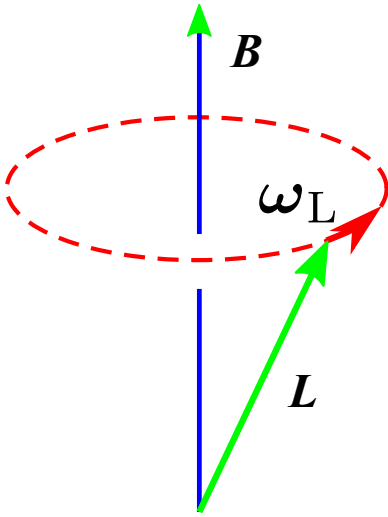


Fig. 2.1 Schematics of Larmor precession. The electron angular momentum L precesses around the axis of magnetic field B with angular frequency ω_L .

From the axial symmetry of magnetic field B and the spherical symmetry of potential, L_z is a constant of motion, which commutes with the hamiltonian. For the residual L_x, L_y , from

$$\frac{dL_x}{dt} = -\omega_L L_y, \quad \frac{dL_y}{dt} = \omega_L L_x \quad (2.12)$$

we obtain

$$L_x(t) = L_0 \cos(\omega_L t + \theta_0), \quad L_y(t) = L_0 \sin(\omega_L t + \theta_0), \quad (2.13)$$

which means L_x, L_y undergo a circular motion with angular frequency ω_L , and the total momentum precesses as illustrated in Fig. 2.1. This is called **Larmor precession**.

This is generalized into **Larmor theorem**[4], which tells that the motion of electronic systems in magnetic field B is the same as that in the zero-magnetic field if we see that on the coordinate system rotating with angular frequency ω_L under the condition (i) the central force potential sits still, (ii) the axial symmetry around the magnetic field B , (iii) the phenomenon up to the first order of magnetic field.

The above is for the orbital angular momentum. In the case of spin angular momentum, the expression of the magnetic moment has g-factor, then the Larmor frequency has the g-factor as

$$\omega_L = g \frac{eB}{2m} \approx \frac{eB}{m}. \quad (2.14)$$

Further, the expression ω_L is also used for nuclear magnetic moment etc. The coefficient of B for ω_L is often written as γ (that is $\omega_L = \gamma B$), where γ is called **gyromagnetic ratio**. These are the basis of magnetic resonance experiment, and we revisit the magnetic resonance experiments afterwards.

2.2 Magnetism of inert gas atoms and closed shell ion cores

At the beginning of chapter 1, I wrote that what we feel the magnetism is from the permanent magnet. In comparison with that, it may be a bit hard to feel that the gases also have the magnetism. However, if the isolated atoms or molecules have the magnetism, the gases of those particles naturally have magnetic moments. An example of important role played by the gas magnetism, is the birth of stars, in which the interstellar magnetic field ($\sim 10^{-10}$ T) is said to work for the integration of gases as well as the gravitational force^{*1}. Another example is the trapping and cooling of laser cooled gases

^{*1} However, according to recent observation by Alma telescope, it is deduced that the effect of magnetic field may be weaker than that of gravitation[5]

| Z | Element | Susceptibility |
|-----|---------|------------------------|
| 2 | He | -1.9×10^{-6} |
| 10 | Ne | -7.2×10^{-6} |
| 18 | Ar | -19.4×10^{-6} |
| 36 | Kr | -28×10^{-6} |
| 54 | Xe | -43×10^{-6} |

Tab. 2.1 Measured mole magnetic susceptibility of inert gases.

of neutral atoms. By adding a spatial distribution to the Zeeman split due to the magnetic moment by the magnetic field gradient, atoms with the magnetic moment can be collected near one point in space (magnetic trap). Atoms with higher kinetic energies tends to distribute positions far from the center of trap and the radio frequency wave rotates spins around there and selectively expels out the high energy atoms, which leads to the cooling (evaporation cooling).

We consider the case, in which the orbitals (n, l) are important. The orbital angular momentum \mathbf{L} , the spin angular momentum \mathbf{S} , and the total angular momentum \mathbf{J} are written as

$$\mathbf{L} = \sum_j \mathbf{l}_j = \sum_{\sigma} \sum_{mm'} \langle m | \mathbf{l} | m' \rangle_{nl} a_{m\sigma}^\dagger a_{m'\sigma}, \quad (2.15a)$$

$$\mathbf{S} = \sum_j \mathbf{s}_j = \sum_m \sum_{\sigma\sigma'} \left(\frac{\sigma}{2} \right)_{\sigma\sigma'} a_{m\sigma}^\dagger a_{m\sigma'}, \quad (2.15b)$$

$$\mathbf{J} = \sum_j \mathbf{j}_j = \mathbf{L} + \mathbf{S}. \quad (2.15c)$$

In inert gases like He, Ne, Ar, or in ion cores like Ag^+ , which have closed shell structures, the total orbital and spin angular momentums are zero ($L = S = 0$) due to the cancelling between electrons. Then the paramagnetic term is zero in these cases. This is, of course, an important information and this leads to the survival of the diamagnetic term (second term) in eq. (1.80). The magnetic moment due to this term is

$$\boldsymbol{\mu}_{\text{dia}} = -\frac{e^2}{4m} \sum_n [\mathbf{r}_n \times (\mathbf{B} \times \mathbf{r}_n)] = -\frac{e}{2} \sum_n [\mathbf{r}_n \times (\boldsymbol{\omega}_L \times \mathbf{r}_n)] = -\frac{\mu_B}{\hbar} \sum_n [\mathbf{r}_n \times (m\mathbf{v}_n)], \quad (2.16)$$

where $\boldsymbol{\omega}_L$ is a vector of the Larmor frequency produced with replacing B in eq. (2.10) with the vector \mathbf{B} . Equation (2.16) indicates that the diamagnetism arises from the outer product of momentum and coordinate created by the Larmor precession, that is, the angular momentum of the Larmor precession. Hence we call the diamagnetism as **Larmor diamagnetism**. We have calculated classically the magnetic moment induced by the magnetic field in zero-field and without angular moment ($L = 0$) in Sec. 1.3.2. The quantum mechanical calculation of eq. (2.16) gives the same results as

$$\mu_d = -\frac{e^2}{4m} \langle x^2 + y^2 \rangle B = -\frac{e^2}{6m} \langle r^2 \rangle B, \quad (2.17)$$

where we have used the fact that $\langle x^2 + y^2 \rangle = (2/3) \langle r^2 \rangle$ in the radial wavefunction in eq. (2.4). The molar susceptibility of inert gases of atomic number Z is then

$$\chi = -\frac{N_A Z e^2 \langle r^2 \rangle}{6m}. \quad (2.18)$$

This leads to the estimation of radius of atoms (ions) from the susceptibility measurement[6]. The experimental values in Tab. 2.1 tells that

$$\langle r^2 \rangle \sim a_B^2. \quad (2.19)$$

2.3 Electronic state of magnetic ions

Next we proceed the most important example of the appearance of paramagnetic term, which is zero in inert gases. That is, the **magnetic ions**, which have open shells and really big effects on the magnetism like ferromagnetism, etc.

2.3.1 Ground multiplex – Hund’s rule –

The orbital with angular momentum l can take the eigenvalue m of z -component as $m = -l, -l + 1, \dots, l$ and with the spin degree of freedom, the number of possible states is $2(2l + 1)$. The many-body state accommodating multiple electrons can be indexed with L and S in eq. (2.15), which can be written as (L, S) .

These are degenerated for \mathcal{H}_{L0} in eq. (2.1) though the Coulomb interaction \mathcal{H}_C causes splitting in (L, S) state. Each of them is degenerated by $(2L + 1)(2S + 1)$ folds. These are called LS multiplex.

To consider which state is the ground state, we represent the Coulomb interaction as

$$\mathcal{H}_C = \frac{1}{2} \sum_{m_1, \dots, m_4} \sum_{\sigma_1 \sigma_2} \left\langle m_1 m_2 \left| \frac{e^2}{4\pi\epsilon_0 r} \right| m_3 m_4 \right\rangle a_{m_1 \sigma_1}^\dagger a_{m_2 \sigma_2}^\dagger a_{m_3 \sigma_3} a_{m_4 \sigma_4}, \quad (2.20)$$

where l is not written. The bracket term in the coordinate representation is

$$\left\langle m_1 m_2 \left| \frac{e^2}{4\pi\epsilon_0 r} \right| m_3 m_4 \right\rangle = \int d\mathbf{r}_1 d\mathbf{r}_2 u_{m_1}^*(\mathbf{r}_1) u_{m_2}^*(\mathbf{r}_2) \frac{e^2}{4\pi\epsilon_0 |\mathbf{r}_1 - \mathbf{r}_2|} u_{m_3}(\mathbf{r}_2) u_{m_4}(\mathbf{r}_1). \quad (2.21)$$

The number of this combination of (m_1, \dots, m_4) is $5^4 = 625$ for d -orbital and much more for f -orbital. Then we need to consider the contribution of dominant terms. From eq. (2.21), the term of $m_1 = m_2 = m_3 = m_4$ is the largest and

$$\left\langle m_1 m_1 \left| \frac{e^2}{4\pi\epsilon_0 r} \right| m_1 m_1 \right\rangle a_{m_1 \uparrow}^\dagger a_{m_1 \downarrow}^\dagger a_{m_1 \uparrow} a_{m_1 \downarrow} = U_0 \sum_m \hat{n}_{m \uparrow} \hat{n}_{m \downarrow} \quad (\hat{n}_{m \sigma} = a_{m \sigma}^\dagger a_{m \sigma}). \quad (2.22)$$

In the rhs, the spin state is (\uparrow, \downarrow) due to the Fermi statistics (the Pauli principle) on the spin-term in eq. (2.20). In consequence, the above represents the effect of the Coulomb repulsion between the electrons with spin $(\uparrow\downarrow)$ accommodated in the same orbital.

The next is the term of $m_1 = m_4 \neq m_2 = m_3$, given as

$$\frac{1}{2} \sum_{m_1 \neq m_2} U(m_1, m_2) \hat{n}_{m_1} \hat{n}_{m_2} \quad \left(\hat{n}_m = \sum_{\sigma} n_{m \sigma} \right). \quad (2.23)$$

This represents the Coulomb repulsion between the electrons in different orbitals.

And the next is the case of $m_1 = m_3 \neq m_2 = m_4$. The contribution is written as

$$\frac{1}{2} \sum_{m_1 \neq m_2} \sum_{\sigma_1 \sigma_2} J(m_1, m_2) a_{m_1 \sigma_1}^\dagger a_{m_2 \sigma_2}^\dagger a_{m_1 \sigma_2} a_{m_2 \sigma_1} = -\frac{1}{2} \sum_{m_1 \neq m_2} J(m_1, m_2) \left(\frac{1}{2} \hat{n}_{m_1} \hat{n}_{m_2} + 2\mathbf{s}_{m_1} \cdot \mathbf{s}_{m_2} \right). \quad (2.24)$$

| Element | Configuration | Ion | Configuration | L | S |
|---------|----------------|----------------------------------|---------------|-----|-----|
| Sc | $3d^1 4s^2$ | | | | |
| Ti | $3d^2 4s^2$ | $\text{Ti}^{3+}, \text{V}^{4+}$ | $3d^1$ | 2 | 1/2 |
| V | $3d^3 4s^2$ | V^{3+} | $3d^2$ | 3 | 1 |
| Cr | $3d^5 4s^1$ | $\text{Cr}^{3+}, \text{V}^{2+}$ | $3d^3$ | 3 | 3/2 |
| Mn | $3d^5 4s^2$ | $\text{Mn}^{3+}, \text{Cr}^{2+}$ | $3d^4$ | 2 | 2 |
| Fe | $3d^6 4s^2$ | $\text{Fe}^{3+}, \text{Mn}^{2+}$ | $3d^5$ | 0 | 5/2 |
| Co | $3d^7 4s^2$ | $\text{Co}^{3+}, \text{Fe}^{2+}$ | $3d^6$ | 2 | 2 |
| Ni | $3d^8 4s^2$ | Co^{2+} | $3d^7$ | 3 | 3/2 |
| Cu | $3d^{10} 4s^1$ | Ni^{2+} | $3d^8$ | 3 | 1 |
| Zn | $3d^{10} 4s^2$ | Cu^{2+} | $3d^9$ | 2 | 1/2 |

Tab. 2.2 Electronic configurations of $3d$ metal ions, ground state L and S derived from Hund’s rule.

Here, s_m is the spin operator of orbital m , which is already defined in eq. (2.15b). We here write down it again as

$$s_m = \sum_{\sigma_1 \sigma_2} \left(\frac{\sigma}{2} \right)_{\sigma_1 \sigma_2} a_{m\sigma_1}^\dagger a_{m\sigma_2}. \quad (2.25)$$

In eq. (2.24), the term $2s_{m_1} \cdot s_{m_2}$ appears. At the first sight this is a bit strange. However, if we write the matrix representation for two-electron spin space ($2 \times 2=4$ dimensional), the lhs and the rhs are the same. Which means this representation is possible.

The matrix element $J(m_1, m_2)$ is called **exchange integral**. By using Fourier transformation of Coulomb potential, we obtain

$$J(m_1, m_2) = \int d\mathbf{r}_1 d\mathbf{r}_2 u_{m_1}^*(\mathbf{r}_1) u_{m_2} \frac{e^2}{4\pi\epsilon_0 |\mathbf{r}_1 - \mathbf{r}_2|} u_{m_1}(\mathbf{r}_2) u_{m_2}^*(\mathbf{r}_2) \quad (2.26a)$$

$$= \int d\mathbf{r}_1 d\mathbf{r}_2 u_{m_1}^*(\mathbf{r}_1) u_{m_2} \left[\int d\mathbf{q} \frac{e^2}{\epsilon_0 q^2} e^{i\mathbf{q} \cdot (\mathbf{r}_1 - \mathbf{r}_2)} \right] u_{m_1}(\mathbf{r}_2) u_{m_2}^*(\mathbf{r}_2) \quad (2.26b)$$

$$= \int d\mathbf{q} \frac{e^2}{\epsilon_0 q^2} \left| \int d\mathbf{r}_1 u_{m_1}^*(\mathbf{r}_1) u_{m_2}(\mathbf{r}_1) e^{i\mathbf{q} \cdot \mathbf{r}_1} \right|^2 > 0. \quad (2.26c)$$

That is $J(m_1, m_2)$ is always positive. Hence the two spins in two orbitals tend to be parallel. Most naive explanation is that the electrons in the same state try to avoid each other and as a result the Coulomb energy is lowered.

From the above, the ground multiplex can be determined from the following **Hund's rule**.

Hund's rule

1. Multiplex with maximum S
2. Multiplex with maximum L among those have maximum S

The LS multiplexes in Tab. 2.2 are determined from the Hund's rule.

Appendix 2A: Second quantization method

We hve short review of second quantzation method, which will be frequently used. For the knowledges of the physical meanings, the mathematical proofs, you are recommended to refer to famous textbooks like Ref. [7, 8]. The explanation of the physical meaning in Ref. [1] also has good reputation.

2A.1 Creation and annihilation operators

In **number representation** of a homogeneous multi-particle system, a many-body state is represented by the numbers of particles $\{n_j\}$, where $j = 1, 2, \dots$ are the indices of single particle states. Let \mathbf{n} be the vector of elements $\{n_j\}$ and we write the state in number representation as

$$|\mathbf{n}\rangle = |n_1, n_2, \dots\rangle. \quad (2A.1)$$

When every single-particle state is empty, we call the many-particle state "vacuum" and write it as $|0\rangle$. We consider an operator that add a particle to the j -th state and call it a **creation operator**. Writing a creation operator as a_j^\dagger , the definition is given by

$$a_j^\dagger |0\rangle = |1_j\rangle. \quad (2A.2)$$

a_j , the hermitian conjugate of a_j^\dagger , decreases the number of particles at j -th state by one. The operation of a_j on the vacuum produces zero. a_j is called an **annihilation operator**.

Henceforth we need to specify the statistics of homogeneous particles. In the case of fermions, a single state can only be occupied with a single particle and the number cannot be increased with repetitive operation of a_j^\dagger . Namely, $(a_j^\dagger)^2 = (a_j)^2 = 0$. Similar thought gives $a_j a_j^\dagger |0\rangle = |0\rangle$, $a_j^\dagger a_j |1_j\rangle = |1_j\rangle$. In consequence, the creation and annihilation operators of fermionic particles satisfy the following anti-commutation relations.

$$[a_i, a_j]_+ = [a_i^\dagger, a_j^\dagger]_+ = 0, \quad [a_i, a_j^\dagger]_+ = \delta_{ij}, \quad (2A.3)$$

where $[A, B]_+ = AB + BA$. Then applying the operator $\hat{n}_j \equiv a_j^\dagger a_j$ on the state $|\mathbf{n}\rangle$ gives

$$\hat{n}_j |\mathbf{n}\rangle = n_j |\mathbf{n}\rangle. \quad (2A.4)$$

This is understood by considering the cases of $n_j = 0, 1$. This tells that \hat{n}_j is a **number operator** that has the eigenstates of particle numbers in j -th state.

For bosons, creation and annihilation operators b_j^\dagger, b_j satisfy the following commutation relation

$$[b_i, b_j] = [b_i^\dagger, b_j^\dagger] = 0, \quad [b_i, b_j^\dagger] = \delta_{ij}. \quad (2A.5)$$

$b_j |0\rangle = 0$ is the same as fermions. Also the same for number operators.

$$\hat{n}_j |\mathbf{n}\rangle = b_j^\dagger b_j |\mathbf{n}\rangle = n_j |\mathbf{n}\rangle. \quad (2A.6)$$

We can obtain the expression of $|n_j\rangle$ by the creation operator and the vacuum as

$$|n_j\rangle = \frac{1}{\sqrt{n_j!}} (a_j^\dagger)^{n_j} |0\rangle \quad (2A.7)$$

after some algebra to calculate the normalization constant.

2A.2 Expression of operators

In the expression of second quantization, the particle statistics can be represented by the (anti-)commutation relations between creation and annihilation operators. Hence for human, the second quantization expression is generally simpler than the direct treatment of many-body wavefunctions like the Slater determinant. Thus in the discussion of many-body problem, the second quantization is mostly used.

We consider the simplest case, in which a many-body operator is actually written as a sum of single-particle operators. That can be expressed in the coordinate representation as

$$\mathcal{F}(\mathbf{r}_1, \mathbf{r}_2, \dots) = \sum_i f(\mathbf{r}_i). \quad (2A.8)$$

For fermions, by letting the Slater determinant be $|\psi_{1,2,\dots}\rangle$, a matrix element is expressed as

$$\langle \psi_{m_1, m_2, \dots} | \mathcal{F} | \psi_{n_1, n_2, \dots} \rangle = \sum_i \langle \psi_{m_1, m_2, \dots} | f(\mathbf{r}_i) | \psi_{n_1, n_2, \dots} \rangle, \quad (2A.9)$$

which contains many complicated terms.

In second quantization, defining an operator

$$F = \sum_{mn} \langle m | f | n \rangle a_m^\dagger a_n$$

$$\langle m | f | n \rangle = \int d\mathbf{r} \phi_m^*(\mathbf{r}) f(\mathbf{r}) \psi_n(\mathbf{r}), \quad (2A.10)$$

we can write the matrix element as

$$\langle \psi_{m_1, m_2, \dots} | \mathcal{F} | \psi_{n_1, n_2, \dots} \rangle = \langle \mathbf{m} | F | \mathbf{n} \rangle, \quad (2A.11)$$

where $|m\rangle$ are the number representation of corresponding states. The matrix elements and the operators representing the statistics can be treated separately. This gives a better view of the calculation.

For multiparticle operators the same approach is possible. For example in the case of a two-particle operator $g(\mathbf{r}_1, \mathbf{r}_2)$ we can write

$$G = \frac{1}{2} \sum_{klmn} \langle kl|g|mn\rangle a_k^\dagger a_l^\dagger a_n a_m. \quad (2A.12)$$

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