SCPY 371: Solid State Physics **1^{st} Semester 2016**

Lecture 11: Magnetism

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As you have already known, charge and spin are two fundamental physical properties of electrons and other elementary particles. In this class so far, we have only discussed about the charge degree of freedom; how electron charges interact to give rise to measurable quantities. In this chapter, we will switch gears and consider the spin degree of freedom, which gives rise to magnetic properties of the interest systems.

Magnetic moments in matters, which can generate magnetic field, arises from three sources.

1. Electron spin
2. Orbital angular momentum due to electron motion around the nucleus
3. Nuclear spin

However, since the magnetic moment due to nuclear spin is very smaller compared to that due to electron spin and orbital angular momentum (10^3 times smaller), we will ignore nuclear spin and only consider the first two sources of magnetic moments. First, we will consider how electrons arrange themselves in orbitals to obtain a certain value of spin and orbital angular momentum.

We will first start considering the simplest case where there is no interaction between spins. It is pretty much like the free electron model but now we will consider free spin (angular-momentum) model. We can induce the magnetic moments from these free spins and angular momenta by applying the magnetic field and measure the magnetization, which is defined as the magnetic moment per unit volume. To first approximation, the magnetization is linearly proportional to the applied magnetic field B, that is,

$$M = \chi B,$$

where χ is the magnetic susceptibility per unit volume, which indicates how easy or difficult it is to align magnetic moments by the external field for a given magnetic materials. Based on the sign of χ, we can divide materials into two groups. The first group is called **diamagnetic** where χ is negative, that is, the direction of the magnetization is opposite to the direction of the applied field. The second group is called **paramagnetic** where χ is positive.

11.1 Diamagnetism

Classically, we can think of diamagnetism as the result of 'electric current' around the nucleus. One can assume that without magnetic field this current is zero. Then, when we apply the magnetic field, the field will induce the current in the opposite direction to the change of the field according to Lenz's law. This current can be calculate from the Larmor precession of electrons. Suppose that there are Z electrons, where Z is the atomic number, then the current is equal to

$$I = -Ze\left(\frac{\omega_L}{2\pi}\right) = -\frac{Ze^2B}{4\pi mc},$$

where $\omega_L = \frac{eB}{2m}$ is the Larmor frequency and $\frac{2\pi}{\omega_L}$ is the time each electron takes to complete one orbit around the nucleus. From classical electromagnetism, we have already learned that the magnetic moment μ of the current loop is equal to

$$\mu = IA/c,$$

where A is the area of the loop. For our system, that means,

$$\mu = -\frac{Ze^2B}{4mc^2}\langle\rho^2\rangle,$$

where ρ is the radius of the orbit. If there are N atoms, then the magnetization is equal to

$$M = N\mu = -\frac{NZe^2}{4mc^2}\langle\rho^2\rangle B.$$

Now since $\rho^2 = x^2 + y^2$, we have $\langle\rho^2\rangle = \langle x^2\rangle + \langle y^2\rangle$. For the spherical symmetric distribution, $\langle x^2\rangle = \langle y^2\rangle = \langle z^2\rangle$. Therefore, in term of $\langle r^2\rangle = \langle x^2\rangle + \langle y^2\rangle + \langle z^2\rangle$, we have $\langle\rho^2\rangle = \frac{2}{3}\langle r^2\rangle$. The magnetic susceptibility is hence equal to

$$\chi = -\frac{NZe^2}{6mc^2}\langle r^2\rangle.$$

This result of called the classical Langevin diamagnetism. Note that χ is negative. Next we will try to calculate this magnetic susceptibility using quantum mechanics. For electron, we know that in the presence of magnetic field, the momentum term becomes

$$\vec{p} \to \vec{p} + \frac{e}{c}\vec{A}.$$

Therefore, the Hamiltonian becomes

$$\mathscr{H} = \frac{1}{2m}\left(\vec{p} + \frac{e}{c}\vec{A}\right)^2.$$

We will assume that we apply the uniform magnetic field along the z direction, that is, $\vec{B} = B\hat{z}$. Therefore, we can write the vector potential as

$$A_x = -\frac{1}{2}yB, \quad A_y = \frac{1}{2}xB, \quad A_z = 0,$$

or equivalently as

$$\vec{A} = -\frac{1}{2}\vec{r}\times\vec{B}.$$

Then, the Hamiltonian becomes

$$\begin{aligned} \mathscr{H} &= \frac{1}{2m}\left(\vec{p} - \frac{e}{2c}\vec{r}\times\vec{B}\right)^2 \\ &= \frac{\vec{p}^2}{2m} - \frac{e}{4mc}\left(\vec{p}\cdot(\vec{r}\times\vec{B}) + (\vec{r}\times\vec{B})\cdot\vec{p}\right) + \frac{e^2}{8mc^2}(\vec{r}\times\vec{B})\cdot(\vec{r}\times\vec{B}) \\ &= \frac{\vec{p}^2}{2m} + \frac{e}{2mc}(\vec{r}\times\vec{p})\cdot\vec{B} + \frac{e^2B^2}{8mc^2}\left(x^2+y^2\right). \end{aligned}$$

But we know that

$$\hbar\vec{L} = \vec{r}\times\vec{p}.$$

Therefore, we obtain

$$\mathscr{H} = \frac{\vec{p}^2}{2m} + \frac{e\hbar}{2mc}\vec{L}\cdot\vec{B} + \frac{e^2B^2}{8mc^2}\left(x^2+y^2\right).$$

As we can see from this expression, the first term is the kinetic energy in the absence of the magnetic field. Furthermore, the second term give rise to the paramagnetic contribution from the angular momentum, which we will consider later. The third term is the diamagnetic contribution. We can calculate the shift of the ground state due to this last term using the first-order perturbation theory. Let $\mid \phi_0 \rangle$ be the unperturbed ground state.

$$\varepsilon_B = \frac{e^2B^2}{8mc^2}\langle \phi_0 \mid \left(x^2+y^2\right) \mid \phi_0 \rangle = \frac{e^2B^2}{12mc^2}\langle \phi_0 \mid r^2 \mid \phi_0 \rangle.$$

For N atoms with the atomic number Z, the shift in energy becomes

$$E_B = \frac{NZe^2B^2}{12mc^2}\langle r^2 \rangle.$$

Since the magnetization is equal to

$$M = -\frac{\partial E_B}{\partial B} = -\frac{NZe^2}{6mc^2}B\langle r^2 \rangle,$$

we obtain

$$\chi = -\frac{NZe^2}{6mc^2}\langle r^2 \rangle,$$

which is in agreement with the classical Langevin result.

11.2 Paramagnetism

We have learned that the classical and quantum description do agree on the diamagnetism. In fact, both give exactly the same result. However, the classical description fails to provide the explanation for paramagnetism, which can only emerge in the quantum picture. The origin of the paramagnetism is due to the second term of the Hamiltonian written above. This term basically gives rise to the discrete energy states since the operation $\vec{L}$ is now quantized. However, as we mentioned at the beginning of this chapter that the contribution to the magnetism comes not only from the orbital angular momentum $\vec{L}$ but also the electron spin $\vec{S}$, which is an intrinsic property of electron and at this stage cannot be derived. Therefore, we will manually combine $\vec{L}$ and $\vec{S}$ and create another operator called $\vec{J}$, which is the combination of $\vec{L}$ and $\vec{S}$. So, for the given $\vec{L}$ and $\vec{S}$, how can we find $\vec{J}$? In order to answer this question, we will have to rely on Hund Rules.

Hund Rules The arrangement of electrons in orbitals is governed by the so called 'Hund Rules'. In order to be in the ground state, electrons have to reside in the orbitals according to the following rules. Note that the rules have to be applied in the exact order from No. 1 to No. 3.

1. Maximize the value of total spin S.
2. Maximize the value of the orbital angular momentum L, which is still consistent with No. 1.
3. The value of the total angular momentum J, which includes both spin and orbital part, is equal to $|L-S|$ for the less-than half-filled shell and $L+S$ for the more-than half filled shell. In other words, for the less-than half filled shell, the direction of electron spins is opposite to the orbital angular momentum, whereas for the more-than half-filled shell, the direction of spins is along the orbital angular momentum.

Hund rules are the results of the exclusion principle and the spin-orbit interaction. The first Hund rule is due to the exclusion principle that prohibits two electrons to be in the same state. Furthermore, it is energetic favorable for two electrons to have the same spins to lower the Coulomb repulsion. As you know, the total wave function for electrons, which is consisted of spatial and spin parts, has to anti-symmetric since electrons are fermions. To reduce the Coulomb energy, two electrons prefers being apart, and hence the spatial part of the wave function must be anti-symmetric, which means the spin part of the same function has to be symmetric. Therefore, two electron spins point along the same direction. The second rule and the third rule are the result of the spin-orbit coupling, which prefers the anti-parallel alignment of the spin and orbital angular momentum. The spin-orbit coupling is proportional to $\vec{S}\cdot\vec{L}$.

Application of Hund Rules To illustrate Hund Rules described above, we will consider the filling of electrons in the $d-$orbital. The $d-$orbital consisted of 5 states ($m_l = \pm 2, \pm 1, 0$) can afford ten electrons. The table below shows the arrangement of electrons in the $d-$orbital as well the $J-$value and the symbol for each state. The symbol is written as $^{2S+1}X_J$, where $X = S, P, D, F, G, H, I$ for $L = 0, 1, 2, 3, 4, 5, 6$, respectively.

Table 11.1: Ground state of ions in $d-$orbitals

n	S	$L = \lvert\sum m_l\rvert$	J	$^{2S+1}X_J$
1	1/2	2	3/2	$^2D_{3/2}$
2	1	3	2	$^3F_2$
3	3/2	3	3/2	$^4F_{3/2}$
4	2	2	0	$^5D_0$
5	5/2	0	5/2	$^6S_{5/2}$
6	2	2	4	$^5D_4$
7	3/2	3	9/2	$^4F_{9/2}$
8	1	3	4	$^3F_4$
9	1/2	2	5/2	$^2D_{5/2}$
10	0	0	0	$^1S_0$

Now we are ready to consider the result of the second term in the Hamiltonian. In the presence of the magnetic field, this term lifts the spin and angular momentum degeneracy and the total magnetic moment can be represented by the quantum number J and m_J, where $J^2 \to \hbar^2 J(J+1)$ and $m_J = \pm J, \pm J-1, \pm J-2, \ldots$. In the lieu of $\frac{e\hbar}{2mc}\vec{L}\cdot\vec{B}$, after taking into account the spin part we can rewrite the second term of the Hamiltonian as

$$H_J = -\vec{\mu}\cdot\vec{B},$$

where $\vec{\mu} = -g\mu_B\vec{J}$. $\mu_B = \frac{e\hbar}{2mc}$ is the Bohr magneton and g is the Landé equation, which can be written as

$$g = \frac{3}{2} + \frac{1}{2}\left[\frac{S(S+1) - L(L+1)}{J(J+1)}\right].$$

Alternatively, we can expressed μ as

$$\mu = \gamma\hbar\vec{J},$$

where γ is called the gyromagnetic ratio or magnetogyric ratio.

As mentioned above, the second term or H_J causes the splitting of the formerly degenerate states with different m_J and there are $2J+1$ states. In order to calculate the magnetization, we first need to know the energy as a function of field. Since the energy in this case is not a single value and thermal energy can change the occupation number of each state. Therefore, to calculate the total energy, which in this case is the average total energy, we need to rely on the statistical mechanics and calculate the free energy F of the system. The equation for the free energy can be written as

$$e^{\beta F} = \sum_{m_J=-J}^{J} e^{-\beta g\mu_B B m_J}.$$

This is simply a geometric sum with the initial term $e^{\beta g \mu_B J}$. The sum can be evaluated to give

$$
\begin{aligned}
e^{-\beta F} &= \frac{e^{\beta g \mu_B B J} - e^{-\beta g \mu_B B (J+1)}}{1 - e^{-\beta g \mu_B B}} \\
&= \frac{e^{\beta g \mu_B B \left(J+\frac{1}{2}\right)} - e^{-\beta g \mu_B B \left(J+\frac{1}{2}\right)}}{e^{\beta g \mu_B B/2} - e^{-\beta g \mu_B B/2}} \\
&= \frac{\sinh\left[\beta g \mu_B B \left(J+\frac{1}{2}\right)\right]}{\sinh\left(\beta g \mu_B B/2\right)}.
\end{aligned}
$$

We can write the free energy F by taking the logarithmic of the above expression.

$$
F = -\frac{1}{\beta}\left\{\log\left(\sinh\left[\beta g \mu_B B \left(J+\frac{1}{2}\right)\right]\right) - \log\left[\sinh\left(\beta g \mu_B B/2\right)\right]\right\}.
$$

Given that there are N magnetic ions, we can calculate the magnetization by taking the derivative of the free energy with respect to B, that is,

$$
\begin{aligned}
M &= -N\frac{\partial F}{\partial B} \\
&= N g \mu_B \left\{\frac{2J+1}{2}\frac{\cosh\left[\beta g \mu_B B \left(J+\frac{1}{2}\right)\right]}{\sinh\left[\beta g \mu_B B \left(J+\frac{1}{2}\right)\right]} - \frac{1}{2}\frac{\cosh\left[\beta g \mu_B B/2\right]}{\sinh\left[\beta g \mu_B B/2\right]}\right\} \\
&= N g \mu_B J \left\{\frac{2J+1}{2J}\coth\left[\beta g \mu_B B J\left(\frac{2J+1}{2J}\right)\right] - \frac{1}{2J}\coth\left[\frac{\beta g \mu_B B J}{2J}\right]\right\} \\
&\equiv N g \mu_B J B_J(\beta g \mu_B B J),
\end{aligned}
$$

where $B_J(x)$ is called the Brillouin function, which can be written as

$$
B_J(x) = \frac{2J+1}{2J}\coth\left[\frac{2J+1}{2J}x\right] - \frac{1}{2J}\coth\left[\frac{x}{2J}\right].
$$

We can see that as $x \to \infty$, $B_J(x) \to 1$. That is, as temperature goes to zero at the fixed magnetic field, the magnetization approaches the saturated value of $N g \mu_B J$. This is what we expected since the ground state at zero temperature is where all spins (orbital angular momenta) point along the same direction as the applied field. On the other hand, if x is small, that is, at high temperature or low field, we can approximate the hyperbolic cosince as

$$
\coth x \approx \frac{1}{x} + \frac{x}{3}
$$

Therefore, the Brillouin function becomes

$$
B_J(x) \approx \frac{2J+1}{2J}\cdot\frac{2J}{2J+1}\cdot\frac{1}{x} + \left(\frac{2J+1}{2J}\right)^2\cdot\frac{x}{3} - \frac{1}{2J}\cdot 2J\cdot\frac{1}{x} + \left(\frac{1}{2J}\right)^2\cdot\frac{x}{3} = \frac{J+1}{J}\cdot\frac{x}{3},
$$

and the magnetization becomes

$$
M = N g \mu_B J \cdot \frac{J+1}{J}\cdot\frac{\beta g \mu_B B J}{3} = \frac{N\left(g\mu_B\right)^2}{3}\frac{J(J+1)}{k_B T}\cdot B.
$$

Therefore, for the limit where $x = \beta g \mu_B J B \ll 1$, the magnetic susceptibility χ can be approximated by

$$
\chi = \frac{N\left(g\mu_B\right)^2}{3}\frac{J(J+1)}{k_B T}.
$$

This temperature dependence of the susceptibility is known as the Curie's law, which basically indicates that the magnetic susceptibility increases at low temperature and diverges at $T \to 0$ as $1/T$. We often write it as $\chi = \frac{C}{T}$, where C is called the Curie's constant. Experimentally, the Curie's law can be written as

$$\chi = \frac{N}{3}\frac{\mu_B^2 p^2}{k_B T},$$

where p is the effective Bohr magneton number, which is given by

$$p = g\,(J(J+1))^{1/2}.$$

We can in fact experimentally measure p and compare with the calculated value. We found that for the $3d-$electrons of the transition metals the agreement is not that great. However, for the $4f-$electrons of the rare earths, the agreement between experimental and calculated values is excellent. The fact that our free spin model fails to explain the magnetization of the $d-$electrons is due to the crystal field splitting. The crystal field splitting is caused by the influence of the crystalline environment due to the electric fields. In the case of the $4f-$electrons, the $f-$orbitals lie very deep in energy and are shielded from the crystalline electric fields by the $5s-$ and $5p-$orbitals. On the other hand, the $d-$orbitals are the outermost orbitals and hence can be most affected by the crystalline electric fields. The result of the crystal field on the $3d-$electrons is that their orbital component is *quenched* and averages to zero.

As we have learned, the Hund Rules are the results of the spin-orbit coupling. It turns out that for the transition metals the crystal field can dominate the spin-orbit coupling and hence the Hund Rules can no longer be applied. The crystal field will lift the L degeneracy, which results in the ground state with the average value of m_l is zero; though L^2 is still a good quantum number. In this case, the quantum number can be simply represented by S. Therefore, the effective Bohr magneton number for the transition metals is well compared with

$$p = g\,(S(S+1))^{1/2},$$

where S now replaces J.

Furthermore, there can be the temperature-independent paramagnetism, which is called the **van Vleck paramagnetism**. The underlying physics of magnetism in this case is due to the unbalanced populations of spins in the ground state and the excited state, which are separated by the energy gap Δ. If $\Delta \ll k_B T$, then we recovered the temperature-dependent paramagnetism with the Curie's form. However, if $\Delta \gg k_B T$, then most spins will be in the ground state and the magnetization becomes temperature-independent.

11.3 Magnetism in metals

So far, we have not discussed the magnetism due to the conduction electrons. Therefore, in this section we will examine the non-localized spins. At zero field, we know that the number of spin-up and spin-down electrons must be the same. Let $g_\pm(E)dE$ be the density of electron with spin-up (+) and spin-down(-) between the energy range E and $E+dE$. Then, at zero field we have

$$g_\pm(E) = \frac{1}{2}g(E),$$

and hence the magnetization is equal to

$$M = -\mu_B(n_+ - n_-) = 0,$$

where $n_\pm$ is the number of electrons with spin-up and spin-down. Now if the magnetic field H is not equal to zero, then we have

$$g_+(E) = \frac{1}{2}g(E - \mu_B H)$$

and

$$g_{-}(E) = \frac{1}{2} g(E + \mu_B H).$$

Therefore, the number of electrons with spin-up and spin-down also charges. Since $\mu_B H$ is very small compared to the Fermi energy, we can expand the term in the parentheses around the Fermi energy as

$$g_{\pm}(E) = \frac{1}{2} g(E_F) \mp \frac{1}{2} \mu_B H \frac{dg}{dE}.$$

Now we let $n = n_{+} - n_{-}$, where $n_{\pm} = \int g_{\pm}(E)\, f(E)\, dE$. Therefore, we have

$$M = \mu_B^2 H \int g'(E)\, f(E)\, dE = \mu_B^2 H g(E_F),$$

where we assume that the temperature is so small that we can approximate $f(E) = 1$ for $0 < E < E_F$ and zero otherwise. Hence, the magnetic susceptibility becomes

$$\chi = \mu_B^2 H g(E_F).$$

This is known as the Pauli paramagnetic susceptibility, which can be measured independently by nuclear magnetic resonance, and it is temperature independent in contrast to the Curie's law.

The conduction electrons can also contribute to diamagnetism since an applied magnetic can induce free electrons to travel in orbits similar to the classical picture of the core electrons that we discussed in the beginning of this chapter. However, the calculation in this case is quite complicated and we will not attempt to do it. We will just simply quote the result. This diamagnetism is called the *Landau diamagnetism*, which is given by

$$\chi_{\text{Landau}} = -\frac{1}{3} \chi_{\text{Pauli}}.$$

At the end, since the Landau diamagnetism is also temperature-independent, its effect will be combined with χ_{Pauli} and χ_{core} leaving only one temperature-dependent term, which is the paramagnetic term we discussed in the previous section.

11.4 Cooling by adiabatic demagnetization

We can use the demagnetization to cool a system down to temperature as low as 10^{-3} K. The principle behind this method is that in the applied magnetic field, the system becomes more ordered, that is, spins point along the same direction, which means that the entropy of the system is lower than without the applied field. Now we can stop applying the magnetic field and keep the system in the adiabatic state, that is, we do not allow the heat transfer; hence the entropy cannot. But the system will now to go the state with "free expansion". In this case, it means that the spins will become random again. In doing so, the spins will absorb heat from the environment. However, sine the system is isolated, the temperature of the system must be lower. The relation between magnetic fields, final and initial temperatures can be expressed by

$$T_{\text{final}} = T_{\text{initial}} \frac{B_{\text{final}}}{B_{\text{initial}}},$$

where B_{final} is the effective magnetic field corresponding to the local magnetic interaction. Normally, as temperature is lowered, the spins interaction becomes more dominated and the magnetization for most materials will no longer vary as $1/T$;hence neither will the entropy. Therefore, the equation above can be no longer applied. In order to reach as lower temperature as possible, we will need paramagnetic salts such as $Ce_2Mg_3(NO_3)_{12}{\cdot}(H_2O)_{24}$ with minimum crystal field splitting and minimize magnetic interactions.

11.5 Interacting spins

From the free spin model, we learned that without magnetic field spins are randomly oriented, giving rise to no net magnetization. However, in reality we observe spontaneous magnetization at zero field in some magnetic materials such as some types of iron oxides. Therefore, there must be an interaction among spins that forces spins in the iron oxides to align along the same direction and give rise to the magnetization at zero field. The question that we have to answer is what kind of interaction the spins exert on one another.

The first force that comes to mind to most of us who have taken electromagnetism is the dipole-dipole interaction, since spins and give rise to magnetic moment, which in turn creates magnetic field that can exert force on other spins. So, first let us consider the magnitude of interaction among spins via the dipole-dipole interaction.

From electromagnetism, we know that the magnetic energy between two magnetic dipole can be written as

$$U = \frac{1}{r^3}\left(\vec{m}_1 \cdot \vec{m}_2 - 3\left(\vec{m}_1 \cdot \hat{r}\right)\left(\vec{m}_2 \cdot \hat{r}\right)\right).$$

Let us assume that $\vec{m}_1$ is parallel to $\vec{m}_2$ and both are perpendicular to $\hat{r}$. The magnitudes of $\vec{m}_1$ and $\vec{m}_2$ are approximately equal to $g\mu_B$. Therefore, the energy of the magnetic interactions between two spins via dipole-dipole interaction can be estimated by

$$U \approx \frac{(g\mu_B)^2}{r^3} \lesssim 10^{-4} \quad \text{eV}.$$

This energy is equivalent to the thermal energy of no more than a few Kelvins, which much lower than the temperature at which spins in the iron oxides align along the same direction. Therefore, the dipole-dipole interaction cannot be responsible for the spontaneous magnetization in the iron oxides.

It turns out the mechanism of the magnetic interactions that give rise to the spontaneous magnetization derives from the following interactions among electrons:

1. Kinetic energy or delocalization of electrons.
2. Potential energy or Coulomb repulsion between electrons.
3. Pauli exclusion principle.

The combination or the competition among these interactions will determine the coupling between spins, which can be of two types; one is called **ferromagnetic coupling** and the other is called **antiferromagnetic coupling**. For the ferromagnetic coupling, it is more energetically favorable for two spins to align along the same direction whereas for the antiferromagnetic coupling it is more favorable for the two spins to point into the opposite direction.

Ferromagnetic coupling We will consider two electrons whose wavefunctions are spatial close to each other. In order to minimize the overlapping, the spatial part of the wave function has to be antisymmetric. Therefore the spin part of the wave function has to be symmetric, which means spins point along the same direction. This result is the same as the Hund rules. Therefore, the ferromagnetic coupling is favorable for two electrons that occupy the same space and have orthogonal wave function. We can say that the emergence of the ferromagnetic coupling is the result of the attempt to lower the potential energy of Coulomb repulsion between two electrons in combination with the Pauli exclusion principle. The ferromagnetic coupling is the result of the first order perturbation theory.

Antiferromagnetic coupling The antiferromagnetic coupling often emerges in the system where spins are localized at different positions. In the case, the kinetic energy of the electrons can be lowered if the electrons are allowed to move around or becomes **delocalized**. The parameter that governs the "hopping" of electrons from site to site is called

t, the hopping parameter. This hopping term is the kinetic energy term in the Hamiltonian. Furthermore, since it cost energy (potential energy) for two electrons to occupy the same space due to Coulomb repulsion. This interaction is called the **on-site** repulsion, which can be denoted by U.

We will assume that t is much smaller than U and treat t as the perturbation term. In this case, the system can be in 4 states; those are:

1. One spin with spin up in the left state and the other spin with spin down in the right state: $|\uparrow,\downarrow\rangle$.
2. One spin with spin down in the left state and the other spin with spin up in the right state: $|\downarrow,\uparrow\rangle$.
3. Two spins in the same state on the left: $|\uparrow\downarrow,0\rangle$.
4. Two spins in the same state on the left: $|\,0,\uparrow\downarrow\rangle$.

Note that $|\uparrow\uparrow,0\rangle$, $|\downarrow\downarrow,0\rangle$, $|\,0,\uparrow\uparrow\rangle$, and $|\,0,\downarrow\downarrow\rangle$ are not allowed since two electrons with the same spin state cannot occupy the same space. The first two states are the ground state while the other two states are the excited states. As you might be able to see that the first order perturbation term vanished since the hopping term only connects the ground states to the excited states. Therefore, we need to use the second order perturbation calculation, which can be written as:

$$E_2 = \sum_n \frac{|\langle n \mid H_t \mid 0\rangle|^2}{E_0 - E_n}.$$

Since the energy of the excited state is U and the energy of the hopping term is t, we can write E_2 as

$$E_2 = -\frac{2t^2}{U}.$$

As we can see that E_2 is always negative since E_0 is always smaller than E_n. Therefore, by means of hopping around, an electron can lower its kinetic energy. Since $|\uparrow,\uparrow\rangle$ and $|\downarrow,\downarrow\rangle$ do not allow the hopping to occurs, these two states have higher energy when hopping is allowed. Therefore, the spin state with opposite spins on different sites is more favorable. The spin interaction, hence, becomes antiferromagnetic with the energy different between the ground state and the excited state in an order of $\frac{t^2}{U}$.

Experimentally, we can measure the magnetic susceptibility to determine whether the interested material is ferromagnetic or antiferromagnetic. The temperature dependence of the susceptibility for the ferromagnetic and antiferromagnetic materials in the paramagnetic state, that is, at high temperature is similar to the Curie's law except that the susceptibility diverges not at $T = 0$ but at a finite T. Therefore, the Curie's law becomes

$$\chi = \frac{C}{T - \Theta},$$

where Θ is the same order as the ordering temperature. If Θ is positive, the material is ferromagnetic whereas if Θ is negative, the material is antiferromagnetic. This expression is called the **Curie-Weiss law**.

References

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