Quantum theory of diamagnetism

Consider the case of a solid composed of atoms/ions whose all electronic ~~sheet~~ shells are filled. An ion has zero spin and orbital angular momentum in its ground state ~~&~~ represented by the wavefunction ϕ_0, i.e

$$J|\phi_0\rangle = L|\phi_0\rangle = S|\phi_0\rangle = 0 .$$

In this case, only the second term in equation (5) ~~sur~~ survive.

change in ground state energy

$$\Delta E_0 = \frac{e^2}{8m} B_0^2 \langle \phi_0 | \sum_i (x_i^2 + y_i^2) | \phi_0 \rangle$$

$$= \cancel{\frac{e^2}{8m} B_0^2 \langle \phi_0}$$

$$= \frac{e^2}{8m} B_0^2 \, \frac{2}{3} \langle \phi_0 | \sum_i r_i^2 | \phi_0 \rangle$$

[For completely filled shell electron distribution is spherically symmetric $\langle \phi_0 | \sum_i x_i^2 | \phi_0 \rangle = \langle \phi_0 | \sum_i y_i^2 | \phi_0 \rangle = \frac{1}{3} \langle \phi_0 | \sum_i r_i^2 | \phi_0 \rangle$]

$$\Delta E_0 = \frac{e^2 B_0^2}{12 m} \langle \phi_0 | \sum_i r_i^2 | \phi_0 \rangle$$

In the state of thermal equilibrium ions are generally in their ground state, excepting the situation at high temperature. Therefore, the susceptibility of a solid with N atoms or ions per unit volume at room temp. is given by

$$\chi = \mu_0 \frac{\partial M}{\partial B_0} = \mu_0 \frac{\partial}{\partial B_0}\left[-N \frac{\partial E_0}{\partial B_0}\right] = -\mu_0 N \frac{\partial^2 (\Delta E_0)}{\partial B_0^2}$$

$$= -\cancel{\mu_0 N \frac{e^2 B_0^2}{12 m}} = -\mu_0 N \frac{e^2}{6m} \langle \phi_0 | \sum_i r_i^2 | \phi_0 \rangle$$

If there are Z electrons in an atom/ion, mean square radium of the ion may be defined by

$$\langle r^2 \rangle = \frac{\langle \phi_0 | \sum_i r_i^2 | \phi_0 \rangle}{Z}$$

This leads to

$$x = -\frac{\mu_0 N Z e^2}{6m} \langle r^2 \rangle$$

This is the same expression we obtained with classical formulation.

Quantum theory of paramagnetism

Consider the case of a solid composed of atoms/ions whose electronic shell is partially filled. In this case for all completely filled shell $L=0$, $S=0$, but for the partially filled shell $L \neq 0$, $S \neq 0$.

In this situation ($L \neq 0$, $S \neq 0$), two cases may arise.

(i) $J=0$ (partially filled shell is one electron short of being half filled)

An example

$\uparrow$	$\uparrow$	
$m_\ell = +1$	0	-1

$S=1$
$L=1$

Since the shell is less than half filled
$J = L - S = 0$.

~~(ii) $J \neq 0$, all other cases of partially filled shell.~~

In this case first term of energy shift vanish

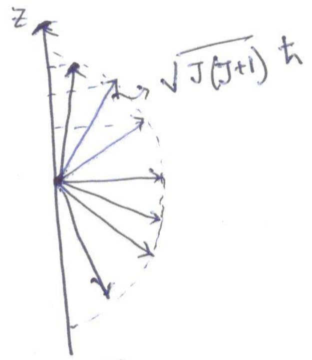
$$\Delta E_0 = \underbrace{\mu_B \vec{B}_0 \cdot \langle \phi_0 | \vec{L} + g_s \vec{S} | \phi_0 \rangle}_{\substack{0 \text{ for } J=0 \\ (\text{will prove it})}} + \frac{e^2}{8m} B_0^2 \langle \phi_0 | \sum_i x_i^2 + y_i^2 | \phi_0 \rangle + \sum_{n'} \frac{|\langle \phi_0 | \mu_B \vec{B}_0 \cdot (\vec{L} + g_s \vec{S}) | \phi_{n'} \rangle|^2}{E_0 - E_{n'}}$$

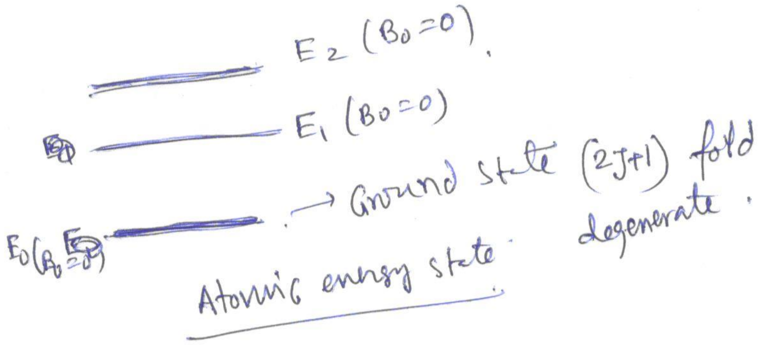
In this case other two terms contribute to magnetic behavior of solid.
Second term is the expression in diamagnetic contribution, and third term gives positive contribution (opposite to diamagnetic term) in ~~tem~~ terms of paramagnetism, known as 'Van Vleck paramagnetism'.

(ii) Second case, $J \neq 0$ in other situations of partially filled shell.
Then first term becomes so much larger than the other two terms that they can safely be ignored.

Thus, $\Delta E_0 \simeq \mu_B \vec{B}_0 \cdot \langle \phi_0 | \vec{L} + g_s \vec{S} | \phi_0 \rangle$

In this case also, at temperature not too high, atoms/ions ~~rem~~ mainly remain in their ground state. The ground state [with $J \neq 0$] is $(2J+1)$ fold degenerate ($m_J = -J, \cdots 0, \cdots +J$).





When $\vec{B}_0 = 0$,
all these $(2J+1)$ states are degenerate.

When magnetic field is applied ($\vec{B}_0 \neq 0$), the degenerate states of ground states, acquire different energy, so degeneracy is lifted.

Let me first calculate ΔE_0.

$$\Delta E_0 = \mu_B \vec{B}_0 \cdot \langle \phi_0 | \vec{L} + g_s \vec{S} | \phi_0 \rangle = \mu_B B_0 \langle \phi_0 | L_z + g_s S_z | \phi_0 \rangle$$

This is a problem of diagonization $(2J+1)$ fold square matrix.

$|\phi_0\rangle \rightarrow |J L S J_z\rangle$ with different J_z. {According to Hund's third rule, all possible $J_z = -J \cdots 0, +J$, have same energy for given J, L, S.

~~$\mu_B \vec{B}_0 \langle J L S J_z | \vec{L} + g_s \vec{S} | J L S J_z \rangle$~~

~~Hence, ΔE_0~~

~~Use~~ We can diagonize the matrix simply by Wigner-Eckart theorem, which states that matrix elements of any vector operator in the $(2J+1)$-dimensional space of eigenstates of J^2 and J_z with a given value of J, are proportional to the matrix elements of J itself:

Wigner - Eckart theorem

$$\langle J L S J_z | \vec{L} + g_s \vec{S} | J L S J_z' \rangle = g(JLS) \langle J L S J_z | \vec{J} | J L S J_z' \rangle$$

Sometimes it is written in shorthand notation

$\vec{L} + g_s \vec{S} = g \vec{J}$ (equality is valid for their matrix elements).

For ~~out~~ our given problem

$$\langle J L S J_z | L_z + g_s S_z | J L S J_z' \rangle = g(JLS) \langle J L S J_z | J_z | J L S J_z' \rangle$$

$$= g J_z \delta_{J_z, J_z'} \quad \text{--- (1)}$$

Lange-g factor $g = \frac{1}{2}(g_s+1) - \frac{1}{2}(g_s-1) \frac{L(L+1) - S(S+1)}{J(J+1)}$

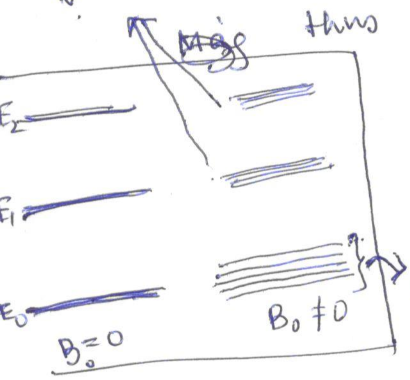
taking $g_s = 2$ for electron

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

Using result (1) we can get

$$\Delta E_0 = \mu_B B_0 g J_z \quad \text{--- (2)}$$

occupancy is very less



thus energy of the ground state ~~(...)~~ ~~for~~ now modifies to

~~$E_0(B) = E_0(B=0) + \Delta E_0(\mu_0 B_0 g J_z)$~~

$$E_0(B) = E_0(B=0) + \Delta E_0$$

$$E_0(B) = E_0(B=0) + \mu_B B_0 g J_z \quad \text{--- (3)}$$

We know Magnetization $M = -N \frac{\partial F}{\partial B_0}$

Susceptibility $\chi = \mu_0 \frac{\partial M}{\partial B_0}$

where $e^{-F/k_BT} = \sum_i e^{-E_n/k_BT}$

$$e^{-F/K_BT} = \sum_{J_z=-J}^{+J} e^{-\left[\frac{E_0(B_0=0) + \mu_B B_0 g J_z}{K_BT}\right]}$$

$$e^{-F/K_BT} = e^{-\frac{E_0(B_0=0)}{K_BT}} \sum_{J_z=-J}^{+J} e^{-\frac{\mu_B B_0 g J_z}{K_BT}}$$

$$\ln\left(e^{-F/K_BT}\right) = \ln\left(e^{-\frac{E_0(B_0=0)}{K_BT}}\right) + \ln\left(\sum_{J_z=-J}^{J} e^{-\frac{\mu_B B_0 g J_z}{K_BT}}\right)$$

taking derivative w.r.t B_0.

$$\frac{\partial}{\partial B_0}\left[\ln e^{-F/K_BT}\right] = \frac{\partial}{\partial B_0}\left[\ln \sum_{J_z=-J}^{+J} e^{-\frac{\mu_B B_0 g J_z}{K_BT}}\right]$$

Let $\beta = \frac{1}{K_BT}$ and $\gamma = g\mu_B$.

$$\frac{\partial}{\partial B_0}\left[\ln e^{-\beta F}\right] = \frac{\partial}{\partial B_0}\left[\ln \sum_{J_z=-J}^{+J} e^{-\beta\gamma B_0 J_z}\right]$$

$$\frac{e^{-\beta F}}{e^{-\beta F}} \times \left(-\beta\frac{\partial F}{\partial B_0}\right) = \frac{\sum\left[(-\beta\gamma J_z)\, e^{-\beta\gamma B_0 J_z}\right]}{\sum_{J_z=-J}^{+J} e^{-\beta\gamma B_0 J_z}}$$

$$+\beta\frac{\partial F}{\partial B_0} = \frac{\sum +(\beta\gamma J_z)\, e^{-\beta\gamma B_0 J_z}}{\sum_{J_z=-J}^{+J} e^{-\beta\gamma B_0 J_z}}$$

$$\cancel{\beta}\frac{\partial F}{\partial B_0} = \frac{\beta\gamma\left[J e^{-\beta\gamma B_0 J} + (J-1)\, e^{-\beta\gamma B_0 (J-1)} + \cdots + (-J)\, e^{\beta\gamma B_0 J}\right]}{\left[e^{-\beta\gamma B_0 J} + e^{-\beta\gamma B_0 (J-1)} + \cdots + e^{\beta\gamma B_0 J}\right]}$$

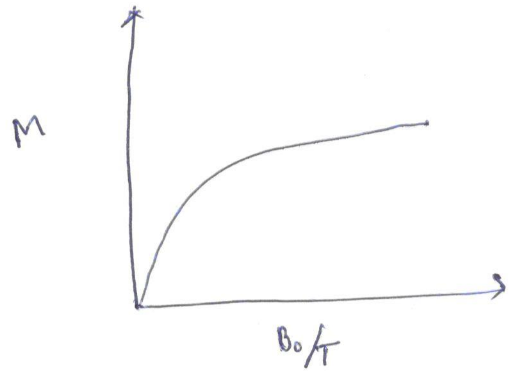
$$\frac{\partial F}{\partial B_0} = -\gamma J\, B_J(\beta\gamma J B_0) = -\gamma J\, B_J(x) \quad \text{where } x = \beta\gamma J B_0$$

where $B_J(x) = \frac{2J+1}{2J}\coth\frac{2J+1}{2J}x - \frac{1}{2J}\coth\frac{1}{2J}x$

thus magnetization

$$M = -N \frac{\partial F}{\partial B_0}$$

$$= N \gamma J B_J(x)$$



The behavior matches very well with experiment.

→ over a wide temp. range $g\mu_B B_0 << k_B T$

then x $\left(= \frac{g\mu_B J B_0}{k_B T}\right)$ is very small.

we can expand 'coth' function in $B_J(x)$ &

$$B_J(x) \simeq \frac{(2J+1)}{2J}\left[\frac{2J}{(2J+1)x} + \frac{(2J+1)x}{3\times(2J)}\right] - \frac{1}{2J}\left[\frac{2J}{x} + \frac{1}{3}\frac{x}{2J}\right]$$

$$= \left(\frac{J+1}{3J}\right)x$$

thus $g\mu_B B_0 << k_B T$ limit

$$M = N\gamma J B_J(x) = N\gamma J\left(\frac{2J+1}{3J}\right)x$$

$$M = N(\mu_B g) J\left(\frac{J+1}{3J}\right)\left(\frac{g\mu_B J B_0}{k_B T}\right)$$

$$= \frac{N J(J+1) g^2 \mu_B^2}{3 k_B T} B_0$$

$$\chi = \mu_0 \frac{\partial M}{\partial B_0} = \frac{\mu_0 N J(J+1) g^2 \mu_B^2}{3 k_B T} = \frac{C}{T}$$