Chapter 18

# Magnetism

## Chapter Outline

Magnetism was discovered in Magnesia, a place in Greece, around 800 BCE and that is the origin of its name. The writing of Thales, a Greek writer, shows that magnetite or loadstone was known to attract iron pieces. The Chinese made a magnetic compass sometime around 200 BCE. Today, we can observe that most of the elements in the periodic table exhibit magnetism of varying strength. The type of magnetization that occurs when an external magnetic field is applied to an element varies:

1. In some elements of the periodic table, magnetization is induced in a direction opposite to the applied magnetic field. The induced magnetization lasts only for the time the applied magnetic field exists. Such elements are called diamagnetic elements and are repelled by the magnetic field.
2. In many elements, weak magnetization is produced in the direction of the applied magnetic field. Moreover, the magnetization lasts so long as the applied field is finite. Such elements are called paramagnetic elements and are weakly attracted by the magnetic field.
3. In some elements, remarkably strong magnetization is produced in the direction of the applied magnetic field. Further, the magnetization exists even in the absence of the applied field. Such elements are called ferromagnetic elements and are strongly attracted by the magnetic field.

In addition, there exist antiferromagnetic and ferrimagnetic elements, which will be discussed in reasonable detail in the coming chapters. The atomic magnetic dipole moment, induced or intrinsic, is basically responsible for the existence of magnetism in the various elements.

## 18.1 ATOMIC MAGNETIC DIPOLE MOMENT

In an atom, electrons revolve around the nucleus and the nucleus contains protons and neutrons. An atom as a whole is electrically neutral, but it consists of moving charged particles that may behave as magnetic dipoles. An electron in an atom has two motions: orbital and spin. Similarly, protons and neutrons also possess orbital and spin motions inside the nucleus. Therefore, the magnetic moment of an electron has two principal contributions, which are the orbital and spin magnetic moments. There is also a third contribution to the magnetic moment arising from the spin-orbit interaction. If the spin and orbital motions are assumed to be independent of each other, then the spin-orbit contribution vanishes and the total magnetic moment of the ith electron $\vec{\mu}_{\mathrm{ei}}$ is the vector sum of its orbital and spin contributions, i.e.,

$$\vec{\mu}_{\mathrm{ei}} = \vec{\mu}_{\mathrm{eil}} + \vec{\mu}_{\mathrm{eis}} \tag{18.1}$$

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where $\vec{\mu}_{\mathrm{eil}}$ and $\vec{\mu}_{\mathrm{eis}}$ are the orbital and spin contributions to the magnetic moment of the ith electron. The total electronic contribution to the magnetic moment of an atom $\vec{\mu}_{\mathrm{e}}$, therefore, is the vector sum of the magnetic moments of all the electrons, i.e.,

$$\vec{\mu}_{\mathrm{e}}=\sum_{\mathrm{i}}\vec{\mu}_{\mathrm{ei}} \tag{18.2}$$

The protons in a nucleus, being charged particles, possess both orbital and spin magnetic moments, just like electrons. The neutrons, being neutral particles, do not possess an orbital magnetic moment in spite of their orbital motion, but they do possess an intrinsic spin magnetic moment. The total magnetic moment of a nucleus $\vec{\mu}_{\mathrm{N}}$ is the vector sum of the magnetic moments of the neutrons and protons and is given by

$$\mu_{\mathrm{N}}=\sum_{\mathrm{j}}\mu_{\mathrm{pj}}+\sum_{\mathrm{k}}\mu_{\mathrm{nk}} \tag{18.3}$$

where $\mu_{\mathrm{pj}}$ and $\vec{\mu}_{\mathrm{nk}}$ are the total magnetic moment of the jth proton and kth neutron. From Eqs. (18.2) and (18.3) the magnetic moment of an atom is given by

$$\vec{\mu}=\vec{\mu}_{\mathrm{e}}+\vec{\mu}_{\mathrm{N}} \tag{18.4}$$

We shall see later that the magnetic moment of a nucleus is negligible compared with the electronic contribution (about 2000 times smaller); therefore, the magnetic moment of an atom is determined mainly by the electrons. In the coming discussion the magnetic moment of an atom $\vec{\mu}$ is assumed to include only the electronic contribution.

### 18.1.1 Orbital Magnetic Moment

Consider an atom in which an electron is moving in an elliptical orbit with a nucleus at one of its foci, say O (Fig. 18.1). Let T be the time period of revolution of the electron around the nucleus. The revolving electron constitutes an electric current $\mathrm{I_L}$ given by

$$\mathrm{I_L}=-\frac{\mathrm{e}}{\mathrm{T}} \tag{18.5}$$

The total area of the elliptical orbit swept by the electron in time T is given by

$$\mathrm{A}=\frac{1}{2}\int_0^{2\pi}\mathrm{r}^2\,\mathrm{d}\varphi \tag{18.6}$$

where $\varphi$ is the angle formed by the major axis of the ellipse with the radius vector r (from the focus) of the electron at any time t. From elementary electricity, the orbital magnetic moment arising from the current $\mathrm{I_L}$ is given by

$$\mu_{\mathrm{L}}=\frac{\mathrm{I_L A}}{\mathrm{c}} \tag{18.7}$$

where c is the velocity of light. The angular momentum of the electron is given by

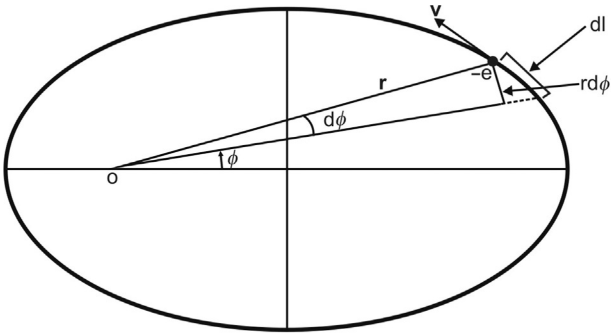

**FIG. 18.1** Motion of an atomic electron in an elliptical orbit with a nucleus at one of its foci O. The electron with position vector **r** is moving with velocity **v** in the orbit.

$$p_\varphi = m_e r^2 \omega_\varphi = m_e r^2 \frac{d\varphi}{dt} \tag{18.8}$$

where $m_e$ is the mass and $\omega_\varphi$ is the angular velocity of the electron. Substituting the value of $r^2$ from Eq. (18.8) into Eq. (18.6), we write

$$A = \frac{1}{2}\int_0^{2\pi} \frac{p_\varphi}{m_e} \frac{1}{{}^{d\varphi}/_{dt}} d\varphi = \frac{1}{2}\frac{p_\varphi}{m_e}\int_0^T dt = \frac{1}{2}\frac{p_\varphi T}{m_e} \tag{18.9}$$

Substituting Eqs. (18.5) and (18.9) into Eq. (18.7), we get

$$\mu_L = -\frac{e}{2m_e c} p_\varphi \tag{18.10}$$

From Bohr's quantization rule for orbits, the angular momentum $p_\varphi$ can be written as

$$p_\varphi = \hbar L \tag{18.11}$$

Here L is called the orbital quantum number and has integral values 1, 2, 3, … Sometimes L is also called the orbital angular momentum in units of $\hbar = h/2\pi$ where h is the Planck constant. From Eqs. (18.10) and (18.11) one can write

$$\mu_L = -\mu_B L \tag{18.12}$$

where $\mu_B$ is called the Bohr magnetron defined as

$$\mu_B = \frac{e\hbar}{2 m_e c} \tag{18.13}$$

In vector notation Eq. (18.12) can be written as

$$\vec{\mu}_L = -\mu_B \mathbf{L} \tag{18.14}$$

The negative sign indicates that the orbital magnetic moment is in a direction opposite to the orbital angular momentum and is basically due to the negative charge of the electron. The above expression is valid only for orbital motion. An alternate method for calculating $\mu_L$ for an electron moving in a circular orbit is given in Appendix L.

### 18.1.2 Spin Magnetic Moment

The orbital theory does not explain the multiplicity of atomic spectra, e.g., the doublet of d-states. In addition, it also does not explain the Zeeman levels in some of the elements. These difficulties were resolved by assuming that an electron possesses intrinsic spin angular momentum **S**, which has eigenvalues ±(1/2) in units of $\hbar$. Note that spin is purely a relativistic property of an electron and arises from quantum effects. The magnetic moment arising from the spin angular momentum is given by

$$\vec{\mu}_S = -2\mu_B \mathbf{S} \tag{18.15}$$

From Eq. (18.15) the value of the spin magnetic moment is numerically equal to the Bohr magnetron. Hence the total magnetic moment of an electron becomes

$$\begin{aligned} \vec{\mu}_J &= \vec{\mu}_L + \vec{\mu}_S \\ &= -\mu_B(\mathbf{J} + \mathbf{S}) \end{aligned} \tag{18.16}$$

where the total angular momentum **J** of an electron is given by

$$\mathbf{J} = \mathbf{L} + \mathbf{S} \tag{18.17}$$

The vector **S** is spinning around the direction of **J** (see Fig. 18.2). So, the average value of the magnetic moment $\vec{\mu}_J$ is obtained by substituting the average value of **S** along the direction of **J**, that is, $\langle \mathbf{S} \rangle$ in Eq. (18.16), allowing us to write

$$\vec{\mu}_J = -\mu_B[\mathbf{J} + \langle \mathbf{S} \rangle] \tag{18.18}$$

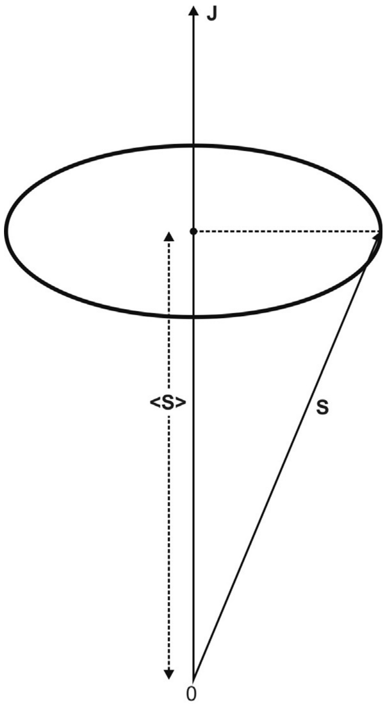

**FIG. 18.2** The spinning of an electron spin **S** around the total angular momentum **J** of the electron. The vector $\langle \mathbf{S} \rangle$ gives the average value of spin **S** along the **J** vector.

Here $\mathbf{J}+\langle \mathbf{S} \rangle$ gives the diagonal element of $\mathbf{J}+\mathbf{S}$. The average value of $\langle \mathbf{S} \rangle$ is given by

$$\langle \mathbf{S} \rangle = \frac{\mathbf{J}\cdot\mathbf{S}}{|\mathbf{J}|}\hat{\mathbf{J}} = \frac{\mathbf{J}\cdot\mathbf{S}}{|\mathbf{J}|^2}\mathbf{J} \tag{18.19}$$

where $\hat{\mathbf{J}}$ is a unit vector in the direction of **J**. From Eq. (18.17) we write

$$\mathbf{J}-\mathbf{S}=\mathbf{L} \tag{18.20}$$

Squaring both sides, we find

$$\mathbf{J}\cdot\mathbf{S}=\frac{1}{2}\left(J^2+S^2-L^2\right) \tag{18.21}$$

From Eqs. (18.19) and (18.21) the average value of the spin becomes

$$\langle \mathbf{S} \rangle = \frac{J^2+S^2-L^2}{2J^2}\mathbf{J} \tag{18.22}$$

The eigenvalues of $L^2$, $S^2$, and $J^2$ are $L(L+1)$, $S(S+1)$ and $J(J+1)$. Therefore, the average value of spin along the direction of **J** is given by

$$\langle \mathbf{S} \rangle = \frac{J(J+1)+S(S+1)-L(L+1)}{2J(J+1)}\mathbf{J} \tag{18.23}$$

Substituting the value of $\langle \mathbf{S} \rangle$ from Eq. (18.23) into Eq. (18.18), we get the average value of the magnetic moment as

$$\vec{\mu}_J = -g_J\mu_B\mathbf{J} \tag{18.24}$$

where

$$g_J = 1+\frac{J(J+1)+S(S+1)-L(L+1)}{2J(J+1)} \tag{18.25}$$

The factor $g_J$ is usually called Lande's splitting factor. The above expression gives the magnetic moment of an electron due to its total angular momentum **J**. It can be easily proved from Eq. (18.25) that $g_J = 2$ if there is only the spin motion and that it is equal to 1 if there is only the orbital motion. From experiments, the actual value of $g_J$ for electron spin is found to be 2.0023.

### 18.1.3 Nuclear Magnetic Moment

One can also calculate the magnetic moment of a proton $\vec{\mu}_p$ and neutron $\vec{\mu}_n$ in exactly the same way as for an electron. The expressions for the magnetic moments are

$$\vec{\mu}_p = \mu_{Bp}\mathbf{I}_p \tag{18.26}$$

and

$$\vec{\mu}_n = \mu_{Bn}\mathbf{I}_n \tag{18.27}$$

where

$$\mu_{Bp} = \frac{e\hbar}{2M_p c},\ \mu_{Bn} = \frac{e\hbar}{2M_n c} \tag{18.28}$$

$\mathbf{I}_p$ and $\mathbf{I}_n$ are the total angular momenta for the proton and neutron, respectively. $\mathbf{I}_p$ arises from both the orbital and spin motions, while $\mathbf{I}_n$ arises from the spin motion only. From Eq. (18.26) it is evident that the angular momentum and magnetic moment of a proton are in the same direction, in contrast with an electron, and this is because of the positive charge on the proton. In the case of a neutron, the angular momentum and magnetic moment are also in the same direction, although the neutron is a neutral particle. Further, due to the large mass of the proton, the Bohr magnetron of a proton $\mu_{Bp}$ is about 2000 times smaller than the Bohr magnetron of an electron $\mu_B$. The same applies to the neutron Bohr magnetron $\mu_{Bn}$. Therefore, the nuclear magnetic moment is very small compared with the electronic magnetic moment in an atom. In other words, the atomic magnetic moment arises mainly from the electron contribution.

## 18.2 MAGNETIZATION

When a solid is placed in a magnetic field, it gets magnetized. Therefore, one can talk about the strength of magnetism produced inside the solid, which is determined by a physical quantity called magnetization. *Magnetization is defined as the atomic/molecular magnetic moment per unit volume*. For weak magnetic fields, magnetization $\mathbf{M}(\mathbf{r})$ is linearly proportional to the applied magnetic field $\mathbf{H}(\mathbf{r})$. For inhomogeneous and anisotropic solids.

$$\mathbf{M}(\mathbf{r}) = \sum_{\mathbf{r}'} \chi_M(\mathbf{r},\mathbf{r}')\mathbf{H}(\mathbf{r}') \tag{18.29}$$

$\mathbf{M}(\mathbf{r})$ is the magnetization produced in the $\mathbf{r}$ direction, while the magnetic field $\mathbf{H}(\mathbf{r}')$ is applied in the $\mathbf{r}'$ direction. Here $\chi_M(\mathbf{r},\mathbf{r}')$ is the proportionality constant and is, in general, a tensor for an inhomogeneous and anisotropic solid. $\chi_M(\mathbf{r},\mathbf{r}')$ is usually called the magnetic susceptibility tensor. According to the above expression, the magnetic field applied in all possible directions of $\mathbf{r}'$, contributes to magnetization along the $\mathbf{r}$ direction. If the solid is homogeneous and isotropic, then both the magnetic field and magnetization are in the same direction and one can write

$$\mathbf{M}(\mathbf{r}) = \chi_M(\mathbf{r})\mathbf{H}(\mathbf{r}) \tag{18.30}$$

For such solids the magnetic susceptibility $\chi_M(\mathbf{r})$ becomes a scalar quantity. A uniform magnetic field produces a constant magnetization and, therefore, the magnetic susceptibility $\chi_M$ becomes a constant. It can easily be shown from the above expression that the magnetic susceptibility is dimensionless.

## 18.3 MAGNETIC INDUCTION

In the presence of an externally applied magnetic field, a solid is magnetized. Therefore, the magnetic field inside the solid $\mathbf{B}(\mathbf{r})$, usually called the magnetic induction, is different than the applied field and is given by

$$\mathbf{B}(\mathbf{r}) = \mathbf{H}(\mathbf{r}) + 4\pi\mathbf{M}(\mathbf{r}) \tag{18.31}$$

Substituting the value of $\mathbf{M(r)}$ from Eq. (18.29) into Eq. (18.31), one gets

$$\mathbf{B(r)} = \mathbf{H(r)} + 4\pi \sum_{\mathbf{r}'} \chi_{\mathrm{M}}(\mathbf{r}, \mathbf{r}')\, \mathbf{H}(\mathbf{r}') \tag{18.32}$$

The above expression can be written as

$$\mathbf{B(r)} = \sum_{\mathbf{r}'} \mu(\mathbf{r}, \mathbf{r}')\, \mathbf{H}(\mathbf{r}') \tag{18.33}$$

where

$$\mu(\mathbf{r}, \mathbf{r}') = \delta_{\mathbf{r},\mathbf{r}'} + 4\pi \chi_{\mathrm{M}}(\mathbf{r}, \mathbf{r}') \tag{18.34}$$

Here $\mu(\mathbf{r}, \mathbf{r}')$ is called the magnetic permeability tensor of the material. As already discussed, for a homogeneous and isotropic material the magnetic susceptibility is a scalar, therefore, from Eq. (18.34) the magnetic permeability also becomes a scalar and is given as

$$\mu(\mathbf{r}) = 1 + 4\pi \chi_{\mathrm{M}}(\mathbf{r}) \tag{18.35}$$

As the magnetic susceptibility is dimensionless, the magnetic permeability is also dimensionless.

## 18.4 POTENTIAL ENERGY OF MAGNETIC DIPOLE MOMENT

Consider an electron moving in an elliptical orbit with its magnetic dipole moment always perpendicular to it. Let a uniform magnetic field **H** be applied in the z-direction, as shown in Fig. 18.3. In the presence of **H**, torque will act on the current loop or the magnetic dipole moment, which is given by

$$\vec{\tau} = \vec{\mu} \times \mathbf{H} \tag{18.36}$$

The magnitude of the torque is given by

$$\tau = \mu \mathrm{H} \sin\theta \tag{18.37}$$

Work will be done by the torque on the magnetic moment, which will change the orientation of the dipole moment. The work done will be stored as the potential energy of the magnetic dipole moment. The zero of the potential energy (reference level) may be taken in any direction of the dipole moment. To be consistent with Eq. (18.37) we usually assume potential energy to be zero when $\vec{\mu}$ and **H** are perpendicular to each other. The potential energy of the magnetic dipole moment in the

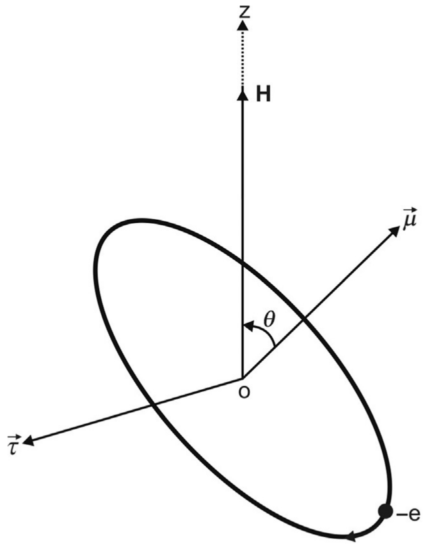

**FIG. 18.3** The torque $\vec{\tau}$ acting on the magnetic moment $\vec{\mu}$, arising from a current loop, in the presence of applied magnetic field **H**.

presence of a magnetic field is the work required to rotate the magnetic dipole from the zero energy position ($\theta = 90°$) to an angle $\theta$, i.e.,

$$E = \int_{90}^{\theta} \tau d\theta = \mu H \int_{90}^{\theta} \sin\theta d\theta \tag{18.38}$$

The above integral can easily be solved to get

$$E = -\vec{\mu} \cdot \mathbf{H} \tag{18.39}$$

It should be noted that the choice of the zero energy configuration for E is arbitrary as one is usually interested in the changes in potential energy that occur when a dipole moment is rotated.

## 18.5 LARMOR PRECESSION

Consider an orbital magnetic moment $\vec{\mu}_L$, associated with an electron, in a uniform magnetic field **H,** as shown in Fig. 18.4. The torque acting on the magnetic moment, from Eqs. (18.14) and (18.36), is given by

$$\vec{\tau}_L = \vec{\mu}_L \times \mathbf{H} = -\mu_B \mathbf{L} \times \mathbf{H} \tag{18.40}$$

So, the magnitude of the torque is given by

$$\tau_L = \mu_B H L \sin\theta \tag{18.41}$$

Depending on the direction of motion, the torque will either accelerate or retard the electron in motion, thereby inducing additional current in the current loop. According to Newton's second law of motion the torque produces a change in the orbital angular momentum **L**, which is at a right angle to itself. Torque can also be defined as the rate of change of angular momentum and is given by

$$\vec{\tau}_L = \frac{d\mathbf{p}_\varphi}{dt} = \hbar \frac{d\mathbf{L}}{dt} \tag{18.42}$$

So, the torque causes **L** to precess about the direction of **H** with an angular frequency $\omega_L$. The precession of the orbital angular momentum about the direction of a magnetic field is called the Larmor precession and $\omega_L$ is called the Larmor frequency. An alternate simple method for calculating $\omega_L$ is presented in Appendix M. From Fig. 18.4, the change in orbital angular momentum **L** in time dt is given by

$$dL = L \sin\theta \, (\omega_L dt)$$

The above equation gives the torque $\tau_L$ as

$$\tau_L = \hbar \frac{dL}{dt} = \hbar \omega_L L \sin\theta \tag{18.43}$$

From Eqs. (18.41) and (18.43) one can immediately write

$$\hbar \omega_L = \mu_B H \tag{18.44}$$

From this equation the Larmor precession frequency becomes

$$\omega_L = \frac{eH}{2m_e c} \tag{18.45}$$

Diamagnetism is related to the Larmor precession of the electrons. Diamagnetism is the tendency of electrical charges to partially shield the interior of the solid from the applied magnetic field. The basic principle of diamagnetic behavior can be illustrated with the Lenz law of electricity. Consider an atom with Z electrons revolving around its nucleus in different orbits. When an external magnetic field **H** is applied, the magnetic force acts on every electron. The magnetic force accelerates some of the electrons, while others are retarded depending on the direction of their motion. The change in velocity of

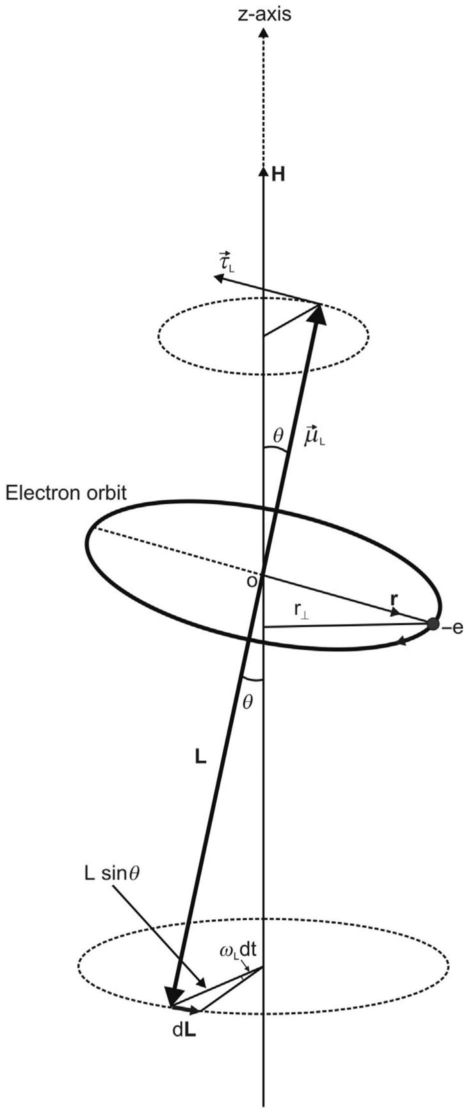

**FIG. 18.4** The torque $\vec{\tau}_L$ acting on an orbital magnetic moment $\vec{\mu}_L$ in the presence of an applied magnetic field **H** in the z-direction. The figure also depicts the change in orbital angular momentum d**L** due to the torque.

the electrons gives rise to an induced current that opposes the applied magnetic field (Lenz law). The induced current is responsible for inducing an orbital magnetic moment $\vec{\mu}_L$ on the atom. If $T_L$ is the time period for Larmor precession of the electrons around the magnetic field, the induced current $I_L$ is given by

$$I_L = -\frac{Ze}{T_L} \tag{18.46}$$

But the Larmor frequency is given by

$$\omega_L = \frac{2\pi}{T_L} = \frac{eH}{2m_e c} \tag{18.47}$$

Substituting the value of $T_L$ from Eq. (18.47) into Eq. (18.46), we find

$$I_L = -\frac{Ze^2 H}{4\pi m_e c} \tag{18.48}$$

Let $\langle r_\perp^2 \rangle$ be the average of the square of the radius of the electron from the nucleus perpendicular to the direction of the magnetic field. Then the average area of the electron orbit perpendicular to the magnetic field becomes

$$A = \pi \langle r_\perp^2 \rangle \tag{18.49}$$

As the magnetic field is in the z-direction, $\langle r_\perp^2 \rangle$ is in the xy-plane. One can write

$$\langle r_\perp^2 \rangle = \langle x^2 \rangle + \langle y^2 \rangle \tag{18.50}$$

In general, the mean square distance $\langle r^2 \rangle$ of the electrons from the nucleus in three dimensions is given by

$$\langle r^2 \rangle = \langle x^2 \rangle + \langle y^2 \rangle + \langle z^2 \rangle \tag{18.51}$$

In order to estimate the induced magnetic moment, we consider a simple case in which the charge distribution is spherically symmetric, that is,

$$\langle x^2 \rangle = \langle y^2 \rangle = \langle z^2 \rangle \tag{18.52}$$

From Eqs. (18.50), (18.51), and (18.52) one can easily write

$$\langle r_\perp^2 \rangle == \frac{2}{3} \langle r^2 \rangle \tag{18.53}$$

Substituting Eqs. (18.48), (18.49), and (18.53) into Eq. (18.7), the induced magnetic moment due to the Larmor precession is given by

$$\mu_L = -\frac{Ze^2 H}{6m_e c^2} \langle r^2 \rangle \tag{18.54}$$

If there are $\rho^a$ atoms per unit volume, the diamagnetic susceptibility is given by

$$\chi_d = \frac{M}{H} = \frac{\rho^a \mu_L}{H} = -\frac{Ze^2 \rho^a}{6m_e c^2} \langle r^2 \rangle \tag{18.55}$$

This is called the Langevin result. From Eq. (18.55) it is evident that the problem of calculating the diamagnetic susceptibility is reduced to the calculation of $\langle r^2 \rangle$ for the atomic electron distribution in an atom, which can be estimated using a quantum mechanical approach.

The units of $\chi_d$ can be calculated from Eq. (18.55). Z is a number but $\rho^a$, as the density of atoms, has dimensions of $1/L^3$ and so, from Eq. (18.55), one can write

$$\chi_d = \frac{1}{L^3} \frac{e^2}{M\left(LT^{-1}\right)^2} L^2 = \frac{e^2}{L} \frac{1}{ML^2T^{-2}} \tag{18.56}$$

Now $e^2/L$ have the units of energy (work) with dimensions

$$\frac{e^2}{L} = maS = M\left(LT^{-2}\right)L = ML^2T^{-2} \tag{18.57}$$

From Eqs. (18.56) and (18.57), $\chi_d$ is found to be dimensionless. The value of $\chi_d$ is specified in the same way as the density $\rho^a$ is defined. If the density $\rho^a$ is defined per unit volume, then the values of $\chi_d$ are listed per unit volume, but if $\rho^a$ is taken per gram mole, then $\chi_d$ is specified per gram mole.

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*Problem 18.1*

Calculate the diamagnetic susceptibility for a He atom in the ground state, i.e., the 1 s state, taking its radius as the Bohr radius $a_0$. The density of He atoms is given by $\rho^a = 2.7 \times 10^{24}\,\text{cm}^{-3}$.

## 18.6 QUANTUM THEORY OF DIAMAGNETISM

The Hamiltonian of an electron in an atom (say the Bohr atom) is given by

$$\widehat{H}_0 = \frac{p^2}{2m_e} + V \tag{18.58}$$

where p and $m_e$ are the momentum and mass of the electron, respectively. If the atom is placed in electric and magnetic fields represented by **E** and **H**, respectively, then the Lorentz force acting on the electron is given by

$$\mathbf{F} = -e\mathbf{E} - \frac{e}{c}\mathbf{v} \times \mathbf{H} \tag{18.59}$$

The magnetic field in terms of the vector potential **A** is given by

$$\mathbf{H} = \nabla \times \mathbf{A} \tag{18.60}$$

The momentum of an electron in the presence of an electromagnetic field changes as follows:

$$\mathbf{p} \rightarrow \mathbf{p} - \frac{e}{c}\mathbf{A} \tag{18.61}$$

Therefore, the Hamiltonian of an electron in the presence of a magnetic field becomes

$$\widehat{H} = \frac{1}{2m_e}\left(\mathbf{p} - \frac{e}{c}\mathbf{A}\right)^2 + V \tag{18.62}$$

$\widehat{H}$ can be split up into two parts as

$$\widehat{H} = \widehat{H}_0 + \widehat{H}_1 \tag{18.63}$$

where

$$\widehat{H}_0 = \frac{p^2}{2m_e} + V \tag{18.64}$$

$$\widehat{H}_1 = -\frac{e}{2m_e c}(\mathbf{p} \cdot \mathbf{A} + \mathbf{A} \cdot \mathbf{p}) + \frac{e^2}{2m_e c^2}A^2 \tag{18.65}$$

Here $\widehat{H}_0$ is the unperturbed Hamiltonian and $\widehat{H}_1$ is the perturbation. Suppose **H** is uniform and is applied in the z-direction, then the components of the magnetic field from Eq. (18.60) are given as

$$H_x = \frac{\partial A_z}{\partial y} - \frac{\partial A_y}{\partial z} = 0 \tag{18.66}$$

$$H_y = \frac{\partial A_x}{\partial z} - \frac{\partial A_z}{\partial x} = 0 \tag{18.67}$$

$$H_z = \frac{\partial A_y}{\partial x} - \frac{\partial A_x}{\partial y} = H \tag{18.68}$$

The above equations are satisfied if the components of the vector potential are given by

$$A_x = -\frac{1}{2}yH, A_y = \frac{1}{2}xH, A_z = 0 \tag{18.69}$$

This can be written in vector form as

$$\mathbf{A} = \frac{1}{2}\mathbf{H} \times \mathbf{r} \tag{18.70}$$

Substituting $\mathbf{p} = -\imath\hbar\nabla$ into Eq. (18.65), $\widehat{H}_1$ can be written as

$$\widehat{H}_1 = \frac{\imath\hbar e}{2m_e c}(\nabla \cdot \mathbf{A} + \mathbf{A} \cdot \nabla) + \frac{e^2}{2m_e c^2}A^2 \tag{18.71}$$

In terms of Cartesian components $\widehat{H}_1$, from Eq. (18.65), can be written as

$$\widehat{H}_1 = -\frac{e}{2m_e c}\left(p_x A_x + p_y A_y + A_x p_x + A_y p_y\right) + \frac{e^2}{2m_e c^2}\left(A_x^2 + A_y^2\right) \tag{18.72}$$

From Eqs. (18.69) and (18.72) it is straightforward to write

$$\widehat{H}_1 = -\frac{eH}{2m_e c}\left(xp_y - yp_x\right) + \frac{e^2 H^2}{8m_e c^2}\left(x^2 + y^2\right) \tag{18.73}$$

The orbital angular momentum, defined as $\mathbf{L} = \mathbf{r} \times \mathbf{p}$, can be used to write

$$\widehat{H}_1 = -\frac{eH}{2m_e c}L_z + \frac{e^2 H^2}{8m_e c^2}\left(x^2 + y^2\right)$$

or

$$\widehat{H}_1 = -\mu_z H + \frac{e^2 H^2}{8m_e c^2}\left(x^2 + y^2\right)$$

or

$$\widehat{H}_1 = -\vec{\mu}\cdot\mathbf{H} + \frac{e^2 H^2}{8m_e c^2}\left(x^2 + y^2\right) \tag{18.74}$$

The expectation value of $\widehat{H}_1$ gives us the change in energy due to the application of the magnetic field. The lowest order change in energy is given by the first-order correction in perturbation theory. Let $|\psi_0\rangle = |0\rangle$ represent the ground state of the system. For diamagnetic substances the atomic or molecular magnetic moment is zero in the ground state, therefore,

$$\langle 0|\mu_z|0\rangle = 0 \tag{18.75}$$

Hence the first-order correction to energy in a diamagnetic substance comes from the expectation value of the second term in Eq. (18.74), i.e.,

$$E_1 = \frac{e^2 H^2}{8m_e c^2}\langle 0|x^2 + y^2|0\rangle \tag{18.76}$$

$\langle 0|\, x^2 + y^2|0\rangle$ is the average value of the area of the electron loop perpendicular to the direction of the magnetic field and is given by

$$\langle 0|x^2 + y^2|0\rangle = \left\langle r_\perp^2\right\rangle = \frac{2}{3}\left\langle r^2\right\rangle \tag{18.77}$$

Substituting Eq. (18.77) into Eq. (18.76), we obtain

$$E_1 = \frac{e^2 H^2}{12m_e c^2}\left\langle r^2\right\rangle \tag{18.78}$$

We know that the magnetic energy is given by

$$E = -\vec{\mu}\cdot\mathbf{H} = -\mu_z H \tag{18.79}$$

Therefore, the magnetic moment is given by

$$\mu_z = -\frac{\partial E}{\partial H} \tag{18.80}$$

Substituting Eq. (18.78) into Eq. (18.80), one gets

$$\mu_z = -\frac{e^2 H}{6m_e c^2}\left\langle r^2\right\rangle \tag{18.81}$$

This is the same result for the magnetic moment as that obtained classically.

Let us find the expectation value of the Hamiltonian of the perturbed ground state. Suppose $|n\rangle$ represents the nth state of the unperturbed system with energy $E_n$. The matrix element of the magnetic moment between the ground state $|0\rangle$ and the nth state $|n\rangle$ is $\langle n|\mu_z|0\rangle$. When a magnetic field **H** is applied, the perturbed ground state of the system is written as

$$|0'\rangle = |0\rangle + \sum_{n\neq 0} \frac{\langle n|\mu_z H|0\rangle}{E_n - E_0} |n\rangle \tag{18.82}$$

The first-order correction to the magnetic moment with respect to the perturbed ground state of the system, neglecting terms of second and higher order in H, is given by

$$\begin{aligned} \Delta\mu = \langle 0'|\mu_z|0'\rangle = \langle 0|\mu_z|0\rangle + H \sum_{n\neq 0} \frac{\langle 0|\mu_z|n\rangle\langle n|\mu_z|0\rangle}{E_n - E_0} \\ + H \sum_{n'\neq 0} \frac{\langle 0|\mu_z|n'\rangle\langle n'|\mu_z|0\rangle}{E_{n'} - E_0} \end{aligned} \tag{18.83}$$

The first term on the right side of Eq. (18.83) is zero. Further, the second and third terms are equal, yielding

$$\Delta\mu = 2H \sum_{n\neq 0} \frac{|\langle n|\mu_z|0\rangle|^2}{E_n - E_0} \tag{18.84}$$

If there are $\rho^a$ atoms or molecules per unit volume of the solid, then the magnetization produced is given by

$$\Delta M = \rho^a \Delta\mu = 2\rho^a H \sum_{n\neq 0} \frac{|n|\mu_z|0\rangle|^2}{E_n - E_0} \tag{18.85}$$

Therefore, the magnetic susceptibility contribution is given by

$$\Delta\chi_M = \frac{\Delta M}{H} = 2\rho^a \sum_{n\neq 0} \frac{|\langle n|\mu_z|0\rangle|^2}{E_n - E_0} \tag{18.86}$$

Here $E_n > E_0$, therefore, $\Delta\mu$ and hence $\Delta\chi_M$ is positive. With respect to $E_n - E_0$ two cases arise:

1. If $E_n - E_0 \gg k_B T$, i.e., the excited state has energy much greater than the thermal energy, then most of the electrons will be in the ground state. In this case, $\Delta\chi_M$ is positive and independent of temperature. This type of contribution to the magnetic susceptibility of a diamagnetic substance is known as *Van Vleck paramagnetism*.
2. If $E_n - E_0 \ll k_B T$, the excited state has an energy much less than the thermal energy. In this situation, both the ground and excited states are occupied with electrons, but the ground state has a higher population compared with the excited state. The excess population in the ground state is $\rho^a (E_n - E_0)/2k_B T$. Hence the resultant magnetization in the ground state of the system is given by

$$\Delta M = \rho^a \Delta\mu (E_n - E_0)/2k_B T$$

Substituting the value of $\Delta\mu$ from Eq. (18.84) into the above equation, we find

$$\Delta M = \frac{\rho^a H}{k_B T} \sum_{n\neq 0} |\langle n|\mu_z|0\rangle|^2 \tag{18.87}$$

Hence the magnetic susceptibility becomes

$$\Delta\chi_M = \frac{\rho^a}{k_B T} \sum_{n\neq 0} |\langle n|\mu_z|0\rangle|^2 \tag{18.88}$$

$\Delta\chi_M$ has a behavior similar to that of the Curie susceptibility, but the origin of this contribution is entirely different: $\Delta\chi_M$ arises due to the polarization of the states of the system. It should be noted that the energy separation $E_n - E_0$ does not enter in Eq. (18.88). We should also note that if $E_n \to E_0$, then the electrons become free and the solid becomes a metal; in this case, Eq. (18.88) is not valid.

The above treatment can be generalized for the $n^{th}$ perturbed excited state given by

$$|n'\rangle = |n\rangle - \sum_{n\neq 0} \frac{\langle 0|\mu_z H|n\rangle}{E_n - E_0} |0\rangle$$

The expectation value of the magnetic moment in the perturbed state is given by

$$\Delta\mu' = \langle n'|\mu_z|n'\rangle = -2H \sum_{n\neq 0} \frac{|\langle n|\mu_z|0\rangle|^2}{E_n - E_0}$$

## 18.7 PARAMAGNETISM

In a paramagnetic substance each atom or molecule possesses an intrinsic magnetic dipole moment $\vec{\mu}$. At finite temperature, all of the magnetic dipole moments are oriented randomly in the form of closed chains yielding zero magnetization. In the presence of an applied magnetic field, two opposing forces act on each atomic dipole moment in a paramagnetic substance:

1. The magnetic field tries to align the dipole moments in the direction of the field, thereby producing finite magnetization along the magnetic field.
2. At finite temperature, the thermal energy tries to randomize the magnetic moments to form closed chains and hence tends to decrease magnetization.

### 18.7.1 Classical Theory of Paramagnetism

In the classical description, the magnetic dipole moment $\vec{\mu}$ is taken to be a constant physical quantity independent of the quantum numbers. Under the action of the competing forces mentioned above, some dipole moments align in the direction of the applied magnetic field, while others make some angle $\theta$, which is different for different dipole moments. Therefore, a solid shows finite magnetic dipole moment and hence finite magnetization in the direction of the magnetic field. The maximum magnetization is produced when all of the dipole moments align along the direction of the applied field. In the presence of a magnetic field, the potential energy of the magnetic dipole moment is given by

$$E = -\vec{\mu}\cdot\mathbf{H} = -\mu H\cos\theta \tag{18.89}$$

According to classical statistics, the probability P of a dipole moment making an angle $\theta$ with the magnetic field is given by

$$P \propto \exp\left(-\frac{E}{k_B T}\right) \propto \exp\left(\frac{\mu H}{k_B T}\cos\theta\right) \tag{18.90}$$

The component of the magnetic moment along the direction of the magnetic field is $\vec{\mu}\cdot\hat{\mathbf{H}} = \mu\cos\theta$ where $\hat{\mathbf{H}}$ is a unit vector in the direction of the field. Hence the average component of magnetic moment in the direction of the magnetic field is given by

$$\mu_{avg} = \frac{\int \left(\vec{\mu}\cdot\hat{\mathbf{H}}\right) \exp\left(\frac{\mu H}{k_B T}\cos\theta\right) d\Omega_s}{\int \exp\left(\frac{\mu H}{k_B T}\cos\theta\right) d\Omega_s} \tag{18.91}$$

Here $d\Omega_s$ is the elemental solid angle. Solving the above integral, one gets

$$\mu_{avg} = \mu L\left(\frac{\mu H}{k_B T}\right) \tag{18.92}$$

where

$$L(y) = \coth y - \frac{1}{y} \tag{18.93}$$

L(y) is the Langevin function (see Section 15.15). If $\rho^a$ is the number of atoms per unit volume, then the magnetization is given by

$$M = \rho^a \mu L\left(\frac{\mu H}{k_B T}\right) \tag{18.94}$$

The magnetic susceptibility $\chi_M$ becomes

$$\chi_M = \frac{\rho^a \mu}{H} L\left(\frac{\mu H}{k_B T}\right) \tag{18.95}$$

It is interesting to study M and $\chi_M$ in limiting cases. If the magnetic field is very high and the temperature is very low then,

$$\mu H \gg k_B T \tag{18.96}$$

In this limiting case the Langevin function goes to unity, i.e., $L(\mu H/k_B T) = 1$ and therefore

$$M = \rho^a \mu \tag{18.97}$$

which is the saturation magnetization when all the magnetic dipole moments are aligned in the direction of the magnetic field. Hence saturation magnetization is obtained either at very low temperatures or at very high magnetic field values. The other limiting case occurs when the magnetic field is low, but the temperature is high and, according to this.

$$\mu H \ll k_B T \tag{18.98}$$

If y is small, $L(y) \approx y/3$ [see Eq. (15.84)] and hence the magnetization from Eq. (18.94) becomes

$$M(T) = \rho^a \mu \frac{\mu H}{3 k_B T} = \frac{\mu^2 \rho^a}{3 k_B T} H \tag{18.99}$$

The behavior of the magnetization M(y) as a function of y is shown in Fig. 18.5. M(y) acquires the saturated value $\rho^a \mu$ at very large values of y, but the slope of the M(y) curve at $y = 0$ is $\rho^a \mu/3$. From Eq. (18.99) the paramagnetic susceptibility is given by

$$\chi_M(T) = \frac{C_M}{T} \tag{18.100}$$

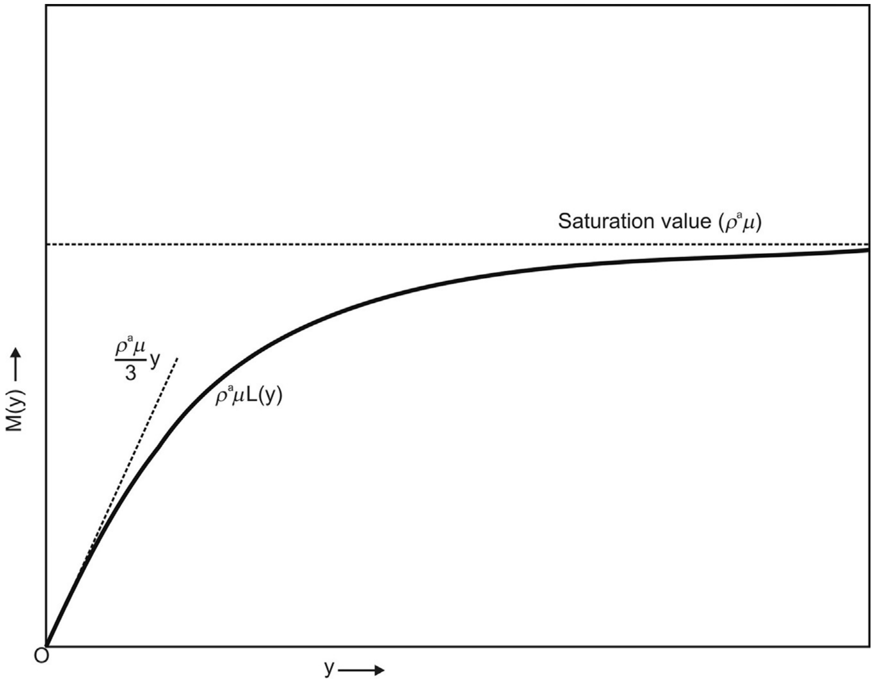

**FIG. 18.5** The magnetization M(y) in a paramagnetic solid as a function of parameter $y = \mu H/k_B T$ in the classical theory. The slope of the magnetization curve at the origin is shown by the *dashed line*.

where $C_M$ is the Curie constant and is given by

$$C_M = \frac{\mu^2 \rho^a}{3k_B} \tag{18.101}$$

Eq. (18.100) is the usual Curie law. The limitation of the classical theory is that the distribution of magnetic dipole moments is assumed to be continuous, i.e., all values of $\theta$ are allowed. But according to quantum mechanics, the distribution of magnetic dipoles must be discrete.

---

*Problem 18.2*

Let the paramagnetic susceptibility be given by

$$\chi_M = \frac{\rho^a \mu_B^2}{3k_B T}$$

where $\mu_B$ is the Bohr magnetron. If the density of atoms is $\rho^a = 2 \times 10^{22}$ atoms/cm$^3$, find the paramagnetic susceptibility at room temperature taken as $T = 300\,K$.

---

*Problem 18.3*

If one retains the first two terms in the series expansion of the Langevin theory of paramagnetism, prove that the susceptibility is given by

$$\chi_M = \frac{M}{H} = \frac{\rho^a \mu^2}{3k_B T}\left[1 - \frac{1}{15}\left(\frac{\mu H}{k_B T}\right)^2\right]$$

---

## 18.7.2 Quantum Theory of Paramagnetism

Eq. (18.14) yields discrete values for the orbital magnetic moment $\vec{\mu}_L$, which means that it is quantized. Similarly, the spin magnetic moment $\vec{\mu}_S$ is also discrete, having two values [Eq. (18.15)]: $\mu_B$ and $-\mu_B$. Therefore, the total magnetic moment $\vec{\mu}_J$ has discrete values. The general expression for the magnetic moment of an atom or an ion in free space is given by

$$\vec{\mu}_{\mathbf{J}} = \gamma_J \hbar \mathbf{J} \tag{18.102}$$

where $\mathbf{J}$ is the total angular momentum. The constant $\gamma_J$ is the ratio of the magnetic moment to the angular momentum and is called the magneto-mechanical or gyromagnetic ratio. Comparing Eq. (18.102) with Eq. (18.24), one can write

$$g_J \mu_B = -\gamma_J \hbar \tag{18.103}$$

Lande's spectroscopic splitting factor $g_J$ represents the ratio of the number of Bohr magnetrons to the angular momentum in units of ħ.

Suppose a magnetic field $\mathbf{H}$ is applied to a paramagnetic substance along the z-direction. The Hamiltonian of the system is given by

$$\widehat{H} = -\vec{\mu}_J \cdot \mathbf{H} = g_J \mu_B J_z H \tag{18.104}$$

$J_z$ is the z-component of the angular momentum $\mathbf{J}$. If $M_J$ is the eigenvalue of $J_z$, the interaction energy is given by

$$E = g_J \mu_B H M_J \tag{18.105}$$

$M_J$ is the azimuthal quantum number having the values $-J, -(J-1), \ldots\ldots\ldots -1, 0, 1, \ldots\ldots (J-1), J$, which are $2J+1$ in number. In a paramagnetic substance the occupation probability is given by the Boltzmann distribution as

$$P \propto \exp\left(-\frac{E}{k_B T}\right) \propto \exp\left(-\beta_0 g_J \mu_B H M_J\right) \tag{18.106}$$

The constant $\beta_0$ is given by Eq. (8.22). The component of the magnetic moment in the direction of the magnetic field is

$$\mu_z = \vec{\mu}_J \cdot \hat{z} = -g_J \mu_B M_J \tag{18.107}$$

Hence the average magnetic moment in the direction of the magnetic field is given by

$$\mu_{avg} = \frac{\sum_J (-g_J \mu_B M_J) \exp(-\beta_0 g_J \mu_B H M_J)}{\sum_J \exp(-\beta_0 g_J \mu_B H M_J)} \tag{18.108}$$

Substituting

$$y = \beta_0 g_J \mu_B H \tag{18.109}$$

Eq. (18.108) can be written as

$$\begin{aligned} \mu_{avg} &= \frac{-g_J \mu_B \sum_J M_J \exp(-yM_J)}{\sum_J \exp(-yM_J)} \\ &= g_J \mu_B \frac{d}{dy} \ln\left(\sum_J \exp(-yM_J)\right) \end{aligned} \tag{18.110}$$

It can easily be shown that

$$\sum_J \exp(-yM_J) = \frac{\exp\left(\frac{2J+1}{2} y\right) - \exp\left(-\frac{2J+1}{2} y\right)}{\exp\left(\frac{y}{2}\right) - \exp\left(-\frac{y}{2}\right)} \tag{18.111}$$

Substituting Eq. (18.111) into Eq. (18.110) and simplifying, we obtain

$$\mu_{avg} = g_J \mu_B J B_J(x) \tag{18.112}$$

where

$$B_J(x) = \frac{2J+1}{2J} \coth\left(\frac{2J+1}{2J} x\right) - \frac{1}{2J} \coth\left(\frac{1}{2J} x\right) \tag{18.113}$$

and

$$x = yJ = \beta_0 g_J \mu_B H J \tag{18.114}$$

The function $B_J(x)$ is called the Brillouin function. If $\rho^a$ is the number of dipole moments per unit volume, the magnetization is given by

$$M_J(x) = \rho^a g_J \mu_B J B_J(x) \tag{18.115}$$

One can study the particular case in which there is only spin ($L=0$). In the case of spin $J=S=1/2$ and $g_J = g_S = 2$, we find

$$x = \frac{\mu_B H}{k_B T} \tag{18.116}$$

Substituting the above mentioned values, the Brillouin function for spin becomes

$$B_{1/2}\left(\frac{\mu_B H}{k_B T}\right) = 2\coth\left(2\frac{\mu_B H}{k_B T}\right) - \coth\left(\frac{\mu_B H}{k_B T}\right) \tag{18.117}$$

which can be simplified to get

$$B_{1/2}\left(\frac{\mu_B H}{k_B T}\right) = \tanh\left(\frac{\mu_B H}{k_B T}\right) \tag{18.118}$$

Substituting Eq. (18.118) into Eq. (18.115) one can write

$$M_{1/2} = \rho^a \mu_B \tanh\left(\frac{\mu_B H}{k_B T}\right) \tag{18.119}$$

The value of the magnetization and magnetic susceptibility can be obtained in a simpler form in the limiting cases. From Eq. (18.114) one can write

$$x = \frac{g_J \mu_B H J}{k_B T} \tag{18.120}$$

In the limit $x \to 0$, i.e., when the magnetic field is very small or the temperature is very large, one can expand coth x as in Eq. (15.83) and use this in Eq. (18.113) to get

$$B_J(x) = \frac{J+1}{J}\frac{x}{3} \tag{18.121}$$

Therefore, in the limit $x \to 0$, the magnetization from Eq. (18.115) is given by

$$M_J(x) = \frac{\rho^a g_J^2 \mu_B^2 J(J+1)}{3k_B T} H = \rho^a g_J \mu_B \frac{J+1}{3} x \tag{18.122}$$

Hence the magnetic susceptibility becomes

$$\chi_M = \frac{C_J}{T} \tag{18.123}$$

where

$$C_J = \frac{\rho^a g_J^2 \mu_B^2 J(J+1)}{3k_B} \tag{18.124}$$

Eq. (18.123) is just the Curie law with Curie constant $C_J$, which depends on the total quantum number J. If we compare Eq. (18.124) with Eq. (18.101), we can say that the magnetic moment $\mu_J$ associated with an atom having quantum number J is

$$\mu_J = \mu_B p_J \tag{18.125}$$

where

$$p_J = g_J \sqrt{J(J+1)} \tag{18.126}$$

Here $p_J$ gives the effective number of Bohr magnetrons in an atom. The Curie constant in terms of $\mu_J$ is given by

$$C_J = \frac{\rho^a \mu_J^2}{3k_B} \tag{18.127}$$

In the limiting case of $x \to \infty$, either the magnetic field is very high or the temperature is very low. In this limit the Brillouin function (Eq. 18.113) goes to unity and, therefore, the magnetization from Eq. (18.115) is given by

$$M_J = \rho^a g_J \mu_B J \tag{18.128}$$

which gives the saturation magnetization of the substance. The variation of $M_J(x)$, given by Eq. (18.115) as a function of x, is shown in Fig. 18.6, which is similar to the magnetization curve obtained in the classical case. $M_J(x)$ increases with an increase in x and approaches the saturation value for large values of magnetic fields.

One can obtain the classical result of paramagnetism from the quantum theory in the limiting case. Let us suppose that the angular momentum **J** makes an angle $\theta$ with the direction of **H** (Fig. 18.7). The eigenvalue of **J** is $[J(J+1)]^{1/2}$ and, therefore, the value of the z-component of **J**, i.e., $J_z$, is given by

$$J_z = \sqrt{J(J+1)} \cos\theta \tag{18.129}$$

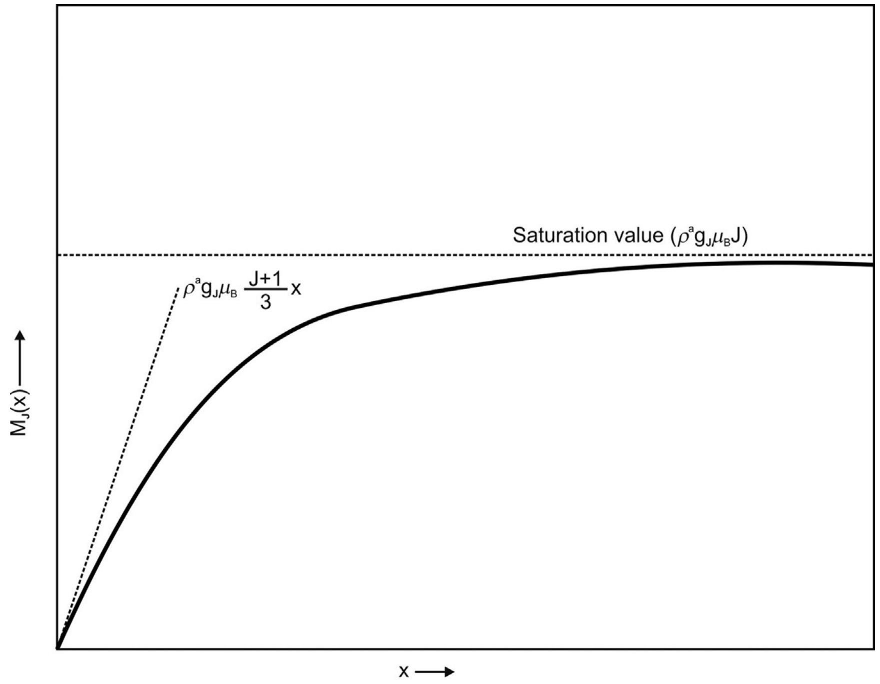

**FIG. 18.6** The magnetization $M_J(x)$ for a paramagnetic solid as a function of parameter $x = \beta_0 g \mu_B J H$. The magnetization curve is similar to that shown in Fig. 18.5 except that the saturation magnetization and slope of the curve at the origin are different.

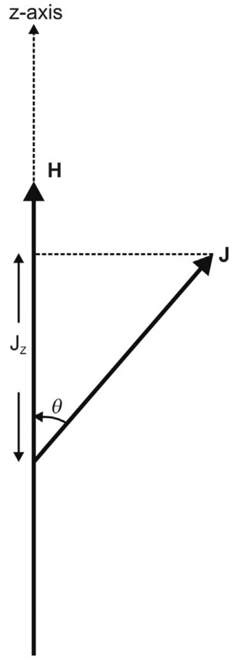

**FIG. 18.7** Orientation of total angular momentum **J** with respect to the applied magnetic field **H** in the z-direction.

From quantum mechanics $J_z$ has $2J+1$ eigenvalues ranging from $-J$ to J through zero. Therefore, the values of $\cos\theta$ are given by

$$\cos\theta = \pm\frac{J}{\sqrt{J(J+1)}} = \pm\frac{1}{\left(1+\frac{1}{J}\right)^{1/2}} \tag{18.130}$$

As the values of J are discrete, so are the values of $\theta$. If J has an infinite number of values, then J becomes very large. Hence from Eq. (18.130) $\cos\theta$ has an infinite number of values lying between $-1$ and $+1$. In other words, the value of $\theta$ becomes continuous, that is, the distribution becomes continuous (classical case). In the limit of $J \rightarrow \infty$, it is easy to prove from Eq. (18.113) that

$$\mathrm{Lim}_{J \rightarrow \infty} B_J(x) = \coth x - \frac{1}{x} = L(x) \tag{18.131}$$

Hence the magnetization from Eq. (18.115) in the limit $J \rightarrow \infty$ is given by

$$M_J = \rho^a \mu_J L(x) \tag{18.132}$$

where

$$\mu_J = g_J \mu_B J \tag{18.133}$$

and

$$x = \frac{\mu_J H}{k_B T} \tag{18.134}$$

Eq. (18.132) gives the familiar Langevin paramagnetism.

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*Problem 18.4*

Consider an ion with a partially filled shell of angular momentum J and Z additional electrons in filled shells. Show that the ratio of paramagnetic susceptibility at high temperatures (Curie law) to the diamagnetic susceptibility is given by

$$\frac{\chi_M}{\chi_d} = \frac{g_J{}^2}{4} \frac{2J(J+1)}{Zk_B T} \frac{\hbar^2}{m_e \langle r^2 \rangle}$$

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## 18.8 HUND'S RULE

The magnetic moment of an atom can be predicted using the knowledge of quantum mechanics in combination with the Pauli exclusion principle and Hund's rule. The Pauli principle says that, in a paramagnetic substance, an electron state can be occupied by two electrons with the same principal (n), orbital ($\ell$), and magnetic ($m_\ell$) quantum numbers, but with opposite spins (s). In an atom the filled electron states do not contribute to the magnetic moment, but rather its finite value results from the partially filled states.

Hund's rule states that in the ground state of an atom

1. The electron spins add to give the maximum possible total spin S consistent with the Pauli exclusion principle. This rule has its origin in the Coulomb repulsive interaction energy between two electrons.
2. The orbital angular momenta of electrons combine to give the maximum possible total angular momentum L that is consistent with point 1. This rule is based on model calculations of spectral terms.
3. For a partially filled shell, the total angular momentum is given as follows:

$$\begin{aligned} J &= |L - S| \text{ for a shell less than half filled} \\ &= L + S \text{ for a shell more than half filled.} \end{aligned} \tag{18.135}$$

This rule is a consequence of the spin-orbit interaction.

### 18.8.1 Applications of Hund's Rule

In the paramagnetic elements each atom or molecule has a finite intrinsic magnetic moment. In the periodic table most of the paramagnetic elements are either d-shell or f-shell elements, which possess partially filled electron shells. For example, elements of the iron group, with atomic number Z ranging from 21 to 28, possess incomplete 3d-shells. The elements of the palladium group, with Z ranging from 39 to 46, possess incomplete 4d- shells, while the platinum group elements, with Z ranging from 71 to 78, possess incomplete 5d-shells. The rare-earth elements, with Z ranging from 57 to 72, possess incomplete 4f-shells. The uranium group elements, with Z ranging from 89 to 103, possess incomplete 5f and 6d-shells. To illustrate the method of calculating the atomic magnetic moment, we consider a few different elements.

#### 18.8.1.1 Rare-Earth Group

The rare-earth element $Ce^{58}$ is paramagnetic in nature and has the following electronic configuration.

$$\mathrm{Ce}^{58} : 4f^2 5s^2 5p^6 6s^2$$

In the above representation the electronic configuration starting from the first partially filled shells is written. Here the 4f-shell is partially filled and is responsible for the magnetic moment. The ion of $Ce^{58}$ is trivalent and has the configuration.

$$\mathrm{Ce}^{+3} : 4f^1 5s^2 5p^6$$

The valence is contributed by one electron in the 4f-shell and two electrons in 6 s-shell. The 4f-shell has 7 subshells with orbital magnetic quantum number $m_\ell$ from −3 to 3, while the spin quantum number $m_s$ has two values 1/2 and −1/2. The distribution of 4f-electrons in the subshells is given below:

$$\begin{array}{lcccccccc} m_\ell & : & 3 & 2 & 1 & 0 & -1 & -2 & -3 \\ m_{s\uparrow} & : & \frac{1}{2} & & & & & & \end{array}$$

The above distribution gives as a maximum value of the orbital quantum number L = 3 and a maximum value of spin S = 1/2 consistent with Hund's rule. As the 4f-shell is less than half filled, the total angular momentum J is given as

$$J = |L - S| = 3 - ½ = 5/2$$

With these values of J, L, and S, the value of $g_J$ can be calculated using Eq. (18.25) yielding

$$g_J = 1 + \frac{\frac{5}{2}\cdot\frac{7}{2} + \frac{1}{2}\cdot\frac{3}{2} - 3\times 4}{2\cdot\frac{5}{2}\cdot\frac{7}{2}} = \frac{6}{7}$$

Hence the effective number of Bohr magnetrons from Eq. (18.126) becomes

$$p_J = \frac{3}{7}\sqrt{35} \cong 2.5$$

The experimental value of the effective number of Bohr magnetrons is $p_{exp} = 2.4$, which is in good agreement with the calculated value.

Another interesting example of the rare-earth elements is $Pr^{59}$ with the following electronic configuration.

$$\mathrm{Pr}^{59} : 4f^2 5s^2 5p^6 6s^2 6p^1$$

Here the 4f-shell is partially filled and is responsible for the magnetic moment in paramagnetic Pr. The ion of $Pr^{59}$ is trivalent and has the configuration.

$$\mathrm{Pr}^{+3} : 4f^2 5s^2 5p^6$$

The distribution of electrons of $Pr^{+3}$ in the 4f-subshells is given below:

$$\begin{array}{lcccccccc} m_\ell & : & 3 & 2 & 1 & 0 & -1 & -2 & -3 \\ m_{s\uparrow} & : & \frac{1}{2} & \frac{1}{2} & & & & & \end{array}$$

According to Hund's rule, L = 3+2 = 5 and S = ½+½ = 1. As the f-shell is less than half filled, therefore,

$$J = |L - S| = 4$$

The value of Lande's splitting factor becomes

$$g_J = 1 - \frac{1}{5} = \frac{4}{5}$$

The effective number of Bohr magnetrons $p_J$ can be found immediately and has the value

$$p_J = \frac{4}{5}\cdot\sqrt{20} = 3.58$$

The experimental value is $p_{exp} = 3.50$, which is in reasonable agreement with theory. The agreement between theory and experiment in the ionic magnetic moment of Ce and Pr is good, but there is a large discrepancy in the case of $Eu^{+3}$ and $Sm^{+3}$ ions.

### *18.8.1.2 Iron Group*

Mn is an important element of the iron group with its atom having the electronic configuration:

$$\mathrm{Mn}: 3d^5 4s^2$$

Here the 3d-shell is incomplete and is expected to contribute to the magnetic moment. The electronic configuration of a divalent Mn ion becomes

$$\mathrm{Mn}^{+2}: 3d^5$$

The distribution of electrons among the d-subshells is given below:

$$\begin{array}{lcccccc} m_\ell & : & 2 & 1 & 0 & -1 & -2 \\ m_{s\uparrow} & : & \frac{1}{2} & \frac{1}{2} & \frac{1}{2} & \frac{1}{2} & \frac{1}{2} \end{array}$$

Hund's rule yields the following values for the quantum numbers L and S:

$$L = 0, \ S = 5/2$$

One should note that the 3d-shell is half filled and the value of J is the same using both formulas: one for a shell less than half filled and the other for a shell more than half filled, that is,

$$J = |L - S| = |L + S| = 5/2.$$

The $g_J$ factor has the value 2 because this is a case with spin only. With the above values one can easily find the value of $p_J$ as

$$p_J = g_J \sqrt{J(J+1)} = g_S \sqrt{S(S+1)} = \sqrt{35} = 5.9$$

The experimental value is also the same, that is, $p_{exp} = 5.9$. Hence both the calculated and experimental values agree with each other.

Another peculiar element of the iron group is $Cr^{24}$ with the following electronic configuration:

$$\mathrm{Cr}^{24}: 3d^5 4s^1$$

If the valence of Cr is taken to be three, then the electronic configuration of $Cr^{+3}$ becomes

$$\mathrm{Cr}^{+3}: 3d^3$$

Here two d-electrons and one s-electron contribute to the valence. The three electrons in the d-subshells of $Cr^{+3}$ contribute to the magnetic moment and their arrangement is given below:

$$\begin{array}{lcccccc} m_\ell & : & 2 & 1 & 0 & -1 & -2 \\ m_{s\uparrow} & : & \frac{1}{2} & \frac{1}{2} & \frac{1}{2} & & \end{array}$$

The values of L, S, and J become 3, 3/2, and 3/2, which yield a value of $g_J = 2/5$. The value of $p_J$ becomes

$$p_J = \frac{1}{5} \sqrt{15} = 0.77$$

But $p_{exp} = 3.8$, which clearly shows a disagreement between theory and experiment. The disagreement may possibly be due to the valence as the Cr atom exhibits variable valence. Let us take the Cr atom as divalent with electronic configuration

$$\mathrm{Cr}^{+2}: 3d^4$$

In this case the distribution of electrons is given below:

$$\begin{array}{lcccccc} m_\ell & : & 2 & 1 & 0 & -1 & -2 \\ m_{s\uparrow} & : & \frac{1}{2} & \frac{1}{2} & \frac{1}{2} & \frac{1}{2} & \end{array}$$

The above distribution yields values of $L = 2,\ S = 2$ and $J = 0$ (d-shell is less than half filled). These values yield zero magnetic moment ($p_J = 0$) for the $Cr^{+2}$ ion, which is again in disagreement with the experimental value. This shows that there is some other factor that may yield the correct value of the magnetic moment in Cr. Let us examine the case of $Cr^{+3}$ assuming that only the spin contributes to the magnetic moment of the ion. Then

$$p_S = g_S\sqrt{S(S+1)} = 2\sqrt{\frac{3}{2}\cdot\frac{5}{2}} = \sqrt{15} = 3.87$$

The value of $p_S$ is in reasonable agreement with $p_{exp} = 3.8$. Therefore, a $Cr^{+3}$ ion behaves as if it had zero orbital angular momentum. Similarly, it can be shown that in the $Fe^{+3}$ ion, the magnetic moment turns out to be 5.9 if the orbital angular momentum is assumed to be zero, which agrees with the experimental value. One should note that, in general, the ions from the iron group behave as if there were no orbital angular momentum associated with them. In other words, one can say that the orbital angular momentum is quenched in iron group elements.

## 18.9 CRYSTAL FIELD SPLITTING

Inside a crystal, every atom or molecule experiences a crystal field, which has a significant effect on the atomic/molecular magnetic moment. The 4f-shell in the rare-earth elements is responsible for paramagnetism and lies deep inside the ion. Therefore, the 4f-shell is well shielded from the crystal field by the 5 s- and 5p-shells. On the other hand, in the iron group elements, the 3d-shell is responsible for paramagnetism. The 3d-shell is the outermost shell in an ion and experiences an intense local crystal field produced by the neighboring ions, which is generally inhomogeneous in nature. The interaction of ions with the inhomogeneous crystal field has two major effects.

1. The coupling of the **L** and **S** vectors (**L** − **S** coupling) is largely broken, so the states can no longer be specified by the total angular momentum **J**.
2. The $2L+1$ sublevels (given by $m_\ell$) belonging to a given L value are degenerate in a free ion, but they get split up by the inhomogeneous crystal field. The splitting diminishes the contribution of the orbital magnetic moment.

### 18.9.1 Quenching of Orbital Angular Momentum

In a central field directed toward the nucleus, the plane of the electron orbit is fixed in space, yielding constant components of orbital angular momentum $L_x$, $L_y$, and $L_z$. According to quantum mechanics, in the central field approximation, $\widehat{H}, L_z,$ and $L^2$ are constants of motion, which means that they commute with one another. On the other hand, in the presence of a noncentral crystal field, the plane of the electron orbit is not fixed, but rather it is moving about its center in all possible directions. As a result, the components of orbital angular momentum are continuously changing and they may average out to zero. In such a situation $\widehat{H}$ and $L_z$ are no longer constants of motion, although $L^2$ may continue to be a constant of motion. In other words, $\widehat{H}$ and $L_z$ do not commute with each other, i.e.,

$$\left[\widehat{H}, L_z\right] \neq 0 \tag{18.136}$$

In this case $L_z$ may average out to zero, leading to quenching of the orbital angular momentum.

The magnetic moment of an atom or molecule depends on the magnetic moment operator $\mu_B(\mathbf{L}+2\mathbf{S})$. If a magnetic field is applied in the z-direction, the orbital magnetic moment is proportional to the expectation value of $L_z$. If $L_z$ is quenched, the orbital magnetic moment is also quenched. In such elements, the magnetic moment arises from the spin angular momentum only.

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*Problem 18.5*

Derive the expression for the paramagnetic susceptibility in a metal with free electrons contributing to magnetization.

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## SUGGESTED READING

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