1. Magnetic Properties of Electron and Nuclear Spins

1.1 Scalar and Vector Products

In this volume, we will often use the scalar and vector products of two vectors. Thus, we will start with a review of vector algebra. The scalar product of vectors **a** and **b** is defined as

$$\mathbf{a} \bullet \mathbf{b} = a_x b_x + a_y b_y + a_z b_z = ab\cos\theta. \quad (1\text{-}1)$$

Here, θ is the angle between **a** and **b** as shown in Fig. 1-1(a). The scalar product is also called the inner product, which means the degree of the overlap between **a** and **b**.

The vector product (**a** × **b**) of vectors **a** and **b** is defined as

$$(\mathbf{a} \times \mathbf{b})_x = a_y b_z - a_z b_y, \quad (1\text{-}2a)$$

$$(\mathbf{a} \times \mathbf{b})_y = a_z b_x - a_x b_z, \quad (1\text{-}2b)$$

$$(\mathbf{a} \times \mathbf{b})_z = a_x b_y - a_y b_x. \quad (1\text{-}2c)$$

Here, θ is the angle between **a** and **b** as shown in Fig. 1-1(b). The vector product is also called the outer product, which means that its value is the space (S) spanned between **a** and **b** and that its direction is the right-handed screw one turning from **a** to **b**.

$$|\,\mathbf{a} \times \mathbf{b}\,| = ab\sin\theta. \quad (1\text{-}3)$$

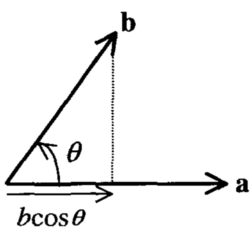

Fig. 1-1(a). The scalar product of **a** and **b**.

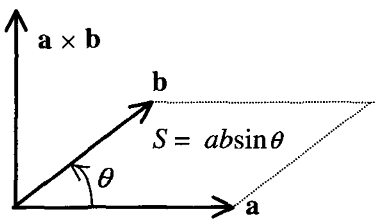

Fig. 1-1(b). The vector product of **a** and **b**.

1.2 Lorentz Force

In the 19th century, H. A. Lorentz found experimentally that a charge with q moving with a velocity of **v** in a magnetic field (**B**) felt the following force (**F**): (1) The magnitude of **F** was found to be proportional to $qvB\sin\theta$. (2) **F** was found to be directed at right angles to the plane of spanned by **v** and **B** as shown in Fig. 1-2. Thus, **F** can be represented by the vector product of **v** and **B**.

$$\mathbf{F} = \alpha q\mathbf{v} \times \mathbf{B}. \quad (1\text{-}4)$$

Here, α is the proportional coefficient.

If α is assumed to be a dimensionless constant having α=1, B can be defined as follow:

$$\mathbf{F} = q\mathbf{v} \times \mathbf{B}. \quad (1\text{-}5)$$

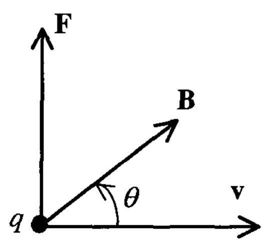

Fig. 1-2. The Lorentz force.

The dimension of **B** defined by Eq. (1-5) is called Tesla (T). Thus, we can obtain the dimension of T ([T]) with those of **F** ([F] = [N] = [kg m s^{-2}]), q ([q] = [C] = [A s]), and **v** ([v] = [m s^{-1}]), using Eq. (1-5).

$$[\mathrm{kg\ m\ s^{-2}}] = [\mathrm{A\ s}]\,[\mathrm{m\ s^{-1}}]\,[\mathrm{T}], \tag{1-6a}$$

$$[\mathrm{T}] = [\mathrm{kg\ s^{-2}\ A^{-1}}]. \tag{1-6b}$$

Conventionally, the unit of gauss (G) is also used for **B**, where 1 G = 10^{-4} T = 10^{-1} mT.

More generally, the force induced on a charge in the presence of both the electric (**E**) and magnetic fields is given by

$$\mathbf{F} = q(\mathbf{E} + \mathbf{v} \times \mathbf{B}). \tag{1-7}$$

This force is called the Lorentz force.

1.3 Potential Energy of a Magnetic Moment

Let us consider a charge with its charge density of ρ which moves at its velocity of **v** as shown in Fig. 1-3. In this case, its current density (**j**) becomes

$$\mathbf{j} = \rho\mathbf{v}. \tag{1-8}$$

Thus, the force (**f**) induced to this unit volume by a magnetic field of **B** is given from Eq. (1-5) by

$$\mathbf{f} = \rho\mathbf{v} \times \mathbf{B} = \mathbf{j} \times \mathbf{B}. \tag{1-9}$$

When the cross section of this wire is S, the force (**dF**) induced to the wire with its length of **dL** becomes as follows:

$$\mathbf{dF} = \mathbf{f}SdL = \mathbf{j} \times \mathbf{B}\,SdL. \tag{1-10}$$

Because the total current of this wire (**I**) is $S\mathbf{j}$, **dF** can be represented as

$$\mathbf{dF} = \mathbf{I} \times \mathbf{B}\,dL = I\mathbf{dL} \times \mathbf{B}. \tag{1-11}$$

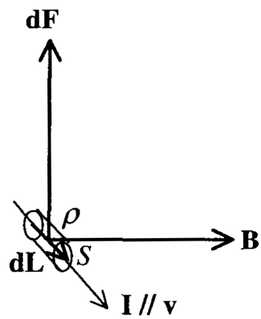

Fig. 1-3. The force induced by **B** to **I** in a wire.

Here, it is obvious that $\mathbf{I}dL = I\mathbf{dL}$, because **I** // **dL** as shown in Fig. 1-3.

Then let us consider the forces induced by **B** to a rectangular coil ($a \times b$) with a current of I as shown in Fig. 1-4.

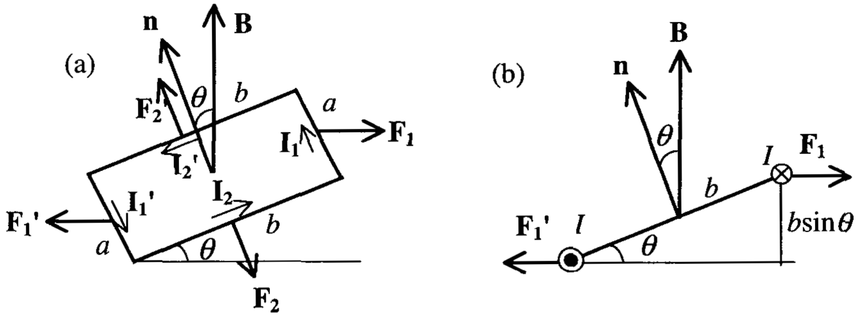

Fig. 1-4. Forces induced by **B** to a rectangular coil ($a \times b$) with a current of I.

F_1 and F_2 are given from Eq. (1-11) by

$$F_1 = |\mathbf{F}_1| = |\mathbf{F}_1'| = BIa, \quad (1\text{-}12)$$

$$F_2 = |\mathbf{F}_2| = |\mathbf{F}_2'| = BIb\cos\theta. \quad (1\text{-}13)$$

The torque (**N**) induced by $\mathbf{F}_1$ and $\mathbf{F}_1'$ to this coil can be obtained as shown in Fig 1-4(b).

$$N = F_1 b\sin\theta = BIab\sin\theta. \quad (1\text{-}14)$$

Thus, **N** can be represented in terms of a vector product as follows:

$$\mathbf{N} = Iab\mathbf{n} \times \mathbf{B}. \quad (1\text{-}15)$$

Here, **n** is the unit vector perpendicular to the coil plane as shown in Fig. 1-4.

Let us define an important vector in spin chemistry, which is the magnetic moment (**m**) induced by a moving charge. For this coil, **m** is given by

$$\mathbf{m} = Iab\mathbf{n}. \quad (1\text{-}16)$$

Using **m**, we can write **N** as

$$\mathbf{N} = \mathbf{m} \times \mathbf{B}. \quad (1\text{-}17)$$

From Eq. (1-17), we can see that the torque tends to turn **m** toward **B**. This means that the loop ($\theta = 0$) shown in Fig. 1-5(a) is more stable than that ($\theta > 0$) shown in Fig. 1-5(b). In other words, **N** tends to decrease θ and the magnitude of **N** at θ is represented by

$$N(\theta) = |\mathbf{N}(\theta)| = mB\sin\theta. \quad (1\text{-}18)$$

In order to keep the coil at θ, the external force ($\mathbf{N}_{ext}(\theta)$) must be put on the loop.

$$\mathbf{N}_{ext}(\theta) = -\mathbf{N}(\theta) = -\mathbf{m} \times \mathbf{B}. \quad (1\text{-}19)$$

When this coil is rotated from θ to $\theta + \delta\theta$, the work (δU) done in this rotation is

$$\delta U(\theta) = |\mathbf{N}_{ext}(\theta)|\,\delta\theta = mB\sin\theta\delta\theta = -mB\delta(\cos\theta). \quad (1\text{-}20)$$

Thus, the total work necessary for the rotation of this coil from $\theta = 0$ to $\theta = \alpha$ is obtained as

$$U(\alpha) = \int_0^\alpha \delta U(\theta) = -\int_0^\alpha mB\delta(\cos\theta) = -mB[\cos\theta]_0^\alpha = -mB\cos\alpha + \text{const.} \quad (1\text{-}21)$$

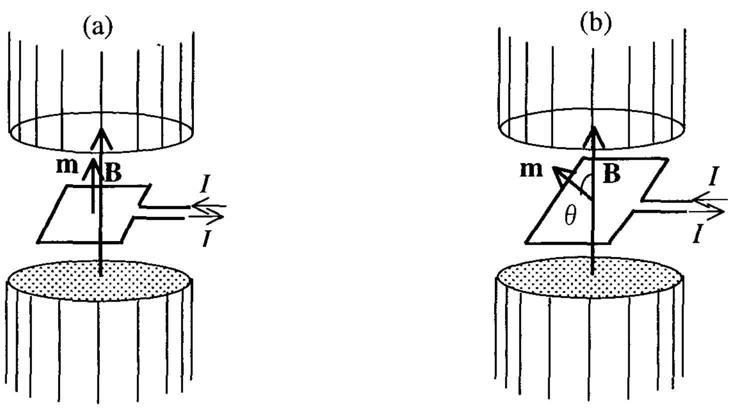

Fig. 1-5. A coil with the magnetic moment of **m** is placed in a magnetic field of **B**: (a) $\theta = 0$ and (b) $\theta > 0$.

This is called the potential energy of this coil, which is defined without the constant term of Eq. (1-21) as

$$U(\alpha) = -mB\cos(\alpha) = -\mathbf{m} \bullet \mathbf{B}. \quad (1\text{-}22)$$

From Eq. (1-22), it can clearly be seen that the potential energy at α=0 is smaller than that at $\alpha \neq 0$ $(0 < |\alpha| \leq \pi/2)$.

$$U(\alpha = 0) = -mB < U(\alpha \neq 0) = -mB\cos\alpha. \quad (1\text{-}23)$$

In other words, the position at α=0 is more stable than that at $\alpha \neq 0$ $(0 < |\alpha| \leq \pi/2)$.

1.4 Orbital Magnetic Moment

An electron moving in an orbit as shown in Fig. 1-6 has its magnetic moment ($\boldsymbol{\mu}_0$) from Eq. (1-16).

$$\boldsymbol{\mu}_0 = IS\mathbf{n}. \quad (1\text{-}24)$$

S in Eq. (1-16) is ab, but S is πr^2 in Eq. (1-24).

I is given as

$$I = q/T = -ev/2\pi r. \quad (1\text{-}25)$$

Here, q is the charge of an electron ($-e$) and T is the time for its single revolution ($T = 2\pi r/v$). Thus, $\boldsymbol{\mu}_0$ can be given as follows:

$$\boldsymbol{\mu}_0 = -(ev/2\pi r)(\pi r^2)\mathbf{n} = -(evr/2)\mathbf{n}. \quad (1\text{-}26)$$

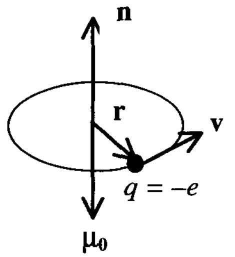

Fig. 1-6. The orbital motion of an electron.

Problem 1-1. Show that $[\mu_0] = [\mathrm{A\ m^2}]$.

From quantum mechanics, the angular momentum ($\boldsymbol{l}$) of an electron moving as shown in Fig. 1-6 is expressed by

$$\boldsymbol{l} = \mathbf{r} \times \mathbf{p}. \quad (1\text{-}27)$$

Because $\mathbf{p}$ *is* $m_e\mathbf{v}$ where m_e is the electron mass, $\boldsymbol{l}$ can be rewritten by

$$\boldsymbol{l} = r\, m_e v\mathbf{n}. \quad (1\text{-}28)$$

Problem 1-2. Show that $[l] = [\mathrm{J\ s}]$. Note that this is the same dimension as $\hbar\ (=h/2\pi)$.

Thus, $\boldsymbol{\mu}_0$ can be represented by $\boldsymbol{l}$ as

$$\boldsymbol{\mu}_0 = -(e/2m_e)\,\boldsymbol{l} = -(e\hbar/2m_e)(\boldsymbol{l}/\hbar) = -\mu_B\mathbf{L}. \quad (1\text{-}29)$$

Here, μ_B is called Bohr magneton and $\mathbf{L}$ is the dimensionless operator corresponding to the orbital angular momentum of an electron. They are defined as

$$\mu_B = (e\hbar/2m_e), \quad (1\text{-}30)$$

$$\mathbf{L} = (\boldsymbol{l}/\hbar). \quad (1\text{-}31)$$

Problem 1-3. Confirm that $\mu_B = 9.2740\times10^{-24}\ \mathrm{J\ T^{-1}}$.

It is very convenient to use $\mathbf{L}$, which is a dimensionless operator instead of $\boldsymbol{l}$ which has the unit of $\hbar$. According to quantum mechanics, these operators obey the following relations:

$$l^2|l, m_l\rangle = l(l+1)\hbar^2|l, m_l\rangle, \quad (1\text{-}32a)$$

$$l_z|l, m_l\rangle = m_l\,\hbar\,|l, m_l\rangle, \quad (1\text{-}32b)$$

$$l^+|l, m_l\rangle = \sqrt{l(l+1) - m_l(m_l+1)}\;\hbar\,|l, m_l+1\rangle, \quad (1\text{-}32c)$$

$$l^-|l, m_l\rangle = \sqrt{l(l+1) - m_l(m_l-1)}\;\hbar\,|l, m_l-1\rangle, \quad (1\text{-}32d)$$

and

$$L^2|L, m_L\rangle = L(L+1)\,|L, m_L\rangle, \quad (1\text{-}33a)$$

$$L_z|L, m_L\rangle = m_L\,|L, m_L\rangle, \tag{1-33b}$$

$$L^+|L, m_L\rangle = \sqrt{L(L+1) - m_L(m_L+1)}\;|L, m_L+1\rangle, \tag{1-33c}$$

$$L^-|L, m_L\rangle = \sqrt{L(L+1) - m_L(m_L-1)}\;|L, m_L-1\rangle. \tag{1-33d}$$

Here,

$$l^{\pm} = l_x \pm i l_y, \tag{1-34a}$$

$$l_x = (l^+ + l^-)/2, \tag{1-34b}$$

$$l_y = (l^+ - l^-)/2i. \tag{1-34c}$$

The same relations as Eq. (1-34) are also applied to L. In the right sides of Eqs. (1-32) and (1-33), l and L are called the orbital quantum number and they are integers of 0, 1, 2..... The m_l and m_L values are called the magnetic quantum numbers and they take on the values $-l$, $-l+1$,.....$l-1$, l and $-L$, $-L+1$,.....$L-1$, L, respectively.

1.5 Spin Magnetic Moments

According to quantum mechanics, the electron and many other elementary particles such as proton and neutron have their own angular momentum, which is independent of the angular momentum. This independent angular momentum is called "spin" because spin is similar to (but not the same as) the rotation of the earth. For the electron, the magnetic moment (μ_S) due to its spin (**s** and **S**) is given by

$$\mu_S = -g\mu_B(\mathbf{s}/\hbar) = -g\mu_B\mathbf{S}. \tag{1-35}$$

Here, g is called the g-factor, which is 1 for the orbital magnetic moment as shown in Eq. (1-29) but about 2 for the spin magnetic moment of a free electron as shown below.

The operators for the electron spin angular momentum obey the following relations, which are similar to those shown in Eqs. (1-32) and (1-33):

$$S^2|S, m_S\rangle = S(S+1)\,|S, m_S\rangle, \tag{1-36a}$$

$$S_z|S, m_S\rangle = m_S\,|S, m_S\rangle, \tag{1-36b}$$

$$S^+|S, m_S\rangle = \sqrt{S(S+1) - m_S(m_S+1)}\;|S, m_S+1\rangle, \tag{1-36c}$$

$$S^-|S, m_S\rangle = \sqrt{S(S+1) - m_S(m_S-1)}\;|S, m_S-1\rangle. \tag{1-36d}$$

$S^{\pm}$, S_x, and S_y are also defined by the relations similar to those given in Eq. (1-34). In the right side of Eq. (1-36), S is called the spin quantum number and m_S the magnetic quantum number of electron spin. For a single electron, $S = 1/2$ and $m_S = \pm 1/2$.

Combining quantum mechanics and the principle of relativity, Dirac introduced theoretically the existence of electron spin, which had the g-factor of 2 for a free electron. Experimentally, its g-factor (g_e) has been measured very precisely as

$$g_e = 2.002319304. \tag{1-37}$$

This value can be explained theoretically in terms of quantum electrodynamics. If a molecule has an odd electron, this is called a free radical. The g-factor of a free radical is generally different from g_e. This difference is due to the spin-orbit interactions of component atoms.

As the electron has the magnetic moment due to its spin, many nuclei such as ^1H and ^{13}C have the moment (μ_N) due to nuclear spins (**i** and **I**).

$\mu_N = g_N \mu_N (\mathbf{i}/\hbar) = g_N \mu_N \mathbf{I}.$ (1-38)

Here, g_N is the g-factor of a nuclear spin and the nuclear magneton (μ_N) is defined with the mass of proton (m_P) as follows:

$\mu_N = (e\hbar/2\, m_P).$ (1-39)

Problem 1-4. Confirm that $\mu_N = 5.05079\times10^{-27}$ J T^{-1}.

It is noteworthy that there is no minus factor in Eq. (1-38) for nuclear spins in contrast to Eq. (1-35) for electron spin because nuclei have positive charge. It is also noteworthy that μ_N is as small as about 10^{-3} of μ_B because m_P is much larger than m_e.

The operators for the nuclear spin angular momentum obey the following relations, which are similar to those shown in Eqs. (1-32), (1-33), and (1-36):

$I^2|I, m_I\rangle = I(I+1)\,|I, m_I\rangle,$ (1-40a)

$I_z|I, m_I\rangle = m_I\,|I, m_I\rangle,$ (1-40b)

$I^+|I, m_I\rangle = \sqrt{I(I+1) - m_I(m_I+1)}\,|I, m_I{+}1\rangle,$ (1-40c)

$I^-|I, m_I\rangle = \sqrt{I(I+1) - m_I(m_I-1)}\,|I, m_I{-}1\rangle.$ (1-40d)

Table 1-1 shows the g_N values of typical nuclei together with their I values and natural abundance. It is worth while to remark from this table that many nuclei such as ^{12}C and ^{16}C have no spin ($I = 0$). The isotopes with and without spin, therefore, are called "magnetic and non-magnetic isotopes", respectively. Even now, it is very difficult to explain theoretically the observed I and g_N values. This is one of the frontiers of modern physics.

Solutions to the Problems

1-1. From Eq. (1-24), $[\mu_o] = [I]\,[S] = [\mathrm{A\ m^2}]$.

1-2. $[l] = [r\, m_e v] = [\mathrm{m}]\,[\mathrm{kg}]\,[\mathrm{m/s}] = [\mathrm{kg\ m^2\ s^{-2}}]\,[\mathrm{s}] = [\mathrm{J\ s}]$.

1-3. $\mu_B = \dfrac{e\hbar}{2m_e} = \dfrac{1.60218\times10^{-19}C \bullet 1.05457\times10^{-34}Js}{2\bullet 9.10939\times10^{-33}kg} = 9.2740\times10\text{-}24$ JCs/kg.

Using [C] = [As], [JCs/kg] = $[\mathrm{JAs^2/kg}]$.

Using [A] = $[\mathrm{kg/s^2T}]$ from Eq. (1-6b), $[\mathrm{JAs^2/kg}] = [\mathrm{J}]\,[\mathrm{kg/s^2T}]\,[\mathrm{s^2/kg}] = [\mathrm{J\ T^{-1}}]$.

Thus, $\mu_B = 9.274\times10^{-24}$ J T^{-1}.

1-4. If m_e of the above μ_B calculation is replaced by m_P (= 1.67262×10^{-27}kg), the μ_N value can be obtained to be 5.05079×10^{-27} J T^{-1}.

Table 1-1. Nuclear spin properties.

Isotope	Natural Abundance (%)	Spin (I)	g-factor (g_N)
^{1}H	99.985	1/2	5.58570
^{2}H	0.015	1	0.85744
^{12}C	98.90	0	–
^{13}C	1.10	1/2	1.40482
^{14}N	99.634	1	0.40376
^{15}N	0.366	1/2	–0.56638
^{16}O	99.762	0	–
^{17}O	0.038	5/2	–0.75752
^{18}O	0.200	0	–
^{19}F	100	1/2	5.25774
^{28}Si	92.23	0	–
^{29}Si	4.67	1/2	–1.1106
^{30}Si	3.10	0	–
^{32}S	95.02	0	–
^{33}S	0.75	3/2	0.42921
^{34}S, ^{36}S		0	–
^{35}Cl	75.77	3/2	0.54791
^{37}Cl	24.23	3/2	0.45608
^{55}Mn	100	5/2	1.38748
^{73}Ge	7.73	9/2	–0.19544
^{70}Ge, ^{72}Ge, ^{74}Ge, ^{76}Ge,		0	–
^{234}U	0.0055	0	–
^{235}U	0.7200	7/2	–0.109
^{238}U	99.2745	0	–