CHB 604 **Physical Chemistry-IV** **Credits : 3**

1. **Quantum Mechanics of Simple Systems:** Schrӧdinger's wave equation, eigen functions, eigen values and quantum mechanical operators, expectation value of a physical quantity, orthogonality of wave functions, the particle in a one dimensional box problem and its solutions, particle in a three dimensional box, degeneracy, rigid rotor and harmonic oscillator.
2. **Molecular Spectroscopy:** Region of electromagnetic spectrum, emission and absorption spectra, signal to noise ratio and resolving power, width and intensity of spectral transitions, pure rotational spectra, diatomic rigid rotor molecules, effect of isotope substitution, vibrational and vibration- rotational spectra of diatomic molecules, harmonic oscillator-rigid rotor approximation, anharmonicity effect, normal modes of vibration, infrared spectra of linear and bent AB_2 molecules, electronic spectra of diatomic molecules, vibrational structure, Franck-Condon principle.
3. **Nuclear Magnetic Resonance Spectroscopy:** Introduction, chemical shifts, spin-spin splitting, relaxation times.
4. **Molecular Statistics:** The Boltzmann distribution, Maxwell distribution law for distribution of molecular speeds, Maxwell-Boltzmann distribution law for the distribution of molecular energies, partition functions, thermodynamic quantities from partition functions, Sackur- Tetrode equation for molar entropy of monatomic gases, rotational and vibrational partition functions, calculation of Gibbs free energy changes and equilibrium constant in terms of partition functions

References:

1. Fundamentals of Molecular Spectroscopy, C. N. Banwell and E.M. Mc Cash, Tata McGraw Hill, New Delhi.
2. Modern Spectroscopy, J. M. Hollas, John Wiley & Sons, Ltd., Chichester.
3. Nuclear Magnetic Resonance Spectroscopy, R. K. Harris, (1986), Addison Wesley, Longman Ltd, London

Introduction of Spectroscopy: **(Already done in the class)**

Rotational/Microwave Spectroscopy: **(Already done in the class)**

Vibrational/Infra-Red Spectroscopy: **(Already done in the class)**

Electronic Spectroscopy:

Introduction: Electronic spectra is observed when there occurs redistribution of electrons in a molecule. When the electrons transit from filled molecular orbital (HOMO) to the vacant or partially filled molecular orbital (LUMO), photons are absorbed by the molecules for transition. The frequency of radiation for such transition falls in the visible and ultraviolet region since energy required for electronic transition is about $3 \times 10^{14} - 3 \times 10^{16}$ Hz. That's why electronic spectra is called UV-Vis spectroscopy.

Electronic spectra are studied in both absorption and emission spectroscopy. Electronic transition are always associated with vibrational and rotational spectra and hereby it becomes most complicated.

Advantage: Instead of complex nature of the electronic spectra, it has certain advantages also.

1. This spectra are studied in the visible and ultraviolet region of radiation and so experimental handling is easy. This means that recording is easy but interpretation is difficult.
2. Homonuclear diatomic molecules give electronic spectra and molecular information about them can be obtained from the study of electronic spectra. These molecules do not show microwave and infrared spectra.
3. Information about the excited state of the molecule and bond dissociation energy can be easily obtained from the study of electronic spectra.

ELECTRONIC SPECTRA OF DIATOMIC MOLECULES:

The Born-Oppenheimer Approximation: We know that a typical diatomic molecule has distinct rotational energy separation ($1 - 10$ cm^{-1}), vibrational energy separation ($\sim 10^3$ cm^{-1}) and electronic energy separation. So as a first approximation we may consider that a diatomic molecule can executes rotations, vibrations and electronic motions quite independently. This approximation is known as Born-Oppenheimer approximation. According to this we the total energy of a diatomic molecule can be written as

$$E_{total} = E_{electronic} + E_{vibration} + E_{rotation} \qquad (Joules)$$

A change in the total energy of the molecule may then be written as

$$\Delta E_{total} = \Delta E_{elec.} + \Delta E_{vib.} + \Delta E_{rot.} \qquad (joules)$$

or

$$\Delta \varepsilon_{total} = \Delta \varepsilon_{elec.} + \Delta \varepsilon_{vib.} + \Delta \varepsilon_{rot.} \qquad (cm^{-1})$$

The approximate orders of magnitude of these changes are

$$\Delta \varepsilon_{elec.} \approx \Delta \varepsilon_{vib.} \times 10^3 \approx \Delta \varepsilon_{rot.} \times 10^6$$

So when a diatomic molecule transits from lower electronic state to the higher electronic state, there occurs innumerable change of vibrational and rotational levels. Changes in vibrational level are shown by ***coarse structure*** and each coarse structure is also associated with ***fine structure*** due to rotational transitions.

Vibrational Coarse Structure: Progressions

For vibrational transition in the coarse structure of electronic spectra, Born-Oppenheimer approximation is

$$E_{total} = E_{elec.} + E_{vib.} \qquad (Joules)$$

or

$$\varepsilon_{total} = \varepsilon_{elec.} + \varepsilon_{vib.} \qquad (cm^{-1})$$

$$\varepsilon_{total} = \varepsilon_{elec.} + \left(v + \frac{1}{2}\right)\overline{\omega}_e - x_e\left(v + \frac{1}{2}\right)^2 \overline{\omega}_e \qquad (cm^{-1})$$

The energy levels of this according to this equation are shown in **Figure 1**. The relative separations between levels of different $\varepsilon_{elec.}$ are approximate one.

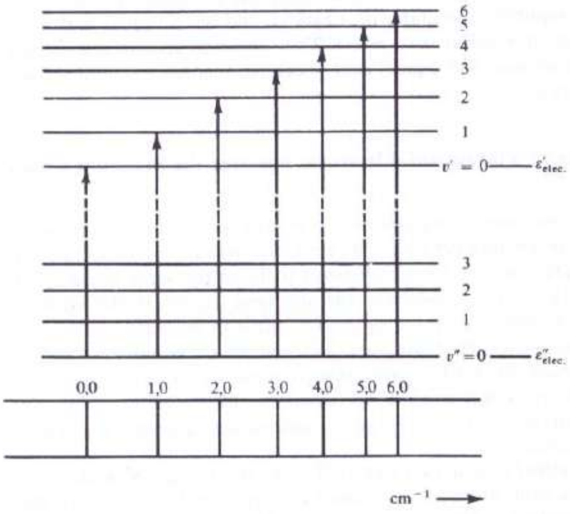


Figure 1: *The vibrational coarse structure of the band formed during electronic absorption from the ground state (v" = 0) to a higher state.*

There is ***essentially no selection rule*** for v when a molecule undergoes an electronic transition i.e. every transition $v'' \rightarrow v'$ has some probability, and so many spectral lines be expected. However, as we know virtually all the molecules exist in the lowest vibrational state, that is $v'' = 0$, and so only transitions to be observed with appreciable intensity are those indicated in **Figure 1**. These are conventionally labelled according to their (v'', v') numbers (upper state first) that is (0, 0), (1, 0), (2, 0), etc. Such a set of transitions is called ***band*** since under low resolution, each lines of set appears somewhat broad and diffuse, and called a ***v' progression*** since the value v' of increases by unity for each line in the set.

Analytical expression for these spectrum

$$\Delta\varepsilon_{total} = \Delta\varepsilon_{elec.} + \Delta\varepsilon_{vib.}$$

So

$$\nu_{spec} = (\varepsilon' - \varepsilon'') + \left\{\left(v' + \frac{1}{2}\right)\bar{\omega}'_e - x'_e\left(v' + \frac{1}{2}\right)^2 \bar{\omega}'_e\right\} - \left\{\left(v'' + \frac{1}{2}\right)\bar{\omega}''_e - x''_e\left(v'' + \frac{1}{2}\right)^2 \bar{\omega}''_e\right\}$$

Observations of a band spectrum leads not only to values of the vibrational frequency ($\bar{\omega}''_e$) and anharmonicity constant (x''_e) in the ground state but also the parameters in the excited state ($\bar{\omega}'_e$ *and* x'_e).

Excited state information is valuable as excited states is extremely unstable and the molecule exist in them for very short times.

Normally, molecules have many excited electronic state energy levels, so that the whole absorption spectrum of a diatomic molecule is more complicated than **Figure 1**.

Emission spectra are extremely complicated as excited molecule may be in one of a large number of available states (ε' v') and has a similar multitude of (ε'' v'') states to which it may revert.

Intensity of Vibrational-Electronic Spectra: Franck-Condon Principle

Although for a given electronic transition, there is no quantum mechanical restriction on the change in the vibration quantum numbers however, all the vibrational lines in a progression are not equally intense. Only those transitions are intense which are in accordance to *Frank-Condon Principle* which state that ***"an electronic transition takes place so rapidly that a vibrating molecule***

does not change its internuclear distance appreciably during the transition”. Thus electronic transitions are vertical transitions.

Now if a diatomic molecule undergoes a transition into an upper electronic state, there will be (probably but not necessarily) differences in various parameters such as vibrational frequency, internuclear distance, or dissociation energy between the two states. This simply means that we can consider each excited molecule as a new but rather similar molecule with a different but also rather similar Morse curve.

Figure 2 shows four possibilities. In **Figure 2(a)**, upper electronic state have the same equilibrium internuclear distance as lower. So according to Franck-Condon principle the most probable transition is that indicated by the vertical line in **Figure 2(a)** and the strongest spectral line of $v'' = 0$ progression will be the (0, 0). As according to the quantum theory at $v = 0$ the atom is most likely to be found at the centre of its motion i.e. at the equilibrium internuclear distance req. For $v = 1, 2, 3, \ldots$ the most probable position steadily approaches to extremities and for high v the quantum and classical pictures merge i.e. oscillating atom spend more

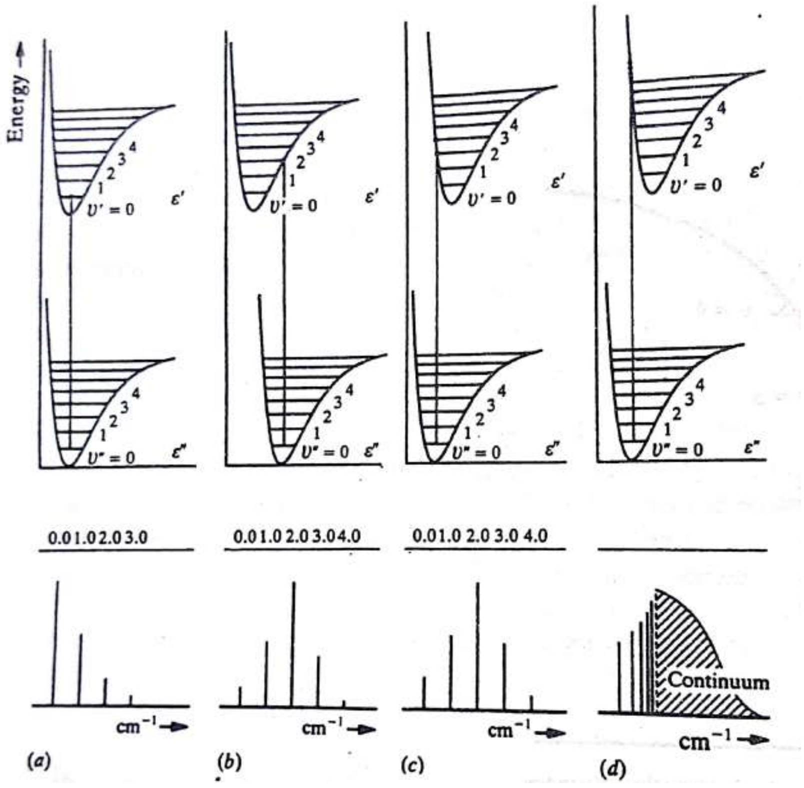


Figure 2: *The operation of the Franck-Condon principle for (a) internuclear distances equal in the upper and lower states, (b) upper state internuclear distance is little less than that in the lower state, (c) upper state distance a little greater than in the lower, and (d) upper state distance considerably greater.*

of its time on the curve at the turning point of its motion. However, the quantum theory only says that the probability of finding the oscillating atom is more at the equilibrium distance in the $v = 0$; it allows some although small chance of the atom being near the extremities of its vibration motion. Hence there is some chance of the transition starting from the ends of the $v'' = 0$ state and finishing in the $v' = 1, 2,$ etc., states. The intensity of the (1, 0), (2, 0), etc lines diminishes rapidly as shown in the foot of **Figure 2(a)**.

In **Figure 2(b)**, the excited state has a slightly smaller internuclear separation than the ground state. A vertical transition from $v'' = 0$ level will be most likely to occur into the upper vibrational state $v'' = 2$. Transitions to lower and higher v' state being less likely.

In **Figure 2 (c)**, the excited electronic state has slightly larger internuclear separation than the ground state, but the resulting transitions and spectrum are similar.

In **Figure 2(d)**, the upper state separation is considerably greater than that in the lower state. So, the vibrational level to which a transition takes place has a high v' value. Furthermore, transitions now occur to a state where the excited molecule has energy in excess of its own dissociation energy. From such states the molecule will dissociate without any vibrations and the atoms which are formed can take any value of kinetic energy, the transitions are not quantized and a continuum results.

Dissociation Energy and Dissociation Products

Figure 3(a) and (b) shows two of the ways in which electronic excitation can lead to dissociation. **Figure 3(a)** represents the case where the equilibrium nuclear separation in the upper state is considerably greater that in the lower. The dashed line limits of the Morse curves represent the dissociation of the normal and excited molecule into atoms, the dissociation energies being D_0'' and D_0' from the $v = 0$ state in each case. The total energy of the dissociation products (i.e. atoms) from the upper state is greater by an amount called E_{ex} than that of the products of dissociation in the lower state. So the continuum limits is

$$\bar{\upsilon}_{continuum\ limit} = D_0^{''} + E_{ex} \qquad cm^{-1}$$

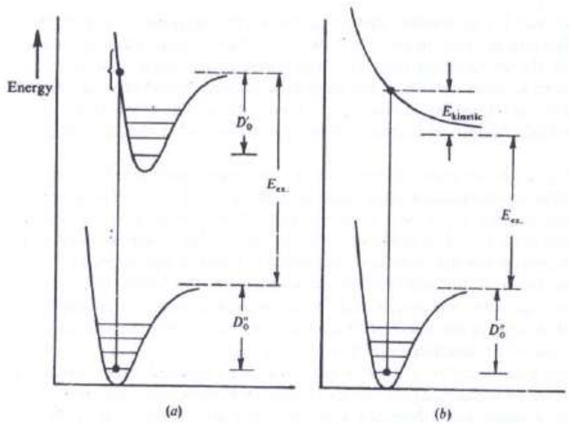


Figure 3: *illustrating dissociation by excitation into (a) a stable upper state and (b) a continuous upper state.*

So we can measure *D₀"*, if we know E_{ex}, excitation energy of the products. The excitation energy of atoms to various electronic states is readily measurable by atomic spectroscopy.

In **Figure 3(b)**, the upper electronic state is unstable: there is no minimum in the energy curve and as soon as a molecule is raised to this state by excitation, the molecule dissociates into products with total excitation energy E_{ex}. The products will fly apart with kinetic energy $E_{kinetic}$. Since $E_{kinetic}$ is not quantized the whole spectrum for this system will exhibit a continuum.

PROBLEM 1: Find out the v_{max} for the dissociation limit of a molecule.

SOLUTION: We know the vibrational energy

$$\varepsilon_v = \left(v + \frac{1}{2}\right)\bar{\omega}_e - x_e\left(v + \frac{1}{2}\right)^2 \bar{\omega}_e \qquad cm^{-1}$$

So the separation between neighbouring levels Δε is

$$\Delta\varepsilon = \varepsilon_{v+1} - \varepsilon_v$$
$$= \bar{\omega}_e\{1 - 2x_e(v+1)\}$$

This separation decreases continuously with increasing v and dissociation limit is reached when $\Delta\varepsilon \to 0$. Thus the maximum value of v is given by v_{max}, where:

$$\bar{\omega}_e\{1 - 2x_e(v+1)\} = 0$$

or

$$v_{max} = \frac{1}{2x_e} - 1$$

We know anharmonicity constant x_e is of the order of 10-2; hence v_{max} is about 50.

Example: For HCL, $\bar{\omega}_e$= 2990 cm-1, x_e = 0.0174, So v_{max} = 27.

Nuclear Magnetic Resonance (NMR) Spectroscopy

Introduction:

In most of the spectroscopy, we see the molecules have a set of energy levels and that the lines we see in spectra are due to transitions between these energy levels. Such a transition can be caused by a photon of light whose frequency, ν, is related to the energy gap, ΔE, between the two levels according to:

$$\Delta E = E_2 - E_1 = h\nu$$

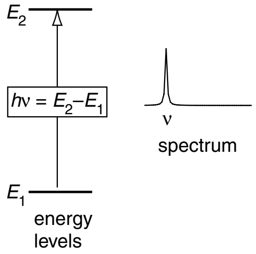


Figure 1: *A line in the spectrum is associated with a transition between two energy levels.*

But in NMR spectroscopy we don’t use this approach of energy levels and the transitions between them. Rather we will use the spin of nuclei.

Quantization of Angular Momentum:

One of the fundamental postulates of quantum physics is that the total angular momentum of any isolated particle cannot have any arbitrary magnitude but may only take certain discrete values or angular momentum is said to be quantized and its magnitude P, can be specified in terms of a quantum number R by

$$P = \hbar\sqrt{R(R+1)}$$

The constant $\hbar$ is $h/2\pi$, where h is known as Planck’s constant; R is either integral or half-integral.

Quantization of angular momentum implies quantization of energy. Each energy state of the particle may be specified by appropriate numbers and has a stationary state wave function.

Angular momentum is actually a vector property, so that for a full description direction has to be specified as well as magnitude. In quantum-mechanical terms this is done by using another quantum number, m_R, such that the component of angular momentum P_z along the direction considered is given by

$$P_z = \hbar m_R$$

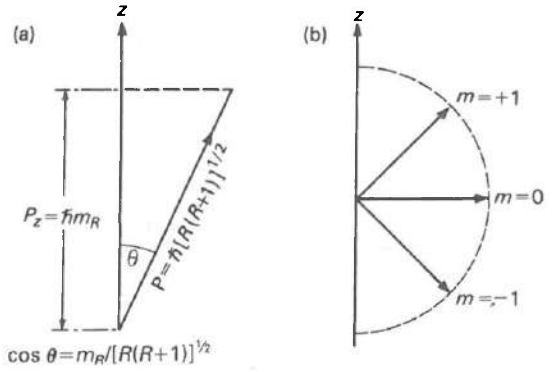


Figure 1: *Angular momentum vectors: (a) the general case, showing the use of quantum numbers R and* m_R*, (b) the possible orientations for an angular momentum vector of quantum number R = 1. Note that R and* m_R *do not specify direction in the xy plane at all.*

Figure 1 illustrates the general situation for a quantized angular momentum vector. Quantum mechanics shows that the allowed values of m_R are

$$m_R = R, R-1, R-2, \ldots\ldots\ldots, -R$$

Electron and Nuclear Spin:

The postulate that electrons possessed angular momentum which could be attributed to a spinning motion was first made in 1925, in order to explain both the fine structure of bands observed in atomic spectra, and the effect of a magnetic field on such spectra (the anomalous Zeeman effect).

The spin quantum number of a single electron is $S = \frac{1}{2}$ and the associated angular momentum is $\sqrt{s(s+1)}(h/2\pi) = \sqrt{3/2}$ units. The possible values of the directional quantum number, m_s, are therefore $\frac{1}{2}$ and $-\frac{1}{2}$.

The existence of nuclear spin was first suggested by Pauli in 1924, a year before the idea of electron spin was mooted, in order to explain further splitting's in atomic spectra (hyperfine structure). These splitting's demonstrate that nuclei of different elements (and different isotopes of the same element) differ in spin angular momentum. This fact may be traced to details of the internal construction of nuclei. The proton has a spin quantum number, I, of $\frac{1}{2}$ as does the neutron.

So, if a nucleus is composed p protons and n neutrons, its total mass $p+n$, its total charge $+p$, and its total spin will be a vector combination of $p+n$ spins each of magnitude of $\frac{1}{2}$.

So, in case hydrogen nucleus spin $\frac{1}{2}$ since it has only one proton. Deuterium contains one proton and one neutron. So, spin will be either 1 or 0 depending on whether the proton and neutron spins are parallel (↑↑) or antiparallel (↑↓) but it is observed to be 1.

Unfortunately, the laws governing the vector addition of nuclear spins are not yet known, so the spin of a particular nucleus cannot be predicted in general. However, from the observation of nuclear spin and corresponding number of protons and neutron, certain systematic features may be noted as follows:

1. Nuclei with both *p* and *n* even (hence charge (+ *p*) and mass (*p* + *n*) even) have zero spin. For example, ^{4}He, ^{12}C, ^{16}O etc.
2. Nuclei with both *p* and *n* odd (hence charge odd (+ *p*) but mass (*p* + *n*) even) have integral spin. For example, ^{2}H, ^{14}N (I = 1); ^{10}B (I = 3), etc
3. Nuclei with odd mass have half integral spins. For example, ^{1}H, ^{13}C, ^{15}N, ^{19}F, ^{29}Si, ^{31}P (I = $\frac{1}{2}$), 11B (I = $\frac{3}{2}$), ^{17}O (I = $\frac{5}{2}$), etc.

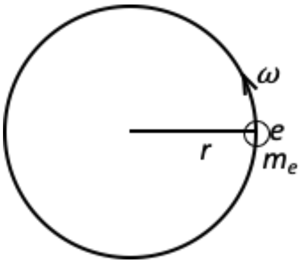
The magnitude of the nuclear spin angular momentum is

$$P = \hbar\sqrt{I(I+1)}$$

The direction of a spin angular momentum vector is conventionally defined such that the spinning body, viewed along the vector, twists in the same sense as a right-handed screw.

Nuclear Magnetic Moments:

Any motion of a charged body has an associated magnetic field. Consider the electric current, which is due to the motion of electrons along a conductor, produces a magnetic dipole moment. This phenomenon also occurs on an atomic scale, for whenever electrons or nuclei possess angular momentum there is a magnetic moment. Since angular momentum is quantized on this scale, so are magnetic moments. The magnitude of such moments is most easily discussed from the classical standpoint by considering orbital electronic motion.



Suppose an electron is travelling in an orbital at an angular velocity *ω*. Such motion is equivalent to an electrical current in the opposite direction of magnitude

$i = e\omega/2\pi$, where e is the magnitude of the charge on the electron. The orbital angular momentum, $P = m_e r^2 \omega$ where m_e is the mass of the electron and r its distance from the nucleus. Thus, the current is

$$i = e\omega/2\pi = eP/2\pi m_e r^2$$

The magnetic moment μ generated by such motion is given in electromagnetic theory by $\mu = Ai$, where A is the area marked out by the orbital. If it is supposed, for simplicity, that the electron moves in a circular orbit, $A = \pi r^2$, then,

$$\mu_e = -(\pi r^2)(eP/2\pi m_e r^2)$$

$$\mu_e = -\frac{e}{2m_e}P$$

$$= -\frac{eh}{4\pi m_e}\sqrt{S(S+1)}$$

[Note that because of the negative charge of the electron, μ_e is negative.]

When we remove the fiction that electrons and nuclei are point charges, then it is convenient to introduce a factor g (known as the Landé splitting factor, or simply the g-factor) to take account of this fact. Thus, we write

$$\mu_e = -\frac{geh}{4\pi m_e}\sqrt{S(S+1)} = -g\beta_e\sqrt{S(S+1)} \qquad (1)$$

$\beta_e = eh/4\pi m_e$, is an important quantity, known as the *Bohr magnetron*. It has a value of 9.274×10^{-24} JT^{-1}. (e = 1.60×10^{-19} C and me = 9.11×10^{-31} kg).

Analogous equations may be used for the spin motion of nuclei. As μ and P depends on the mass of the particle and on its charge, the appropriate equation for nuclei is therefore:

$$\mu \propto (Ze/2m_N)P$$

where m_N is the mass of the nucleus and Z its charge number. For nuclei it is conveniently used a unit of magnetic moment by the term *nuclear magnetron*, $\mu_N = eh/4\pi m_p$, where m_p is the mass of the proton. The magnitude of β_N is 5-05095 × 10^{-27} JT^{-1}. For other nuclei the charge number and the difference in mass from that of the proton are both included in the nuclear g-factor, which also allows for quantum-mechanical effects. Thus

$$\mu_e = \frac{gZeh}{4\pi m_p}\sqrt{I(I+1)} = g_N\beta_N\sqrt{I(I+1)} \qquad (2)$$

where g_N is the nuclear g-factor. It should be noted that unlike Equation 1, which includes a negative sign explicitly (so that g is positive for electrons), Equation 2 allows the nuclear g-factor to be either positive or negative. It might be thought that, since all nuclei are positively charged, all nuclear g-factors must be positive. However, this is not so, and the reason for this may be traced to the structure of the nucleus. Negative nuclear g-factors imply that the spin magnetic moment is anti-parallel to the angular momentum (as for the electron); positive values indicate that μ and P are parallel.

Magnetogyric Ratios / Gyromagnetic Ratios: Usually, nuclear magnetic moments are described in terms of magnetogyric ratios or gyromagnetic ratios, γ, rather than nuclear g-factors. The value of y is defined as the ratio of the magnetic moment to the angular momentum (taking explicit account of the sign of the relationship):

$$\mu = \gamma P \tag{3}$$

From Equation 2 and 3 it can be seen that

$$\gamma\hbar = g_N \beta_N$$

So

$$\mu_N = g_N \beta_N \sqrt{I(I+1)} = \gamma\hbar\sqrt{I(I+1)} \tag{4}$$

Nuclear g-factors are small numbers (as are electron g-factors) since the effects of charge and mass are partially compensatory. Nuclear magnetic moments are, however, only ca. 10^{-3} times as large as electronic magnetic moments due to the effect of the mass to charge ratio—the value β_N/β_e of depends on m_e/m_p.

Interaction Between Spin and a Magnetic Field (Nuclei in a Magnetic Field):

In the absence of a magnetic field the energy of an isolated nucleus is independent of the quantum number mf. This is equivalent to stating that the energy of a magnet is independent of its orientation when no magnetic field is present. However, when a magnetic field of strength B is applied in a direction defined as z, a magnetic moment μ would have, in classical terms, an energy E given by

$$E = -\mu \cdot B = -\mu_z B \tag{5}$$

where μ_z is the component of μ in the direction z. This component is, in the case of nuclear spin, defined by m_I and, using an equation analogous to Equation 4, is given by

$$\mu_z = g_N \beta_N m_I = \gamma\hbar m_I \tag{6}$$