CHAPTER –I
Review of Theory

1.1 Introduction

The phenomenon of the emission or absorption of gamma-ray without loss of energy due to recoil of the nucleus and without thermal broadening is known as the Mossbauer effect. It was discovered by Rudolf Mossbauer in 1958 [1].

It has an important influence in many branches of sciences and engineering. Its unique feature is in the production of monochromatic electromagnetic radiation with a very narrowly defined energy spectrum, so that it can be used to resolve minute energy differences. The direct application of the Mossbauer effect to chemistry arises from its ability to detect the slight variation in the energy of interaction between the nucleus and the extra-nuclear electrons, variations which had previously been considered negligible.

On the physical basis, the Mossbauer effect and the importance of recoilless emission of gamma-rays, discussed as follows [2-9].

1.1.1 Energetics of Free-atom Recoil and Thermal Broadening

Let us consider an isolated atom in the gas phase. The energy difference between the ground state ($E_g$) of the nucleus and its excited state ($E_e$) is given by

$$E_0 = E_e - E_g \quad (1.1)$$

The following treatment refers only one dimension for simplicity, that in which direction a gamma-ray photon is emitted and in which direction the atom
recoils. This simplification causes no loss of generality as the components of motion in other two dimensions remain unchanged. If the photon is emitted from a nucleus of mass M moving with an initial velocity $V_x$ in the direction X at the moment of emission, then its total energy above the ground state nucleus at rest is $E_0 + \frac{1}{2} M V_x^2$. After emission the gamma ray will have an energy $E_\gamma$ and the nucleus a new velocity $(V_x + v)$ due to recoil ($v$ is a vector so that its direction can be opposite to $V_x$) as shown in Fig.1.1.

![Diagram of recoiling nucleus](image)

**Before the emission**
- Velocity $V_x$
- Energy $E_0 + \frac{1}{2} M V_x^2$
- Momentum $M V_x$

**After the emission**
- Velocity $V_x + v$
- Energy $E_\gamma + \frac{1}{2} M (V_x + v)^2$
- Momentum $M (V_x + v) + \frac{E_\gamma}{c}$

**Fig.1.1.** The energy and momentum are conserved in the gamma emission process.

The total energy of the system is $E_\gamma + \frac{1}{2} M (V_x + v)^2$. By conservation of energy

$$E_0 + \frac{1}{2} M V_x^2 = E_\gamma + \frac{1}{2} M (V_x + v)^2.$$  \hspace{1cm} (1.2)

The energy difference between the nuclear transition ($E_0$) and the emitted gamma-ray ($E_\gamma$) is

$$\delta E = E_0 - E_\gamma = \frac{1}{2} M v^2 + M v V_x$$
The $\gamma$-ray energy is seen to differ from the nuclear energy level separation by an amount which depends on the recoil kinetic energy ($E_R = \frac{1}{2} Mv^2$) which is independent of the velocity $V_x$ and the term $E_D = MvV_x$ which is proportional to the atom velocity $V_x$ and is a Doppler-effect energy.

The mean kinetic energy per degree of freedom of a free atom in a gas with random thermal motion is given by

$$\bar{E}_K = \frac{1}{2} M \overline{V}_x^2 \simeq \frac{1}{2} KT \simeq 1.25 \times 10^{-2} \text{eV at } 300 \text{ K},$$

where $\overline{V}_x^2$ is the mean square velocity of the atoms, $k$ is the Boltzmann constant and $T$ is the absolute temperature.

Hence, $\overline{V}_x = (2 E_K/M)^{1/2}$

and the mean broadening

$$\bar{E}_D = Mv(\overline{V}_x^2)^{1/2} = (2\bar{E}_K . Mv^2)^{1/2} = 2(\bar{E}_K E_R)^{1/2}. \quad (1.5)$$

The recoil energy of the $\gamma$-ray emitting nucleus is given by

$$E_R = \frac{1}{2} Mv^2 = \frac{(Mv)^2}{2M} = \frac{p^2}{2M}, \quad (1.6)$$

where $p$ is the linear momentum of the recoiling nucleus. Since the momentum must be conserved, this will be equal and opposite to the momentum of the $\gamma$-ray photon $(p_\gamma)$,

$$p = -p_\gamma = -\frac{E_\gamma}{c}$$
\[ E_R = \frac{E_\gamma^2}{2Mc^2} \]  

\( \simeq 1.95 \times 10^{-3} \text{ eV (The 14.4 KeV } ^{57}\text{Fe transition at 300 K)}. \)

Thus,

\[ E_D = 2 \left( \bar{E}_K E_R \right)^{1/2} = E_\gamma \left( \frac{2\bar{E}_K}{Mc^2} \right)^{1/2}. \]  

The effect of the recoil energy and thermal broadening on the line shape are shown in Figs. 1.3 and 1.4.

Fig. 1.2. The statistical energy distribution of the emitted \( \gamma \)-ray showing the inter relationship of \( E_0, E_R \), and \( \bar{E}_D \).

The dotted curve is the natural line shape without recoil and thermal broadening whereas other curve has the effect of recoil energy and thermal broadening.
According to the fundamental radiation theory the proportion of absorption is determined by the overlap between the exciting and excited energy distributions. This gamma-ray has lost energy $E_R$ due to recoil of the emitting nucleus. It can easily be seen that for the reverse process where a gamma-ray is reabsorbed by a nucleus a further increment of energy $E_R$ is required since the gamma-ray must provide both the nuclear excitation energy and the recoil energy of the absorbing atom ($E_0+E_R$). For example, for $E_\gamma = 10^4$ eV and a mass of the atom (M) = 100 a.m.u., it is found that $E_R = 5.4 \times 10^{-4}$ eV and $E_D = 5 \times 10^{-3}$ eV at 300 K. The amount of resonance is the shaded area in Fig.1.4 and is extremely small. But in the resonance absorption of ultraviolet radiation by atoms, the values of $E_R$ and $E_D$ are found only $2.1 \times 10^{-10}$ eV and $\sim 3 \times 10^{-6}$ eV respectively, for this typical values of $E_0= 6.2$ eV (50,000 cm$^{-1}$) and M = 100 a.m.u. In this case a strong resonance absorption is expected because the emission and absorption profiles overlap strongly.

Fig. 1.4. The figure shows the line shape in the emission and absorption processes and the resonance overlap for free-atom nuclear resonance is small and shown shaded in black.
The recoil energy $2E_R$ can be compensated if the source is moved with a large closing Doppler velocity ($2v$).

$$2v = \frac{2p}{M} = \frac{2p_\gamma}{M} = \frac{2E_\gamma}{Mc}.$$  \hspace{1cm} (1.9)

P.B. Moon [10] had performed the experiment successfully in 1950 using ultra centrifuge.

**1.1.2 Heisenberg Natural Line Width**

The most important influence on a gamma-ray energy distribution is the mean life time of the excited state. The uncertainties in energy and time are related to Planck’s constant $\hbar (=2\pi \hbar)$ by the Heisenberg uncertainty principle

$$\Delta E \Delta t \geq \hbar.$$  \hspace{1cm} (1.10)

The ground state nuclear level has an infinite lifetime and hence a zero uncertainty in energy. However, the excited state of the source has a mean life $\tau$ of a micro second or less, so that there will be a spread of gamma-ray energies of width $\Gamma_s$ at half height, then

$$\Gamma \tau = \hbar$$  \hspace{1cm} (1.11)

$$\Gamma = \frac{\hbar}{\tau}.$$  \hspace{1cm} (1.12)

The mean life $\tau$ is related to the half-life $t_{1/2}$ by the relations $\tau = \ln2 \times t_{1/2}$.

Whence, substituting numerical values we get,

$$\Gamma (\text{eV}) = \frac{4.562 \times 10^{-16}}{t_{1/2} (\text{s})}.$$  \hspace{1cm} (1.13)
For the case of $^{57}$Fe, $t_{1/2} = 97.8$ ns, then $\Gamma = 4.67 \times 10^{-9}$ eV. This is some $10^6$–$10^7$ times less than the values of $E_R$ and $D_E$ for a free atom and so can be neglected in that case. However, it can be seen that if the recoil and thermal broadening could be eliminated, radiation with monochromaticity approaching 1 part in $10^{12}$ could be obtained.

1.1.3 Elimination of the Recoil Energy ($E_R$) and the Doppler Broadening

The lattice energies and chemical binding in solids are of the order of 1-10 eV. These energies are greater than the free atom recoil energies ($E_R$). If the emitting atom is unable to recoil freely because of chemical binding, the recoiling mass can be considered to be the mass of the whole crystal rather than the mass of the single emitting atom. Using the equation $E_R = \frac{E^2}{2Mc^2}$, where $M$ is the mass of the whole crystallite which even in a fine powder contains at least $10^{15}$ atoms. Due to this factor, $E_R$ is reduced and when the whole mass of a lattice participates $E_R$ reduces further. This makes $E_R$ and $E_D (=2(\bar{E}_kE_R)^{1/2})$ completely negligible. Hence, the recoilless gamma-rays with out thermal broadening are obtained. This is called Mossbauer effect.

1.1.4 Energy and Momentum Transfer to the Lattice

In the Mossbauer experiment the emitting and absorbing nuclei are embedded in a solid lattice or matrix, this result in the recoil momentum being taken up by the crystal as a whole since the free atom recoil energy ($\leq 10^{-1}$ eV) is insufficient to eject the atom from the lattice site (binding energy 1-10 eV). Thus,
precluding momentum transfer to linear translational motion of the nucleus, and
the lattice vibrations cannot take up the momentum because a time-average of zero
is established within the decay time. Similarly, the total energy of the $\gamma$-transition
$(E_0)$ must be conserved and can only be shared between:

(i) The energy of the $\gamma$-photon, $E_\gamma$;
(ii) The lattice vibrations;
(iii) The translational kinetic energy of the individual atom;
(iv) The translational kinetic energy of the solid as a whole.

The third of these possibilities is eliminated by the high chemical binding
energy and the fourth has been shown to be minute because of the large mass
involved. The gamma-ray energy of the transition is thus shared between the
$\gamma$-photons and the lattice vibration phonons. Because of quantisation conditions, a
fraction of events, $f$, occur with no change in the lattice vibrations and the entire
transition energy $E$ is manifested in the $\gamma$-photon energy ($E_0= E_\gamma$).

1.1.5 Conditions to Observe Mossbauer Effect

Now we conclude that the Mossbauer’s analysis of the emission and
scattering of gamma-rays by atoms bound in solids indicated that the three
different cases should be distinguished as:

(i) If the free-atom recoil energy is large in comparison to the binding
energy of the atom in solid, the atom will be dislodged from its lattice
site, resulting in no resonance scattering.
(ii) If the free-atom recoil energy is larger than the characteristic energy of the lattice vibrations (i.e. the phonon energy) but less than the energy required to dislodge the atom, the atom will remain at its lattice site and will dissipate its recoil energy by heating the crystal (generation of phonon).

(iii) If the recoil energy is less than the typical phonon energy, a new effect arises because the lattice is a quantized system which cannot be excited in an arbitrary fashion. This energy ($E_R$) cannot be absorbed in the crystal. This effect is responsible for the unexpected increase in the scattering of gamma-rays at low temperature first observed by Mossbauer.

1.1.6 The Recoil Free Fraction

Due to thermal behaviour of the crystal in which the radiating nucleus is embedded, there is a mixture of recoil and nonrecoil transitions, and the recoil free fraction is given by

$$f = \frac{\text{Recoil free transitions}}{\text{Total number of transitions}}.$$  

The recoil free fraction depends upon the Debye model of solids, then

$$f = \exp \left[ -\left( \frac{E_R}{K\theta_D} \right) \left( \frac{3}{2} + \frac{\pi^2 T^2}{\theta_D^2} \right) \right].$$  

(1.14)

The following conclusions [11-13] can be derived from Eq. (1.14)
(i) The recoilless fraction increases as the temperature goes down, this is what Mossbauer observed with $^{191}$Ir.

(ii) The higher the Debye temperature ($\theta_D$) of the solid, the larger is the Mossbauer recoilless fraction.

(iii) The Mossbauer effect is limited to relatively low energy gamma-radiation emission since Eq. (1.14) decreases rapidly with the transition gamma-ray energy. The effect has been observed up to the 155 KeV gamma-radiation.

The expression (1.14) is only valid for a mono atomic lattice of identical atoms. Two frequent situations occur. The emitting nucleus is an impurity in a host lattice and in solids besides the acoustic modes of vibration one can also excite optical modes. Both these cases cannot be described by Eq. (1.14) and a detailed knowledge of the frequency distribution must be available in order to derive the appropriate relation for the recoilless fraction ($f$).

In the expression for $f$-fraction it is presumed that crystal is a microscopic dimension so that low frequency limit of the non-modes could be extended down to zero. This assumption is not valid in the case of the microcrystal where size limitation determines the low frequency cut off and thus effecting the results derived in Eq. (1.14).

1.1.7 Line Shape of the Source and Absorber

The gamma-ray absorption cross section for the nucleus going from ground state to the excited state is given by [14],
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\[
\sigma_0 = \frac{2\pi \hbar^2 (2I_e + 1) I}{(2I_g + 1) (\alpha + 1)},
\]

where \( I_e \) and \( I_g \) are the spins of excited and ground states of the decaying nucleus respectively and \( \alpha \) is the total internal conversion coefficient of the excited state. For \(^{57}\text{Fe} \), the resonance cross section comes out to be \( 2.2 \times 10^{-18} \text{ cm}^2 \) which is 200 times greater than that of photoelectric absorption and Rayleigh scattering \([15]\) cross section at that energy. As a result, the resonant absorption is detectable even when the resonant isotope is a minor constituent of the absorbing solid.

The energy dependence of the absorption cross section is given by the Breit-Wigner formula

\[
\sigma_{(E)} = \sigma_0 \left[ 1 + 4 \left\{ (E - E_0)/\Gamma_a \right\}^2 \right]^{-1},
\]

(1.16)

where \( E_0 \), \( E \) and \( \Gamma_a \) are the nuclear transition energy, photon energy and width of the resonance at half maximum absorption respectively. The Lorentzian line shape defined by this expression applies both to the emitted radiation and to the absorption cross section. The experimentally observed line shapes are a result of folding the source and absorber line shapes and the result is

\[
\sigma_{\text{exp}} (E) = \sigma_0 \left[ 1 + 4 \left\{ (E - E_0)/(\Gamma_s + \Gamma_a) \right\}^2 \right]^{-1}.
\]

(1.17)

Thus, the line widths of the source and the absorber are additive. If the natural line widths are realized in both, the observed Mossbauer resonance line width is just twice the natural line width of the excited state.
The cross section of Eq. (1.15) is the total cross section at the resonance absorption. The effective cross section in the Mossbauer experiment is further reduced by the product of recoil-free fractions applicable to the emission as well as absorption processes separately [16].

1.1.8 Thickness Effect

The Mossbauer spectrum can be obtained either using the scattering geometry [15] or a transmission one [17]. In either of the cases, it is essential to see how a line shape gets affected due to thickness of the absorber. Further, the transmission line shape gets modified due to thickness of the source itself since the accuracy of hyperfine field measurements depend upon the line width of the Mossbauer transition. It is imperative to have the information that how it gets affected due to thickness of the source and the absorber.

The absorber thickness plays a significant role in the quantitative analysis of the spectra. The effective absorber thickness $t_A$ (for a single absorber) is usually defined by

$$t_A = \sigma_0 f_A n_a d_A a_a,$$

(1.18)

where, $\sigma_0$, $f_A$, $n_a$, $d_A$ and $a_a$ are the maximum absorber cross section, the recoil free fraction in the absorber, the number of atoms / cm$^3$ of the particular element, the physical thickness of the absorber in cm and the isotopic abundance of the resonance isotope respectively.

If $t_A \ll 1$ the intensities of the resonance lines are rather small, however, in this case the lines can be fitted to a good approximation by Lorentzian curves. If
t_A \gg 1\) the lines are broadened by saturation effects and fitting by a sum of Lorentzian lines of hyperfine pattern fails usually experiments are carried out with a thickness of \(t_A \approx 1\). Under these conditions the deviation from the thin absorber approximation in split spectra can be significant because of overlap effects. For a quantitative analysis the transmission integral has to be evaluated.

Fitting procedures in conjunction with various computer programs have been discussed extensively in the literature [18, 19].

1.1.9 Importance of Mossbauer Effect

Mossbauer effect has become an important experimental tool for the investigation of hyperfine interactions in solids in a short time soon after its discovery in 1958 [16, 17]. The Mossbauer spectroscopy has number of advantages over other methods because it is more selective and it singles out a specific isotope such as \(^{57}\text{Fe}\) etc. Properties of the surrounding environment can be studied, although indirectly, via hyperfine interactions [20, 21]. The Mossbauer spectroscopy can be used as an analytical tool to determine the total amount of a given isotope, to check the inhomogeneity of the sample or to identify the various components it may contain [22]. The line width of \(^{57}\text{Fe}\) is \(4.5 \times 10^{-9}\) eV and the quality factor \((Q = E_r/\Delta E = 14.4 \times 10^3/4.5 \times 10^{-9})\) gives a high sensitivity of about 3 parts in \(10^{12}\). A few other isotopes known for their higher selectivity are \(^{181}\text{Ta}\) (\(Q \approx 10^{14}\)) and \(^{62}\text{Zn}\) (\(Q \approx 2 \times 10^{15}\)) but they are too difficult to perform experiments
with [23]. Thus, the Mossbauer resonance furnishes important information about the very small perturbations.

The limitations of the method are obvious, too. The number of useful isotopes is relatively small. In biological studies, in particular, the only nuclei of immediate significance are $^{57}$Fe and its radioactive parent $^{57}$Co and the two iodine isotopes $^{127}$I and $^{129}$I. Other limitations are the fixed energy resolution determined by the nuclear half life time and the fact that only the immediate environment of the Mossbauer isotopes can be studied. A further serious restriction is that the system must be in the solid form.

## 1.2 Hyperfine Interactions in the Mossbauer Effect

In the Mossbauer effect, the line width of the nuclear transition is small and the resonant absorption is extremely sensitive to energy variation of the gamma radiation. Therefore, the minute interactions between the nucleus and the orbital electrons which are not observed generally by other methods, can easily be observed in the Mossbauer effect. It is thus the influence of the electronic environment on the nuclear gamma transition both in emission and absorption which determines the hyperfine structure of the Mossbauer radiation [24, 25].

The principal interactions in the Mossbauer effect are

1.2.1 Nuclear Isomer-Shift

1.2.2 Nuclear Quadrupole Interaction

1.2.3 Nuclear Magnetic Hyperfine Interaction
1.2.1 Isomer-Shift

The nuclear electric charge is extended in space and is surrounded by the orbital electronic cloud. We know that the s-electrons are nearest to the nucleus. Therefore, the electrostatic interaction is different for point charges and extended charge distributions. A change in the s-electron density will result in an altered coulombic interaction that produces a shift of the nuclear energy level [26, 27]. The effect could be called the electric monopole interaction. The effect depends upon the difference in the nuclear radii of the ground and isomeric excited states, is known as the Isomer-Shift as shown in Fig.1.5.

Fig.1.5. a and b. Origin of isomer shift. (a) Electric monopole interaction shifts nuclear energy levels without lifting the degeneracy, (b) Resultant Mossbauer spectrum (schematic)
The isomer shift (I.S.) = $E_a - E_s$

$E_a$ and $E_s$ are the energy difference for absorber and source respectively.

$$\text{I.S.} = (2\pi Ze^2/5) \left\{ |\Psi_a(o)|^2 - |\Psi_s(o)|^2 \right\} \left[ R_e^2 - R_g^2 \right], \quad (1.19)$$

where $|\psi_a(o)|$ and $|\psi_s(a)|$, $R_e$ and $R_g$ are respectively the electron density at absorber, source, radii of the nucleus, in excited and the ground states.

Or

$$\text{I.S.} = (2\pi Ze^2/5) R^2 (\delta R/R) \left\{ |\Psi_a(o)|^2 - |\Psi_s(o)|^2 \right\}, \quad (1.20)$$

where $R_e - R_g = \delta R$

and

$R_e^2 - R_g^2 = (R_e - R_g) (R_e + R_g) \approx \delta R (2R)$.

The Eq. (1.20) consists of two factors, one is that of nuclear radius effect and the second being the electronic charge density at the nucleus which is basically an atomic or chemical parameter since it is affected by the valence state of the atom. Therefore, to observed the isomer-shift we must have that,

(i) The mean square radius of the nuclear ground state must be different from that of the nuclear excited state.

(ii) The chemical make up in the source and absorber must be different. For example, two different valence states may be used that the electron density at the nucleus is different in source and absorber.

### 1.2.2 Quadrupole Interaction

In the case of isomer shift, the effect of the electrostatic interaction between nuclear and electronic charges was derived by assuming the nucleus to be spherical and the charge density to be uniform. If these conditions are relaxed,
other effects appear which are in fact higher order terms in the multipole expansion of the electrostatic interaction. These terms do not shift the nuclear levels, they split them, i.e., they lift all or part of their \((2I+1)\) fold degeneracy (where \(I\) is the nuclear spin quantum number as shown in Fig. 1.6.

![Fig. 1.6](image_url)  

**Fig. 1.6.** Schematic diagram of the hyperfine interaction and corresponding Mossbauer spectra of \(^{57}\text{Fe}\). (a) Electronic monopole interaction (b) Electric quadrupole interaction. (c) Magnetic dipole interaction.

The second nonvanishing term of the electrostatic interaction of a nucleus with its surrounding electronic charge is the quadrupole coupling. This is the result of the interaction of the nuclear quadrupole moment with the gradient of the electric field due to other charges in the crystal etc. The nuclear quadrupole moment reflects the deviation of the nucleus from spherical symmetry. An oblate (flattened) nucleus has a negative quadrupole moment while a prolate (elongated) has a positive moment. Nuclei whose spin zero or \(1/2\) are spherically symmetric
and have a zero quadrupole moment. Thus the ground state of $^{57}$Fe with I=1/2 cannot exhibit nuclear quadrupole splitting.

Any nucleus with a spin quantum number of greater than I = 1/2 has a non-spherical charge distribution, which if expanded as series of multipoles contains a quadrupole term [28]. The quadrupole interaction Hamiltonion is given by

$$H_Q = \frac{e^2qQ}{4I(2I-1)} [3I_z^2 - I(I+1) + \frac{\eta}{2} (\hat{I}_+^2 + \hat{I}_-^2)],$$

(1.21)

where I, Q, q, $\eta$, $I_+$ and $I_-$ are the nuclear spin, quadrupole movement, electric field gradient, asymmetry parameter and shift operators respectively.

A Mossbauer transition occurs between two nuclear levels, each of which may have a nuclear spin and quadrupole moment. This means that both the ground state and excited state levels may show a quadrupole interaction. The law of conservation of angular momentum and of parity leads to the formulation of definite selection rules which characterize the transition between the two states and these ensure that there is a high probability for transitions in which the change in the $I_z$ quantum numbers $[I_{z_e} - (I_{z_g})] = m$ is 0 or ± 1. The magnitude of the quadrupole interaction is a product of two factors, $eQ$ is a nuclear constant for the resonant isotope, while eq. is a function of chemical environment. For a $\left| \frac{3}{2} \right> \rightarrow \left| \frac{1}{2} \right>$ transition, it is not possible to determine the sign of $e^2qQ$ or the magnitude of $\eta$ from the line positions. This is not the case for higher spin states where the sign of $e^2qQ$ can be uniquely determined from the unequally spaced lines.
The contributions of the electric field gradient at the nucleus comes from three sources [29, 30].

(i) **Electrons belonging to the atom:** In transition metal ions the inner d- or f-electrons are not completely filled and cause electric field gradient at the nucleus.

(ii) **Polarization of inner shells of the atoms:** The electrons of the filled inner shells have spherical symmetry and normally have no contribution to the field gradient. However, both external charges outside the atom and its own unpaired electrons can polarize these inner shells leading to the induction of the field gradient at the nucleus.

(iii) **Charges external to the atom:** The ionic charges of the lattice produce a field gradient at the Mossbauer nuclear site.

The relative importance of these factors depends on the type of solid considered. For instance the lattice contribution will be dominant in ionic crystals of non-transition elements, whereas in transition elements the electrons in the unfilled shells will give the largest contribution. In molecular solids the asymmetric \( \pi \)-electrons or the presence of \( \pi \)-bounding will give the main contribution to the electric field gradient.

### 1.2.3 Magnetic Hyperfine Interaction

The most familiar part of the hyperfine interaction without doubt is the magnetic part arising from the interaction of the nuclear magnetic dipole moment
\( \mu \) with the magnetic field \( H \) due to the atom’s own electrons [31-33]. The Hamiltonian for the magnetic interaction is
\[
H_m = -\mu \cdot H = -g \mu_N \ I \cdot H,
\]
and the energy levels are
\[
E_m = -\mu \cdot H_m / I = -g \mu_N \ H_m / I ,
\]
with \( m_1 = I, I-1, \ldots, -I \) and \( \mu_N \) is the nuclear magneton and \( g \) is the nuclear ‘g’ factor. According to Eq. (1.23) there are \((2I+1)\) equally spaced energy levels as shown in Fig.1.6. In general, a gamma transition between the ground and excited states of spins \( I_g \) and \( I_e \) must conserve the Z-component of angular momentum, i.e., the angular momentum, \( L \), carried off by the gamma-ray must satisfy,
\[
|I_g - I_e| \leq L \leq |I_g + I_e| \text{ with } L \neq 0.
\]
A transition with \( L = 1 \) is called an electric dipole E1 transition by a change in parity, otherwise it is a magnetic dipole M1 transition. The effective magnetic field acting at the nucleus arising from the atom’s own electrons is usually called the internal field. The main contributions of internal fields are

(i) **The Fermi contact interaction:** Direct interaction between the nucleus and unpaired s-electron density is
\[
H_s = -(16 \pi \beta / 3) \ \langle \Sigma (\uparrow \Psi_s^2(o) - \downarrow \Psi_s^2(o)) \rangle
\]
Where \( \uparrow \Psi_s^2(o) \) and \( \downarrow \Psi_s^2(o) \) are the s-electron spin densities at the nucleus with spin-up and spin-down respectively and \( \beta \) is the electron Bohr magneton.
Differences in spin-up and spin-down charge densities appear even in filled s-shells of the atoms containing partially filled magnetic 3d-shell.

There is a number of other mechanisms which gives rise to magnetic fields at the nucleus

(ii) **The orbital magnetic moment gives rise to a field**

\[ H_L = -2 \beta \langle 1/r^3 \rangle \langle L \rangle = -2 \beta \langle 1/r^3 \rangle (g-2) \langle S \rangle, \]  

(1.25)

Where \( \langle L \rangle \) is angular momentum.

(iii) **Internal field** This term is used for the field resulting directly from the application of a external field \( H_0 \), taking into account the Lorentz and demagnetizing fields

\[ H_i = H_0 + \frac{4}{3} \pi M - DM \]  

(1.26)

(iv) **Dipolar interaction with the electron spins of the parent atom give rise to**

\[ H_D = -2\beta \langle 3r (S.r)/r^5 - S/r^3 \rangle \]  

(1.27)

The relative contribution of these terms depends on the electron configuration in the atom, the most important contribution being that of the Fermi contact term. It is important to observe that unpaired spin densities appear even in filled s-shell of transition ions. This is due to the fact that the exchange interaction between the spin-up polarized d-shell and a spin-up s-electron is attractive while that between the d-shell and a spin-down s-electron is repulsive. As a
consequence, the radial parts of the two s-electron wave functions are distorted, one being pushed closer to the nucleus and the other being pulled further out.

The hyperfine structure of the Mossbauer spectra depends essentially on the character of the magnetic state of the sample paramagnetic, ferromagnetic or antiferromagnetic. For paramagnetic samples it is important to consider the time elapsed between two successive flips of the electron spin. These flips can be due to electronic relaxation, if the frequency of the flip is much larger than the Larmer frequency related to the nuclear spin due to other internal field there is no hyperfine structure as the value of the internal field seen by the nucleus averages out to zero over the time of the Larmer precessions, on the other hand if the electron-flip frequency is comparable to or smaller than the frequency of the nuclear spin, the spectrum will show a magnetic hyperfine pattern. With ferro, ferri-, and antiferro magnetic materials, the electron spin-spin coupling is much higher than the nuclear Zeeman coupling, as a consequence, the nuclear spin interacts with the average value of the internal field and the Mossbauer spectra represent the typical magnetic hyperfine structures.

1.3 Static and Dynamic Aspects of Lattice Structure

The lattice effects are contained in the recoilless factor as the temperature dependant measurements of the resonance cross-section determines, the mean square vibrational amplitude of the Mossbauer nucleus in the solid under investigation. In recent years several experimental and theoretical investigations have established that the phonon relaxations under the defusing motions of atomic
mass point are readily measurable with the help of Mossbauer technique. Similarly, the microcrystal effects have been of intense study using the iron and tin Mossbauer isotopes. However, in all these investigations of the microcrystal no effect of the recoil energy loss when the crystal size is very small, is taken into account. The recoil energy losses in microcrystal of measureable dimensions are as large as the line width. Therefore, the effects arising from the recoil energy losses should also be taken into account in the determinations of the line shifts.
References


