

CHAPTER IV

MÖSSBAUER SPECTROSCOPY

4.1 Introduction

The Mössbauer effect, also known as nuclear resonance fluorescence, was discovered by Rudolf L. Mössbauer in 1957 while he was a graduate student at the University of Heidelberg in Germany. Mössbauer was interested in the line shape (profile) of the gamma radiation (high energy photons) emitted after a nuclear resonant absorption event. As is well known, an excited state of a nucleus can decay to the ground state via the emission of a gamma ray of energy equal to the difference in the energies of the excited state and ground state. Because of the time reversal symmetry of most quantum mechanical processes, the ground state can be excited to the "excited state" by the absorption of a gamma ray with "exactly" the energy required for the transition. Due to the loss in energy of the gamma ray (emitted by the excited nucleus) from the recoil of the nucleus during the emission of the gamma ray, the same gamma ray can not be used to excite the nuclide back to its excited state. By moving either the emitting nuclide or the absorbing nuclide, the energy of the gamma ray (as seen by the absorbing nuclide) can be increased or decreased (via the Doppler effect). Mössbauer also pointed out that under certain situations, the emission of the gamma ray is not accompanied by recoil. In

these cases, the gamma ray has the energy needed to excite the ground state of the nucleus without having to move either the absorbing or emitting nuclei. When recoilless emission occurs, any non resonance between the energy differences existing in the two nuclides would be due to shifts in the energy levels due to perturbation of states in one of the nuclide. In 1960, the Mössbauer effect was widely applied to the study changes in the chemical environment inside various chemical complexes (chemical shift) containing iron. The importance of the Mössbauer technique to mineralogical research was not realized until 1965. At present, Mössbauer spectroscopy has become a powerful tool in physics, chemistry, metallurgy, geology and biology.

4.2 Mössbauer Effect.

From fundamental radiation theory, we knew that the rate of absorption is related to the overlap of the emission and absorption profiles (see Figure 4.1). The Gaussian distributions for the emission (exciting) energy spectrum (the left side distribution in Figure 4.1) is partly quantum mechanical and partly classical. Since the excited states of the nucleus (and atom) have a finite life time, there is an uncertainty in their energies (Heisenberg Uncertainty Principle),

$$\Delta E \Delta T \geq h \quad (4.1)$$

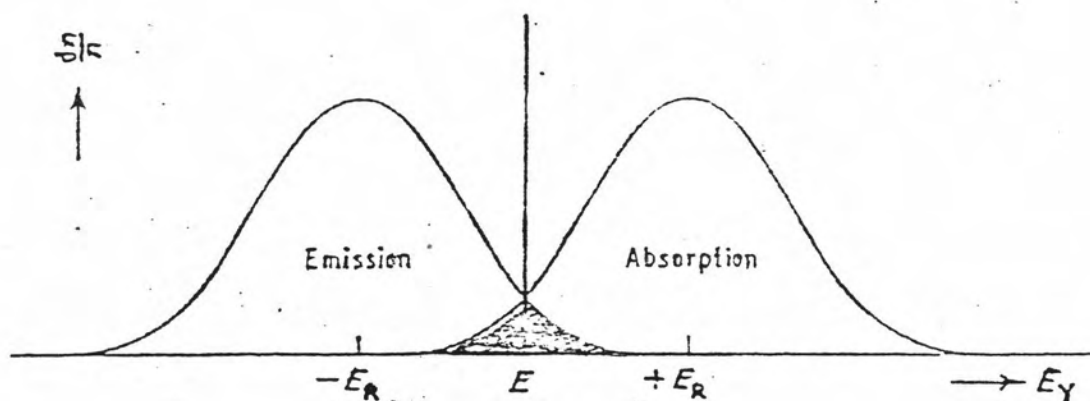


Figure 4.1 The resonance overlap for free atom nuclear resonance is small and is shown shaded in black.

The ground state, however, has an infinite life time and so there is no uncertainty in its energy. Since the principle of conservation of energy (applied to the decay of the excited state of the nucleus to its ground state) requires the energy of the γ -ray be equal to the difference in the energies of the excited state and the ground state, there will be a spread in the energies of γ -ray (see Figure 4.2). The width of the Lorentzian (Gaussian) distribution would be just the uncertainty in the energy of the excited state, i.e.,

$$\Gamma_3 = \hbar/\tau \quad (4.2)$$

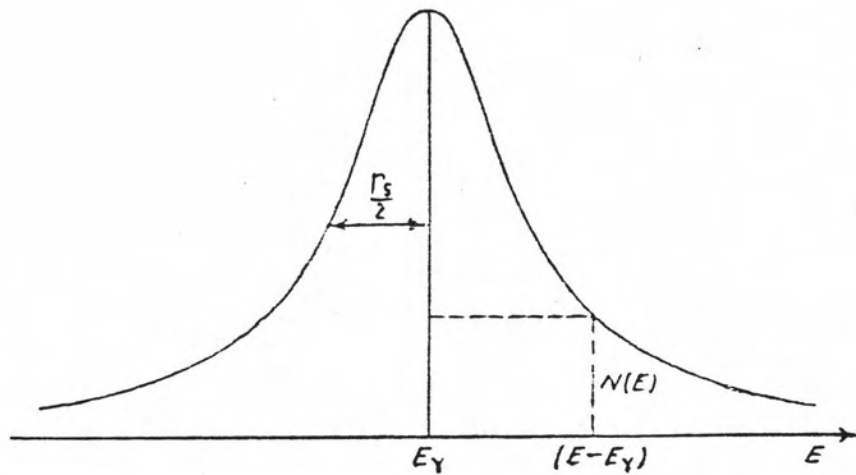


Figure 4.2. The Lorentzian energy distribution of the source recoilless radiation.

where τ is the mean life time. The mean life time is related to the half life $T_{1/2}$ by

$$\tau = T_{1/2} / 0.693 \quad (4.3)$$

Thus, the half width of the Lorentzian distribution appearing in Figure 4.2 is given by

$$\Gamma_3 \text{ (eV)} = 4.562 * 10^{-16} / T_{1/2} \text{ (sec)} \quad (4.4)$$

The classical contribution to the energy spectrum arises as follows: Consider a radioactive nucleus of mass M and rest mass energy E_e moving with an initial velocity v_x moving in the x

direction. After it emits a gamma ray of energy E_γ , it will move with a new velocity $v_x + v$. If E_g is the ground state energy of the nucleus, we have for the total energy of the nucleus (see Figure 4.3) before the emission

$$E_e + (1/2)Mv_x^2$$

and after the emission

$$E_g + E_\gamma + (1/2)M(v_x + v)^2$$

By conservation of energy, we have

$$E_e + (1/2)Mv_x^2 = E_g + E_\gamma + (1/2)M(v_x + v)^2 \quad (4.5)$$

or

$$E_e - E_g - E_\gamma = (1/2)Mv^2 + Mv_x v \quad (4.6)$$

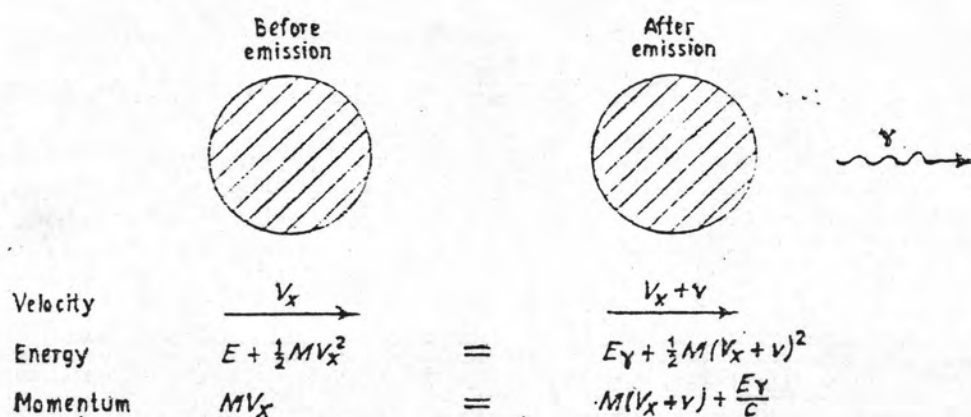


Figure 4.3 The energy and momentum in a gamma emission process.

If E is the difference between the energies of the excited state and the ground state, i.e.,

$$E = E_e - E_g \quad (4.7)$$

then eqn. (4.6) becomes

$$E - E_\gamma = (1/2)Mv^2 + Mv_x v \quad (4.8)$$

The first term on the RHS of eqn. (4.8) can be identified as being the energy of recoil (E_R) of the nucleus, while the second can be identified as being the Doppler effect energy (E_D). In terms of these energies, eqn. (4.8) becomes

$$E - E_\gamma = E_R + E_D \quad (4.9)$$

It should be noted that E_D is proportional to v_x while the E_R is not. To obtain an expression for E_D which can be used in a direct manner, we recall that for random thermal motion of free particles, the mean kinetic energy is given by

$$\bar{E}_k = (1/2)M\bar{v}_x^2 \approx k_B T \quad (4.10)$$

where \bar{v}_x^2 is the mean square velocity of the atom, k_B is the Boltzmann constant and T is the absolute temperature. Therefore,

$$\bar{v}_x = (2k_B T/M)^{1/2} \quad (4.11)$$

The recoil energy E_R can be expressed in terms of the γ -ray energy as follows

$$E_R = p^2/2M \quad (4.12)$$

where p is the recoil momentum of the atom. From the principle of conservation of momentum,

$$p = -p_\gamma = -E_\gamma/c \quad (4.13)$$

where p is the momentum of the γ -ray. Substituting eqn. (4.13) into eqn. (4.12), we get

$$E_R = E_\gamma^2 / 2Mc^2 \quad (4.14)$$

We also have

$$v = (2E_R/M)^{1/2} \quad (4.15)$$

which shows that v is proportional to the γ -ray energy. The mean value of the Doppler effect energy is also proportional to the γ -ray energy, i.e.,

$$\begin{aligned} \bar{E}_D &= M\bar{v}_x v \\ \bar{E}_D &= 2(k_B T E_R)^{1/2} = 2(\bar{E}_k E_R)^{1/2} \end{aligned} \quad (4.16)$$

$$\bar{E}_D = E_\gamma (2\bar{E}_k / Mc^2)^{1/2} \quad (4.17)$$

Due to the recoil and the thermal motion of the atom, the energy spectrum of the γ -ray emitted is broadened into a Lorentzian or Gaussian distribution (see Figure 4.4).

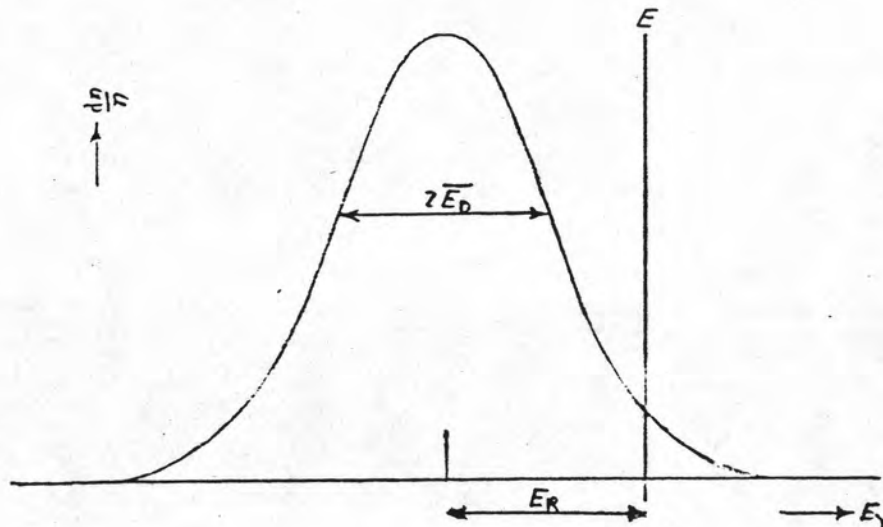


Figure 4.4 The statistical energy distribution of the emitted γ -ray showing the interrelationship of E , E_R and \bar{E}_D .

As is clear from the above discussion, the spread of the energy distribution is due to many factors which may or may not play a significant role in the Mössbauer effect. By selecting the right radioactive sources and embedding them into correct matrix, many of the above factors can be minimized so that the width of the energy distribution becomes very small. Then any unequal shifts (due to perturbations) of the energy levels of the nuclei when they sit in different environments will cause any overlaps of the distributions to cease to exist. Only by moving one set of the nuclei (in the absorber or emitter), can the Doppler effect bring the two distributions back into resonance.

4.3 Mössbauer Spectra

The Mössbauer effect occurs when either of the nuclides moves and a Doppler shift of the gamma ray energy moves the energy of the gamma ray back into resonance with the difference in the energy levels of the absorbing nuclide. By measuring the Doppler shift energy necessary to bring things back into resonance, one would have a measure of the energy level differences in the emitting and absorbing nuclides. Measurement of the Mössbauer effect provides information mainly about;

1. Chemical Isomer Shift.
2. Electric Field Gradient/Quadrupole Moment.
3. Magnetic Hyperfine Field.

The shifts in the energy levels related to the above three

quantities are due to the perturbations caused by :

- a. Interaction of the nucleus of the atom with its own (lowest lying) electronic cloud.
- b. Interaction of the quadrupole moment of the non spherical nucleus with the crystal field produced by the neighboring atoms.
- c. Interaction of the magnetic moment of the nucleus with the magnetic field produced by the atomic magnetic moments of the neighboring atoms or by an external magnet.

The shifts are calculated using either first or second order perturbation theory. What follows are simplified calculations of energy corrections due to these interaction.

4.3.1 Isomer Shift. (13)

When an element reacts chemically with another or finds itself in any environment other than that of the free state, its electronic clouds are altered. The modifications extend down to the lowest lying states (1 s electrons) which for the heavier elements are inside the nucleus. Modifications of the electronic clouds within the nucleus will lead to changes in nuclear energy levels. The usual calculations of the electrostatic potential energy is based on all the charges being point charges. This assumption is valid as long as the charge for which the potential is being calculated for lies outside the region containing the charges which produce the potential $V(r)$.

When the charge lies within the region, then the potential energy is given by

$$E = -e \int \rho_n \phi_e dv \quad (4.18)$$

where $e \rho_n$ is the charge density of the nucleus and ϕ_e is the electrostatic potential of the electron. The change W in the potential energy due to the fact that the nuclear charge is not a point charge is the difference between the Coulomb potential energy for point charges and eqn. (4.18),

$$W = e \int_0^R \rho_n \phi_e dv - Ze^2 \int_0^R (\rho_e/r) dv \quad (4.19)$$

where $-e \rho_e$ is the charge density of the orbital electrons within the volume element dv . The probability density of an s electron in the neighborhood of a point charge is given by

$$\rho_e = \frac{2(\rho+1)|\psi_s(0)|^2}{\Gamma^2(2\rho+1)} \left(\frac{2Z}{a_H}\right)^{2\rho-2} r^{2\rho-2} \quad (4.20)$$

where $\rho = (1-\alpha^2 Z^2)^{1/2}$, $\alpha = e^2/\hbar c$, a_H is the first Bohr radius, $\psi_s(0)$ is the nonrelativistic Schrödinger wave function at $r = 0$ and $\Gamma(n)$ is the gamma function. Assuming that the nuclear charge density is uniform and that the nucleus is spherical, then W becomes

$$W = \frac{24\pi(\rho+1)|\psi_s(0)|^2 Ze^2}{(2\rho+1)(2\rho+3)\Gamma^2(2\rho+1)} \left(\frac{2Z}{a_H}\right)^{2\rho-2} R^{2\rho} \quad (4.21)$$

where R is the radius of the nuclide. When the nucleus is excited, it is expected that there is a change in the radius R . This change in the radius in turn causes a change in W , i.e.,

$$\Delta W = \frac{24\pi(\rho+1)|\psi_s(0)|^2 Ze^2}{(2\rho+1)(2\rho+3)r^2(2\rho+1)} \left(\frac{2Z}{a_H}\right)^{2\rho-2} R^{2\rho} \frac{\delta R}{R} \quad (4.22)$$

The chemical isomer shift δ is the difference between ΔW , eqn.(4.22) for two nuclide sitting in different chemical environments A and B. Since the only quantity in eqn. (4.22) which is electronic and which can be expected to change when the environment changes is the non relativistic wave function $\psi(0)$, the isomer shift would be given by

$$\delta = \frac{24\pi(\rho+1)\{|\psi_s(0)_A|^2 - |\psi_s(0)_B|^2\} Ze^2}{(2\rho+1)(2\rho+3)r^2(2\rho+1)} \left(\frac{2Z}{a_H}\right)^{2\rho-2} R^{2\rho} \frac{\delta R}{R} \quad (4.23)$$

where $\psi(0)_A$ is the wave function for the s-electron moving inside the nuclear radius of the absorber nuclide and $\psi(0)_B$ is the wave function for the s-electron moving inside the radius of the source nuclide.

The isomer shift for Fe^{57} Mössbauer studies is usually measure with reference to natural iron even though the source Fe^{57} nuclides are not embedded in a natural iron matrix. The determination of the isomer shift is accomplished by obtaining two Mössbauer spectrums, one for the Fe^{57} nuclides in natural iron and the other for the Fe^{57} nuclides in the material under study. The isomer shift is the difference between the central positions in the sextet or doublet Mössbauer patterns of the two spectrum.

4.3.2 Electric Quadrupole Splitting.

Nucleus having nuclear spin quantum number I not equal to $1/2$ have non spherical charge distributions. These distributions can be expressed as a linear combination of the multipole contributions (moments). The electric multipole moments are defined as

$$\int \rho(r, \theta, \phi) Y_{1m}(\theta, \phi) dv \quad (4.24)$$

where $Y_{1m}(\theta, \phi)$ are the spherical harmonics. The nuclear quadrupole moment Q represents the first correction to the spherical distribution, i.e.,

$$eQ = \int \rho r^2 (3\cos^2\theta - 1) dv \quad (4.25)$$

where the z -axis is the nuclear spin quantization axis. The sign of the quadrupole moment, $+$ or $-$, indicates whether the nucleus is oblate or prolate in shape.

In 'real' solids, the electronic charge distribution is not uniform and so the charge distribution about any point inside the solid is not spherically symmetric. This non spherical charge distribution will lead to a non zero electric field gradient tensor whose components are

$$E_{ij} = -V_{ij} = -\partial^2 V / \partial x_i \partial x_j \quad (4.26)$$

$$(x_i, x_j = x, y, z)$$

where V is the electrostatic potential at the point x_0, y_0, z_0 . The z axis of the reference frame describing the electric gradient is taken to be the axis along which the gradient is the maximum, i.e.,

$$V_{zz} = eQ$$

Since Laplace equation requires that the electric field gradient be traceless, i.e.,

$$V_{xx} + V_{yy} + V_{zz} = 0,$$

only two of the V_{ii} 's are dependent quantities. The electric field gradient can be completely defined by the value of V_{zz} and of the asymmetry parameter η , defined as

$$\eta = \frac{V_{xx} - V_{yy}}{V_{zz}} \quad (4.27)$$

Assuming that $V_{zz} > V_{yy} \geq V_{xx}$, then $1 \geq \eta \geq 0$.

The interaction Hamiltonian describing the interaction of the nuclear quadrupole moment with electric field gradient is

$$H = \frac{eQ}{2I(2I-1)} (V_{xx} \hat{I}_{xx}^2 + V_{yy} \hat{I}_{yy}^2 + V_{zz} \hat{I}_{zz}^2) \quad (4.28)$$

where $\hat{I}_{x,op}$, $\hat{I}_{y,op}$ and $\hat{I}_{z,op}$ are the three components of the nuclear spin operator I_{op} . The nuclear levels (states) of the nuclide are eigenstates of the two operators \hat{I}_{op}^2 and $\hat{I}_{z,op}$. The eigenvalues of these two operators are $I(I+1)$ and I_z . The eigenstates with these eigenvalues are usually denoted in the Dirac notation as $|I, I_z\rangle$. The operator $\hat{I}_{z,op}$ is the z component of the angular momentum type operator I_{op} , i.e.,

$$\hat{I}_{op} = \hat{I}_{x,op} \hat{i} + \hat{I}_{y,op} \hat{j} + \hat{I}_{z,op} \hat{k}, \quad (4.29)$$

and so

$$\hat{I}_{op}^2 = \hat{I}_{x,op}^2 + \hat{I}_{y,op}^2 + \hat{I}_{z,op}^2 \quad (4.30)$$

The operators $\hat{I}_{x,op}$ and $\hat{I}_{y,op}$ can be combined together to form the step up and step down operators \hat{I}_+ and \hat{I}_- whose operations produce the nuclear quantum states with I constant but with I_z equal to $I_z + 1$ or $I_z - 1$, i.e.,

$$\begin{aligned}\hat{I}_+ |I, I_z\rangle &\propto |I, I_z+1\rangle \\ \hat{I}_- |I, I_z\rangle &\propto |I, I_z-1\rangle\end{aligned}$$

Eqn. (4.28) can be rewritten as

$$H = \frac{e^2qQ}{4I(2I-1)} [3\hat{I}_z^2 - I(I+1) + \eta(\hat{I}_x^2 - \hat{I}_y^2)] \quad (4.31)$$

and then as

$$H = \frac{e^2qQ}{4I(2I-1)} [3\hat{I}_z^2 - I(I+1) + \frac{\eta}{2}(\hat{I}_+^2 + \hat{I}_-^2)] \quad (4.32)$$

If the electric field has axial symmetry, i.e., $V_{xx} = V_{yy}$, then the asymmetry parameter is zero and the interaction Hamiltonian is just

$$H = \frac{e^2qQ}{4I(2I-1)} \{3\hat{I}_z^2 - I(I+1)\} \quad (4.33)$$

The energy correction due to this Hamiltonian can be calculated according to first order perturbation theory, i.e.,

$$E^1 = \langle I, I_z | H | I, I_z \rangle \quad (4.34)$$

or

$$E_Q = \frac{e^2 q Q}{4I(2I-1)} [3\hat{I}_z^2 - I(I+1)] \quad (4.35)$$

Since the square of I_z appears in eqn. (4.35), the $I = 3/2$ nuclear level is split into only two distinct states corresponding to $I_z = \pm 3/2$ and $\pm 1/2$ with their energies shifted to $E_{3/2} \pm (e^2 q Q/4)$ where $E_{3/2}$ is the energy of the unperturbed $I = 3/2$ level. The $I = 1/2$ nuclear level will not be split into two states but will only have its energy shifted. The transition from the $I = 1/2$ nuclear state to the $I = 3/2$ nuclear state (via resonant absorption) will give rise to the Kramer doublet (see Figure 4.5).

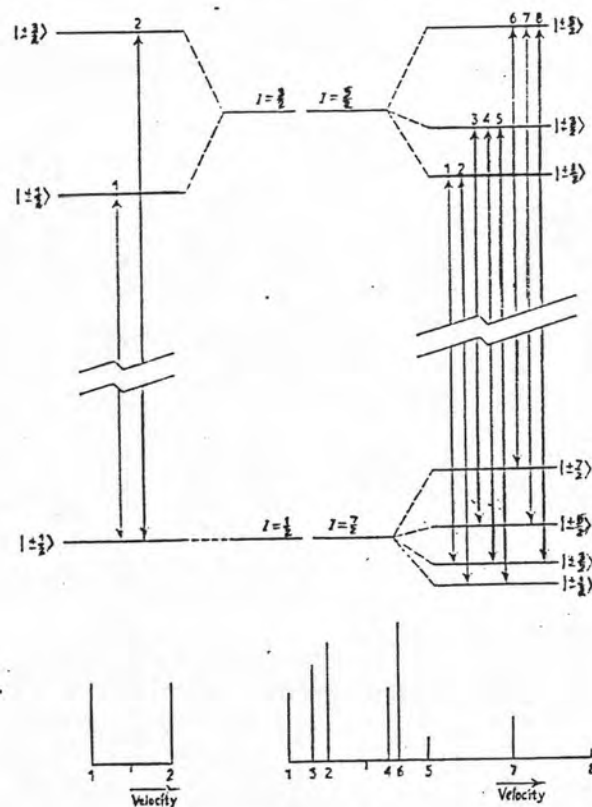


Figure 4.5 Typical energy level schemes and observed spectra for $3/2 \rightarrow 1/2$ and $5/2 \rightarrow 7/2$ transitions with quadrupole hyperfine interactions.

If the electric field is not axial symmetric, then the part in eqn. (4.35) which depends on will have to be treated using de-generate perturbation theory. The following off diagonal matrix elements

$$\langle I, I_z | H | I, I_z + 1 \rangle \text{ and } \langle I, I_z | H | I, I_z - 1 \rangle$$

have to be taken into account. Diagonalizing the matrix

$$\langle I, I'_z | H | I, I_z \rangle$$

for the $I = 3/2$ level yields

$$E_Q = \frac{e^2 q Q}{4I(2I-1)} [3\hat{I}_z^2 - I(I+1)] (1 + \eta^2/3)^{1/2} \quad (4.36)$$

4.3.3 Magnetic Hyperfine Interaction.

Just as the atomic magnetic moment will interact a magnetic field to produce the Zeeman effect, the nuclear magnetic moment will interact with any magnetic field which exist at the nucleus to produce the nuclear analog of the Zeeman effect. The interaction Hamiltonian is simply

$$H = -\bar{\mu} H_{\text{field}} \quad (4.37)$$

where $\bar{\mu}$ is the magnetic moment associated with the nuclear spin I , i.e.,

$$\mu = g \mu_N I \quad (4.38)$$

with g being the nuclear g factor and μ_N being the nuclear Bohr magneton ($e\hbar/2Mc$). If the direction of H_{field} is taken to be the axis of quantization, then the energy shifts are given by

$$E_m = -g \mu_N H_{\text{field}}^m \quad (4.39)$$

where $m = I, I-1, I-2, \dots, 1-I, -I$. Due to certain other factors, the change in the value of $m (=I_z)$ as the nucleus makes a transition from one nuclear level $|I, I_z\rangle$ to another nuclear level $|I', I'_z\rangle$ must be equal to 0 or ± 1 . For the transition from the $I = 3/2$ state to the $I = 1/2$ state (see Figure 4.6), we get the sextet pattern shown.

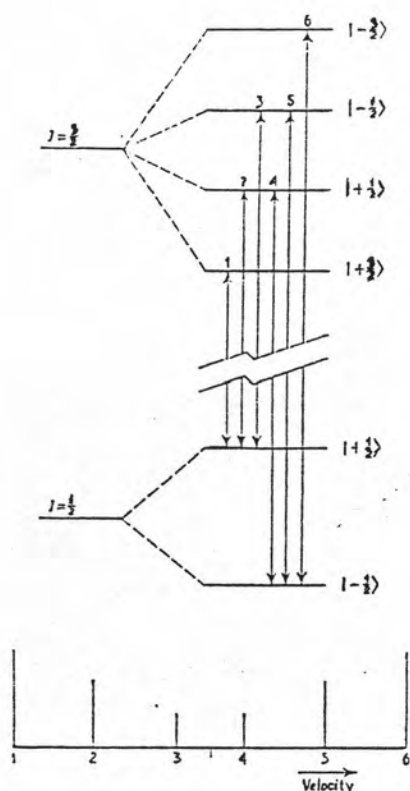


Figure 4.6 Magnetic splitting for a $3/2 \rightarrow 1/2$ transition. The relative inversion of the $3/2$ and $1/2$ multiplets signifies a change in sign of the nuclear magnetic moment. Only transition for a change in m of $0, \pm 1$ are shown.

The magnetic field at the nucleus can arise from several different sources. First, there is the field produced by an external magnetic. Accompanying this field, explanations for their origins can be found in any standard text on electricity and magnetism. Then there are the contributions from the electronic structure of the parent atom. First there is the Fermi contact field which arises from the interaction of the nucleus with the charge imbalance in the s-electron spin density inside the nucleus. The dependence of this field on the parameters of the atom is given by

$$H_S = -(16\pi/3) \mu_B \langle \sum_i S_i^2 \delta(r_i) \rangle \quad (4.40)$$

where $\langle \dots \rangle$ denotes an expectation value. The imbalance of the s-electron spin density is usually due to the polarization of the spins by net spins of the unpaired electrons in the outer orbits. If the angular momentum of the parent atom is non zero, then it has an orbital magnetic moment which can interact with nucleus via

$$H_L = -2 \mu_B \langle r^{-3} \rangle \langle L \rangle$$

or

$$H_L = -2 \mu_B \langle r^{-3} \rangle (g-2) \langle S \rangle \quad (4.41)$$

where $\langle L \rangle$ and $\langle S \rangle$ are the expectation values of the orbital and spin angular momenta. In addition, there is a field which arises from dipolar interaction of the nucleus with the spin moment of the atom, i.e.,

$$H_D = -2 \mu_B \langle 3\bar{r} (\bar{r} \cos \theta) r^{-5} - \bar{r} r^{-3} \rangle \quad (4.42)$$

where θ is the angle between the spin axis and the principal axis.

The most important component of the hyperfine field in magnetic materials is the effective field which arises from the interactions between spins belonging to neighboring atoms. The details of these interactions and how Mössbauer spectroscopy can elucidate the physics of these interactions is beyond the scope of the present work.