Nuclear resonance scattering of gamma rays: Mössbauer effect and its Applications

A Graduate project Presented to

School of graduate Studies

Addis Ababa University

By

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In the Partial Fulfillment

of the Requirement for the Degree of

Master of Science in Physics

Addis Ababa University

Addis Ababa

Ethiopia

April 2007

Addis Ababa University

School of graduate Studies

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Abstract

The aim of this paper is briefly to discuss the innovation which nuclear recoilless emission and absorption of gamma ray (Mössbauer effect) entails over pervious fluorescence techniques, with enough theoretical discussion to understand how and when the Mössbauer effect occurs and with the description of small number applications to gain an appreciation of the importance of the Mössbauer effect.

This effect, which is also called the nuclear resonance fluorescence of gamma rays or nuclear recoilless emission and absorption of gamma rays or zero phonon emission and absorption of gamma rays, is nuclear process permitting the resonance absorption of gamma rays. It is made possible by fixing atomic nuclei in the lattice of solids so that energy is not lost in the recoil during the emission and absorption radiation. The process, discovered by a Germen-born physicist, Rudolf L. Mössbauer in 1957, constitutes a useful tool for studying diverse scientific phenomena. Fields in which Mössbauer spectroscopy has been applied include Nuclear physics, general physics, solid-state physics, surface physics, astronomy, metallurgy, chemistry, biochemistry, geology, and medicine.

Acknowledgements

First and foremost I would like to thank God for he made everything possible and for enabling me to start and to accomplish the study to an end.

I wish to express my deep gratitude to my advisor and instructor Prof. Ashok K. Chaubey for his constant assistant, invaluable guidance and encouragement with out any reservation during the whole period of my project work. I also wish to thank my four colleagues in Nuclear physics class, in particular Nigussie Abebe, for the many stimulating discussions which we have had together.

I would also like to thank Tigray Educational Bureau for sponsoring me to join and continue my graduate studies. My special thanks also go to all my families and friends in Mekele for their valuable assistance and moral support throughout the course of my Msc study.

Finally, I would like to acknowledge the department of physics and school of graduate studies A.A.U. for all co-operations I had during my Msc study. Thank you all very much!

Chapter 1

Introduction and Background

1.1 Introduction

The beauty and fascination of physics rarely becomes more apparent when one follows a particular topic through the various stages of its development. The history of the neutrino, the most elusive of all particles, is an example. Another is the story of nuclear resonance fluorescence, the subject of this paper. In this paper, we outline briefly some phases in the history of atomic and nuclear resonance fluorescence, the Mössbauer effect, and its applications [3].

For several years physicists have been attracted and challenged by the task of doing experiments with nuclear gamma-ray fluorescence. By nuclear gamma ray fluorescence we mean the process in which gamma rays from the decay of an excited state in the nuclei of a source are *resonantly* absorbed or scattered by the excitation of the same state in the identical nuclei of the target [5].

There are many other techniques known, besides resonant absorption, for the observation of gamma rays from nuclear excited states. These are usually adequate for the measurement of the energy difference between the initial and the final states, the lifetime of sufficiently long-lived excited states, and the multipole character of the radiation (which in turn helps to determine the spins and parties of the levels).The special importance of the nuclear fluorescence technique derives from the fact that, *for shapely defined levels*, even every slight difference in the levels of the source and absorber nuclei, or a very slight change in the energy of the emitted gamma rays, will prevent resonance absorption. They may then hope to measure these differences and changes by restoring the fluorescence effect through the addition of known amounts of energy from the outside. Furthermore, since the energies of the nuclear levels are, in fact, not sharply defined, they may hope by similar techniques to determine the spread about the central energy of the excited level and from this to calculate the lifetime of the level.

Nuclear gamma-ray fluorescence is thus potentially useful in the following branches of physics:

(1) By permitting the determination of half-lives and of such properties as nuclear

magnetic moments (through measurement of the energy shift in the magnetic field) it helps to explore nuclear structure and the nuclear forces

(2) By enabling us to measure, with great precision, predicted small changes in the frequency of radiation due to such external influences as the presence of a gravitational field, it helps to test the validity of general physics laws of the most transcending importance.

(3) By enabling us to measure the fraction of gamma rays emitted or absorbed without energy loss as a function of temperature T, it helps to probe the dynamics of the probe nucleus.

However, before the discovery of recoilless gamma emission and absorption, the full potentialities of the fluorescence technique could not begin to be realized. The main difficultly is that, to satisfy conservation of momentum, both the emitting and absorbing nuclei must carry off some recoil energy; the gamma rays therefore do not have the full amount of energy which is needed to raise the target nuclei from the ground state to the excited state and resonant absorption can not occur.

To be sure, several ingenious methods were devised to supply the energy deficit. However the nuclear recoil effect and Doppler broadening had the inevitable effect of broadening of the natural width of the gamma lines; i.e., of making indeterminacy in the energy of narrow gamma rays much larger than required by the uncertainty principle. The expected shifts in the energy which one would have liked to measure, e.g., that due to the presence of a gravitational field, or the magnetic hyperfine splitting, are exceedingly small. They can not be seen if the gamma ray energy spectrum is not reasonably sharp. On the other hand, it *was* possible, in spite of the recoil effect and Doppler broadening broadening, to make indirect measurements of the width of themselves, of fairly broad levels, and by an application of the uncertainty principle to determine the lifetimes of these states. Thus, the usefulness of fluorescence experiments was limited, before Mössbauer's discovery, to the task of measuring short half-lives.

What Mössbauer discovered was that under suitable conditions, a certain fraction of nuclei which are *bound in crystals do not recoil*. Instead the entire massive crystal takes up the recoil momentum and this result in a negligible energy loss by the gamma rays. This discovery opened the way to direct measurement of narrow transition lines, as well as to the observation of the small energy shifts due to the nuclear, atomic, and macroscopic causes. Nuclear resonance scattering thus became an important tool not only in nuclear physics, in

general physics, and solid state physics, but also in Astronomy, Chemistry, Biology Geology, and in Metallurgy.

1.1 Background information to Mössbauer effect

A nucleus consists of neutrons and protons arranged in different energy levels. Radioactive nuclei are those in which either neutrons and/or protons are in high energy levels from which they decay emitting various types of radioactivity. The excited states of a nucleus are produced in a nuclear reaction and also in natural radioactivity after α or β decay. An excited state having energy of excitation lower than the separation energy of nucleon comes to ground state or lower energy state by emission of energy in the form of an electromagnetic radiation which means higher energy X-ray or gamma ray. Here we are concerned with gamma rays. Gamma rays are like light but with the much a higher energy. Sometimes the energy of a proton or neutron changing the energy level is not emitted as a gamma ray, but instead transferred directly to an electron in the atomic shell. This electron is subsequently kicked out of the shell due to this energy burst. An electron from somewhere else in the atomic shell then takes the prized place in the lower energy spot. By doing so it emits X-rays. This process is called *internal conversion*. Similarly, a nucleus can absorb a gamma-ray, putting a neutron or a proton on a higher energy level and thus forming a radioactive nucleus [8].

The fundamental physics of Mössbauer effect involves the transition (decay) of a radioactive nucleus from an excited state of energy E_e to a ground state of energy of E_g with the emission of a gamma ray of energy E_γ subsequent absorption of γ-ray by a second nucleus of the same type as the first. The basis of the Mössbauer effect is the recoilless resonance absorption of γ-rays: a γ-ray emitted in the de-excitation of a nuclear excited state can be absorbed by another nucleus of the same kind and excites it. Nuclear resonance will only occur when the energy of the gamma-quantum and the transition energy of the absorbing nucleus are the same. The excited states in nuclei, however, have very narrow energy widths. Therefore, in order to observe a good resonant absorption of gamma rays by nuclei we need highly precise and sharply defined incident gamma ray energy. For example, a ^{57}Fe nucleus on its first excited state can decay by emitting a photon with energy of 14.4 KeV. Since the energy levels in the nucleus have a very narrow width (long lifetime), only a 14.4 KeV photon can be absorbed by another such nucleus.

Chapter 2

Nuclear Resonance Scattering

2.1 Resonance absorption and fluorescence

Atomic resonant fluorescence was predicted and discovered just after the turn of the last century, and within a few years the underlying theory had been developed. From the simplified view point, an atom in an existed electronic state can decay to its ground state by the emission of a photon to carry off the excess energy. This photon can then be absorbed by a second atom of the same kind by electronic excitation. Subsequent de-excitation re-emits the photon, but not necessarily in the initial direction so that scattering or resonance fluorescence occurs. Thus if the monochromatic yellow light from the sodium lamp is collimated and passed through a glass vessel containing sodium vapour, one would expect to see a yellow glow as the incident beam is scattered by the resonant fluorescence [4].

A close parallel can be drawn between atomic and nuclear resonance absorption. The primary decay of the majority of radioactive nuclides produces a daughter nucleus which is in a highly excited state. The letter then de-excitation by emitting a series gamma ray photons until by one or more router, depending on the complexity of the gamma cascade, it reaches a stable ground state. This clearly analogues to electronic de-excitation, the main difference being in the much higher energies involved in nuclear transitions. It was recognized in the 1920's that it should be possible to use the gamma ray emitted during a transition to a nuclear ground state to excite a second stable nucleus of the same isotope, thus giving rise to nuclear resonance absorption and fluorescence.

The first experiments to detect these nuclear resonance processes by Kuhu 1929 were failure, although it was already recognized that the nuclear recoil & Doppler broadening effects were probably responsible. Several unsuccessful attempts were made since the early experiments of Kuhn (1929). Continuing attempts to observe nuclear resonant absorption were inspired by the realization that the emitted γ-rays should be an unusually good source of monochromatic radiation.

It was in 1957 that the German-born physicist R.L Mössbauer demonstrated the feasibility of observing resonance scattering of gamma rays by embedding the absorbing

and the emitting nuclei in well bound crystalline solids. In order to appreciate the difficulties in observing resonance absorption of gamma rays and at the same time the importance of Mössbauer's discovery, it is necessary to look more closely into the process of resonance absorption.

Suppose a nucleus in the excited state of energy E_e undergoes transition to the ground state of energy E_g by emitting gamma quantum of energy $E_o = E_e - E_g$. Under certain conditions which we shall discuss below, the quantum energy E_o may be totally absorbed by a nucleus of the same kind (same number of protons Z and the same number of neutron N) in the ground state, whereby transition to the excited state of energy E_e takes place. The phenomenon, called *nuclear resonance absorption* of gamma rays, is visualized in Fig 2.1.

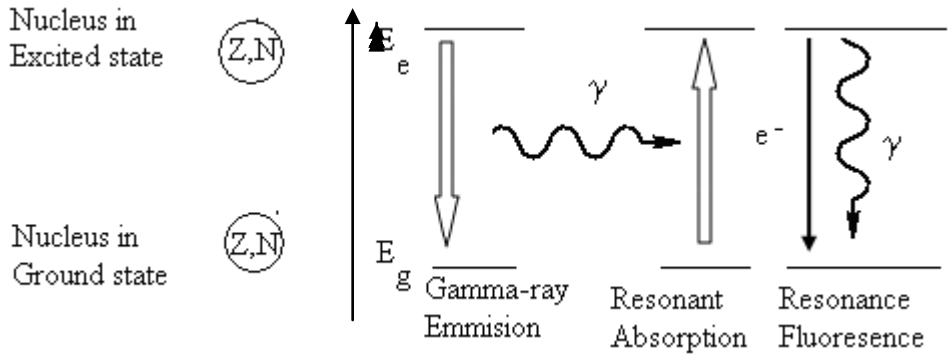


Fig.2.1. Schematic representation of nuclear resonance absorption of gamma rays and nuclear resonance fluorescence.

After the resonant γ-ray absorption the nucleus remains in the excited state of energy $E_o = E_e - E_g$ for a very short time (lifetime of the excited state) with mean life τ and then undergoes transition back to the ground state by isotropic emission of a γ-ray or conversion electrons due to internal conversion (energy transfer from the nucleus to the electron shell), which is most Mössbauer active nuclei competes with γ-ray emission, Here we speak of *Nuclear resonance fluorescence*.

Even though, problem in atomic and nuclear resonance seen very similar, there exist marked differences which render nuclear experiments much more difficult. In order to out line these difficulties, the process of resonance fluorescence must be discussed in more detail.

2.2. Limitations of Earlier Scattering Experiments

In this section, we discuss some of the parameters which enter into scattering experiments and the relationship which must hold between them to make the experiment possible. The aim of this discussion is to make clear the insuperable difficulties with which experiments were faced before Mössbauer discovery. The various energies which come into a typical experiment are:

1. the energy E_o of the excited nuclear state above the ground state
2. the change ΔE in E_o, or the gamma energy, which we wish to measure
3. the natural line width Γ of the emitted gamma radiation
4. the recoil energy E_R which is given to the emitting and to the absorbing nuclei and thermal (Doppler) broadening.

2.2.1 Excitation Energy E_o

The energies E_o, above the ground state, of the discrete nuclear excited states, range from few Kev to few Mev. In order to be able to do a scattering experiment, it is necessary that (a) the excited state decay to the ground state (in order to permit resonant excitation of the target nuclei, which is in the ground state), (b) the excited state must be produced with sufficient abundance, (c) the de-excitation by gamma emission be at least comparable to that by competing processes and the probability of resonant nuclear scattering in the absorber be large in relation to other processes, such as atomic scattering and inelastic scattering. These requirements limit the available candidates, by and large, to the low lying bound states in the region below 1Mev; they are frequently produced following beta decay [5].

2.2.2 Experimental Effect ΔE

The effects which remain to be investigated, whether nuclear or macroscopic origin, are expected to result in energy shifts that are exceedingly small. It this aspect which makes gamma-ray fluorescence experiments at once so difficult and so intriguing. As we shall show explicitly in chapter 3 for the gravitational Doppler shift, ΔE is often proportional to E_o, with the proportionality constant a very small number. This would say that the bigger the excitation energy E_o, the better. But as we have stated already, only the less energetic gamma rays, from low lying levels, can be used.

2.2.3 Natural line width Γ

While considering the energy states of the atomic nuclear, we have so far assigned definite energy value to them. However, this is not quite true. An excited state (nuclear or electronic) of mean life time τ can never be assigned a sharp energy value. Instead the energy level spreads over a certain energy range of width ΔE (See Fig 2.2), which correlates with the uncertainty in time Δt via the Heisenberg uncertainty relation in the form of the conjugate variables energy and time,

$$\Delta E \Delta t \geq \hbar \qquad (2.1)$$

(h = $2\pi\hbar$ = Planck's constant). Δt, also considered as the time interval available to measure the energy E, is in the order of the mean lifetime: $\Delta t \approx \tau$ .From (Eq.2.1) we see that a ground state of infinite lifetime has zero uncertainty in energy.

Nuclear transition from an excited state (e) to the ground state (g), or vice versa, involve all possible energies within the range of ΔE. The transition probability or intensity as a function of the transition energy, I(E), yields a Lorentzian or Breit-Winger curve centered around the most probable transition energy E_o, whose width at half-maximum Γ is called the line width (see Fig 2.2). This width, or uncertainty, in the energy arises, qualitatively, in the following way. The excite state of the nucleus has a finite, rather than an infinite (mean) lifetime τ. The time of emission of the particular gamma ray photon is therefore unknown, on the average, to within the interval τ. Its energy must then be uncertain by an amount Γ given by $\Gamma\tau \approx \hbar$.

Weisskopf and Winger have shown that in general

$$\Gamma\tau = \hbar \qquad (2.2)$$

holds, if Γ = ΔE stands for the full width of the transition spectral line at half maximum. They also find that the spectral line has Lorentzian or Breit winger form and follows the formula

$$I(E) = \frac{I_0}{(E - E_0)^2 + (\Gamma/2)^2} \qquad (2.3)$$

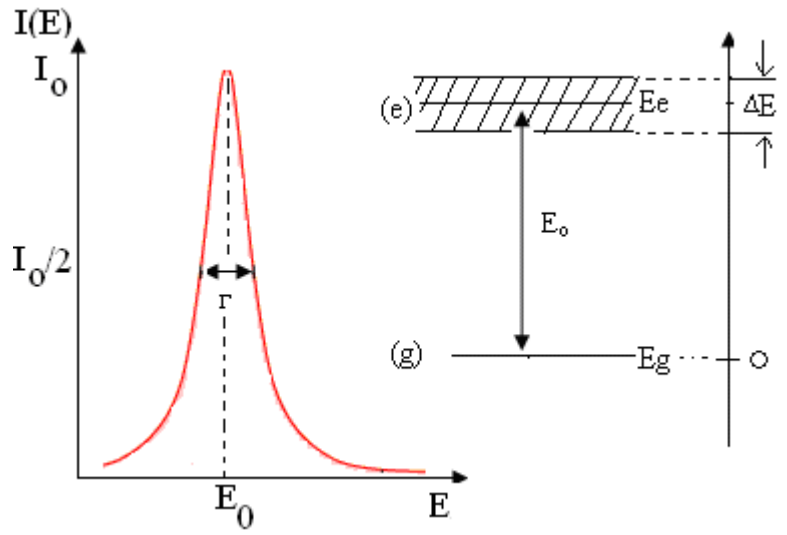


Fig.2.2 Intensity I(E) as a function of transition energy E. $\Delta E=\Gamma=\hbar/\tau$ is the energy width of the excited state (e) with the mean lifetime τ.

The low-lying isomeric states to which we are restricted in fluorescence experiments have lifetimes ranging from about 10^{-11}sec to the longest known. A practical upper limit of about 10^{-6} sec is set by the fact that longer lived, and, hence, narrower resonance would be destroyed by unavoidable extraneous interactions with the environment, e.g., with small magnetic field or small mechanical vibrations. The uncertainty relation gives 10^{-6}ev to 10^{-11}ev as the corresponding range of the line widths.

The line width is of the great importance in deciding whether a particular experiment can be successfully undertaken. For it is clear that if the line width Γ is much greater than the expected shift ΔE in the central region due to the effect under investigation, this shift will be irretrievably covered up by the spread Γ. We thus have the condition for the excited shift

$$\Delta E = \alpha Eo \geq \Gamma. \qquad (2.4)$$

This condition does not appear impossible to satisfy. Even for an effect as small as the gravitational Doppler shift ($\alpha \approx 10^{-15}$), for a level 100Kev above the ground state, a width of about 10^{-10}ev will do. There are a few isomers with sufficiently long lifetimes to satisfy this requirement. It is here, however, that the elementary conservation laws make their, in this case, unwelcome appearance.

2.2.4 Nuclear Recoil Energy E_R and Doppler Broadening E_D

If a γ-ray (photon) is emitted from an excited nucleus of mass M and of mean energy E_o, which is supposed to be at rest before the decay, a recoil is imparted to the nucleus, due to which the nucleus moves with the velocity **V** in opposite direction to the direction of the γ-ray emission (see Fig.2.3) and takes up the recoil kinetic energy

$$E_R = \frac{1}{2} MV^2 = \frac{P_n^2}{2M} \qquad (2.5)$$

The low of conservation of momentum requires that

$$P_n = -P_\gamma = -E_\gamma / c \qquad (2.6)$$

Where $\mathbf{P}_n$ and $\mathbf{P}_\gamma$ are the linear momentum of the nucleus and the γ-ray respectively, c is the velocity of light, and

$$E_\gamma = E_o - E_R \qquad (2.7)$$

is the energy of the emitted γ-ray. Because of the large mass of the nucleus, we may write in the non relativistic approximation

$$E_R = P_n^2/2M = E^2_\gamma /2Mc^2 \qquad (2.8)$$

Since E_R is very small compared to E_o it is reasonable to assume $E_\gamma \approx E_o$; then we may use the following formula for computing the recoil energy of a nucleus in an isolated atom or molecule:

$$E_R = E_o^2/2Mc^2 = 5.37 \times 10^{-4} E_o^2/A \text{ ev} \qquad (2.9)$$

Where A is the atomic mass number of the nucleus and E_o is given in Kev.

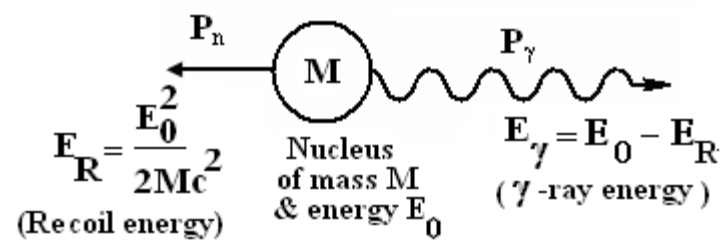


Fig. 2.3.Recoil of momentum $\mathbf{P}_n$ and energy E_R imparted to an isolated nucleus upon γ-ray emission.

As an example, for the Mössbauer transition between the first excited state and the second excited state of ^{57}Fe ($E_o = E_e - E_g$ =14.4 Kev), E_R is evaluated to be 1.95 x 10^{-3} ev. This is about six orders of magnitude larger than the natural width of the spectral line under consideration ($\Gamma = 4.55 \times 10^{-9}$ev)

The recoil effect causes a displacement of the emission line from the position E_o to smaller energies by an amount E_R (see Fig.2.4). In the absorption process, the γ-ray to be

absorbed by a nucleus requires the total energy $E_\gamma = E_o + E_R$ to make up for the transition from the ground to the excited state and the recoil effect (for which $\mathbf{P}_n$ and $\mathbf{P}_\gamma$ have the same directions now). As shown schematically in Fig.2.4, the transition lines for emission and absorption are separated by a distance of $2E_R$ on the energy scale, which is about 10^6 times larger than the natural line width Γ. There is thus an energy deficit of

$$2E_R = \frac{E_0^2}{Mc^2} \approx \frac{E_\gamma^2}{Mc^2}$$

This difference becomes serious for nuclear levels because their line widths are usually much smaller than $2E_R$ [7]

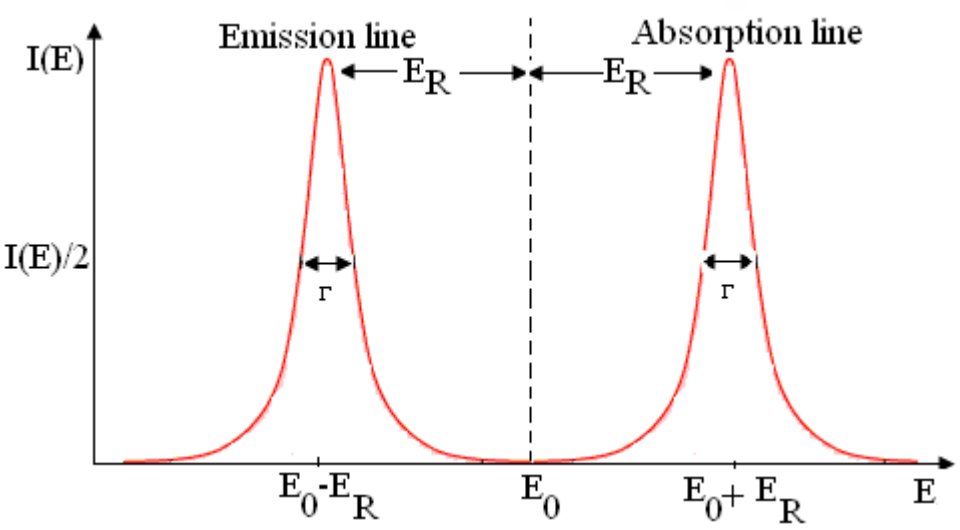


Fig.2.4 Consequences of the recoil effect caused by γ-ray emission and absorption in isolated nuclei.

The transition lines are separated by $2E_R \approx 10^6 \Gamma$. There is no overlap between emission and absorption line and hence no resonant absorption possible. Fluorescence absorption will, however, occur to the extent that the line width produces an overlap in the emission and absorption spectrum. The situation is illustrated in Fig.2.5. It is clear that in order to get a significant amount of fluorescence, it is necessary that

$$2E_R \leq \Gamma \qquad (2.10)$$

The energy difference $2E_R$ can be compensated by the Doppler shift in the energy and resonance absorption spectrum can be observed.

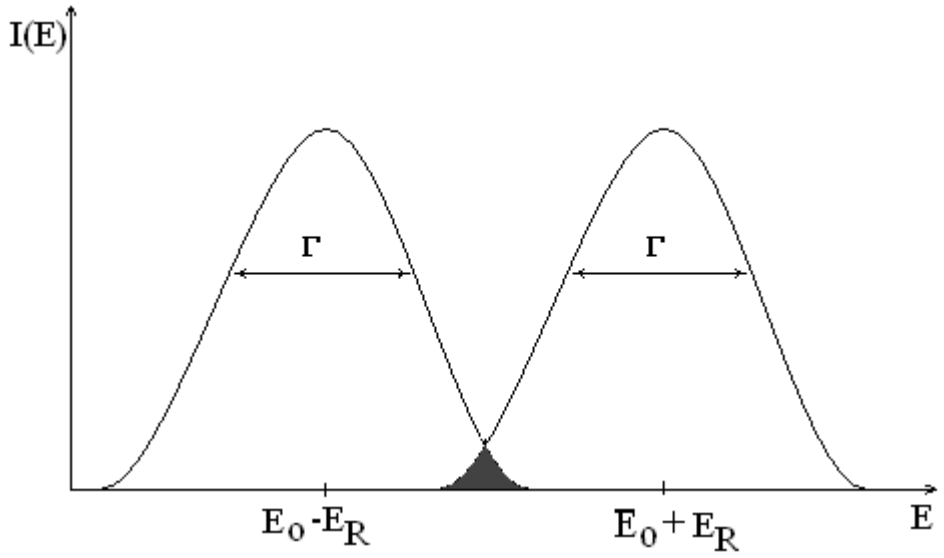


Fig. 2.5 Overlap of emission and absorption curves when the nuclei receives a recoil energy E_R. E_o is the energy of the excited state, Γ its width.

Besides natural broadening there is yet another important process which tends to broaden the spectral lines. This broadening is essentially due to Doppler effect and arises out of the movement of the emitting and absorbing nuclei as a result of temperature. In the discussion so far, the emitting and absorbing nuclei were assumed to be at rest. Actually, however, atoms of the gas are never at rest, thus the sources and the target atoms are in thermal motion as a result of temperature, and this motion introduces an additional widening of the emission and the absorption lines, called *Doppler broadening*. In order to see this effect quantitatively, consider an isolated nucleus of mass M with an excited state level at an energy E_o and moving with the velocity **V** along the direction in which the γ-ray is to be emitted (the components of the notion perpendicular to this direction remains unaffected by the decay may be ignored). The energy above the ground state *at rest* is (E_o + 1/2M$\mathbf{V}^2$). When a γ-ray of energy E_γ is emitted, the nucleus recoil and has a new velocity **V** + **v** (which is the vector sum in that **V** and **v** may be opposed) and a total energy of 1/2M$(\mathbf{V} + \mathbf{v})^2$. By the conservation of energy

$$E_o + 1/2MV^2 = E_\gamma + 1/2M\,(V + v)^2 \qquad (2.11)$$

So that the actual energy of the photon emitted is given by

$$E_\gamma = E_o - 1/2Mv^2 - Mv.V$$

$$E_\gamma = E_o - E_R - E_D$$

The γ-ray is thus deficient in energy by a recoil kinetic energy ($E_R = 1/2Mv^2$) Which is independent of the initial velocity V, and by thermal or Doppler energy ($E_D = Mv.V$) which depends on V and can therefore be positive and negative. Doppler energy E_D is dependent on the thermal motion of the nucleus, and will therefore have a distribution of values which is temperature dependent. A mean value, $\overline{E_D}$, can be defined which is related to the mean kinetic energy per translational energy of $\overline{E_R} \approx 1/2$ kT, by

$$E_D = 2\sqrt{E_K E_R} > E\gamma\sqrt{\frac{2E_K}{Mc^2}} \qquad (2.12)$$

Where K is Boltzmann's constant and T is absolute temperature.

As a result, the statistical distribution of the energy of the emitted γ-rays is displaced from true excited-state energy by $-E_R$ and broadened by E_D into a Gaussian distribution of width $2\overline{E_D}$. The distribution for absorption has the same shape but is displaced by $+E_R$. This is illustrated schematically in Fig. 2.6 and the order of magnitude of E_R and E_D is indicated in Table 2.1 [4].

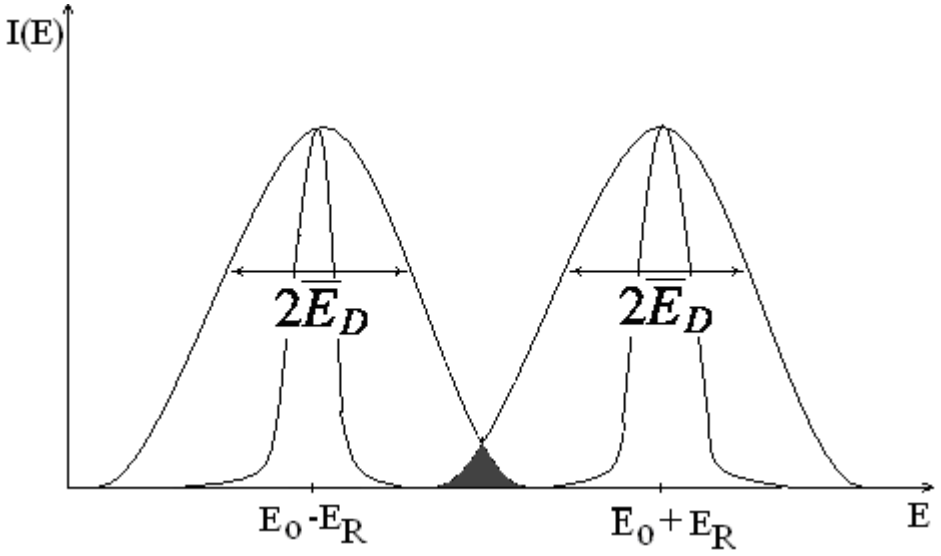


Fig.2.6. Doppler broadening of the emission and absorption lines

The expression for the Doppler broadening (2.12) shows that the Doppler breadth is proportional to the energy of the emitted photon and square root of the absolute temperature. Fig.2.7. shows the variation of recoil energy, Doppler broadening for spectral lines with energies ranging from few ev to few Mev [1].

It is obvious that the emission and the absorption lines would overlap even partially making resonance fluorescence possible if the Doppler broadening E_D is greater than the recoil energy. i.e. if $2E_D > 2E_R$.In general, for the spectral lines in the visible region $E_D > \Gamma > E_R$ making the observation of resonance fluorescence possible. However, for γ-rays

emitted by nuclei the recoil energy, E_R, is comparable or at times even greater than the Doppler broadening making it difficult to observe resonance fluorescence.

Table 2.1. Typical energies of nuclear and chemical interactions

Mössbauer γ-ray energies (E_γ)	10^6 — 10^7 kJMol^{-1}
Chemical bonds & lattice energy	10^2 — 10^3 kJMol^{-1}
Electronic transitions	50 — 500 kJMol^{-1}
Molecular vibrations	5 — 50 kJMol^{-1}
Lattice vibrations	0.5 — 5 kJMol^{-1}
Nuclear recoil & Doppler energies(E_R& E_D)	10^{-2} — 1 kJMol^{-1}
Nuclear quderapole coupling constant	< 10^{-3} kJMol^{-1}
Nuclear Zeeman splitting	< 10^{-3} kJMol^{-1}
Hisenberg linewidth Γ	10^{-7} — 10^{-4} kJMol^{-1}

1ev=1.60219 x 10^{-19} J & is equivalent to 96.49 kJMol^{-1}

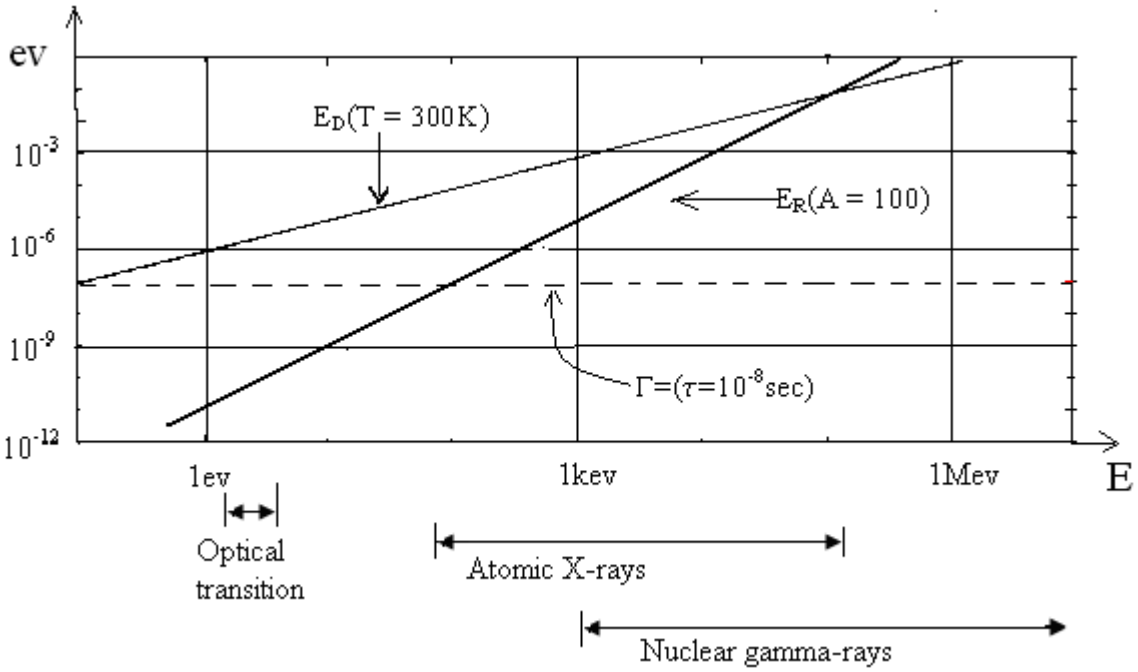


Fig.2.7.Recoil energy E_R and Doppler broadening E_D (for a gas at 300K) as a function of transition energy E for a nucleus of mass number 100. For comparison, the natural line width Γ corresponding to a lifetime of 10^{-8}sec [3].

2.3 Cross-section for resonance Scattering

Resonance experiments with gamma rays are usually performed by either measuring the scattered intensity (resonance fluorescence or resonance scattering) or by determining the attenuation of the beam due to resonance absorption. Both these processes have a certain cross-section which is determined for thin absorber by wavelength of the incident radiation. The cross-section for these processes, for an incident gamma ray of energy E and wavelength λ, and thin absorbers, the cross-sections can be written as [3]

$$\sigma_{Scatt}(E) = \sigma_0 \frac{\Gamma_\gamma^2}{4(E-E_0)^2 + \Gamma^2} \tag{2.13}$$

$$\sigma_{abs}(E) = \sigma_0 \frac{\Gamma\Gamma_\gamma}{4(E-E_0)^2 + \Gamma^2} \tag{2.14}$$

In this expression Γ is the total line width of the resonance absorption line, Γ_γ its gamma ray width, and σ_0 the maximum resonance cross-section given

$$\sigma_0 = \frac{2I_e + 1}{2I_g + 1}\frac{\lambda^2}{2\pi}$$

where I_e and I_g are spins of the resonant nucleus in the excited state and the ground state.

Scattering and absorption cross-sections as given by (2.13) and (2.14) show a characteristic energy dependence of the form

$$\text{I (E)} = \frac{\Gamma/2\pi}{(E-E_0)^2 + (\Gamma/2)^2} \qquad \text{which is normalized to } \int_0^\infty I(E)dE = 1$$

Corresponding curves have sketched in Fig.2.4.This distribution are said to show a Breit-Wigner or Lorentz shape. The parameter Γgives the full width of the distribution at half maximum.

The width of the level is given entirely by decay processes. In nuclei, the two competing modes are γ-ray emission and internal conversion. The total width and gamma-ray width are then related by the equation $\Gamma_\gamma = \frac{1}{1+\alpha}\Gamma$

where α is the coefficient of internal conversion which describes the probability of re-emission of a photon and not.

Consequently, scattering and absorption cross-sections assume the forms [1]

$$\sigma_{Scatt}(E) = \frac{\lambda^2}{4\pi}\frac{2I_e + 1}{2(2I_g + 1)}\frac{\Gamma^2}{(E-E_0)^2 + \frac{\Gamma^2}{4}}\frac{1}{(1+\alpha)^2}$$

$$\sigma_{abso}(E) = \frac{\lambda^2}{4\pi}\frac{2I_e+1}{2(2I_g+1)}\frac{\Gamma^2}{(E-E_0)^2+\frac{\Gamma^2}{4}}\frac{1}{(1+\alpha)}$$

It is easy to see that both σ_{abs} and σ_{scatt} vary as the square of the wavelength of the the incoming radiation. Thus, the maximum resonance cross-section for γ-rays with energies ranging from few kev to few Mev is 10^6 to 10^{12} times smaller than the corresponding cross section for optical radiation. For both σ_{abs} and σ_{scatt} to be large, both E_γ and α should be small.

2.4 Recoilless fraction

In the solid-state, atoms under consideration are more or less rigidly bound to the lattice and they can not recoil as if they were free. If a γ-ray is emitted from the excited nucleus, the concomitant recoil energy may be assumed to consist of two parts [11],

$$E_R = E_{tr} + E_{vib}. \qquad (2.15)$$

E_{tr} is the translational energy transferred through a linear momentum to the crystallite as a whole, which accommodates the nucleus under consideration. E_{tr} may be evaluated using the formula (2.9), in which M stands now for the mass of the whole crystallite. Because of very large mass of the crystalline, E_{tr} can be neglected.

Due to the fundamental quantum nature of solids, atoms bound in solids are restricted to a specific set of vibration called phonon energies. The phonon energies are quantized and the recoil energy only be transferred to the lattice if it is corresponds closely to an allowed quantum jump. If the recoil energy is larger than phonon energy, the lattice will absorb the recoil energy. However, if the recoil energy of a free nucleus is smaller than the phonon energy ($\hbar\omega_E$), the probability of emission of a phonon will be small, the lattice will not be excited and the γ-ray will escape with the full transition energy.Thus, there is a certain probability f that no lattice excitation (energy transfer of $0\hbar\omega_E$, called Zero phonon – process) takes place during the γ-emission or γ-absorption process. The probability f for a transition without energy loss is called the *recoil free fraction* and denotes the fraction of nuclear transitions which occur without recoil. We may therefore write (for $E_R << \hbar\omega_E$)

$$E_R = (1 - f)\hbar\omega_E \qquad (2.16)$$

and

$f = 1 - E_R / \hbar\omega_E = 1 - k^2\langle x^2\rangle$, (2.17)

where $\langle x^2\rangle$ is the expectation value of the squared vibrational amplitude in the x-direction and k is propagation vector. The recoil free fraction in Mössbauer spectroscopy is equivalent to the fraction of scattering processes of x-rays without lattice excitation. The more general expression for f is :

$f = \exp(-E_R / \hbar\omega_E) = \exp(-k^2\langle x^2\rangle)$. (2.18)

From (2.18) we obtain (2.17) by taking $E_R << \hbar\omega_E$.

The Debye model for solids leads to the following expression for the recoil-free fraction [11]:

$$f = \exp\left[\frac{-6E_R}{k_B\Theta_D}\left\{\frac{1}{4} + \left(\frac{T}{\Theta_D}\right)^2 \int_0^{\Theta D/T} \frac{x}{e^x - 1} dx \right\}\right]$$

which reduced to the approximations

$$f = \exp\left[-\frac{E_R}{k_B\Theta_D}\left(\frac{3}{2} + \frac{\pi^2 T^2}{\Theta_D^2}\right)\right] \quad \text{for } T << \Theta_D, \qquad (2.19)$$

$$f = \exp\left(-\frac{6E_R T}{k_B\Theta_D^2}\right) \quad \text{for } T > \Theta_D \qquad (2.20)$$

k_B is the Boltzmann factor and $\Theta_D = \hbar\omega_D / k_B$ the Debye temperature of the host matrix. From these formulae we notice that

(i) f increases with decreasing recoil energy, i.e., decreasing transition energy Eγ;

(ii) f increases with decreasing temperature;

(iii) f increases with increasing Debye temperature Θ_D. Θ_D may be considered a measure for the strength of the bonds between the atoms and the lattice.

f is generally is called the Lamb-Mössbauer factor.

2.5 Why atomic resonance scattering is readily observable, but not nuclear?

It might be instrunctive to compare nuclear resonance with atomic resonance. For example, consider a system initially in the state of energy E_i making a transition to a final state E_f, through the absorption or emission of a photon of frequency ν. In such a process, we have what is known as a resonant or recoilless transition, for which we have the relationship

$$h\nu = \pm (E_i - E_f) \qquad (2.21)$$

Where "-"corresponds to absorption and "+" to emission. Thus measuring ν determines the level spacing, because of recoil effect and conservation of energy

$$E_i - E_f = \pm h\nu + E_R$$

or
$$h\nu = \pm (E_i - E_f - E_R) \qquad (2.22)$$

where E_R denotes the recoil energy of the system.

we also know that with every unstable energy level there is associated a width ΔE of the nuclear state and a natural lifetime τ of the nuclear state, related through the uncertainty principle as

$$\tau \, \Delta E \approx \hbar$$

Or
$$\Delta E \approx \hbar / \tau \sim \text{uncertainty in } (E_i - E_f)$$

In other words, the exact value of each energy level is uncertain, and can not be defined better than ΔE. Consequently, if the recoil energy is such that $E_R << \Delta E$, then the eq.2.22 is equivalent to eq.2.21 and resonance absorption can take place. For most atomic systems, this condition is satisfied and hence resonance fluorescence is observed whereas in the nuclear system emitting γ-rays, this condition in most cases is not satisfied and hence fluorescence is not observed. That is, if $E_R >> \Delta E$ it is then impossible to excite the system to a higher level through resonant absorption within the bound provides by the uncertainty relation [9].

To appreciate this more fully, consider an atom with A=100. The typical spacing of atomic levels is of the order of 1 ev ; let us therefore consider absorption of a photon of energy of $h\nu = 1$ ev. For this case, $Mc^2 \approx 100 \times 10^3$ Mev $= 10^{11}$ ev, and, consequently,

$$E_R = \frac{(h\nu)^2}{2Mc^2} = \frac{(1ev)^2}{2x10^{11} ev} = 5 \times 10^{-12} \text{ev} \qquad (2.23)$$

Because typical lifetimes associated with excited atomic levels are about 10^{-8} sec, we see that

$$\Delta E \approx \hbar / \tau \approx \frac{6.6x10^{-22} Mev - \sec}{10^{-8} \sec} = 6.6 \times 10^{-8} \text{ev}$$

Consequently, $E_R << \Delta E$, and for atomic transitions resonant absorption can take place. On the other hand, the small excitation energies lead to so small an experimental effect, that eq. 2.4 can not be satisfied. Optical spectra are therefore not suitable for investigation of very small energy shifts which arises in the theory of relativity or from other macroscopic causes.

In contrast, typical nuclear spacing have hν ≈ 100 Kev = 10^5 ev. If we consider a nucleus with A = 100, we again have $Mc^2 \approx 10^{11}$ev and, therefore, in this case, the recoil energy is given by

$$E_R = \frac{(h\nu)^2}{2Mc^2} = (10^5 \text{ ev})^2 / 2\text{x}10^{11}\text{ev} = 5\text{x}10^{-2}\text{ev}$$

A typical lifetime for nuclear levels can be taken as about 10^{-12}sec, so that

$$\Delta E \approx \hbar/\tau = \frac{6.6x10^{-22} Mev - s}{10^{-12} s}$$

$$= 6.6 \text{ x } 10^{-10} \text{ Mev} = 6.6 \text{ x } 10^{-4} \text{ ev}$$

It is clear, therefore, that for these nuclear transitions $E_R >> \Delta E$, and resonant absorption is not possible. For resonant absorption to take places in nuclei, the recoil energy must some how be reduced, and this done beautifully through what is known as Mössbauer effect. Table2.2 gives the values of natural width & recoil energies for some typical spectral lines in the visible range and the γ-ray region [1].

Table 2.2 Comparison of the characteristics of the Atomic & Nuclear transition.

Transition system	Transition energy E_o	Recoil energy E_R	Natural width Γ
Atomic Hg	4.9 ev	$1.5\text{x}10^{-10}$ ev	$5.6\text{x}10^{-9}$ev
Nucleus ^{198}Hg	412 kev	0.92 ev	$1.8\text{x}10^{-5}$ev
Atomic Sodium D line	2.10 ev	19^{-10} ev	$4.4\text{x}10^{-8}$ev
Nuclear γ-rays from ^{119}Sn	23.8 kev	$2.5\text{x}10^{-3}$ ev	$2.4\text{x}10^{-8}$ev

2.6 Methods to observe resonance scattering

Before Mössbauer's discovery people had tried varies methods to artificially make up for the recoil energy loss and to achieve at least a partially overlap of the emission and the absorption lines [7].This method consisted in supplying from the out side the $2E_R$ difference between the energy of the emitted gamma ray and the energy needed for absorption.

One way to supply this difference is to spin the source on a high speed rotor in order to increase the energy of the gamma rays by giving them a Doppler shift. The magnitude of this Doppler shift may obtained, correct to first order in v/c (where v is the velocity of gamma ray source in the direction of emission) by a simple nonrelativistic calculation [5].

Let us assume that a wave is emitted by the source starting at a time t = 0 and let us take snapshot of this wave at the latter time t =T, where T is the period of the wave (see Fig.2.8).

If the source were at rest, the wave would be represented by the upper curve and would have a length $\lambda = cT$. But because the source is in motion with velocity v, the back end of the wave is emitted a distance vT to the right of where the front end had been emitted and hence the wave length is shorted by an amount $\Delta\lambda = VT = V/\nu$, where ν is the unperturbed frequency of the radiation.[5]

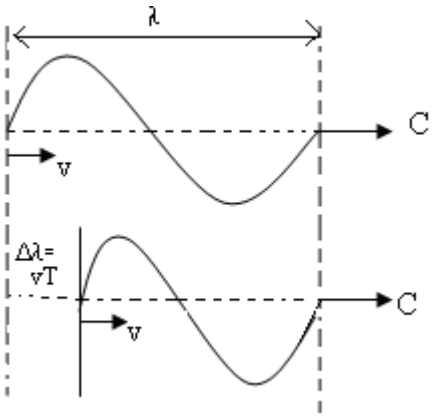


Fig.2.8. Doppler shift in wavelength and frequency of radiation emitted by a moving nucleus

Since the velocity of the radiation is unaffected by the velocity of the source we have, from $\upsilon = c/\lambda$, that the frequency is increased by an amount

$$\Delta\upsilon = \left(\frac{V}{c}\right)\upsilon_0$$

The energy of the radiation is therefore increased by an amount

$$\Delta E = \hbar\,\Delta\upsilon = \left(\frac{V}{c}\right)E_0$$

Thus we see that a Doppler shift of $\Delta E = 2E_R$ requires a linear velocity of E /Mc, which amounts to about 3×10^4 cm/sec for a typical case (E = 100 kev, A = 100)

Another method involves varying the temperatures of the source and the absorber over wide ranges, to Doppler broaden the gamma spectra. Temperature ranges comparable to the recoil energy must be used in order to obtain an observable overlap of the emission and the absorption spectra.

A third method utilizes as a source a nucleus which is recoiling from the previous decay. The decay product is required, by coincidence techniques, to be traveling in a specified direction relative to the direction of the subsequently emitted gamma, thus fixing the component of the velocity of the nucleus along that direction and the Doppler shift in the gamma energy.

Despite these very ingenious experiments, classical nuclear resonances fluorescence experiments did not attain much success since the emission and absorption lines are Doppler broadened and the cross-section for fluorescence is very small. Their most serious drawback is that they can not restore the natural width of the lines from their recoil broadened state. In spite of these difficulties many interesting experiments have been performed since 1950. The difficulties explain to a large extent the slow development of the resonance fluorescence of gamma rays.

2.7 The Mössbauer Effect

The real breakthrough in nuclear resonance scattering of γ-rays came with Mössbauer's discovery at Heidelberg. The Germen Physicist Rudolf L. Mössbauer working in Heidelberg in 1957 demonstrated dramatically and yet accidentally from a completely different side the feasibility of observing nuclear resonance fluorescence by embedding the emitting and absorbing nuclei in a well-bound crystal lattice. He was investigating nuclear resonance scattering of the 129kev gamma rays from ^{191}Ir. For this transition, the free energy recoil E_R is 0.05 ev whereas the Doppler broadening at room temperature is about 0.1 ev. At room temperature, because of the fact $E_D > E_R$, there is an overlap of absorption and emission lines yielding some resonance absorption. In order to determine the background in his experiment, Mössbauer cooled both the source and the absorber with the hope of reducing the Doppler broadening and eliminating the overlap of the absorption and the emission lines. Contrast to his expectation, the resonance fluorescence increased considerably [1].

In order to explain this strange result, Mössbauer used a theory developed by Lamb (1939), this effect was attributed to the fact that in solids the recoil momentum does not always produces a change in the vibrational state of the crystal lattice. Instead, for a fraction of the gamma transitions, the solid as the whole can take up the recoil momentum. Thus, according to this theory, the emission and absorption lines contain very sharp lines of natural width superposed over a broad distribution resulting from the thermal motion of the atoms bound in a crystal lattice. In this case, the correlation between the recoil momentum and energy of the emitting (absorbing) nucleus suffers a discontinuity, since the recoil energy E_R is practically equal to zero on account of a large mass of the crystal: $E_R << \Gamma$. Because of extremely small recoil energy losses, emission and absorption lines appear undisplaced at the resonance energy position, in other words, the shift between these lines

disappears: $E_{em} = E_{ab}$. Consequently, a recoilless emission and absorption of gamma rays becomes possible [6].

Simultaneously, for these acts of emission and absorption the Doppler broadening E_D must disappear, since it will be less than the intrinsic line width Γ. In other words, under the conditions (a very low transition energy and low temperature in comparison with the Debye temperature of the crystal), a sharp recoilless resonance with width equal to the intrinsic line width must be observed. Mössbauer, in one single experiment, achieved the compensation of the recoil and eliminated the Doppler broadening. Mössbauer brilliantly proved this explanation in his famous second experiment.

Mössbauer (1959) demonstrated the existence of these unshifted resonance lines by means of a centrifuge method, employing a velocity of only a few centimeters per second. The experimental arrangement used by Mössbauer is shown schematically in Fig.2.9. Here a ^{191}Ir source emits gamma radiation with energy 129 kev and the absorber is made of iridium. The source and the absorber were placed in cryostats* 1 and 2 in which the temperature of 88 K is maintained. Cryostat 2 containing the source is capable of rotation on heavily marked line. Upon rotation of the cryostat in one direction, the source moves towards the absorber with approximately constant velocity while for rotation in the opposite direction, the source moves away from absorber with the same velocity.

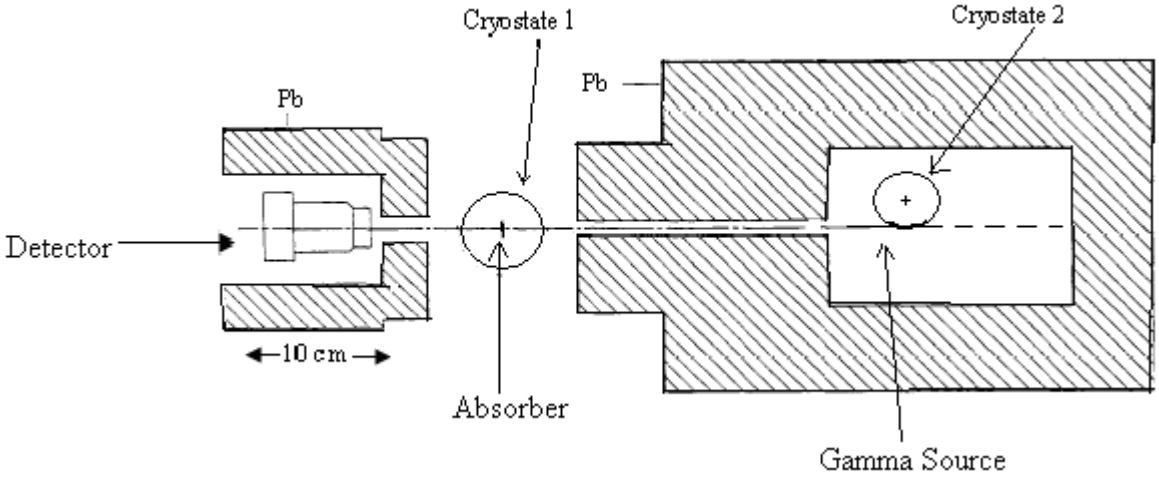


Fig.2.9. Schematic set-up of the original experiment of Mössbauer [1]

* A cryostat is a thermostat for maintaining temperature below 0^0c .

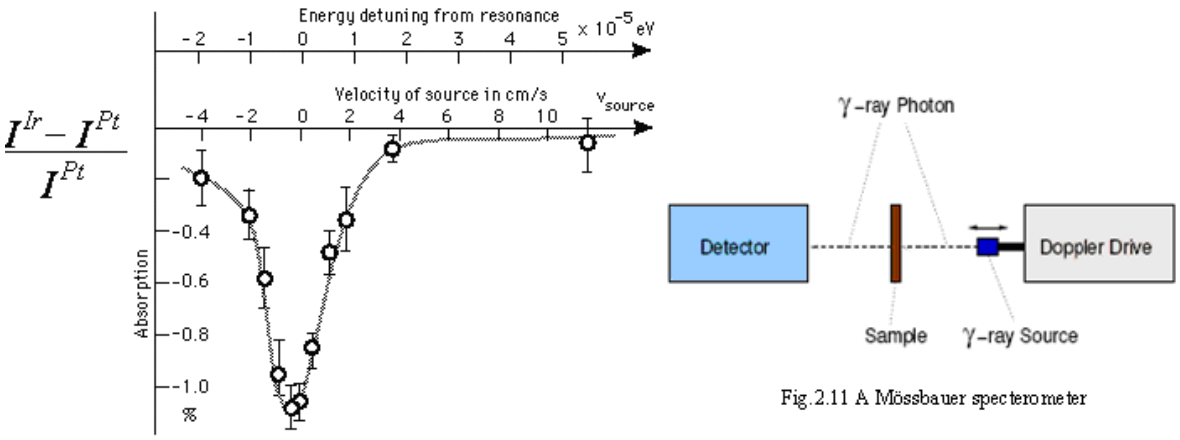


Fig.2.11 A Mössbauer spectrometer

Fig.2.10.Variation of $I^{Ir} - I^{Pt} / I^{Pt}$ as a function of relative velocity between the source and the absorber, I^{Pt} is the count rate with the platinum absorber

The absorption of γ-ray was measured in the experiment for different source velocities. Fig.2.10 shows the result obtained for the129 kev transition in ^{191}Ir. The relative velocity of the source and the absorber, and the corresponding change ΔE in the energy of the emitted rays (due to Doppler effect) are plotted along the abscissa axis. The relative difference in the intensities of the gamma radiation passing through the iridium absorber and a platinum absorber of the same thickness (to estimate the background) are plotted along the ordinate axis. As the figure demonstrates, a maximum resonance absorption was actually present at zero relative velocity as a result of the complete superposition of the recoilless emission and absorption lines; therefore, minimal radiation intensity passing through the absorber was observed in the detector. With increasing relative velocity the emission line was shifted to higher or lower energies, the resonance absorption decreased, and the observed intensity correspondingly increased.

It can be seen from the figure that even at velocities of a few centimeter per second, corresponding to a Doppler shift of less than 10^{-5} ev in the energy of γ-ray, the resonance is disrupted. From the figure, full width at half maximum is about 2cm/s or $1.0\text{x}10^{-5}$ev. This agrees well with the expectation that it should be twice the natural width Γ of the two nuclear states involved, since their measured lifetimes of $\tau = 1.4\text{x}10^{-10}$sec yields $\Gamma = 4.7\text{x}10^{-6}$ev. This means that a recoilless line with intrinsic width $\Gamma \approx 5\text{x}10^{-6}$ ev of gamma transition was indeed observed in the experiment.

In a conventional Mössbauer effect apparatus consists of a radioactive source, an absorber containing the same type of nucleus in the ground state and a radiation detector

such as proportional counter. In a conventional Mössbauer transmission spectrometer shown in Fig. 2.11, a γ-ray source is mounted on a Doppler drive, which usually moves back and forth at a speed on the order of 10-100 mm/s. The photons emitted by the source travel through a thin sample containing an appropriate Mössbauer isotope and the intensity of transmitted photons are measured against the velocity of the source. Nuclear resonance shows up in the spectrum as dips. The extreme sharpness of the nuclear resonance makes this technique useful in many areas of science research. The resonance absorption method can be used for measuring very small energy variations. The measure of the accuracy of this method is the ratio of Γ/E which is equal to $4x10^{-11}$ for the example considered here. Actually, the relative accuracy of measurements is still higher, since it possible to observe experimentally a change in absorption when a line shifts by 1/100 of its intrinsic width.

The various phases in the still young history of the Mössbauer effect are summarized in Table 2.3. [3]

Table 2.3 History of Mössbauer effect

Period	date	Remark
Prehistory	Before 1958	Might have been discovered but not wasn't
Early iridium age	1958	Discovered, but not noticed
Middle iridium age	1958-1959	Noticed, but not believed
Late iridium age	1959-1960	Believed ,but not interesting
Iron age	After 1960	Wow !!

Mössbauer, with Robert Hoftstadtor of the united state, was awarded the Noble Prize in physics in 1961 for the discovery of recoilless emission and absorption of γ-rays.

2.8 Importance of Mössbauer's Discovery

Mössbauer's discovery not only demonstrated for the first time the feasibility of observing resonance fluorescence of γ-rays but it also opened out a possibility of studying a variety of hyperfine interactions between positively charged nucleus and the surrounding electron cloud. Much more important than the zero phonon emission or recoilless emission of γ-rays is the fact that the γ-ray emitted under conditions appropriate to the Mössbauer effect has the natural width determined entirely by the lifetime of the nucleus in the excited state (i.e the possibility of observing nuclear γ-rays with their natural width). Taking the example of the most popular and most worked Mössbauer isotope ^{57}Fe, the 14.4 kev γ-ray emitted as a result of transition from 3/2 state to ½ state has a line width of $4.55x10^{-9}$ ev

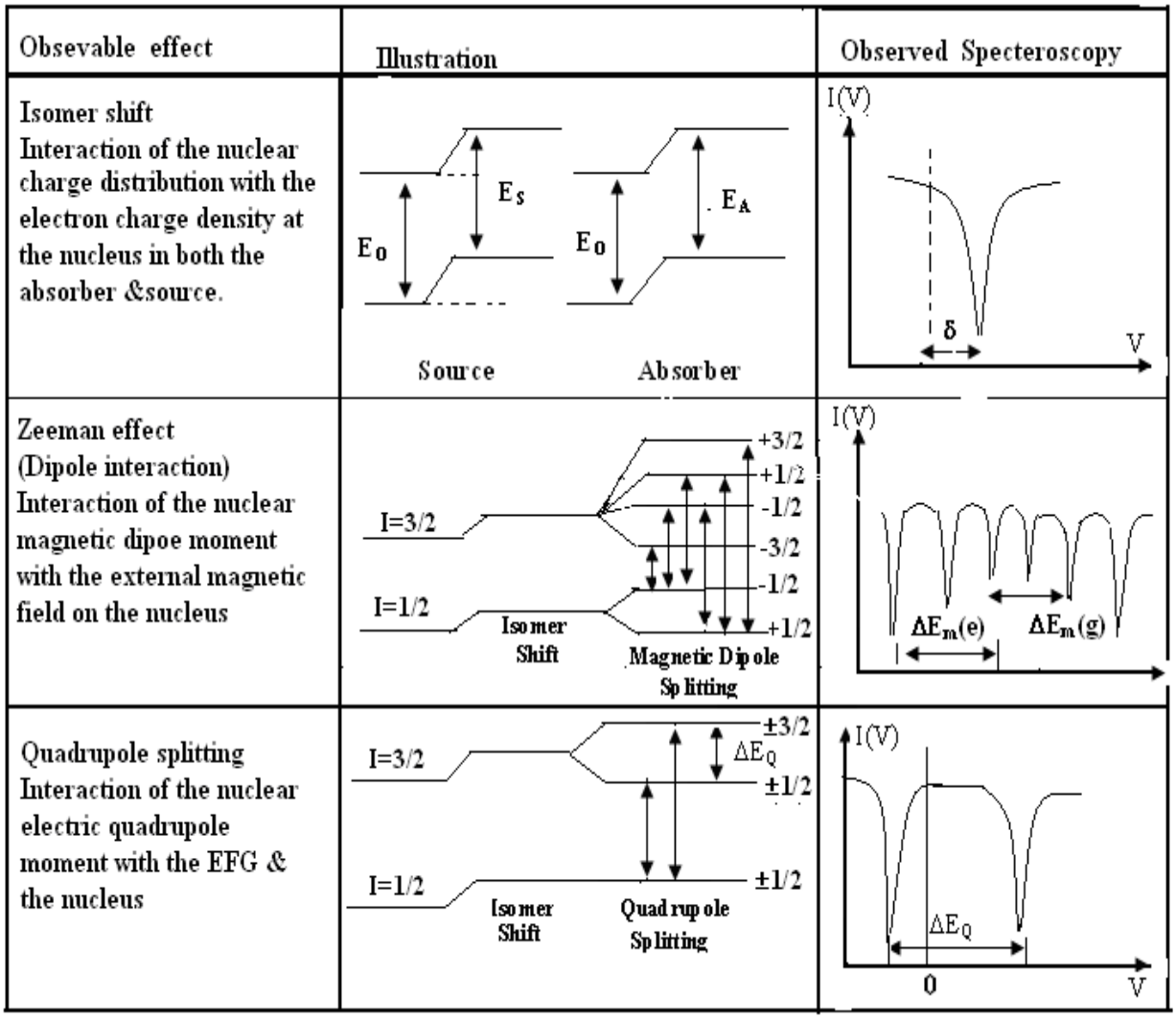
determined entirely by the mean lifetime of the nucleus ^{57}Fe in excited state ($\tau \cong 1.43 \times 10^{-7}$ sec). This is a very small quantity in comparison with the gamma transition energy E =14.4 kev. We can state the same result by saying that the fractional line width of the 14.4 kev γ-ray emitted by ^{57}Fe nucleus $\frac{\Gamma}{E} \cong \frac{4.55x10^{-9}}{14.4x10^{3}} \cong 10^{-13}$. This amounts to saying that we can measure the energy of the γ-ray and in turn the nuclear levels to an accuracy of one part in 10^{13}. This makes Mössbauer emission the most precisely determined electromagnetic radiation available for the physical measurements. With this effect one could investigate any change in the nuclear levels greater than 10^{-9}ev. Significantly, the variety of hyperfine interactions which causes either the shift or the splitting of the levels are greater than this value. Mössbauer effect thus provides a power full tool to investigate a variety of hyperfine interactions [1].

There are three main hyperfine interactions:

- Electric monopole interaction; the nuclear isomer shift
- Electric quadrupole interaction; the nuclear quadrupole splitting
- Magnetic dipole interaction; the nuclear Zeeman effect

Only these three kinds of interaction have to be considered in practical Mössbauer spectroscopy. Electric dipole interaction does not exist because of symmetry arguments (invariance of nuclear forces relative to change in size of coordinates). Interactions of higher order are negligible; their energy effects are so small that they can not be resolved in Mössbauer spectrum. Most valuable chemical information can be extracted from these Mössbauer parameters δ, ΔE_Q, ΔE_M.

Fig.2.12 Nuclear Hyperfine Interactions Observable with Mössbauer spectroscopy



The simplicity of the equipment required to observe it, the elegance of the technique and the phenomenal accuracy it yields has caught the imagination of several physicists all over world and its investigations have led to various application to diverse domains of science such as Nuclear physics, Solid state physics, Chemistry, Biology, etc.

In the chapter 3 we shall attempt to bring out some of the application of this remarkable effect.

Chapter 3

Applications of Mössbauer effect

Mössbauer's discovery has had far-reaching consequences because it has made available electromagnetic radiation (gamma rays) whose energy is more precisely defined then any other known to date and has provided a new technique for measuring the interaction of nuclei with their environment and answering many of the most interesting questions we have in science examples include investigation the surface of Mars, developing an understanding of the nano-world and the studies of corrosion. Energy resolution better than one part in 10^{12} has been achieved with recoil-free gamma rays. This is the same ratio as 1 second compared with 3000 years. Electromagnetic radiation with comparable stability and line width has not yet been obtained by other means. The narrow-line gamma rays have made it possible to perform experiments which had been post pond in the hope that more stable oscillations or clocks would become available. Here we consider some examples from nuclear physics, general physics, solid-state physics and chemistry.

3.1 Measurement of Lifetime of excited state

In conventional nuclear resonance scattering experiments one can measure the scattering cross-section and able to deduce the gamma ray width Γ_γ by using equation (2.13). This procedure is rather indirect, and the Mössbauer effect permits a more straight forward approach, yielding both Γ_γ and Γ. The total line width Γ_{exp} is found by tracing out the absorption or the scattering line by using the Doppler effect, as sketched in Fig.2.10 [3].

The value of Γ_{exp}, depends primarily on the effective thickness T_s and T_a of the source and the absorber. In the limit of thin source and absorber thicknesses, the value is exactly twice the natural line width Γ_γ of the source (i.e. $\Gamma_{exp} = 2\,\Gamma_\gamma$). The Natural line width is related to the nuclear state life time τ vie the uncertainty principle as $\Gamma_\gamma \tau = \hbar$. From the experimental line width one immediately gets the lifetime of the excited state τ by using

$$\tau = \hbar / \Gamma_\gamma \quad \text{or} \quad \tau = 2\hbar / \Gamma_{exp}$$

Measuring line width is a standard technique for measuring lifetimes that are too short for direct measurements.

The measurement Γ of the line width to determine the lifetime was first used by Mössbauer in the a case of ^{191}Ir . This goal was attained, but at the same time a powerful tool for solving other problems was created (Mössbauer effect). In a letter investigation, Mössbauer and Wiedmann (1960) were able to found a value of $\tau = (1.5\pm0.2)\text{x}10^{-11}$ sec for the lifetime of the 134Kev excited state in ^{187}Re. This lifetime was registered as the shortest one that has been determined by the Mössbauer effect.

3.2 Measurement of magnetic moment of excited state

A nucleus with spin will interact with the magnetic field exerted on it and cause splittings of its energy levels. The splittings of the ground state and first-exited state of ^{57}Fe are shown in Fig. 3.2.

The energy associated with this interaction is ΔE

$$\Delta E = -\vec{\mu}.H \qquad (3.2)$$

A nuclear magnetic dipole is related to its spin by

$$\vec{\mu}(S) = g\mu_N S$$

where g is the gyromagnetic ratio, and $\mu_N = \frac{\hbar e}{2m_p}$ is the nuclear magneton. The eigenstates of the Hamiltonian of Eq. 3.2 should be the same eigenstates of operator Sz, where z is the direction of the hyperfine magnetic field $\mathbf{H}_{hf}$. For a nucleus of total spin I, define

$$\mu = g\,\mu_N I$$

The energy eigenvalues are the

$$\Delta E = -g\mu_N H_{hf} M = -\mu H_{hf}\frac{M}{I} \qquad (3.3)$$

where M is the spin eigenvalue in the z-direction. The possible values for M are –I, -I + 1, ..., I.

Thus, the scale of hyperfine splitting is determined by the product of the nuclear magnetic moment ($\mu_n \approx \mu_B = 5.05\text{x}10^{-24}$ erg/G) and the average magnetic field produced by the atomic shell electrons in the region of the nucleus ($\overline{H_e} \approx 10^5$G):

$$\Delta E \approx \mu_B \overline{H_e} \approx 10^{-7}\text{-}10^{-6} \text{ ev.}$$

The typical value of E_n, the energy of transition between nuclear levels, is in the order of 10^4-10^5ev. Hence the relative value of the hyperfine splitting of the nuclear levels is

$$\Delta E/E_n \approx (10^{-7}\text{-}10^{-6})/(10^4\text{-}10^5) = 10^{-12}\text{-}10^{-10}$$

Splitting of this order can be measured only with the help of the Mössbauer effect [6].

Hyperfine splitting of nuclear levels was first discovered in the iron ^{57}Fe. The properties of one of the most widely used nuclie57Fe are given in Table 3.1 and the decay of ^{57}Co to ^{57}Fe is shown in Fig.3.1 [2]. The splitting of nuclear levels of ^{57}Fe is shown in Fig.3.2. For ^{57}Fe the ground state of the spin ½ splits into 2 sublevels, and the first excited state of the spin 3/2 splits into 4 sublevels (Fig.3.2). The two g-factors are

$$g_0 = +0.18121$$

$$g_1 = -0.10348$$

Table 3.1 PROPERTIES OF ^{57}Fe

	Ground State	First excited State
Energy (keV)	0	14.36
Spin & Parity	-1/2	-3/2
Magnetic moment (nm)	0.0903	-0.153
Qudrpole moment (barn)	0	0.29
Mean life (Sec)	stable	1.4×10^{-7}

α Internal conversion coefficient: 9.7 ± 0.2

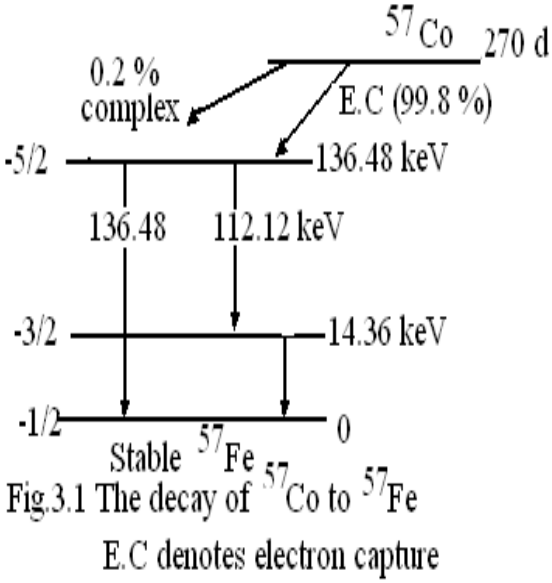


Fig.3.1 The decay of ^{57}Co to ^{57}Fe
E.C denotes electron capture

Consequently, the ground must split into two sublevels with values m = +1/2 and m = -1/2, while the excited state must split into four sublevels with values m equals to +3/2, +1/2, -1/2,-3/2. Between these levels, six gamma transitions are allowed by the selection rules for magnetic dipole transition $\Delta m = 0, \pm 1$. The six allowed transition in ^{57}Fe are shown in Fig.3.2. Such a structure of sublevels is possessed by the emitter nuclei as well as by absorber nuclei. Hence the dependence of the resonance absorption on the velocity of the source must be quite complicated. To simplify this patter the emitter nuclei were placed in a diamagnetic stainless steel grating. In this case, there is no hyperfine splitting for these nuclei and the number of valleys on the experimental Mössbauer spectrum is the same as the number of transitions in the absorber nucleus ^{57}Fe (Fig.3.3).

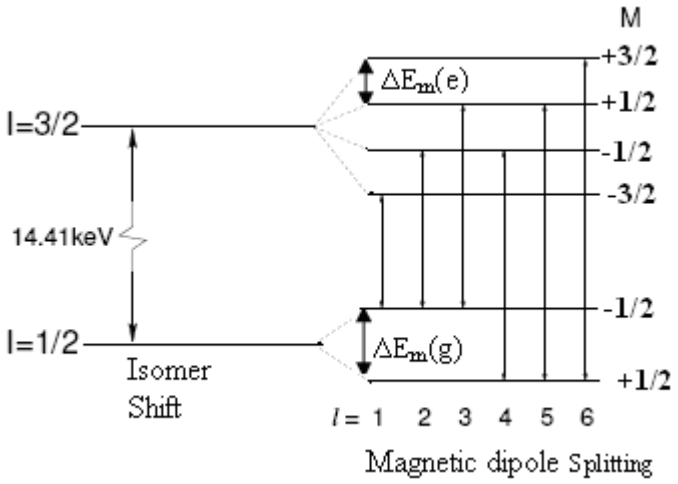


Fig. 3.2-Magnetic hyperfine splitting of nuclear levels in ^{57}Fe, showing allowed transitions.

The splitting $\Delta E_m(g)$ and $\Delta E_m(e)$ for the ground and excited states of ^{57}Fe, as well as the sequential order of the magnetic quantum number m for excited state sublevels (Fig. 3.2), can be calculated by analyzing the experimental curve (Fig.3.3). This allows us to calculate the average magnetic field due to electrons in the region of the nucleus ^{57}Fe from $\Delta E_m(g)$ and known value of the magnetic moment of ^{57}Fe in the ground state ($\mu_{gr} = 0.09\ \mu_B$):

$$\overline{H_e} = 3.33 \times 10^5 \text{G}.$$

In turn, the value of $\overline{H_e}$ obtained in this way can be used to determine the numerical value and sign of the magnetic moment of the excited state of the nucleus ^{57}Fe with help of the value $\Delta E_m(e)$ and the alternation of the quantum number m.

$$\mu_{exc} = -0.153\mu_B$$

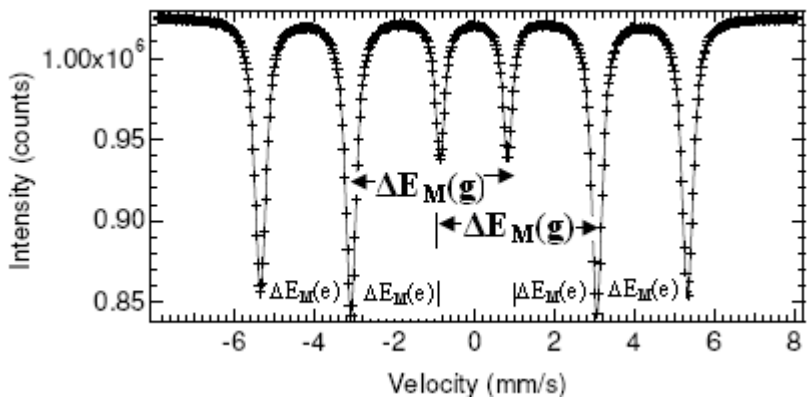
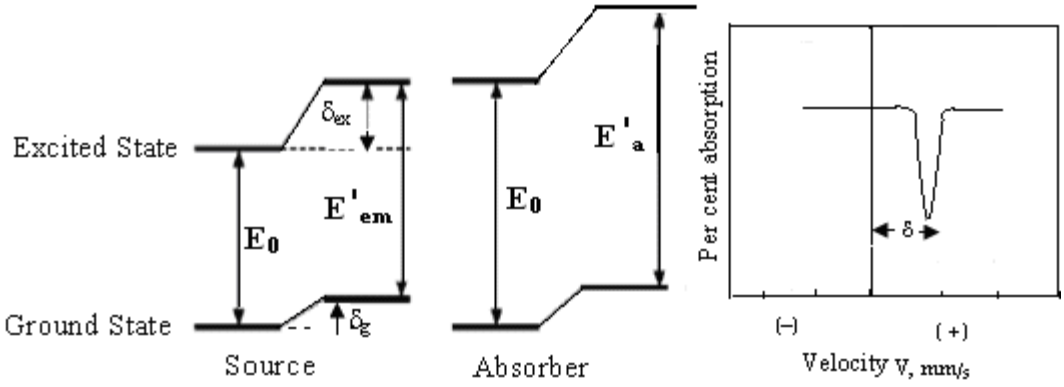


Fig. 3.3 Atypical Mössbauer Spectrum of natural Fe

3.3 Estimation of nuclear radius in the excited state

So far, by the energy of the Mössbauer transition we have meant the difference in the nuclear energies in the excited and the ground states. However, experiments are conducted not with bare nuclei but with atoms, i.e. with nuclei surrounded by electrons. The interaction of the nucleus with electron shell leads to a shift of nuclear and electron levels (in the same way as the hyperfine splitting which is manifested for nuclear as well as electron levels).



(a) (b)

Fig.3.4 (a)Isomer shift. The effect of the electric monopole interaction is to shift nuclear levels without lifting the spin degeneracy.
(b) resultant Mössbauer spectrum (schematic)

The magnitude δE of this shift depends on the binding energy of the electrons with the nucleus, which is determined by the electron density e$|\psi(0)|^2$ in the region of the nucleus, the nuclear radius R, and its charge Ze. The magnitude of the shift in nuclear level is given by [6]

$$\delta E = \left(\frac{2\pi}{5}\right) Ze^2 |\psi(0)|^2 R^2 . \qquad (3.4)$$

If the dimensions of the nucleus in the ground and excited states are different ($R_{gr} \neq R_{ex}$), the energy shifts for the two states will also be different, i.e. $\delta E_{gr} \neq \delta E_{ex}$ (Fig 3.4).The difference ΔE between these quantities gives the correction to the transition energy E_o:

$$E' = E_o + \Delta E, \qquad (3.5)$$

Where $\Delta E = \delta E_{ex} - \delta E_{gr} = \left(\frac{2\pi}{5}\right) Ze^2 |\psi(0)|^2 \{R_{ex}^2 - R_{gr}^2\}$ (3.6)

If the emitter and the absorber atoms are identical, this correction will also be the same for both atoms ($\Delta E_{em}=\Delta E_{ab}$) and would not detune the resonance. However, if the chemical compositions of the emitter and the absorber are different (for identical nuclei), the difference between the binding energies of the electron with emitter and the absorber nuclei (on account of different electron shells, we have $|\psi(0)|^2_{em} \neq |\psi(0)|^2_{ab}$) will cause different shifts in the nuclear levels of the absorber and the emitter ($\Delta E_{em}\neq\Delta E_{ab}$). This will lead to different corrections to the transition energy E' for absorber (E'_a) and the emitter (E'_e). The difference $E'_a - E'_e$ is called the *chemical shift* or *isomeric* shift (δ) of the nuclear levels:

$$\delta = E'_a - E'_e = \Delta E_{ab} - \Delta E_{em} \qquad (3.7)$$

According to the formula (3.6), the chemical shift is given by

$$\delta = \left(\frac{2\pi}{5}\right) Ze^2 \{R^2_{ex} - R^2_{gr}\}\left[|\psi(0))|^2_{ab} - |\psi(0)|^2_{em}\right] \qquad (3.8)$$

The first quantity is of interest of nuclear physicists who want to know if the proton distribution changes when the nucleus is excited while the second quantity is of the interest to solid state physicists and chemists who want information about the electron distribution in a solid.

In some cases (under certain assumption), the expression in the brackets can be calculated. For example, a measurement of the relative velocity which tunes the system to maximum absorption can be used to investigate

either $\{R^2_{ex} - R^2_{gr}\}$ or $\left[|\psi(0))|^2_{ab} - |\psi(0)|^2_{em}\right]$ provided other quantities are known [12]. Hence the measurement of δ can provide an estimate for the radius of the nucleus in the excited state.

The chemical shift is very small ($\delta \approx 10^{-7}$ ev, $\Delta E/E \approx 10^{-12}$) but can be certainly measured with the help of the Mössbauer method. Measurements have shown that a nucleus in the excited state can have a larger or a smaller radius in comparison with the radius of the nucleus in the ground state [6].

$R_{exc}(^{57}Fe) < R_{gr}(^{57}Fe)$ by 0.1 %

$R_{exc}(^{119}Sn) > R_{gr}(^{119}Sn)$ by0.01%

Doppler velocities of about 0.1 mm/sec are required for such measurements

3.4 Measurement of gravitational red shift under laboratory conditions

In relativity studies, the high precision with which the energy of gamma ray can be measured has made possible a direct demonstration of the gravitational red-shift under laboratory conditions, or, equivalently, a test the prediction of Einstein's general relativity prediction that a gamma photon with energy E_γ must behave in the gravitational field as a particle with gravitational mass $m = E_\gamma/c^2$ under laboratory conditions. In essence the gravitational red shift implies a change in the energy of a photon as it moves from a region of one gravitational potential to another. The magnitude of the excited state can be obtained from a simple argument based only the conservation of energy and the relativistic mass-energy equivalence.

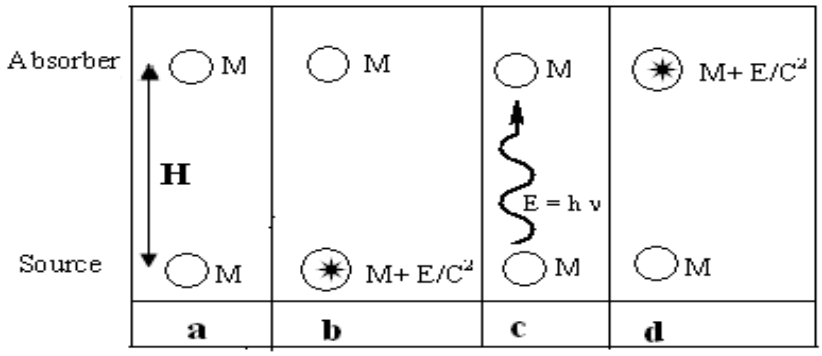


Fig.3.5. Determination of the equation for gravitational red shift

Let us consider a source of mass M at the ground level an identical resonant absorber of mass M at a height H. Let us also assume that one of the nuclei in the source is in the excited state E. The mass of the source becomes, following equivalence principle, $M+E/c^2$. As this nucleus decays to the ground state, it emits a photon of energy $E=h\nu$ and the mass of the source decreases from $M+E/C^2$ to M. As the photon is incident on the absorber, it is absorbed raising the absorbing nucleus to the excited state E. This causes the change in the mass of the absorber from M to $M+E/c^2$.In the effect during emission and absorption processes, we have raised a mass $\Delta M=E/c^2$ through a height H. If the photon does not interact with the gravitational field or if its energy does not change as it moves through a height H, we have in effect got an energy equivalent to $(E/c^2)gH$ out of noting. Indeed in such a case we have made available a system which will be capable of giving perpetual work. If the conservation of energy is to be valid, the photon must interact with the gravitational field or in other words its energy must decrease as it moves up by an amount

$(E/c^2)gH$ (i.e as though it had a mass equal to E/c^2). This would imply a change in the frequency of the photon. The change in the frequency $\Delta\nu$ would be

$$h\Delta\nu = (E/c^2)gH = (h\nu/c^2)gH \qquad (3.9)$$

or $$\Delta\nu = (E/h\,c^2)gH = (E_\gamma/hc^2)gH \quad \text{(redshifted)} \qquad (3.10)$$

The expression for the fraction shift in the energy of the photon may be written as

$$\frac{\Delta E}{E} = \frac{gH}{c^2} \qquad (3.11)$$

The fractional shift in the energy of the photon according to this eq.3.11 is 1 part in 10^{16} per meter path at surface of the earth.

The experiment was carried out in 1959 by Pound and Rebka in 22.6 m high tower of physics laboratory of Harvard University. For such a length of the path of a photon, the fractional shift in energy was $\Delta E/E \approx 2.5 \times 10^{-15}$, which is about 1/150 of the fractional line width $\Gamma/E \approx 3 \times 10^{-12}$ for the ^{57} Fe isotope used in the experiment. The experiment of Pound and Rebka was done in the transmission geometry with the source at the top and the absorber ^{57}Fe foil and the detector at the bottom of a 22.6m tower. Their experimental set-up is shown in Fig.3.6

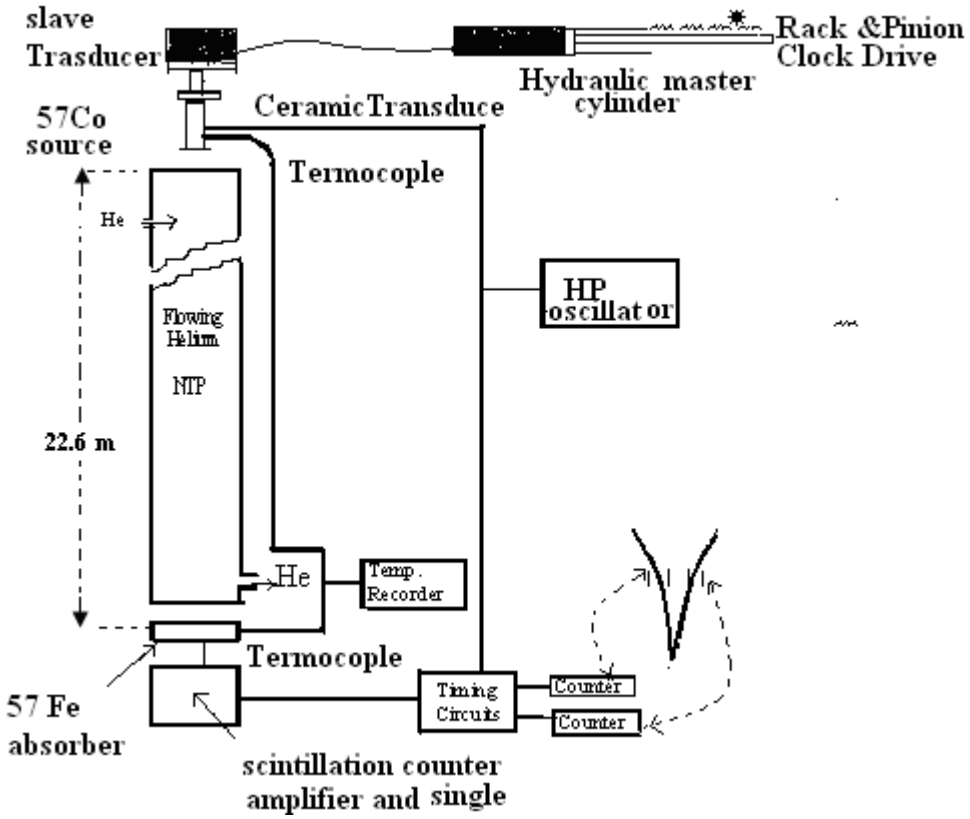


Fig 3.6 The experimental set-up of Pound and Rebka (1960) for red shift experiment[2].

To measure the small shift, which is only a fraction of the natural linewidth, they used the velocity modulation method. In this method one shifts the source of gamma ray energy back and fourth between the steepest parts of the resonant absorption curve. The difference in the counting rate provides information on narrow shifts. It is also advantageous to provide an additional superposed velocity so as to compensate the red shift. The required velocity is 0.75 μm/s. This relative velocity was provided by a hydraulic cylinder. The result obtained is consistent with the shift predicted by eq. 3.11. Thus, they confirmed the prediction of the theory of relativity that the photon energy changes as it moves from a region of one gravitational potential to another. It is interesting to note that the registered terrestrial effect is 10^9 weaker than the solar effect measured by astrophysics method.

3.5 **Mössbauer effect and Solid state physics**

Applications in solid-state physics fall broadly into categories of lattice dynamics and hyperfine interactions, although contributions have been made in other science. Quantities such as the Lamb-Mössbauer factor, the line shape, the line splitting, and line shift can be measured in a Mössbauer experiment. The fact that these quantities can be determined under a wide variety of conditions and with a wide range of parameters makes the recoilless gamma ray emission and absorption such a power full tool in solid-state physics. The choice of the parameters to be varied determines which solid-state properties will be investigated [3].

Mössbauer effect probes the dynamics of the probe nucleus and gives information regarding the atomic motion of the probe nucleus. It can also give considerable information about the dynamical properties of the impurity atoms in the crystal. There dose not seem to be any other method at the present time yielding information about the mean square amplitude and mean square velocity of the atom in the crystal.

Magnetic hyperfine interactions have been particularly useful in the study of magnetically ordered material, i.e., ferromagnets, ferrimagnet, and antiferromagnets. The hyperfine interaction gives an indirect measure of the magnetization of their lattice of magnetic ions and has been used to elucidate the details of magnetic interactions as well as their temperature dependence.

The Mössbauer effect is the youngest of the nuclear guests in solid-state physics. It fits in well indeed with the older ones, complementing them in some areas and allowing

checks in others. Table 3-2 lists the major nuclear tools in solid-state physics and indicates the areas of information, which they have in common with the Mössbauer effect.

Table 3-2 Nuclear Tools in Solid-state physics

Tools	Topics in common with Mössbauer effect
X-ray diffraction	-Lattice dynamics
Neutron diffraction	-Lattice dynamics -Magnetic properties
Nuclear magnetic resonance	-Internal fields -Atomic wave functions at the nucleus
Angular correlation Oriented nuclei	-internal fields -Aftereffects of radioactive decays

Some of typical applications of Mössbauer effect to solid-state physics are for the studies of [3]

- lattice properties
    - the Lamb-Mössbauer factor
    - phonon spectra
    - diffusion
    - lattice specific heat
    - pressure effects
- impurities and imperfection
- internal fields
- low temperature topics
    - nuclear orientation
    - superconductivity

3.6 Chemical application

The chemical application of Mössbauer's discovery turned out to be particular broad and fruitful. The three components of the hyperfine interaction, namely, the isomer shift δ, the nuclear electric quadrupole splitting ΔE_Q, and the nuclear magnetic dipole splitting $\Delta E_{M,}$ have immediate chemical applications.

3.6.1 Isomer shift

The isomer shift measures the charge density of the atomic electrons at the nucleus (i.e. s-electrons) and is directly related to chemical bonding and covalency. A measurement of isomer shift provides the information about chemical environments (through $\psi_{ab}(0)$). It is used frequently to identify states of oxidation or spin.

The isomer shift has the distinction of yielding information which is unique to Mössbauer experiments, and consequently has attracted the greatest attention. The different isomer shifts associated with common valance states were first reported for ^{57}Fe and ^{119}Sn. More recently, valance-state-dependent isomer shifts have also been established in ^{125}Te, ^{129}Ir, ^{151}Eu, and^{197}Au. There is every indication that this list will continue to grow. The recent discovery of xenon compounds was rapidly followed up by Mössbauer investigations of ^{129}Xe in these the novel materials. The Mössbauer effect of ^{83}Kr bound in clathrates had been previously reported.

3.6.2 Quadrupole splitting

Splitting of nuclear level also occurs if the nucleus has an electric quadrupole moment and is situated in a spatially varying electric field. The quadrupole splitting depends on the gradient of the electric field produced by the other ions in the lattice. It is, therefore, intimately related to the point symmetry of the lattice surrounding atom under study and yields structural information. Then measurement of the Mössbauer peak separation can be used to obtain information about the electric field gradient at the nucleus. For example, Mössbauer studies have been used to determine the number of bonds by atoms in solids.

The quadrupole splitting may help to define chemical structure because it sensitive to the point of symmetry of the immediate environment of the atom under observation. The absence of quadrupole splitting is indicative of cubic or near-cubic site symmetry; its presence, of significant distortion.

3.6.3 Magnetic Dipole Splitting

The Magnetic hyperfine splitting has a number of applications. It allows immediate identification of magnetically ordered structures and makes possible the determination of Curie and Neel temperatures. The field is proportional to the magnetization, which follows Brillion function. Using the Mössbauer effect it is possible to distinguish between ferromagnetism and antiferomagnetes by apply a magnetic field along the axis of magnetization, but generally speaking, a susceptibility measurement is preferable. The technique has been applied to the study of metal-organic compounds of iron and tin, including Mössbauer hemoprotins; to inorganic compounds of iron, tin, iodine, and the rare earths; as well as to catalysts, and glasses containing dilute Mössbauer isotopes.

Generally, the chemical and physical state of a Mössbauer atom in any kind of solid material can be characterized by way of the hyperfine interactions which manifest themselves in the Mössbauer spectrum by the isomer shift and, relevant electric quadrupole and magnetic dipole splitting of the resonance lines. On the basis of all the parameters obtainable from a Mössbauer spectrum it is in most cases possible to identify unambiguously one or more chemical species of a given Mössbauer atom. This, usually called phase analysis by Mössbauer spectroscopy, is widely used in various kinds of physico-chemical studies [13], e.g., studies of

-solid-state reactions
-spin and magnetic transitions
-frozen solutions
-corrosion processes
-catalysis
-aftereffect of nuclear transitions
-biological systems
-problems in metallurgy
-minerals
-ancient pottery, etc.

Chapter 4

Summery and Discussion

(1) Nuclear gamma ray fluorescence is the process in which gamma rays from the decay of an excited state in the nuclei of a source are *resonantly* absorbed or scattered by the excitation of the same state in the identical nuclei of the target.

(2) The difficulties in observing resonance scattering are

i) For nuclear transitions involving gamma emission in the 0.1-1Mev range, the recoil width is typically much greater than the natural line width. The recoil of the emitting nucleus implies that the emitted γ-photon can not be absorbed by an identical nucleus because of its energy is reduced by an amount greater than the natural line width of potential absorbing levels. Thus, it is not possible to observe resonance scattering of γ-rays.

ii) Since the maximum absorption and scattering cross-sections are inversely proportional to the square of the photon energy, even if there is a small overlap of the emission and the absorption lines in the γ-ray region, the small cross-section for both resonance absorption and scattering makes it very difficult to observe resonance scattering of γ-rays.

(3) The Mössbauer effect is the nuclear process permitting recoil-free emission and resonant absorption of nuclear γ-ray *in a solid lattice* without degradation by recoil or thermal broadening and it gives an energy distribution dictated by the Heisenberg uncertainty principle. It is made possible by fixing atomic nuclei in the lattices of solids so that the energy is not lost in recoil during the emission and absorption of radiation. That is ,it can occur if the recoil energy can not excite lattice vibrations and the particular nucleus does not change its state.

- Mössbauer effect is optimized for low energy gamma rays with the nuclei strongly bound in a crystal at low temperature.
- Mössbauer effect is unique in that it produces a means of eliminating the distractive effects of the recoil and thermal energies.
- Mössbauer method is so sensitive that if one solid moves relative to the other with a velocity as small as a 10^{th} of a cm per second or if the energy state the radiating or the absorbing nuclei is disturbed by any external effect the resonance is destroyed by the Doppler shift in the γ-ray energy. Then, by varying the relative

velocity of the radiating and the absorbing solids useful resonant absorption is reestablished, the precise magnitude of the destroying effect can be determined. In this fact lies the usefulness of the Mössbauer effect as a tool of experimental physics.

-Mössbauer effect allows nuclear physicists to probe the state of nuclei and the interaction between nuclei and their environment.

-Mössbauer effect enables precision studies of a wide range of small effects through spectroscopy on nuclei.

(4) Mössbauer resonance to be an easily observable, the following requirements must be fulfilled:-

(i) The energy of the γ-ray must be between 10 and 150 keV preferably less than 50 keV, because the recoil-free fraction f and the resonant cross-section σ_o both decreases as E_γ increases.

(ii) The half-life of the first excited state which determines Γ should be between about 1 and 100ns. If $t_{1/2}$ is very long, then Γ is so narrow that mechanical vibration destroy the resonance condition, and if $t_{1/2}$ is very short then Γ will probably be so broad as to obscure any useful hyperfine effects.

(iii) The internal conversion coefficient α should be small (<10) so there is a good probability of detecting the γ-ray.

(iv) a long-lived precursor should exist which can populate the required excited level. This usually means an isotope which decays by β-decay, electron capture, or isomeric transition

Despite these restrictions, Mössbauer has been observed in more than 100 isotopes and about 120 excited states (transitions) in 44 elements, the majority of the heavy elements in fact. However, most of the practical applications of the effect in the technique known as Mössbauer spectroscopy have been with a much smaller number of isotopes in which the conditions for observing the Mössbauer effect and obtaining useful information from it are particularly favorable.

In the last 50 years, Mössbauer spectroscopy has made a great impact on a wide variety of scientific disciplines: many branches of chemistry and physics, biochemistry, the earth sciences and metallurgy to name a few.

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