

AN INTRODUCTION TO
THE THEORY OF THE MÖSSBAUER
EFFECTS FOR CRYSTALS

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ABSTRACT

Ever since the discovery of the Mössbauer effect in 1958, it has been recognised as a valuable tool in many branches in physics, notably in solid state physics, nuclear physics and relativity. This thesis represents an attempt to give a detail review of the basic theory underlying the Mössbauer effect. It must be understood that no original calculation will appear in this work. However, the purpose is to present, in a clear and straightforward manner, an exposition of the general theory to a reader who is assumed to have little or no previous knowledge of the subject. In the first introductory chapter, an account is given of the basic principles of nuclear resonance fluorescence and the related phenomenon of the Mössbauer effect. Then the existence of the so-called "recoilless fraction" and its approximate expression, the Lamb-Mössbauer factor e^{-2M} , are discussed in Chapter II. An exact expression for this fraction has been found by Kaufman and Lipkin, and Chapter III is devoted to presenting the derivation in detail. It is shown that the exact expression is equal to e^{-2M} multiplied by a product of Bessel functions. The contribution of this multiplicative factor can be important for crystals containing defects. Lastly, in Chapter IV, the Lamb-Mössbauer factor is expressed in

terms of the lattice dynamics of the crystal by the method of double-time Green's functions, the treatment by Maradudin et al. This obviously does not cover all the relevant theoretical work for the Mössbauer effect, but it is hoped that the reader may acquire adequate knowledge for further study of the subject.

I. NUCLEAR RESONANCE FLUORESCENCE AND THE MÖSSBAUER EFFECT

Photons emitted from the decay of excited levels of nuclei in a source material may be absorbed or scattered resonantly by the same levels of the same species of nuclei in an absorber. This effect is called nuclear resonance fluorescence. We shall consider the case of a free nucleus first and thus familiarize ourselves with the basic principles of resonance fluorescence. We then outline briefly the case when the resonant nucleus is bound in a crystal. It is in this latter case that emission and absorption of gamma-rays without recoil of the nucleus, the so-called Mössbauer effect, is observed. As we shall see, the Mössbauer effect provides a remarkable method of producing resonance fluorescence.

A. Nuclear Resonance Fluorescence for a Free Nucleus¹

A nucleus in an excited state, with energy E_r above the ground state, can decay to the ground state by emitting a photon. One might think that the photon would carry the full energy E_r as the same amount is lost by the nucleus during the transition. If this were the case, resonance absorption would be readily attained, for the photon could be absorbed by another nucleus of the same species and the transition from the ground state to the same excited state would result. However, this process will generally not occur because the energy of the photon

is not exactly E_r . While the emitted photon does receive the dominant share of the transition energy E_r , a small part is converted into the kinetic energy of the recoiling nucleus.

To be more specific, we assume the nucleus to be at rest before the gamma-ray emission. This condition is removed later. If we denote the energy, momentum and wave vector of the emitted gamma-ray by E , \vec{p} and \vec{k} respectively, the relations among these quantities are as follows :

$$\vec{p} = \hbar \vec{k} , \quad (1a)$$

$$E = |\vec{p}| c . \quad (1b)$$

In order to conserve momentum, the nucleus must recoil, after the gamma-ray emission, with an equal but opposite momentum $-\vec{p}$, since the total momentum is zero. The recoil energy of the nucleus is then given by

$$R = \frac{p^2}{2M'} = \frac{E^2}{2M'c^2} \quad (2)$$

Here, M' denotes the nuclear mass after the photon emission and is equal to the initial mass less the equivalent photon mass of $\delta M = E/c^2$.

Next, we consider conservation of energy. The photon energy E must equal to the difference between the transition energy E_r and the recoil energy R :

$$E = E_r - R . \quad (3)$$

To facilitate an estimate of R , let us express this recoil energy in terms of E_r only. Substituting Eq.(3) into Eq.(2), we obtain

$$R = \frac{E_r^2}{2M'c^2} \left(1 - \frac{R}{E_r}\right)^2 \quad (4)$$

For those transitions for which R is small in comparison with E_r (and therefore with E also) , Eq.(4) becomes

$$R \doteq \frac{E_r^2}{2M'c^2} \quad (5a)$$

and

$$\frac{R}{E_r} = \frac{E_r}{2M'c^2} \ll 1 \quad (5b)$$

Eq.(5b) may be interpreted as showing that for those transitions whose transition energy E_r is small in comparison to its rest energy $M'c^2$, the corresponding recoil energy R is also small as compared to E_r .

It seems appropriate at this point to make an estimate of the value of R in a typical case, that of the 14 keV transition in Fe^{57} . For this case, E_r is 14×10^3 eV. The magnitude of R is thus approximately 2×10^{-3} eV and is indeed small in comparison with E_r , ($R/E_r \approx 1.4 \times 10^{-7}$), thus justifying the use of the approximate equation (5a).

However, small as this recoil energy is, it is not small enough to be neglected in the consideration of the resonance absorption process. Before discussing this point further, let us introduce the idea of the natural line

widths of nuclear gamma rays. It is well known that the mean life against decay of a nuclear excited level, τ , is finite while that of the ground state may be taken as infinite. According to Heisenberg's uncertainty relation, the energy of a state with life-time τ cannot be measured sharply but only within an uncertainty of Γ , given by $\tau \Gamma \sim \hbar$, Planck's constant. Thus while the energy level of the ground state is sharply defined, that of the excited level is not. In fact, by using a perturbation method², the probability distribution of energy for the state is shown to be Lorentzian, centred at the transition energy E_r and exhibiting the half-width, or the natural line width Γ . When normalised to unity, the energy distribution is given by

$$I(E) = \frac{\Gamma}{2\pi} \frac{1}{(E - E_r)^2 + (\Gamma/2)^2}$$

The emission "line", or the photon energy distribution, also maintains the same natural line shape. However, the centre of the distribution is not located at E_r but is displaced to the value $E_r - R$, with R defined in Eq.(5a). This negative energy shift of the entire emission line is a consequence of the recoil of the decaying nucleus, as discussed before.

In the case of photon absorption, the nucleus recoils with the same energy R defined above. Now, the photon must provide the excitation energy as well as the

nuclear recoil. The entire absorption line is therefore shifted again, now having the centre at $E_r + R$ but still maintaining the natural line shape Γ .

Both the emission and absorption lines are shown in Fig.1. It can be seen that if $R < \frac{\Gamma}{2}$, the lines overlap significantly. For a photon of energy E_r , the emission probability is equal to the absorption probability and the resonance absorption effect is largest. At other energy values within the overlapping region, the corresponding emission and absorption probabilities are unequal. Nevertheless, resonance absorption is still possible, though the effect is much smaller. No resonance absorption is possible outside the overlapping region. Now we recognise the importance of the recoil energy R in the process of resonance absorption. A significant amount of resonance occurs if $2R < \Gamma$. Since the natural line widths Γ of nuclear gamma-rays are of the order of 10^{-5} eV or even smaller, and for the case of the 14 keV transition in Fe^{57} , R is of the order of 10^{-3} eV which is larger than Γ by two orders of magnitude, it is clear that resonance absorption is extremely weak for this case.

Now suppose that the nucleus is not at rest initially. Let \vec{p}_i be its initial momentum. After photon emission, the final nuclear momentum is $\vec{p}_i - \vec{p}$. The kinetic energies of the nucleus, before and after the emission, are given by $p_i^2/2M$ and $(\vec{p}_i - \vec{p})^2/2M'$ respectively. To a good

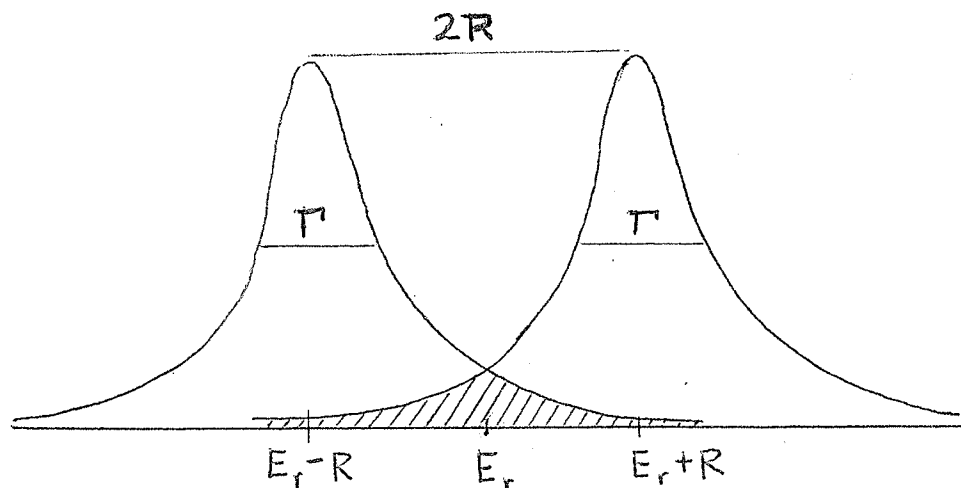


Fig.1. Overlap of emission and absorption lines when a free nucleus, initially at rest, receives a recoil energy R . E_r is the transition energy and Γ , the Γ linewidth of the excited state.

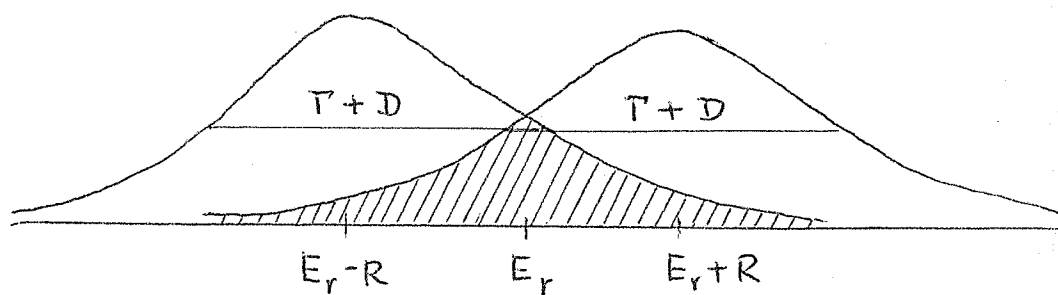


Fig.2. Increased overlap of emission and absorption lines due to Doppler broadening. The linewidth is broadened by an amount of the order D .

approximation, the net recoil energy is therefore given by

$$R' \cong \frac{(\vec{p}_i - \vec{p})^2}{2M} - \frac{\vec{p}_i^2}{2M} \approx \frac{p^2}{2M} - \frac{\vec{p} \cdot \vec{p}_i}{M} \quad (6)$$

The first term on the right hand side is the free recoil energy R . The second term may be written as $D(\vec{p}, \vec{p}_i) \cos(\vec{p}, \vec{p}_i)$ where $D = 2\sqrt{\epsilon R}$ and $\epsilon = p_i^2/2M$. Hence the photon energy becomes

$$E = E_r - R + D(\vec{p}, \vec{p}_i) \cos(\vec{p}, \vec{p}_i) \quad (7)$$

The emission line is thus centred at $E_r - R + D \cos(\vec{p}, \vec{p}_i)$, when the decaying nucleus has an initial momentum \vec{p}_i .

Now, actual experiments are always performed with a large number of nuclei, and a large number of gamma-rays are detected. The initial momentum \vec{p}_i is not the same for every nucleus. Different sets of nuclei with different momenta thus give rise to a spreading of the energy distribution of the emitted gamma-rays. As $\cos(\vec{p}, \vec{p}_i)$ may take any value between -1 and +1, the last term in Eq.(7) essentially broadens the line shape by an amount of the order of D . The height is correspondingly decreased. This effect is called Doppler broadening (see Fig. 2). For an isotropic Maxwellian velocity distribution of the source emitters, this Doppler broadening is of the order of $\bar{D} \cong 2\sqrt{\bar{\epsilon} R}$, where $\bar{\epsilon}$ is the average value of the kinetic energy of the emitters. Similar arguments apply for the case of absorption.

Without going into details, we see that the amount

of resonance fluorescence depends on the amount of overlapping between the emission and the absorption lines, which again depends on the relative magnitudes of R , D and T . At higher temperatures, since the range of nuclear momenta is greater, the lines are broadened further, and hence more overlapping is obtained; while at lower temperatures, the broadening is reduced and hence less overlap occurs. Besides the method of increasing the temperature of the source and the absorber to increase the resonance effect, a more effective method is to shift the lines towards each other, so that complete overlap is obtained if both lines are identical. This may be achieved by moving the source towards the absorber with an appropriate velocity V , for the frequency of the emitted radiation is increased by $\Delta\nu = \left(\frac{V}{c}\right)\nu$, where ν is the frequency of the radiation emitted by a stationary source, and thus a corresponding increase in the photon energy by $\Delta E = h\Delta\nu = \frac{V}{c}E$. It is therefore possible to compensate for the total relative shift of $2R$ due to recoil, by moving the source with a velocity V determined by the relation $\frac{V}{c}E = 2R$.

B. Resonance Fluorescence for a Nucleus Bound
in a Crystal

As we have seen, one of the major difficulties in resonance fluorescence experiments is due to the recoil energy. If the nucleus is bound rigidly to some structure, the recoil will be taken up by the structure as a whole rather than by the nucleus alone. The crystal lattice, though not rigid, provides a suitable structure for this purpose. If the resonant nucleus is bound in a lattice site, the whole system of crystal and nucleus will be involved in any photon emission or absorption process.

In general, the chemical binding energy in crystals is about 15-30 eV. If the free recoil energy R is much larger than this value, the nucleus will be dislodged from its lattice site and the situation simulates the case of a free nucleus. If R is less than this displacement energy and is of the order of the characteristic energy of lattice vibrations (or phonon energy), the nucleus will remain in its site while the recoil energy is transferred into the whole crystal.

Let us now consider the two aspects of momentum and energy transfer during the emission process for a lattice-bound nucleus¹. Momentum and energy must be conserved. As the recoil momentum cannot go into translational motion of the nucleus, it can be taken up by the crystal as a whole or by the lattice vibrations or both.

However, lattice vibrations are standing waves, and the expected value of the momentum is always zero. Thus lattice vibrations cannot store up momentum. The recoil momentum must eventually be taken up by the entire solid. As the mass of the entire solid is very large in comparison to the mass of a single nucleus, we can neglect the translational motion of the solid induced by the momentum transfer. Now, let us turn our attention to energy conservation. The nuclear transition energy E_r can be shared among the gamma-ray, the nucleus, the lattice vibrations and the crystal as a whole. Since the nucleus does not acquire translational energy, and we have neglected the translational energy of the whole crystal already, the transition energy is shared between the gamma-ray and the lattice vibrations, or phonons. This excitation of lattice vibrations, or equivalently the creation of phonons, amounts to an increase in the internal energy of the crystal. We remark that the quantum mechanical average energy transfer to the crystal is just equal to the classical free recoil energy R (see II.B.). We therefore have a situation in which the momentum is picked up by the whole crystal, without any significant amount of accompanying energy going to the centre of mass, while the energy is picked up by the lattice vibrations, without any corresponding momentum transfer to these vibrations.

Now the crystal is a quantised energy system which cannot be excited arbitrarily. There is a finite

probability for each of the many different phonon creation processes at a given energy. In other words, many possible states of excitation of the crystal can occur. In particular there will be a finite probability that the entire solid remains unexcited. In this case, no nuclear energy is converted into the internal energy of the crystal and the emitted gamma-ray carries off the full nuclear transition energy E_r . We shall refer these transitions as the zero-phonon or "recoilless" transitions. It should be understood that the word "recoilless" refers to the transfer of the recoil energy only and not the recoil momentum, as the crystal must carry off the momentum whether the vibrational state of the entire crystal is changed or not during the gamma-ray emission. The existence of these recoilless transitions, i.e. the Mössbauer effect, leads directly to an enhancement in resonance effect as discussed in the next paragraph.

The Mössbauer effect dates back from 1958 when R. Mossbauer was investigating the resonance scattering of the 129 keV gamma-rays from Ir^{191} . For this transition, $R \sim .05$ eV; while, at room temperature, $D \sim .1$ eV. Thus the considerable overlap of the emission and absorption lines accounts for appreciable resonance scattering at room temperature. Mössbauer attempted to reduce this resonance scattering, cooling both source and absorber. Surprisingly, a considerable increase was obtained instead.

This phenomenon was successfully interpreted by Mössbauer, who showed that, at low temperatures, there exists an appreciable fraction of the emitted and absorbed gamma-rays which have participated in recoil-free transitions. The energy distribution of the photons is shown in Fig. 3. The pronounced peak, centred at the transition energy E_r , corresponds to the recoilless fraction, while the "wing" corresponds to those transitions accompanied by phonon excitations. The very narrow linewidth of the unshifted peak is solely determined by the nuclear levels involved, since the lattice is not excited, and is of the order of the natural linewidths of nuclear levels $\sim 10^{-7}$ eV. As the lattice is excited for the other transitions, the "wing" is very much broadened, its effective linewidth being the order of phonon energies $\sim 10^{-2}$ eV.

We have pointed out the condition of low temperatures, when the phonon states are only sparsely populated. It will be shown that the recoilless fraction, and hence the height of the central peak, is very much temperature-dependent, and will become insignificant at high temperatures.

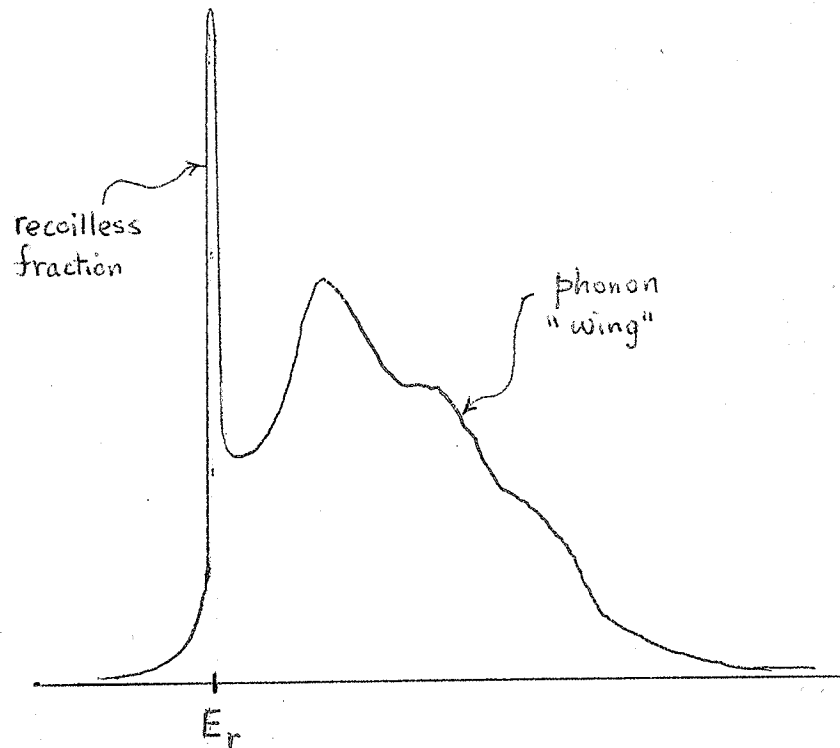


Fig.3. The absorption energy distribution of photons for a nucleus bound in a crystal. The sharp, unshifted line corresponds to recoil-free transitions, or the recoilless fraction; and the broadened "wing" is a consequence of phonon excitation processes.

II. THE RECOILLESS FRACTION AND THE LAMB-MÖSSBAUER FACTOR

In this chapter, the general expression for the recoilless fraction f , i.e. the relative probability for recoilless transitions, is first obtained. The general expression is valid for any model of the crystal lattice because no reference to an explicit model is required for its derivation. For this calculation, the line shape of the nuclear transition is irrelevant, and the Breit-Wigner formula does not come up. The general sum rule due to Lipkin³ is then discussed. Finally, in order to obtain an explicit expression for the recoilless fraction, a more detailed model of the lattice has to be used. For a harmonic crystal, in a state of thermal equilibrium, it is shown that f is given by an exponential e^{-2M} , to a very good approximation. This exponential is called the Lamb-Mössbauer factor or the Debye-Waller factor.

A. General Expression for the Recoilless Fraction

The expression has been shown either by considering the requirements of momentum conservation and Galilean invariance, namely that the transition probability is independent of the velocity of the observer³, or by considering the radioactive transition as a result of the interaction between the electromagnetic field and a nucleon in the decaying nucleus¹. In view of the

elegance intrinsic to the first method, we shall elaborate on it in the following discussion.

First of all, let us consider a state of the entire crystal as an eigenstate of the total Hamiltonian. By the terminology "entire" crystal, we mean the whole system of N nuclei with all the nucleons in each nucleus. In particular, it contains a specified radioactive nucleus, labelled by ℓ , through which gamma-ray emission or absorption occurs as a result of some interaction with the surrounding field. Let us consider the total Hamiltonian more closely. We denote the mass and the position coordinates of the j th nucleon in the k th nucleus by $m_j(k)$ and $\vec{r}_j(k)$ respectively, and the number of nucleons in the k th nucleus by $n(k)$. The total kinetic energy part H_{kin} is readily obtained in terms of these quantities. Let us further denote the potential of the j th nucleon in the k th nucleus by $V(\vec{r}_j(k))$. Then the total Hamiltonian is given explicitly by

$$H = \sum_{k=1}^N \sum_{j=1}^{n_k} \frac{1}{2} m_j(k) [\dot{\vec{r}}_j(k)]^2 + \sum_{k=1}^N \sum_{j=1}^{n_k} V(\vec{r}_j(k))$$

Introducing the centre-of-mass coordinate $\vec{r}_c(k)$ and the relative (or, internal) coordinate $\vec{r}'_j(k)$ for each nucleus k , such that

$$\vec{r}_j(k) = \vec{r}_c(k) + \vec{r}'_j(k) \quad , \quad (1)$$

we can write the kinetic energy part of the Hamiltonian as the sum of two terms, the first term being the kinetic

energy attributed to the centre-of-mass motion of the N nuclei and the second, the internal kinetic energy of the nucleons in each nucleus :

$$H_{kin} = \sum_{k=1}^N \frac{1}{2} m(k) \left[\dot{\vec{r}}_c(k) \right]^2 + \sum_{k=1}^N \sum_{j=1}^{\eta_k} \frac{1}{2} m_j(k) \left[\dot{\vec{r}}_j'(k) \right]^2, \quad (2)$$

where $m(k) = \sum_{j=1}^{\eta_k} m_j(k)$ is the mass of the k th nucleus. Here, we have made use of the fact that the total internal momentum operator of the nucleons in each nucleus is zero, i.e.

$$\sum_{j=1}^{\eta_k} m_j(k) \dot{\vec{r}}_j'(k) = 0 \quad (3)$$

As for the potential energy part, we recognise the fact that the nuclear binding forces among the nucleons in a nucleus are much stronger and more short-ranged than the lattice forces between the nucleus and the other atoms of the crystal. To a very good approximation then, the internal motion of a nucleon inside a nucleus is hardly affected by the external and long-ranged lattice forces, while the centre-of-mass motion of the nuclei is unaffected by the internal, highly-localised nuclear forces. It is equivalent to say that the interaction term involving both internal and centre-of-mass coordinates is negligible in the total Hamiltonian. Hence the potential energy part of the total Hamiltonian, namely H_{pot} , is written as a sum of two terms, one depending on the centre-of-mass coordinates of the nuclei only, the other depending on the internal

coordinates of the nucleons:

$$H_{\text{pot}} = \sum_{k=1}^N V(\vec{r}_c(k)) + \sum_{k=1}^N \sum_{j=1}^{n_k} V(\vec{r}_j'(k)) \quad (4)$$

Combining Eqs.(2) and (4), the total Hamiltonian is expressible as the sum of a lattice part H_{lattice} , and a nuclear part H_{nuclear} :

$$H_T = H_{\text{lattice}} + H_{\text{nuclear}} \quad (5)$$

where

$$H_{\text{lattice}} = \sum_{k=1}^N \frac{1}{2} \frac{(\vec{p}_c(k))^2}{m(k)} + \sum_{k=1}^N V(\vec{r}_c(k)) \quad (6a)$$

and

$$H_{\text{nuclear}} = \sum_{k=1}^N \sum_{j=1}^{n_k} \frac{1}{2} \frac{(\vec{p}_j'(k))^2}{m_j(k)} + \sum_{k=1}^N \sum_{j=1}^{n_k} V(\vec{r}_j'(k)) \quad (6b)$$

Here, $\vec{p}_c(k)$ and $\vec{p}_j'(k)$ are momentum operators conjugate to the position operators $\vec{r}_c(k)$ and $\vec{r}_j'(k)$ respectively.

From Eqs.(5) and (6), we justify a factorisation of a general energy eigenstate $|\Psi\rangle$ for the entire crystal into a direct product of a crystal state vector $|L\rangle$ and a nuclear state vector $|N\rangle$, i.e.

$$|\Psi\rangle = |L\rangle |N\rangle \quad (7)$$

Now $|L\rangle$ depends on the centre-of-mass coordinates of the N nuclei only, whereas $|N\rangle$ depends solely on the internal coordinates of the nuclei.

Following this discussion of the total energy of the entire crystal, let us now consider the total momentum of the same system. We define \vec{P}_T , the total momentum, in terms of the masses and the position coordinates of all the nucleons, thus

$$\vec{P}_T = \sum_{k=1}^N \sum_{j=1}^{n_k} m_j(k) \dot{\vec{r}}_j(k).$$

Again, by the introduction of centre-of-mass coordinates and internal coordinates given by Eq.(1) and the corresponding momentum operators, and using the fact that the total internal momentum of the nucleons in a given nucleus is zero, we see that \vec{P}_T is equal to the sum of the centre-of-mass momentum operators of the N nuclei :

$$\vec{P}_T = \sum_{k=1}^N \vec{p}_c(k). \quad (8)$$

For the sake of later discussion, we single out $p_c(\ell)$ of the ℓ th nucleus which will undergo a nuclear transition accompanied by the emission or absorption of a gamma-ray. Thus we write

$$\vec{P}_T = \vec{p}_c(\ell) + \sum_{k \neq \ell}^N \vec{p}_c(k). \quad (9)$$

We remark that the set of crystal states $\{|L\rangle\}$ and the set of nuclear states $\{|N\rangle\}$ form complete ^{orthonormal} orthonormal sets of eigenstates.

We now proceed to study the energy and momentum transfer to the crystal when a gamma-ray is emitted from the radioactive nucleus, labelled \mathcal{L} , which is bound in the above lattice. For simplicity, let us assume the initial state $|I\rangle$ of the system of the crystal containing a decaying nucleus to be a simultaneous eigenstate of the total Hamiltonian and the total momentum. According to Eq.(7), we then factorise $|I\rangle$ into a product of an initial crystal state $|L_i\rangle$ and an initial nuclear state $|N_i\rangle$, thus $|I\rangle = |L_i\rangle |N_i\rangle$. If the state $|I\rangle$ belongs to the momentum eigenvalue \vec{P}_0 , i.e. $\vec{P}_T |I\rangle = \vec{P}_0 |I\rangle$, then, according to Eq.(9), the initial crystal state $|L_i\rangle$ is also an eigenstate of \vec{P}_T , belonging to the same value \vec{P}_0 . Therefore, we have

$$\vec{P}_T |L_i\rangle = \vec{P}_0 |L_i\rangle \quad (10)$$

Now after the emission of a gamma-ray, a momentum $\hbar\vec{k}$ is carried away from the crystal. Conservation of momentum then requires the total momentum of the crystal to decrease from the initial value \vec{P}_0 to the value $\vec{P}_0 - \hbar\vec{k}$. Thus the final state of the system of crystal and decaying nucleus, denoted by $|F\rangle$, must be a momentum eigenstate belonging to the value $\vec{P}_0 - \hbar\vec{k}$, i.e. $\vec{P}_T |F\rangle = (\vec{P}_0 - \hbar\vec{k}) |F\rangle$. Again the state $|F\rangle$ can be written as a product $|L_f\rangle |N_f\rangle$. Similar to Eq.(10) is the following relation:

$$\vec{P}_T |L_f\rangle = (\vec{P}_0 - \hbar\vec{k}) |L_f\rangle \quad (11)$$

At this point, we remark that we shall limit our discussion

to one particular nuclear transition between the excited state (the initial state $|N_i\rangle$) and a specified ground state (the final state $|N_f\rangle$), so that while there is a probability of finding the crystal in any of its possible final states $|L_f\rangle$, the final nuclear state of the decaying nucleus ℓ is the unique ground state $|N_f\rangle$.

We now come to discuss the transition probability amplitude $c_{i \rightarrow f}$, from the initial state $|I\rangle$ to a final state $|F\rangle$ of the system of crystal including the radioactive nucleus ℓ . It must be the matrix element of some operator A between these two states :

$$c_{i \rightarrow f} = \langle F | A | I \rangle = \langle L_f | \langle N_f | A | L_i \rangle | N_i \rangle . \quad (12)$$

This operator A characterises the interaction between the nucleus and the electromagnetic field around the nucleus. It is unnecessary to go into the detail form of this interaction, but this operator A surely depends on the internal dynamical variables of the nucleons in the nucleus ℓ , namely positions, momenta and spins. We now express A in terms of the centre-of-mass coordinate $\vec{r}_c(\ell)$ of the nucleus, and a set of relative coordinates, denoted by a single symbol q , which includes spins. Thus we have $A = A(\vec{r}_c(\ell); q)$. Furthermore we assume that A may be factored into two separate parts, one depending on the centre-of-mass coordinate only, the other on the relative coordinates q , thus

$$A(\vec{r}_c(\ell); q) = A(\vec{r}_c(\ell)) a(q) . \quad (13)$$

The transition matrix element $c_{i \rightarrow f}$ may now be written as a product of two factors, a lattice part and a nuclear part :

$$c_{i \rightarrow f} = \langle L_f | A(\vec{r}_c(\varrho)) | L_i \rangle \langle N_f | a(\varrho) | N_i \rangle . \quad (14)$$

We are not interested in the absolute transition probability but in the fraction of gamma-rays that are recoilless, i.e. those transitions in which the lattice remains unchanged. This corresponds to the case when the internal state of the lattice in state $|L_f\rangle$ is identical to that in the initial state $|L_i\rangle$. Now we note that the nuclear factor in Eq.(14) is the same for all possible final states of the lattice. Hence for our purpose in calculating the relative probabilities for recoilless transitions or those transitions accompanied by lattice excitations or de-excitations, we may drop this constant factor in our further discussion. The relative probability that a transition to state $|L_f\rangle$ from an initial state $|L_i\rangle$ is then proportional to

$$P(L_i \rightarrow L_f) \propto \left| \langle L_f | A(\vec{r}_c(\varrho)) | L_i \rangle \right|^2 . \quad (15)$$

We now proceed to obtain the form of the operator A, apart from a constant factor, using consideration of Galilean invariance and momentum conservation. Let us consider the matrix element of some operator $A(\vec{X})$ between two arbitrary states $|\psi(\vec{x})\rangle, |\chi(\vec{x})\rangle$ i.e., $\langle \psi(\vec{x}) | A(\vec{x}) | \chi(\vec{x}) \rangle$ where \vec{X} is a position coordinate. From quantum mechanics, this scalar product is invariant under a unitary transformation.

That is, if

That is, if $\langle \psi(\vec{x}') | A(\vec{x}) | \chi(\vec{x}') \rangle = \langle \psi(\vec{x}') | A'(\vec{x}) | \chi(\vec{x}') \rangle$

then
$$A'(\vec{x}) = S A(\vec{x}) S^{-1}, \quad (16)$$

and
$$|\psi(\vec{x}')\rangle = S |\psi(\vec{x})\rangle, \quad (17)$$

where S is a unitary transformation. We may assume S to have an exponential form of e^{iW} , with W hermitian ($W^\dagger = W$). Now let us show the Galilean transformation S_g is also unitary. Thus Galilean invariance is satisfied indeed in non-relativistic quantum mechanics and we may use S_g for S in the above equations (16) and (17).

Under a Galilean transformation, the position and time coordinates are transformed as

$$\vec{x}' = \vec{x} + \vec{x}_0 + \vec{v}t,$$

$$t' = t + t_0,$$

where \vec{x}_0 , t_0 are constants, and \vec{v} is the constant velocity of the primed system relative to the unprimed system. The state vectors are transformed accordingly, and using Taylor's expansion, we have, considering \vec{x}_1 infinitesimal,

$$\begin{aligned} |\psi(\vec{x}')\rangle &= |\psi(\vec{x} + \vec{x}_1)\rangle \\ &= |\psi(\vec{x})\rangle + \vec{x}_1 \cdot \nabla_x |\psi(\vec{x})\rangle + \frac{(\vec{x}_1 \cdot \nabla_x)^2}{2!} |\psi(\vec{x})\rangle + \dots \\ &= |\psi(\vec{x})\rangle + \frac{i}{\hbar} \vec{x}_1 \cdot \vec{p} |\psi(\vec{x})\rangle + \frac{(i/\hbar)^2 (\vec{x}_1 \cdot \vec{p})^2}{2} |\psi(\vec{x})\rangle + \dots \\ &= e^{\frac{i}{\hbar} \vec{x}_1 \cdot \vec{p}} |\psi(\vec{x})\rangle, \end{aligned} \quad (18)$$

since the momentum operator $\vec{p} = -i\hbar \nabla_x$. Hence we see that $S_g = e^{\frac{i}{\hbar} \vec{x}_1 \cdot \vec{p}}$ generates infinitesimal Galilean transformations and effects a shift from \vec{x} to $\vec{x} + \vec{x}_1$ for any

function of \vec{X} . Now \vec{X}_1 and \vec{P} are hermitian operators, hence $\vec{X}_1 \cdot \vec{P}$ is also hermitian. Thus the Galilean transformation S_g is a unitary transformation.

Using this S_g in Eq.(16), the operator $A(X)$ is transformed as

$$A(\vec{X}') = A(\vec{X} + \vec{X}_1) = e^{\frac{i\vec{P} \cdot \vec{X}_1}{\hbar}} A(\vec{X}) e^{-\frac{i\vec{P} \cdot \vec{X}_1}{\hbar}}$$

In particular, for $\vec{X}=0$, $\vec{X}_1=\vec{X}$, we have the general formula

$$A(\vec{X}) = e^{\frac{i\vec{P} \cdot \vec{X}}{\hbar}} A(0) e^{-\frac{i\vec{P} \cdot \vec{X}}{\hbar}}, \quad (19)$$

where $A(0)$ is an operator independent of \vec{X} , and \vec{P} is the momentum operator conjugate to \vec{X} .

Let us now apply this general Eq.(19) to our case of $A(\vec{r}_c(\ell))$ in Eq.(15). It can therefore be written as

$$A(\vec{r}_c(\ell)) = e^{\frac{i}{\hbar} \vec{P}_c(\ell) \cdot \vec{r}_c(\ell)} A(0) e^{-\frac{i}{\hbar} \vec{P}_c(\ell) \cdot \vec{r}_c(\ell)} \quad (20)$$

Now we may replace the momentum operator $\vec{p}_c(\ell)$ by the total momentum \vec{P}_T by using Eq.(9) and the fact that $[\sum_{k \neq \ell} \vec{p}_c(k), \vec{r}_c(\ell)] = 0$. The transition probability is then written as

$$P(L_i \rightarrow L_f) \propto |\langle L_f | e^{\frac{i}{\hbar} \vec{P}_T \cdot \vec{r}_c(\ell)} A(0) e^{-\frac{i}{\hbar} \vec{P}_T \cdot \vec{r}_c(\ell)} | L_i \rangle|^2 \quad (21)$$

Recalling that $|L_i\rangle$ and $|L_f\rangle$ are momentum eigenstates belonging to the values \vec{P}_0 and $\vec{P}_0 - \hbar\vec{k}$ respectively (see Eqs. (10) and (11)), which follows from momentum conservation, Eq.(21) becomes

$$P(L_i \rightarrow L_f) \propto |\langle L_f | e^{\frac{i}{\hbar} (\vec{P}_0 - \hbar\vec{k}) \cdot \vec{r}_c(\ell)} A(0) e^{-\frac{i}{\hbar} \vec{P}_0 \cdot \vec{r}_c(\ell)} | L_i \rangle|^2$$

$$= \left| \langle L_f | e^{-i\vec{k} \cdot \vec{r}_c(\ell)} A(0) | L_i \rangle \right|^2, \quad (22)$$

where $A(0)$ is a constant and may be dropped out in our present calculation of the relative probabilities of occurrences of the various final crystal states. Thus we obtain a general expression for the relative probability that the lattice be excited from state $|L_i\rangle$ to $|L_f\rangle$, with the emission of a gamma-ray of momentum $\hbar\vec{k}$, namely

$$P(L_i \rightarrow L_f) = \frac{|\langle L_f | e^{-i\vec{k} \cdot \vec{r}_c(\ell)} | L_i \rangle|^2}{\sum_f |\langle L_f | e^{-i\vec{k} \cdot \vec{r}_c(\ell)} | L_i \rangle|^2}. \quad (23)$$

Now the denominator is just equal to unity, for the lattice states are normalised. This is seen as follows:

$$\begin{aligned} \sum_f |\langle L_f | e^{-i\vec{k} \cdot \vec{r}_c} | L_i \rangle|^2 &= \sum_f \langle L_i | e^{i\vec{k} \cdot \vec{r}_c} | L_f \rangle \langle L_f | e^{-i\vec{k} \cdot \vec{r}_c} | L_i \rangle \\ &= \langle L_i | e^{i\vec{k} \cdot \vec{r}_c} e^{-i\vec{k} \cdot \vec{r}_c} | L_i \rangle = 1. \end{aligned}$$

Hence the general expression for $P(L_i \rightarrow L_f)$ is given by

$$P(L_i \rightarrow L_f) = \left| \langle L_f | e^{-i\vec{k} \cdot \vec{r}_c(\ell)} | L_i \rangle \right|^2. \quad (24)$$

In particular, the recoilless fraction is given by

$$f = P(L_i \rightarrow L_i) = \left| \langle L_i | e^{-i\vec{k} \cdot \vec{r}_c(\ell)} | L_i \rangle \right|^2. \quad (25)$$

B. A Sum Rule

The sum rule, due to Lipkin³, states that the average energy transferred to the lattice is just equal to the energy the nucleus would have if it recoils freely. It also predicts the existence of recoilless transitions in the crystal. The sum rule, as derived here, is based on two general assumptions. First, the lattice forces are dependent on the positions of the atoms only and not on the velocities. Secondly, the average value of the centre-of-mass momentum of the radioactive nucleus ℓ , in the initial lattice state is zero⁺. For further discussion, let us adopt the abbreviated notation of \vec{r}_k and \vec{p}_k to replace $\vec{r}_c(k)$ and $\vec{p}_c(k)$ in denoting the centre-of-mass coordinate and its conjugate momentum of the k th nucleus, unless specified otherwise. Now that the potential energy is a function of positions \vec{r}_k only, there is only one term in the crystal Hamiltonian $H_{\text{lattice}} = \sum_{k=1}^N \left[\frac{\vec{p}_k^2}{2m_k} + V(\vec{r}_k) \right]$, which does not commute with \vec{r}_ℓ , the centre-of-mass coordinate of the radioactive nucleus ℓ . The term is $\frac{\vec{p}_\ell^2}{2m_\ell}$, the kinetic energy of that nucleus. By the usual method of commutation algebra, we proceed to obtain the following relations.

⁺ Lipkin did not mention this requirement explicitly in his derivation³.

For an arbitrary state $|\psi\rangle$,

$$\begin{aligned}
 [H, e^{-i\vec{k}\cdot\vec{r}_e}]|\psi\rangle &= \frac{1}{2m_e} [\vec{p}_e^2, e^{-i\vec{k}\cdot\vec{r}_e}]|\psi\rangle \\
 &= \frac{1}{2m_e} \left\{ \vec{p}_e [\vec{p}_e, e^{-i\vec{k}\cdot\vec{r}_e}]|\psi\rangle + [\vec{p}_e, e^{-i\vec{k}\cdot\vec{r}_e}] \vec{p}_e |\psi\rangle \right\} \\
 &= e^{-i\vec{k}\cdot\vec{r}_e} \left[\frac{(\hbar\vec{k})^2}{2m_e} + \frac{\hbar\vec{k}\cdot\vec{p}_e}{m_e} \right] |\psi\rangle. \quad (26)
 \end{aligned}$$

Hence, operating $e^{+i\vec{k}\cdot\vec{r}_e}$ from the left on Eq.(26), we obtain

$$e^{i\vec{k}\cdot\vec{r}_e} [H, e^{-i\vec{k}\cdot\vec{r}_e}] = R + \frac{\hbar\vec{k}\cdot\vec{p}_e}{m_e}, \quad (27)$$

where $R = \frac{(\hbar\vec{k})^2}{2m_e}$, is equal to the free nuclear recoil energy. Taking the diagonal matrix element for the lattice state $|L_i\rangle$, we have

$$\langle L_i | e^{i\vec{k}\cdot\vec{r}_e} H e^{-i\vec{k}\cdot\vec{r}_e} | L_i \rangle - \langle L_i | H | L_i \rangle = R + \frac{\hbar}{m_e} \langle L_i | \vec{k}\cdot\vec{p}_e | L_i \rangle. \quad (28)$$

Introducing a complete orthonormal set of energy eigenstates

$\{|L_f\rangle\}$, the left hand side becomes :

$$\begin{aligned}
 &\sum_{ff'} \langle L_i | e^{i\vec{k}\cdot\vec{r}_e} | L_f \rangle \langle L_f | H | L_{f'} \rangle \langle L_{f'} | e^{-i\vec{k}\cdot\vec{r}_e} | L_i \rangle - E_i \\
 &= \sum_f \langle L_i | e^{i\vec{k}\cdot\vec{r}_e} | L_f \rangle \langle L_f | H | L_f \rangle \langle L_f | e^{-i\vec{k}\cdot\vec{r}_e} | L_i \rangle - E_i \\
 &= \sum_f E_f |\langle L_f | e^{-i\vec{k}\cdot\vec{r}_e} | L_i \rangle|^2 - E_i \sum_f |\langle L_f | e^{-i\vec{k}\cdot\vec{r}_e} | L_i \rangle|^2 \\
 &= \sum_f (E_f - E_i) P(L_i \rightarrow L_f), \quad (29)
 \end{aligned}$$

since $\langle L_f | H | L_{f'} \rangle = E_f \delta_{ff'}$ and the relative transition probability $P(L_i \rightarrow L_f)$ has been shown to be $|\langle L_f | e^{-i\vec{k} \cdot \vec{r}_e} | L_i \rangle|^2$ (see Eq.(24)), with $\sum_f P(L_i \rightarrow L_f) = 1$. Hence, we rewrite Eq.(28) as

$$\sum_f (E_f - E_i) P(L_i \rightarrow L_f) = R + \langle L_i | \vec{k} \cdot \vec{p}_e | L_i \rangle \frac{\hbar}{m_e} \quad (30)$$

We have assumed $\langle L_i | \vec{p}_e | L_i \rangle = 0$, i.e. this state is not a propagating wave packet, hence we finally arrive at the sum rule :

$$\sum_f (E_f - E_i) P(L_i \rightarrow L_f) = R. \quad (31)$$

This states that the average energy per event given to the lattice is exactly equal to the free recoil energy R , which is consistent with conservation of energy.

From Eq.(31), we notice that the probability of recoilless transitions, i.e. those transitions in which no nuclear energy is converted into the internal energy of the crystal and the emitted gamma-ray carries the full nuclear transition energy, does not contribute to the sum. One is able to see that if there exists an appreciable probability for an energy transfer which is greater than the free recoil energy R , then there must also be an appreciable probability for zero energy transfer to the lattice. For an illustration, we consider a nucleus moving in a highly-localised potential well, such that only one excited bound state is possible. If the energy

difference is greater than R , say $(3/2)R$, then from the sum rule, the probability of excitation is $2/3$. The sum is exhausted by a probability less than unity. The remaining transition probability of $1/3$ must then apply to recoilless ($E_i = E_f$) transitions, and therefore contributes to the Mössbauer effect.

C. The Lamb-Mössbauer Factor for Harmonic Crystals

We have shown in section II.A that the relative probability of recoilless transitions is given by $f = |\langle L_i | e^{-i\vec{k}\cdot\vec{r}_i} | L_i \rangle|^2$. In an actual experimental situation, one has the lattice in thermal equilibrium rather than in a specific eigenstate. Taking the phonons distributed according to a canonical distribution at temperature T , let us denote the statistical average value for recoilless fraction by $f' = \left\{ |\langle L_i | e^{-i\vec{k}\cdot\vec{r}_i} | L_i \rangle|^2 \right\}_T$. For harmonic crystals of N nuclei, where the crystal Hamiltonian can be written as a sum of $3N$ independent harmonic oscillators Hamiltonians, we shall show that, to a very good approximation, ~~that~~ f' may be expressed in the form of an exponential, namely $f' \cong e^{-2M} \equiv e^{-k^2 \langle u^2 \rangle_T}$, where $\langle u^2 \rangle_T$ is the mean square displacement of the radioactive nucleus in the direction of the wave-vector \vec{k} of the emitted gamma-ray. This approximate expression of an exponential for the recoilless fraction is valid for most cases when the harmonic crystal is large ($N \sim 10^{23}$) and is free from localised modes, which are present in crystals containing lattice defects.

The exponential e^{-2M} is called the Lamb-Mössbauer factor, and is often called the Debye-Waller factor, in analogy with the similar factor in the theory of X-ray scattering in crystals. We see that, for a rigid crystal, $f'=1$. In actual crystals, f' must be less than unity, since at absolute zero temperature, $\langle u^2 \rangle \neq 0$ by virtue of the zero-point motion of the nucleus. f' cannot be zero either, if the nucleus is not dislodged from its site.

Let us derive the Lamb-Mössbauer factor e^{-2M} . The crystal lattice state is a function of the centre-of-mass coordinates of each of the N constituent nuclei. Let us assume, for simplicity, ^{that} all the nuclei are identical with equal mass M . We denote the equilibrium position of the radioactive nucleus ℓ by \vec{r}_ℓ^0 . Then its instantaneous position may be written as

$$\vec{r}_\ell(t) = \vec{r}_\ell^0 + \vec{u}_\ell(t), \quad (32)$$

where $\vec{u}_\ell(t)$ is its displacement vector. Since the interatomic forces are assumed harmonic, we may expand the displacement vector in terms of the $3N$ normal modes⁴, thus

$$\vec{u}_\ell(t) = \sum_{\underline{k}_j} \left(\frac{\hbar}{2M\omega(\underline{k}_j)N} \right)^{\frac{1}{2}} \vec{e}(\underline{k}_j) \left[a_{\underline{k}_j}(t) + a_{-\underline{k}_j}^\dagger(t) \right] \cdot e^{2\pi i \vec{k} \cdot \vec{r}_\ell^0} \quad (33)$$

Here,
$$a_{\underline{k}j}(t) = a_{\underline{k}j}(0) e^{-i\omega(\underline{k}j)t}, \quad (34)$$

and $\vec{e}(\underline{k}j)$ is the unit vector for the j th polarisation component of the mode \vec{k} , $\omega(\underline{k}j)$ being the angular frequency. We now treat the lattice vibrations as a quantum field: then $a_{\underline{k}j}(t)$ and $a_{\underline{k}j}^\dagger(t)$ are hermitian conjugate operators. The commutation relations for a and a^\dagger follow from those relations for the components of $\vec{u}_\ell(t)$ and their conjugate momenta:

$$\begin{aligned} [a_{\underline{k}j}, a_{\underline{k}'s}^\dagger] &= \delta_{\underline{k}\underline{k}'} \delta_{js} \\ [a_{\underline{k}j}, a_{\underline{k}'s}] &= [a_{\underline{k}j}^\dagger, a_{\underline{k}'s}^\dagger] = 0, \end{aligned} \quad (35)$$

and, $a_{\underline{k}j}$ and $a_{\underline{k}j}^\dagger$ may be seen as creation and annihilation operators for phonons in the mode $(\vec{k}j)$. The crystal Hamiltonian H is then separable in the $3N$ harmonic oscillator Hamiltonians H_s

$$H = \sum_{s=1}^{3N} H_s = \sum_{s=1}^{3N} \hbar\omega_s \left(a_s^\dagger a_s + \frac{1}{2} \right) \quad (36)$$

where we use a single index s to denote the pair $\vec{k}j$. The crystal lattice state $|L\rangle$ is therefore products of the harmonic oscillator states $|n_s\rangle$, where the occupation number n_s denotes the excitation state of the corresponding oscillator:

$$H_s |n_s\rangle = \hbar\omega_s \left(a_s^\dagger a_s + \frac{1}{2} \right) |n_s\rangle = \hbar\omega_s \left(n_s + \frac{1}{2} \right) |n_s\rangle \quad (37)$$

with n_s , positive integers, ranging from zero to infinity.

Thus the crystal state $|L\rangle$ is characterised by a set of phonon occupation numbers $\{n_s\}$ of all the oscillators, and we write

$$|L\rangle = \prod_{s=1}^{3N} |n_s\rangle \quad (38)$$

We proceed to evaluate the recoilless fraction given by

$$f' = \left\{ \left| \langle Li | e^{-i\vec{k} \cdot \vec{r}_\ell(t)} | Li \rangle \right|^2 \right\}_T \quad (39)$$

where $\vec{r}_\ell(t)$ is the position of the radioactive nucleus. Without loss of generality, we choose the equilibrium position of the nucleus as the origin by setting $\vec{r}_\ell^0 = 0$, so that $\vec{r}_\ell(t) = \vec{u}_\ell(t)$, the displacement vector. From Eq.(33), replacing the pair of indices kj by s , we have

$$\vec{u}_\ell(t) = \sum_{s=1}^{3N} \left(\frac{\hbar}{2M\omega_s N} \right)^{\frac{1}{2}} \vec{e}_s (a_s + a_s^\dagger) \quad (40)$$

$$= \sum_{s=1}^{3N} b_s \xi_s \vec{e}_s, \quad (41)$$

where $\xi_s = \frac{a_s + a_s^\dagger}{\sqrt{2}}$ (42)

$$b_s = \sqrt{\frac{\hbar}{M\omega_s N}} \quad (43)$$

Substituting Eq.(41) into Eq.(39), we have

$$f' = \left\{ \left| \langle Li | e^{-i \sum_{s=1}^{3N} (\vec{k} \cdot \vec{e}_s) b_s \xi_s} | Li \rangle \right|^2 \right\}_T \quad (44)$$

In view of the factorisation of the lattice state into individual harmonic oscillator states, the expression (44) can be written as a product of matrix elements each acting on a normal mode state, thus

$$f' \approx \left\{ \left| \prod_{s=1}^{3N} \langle n_s | e^{-i(\vec{k} \cdot \vec{e}_s) b_s \xi_s} | n_s \rangle \right|^2 \right\}_T \quad (45)$$

Now, we note that in a macroscopic crystal, N is of the order 10^{23} , which is very large. If all the coefficients $(\vec{k} \cdot \vec{e}_s) b_s$ are approximately of the same order of magnitude, each one must be very small ($\sim 1/\sqrt{N}$), since there are $3N$ of them. We can therefore expand the exponentials in Eq.(45) to obtain, retaining terms up to $(\vec{k} \cdot \vec{e}_s)^2 b_s^2 \xi_s^2 / 2$,

$$f' \approx \left\{ \left| \prod \langle n_s | 1 - i(\vec{k} \cdot \vec{e}_s) b_s \xi_s - \frac{(\vec{k} \cdot \vec{e}_s)^2 b_s^2 \xi_s^2}{2} | n_s \rangle \right|^2 \right\}_T \quad (46)$$

Now the expected value of the linear term in ξ_s vanishes, and Eq.(46) becomes

$$f' \approx \left\{ \left| \prod \left(1 - \frac{(\vec{k} \cdot \vec{e}_s)^2 b_s^2}{2} \langle n_s | \xi_s^2 | n_s \rangle \right) \right|^2 \right\}_T \quad (47)$$

since $|n_s\rangle$ are normalised. Thus we have expressed the recoilless fraction as a product of a large number of factors, each of which is very close to unity. We shall now show that it can further be expressed conveniently to a very good approximation by an exponential of the form e^{-2M} .

To see this, let us write the first three terms of Eq.(47) by performing the multiplication of the factors:

$$f' \equiv \left\{ \left| 1 - \sum_{s=1}^{3N} \frac{(\vec{k} \cdot \vec{e}_s)^2}{2} b_s \langle n_s | \xi_s^2 | n_s \rangle \right. \right. \\ \left. \left. + \sum_{t=1}^{3N} \sum_{s=1}^{3N} \frac{(\vec{k} \cdot \vec{e}_s)^2 (\vec{k} \cdot \vec{e}_t)^2}{8} b_s^2 b_t^2 \langle n_s | \xi_s^2 | n_s \rangle \langle n_t | \xi_t^2 | n_t \rangle \right. \right. \\ \left. \left. + \dots \right|^2 \right\}_T, \quad (48)$$

since $\prod_s (1 - p_s) = 1 - \sum_s p_s + \sum_{t \neq s} p_s p_t / 2 + \dots$.

This expansion (48) is very nearly equal to the expansion of the following exponential

$$f' \equiv \left\{ \left| e^{-\sum_{s=1}^{3N} \frac{(\vec{k} \cdot \vec{e}_s)^2}{2} b_s^2 \langle n_s | \xi_s^2 | n_s \rangle} \right|^2 \right\}_T \quad (49)$$

$$= \left\{ e^{-\sum_{s=1}^{3N} (\vec{k} \cdot \vec{e}_s)^2 b_s^2 \langle n_s | \xi_s^2 | n_s \rangle} \right\}_T \quad (50)$$

The first two terms in the expansion (49) are identical to the corresponding terms in expansion (50). The difference in the third terms between these two expansions lies in the exclusion of the term $s = t$ in the double sum in (48) whereas this term is included into the sum when we expand (49). However, the error thus introduced is very small and is given by

$$\sum_{s=1}^{3N} \frac{(\vec{k} \cdot \vec{e}_s)^4}{8} b_s^4 \langle n_s | \xi_s^2 | n_s \rangle^2 \quad (51)$$

Since $b_s^4 \sim 1/N^2$ and even though there are $3N$ terms in the sum (51), the error is still of order $1/N$. We also note that the first non-vanishing terms neglected in the expansion of the exponentials in (46) are also of the same order of magnitude as the terms in (51) which are proportional to $(\vec{k} \cdot \vec{e}_s)^4 b_s^4$. Thus the above procedure in exponentiating the expression (47) to (50) by considering the product (47) as a whole is a very good approximation and is much better than the more naive approximation by exponentiating each factor separately, although the same result (50) would be obtained. However, the latter approximation would be good to first order in $(\vec{k} \cdot \vec{e}_s)^2 b_s^2$ only and the third term in Eq.(48) would appear to have been ignored completely. But in the above approximation, we see that for large N , the error introduced is not of the order of the second term in (48) only, but is of the order of (51) i.e. of order $1/N$.

The thermal average $\left. \right\}_T$ is now carried out. We take the crystal to be in thermal equilibrium with some heat reservoir at temperature T . For temperatures not too low, we may assume the Boltzmann statistics is applicable. Each state $|n_s\rangle$ should then be weighted by the appropriate Boltzmann statistical factor which gives the probability of finding the system in that state at that temperature. A more detailed analysis of the Mössbauer effect for harmonic crystals in thermal equilibrium will be given in the next chapter. Meanwhile we shall proceed as follows:

We first evaluate $\langle n_s | \xi_s^2 | n_s \rangle$ in Eq.(50), which is

$$\begin{aligned} \langle n_s | \xi_s^2 | n_s \rangle &= \frac{1}{2} \langle n_s | a_s a_s^\dagger + a_s^\dagger a_s + a_s^2 + a_s^{\dagger 2} | n_s \rangle \\ &= n_s + \frac{1}{2} \end{aligned} \quad (52)$$

Use has been made of the relation $a_s a_s^\dagger + a_s^\dagger a_s = 2n_s + 1$ and the fact that $\langle n_s | a_s^2 + a_s^{\dagger 2} | n_s \rangle = 0$. Eq.(50) then becomes

$$f' = \left\{ e^{-\sum_{s=1}^{3N} (\vec{k} \cdot \vec{e}_s)^2 b_s^2 (n_s + \frac{1}{2})} \right\}_T \quad (53)$$

Taking the thermal average of the occupation number n_s , we replace n_s by \bar{n}_s in (52) where \bar{n}_s is given by

$$\begin{aligned} \bar{n}_s &= \frac{\sum_{n_s=1}^{\infty} n_s e^{-n_s \hbar \omega_s / kT}}{\sum_{n_s=1}^{\infty} e^{-n_s \hbar \omega_s / kT}} = -\frac{\hbar}{kT} \frac{\partial}{\partial \omega_s} \left[\ln \sum_{n_s=1}^{\infty} e^{-n_s \hbar \omega_s / kT} \right] \\ &= \left[e^{\hbar \omega_s / kT} - 1 \right]^{-1} \end{aligned} \quad (54)$$

The recoilless fraction now takes the form

$$\begin{aligned} f' &\approx e^{-\sum_{s=1}^{3N} (\vec{k} \cdot \vec{e}_s)^2 b_s^2 (\bar{n}_s + \frac{1}{2})} \\ &= e^{-\sum_{s=1}^{3N} \frac{(\vec{k} \cdot \vec{e}_s)^2}{M \omega_s N / \hbar} (\bar{n}_s + \frac{1}{2})}, \quad \text{since } b_s = \sqrt{\frac{\hbar}{M \omega_s N}} \end{aligned} \quad (55)$$

The expression is then transformed to a particularly simple form by noting the fact that , for a harmonic

oscillator, the average value of the potential energy is equal to one half of the total energy⁵. Thus for our crystal, pictured as a collection of N weakly-interacting three-dimensional oscillators, we may write

$$\left(\bar{n}_s + \frac{1}{2}\right) \hbar \omega_s = NM \omega_s^2 \langle u_s^2 \rangle_T, \quad (56)$$

where $\langle u_s^2 \rangle_T$ is the mean square displacement in the direction of polarisation \vec{e}_s of the oscillator. Now noting $\vec{u}_s = u_s \vec{e}_s$, and $\frac{\vec{u}^2}{\ell} = \sum_{s=1}^{3N} \frac{\vec{u}_s^2}{\ell}$, we arrive at the exponential expression

$$f' \cong \hat{f} \equiv e^{-2M} = e^{-\langle (\vec{k} \cdot \vec{u})^2 \rangle_T}, \quad (57)$$

for the recoilless fraction, to a very good approximation. This exponential \hat{f} is called the Lamb-Mössbauer factor.

III. AN EXACT DERIVATION FOR THE MÖSSBAUER EFFECT FOR A HARMONIC CRYSTAL

In section II.B, we saw that the Mössbauer effect is based on the existence of a finite probability for elastic momentum transfer to an atom in a lattice without energy transfer. Applying the general expression for the recoilless fraction obtained in section II.A for the case of a harmonic crystal in thermal equilibrium, and using a very good approximation, we obtained in section II.C the Lamb-Mössbauer factor e^{-2M} for this recoilless fraction. However, an exact derivation for e^{-2M} is possible, in the case of a harmonic crystal. In this chapter, we shall present this exact and self-contained derivation⁶, which is due to Kaufman and Lipkin. A general and exact expression for those transitions which are accompanied by phonon excitation and de-excitation is also given. We shall start by considering the total absorption cross-section, involving the Breit-Wigner formula for resonance absorption. The total absorption cross-section is written as a linear combination of the transition probabilities $P(L_i \rightarrow L_f)$, whose final forms are obtained by operator algebra.

For the recoilless fraction, it is found that the Lamb-Mössbauer factor is modified by a multiplicative factor consisting of a finite product of Bessel functions. For a large crystal, free of localised modes, each Bessel function factor reduces to unity and the Lamb-Mössbauer

factor represents the recoilless fraction exactly. However the modification may be appreciable when the crystal contains lattice defects which produce localised modes, because the Bessel function factor depends on these modes.

Instead of writing out the form of the total resonance absorption cross-section at the outset, it seems appropriate to include a brief resume of its derivation using time-dependent perturbation theory. However, in order to maintain continuity in the discussion of the Mössbauer effect, we shall relegate a part of the discussion to Appendix A.

A. General Expression for the Total Resonance Absorption Cross-section

From Appendix A, we find that the relative probability that a transition will have occurred from an initial state $|0\rangle$ of energy E_0 to a particular state $|n\rangle$ of energy E_n , after a long duration of time, is given by the Lorentz function

$$|b_n(\infty)|^2 = \frac{|\langle n|H|0\rangle|^2}{\hbar^2 \left[(E_n - E_0)^2 + \frac{\Gamma^2}{4} \right]} \quad (\text{A-11})$$

where H is the interaction term in the system's Hamiltonian which is responsible for the transition, and Γ is the line-width of the state $|n\rangle$.

In our present problem, the system consists of

the entire crystal containing the Mössbauer nucleus and the radiation field. The transition involves the emission or absorption of a gamma-ray by the Mössbauer nucleus, accompanied by energy changes in the nucleus as well as in the entire crystal. Let us consider the absorption process only. We now denote an initial state of the system by a ket vector $|\vec{k}, A, \{n_s\}\rangle$. Here \vec{k} denotes the wave vector of a photon of energy E , which exists in the radiation field prior to absorption. The symbol A represents the ground state of the Mössbauer nucleus, with energy E_a . Furthermore, assuming that the harmonic approximation is valid for the crystal of N atoms, we can decompose the crystal Hamiltonian into $3N$ linearly independent harmonic oscillator Hamiltonians. Thus a state of the crystal is specified by a set of $3N$ integers $\{n_s\}$, where n_s is the number of phonons in the s th normal mode of vibration with frequency ω_s , or simply the occupation number for the s th normal mode which we have already made use of in the previous derivation of e^{-2M} in section II.C. These integers n_s may have values from zero to infinity. Thus the set $\{n_s\}$ gives a picture of the population of phonons among the possible modes. The energy of the crystal is then given by $E\{n_s\} = \sum_{s=1}^{3N} n_s \hbar \omega_s$. Now if the gamma-ray is absorbed by the nucleus, the final state of the system is given by $|0, B, \{m_s\}\rangle$. Here the symbol B labels the particular nuclear excited level, with



energy E_b . The new set of integers $\{m_s\}$ describes fully the final state of the crystal, with energy

$$E\{\{m_s\}\} = \sum_{s=1}^{3N} m_s \hbar \omega_s .$$

It is now clear that the total probability for the absorption of a gamma-ray of momentum $\hbar \vec{k}$ by a nucleus bound in the crystal, is obtained by summation over all possible final states for the crystal and from Eq.(A-11) it is proportional to

$$W[\{\{n_s\}, \vec{k}] = \sum_{\{m_s\}} \frac{|\langle 0, B, \{m_s\} | H | \vec{k}, A, \{n_s\} \rangle|^2}{[(E_a + E + E\{\{n_s\}\}) - (E_b + E\{\{m_s\}\})]^2 + \frac{\Gamma^2}{4}} \quad (1)$$

Here $\sum_{\{m_s\}}$ indicates a summation over all possible final crystal states, each set $\{m_s\}$ labelling one possible state and m_s can take any integral value between zero and infinity for any mode s . The matrix element

$$\langle 0, B, \{m_s\} | H | \vec{k}, A, \{n_s\} \rangle \quad \text{may be decomposed into two}$$

factors. One factor depends on the lattice dynamics only, that is, the centre-of-mass coordinates of the absorbing nucleus and the host lattice atoms. The other factor is a function of the internal nuclear coordinates and also depends on the gamma-ray. We are primarily concerned with the absorption of a particular gamma-ray with wave-vector \vec{k} and a particular nuclear transition $A \rightarrow B$, so that the nuclear factor can be considered as a constant multiplicative factor for all possible lattice transitions in which creation and annihilation of phonons take place. This has

been discussed in section II.A. In that section it was also deduced that the lattice-dependent part of the interaction Hamiltonian H is of the form $e^{+i\vec{k}\cdot\vec{r}_\ell}$, where \vec{r}_ℓ is the centre-of-mass position of the Mössbauer nucleus, as a direct consequence of the requirement of momentum conservation so that the momentum of the crystal is increased by $\hbar\vec{k}$ after gamma-ray absorption. (We note that the process under consideration/was gamma-ray emission, in II.A, thus leading to the form of the Hamiltonian as $e^{-i\vec{k}\cdot\vec{r}_\ell}$, as the crystal's momentum is decreased by $\hbar\vec{k}$). As we are interested only in the relative probability of the numerous possible lattice transitions which can accompany the gamma-ray absorption, we can drop the constant nuclear factor from now on and replace the matrix element in Eq.(1) by the lattice factor only, namely $\langle\{m_s\}|e^{i\vec{k}\cdot\vec{r}_\ell}|\{n_s\}\rangle$.

Hence we rewrite the total absorption probability as proportional to

$$W[\{n_s\}, \vec{k}] = \sum_{\{m_s\}} \frac{|\langle\{m_s\}|e^{+i\vec{k}\cdot\vec{r}_\ell}|\{n_s\}\rangle|^2}{\left[E+E_0 - \sum_{s=1}^{3N} (m_s - n_s)\hbar\omega_s\right]^2 + \frac{\Gamma^2}{4}}, \quad (2)$$

where $E_0 = E_b - E_a$, is the energy difference between the two nuclear states.

Eq.(2) is obtained for the case when the crystal is initially in a specified state $|\{n_s\}\rangle$. As we mentioned before in III.C, one does not know the exact initial state of the crystal in an actual experiment. We only know, at

best, that the crystal is in thermal equilibrium with some heat reservoir at a temperature T . Thus we could only say that, according to statistical mechanics, there is a finite probability of finding the crystal in a state $|\{n_s\}\rangle$, which is given by the Boltzmann factor for the whole assembly of $3N$ weakly interacting oscillators modes characterising the crystal. For a single oscillator mode s , the thermal probability of finding the mode in state $|n_s\rangle$ of energy $\epsilon_s = n_s \hbar \omega_s$, or its Boltzmann factor, is given by the canonical distribution:

$$P(|n_s\rangle, T) = \frac{e^{-\beta \epsilon_s}}{\sum_{\epsilon_s=0}^{\infty} e^{-\beta \epsilon_s}} = \frac{e^{-n_s \beta \hbar \omega_s}}{\sum_{n_s=0}^{\infty} e^{-n_s \beta \hbar \omega_s}} \quad (\beta = \frac{1}{k_B T})$$

Let us denote the Boltzmann factor for the whole crystal by $g\{\{n_s\}\}$. Then it is equal to the product of the individual Boltzmann factor for each of the $3N$ harmonic oscillator modes, considered all linearly independent, if we treat the lattice classically. Introducing a symbol $\gamma_s = e^{-\beta \hbar \omega_s}$ we obtain the Boltzmann factor as

follows:

$$g\{\{n_s\}\} = \prod_{s=1}^{3N} \frac{e^{-n_s \beta \hbar \omega_s}}{\sum_{n_s=0}^{\infty} e^{-n_s \beta \hbar \omega_s}} = \prod_{s=1}^{3N} e^{-n_s \beta \hbar \omega_s} (1 - e^{-\beta \hbar \omega_s}) \quad (3)$$

$$= \prod_{s=1}^{3N} (1 - \gamma_s) \gamma_s^{n_s} \quad (4)$$

We note that this weighting function is normalised since each individual Boltzmann factor is normalised. Thus

$$\sum_{\{n_s\}} g\{\{n_s\}\} = 1.$$

The total absorption probability, including all possible initial states properly weighted, is now proportional to

$$W(E) \approx \sum_{\{m_s\}} \sum_{\{n_s\}} g\{\{n_s\}\} \frac{|\langle \{m_s\} | e^{i \vec{k} \cdot \vec{r}_e} | \{n_s\} \rangle|^2}{\left[E - E_0 - \sum_{s=1}^{3N} (m_s - n_s) \hbar \omega_s \right]^2 + \frac{\Gamma^2}{4}}, \quad (5)$$

where $g\{\{n_s\}\}$ is given by Eq.(4). We have thus arrived at the form, apart from a constant factor, of the resonance absorption cross-section of the nucleus \mathcal{L} in a crystal for a monochromatic gamma-ray of energy E .

Let us examine the expression $W(E)$ more closely. If we consider a particular transition in which the occupation numbers change by a set $\{k_s\}$ so that for each mode s , the final occupation number m_s is equal to the initial occupation number n_s plus k_s :

$$m_s = n_s + k_s, \quad s = 1, 2, \dots, 3N. \quad (6)$$

we recognise that the terms in Eq.(5) satisfying Eq.(6)

for all possible initial states characterised by all possible sets of $\{n_s\}$ will contribute a resonance curve centred at $E = E_0 + \sum_{s=1}^{3N} \hbar \omega_s k_s$, with a width Γ .

Thus $W(E)$ may be regarded as a superposition of resonance curves centring at various energy values of $E_0 + \sum_{s=1}^{3N} \hbar \omega_s k_s$,

corresponding to the possible sets of $\{k_s\}$, and having the same width Γ . We now rewrite Eq.(5) as a superposition of resonance curves:

$$W(E) = \sum_{\{k_s\}} \frac{P_{\{k_s\}}}{[E - E_0 - \sum_{s=1}^{3N} \hbar \omega_s k_s]^2 + \frac{\Gamma^2}{4}}, \quad (7)$$

$$\text{where } P_{\{k_s\}} = \sum_{\{n_s\}} g\{n_s\} \left| \langle \{n_s + k_s\} | e^{i \vec{k} \cdot \vec{r}_e} | \{n_s\} \rangle \right|^2. \quad (8)$$

$P_{\{k_s\}}$ is precisely the normalised transition probability for absorption of a gamma-ray of momentum $\vec{p} = \hbar \vec{k}$ from all initial states, each specified by a set $\{n_s\}$ to all final states $\{n_s + k_s\}$, which differ from an initial state by the quantum numbers $\{k_s\}$. $P_{\{k_s\}}$ is normalised because $g\{n_s\}$ is normalised. In particular, $P_{\{0\}}$ gives the important recoilless fraction for which we now proceed to present the exact derivation for the case of a harmonic crystal.

Let us now expand the nuclear position coordinate \vec{r}_e in the matrix elements of Eq.(8) as a linear combination of the normal coordinates of the crystal. Then we write

$$\vec{k} \cdot \vec{r}_e = \frac{\vec{p} \cdot \vec{r}_e}{\hbar} = \sum_{s=1}^{3N} \sigma_s \xi_s, \quad (9)$$

where the expansion coefficients σ_s depend on the nature of the crystal. They are proportional to the momentum components along the polarisation vectors \vec{e}_s , namely $\vec{p}_s = \hbar(\vec{k} \cdot \vec{e}_s)$. Comparing with Eq.(41) of section II.C :

$\vec{u}_\lambda = \sum_{s=1}^{3N} \sqrt{\frac{\hbar}{M\omega_s N}} \vec{e}_s \xi_s$, we see that $\sigma_s = (\vec{k} \cdot \vec{e}_s) \sqrt{\frac{\hbar}{M\omega_s N}}$, thus varying as $1/\sqrt{N}$, where N is the number of atoms in the crystal. Now from Eqs.(8),(9) and (4), the probability for a transition k_s is then given by

$$P_{\{k_s\}} = \sum_{n_s=0}^{\infty} \prod_{s=1}^{3N} (1-\gamma_s) \gamma_s^{n_s} \left| \langle n_s + k_s | e^{i\sigma_s \xi_s} | n_s \rangle \right|^2, \quad (10)$$

since a lattice state $|\{n_s\}\rangle$ is a product of the $3N$ linearly independent harmonic oscillator states $|n_s\rangle$, namely $|\{n_s\}\rangle = \prod_{s=1}^{3N} |n_s\rangle$, and that $\sum_{n_s=0}^{\infty}$ accounts for all possible occupation numbers for each mode. For the sake of later discussion, we note that in Eq.(10), the order of summation and multiplication may be reversed, since the summation is taken over the infinite set of integers n_s , whereas the product is over the finite set in s , so that Eq.(10) may be written as

$$P_{\{k_s\}} = \prod_{s=1}^{3N} (1-\gamma_s) \sum_{n_s=0}^{\infty} \gamma_s^{n_s} \left| \langle n_s + k_s | e^{i\sigma_s \xi_s} | n_s \rangle \right|^2. \quad (11)$$

In particular, the recoilless fraction is then given by

$$f' \equiv P_{\{0\}} = \prod_{s=1}^{3N} (1-\gamma_s) \sum_{n_s=0}^{\infty} \gamma_s^{n_s} \left| \langle n_s | e^{i\sigma_s \xi_s} | n_s \rangle \right|^2 \quad (12a)$$

which, in the notation of section II.C for the thermal average $\{\}_{T}$, is

$$f' \equiv P_{\{0\}} = \left\{ \left| \langle \{n_s\} | e^{i\vec{k} \cdot \vec{r}_\lambda} | \{n_s\} \rangle \right|^2 \right\}_T. \quad (12b)$$

B. Evaluation of the Total Resonance Absorption Cross-section

The evaluation of the expression $W(E)$ given in Eq.(5), or Eq.(7), is made difficult by the presence of the sum $\sum_{s=1}^{3N} (m_s - n_s) \hbar \omega_s$ in the denominator. It would therefore be desirable to group these terms in (5) together, for which this sum has the same value. One may accomplish this by making use of a possible integral representation of the resonance denominator, namely:

$$\frac{a}{a^2 + b^2} = \text{Re} \int_0^{\infty} e^{(-a+ib)\mu} d\mu \quad (13)$$

The typical resonance denominator in Eq.(5) is then expressible as

$$\frac{1}{[E - E_0 - \sum_s (m_s - n_s) \hbar \omega_s]^2 + \frac{\Gamma^2}{4}} \equiv \left(\frac{2}{\Gamma}\right) \text{Re} \int_0^{\infty} d\mu e^{-\mu \frac{\Gamma}{2} + i\mu(E - E_0) - i\mu \sum_{s=1}^{3N} (m_s - n_s) \hbar \omega_s} \quad (14)$$

Substituting Eq.(14) into Eq.(5), we obtain an integral representation of the cross-section :

$$W(E) = \frac{2}{\Gamma} \text{Re} \int_0^{\infty} d\mu e^{-\mu \frac{\Gamma}{2} + i\mu(E - E_0)} \sum_{\{m_s\}} \sum_{\{n_s\}} e^{-i\mu \sum_{s=1}^{3N} \hbar \omega_s (m_s - n_s)} g_{\{n_s\}} | \langle \{m_s\} | e^{i\vec{R} \cdot \vec{r}} | \{n_s\} \rangle |^2 \quad (15)$$

In other words, the integral transformation has made possible the extraction of the sum $\sum_s (m_s - n_s) \hbar \omega_s$ from the denominator and its inclusion into the double summation $\sum_{\{m_s\}} \sum_{\{n_s\}}$ over all the normal modes. From Eq.(15), we see that the

information about all the lattice transitions is contained in this double sum. To facilitate further discussion, we shall denote the whole double sum by an exponential $e^{g(\mu)}$, so that Eq.(15) is expressed as

$$W(E) = \frac{2}{T} \operatorname{Re} \int_0^{\infty} d\mu e^{-\mu \frac{T}{2} + i\mu(E-E_0)} e^{g(\mu)} \quad (16)$$

Now we recall that each term in the sum is expressible as a product of $3N$ factors (see Eqs.(4),(9) and (10)). Then the double sum in Eq.(15) is

$$e^{g(\mu)} = \sum_{\{m_s\}} \sum_{\{n_s\}} \left[\prod_{s=1}^{3N} e^{-i\mu \hbar \omega_s (m_s - n_s)} (1-\gamma_s) \gamma_s^{n_s} \left| \langle m_s | e^{i\sigma_s \xi_s} | n_s \rangle \right|^2 \right] \quad (17)$$

$$= \prod_{s=1}^{3N} (1-\gamma_s) \sum_{\substack{m_s \\ n_s=0}}^{\infty} \left(e^{-i\mu \hbar \omega_s} \right)^{m_s} \left(\gamma_s e^{i\mu \hbar \omega_s} \right)^{n_s} \left| \langle m_s | e^{i\sigma_s \xi_s} | n_s \rangle \right|^2 \quad (18)$$

The sum in Eq.(17) is directly connected to the transition probabilities $P_{\{k_s\}}$, whose exact expressions are the ultimate goal of the discussion in this section. This is easily seen by substituting $m_s = n_s + k_s$ (see Eq.(6)) into Eq.(17), which then becomes[†]

$$e^{g(\mu)} = \sum_{\{k_s\}} e^{-i\mu \sum_s \hbar \omega_s k_s} \sum_{\{n_s\}} \prod_{s=1}^{3N} (1-\gamma_s) \gamma_s^{n_s} \left| \langle n_s + k_s | e^{i\sigma_s \xi_s} | n_s \rangle \right|^2 \quad (19)$$

$$= \sum_{\{k_s\}} e^{-i\mu \sum_{s=1}^{3N} \hbar \omega_s k_s} P_{\{k_s\}}, \quad (20)$$

[†] We note that the exponent in (20) is negative. In Kaufman and Lipkin's paper, the positive exponent is erroneous. See Eq.(12) in their paper⁶.

since $P\{k_s\}$ is given by Eq.(10). Now we see that the factor $e^{g(\mu)}$ is just a linear combination of all the transition probabilities $P\{k_s\}$. It is clear, therefore, that our next step will consist of evaluating the sum exactly, bring it down to a form $\sum_{\{k_s\}} e^{-i\mu \sum_s \hbar \omega_s k_s} h_{\{k_s\}}$, and then identify these expressions $h_{\{k_s\}}$ with the corresponding probabilities, $P\{k_s\}$. Let us proceed to evaluate $e^{g(\mu)}$, starting with the expression given by Eq.(18). For clarity it is now written as

$$e^{g(\mu)} = \prod_{s=1}^{3N} (1 - \gamma_s) X_s, \quad (21)$$

where the sum X_s is given by

$$X_s = \sum_{m_s, n_s=0}^{\infty} \alpha_s^{m_s} \beta_s^{n_s} \left| \langle m_s | e^{i\gamma_s \xi_s} | n_s \rangle \right|^2, \quad (22)$$

$$\text{with } \alpha_s \equiv e^{-i\mu \hbar \omega_s}, \quad \text{and } \beta_s = \gamma_s e^{i\mu \hbar \omega_s}. \quad (23)$$

Now let us introduce the harmonic oscillator creation, annihilation and number operators, for the mode s , by a_s^\dagger , a_s and $N_s = a_s^\dagger a_s$ respectively. The commutation relations are as follows :

$$[a_s, a_{s'}^\dagger] = \delta_{ss'}, \quad [N_s, a_s] = -a_s, \quad [N_s, a_s^\dagger] = a_s^\dagger. \quad (24)$$

We recall that the normal coordinate ξ_s is related to the creation and annihilation operators by the simple relation in Eq.(42) of section II.C. We rewrite it here :

$$\xi_s = \frac{a_s + a_s^\dagger}{\sqrt{2}}. \quad (25)$$

Furthermore, we note that we are using a representation in which the number operator is diagonal :

$$\langle m_s | N_s | m'_s \rangle = m_s \delta_{m_s m'_s} \quad (26)$$

Using this relation, we may rewrite $\alpha_s^{m_s} \beta_s^{n_s}$ in Eq.(22) in terms of matrix elements of exponentials involving N_s :

$$\alpha_s^{m_s} \beta_s^{n_s} = \langle m_s | (e^{\log \alpha_s})^{N_s} | m_s \rangle \langle n_s | (e^{\log \beta_s})^{N_s} | n_s \rangle \quad (27)$$

The sum is then expressible explicitly as

$$X_s = \sum_{m_s, n_s} \langle m_s | e^{N_s \log \alpha_s} | m_s \rangle \langle m_s | e^{i\sigma_s \xi_s} | m_s \rangle \langle n_s | e^{N_s \log \beta_s} | n_s \rangle \langle n_s | e^{-i\sigma_s \xi_s} | n_s \rangle \quad (28)$$

By virtue of (26) again, the above expression may be written as a fourfold summation over complete sets of linear harmonic oscillator states, and thus reduced to a trace, as follows :

$$X_s = \sum_{\substack{m_s, m'_s \\ n'_s, n_s}} \langle m_s | e^{N_s \log \alpha_s} | m'_s \rangle \langle m'_s | e^{i\sigma_s \xi_s} | n'_s \rangle \langle n'_s | e^{N_s \log \beta_s} | n_s \rangle \langle n_s | e^{-i\sigma_s \xi_s} | m_s \rangle \quad (29)$$

$$= \text{Tr} \left\{ e^{N_s \log \alpha_s} e^{i\sigma_s \frac{(a_s^\dagger + a_s)}{\sqrt{2}}} e^{N_s \log \beta_s} e^{-i\sigma_s \frac{(a_s^\dagger + a_s)}{\sqrt{2}}} \right\}; \quad (30)$$

noting the definition of ξ_s given in Eq.(25).

At this point, in order to evaluate the trace, some exchange rules and the Baker-Hausdorff formula are required. Their detail derivations are given in Appendix B. Using those general relations, we can extract a constant

factor from the trace (30) and X_s becomes (see Appendix B)

$$X_s = e^{\frac{\sigma_s^2 \beta_s - 1}{\beta_s}} \text{Tr} \left\{ e^{N_s \log \gamma_s} e^{i \frac{\sigma_s}{\sqrt{2}} (\beta_s - 1) a_s} e^{i \frac{\sigma_s}{\sqrt{2}} (\frac{1}{\beta_s} - 1) a_s^\dagger} \right\} \quad (31)$$

Then we make use of another relation (see proof in Appendix C):

$$(1-w) \text{Tr} \left(e^{N \log w} e^{u a} e^{v a^\dagger} \right) = e^{\frac{uv}{1-w}}, \quad (32)$$

for arbitrary constants u , v and w . Taking

$$u = i \frac{\sigma_s}{\sqrt{2}} (\beta_s - 1), \quad v = i \frac{\sigma_s}{\sqrt{2}} (\frac{1}{\beta_s} - 1); \quad w = \gamma_s$$

in Eq.(32), and substituting into Eq.(31), the sum X_s becomes, after some simplification,

$$X_s = \frac{1}{1-\gamma_s} \exp \left(-\frac{\gamma_s^2 (1-d_s)(1-\beta_s)}{2(1-\gamma_s)} \right). \quad (33)$$

Thus each factor $(1-\gamma_s) X_s$ in the product (21) is a simple exponential. Writing out α_s and β_s explicitly, (see Eq.(23)), the factor $e^{g(\mu)}$ now becomes

$$e^{g(\mu)} = \prod_{s=1}^{3N} \exp \left\{ -\frac{\sigma_s^2}{2} \frac{(1-e^{-i\mu t h_s})(1-\gamma_s e^{i\mu t h_s})}{1-\gamma_s} \right\}, \quad (34)$$

$$\text{or, } g(\mu) = -\frac{1}{2} \sum_{s=1}^{3N} \sigma_s^2 \left\{ \frac{1+\gamma_s}{1-\gamma_s} - \frac{e^{-i\mu t h_s} + \gamma_s e^{i\mu t h_s}}{1-\gamma_s} \right\}. \quad (35)$$

The exponent $g(\mu)$ is now written as a sum of two parts, the first part containing terms which are independent of μ , and the second part is μ -dependent. In the next section,

it will be shown that the part which is independent of μ in Eq.(35) is precisely the exponent of the Lamb-Mössbauer factor e^{-2M} , as derived in section II.C. Hence we now write

$$e^{g(\mu)} = e^{-2M} e^{G(\mu)}, \quad (36)$$

where

$$e^{G(\mu)} = \exp \left\{ \frac{1}{2} \sum_{s=1}^{3N} \sigma_s^2 \frac{e^{-i\mu \hbar \omega_s} + \gamma_s e^{i\mu \hbar \omega_s}}{1 - \gamma_s} \right\} \quad (37)$$

and

$$-2M = -\frac{1}{2} \sum_{s=1}^{3N} \sigma_s^2 \frac{1 + \gamma_s}{1 - \gamma_s}. \quad (38)$$

The total resonance absorption cross-section, as we recall, is proportional to the quantity $W(E)$ given in Eq.(16) in integral form, with the factor $e^{g(\mu)}$ included in the integrand. Now that $e^{g(\mu)}$ contains a factor e^{-2M} which is independent of μ , e^{-2M} can be taken out of the integral, and the total cross-section is therefore proportional to

$$W(E) = \frac{2}{\Gamma} e^{-2M} \operatorname{Re} \int_0^{\infty} e^{-\mu \frac{\Gamma}{2} + i\mu(E-E_0)} e^{G(\mu)} d\mu, \quad (39)$$

with $e^{G(\mu)}$ given by Eq.(37).

C. Exact Expressions for the Recoilless Fraction

The relation between the factor $e^{g(\mu)}$ and the transition probabilities $P_{\{k_s\}}$ was given in Eq.(20):

$$e^{g(\mu)} = \sum_{\{k_s\}} e^{-i\mu \sum_s \hbar \omega_s k_s} P_{\{k_s\}}. \quad (20)$$

We now show that this factor, as given in the forms (36) and

(37), can be transformed into a similar sum as that of (20), thereby providing a comparison between the two sums, and hence the exact expression for the probability $P_{\{k_s\}}$ for any set $\{k_s\}$ can be obtained. To do this we shall replace the factor $e^{G(\mu)}$ with a Bessel-generating function. Then it will be found that the probability $P_{\{k_s\}}$ contains the Lamb-Mössbauer factor, modified by a product of Bessel function factors.

First, we note that the exponent $G(\mu)$ in (37) can be written as

$$G(\mu) = \frac{1}{2} \sum_{s=1}^{3N} \frac{\sigma_s^2 \sqrt{\gamma_s}}{1-\gamma_s} \left(\frac{e^{-i\mu h \omega_s}}{\sqrt{\gamma_s}} + \sqrt{\gamma_s} e^{i\mu h \omega_s} \right), \quad (40)$$

so that the factor $e^{G(\mu)}$ is now expressible as

$$\begin{aligned} e^{G(\mu)} &= e^{\sum_s \frac{\alpha_s}{2} \left(u_s - \frac{1}{u_s} \right)} \\ &= \prod_{s=1}^{3N} e^{\frac{\alpha_s}{2} \left(u_s - \frac{1}{u_s} \right)}, \end{aligned} \quad (41)$$

where we have introduced the abbreviations[†]:

$$\alpha_s \equiv \frac{i\sigma_s \sqrt{\gamma_s}}{1-\gamma_s} \quad \text{and} \quad u_s \equiv \frac{-ie^{-i\mu h \omega_s}}{\sqrt{\gamma_s}}. \quad (42)$$

Now each factor in the product (41) is a Bessel-generating function⁷:

$$e^{\frac{\alpha_s}{2} \left(u_s - \frac{1}{u_s} \right)} = \sum_{k=-\infty}^{\infty} J_k(\alpha_s) u_s^k. \quad (43)$$

[†]In Kaufmann and Lipkin's paper⁶, the abbreviation of u_s is $-ie^{i\mu h \omega_s} / \sqrt{\gamma_s}$, which may be a printed error, because Eq.(41) cannot be obtained by such a replacement.

Hence $e^{g(\mu)}$ becomes, after substituting (42) into Eq.(43),

$$\begin{aligned}
 e^{g(\mu)} &= e^{-2M} e^{G(\mu)} & (36) \\
 &= e^{-2M} \prod_{s=1}^{3N} \sum_{k_s=-\infty}^{\infty} J_{k_s} \left(\frac{i\sigma_s^2 \sqrt{\gamma_s}}{1-\gamma_s} \right) (i\sqrt{\gamma_s})^{-k_s} e^{-i\mu \hbar \omega_s k_s} \\
 &= e^{-2M} \sum_{\{k_s\}} \prod_{s=1}^{3N} J_{k_s} \left(\frac{i\sigma_s^2 \sqrt{\gamma_s}}{1-\gamma_s} \right) (i\sqrt{\gamma_s})^{-k_s} e^{-i\mu \hbar \omega_s k_s} \\
 &= \sum_{\{k_s\}} e^{-i\mu \sum_s \hbar \omega_s k_s} \left[e^{-2M} \prod_{s=1}^{3N} J_{k_s} \left(\frac{i\sigma_s^2 \sqrt{\gamma_s}}{1-\gamma_s} \right) (i\sqrt{\gamma_s})^{-k_s} \right]. & (44)
 \end{aligned}$$

On comparison with Eq.(20), it follows that the transition specified by $\{k_s\}$ has the probability

$$P_{\{k_s\}} = e^{-2M} \prod_{s=1}^{3N} J_{k_s} \left(\frac{i\sigma_s^2 \sqrt{\gamma_s}}{1-\gamma_s} \right) (i\sqrt{\gamma_s})^{-k_s}. \quad (45)$$

In particular, the recoilless fraction, or the probability of "no-phonon" transitions, specified by $\{0\}$, is then given by

$$f' \equiv P_{\{0\}} = e^{-2M} \prod_{s=1}^{3N} J_0 \left(\frac{i\sigma_s^2 \sqrt{\gamma_s}}{1-\gamma_s} \right). \quad (46)$$

Eq.(45) gives the probability $P_{\{k_s\}}$ that, after the gamma-ray absorption, the crystal suffers a change of internal energy such that among the $3N$ normal modes, the population of any mode s changes from n_s to $n_s + k_s$. We also note that since $0 \leq n_s \leq \infty$, k_s may take any value between $-\infty$ and ∞ . Since our main interest is in the recoilless fraction, we shall not discuss "one- or many-phonon" processes any further. From Eq.(46), we arrive at an exact expression for the recoilless fraction, which shows

the presence of a product of Bessel function factors. We recall that in section II.C, employing a very good approximation, we obtained the purely exponential form e^{-2M} , without this additional Bessel function product for the Mossbauer fraction, and was called the Lamb-Mössbauer factor.

Before discussing further, let us justify Eq.(38) which states that the sum $-\frac{1}{2} \sum_{s=1}^{3N} \sigma_s^2 \frac{1+\gamma_s}{1-\gamma_s}$ is equal precisely to the exponent $-2M$ of the Lamb-Mössbauer factor, which was defined in II.C in Eq.(57) as $-\langle (\vec{k} \cdot \vec{u}_\ell)^2 \rangle_T$ or $-\langle (\vec{k} \cdot \vec{r}_\ell)^2 \rangle_T$, since the equilibrium position of the Mossbauer nucleus, \vec{r}_ℓ^0 , has been chosen to be zero. Here $\langle F \rangle_T$ denotes the quantum-mechanical and thermal average of F over all the oscillator states, and using Eq.(4), we have in general, for any function F ,

$$\langle F \rangle_T = \prod_{s=1}^{3N} \sum_{n_s=0}^{\infty} (1-\gamma_s) \gamma_s^{n_s} \langle n_s | F | n_s \rangle \quad (47)$$

Now we must prove

$$e^{-\frac{1}{2} \langle (\vec{k} \cdot \vec{r}_\ell)^2 \rangle_T} = e^{-\frac{1}{2} \sum_s \langle (\sigma_s \xi_s)^2 \rangle_T} = \exp \left[-\frac{1}{2} \sum_s \sigma_s^2 \frac{1+\gamma_s}{1-\gamma_s} \right], \quad (48)$$

in order to justify the statement (38). For the s th mode,

$$\begin{aligned} \langle (\sigma_s \xi_s)^2 \rangle_T &= \frac{1-\gamma_s}{2} \sum_{n_s=0}^{\infty} \sigma_s^2 \gamma_s^{n_s} \langle n_s | a_s^{\dagger 2} + a_s^{\dagger} a_s + a_s a_s^{\dagger} + a_s^2 | n_s \rangle \left[\text{since } \xi_s^2 = \frac{(a_s + a_s^{\dagger})^2}{2} \right] \\ &= \frac{(1-\gamma_s) \sigma_s^2}{2} \sum_{n_s=0}^{\infty} \gamma_s^{n_s} (2n_s + 1) \left[\text{since } a_s^{\dagger} a_s + a_s a_s^{\dagger} = 2N_s + 1 \right. \\ &\quad \left. \langle n_s | a_s^2 + a_s^{\dagger 2} | n_s \rangle = 0 \right] \\ &= \frac{(1-\gamma_s) \sigma_s^2}{2} \left\{ \left(\sum_{n_s=0}^{\infty} 2n_s \gamma_s^{n_s} \right) + \frac{1}{1-\gamma_s} \right\} \end{aligned}$$

$$= \frac{\sigma_s^2 \gamma_s}{1-\gamma_s} + \frac{\sigma_s^2}{2}, \quad \left[\text{since } \sum_{n_s=0}^{\infty} n_s \gamma_s^{n_s} = \frac{1}{(1-\gamma_s)^2} \right]$$

$$= \frac{\sigma_s^2}{2} \left(\frac{1+\gamma_s}{1-\gamma_s} \right).$$

Thus the sum $\sum_s \frac{\sigma_s^2}{2} \left(\frac{1+\gamma_s}{1-\gamma_s} \right)$ is indeed equal to $-2M$.

We also take this opportunity to distinguish between the two quantities, the exact recoilless fraction f' and the Lamb-Mössbauer factor \hat{f} . According to Eq.(12b), we have

$$f' = \left\{ \left| \langle e^{i\vec{k} \cdot \vec{r}_e} \rangle \right|^2 \right\}_T \quad (12b)$$

Now, by using Eq.(47), we can show that

$$\hat{f} = \left\{ \langle e^{i\vec{k} \cdot \vec{r}_e} \rangle_T \right\}^2 \quad (49)$$

The proof is as follows:

$$\begin{aligned} \langle e^{i\vec{k} \cdot \vec{r}_e} \rangle_T &= \prod_{s=1}^{3N} \sum_{n_s} (1-\gamma_s) \gamma_s^{n_s} \langle n_s | e^{i\sigma_s \xi_s} | n_s \rangle \quad \left[\text{by using Eqs. (47) and (9)} \right] \\ &= \prod_{s=1}^{3N} (1-\gamma_s) \sum_{n_s} \langle n_s | e^{N_s \log \gamma_s} | n_s \rangle \langle n_s | e^{i\sigma_s \xi_s} | n_s \rangle \\ &= \prod_{s=1}^{3N} (1-\gamma_s) \sum_{n_s, n'_s} \langle n_s | e^{N_s \log \gamma_s} | n'_s \rangle \langle n'_s | e^{i\sigma_s \xi_s} | n_s \rangle \quad \left[\text{since } \langle n_s | e^{N_s} | n'_s \rangle = e^{n_s \delta_{n_s, n'_s}} \right] \\ &= \prod_{s=1}^{3N} (1-\gamma_s) \text{Tr} e^{N_s \log \gamma_s} e^{i\frac{\sigma_s}{\sqrt{2}} (a_s^\dagger a_s)} \quad \left[\text{by the definition of a trace} \right] \\ &= \exp \left[-\frac{1}{4} \sum_s \sigma_s^2 \left(\frac{1+\gamma_s}{1-\gamma_s} \right) \right] \quad \left[\text{by using exchange rule (3) in Appendix B} \right] \end{aligned}$$

$$\text{Thus, } \left\{ \langle e^{i\vec{k} \cdot \vec{r}_e} \rangle_T \right\}^2 = \exp \left[-\frac{1}{2} \sum_s \sigma_s^2 \left(\frac{1+\gamma_s}{1-\gamma_s} \right) \right] = e^{-2M} \equiv \hat{f}.$$

The two expressions (12b) and (49) are not the same. In words, the recoilless fraction is the thermal average of the square of the quantum-mechanical average of the operator $e^{i\vec{k}\cdot\vec{r}_\ell}$, namely (12b) and the Lamb-Mössbauer factor is equal to the square of the thermal and quantum-mechanical average of the same operator $e^{i\vec{k}\cdot\vec{r}_\ell}$, namely (49).

We have now completed the exact treatment of the Mössbauer effect. The general expression for the transition probabilities $P\{k_s\}$ is given in Eq.(45). The recoilless fraction is given in Eq.(46). The usual expression for the recoilless fraction is the Lamb-Mössbauer factor, which is a very good approximation. The exact expression, however, consists of this Lamb-Mössbauer factor and a multiplicative factor of a finite product of Bessel functions. Let us examine the validity of the approximate expression once more, and thus distinguish the cases when the exact expression is necessary.

In order to compare the exact result f' for the recoilless fraction with the approximate expression \hat{f} , let us expand the "Bessel function product" factor in powers of σ_s^2 , noting the fact that $J_0(x) = 1 + \frac{x^2}{4} + \dots$,

$$\prod_{s=1}^{3N} J_0\left(\frac{i\sigma_s^2\sqrt{\gamma_s}}{1-\gamma_s}\right) = 1 - \sum_{s=1}^{3N} \frac{\sigma_s^4\gamma_s}{(1-\gamma_s)^2} + \dots \quad (50)$$

The zero-order term is unity, and the first-order term is of the order of $\sum_{s=1}^{3N} \sigma_s^4$. Thus, the approximation which

sets the recoilless fraction equal to e^{-2M} is valid whenever $\sum_{s=1}^{3N} \sigma_s^4$ is small compared to unity. Now we recall from Eq.(9) that these expansion coefficients σ_s are proportional to $1/\sqrt{N}$ (for phonons)⁺, so that σ_s^4 is of the order of $1/N^2$. Now if there is a large number of modes, of the order N , contributing to the sum $\sum_{s=1}^{3N} \frac{\sigma_s^4 \delta_s}{(1-\delta_s)^2}$ in (40), then the sum is of order $1/N$, and the approximation in question is justified. The Lamb-Mössbauer factor will indeed be a very good and adequate expression for the recoilless fraction. However, the validity of this approximation fails when there is only a single mode or a small number of modes having values of σ_s , each of the order unity, with only slight contribution from other modes. This situation would occur if the Mössbauer nucleus is an impurity, vibrating mainly in a localised mode. In general, localised modes occur for crystals containing lattice defects. When these localised modes dominate the motion of the resonant nucleus, the expansion coefficients are of the order unity. Therefore, when only a small number of modes contribute to the sum, the "Bessel function factor" has to be taken into consideration.

⁺ Also see the first line in Page 47.

IV. AN EXPRESSION FOR THE LAMB-MÖSSBAUER FACTOR IN TERMS OF LATTICE DYNAMICS

So far, we have been discussing the general form of the recoilless fraction and the probabilities for transitions accompanied by phonon excitations, for a general harmonic crystal in thermal equilibrium. The exact expression for the recoilless fraction consists of the Lamb-Mössbauer factor e^{-2M} and a multiplicative Bessel function factor. Let us now express the factor e^{-2M} in terms of the lattice dynamics of the host crystal which contains the absorbing nucleus. The double-time Green's function will be used and its properties are described in section B of this chapter. It is also possible to express the Bessel function factor in terms of lattice dynamics, using this double-time Green's function method. However, we shall not undertake this problem, but we shall derive the expression for e^{-2M} only. The treatment follows that of Maradudin et al.⁸.

A. The Lamb-Mössbauer Factor e^{-2M} in terms of Phonon Operators

The Lamb-Mössbauer factor was introduced in Eq.(57) of section II.C :

$$e^{-2M} = e^{-\langle (\vec{k} \cdot \vec{u}(\ell, t))^2 \rangle_T}$$

where \vec{k} is the wave vector of the absorbed gamma-ray, and $\vec{u}(\ell, t)$ is the displacement vector of the absorbing nucleus ℓ

at time t . The notation $\langle \rangle_T$ denotes, as before, a thermal average over the canonical ensemble of the crystal.

First of all, let us see that the factor e^{-2M} is independent of time, so that the exponent may be expressed in terms of $\vec{u}(\lambda, 0)$, thus

$$+2M = \langle (\vec{k} \cdot \vec{u}(\lambda, 0))^2 \rangle_T, \quad (1)$$

where the operator $\vec{u}(\lambda, 0)$ is related to the Heisenberg operator $\vec{u}(\lambda, t)$ by the relation

$$\vec{u}(\lambda, t) = e^{i\frac{t}{\hbar}H} \vec{u}(\lambda, 0) e^{-i\frac{t}{\hbar}H}, \quad (2)$$

where H is the crystal Hamiltonian. Eq.(1) can be seen by evaluating the quantum-mechanical average of the quantity $(\vec{k} \cdot \vec{u}(\lambda, t))^2$ in any crystal lattice state $|m\rangle$, thus

$$\begin{aligned} \langle m | (\vec{k} \cdot \vec{u}(\lambda, t))^2 | m \rangle &= \langle m | e^{i\frac{t}{\hbar}H} (\vec{k} \cdot \vec{u}(\lambda, 0))^2 e^{-i\frac{t}{\hbar}H} | m \rangle \\ &= \langle m | (\vec{k} \cdot \vec{u}(\lambda, 0))^2 | m \rangle. \end{aligned}$$

Hence, from now on, we write the exponent $2M$ in the form

$$\begin{aligned} 2M &= \langle (\vec{k} \cdot \vec{u}(\lambda, 0))^2 \rangle_T \\ &= \langle \vec{k} \cdot \vec{u}(\lambda, 0) \vec{k} \cdot \vec{u}(\lambda, 0) \rangle_T. \end{aligned} \quad (3)$$

Now, the next step is to expand the displacement vector $\vec{u}(\lambda, 0)$ in terms of the $3N$ normal modes, which has been done in Eq.(33) of section II.C :

$$\vec{u}(\underline{r}, 0) = \sqrt{\frac{\hbar}{2MN}} \sum_{\underline{k}_j} \frac{1}{\sqrt{\omega(\underline{k}_j)}} \left[a_{-\underline{k}_j}^\dagger(0) + a_{\underline{k}_j}(0) \right] \vec{e}(\underline{k}_j), \quad (4)$$

where we have taken the mean position of the Mössbauer nucleus to be the origin, so that $e^{\pm i\vec{k} \cdot \vec{r}_c} = 1$ and also $e^{\pm i\omega_s t} = 1$, for $t = 0$. Here, the wave vector \underline{k} has values uniformly and densely distributed throughout the first Brillouin zone of the crystal, and the three branches of the phonon spectrum are denoted by $j=1,2,3$. $\omega(\underline{k}, j)$ is the angular frequency of the normal mode of the unperturbed crystal, described by the wave vector \underline{k} and the branch index j , while $\vec{e}(\underline{k}_j)$ is the associated unit polarisation vector. $a_{\underline{k}_j}^\dagger$ and $a_{\underline{k}_j}$ are creation and destruction operators respectively, for phonons in the mode (\underline{k}_j) .

For convenience, let us introduce the operator $A_{\underline{k}_j}(t)$ which is defined as follows

$$A_{\underline{k}_j}(t) = a_{-\underline{k}_j}^\dagger(t) + a_{\underline{k}_j}(t). \quad (5)$$

It follows immediately from (5) that $A_{\underline{k}_j}(t) = A_{-\underline{k}_j}(t)$. Then the exponent of the Lamb-Mössbauer factor becomes, from Eq.(3)

$$2M = \frac{\hbar}{2NM} \sum_{\underline{k}_j} \sum_{\underline{k}'_j} \frac{(\vec{k} \cdot \vec{e}(\underline{k}_j))(\vec{k} \cdot \vec{e}(\underline{k}'_j))}{[\omega(\underline{k}_j) \omega(\underline{k}'_j)]^{\frac{1}{2}}} \langle A_{\underline{k}_j}(0) A_{\underline{k}'_j}(0) \rangle_T \quad (6)$$

In order to evaluate Eq.(6), we now follow Maradudin et al.⁸ to use the method of double-time Green's functions in evaluating the quantity $\langle A_{\underline{k}_j}(0) A_{\underline{k}'_j}(0) \rangle_T$.

B. Double Time Green's Functions Method⁸

The quantity $\langle A_{k_j}(0) A_{k'_j}(0) \rangle_T$ in Eq.(6) is of the form $\langle A(0)B(0) \rangle_T$ and is a special case of the more general correlation function $\langle A(t)B(0) \rangle_T$ in which $A(t)$ is the time-dependent Heisenberg operator: $A(t) = e^{i\frac{H}{\hbar}t} A(0) e^{-i\frac{H}{\hbar}t}$, where H is the total Hamiltonian of the crystal. Though we are primarily concerned with the Lamb-Mössbauer factor, we remark that this unequal-time correlation function is important when an explicit expression of the Bessel function factor in terms of lattice dynamics is required. Let us call the quantity $\langle A(0)B(0) \rangle_T$ an equal-time correlation function, because $\langle A(t)B(t) \rangle_T = \langle A(0)B(0) \rangle_T$ for all times t , as we shall see. Let us first follow Maradudin's notation to specify an eigenstate of the crystal Hamiltonian H by a single index m , instead of a set of occupation numbers $\{m_s\}$, which was introduced in section III.A. The thermal and quantum-mechanical average of the product of Heisenberg products $A(t)B(t)$, written explicitly, is given by

$$\begin{aligned} \langle A(t)B(t) \rangle_T &= \sum_m g(m) \left| \langle m | e^{i\frac{H}{\hbar}t} A(0) e^{-i\frac{H}{\hbar}t} (e^{i\frac{H}{\hbar}t} B(0) e^{-i\frac{H}{\hbar}t}) | m \rangle \right|^2 \\ &= \sum_m g(m) \left| \langle m | A(0)B(0) | m \rangle \right|^2 \\ &\equiv \langle A(0)B(0) \rangle_T \end{aligned}$$

Here, the thermal weighting factor $g(m)$ is given by $e^{-\beta E_m}/Z$ where Z is the partition function for the crystal and is equal to $\sum_m \exp(-\beta E_m)$ (see also Eqs. (3) and (4) in section III.A.)

Let us now consider two unequal-time correlation functions defined as

$$F_{AB}(t) = \langle A(t) B(0) \rangle_T \quad (7a)$$

$$F_{BA}(t) = \langle B(0) A(t) \rangle_T \quad (7b)$$

Their difference is then

$$F_{AB}(t) - F_{BA}(t) = \langle [A(t), B(0)] \rangle_T \quad (7c)$$

Again, by the definition of the angular brackets Eq. (7a) is written explicitly as

$$\begin{aligned} F_{AB}(t) &= \sum_{m,n} \frac{e^{-\beta E_m}}{Z} \langle m | e^{i\frac{H}{\hbar}t} A(0) e^{-i\frac{H}{\hbar}t} | n \rangle \langle n | B(0) | m \rangle \\ &= \sum_{m,n} \frac{e^{-\beta E_m}}{Z} \langle m | A(0) | n \rangle \langle n | B(0) | m \rangle e^{i\frac{t}{\hbar}(E_m - E_n)} \\ &= \int_{-\infty}^{\infty} d\omega \rho(\omega) e^{-i\omega t}, \end{aligned} \quad (8)$$

which is deliberately written in its spectral representation, with

$$\rho(\omega) = \sum_{m,n} \frac{e^{-\beta E_m}}{Z} \langle m | A(0) | n \rangle \langle n | B(0) | m \rangle \delta\left(\omega + \frac{E_m - E_n}{\hbar}\right) \quad (9)$$

Similarly, the other correlation function may be written as

$$\begin{aligned}
 F_{BA}(t) &= \sum_{m,n} \frac{e^{-\beta E_m}}{Z} \langle m|B(0)|n\rangle \langle n|A(0)|m\rangle e^{i\frac{t}{\hbar}(E_n-E_m)} \\
 &= \int_{-\infty}^{\infty} d\omega \rho'(\omega) e^{-i\omega t}, \quad (10)
 \end{aligned}$$

$$\text{where } \rho'(\omega) = \sum_{m,n} \frac{e^{-\beta E_m}}{Z} \langle m|B(0)|n\rangle \langle n|A(0)|m\rangle \delta\left(\omega + \frac{E_n-E_m}{\hbar}\right). \quad (11)$$

Interchanging the dummy indices m and n and noting

$$\exp(-\beta E_n) = \exp\left[-\beta E_m - \beta(E_n - E_m)\right] = \exp(-\beta E_m) \exp(-\beta \hbar \omega),$$

we have

$$\begin{aligned}
 \rho'(\omega) &= \sum_{m,n} \frac{e^{-\beta E_m}}{Z} \langle m|A(0)|n\rangle \langle n|B(0)|m\rangle \delta\left(\omega + \frac{E_m-E_n}{\hbar}\right) e^{-\beta \hbar \omega} \\
 &= \rho(\omega) e^{-\beta \hbar \omega} \quad (12)
 \end{aligned}$$

Then the function $F_{BA}(t)$ is now expressible in an integral containing the spectral density $\rho(\omega)$ which is defined in Eq.(9), thus

$$F_{BA}(t) = \int_{-\infty}^{\infty} d\omega e^{-\beta \hbar \omega} \rho(\omega) e^{-i\omega t} \quad (13)$$

Combining Eqs.(8) and (13), the difference of the correlation functions is then

$$\begin{aligned}
 F_{AB}(t) - F_{BA}(t) &\equiv \langle [A(t), B(0)] \rangle_T \\
 &= \int_{-\infty}^{\infty} d\omega (1 - e^{-\beta \hbar \omega}) \rho(\omega) e^{-i\omega t}
 \end{aligned}$$

In particular, for the equal-time correlation functions,

$$\langle [A(0), B(0)] \rangle_T = \int_{-\infty}^{\infty} d\omega (1 - e^{-\beta \hbar \omega}) \rho(\omega) \quad (14)$$

At this point, we would like to note that the Fourier transform of $F_{AB}(t)$ is, from Eq.(8),

$$\rho(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dt e^{i\omega t} F_{AB}(t). \quad (15)$$

We now proceed to introduce the retarded and advanced Green's functions in terms of these correlation functions :

$$\begin{aligned} G_{AB}(t)_r &= -i\theta(t) (F_{AB}(t) - F_{BA}(t)) \\ &= -i\theta(t) \langle [A(t), B(0)] \rangle_T \equiv \langle\langle A(t); B(0) \rangle\rangle_r. \end{aligned} \quad (16a)$$

$$\begin{aligned} G_{AB}(t)_a &= i\theta(-t) (F_{AB}(t) - F_{BA}(t)) \\ &= i\theta(-t) \langle [A(t), B(0)] \rangle_T \equiv \langle\langle A(t); B(0) \rangle\rangle_a. \end{aligned} \quad (16b)$$

In these expressions, $\theta(t)$ is the unit step function

$$\begin{aligned} \theta(t) &= 1 & t > 0 \\ &= 0 & t < 0 \end{aligned} \quad (17)$$

It is clear that these Green's functions can be cast into integral forms by the use of Eqs.(8) and (13). However, let us now introduce the Fourier transform of the Green's functions (either retarded or advanced) as a function of energy E first :

$$G(E) = \frac{1}{2\pi} \int_{-\infty}^{\infty} G(t) e^{iEt} dt, \quad (18a)$$

and

$$G(t) = \int_{-\infty}^{\infty} G(E) e^{-iEt} dt. \quad (18b)$$

Then, for the retarded Green's function, its Fourier transform is given by

$$G_r(E) = -\frac{i}{2\pi} \int_{-\infty}^{\infty} d\omega (1 - e^{-\beta\hbar\omega}) \rho(\omega) \int_{-\infty}^{\infty} dt \theta(t) e^{i(E-\omega)t} \quad (19)$$

In order to evaluate this integral, we make use of the integral representation of the step function, (see proof in Appendix D):

$$\theta(t) = \lim_{\delta \rightarrow 0^+} \int_{-\infty}^{\infty} \frac{dx}{2\pi i} \frac{e^{ixt}}{x - i\delta} \quad (20)$$

Substituting this equation into Eq.(19), we have

$$G_r(E) = -\lim_{\delta \rightarrow 0^+} \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} (1 - e^{-\beta\hbar\omega}) \rho(\omega) \int_{-\infty}^{\infty} \frac{dx}{x - i\delta} \frac{1}{2\pi} \int_{-\infty}^{\infty} dt e^{-it(\omega - E - x)}$$

Then recognizing the delta-function in the form :

$$\delta(p) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dt e^{-itp},$$

we finally obtain

$$G_r(E) = \lim_{\delta \rightarrow 0^+} \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} (1 - e^{-\beta\hbar\omega}) \rho(\omega) \frac{1}{E - \omega + i\delta} \quad (21)$$

Following the same method, the Fourier transform of the advanced Green's function is obtained:

$$G_a(E) = \lim_{\delta \rightarrow 0^+} \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} (1 - e^{-\beta\hbar\omega}) \rho(\omega) \frac{1}{E - \omega - i\delta} \quad (22)$$

Up to now, the quantity E is considered to be real. However, we can continue $G_{r,a}(E)$ into the complex E -plane, without imposing too stringent conditions on $G_{r,a}(t)$. We may then combine the two Green's functions together by the following definition:

$$G(E) = \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} (1 - e^{-\beta\hbar\omega}) \rho(\omega) \frac{1}{E - \omega} \quad (23)$$

$$= \begin{cases} G_r(E) & \text{Im}(E) > 0 \\ G_a(E) & \text{Im}(E) < 0 \end{cases} \quad (24)$$

In the following discussion, we shall refer to this Fourier transform $G(E)$ as the Green's function.

Let us now recall that the definition of $G_{r,a}(t)$ by Eq.(16) involves the commutator between the Heisenberg operator $A(t)$ and $B(0)$. So far no restriction is imposed on the commutator in obtaining the integral expression for its Fourier transform $G(E)$. However, let us examine the behaviour of the integral of Eq.(23) as $|E| \rightarrow \infty$, by an expansion of the factor $(E - \omega)^{-1}$ in the integrand, thus

$$G(E) = \frac{1}{E} \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} (1 - e^{-\beta\hbar\omega}) \rho(\omega) + \frac{1}{E^2} \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} \omega (1 - e^{-\beta\hbar\omega}) \rho(\omega) + O(E^{-3}). \quad (25)$$

Here, the first term is seen to be $\frac{1}{2\pi E} \langle [A(0), B(0)] \rangle_T$ precisely (see Eq.(14)). Thus if the operators $A(0), B(0)$ commute, this term vanishes and the Green's function is of order $O(E^{-2})$ as $|E| \rightarrow \infty$. This fact then allows the evaluation of the integrals containing $G(E)$ by the use of contour integration, as will be seen later. In view of this fact, we shall construct Green's functions only for those operators A and B which commute at equal times.

From Eq.(23), we may express the spectral density in terms of the Green's functions. If we denote $f(\omega) = (1 - e^{-\beta\hbar\omega}) \rho(\omega)$, we can write the following equation

$$G(E+i\delta) - G(E-i\delta) = \frac{1}{2\pi} \int_{-\infty}^{\infty} d\omega f(\omega) \left\{ \frac{1}{E+i\delta-\omega} - \frac{1}{E-i\delta-\omega} \right\}.$$

Then, making use of the delta-function as represented in the form of

$$\delta(x) = \frac{i}{2\pi} \left\{ \frac{1}{x+i\delta} - \frac{1}{x-i\delta} \right\},$$

we relate the Green's function directly with $f(E)$, for

$$\begin{aligned} G(E+i\delta) - G(E-i\delta) &= \int_{-\infty}^{\infty} d\omega f(\omega) \delta(E-\omega) \frac{1}{i} \\ &= \frac{1}{i} f(E), \end{aligned}$$

for any value of E . By substituting the value ω for E , we finally express the spectral density in terms of the Green's functions

$$\rho(\omega) = \frac{i}{1 - e^{-\beta\hbar\omega}} \left\{ G(\omega+i\delta) - G(\omega-i\delta) \right\}.$$

It is now possible, through this spectral density function, to relate the correlation functions $F(t)$ to the corresponding Green's functions by means of an integral. To do this, we now rewrite Eq.(15) here, which gives the spectral density as a Fourier transform of $F_{AB}(t)$:

$$\rho(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dt e^{i\omega t} F_{AB}(t). \quad (15)$$

Hence, on comparison between Eqs.(26) and (15), and taking the Fourier transform of $\rho(\omega)$ again, the correlation function $F_{AB}(t)$ is given by

$$F_{AB}(t) = i \int_{-\infty}^{\infty} d\omega \frac{e^{-i\omega t}}{1 - e^{-\beta\hbar\omega}} \left\{ G(\omega+i\delta) - G(\omega-i\delta) \right\}. \quad (27)$$

In particular, the equal-time correlation function becomes

$$F_{AB}(0) = i \int_{-\infty}^{\infty} d\omega \frac{1}{1 - e^{-\beta\hbar\omega}} \left\{ G(\omega+i\delta) - G(\omega-i\delta) \right\}. \quad (28)$$

This is the relevant quantity we want to evaluate for the Lamb-Mössbauer factor. In Eq.(6), this function $F_{AB}(0)$ will be $\langle A_{kj}(0) A_{kj}(0) \rangle_T$.

So far we have taken ω as a real variable. We may write the above integral into more convenient forms, by introducing the complex variable $z = \omega \pm i\delta$, thus[†]

$$F_{AB}(0) = \int_{-\infty+i\delta}^{\infty+i\delta} dz \frac{iG(z)}{1 - e^{-\beta\hbar(z-i\delta)}} - \int_{-\infty-i\delta}^{\infty-i\delta} dz \frac{iG(z)}{1 - e^{-\beta\hbar(z+i\delta)}}. \quad (29)$$

[†]There were several misprints in the corresponding Eq.(4.17) of Maradudin's paper⁸.

The first integral is taken along the line parallel to the real axis with distance $+\delta$ above it ($z=x+i\delta$) and the second integral, along the equidistant parallel line below the axis ($z=x-i\delta$). Now we recall that the Green's functions go to zero like z^{-2} as $|z| \rightarrow \infty$ (see Eq.(25) and the following). We may now close the contour in (29) with an infinite semicircle in the upper half-plane in the first integral, and likewise in the lower half-plane in the second integral (see Fig.4). The contributions to the integrals from the infinite semicircles are then zero. The only contributions come from the residues of the poles of $(1-e^{-\beta\hbar(z-i\delta)})^{-1}$ and $(1-e^{-\beta\hbar(z+i\delta)})^{-1}$ respectively. For the first integral, the poles are given by

$$e^{-\beta\hbar(z-i\delta)} = 1 = e^{2\pi n i} \quad n, \text{ any positive integer}$$

or,
$$z_n = i(\delta + \omega_n)$$

where
$$\omega_n = \frac{2\pi n}{\beta\hbar} \quad n = 0, 1, 2, \dots, \infty.$$

There is thus an infinite number of simple poles all lying along the imaginary axis. In a similar manner, the poles in the second integral are found and are given by

$$z_n = -i(\delta + \omega_n) \quad n = 0, -1, -2, \dots, -\infty.$$

where ω_n is similarly defined as above, with n ranging through all negative integers and zero (see Fig.4). In evaluating the integrals, let us recall the well-known corollary⁹ in complex integration analysis that if there

exists a simple pole along the real axis of integration, only one half of the residue at that pole contributes to the integral. Thus in our case, the contribution to the first integral from the pole ^{at} $z = i\delta$ is $\pi i \text{Res} f(i\delta)$, where the entire integrand is denoted by $f(z) = \frac{iG(z)}{1 - e^{-\beta\hbar(z-i\delta)}}$.

Hence the first integral

$$\begin{aligned} &= \pi i \text{Res} f(i\delta) + \sum_{n=1}^{\infty} 2\pi i \text{Res} f[i(\delta + \omega_n)] \\ &= \frac{\pi G(i\delta)}{\beta\hbar} - \frac{2\pi}{\beta\hbar} \sum_{n=1}^{\infty} G[i(\delta + \omega_n)] \end{aligned} \quad (30)$$

since for a simple pole,

$$\begin{aligned} \text{Res} f[i(\delta + \omega_n)] &= \left. \frac{iG(z)}{\frac{d}{dz}[1 - e^{-\beta\hbar(z-i\delta)}]} \right|_{z=i(\delta + \omega_n)} \\ &= \frac{iG[i(\delta + \omega_n)]}{\beta\hbar e^{-\beta\hbar \omega_n i}} = iG[i(\delta + \omega_n)] \cdot \frac{1}{\beta\hbar} \end{aligned}$$

Again, taking into consideration the clockwise direction of integration, the second integral

$$\begin{aligned} &= -\pi i \text{Res} f(-i\delta) - \sum_{n=1}^{\infty} 2\pi i \text{Res} f[-i(\delta + \omega_n)] \\ &= \frac{\pi G(-i\delta)}{\beta\hbar} + \frac{2\pi}{\beta\hbar} \sum_{n=1}^{\infty} G[-i(\delta + \omega_n)] \end{aligned} \quad (31)$$

Combining Eqs. (30) and (31), the equal-time correlation function becomes, from Eq. (29):

$$\begin{aligned} F_{AB}(0) &= -\frac{\pi}{\beta\hbar} [G(i\delta) + G(-i\delta)] \\ &\quad - \frac{2\pi}{\beta\hbar} \left[\sum_{n=1}^{\infty} G(i\delta + i\omega_n) + \sum_{n=1}^{\infty} G(-i\delta - i\omega_n) \right] \end{aligned}$$

Upon taking the limit $\delta \rightarrow 0$, we finally obtain

$$\begin{aligned} F_{AB}(0) &= -\frac{2\pi}{\beta\hbar} G(0) - \frac{2\pi}{\beta\hbar} \left[\sum_{n=1}^{n=\infty} G(i\omega_n) + \sum_{n=1}^{n=\infty} G(-i\omega_n) \right] \\ &= -\frac{2\pi}{\beta\hbar} \sum_{n=-\infty}^{n=\infty} G(i\omega_n) \end{aligned} \quad (32)$$

since $\sum_{n=1}^{\infty} G(-i\omega_n) = \sum_{n=-1}^{-\infty} G(i\omega_n)$. Thus the function $F_{AB}(0)$ sought for is now expressed as an infinite sum of the Green's functions. For the unequal-time correlation function similar evaluation may be carried out. However, we shall not do this, since it is not presently needed.

connected to Eq. (32) when the relation of $F_{AB}(0)$ with the Green's function is established.

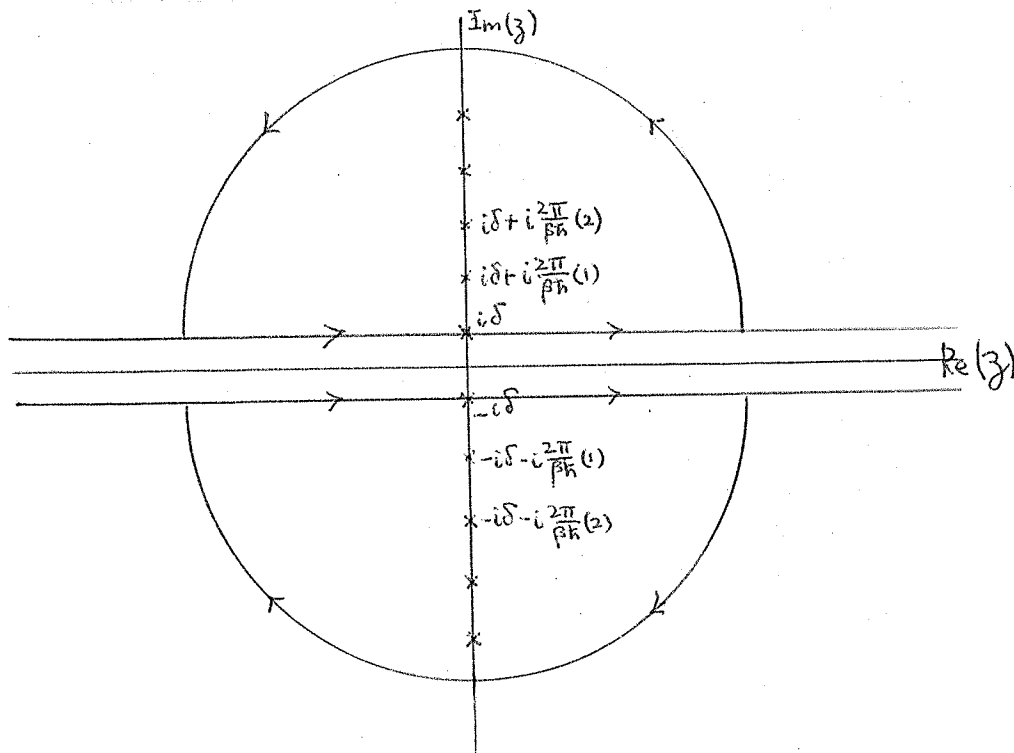


Fig. 4.

We must now see how these Green's functions are obtainable for a particular physical system. Let us return to the definition of the Green's functions $G(t)$, given in Eqs.(16a) and (16b). We can find their equations of motion by taking the time derivative of those equations. Since we can see that both the retarded and advanced functions satisfy the same equation of motion, it is unimportant to distinguish between them. Making use of the relation

$$\frac{d}{dt} \theta(t) = \delta(t)$$

and that the equation of motion for $A(t)$ is given by

$$i\hbar \frac{d}{dt} A(t) = [A(t), H(t)]$$

where $H(t)$ is the Hamiltonian of the system under consideration, we arrive at the equation of motion for $G(t)$, from Eq.(16) :

$$\begin{aligned} i\hbar \frac{d}{dt} G(t) &= \hbar \delta(t) \langle [A(t), B(0)] \rangle_T + \ll i\hbar \frac{d}{dt} A(t); B(0) \gg \\ &= \hbar \delta(t) \langle [A(t), B(0)] \rangle_T + \ll [A(t), H(t)]; B(0) \gg \quad (33) \end{aligned}$$

If the explicit form of the Hamiltonian is known and the solution for $G(t)$ is obtained, the Green's functions $G(E)$ which occur in the right hand side of Eq.(32) are obtainable by means of a Fourier transformation. Then the equal-time correlation $F_{AB}(0)$ is solved.

To apply the above considerations to our main

problem of expressing the Lamb-Mössbauer factor in terms of lattice dynamics, we simply note that $A(0), B(0)$ correspond to $A_{\underline{k}_j}(0), A_{\underline{k}'_j}(0)$, defined in Eq.(5). Let us therefore introduce the notation of a phonon Green's function:

$$G(\underline{k}_j, \underline{k}'_j, t) = \langle\langle A_{\underline{k}_j}(t); A_{\underline{k}'_j}(0) \rangle\rangle \quad (34)$$

Then from Eq.(32), the phonon equal-time correlation function is

$$F_{A_{\underline{k}_j}(0) A_{\underline{k}'_j}(0)} \equiv \langle A_{\underline{k}_j}(0) A_{\underline{k}'_j}(0) \rangle_T = -\frac{2\pi}{\beta\hbar} \sum_{n=-\infty}^{\infty} G(\underline{k}_j, \underline{k}'_j, i\omega_n) \quad (35)$$

In this equation, the Green's functions are the Fourier transforms of those defined in Eq.(34), which in turn are determined in Eq.(43) from the explicit Hamiltonian for the vibrating crystal lattice. Thus substituting this expression into Eq.(6), we finally obtain the exponent of the Lamb-Mössbauer factor, now expressed in terms of lattice dynamics of the crystal :

$$-2M = \frac{\hbar}{2NM} \sum_{\underline{k}_j} \sum_{\underline{k}'_j} \frac{(\vec{k} \cdot \vec{e}(\underline{k}_j)) (\vec{k} \cdot \vec{e}(\underline{k}'_j))}{[\omega(\underline{k}_j) \omega(\underline{k}'_j)]^{\frac{1}{2}}} \times \frac{2\pi}{\beta\hbar} \sum_{n=-\infty}^{\infty} G(\underline{k}_j, \underline{k}'_j, i\omega_n) \quad (36)$$

Eq.(36) is quite general, as we have not introduced any explicit model for the crystal lattice Hamiltonian \hat{H} , which determines the eigenfrequencies $\omega(\mathbf{k}_j)$, the eigenvectors $\vec{e}(\mathbf{k}_j)$ and the Green's functions $G(\mathbf{k}_j, \mathbf{k}'_j; i\omega_n)$ for the crystal. However once the Hamiltonian is given, corresponding to a physical model of the crystal, the Mössbauer effect can be calculated, at least in principle. A comparison with the experimental data would thus provide some insight into the lattice dynamics of the crystal.

V. SUMMARY

The Mössbauer effect has been seen as a special case of nuclear resonance fluorescence. It is characterised by the recoilless fraction, which is the fraction of gamma-rays in an absorption (or emission) process which undergoes no energy exchange with the crystal. The overlapping of the emission and the absorption lines thus gives rise to a large resonance effect. Without specifying a particular model for the crystal lattice, the recoilless fraction is given by thermal and quantum-mechanical average of the operator $e^{-i\vec{k}\cdot\vec{r}_\ell}$, where \vec{k} is the wave vector of the gamma-ray absorbed by the radioactive nucleus of position \vec{r}_ℓ , over the lattice states $|L\rangle$, thus $\left\{ \left| \langle L_i | e^{-i\vec{k}\cdot\vec{r}_\ell} | L_i \rangle \right|^2 \right\}_T$. For a harmonic crystal, using Boltzmann statistics, this fraction is equal to a product of e^{-2M} , the Lamb-Mössbauer factor and a Bessel functions factor. The Bessel functions factor may not be neglected if the crystal contains lattice defects. However, for a large crystal free of localised modes, the Lamb-Mössbauer factor is a very good approximation for this recoilless fraction. The exponent is closely related to the lattice dynamics of the crystal, for $2M = \langle (\vec{k}\cdot\vec{u}_\ell)^2 \rangle_T$, where \vec{u}_ℓ is the displacement vector of the nucleus ℓ from its equilibrium position. A double time Green's function method is then employed to write the Lamb-Mössbauer factor in terms of the lattice dynamics,

which can be solved, in principle, if the crystal Hamiltonian is specified.

APPENDIX A Theory of Natural Linewidth

Let us consider a system whose Hamiltonian consists of two parts: an unperturbed part H_0 and a small perturbation term H_{int} . The free part H_0 is equal to the sum of the Hamiltonians of the composite subsystems, in the absence of interaction, and the term H_{int} accounts for the interaction between these systems. The time evolution of a state $|\psi\rangle$ of the entire system is governed by the time-dependent Schrödinger equation:

$$i\hbar \frac{\partial}{\partial t} |\psi\rangle = H |\psi\rangle \quad (\text{A-1a})$$

where
$$H = H_0 + H_{int} \quad (\text{A-1b})$$

The solutions of this time-dependent equation may be obtained in the Schrödinger picture, where the operators are time-independent and the state vector are time-dependent, or in the Heisenberg picture where the time-dependence is completely transferred to the operators and the state vectors become time-independent. The two pictures (often denoted as "representations") are connected by a unitary transformation :

$$|\psi_H\rangle = e^{iH_S t/\hbar} |\psi_S\rangle \quad (\text{A-2a})$$

$$H_H = e^{iH_S t/\hbar} H_S e^{-iH_S t/\hbar}, \quad (\text{A-2b})$$

where H_H, S denote the Heisenberg and the Schrödinger representations respectively. It is seen that these two

pictures are identical at $t=0$, and that $|\psi_t\rangle$ is indeed time-independent, for

$$i\hbar \frac{\partial}{\partial t} |\psi_t\rangle = -e^{iH_0 t/\hbar} H_0 |\psi_s\rangle + i\hbar e^{iH_0 t/\hbar} \frac{\partial}{\partial t} |\psi_s\rangle = 0$$

from (A-1a).

However, in the study of the interaction as a perturbation, a third picture is often used with advantage. As we shall see, the time variation of the state vector in this picture will be determined by the interaction only, and the time dependence due to the free part H_0 is removed. This picture is called the interaction picture or the Dirac picture and is again related to the Schrödinger and the Heisenberg pictures through unitary transformations. For example, the transformation from the Schrödinger picture to the interaction picture is given by

$$|\psi_I\rangle = e^{iH_0 t/\hbar} |\psi_S\rangle \quad (\text{A-3a})$$

and

$$H_I = e^{iH_0 t/\hbar} H_S e^{-iH_0 t/\hbar} \quad (\text{A-3b})$$

where I denotes the interaction representation. Here we note that the unitary transformation carries the free part H_0 only and not the part H_{int} . Differentiating (A-3a) with respect to time, we have

$$i\hbar \frac{\partial}{\partial t} |\psi_I\rangle = H_{int} |\psi_I\rangle \quad (\text{A-4a})$$

where

$$H_{int} = e^{iH_0 t/\hbar} H_{int} e^{-iH_0 t/\hbar} \quad (\text{A-4b})$$

Thus in the presence of interaction, Eqs. (A-4) show that both the state vector $|\psi_I\rangle$ and operators are time-dependent. The unitary transformation of Eqs. (A-3) has effected a partial shift of the time-dependence from the state vector to the operator. In this sense, the interaction picture stands intermediate between the other two pictures. Now from (A-4a), we recognise that the evolution of $|\psi_I\rangle$ is indeed governed by the interaction only, and from (A-3a) we see that the exponential time-dependence of the non-interacting systems is removed. It is therefore most appropriate to use this interaction picture when interaction is treated as a perturbation. We remark that, in the absence of interaction, the interaction picture is identical to the Heisenberg picture, as can be seen from Eqs. (A-3).

Let us now proceed to solve Eqs. (A-4) ². The subscript S labelling quantities represented in the Schrödinger picture is omitted from now on. We denote $\{|n\rangle\}$ as a complete orthonormal set of eigenstates of the free Hamiltonian H_0 , and E_n , the energy eigenvalue of the state $|n\rangle$. The abbreviation n includes a complete description of the whole system when free of interaction. In particular, the system we are interested in is a system of radiation, and the entire crystal containing a Mössbauer nucleus.

Let us expand the spatial dependence of the interaction state vector $|\psi_I\rangle$ as a linear combination of the stationary eigenstates of H_0 :

$$|\Psi_I\rangle = \sum_m b_m(t) |m\rangle, \quad (\text{A-5})$$

where $|b_m(t)|^2$ is the probability that the system may be observed in the unperturbed state $|m\rangle$ at time t . We now insert (A-5) into (A-4a), multiply throughout by the bra vector $\langle n|$ and integrate over the variables on which $\langle n|$ depends. The result is

$$i\hbar \dot{b}_n(t) = \sum_m \langle n | H'_{int} | m \rangle b_m(t). \quad (\text{A-6})$$

Here, $\langle n | H'_{int} | m \rangle$ is the matrix element for the transition $m \rightarrow n$, and the prime now replaces I in indicating the interaction picture. In terms of H'_{int} , we make use of (A-4b) to bring out the time factors, and thus (A-6) becomes

$$i\hbar \dot{b}_n(t) = \sum_m \langle n | H_{int} | m \rangle e^{i(E_n - E_m)\frac{t}{\hbar}} b_m(t) \quad (\text{A-7})$$

Let us assume that initially, the whole system is in a certain unperturbed state, denoted by $|0\rangle$. Thus, at time $t=0$,

$$b_0(0) = 1, \quad b_n(0) = 0. \quad (\text{A-8})$$

The values of b_n , and therefore the transition probability, will vary with time as a consequence of the interaction. We shall assume that for a time not too long and for a small interaction, the value of b_0 has not changed much from unity while the values of b_n are still very small. Furthermore, we see that, to a first approximation, only those b_n 's for which the numbers of photons in n differs by unity from those in $|0\rangle$ will be different from zero.

Thus (A-7) may now be written as

$$i\hbar \dot{b}_n(t) = \langle n | H_{int} | 0 \rangle e^{i(E_n - E_0) \frac{t}{\hbar}} b_0(t) \quad (\text{A-9a})$$

$$i\hbar \dot{b}_0(t) = \sum_m \langle 0 | H_{int} | m \rangle e^{i(E_0 - E_m) \frac{t}{\hbar}} b_m(t). \quad (\text{A-9b})$$

These equations may be solved by imposing some approximation to $b_0(t)$, the probability amplitude of the state $|0\rangle$ at time t . We shall use a trial function

$$b_0(t) = e^{-\frac{\Gamma t}{2}}, \quad (\text{A-10})$$

satisfying initial condition in (A-8). This function implies the probability of finding the state $|0\rangle$ decreases exponentially with a life-time $\frac{1}{\Gamma}$. In fact, it can be seen² that Γ is just the natural line-width of the state $|0\rangle$, and is equal to the total spontaneous transition probability per unit time. The time integration of (A-9a), using (A-10), gives a general expression for the transition probability amplitude:

$$b_n(t) = \langle n | H_{int} | 0 \rangle \frac{1 - e^{i(E_n - E_0) \frac{t}{\hbar} - \frac{\Gamma}{2} t}}{\left[\frac{E_n - E_0}{2} + i \frac{\Gamma}{2} \right]}$$

The transition probability from state $|0\rangle$ to $|n\rangle$, in time t , is therefore given by

$$|b_n(t)|^2 = |\langle n | H_{int} | 0 \rangle|^2 \frac{1 - e^{-\Gamma t} - e^{-\Gamma t/2} 2 \cos\left(\frac{E_n - E_0}{\hbar} t\right)}{\hbar^2 \left[(E_n - E_0)^2 + \frac{\Gamma^2}{4} \right]}$$

After a long duration $t \gg \frac{1}{\Gamma}$, or taking the limit $t \rightarrow \infty$, we obtain the transition probability as

$$\left| b_n(\infty) \right|^2 = \frac{|\langle n | H_{int} | 0 \rangle|^2}{\hbar^2 \left[(E_n - E_0)^2 + \frac{\Gamma^2}{4} \right]} \quad (\text{A-11})$$

The function is seen to be symmetric about the line $E_n = E_0$, where it attains a maximum value of $|\langle n | H_{int} | 0 \rangle|^2 / \frac{\hbar^2 \Gamma^2}{4}$, and the width of the curve at half-maximum is Γ . This is known as a Lorentz curve, and the denominator is sometimes called the resonance denominator.

APPENDIX B Some exchange rules

We want to prove the following exchange rules:

- (I) For arbitrary constants u, v, w and $N = a^\dagger a$, the number operator,

$$e^{ua+va^\dagger} e^{N \log w} = e^{N \log w} e^{uva + \frac{v}{w} a^\dagger} \quad (\text{B-1})$$

- (II) If the commutator of two operators A and B commutes with each of them, that is $[A, [A, B]] = [B, [A, B]] = 0$, one has the identity

$$e^A e^B = e^{A+B + \frac{1}{2}[A, B]} \quad (\text{B-2})$$

This is called the Baker-Hausdorff formula.

- (III) For arbitrary constants u, v and a^\dagger, a the creation and annihilation operators,

$$e^{\frac{uv}{2} va^\dagger} e^{ua} = e^{ua+va^\dagger} = e^{-\frac{uv}{2}} e^{ua} e^{va^\dagger} \quad (\text{B-3})$$

The proofs are as follows:

- (I): From the commutation relations $[a, a^\dagger] = 1$, $[a^\dagger, a^\dagger] = [a, a] = 0$, one has $[a, N] = a$, $[a^\dagger, N] = -a^\dagger$ or, $aN = (N+1)a$ and $a^\dagger N = (N-1)a^\dagger$.

For arbitrary constants u, v , it follows that

$$\begin{aligned} (ua+va^\dagger)N &= (N+1)ua + (N-1)va^\dagger \\ (ua+va^\dagger)N^k &= (N+1)u a + (N-1)^k v a^\dagger, \end{aligned}$$

where k is a positive integer.

For a constant γ , $e^{\gamma N} = \sum_{k=0}^{\infty} \frac{(\gamma N)^k}{k!}$,

therefore $(uav^+)^{\gamma N} = e^{\gamma(N+1)} uav^+ + e^{\gamma(N-1)} v^+ a^+ u$
 $= e^{\gamma N} [e^{\gamma} uav^+ + e^{-\gamma} v^+ a^+ u]$.

Choosing $\gamma = \log w$ and noting $e^{uav^+} = \sum_{k=0}^{\infty} \frac{(uav^+)^k}{k!}$

we have

$$(uav^+)^k e^{N \log w} = e^{\log w} \left[w uav^+ + \frac{v^+}{w} a^+ u \right]^k$$

Hence $e^{uav^+} e^{N \log w} = e^{N \log w} e^{u w a + \frac{v}{w} a^+} \quad (B-1)$

(II): Let us consider an operator depending on a parameter

$$t: \quad f(t) = e^{At} e^{Bt}$$

One has $\frac{df}{dt} = [A + e^{At} B e^{-At}] f(t)$.

We consider the commutator $[B, e^{-At}] = B e^{-At} - e^{-At} B$.

$$[B, e^{-At}] = \sum_{n=0}^{\infty} (-1)^n \frac{t^n}{n!} [B, A^n]$$

$$= \sum_{n=0}^{\infty} (-1)^n \frac{t^n A^{n-1}}{(n-1)!} [B, A]$$

$$= -e^{-At} t [B, A]$$

$$\left[\begin{array}{l} \text{since} \\ [B, A^n] = n A^{n-1} [B, A] \\ \text{when } A \text{ commutes} \\ \text{with } [B, A] \end{array} \right]$$

Therefore

$$e^{At} B e^{-At} = B - t [B, A],$$

so that

$$\frac{df}{dt} = [A + B + [A, B]t] f$$

Integrating,

$$f(t) = e^{(A+B)t + \frac{1}{2}[A, B]t^2}$$

Setting $t=1$, we have

$$e^A e^B = e^{A+B + \frac{1}{2}[A, B]}$$

(B-2)

(III): Let us denote $A = v a^\dagger$, $B = u a$. Then the commutator $[A, B] = vu [a^\dagger, a] = -vu$, a constant number. Hence the commutator commutes with both A and B , and we may apply the Baker-Hausdorff formula (B-2) and obtain

$$e^{\frac{uv}{2}} e^{v a^\dagger} e^{u a} = e^{\frac{uv}{2}} e^{v a^\dagger + u a + \frac{1}{2}(uv)} = e^{v a^\dagger + u a}$$

Similarly,
$$e^{-\frac{uv}{2}} e^{u a} e^{v a^\dagger} = e^{v a^\dagger + u a} \quad (\text{B-3})$$

We shall now obtain Eq.(31) of section III.B, using the above exchange rules. Dropping the subscript s , we have

$$\begin{aligned} X &= \text{Tr} \left\{ e^{N \log \alpha} e^{i \frac{\sigma}{\sqrt{2}} (a^\dagger a)} e^{N \log \beta} e^{-i \frac{\sigma}{\sqrt{2}} (a^\dagger a)} \right\} && \text{Eq. (30) of III.B} \\ &= \text{Tr} \left\{ e^{N \log \alpha} e^{N \log \beta} e^{i \frac{\sigma}{\sqrt{2}} \beta a^\dagger + i \frac{\sigma}{\sqrt{2}} \beta a} e^{-i \frac{\sigma}{\sqrt{2}} (a^\dagger a)} \right\} && \text{using (B-1)} \\ &= \text{Tr} \left\{ e^{N \log \alpha \beta} e^{i \frac{\sigma}{\sqrt{2}} (\beta-1) a^\dagger + i \frac{\sigma}{\sqrt{2}} (\frac{1}{\beta}-1) a + \frac{\sigma^2}{2} (\frac{\beta^2-1}{\beta})} \right\} && \text{using (B-2)} \end{aligned}$$

Introducing one-half the commutator between $i \frac{\sigma}{\sqrt{2}} (\beta-1) a$ and $i \frac{\sigma}{\sqrt{2}} (\frac{1}{\beta}-1) a^\dagger$, we have

$$\begin{aligned} X &= \text{Tr} \left\{ e^{N \log \alpha \beta} e^{i \frac{\sigma}{\sqrt{2}} (\beta-1) a + i \frac{\sigma}{\sqrt{2}} (\frac{1}{\beta}-1) a^\dagger + \frac{1}{2} \left(\frac{\sigma^2}{2} \right) (\beta-1) \left(\frac{1}{\beta} \right) - \frac{1}{2} \left(\frac{\sigma^2}{2} \right) (\beta-1) \left(\frac{1}{\beta} \right) + \frac{\sigma^2}{2} \left(\frac{\beta^2-1}{\beta} \right)} \right\} \\ &= \text{Tr} \left\{ e^{N \log \alpha \beta} e^{i \frac{\sigma}{\sqrt{2}} (\beta-1) a} e^{i \frac{\sigma}{\sqrt{2}} (\frac{1}{\beta}-1) a^\dagger} \right\} e^{\frac{\sigma^2}{2} \left(\frac{\beta^2-1}{\beta} \right)} && \text{using (B-2)} \end{aligned}$$

which is Eq.(31) of III.B.

APPENDIX C. We want to prove Eq.(32) in section III.B:

$$\text{Tr} \left\{ e^{N \log w} e^{ua} e^{vat} \right\} = e^{\frac{uv}{1-w}},$$

where u, v, w , are arbitrary constants.

Proof : From (B-3), we have the relation :

$$e^{vat} e^{ua} = e^{-uv} e^{ua} e^{vat}. \quad (\text{B-3}')$$

Under similarity transformation, the trace remains invariant,

$$\begin{aligned} \text{Tr} \left\{ e^{N \log w} \right\} &= \text{Tr} \left\{ e^{-Ra^t} e^{-Sa} e^{N \log w} e^{Sa} e^{Ra^t} \right\} \\ &= \text{Tr} \left\{ e^{\frac{-RS}{2}} e^{-Ra^t - Sa} e^{N \log w} e^{\frac{SR}{2}} e^{Ra^t + Sa} \right\} \\ &= \text{Tr} \left\{ e^{N \log w} e^{-Swa - \frac{R}{w} a^t} e^{Ra^t + Sa} \right\} \\ &= \text{Tr} \left\{ e^{N \log w} e^{\frac{RS}{2}} e^{-\frac{R}{w} a^t} e^{S(1-w)a} e^{Ra^t} e^{-\frac{RS}{2}} \right\} \\ &= \text{Tr} \left\{ e^{N \log w} e^{S(1-w)a} e^{R(1-\frac{1}{w})a^t} e^{\frac{RS(1-w)}{w}} \right\} \end{aligned}$$

Setting $u=S(1-w)$, $v=R(1-\frac{1}{w})$, so that $uv = -\frac{RS(1-w)^2}{w}$,

we have

$$\text{Tr} \left\{ e^{N \log w} \right\} = e^{\frac{-uv}{1-w}} \text{Tr} \left\{ e^{N \log w} e^{ua} e^{vat} \right\}$$

$$\text{The left hand side} = \sum_{r=0}^{\infty} w^r = \frac{1}{1-w}$$

$$\text{therefore} \quad \text{Tr} \left\{ e^{N \log w} e^{ua} e^{vat} \right\} = \frac{1}{1-w} e^{\frac{uv}{1-w}}$$

APPENDIX D.

PART II.

We want to show that the step function

$$\theta(t) = \begin{cases} 1, & t > 0 \\ 0, & t < 0 \end{cases}$$

can be represented by the integral
$$I = \lim_{\delta \rightarrow 0^+} \int_{-\infty}^{\infty} \frac{dx}{2\pi i} \frac{e^{ixt}}{x - i\delta}$$

For convenience, let us write $I' = \int_{-\infty}^{\infty} f(x) dx$, where $f(x) = \frac{e^{ixt}}{2\pi i (x - i\delta)}$, then we have $I = \lim_{\delta \rightarrow 0^+} I'$. From the theory

of complex contour integration, it is known that I' can be replaced by an integral over a closed contour containing the real axis, provided the value of the integral over the part of the contour other than the real axis is zero. In this problem, we may use the semi-circle at infinity, either in the upper half-plane or in the lower half-plane, according to whether t is positive or negative. This can be seen by examining the complex integral over the semi-circle. Let $z = Re^{i\theta}$ (see Fig. 5). Now,

$$\begin{aligned} \int_{\text{Semicircle}} f(z) dz &= \int_{\text{Semicircle}} f(Re^{i\theta}) iRe^{i\theta} d\theta \\ &= \int_{\text{Semicircle}} \frac{Re^{i\theta}}{z\pi} \frac{e^{(iR\cos\theta)t}}{R\cos\theta + i(R\sin\theta - \delta)} e^{(-R\sin\theta)t} d\theta \end{aligned}$$

We see that the vanishing of this integral depends on the real exponential $e^{(-R\sin\theta)t}$ which again depends on the signs of t and $\sin\theta$.

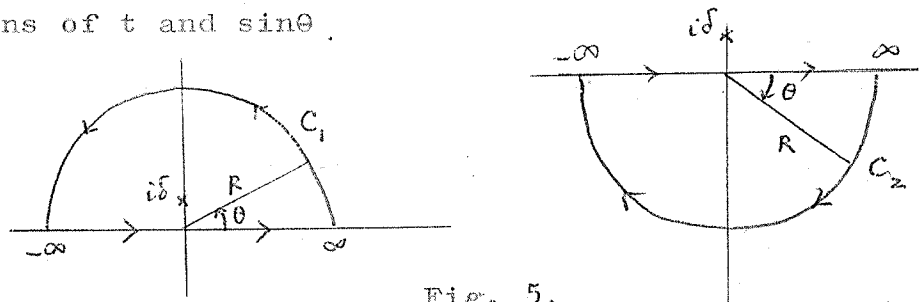


Fig. 5.

In order to ensure that the integral will vanish for $R \rightarrow \infty$, that is $e^{-(R \sin \theta)t} \rightarrow 0$, we must therefore have only two cases: (1) $t > 0$, $\sin \theta > 0$ or (2) $t < 0$, $\sin \theta < 0$. This implies the necessity of choosing the upper semi-circle in an anti-clockwise direction as contour for case (1) and the lower semi-circle in a clockwise direction for case (2) (see Fig.5). The integral I can now be evaluated as follows:

For $t > 0$

$$\begin{aligned} I &= \lim_{\delta \rightarrow 0^+} \left[\int_{-\infty}^{\infty} f(x) dx + \int_{\text{upper semicircle}} f(z) dz \right] \\ &= \lim_{\delta \rightarrow 0^+} \oint_{C_1} f(z) dz = \lim_{\delta \rightarrow 0^+} [2\pi i \operatorname{Res} f(i\delta)] = \lim_{\delta \rightarrow 0^+} e^{-\delta t} = 1. \end{aligned}$$

For $t < 0$

$$\begin{aligned} I &= \lim_{\delta \rightarrow 0^+} \left[\int_{-\infty}^{\infty} f(x) dx + \int_{\text{lower semicircle}} f(z) dz \right] \\ &= \lim_{\delta \rightarrow 0^+} \oint f(z) dz = 0. \end{aligned}$$

Hence the step function may be represented as

$$\theta(t) = \lim_{\delta \rightarrow 0^+} \int_{-\infty}^{\infty} \frac{dx}{2\pi i} \frac{e^{ixt}}{x - i\delta}$$

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