Some Simple Features of the Mossbauer Effect[*]

II. Sum Rules and the Moments of the Energy Spectrum

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General expressions for the moments of the Mössbauer energy spectrum are derived and sum rules for the second moment (dispersion), as well as for the first, are calculated. By examining these results one obtains physical insight into the mechanism of the momentum transfer to the lattice and appreciates the importance of the quantum-mechanical zero-point motion which cannot produce a Doppler shift in the classical sense. The principal effect of the binding forces is not to "hold the atom in the crystal" during the emission of the gamma ray; rather it is to produce zero-point motion before the emission.

The well known expression for the "Mössbauer fraction" in a crystal is derived in a simple way using the sum rule for the second moment.

INTRODUCTION

In processes like neutron capture or gamma ray emission and absorption by nuclei bound in crystal lattices, there is a sudden momentum transfer to a single atom in the lattice. In general this momentum transfer is accompanied by a transfer of energy to the lattice vibrations. The spectrum of this energy transfer has been calculated by Lamb (1). Interest in these processes was renewed following the discovery by Mössbauer (2) that there could be a finite probability for momentum transfer *without energy transfer* to the lattice vibrations.

The striking features of the Mössbauer effect are (1) that the momentum transfer is absorbed by the whole crystal without any internal changes; (2) that there is no Doppler broadening of the line due to thermal motion of the emitting atom in the lattice. Despite attempts to give a simple physical description of these features (3, 4) they still remain somewhat mysterious. In fact some of the simple pictures proposed tend to be confusing and in contradiction with the exact treatment. One example is the argument that the atom is so strongly bound that "it cannot recoil freely but must carry the whole crystal along with it." Examination of the quantum-mechanical calculations show that the opposite is true. The binding forces are considered to be so weak that they can be neglected completely during the process of momentum transfer. The spirit of the calcula-

tion seems to be that of the "impulse approximation" (5), in which the role of the binding forces is simply to determine the possible energy states of the lattice before and after the momentum transfer process.[1] Other misleading arguments involve the lifetimes of the nuclear state and the fact that it is generally long compared to characteristic lattice vibration times. One is tempted to think that the Doppler shifts due to the rapid vibrational motion are somehow averaged out over the long lifetime. It is then surprising to note that the lifetime of the nuclear state does not enter at all in the calculations of the dynamics of the momentum transfer. Again we have the impulse approximation, in which the momentum transfer is considered to take place *instantaneously*, not during the whole lifetime, with the emission of an indivisible quantum.

In this paper, the approach of our previous treatment (3) is generalized to obtain simple exact expressions for the moments of energy transfer distribution associated with momentum transfer to an atom in a lattice. Sum rules having general validity are obtained for the second moment as well as the first. The underlying physical basis of the Mössbauer effect is clarified by comparison of these expressions with the strikingly similar ones obtained in a simple classical model in which the momentum transfer is treated by straightforward billiard-ball kinematics. In particular the crucial role of the quantum-mechanical zero point motion is brought into evidence by this comparison.

A CLASSICAL EXAMPLE

Let us first consider the simple classical kinematics of the emission of a gamma ray of momentum $\mathbf{p}_\gamma$ by an atom of mass M having an initial momentum $\mathbf{p}_i$. The momentum of the atom after the emission of the gamma ray is just $\mathbf{p}_i - \mathbf{p}_\gamma$, and the kinetic energy of the atom is thus

$$E_f = (\mathbf{p}_i - \mathbf{p}_\gamma)^2/2M = E_i + R - (\mathbf{p}_i \cdot \mathbf{p}_\gamma/M) \qquad (1)$$

where

$$E_i = p_i^2/2M$$

is the initial kinetic energy of the atom and

$$R = p_\gamma^2/2M \qquad (2)$$

is the so-called "free recoil energy"; i.e., the energy transfer due to recoil if the atom is initially at rest and recoils freely.

Let us now assume that the atom emitting the gamma ray is bound and moving classically in a crystal lattice, and that the gamma ray emission occurs instantaneously. The kinematics of the momentum and energy transfer is described by Eq. (1) where p_i is the momentum of the atom at the instant before the emission

of the gamma ray. After the gamma ray is emitted, the recoiling atom interacts with the other atoms in the lattice in a complicated way, transferring momentum and energy to the various modes of motion. However, since both energy and momentum are conserved in these interactions, they are of little interest to us. The momentum and energy transfer between the gamma ray and the lattice are determined by the kinematics at the instant of emission, and cannot be changed by the subsequent processes within the lattice after the gamma ray is gone. Thus Eq. (1) is valid also for this case with E_i and E_f now being taken to be the initial and final energies of the *lattice*.

If this "experiment" is repeated a large number of times, the energy of the lattice final state E_f will in general be different each time, as it depends upon the momentum of the emitting atom at the instant before the gamma ray is emitted. We can define a function $P(E_f)$ such that $P(E_f)\, dE_f$ is the probability that the final state of the lattice will be between E_f and $E_f + dE_f$. Since energy is conserved in the emission of the gamma ray, the function $P(E_f)$ is directly related to the spectrum of the emitted gamma rays. We can also talk about the moments of energy distribution. From Eq. (1) we see that the mean value of $(E_f)^n$ is just

$$\langle (E_f)^n \rangle = \langle [E_i + R - (\mathbf{p}_i \cdot \mathbf{p}_\gamma)/M]^n \rangle \tag{3}$$

Thus the moments of the energy distribution are simply related to the moments of the momentum distribution for the emitting atom in the initial state. They are completely independent of the character of the binding forces, except insofar as these forces determine the momentum distribution; i.e., they are the same as for a gas of free atoms with the same momentum distribution. This result is of course not surprising, as it was put into the model in the first place by the assumption that the momentum transfer was instantaneous.

If we assume that the angular distribution of the momentum $\mathbf{p}_i$ is isotropic, then $\langle \mathbf{p}_i \cdot \mathbf{p}_\gamma \rangle = 0$ and $\langle (\mathbf{p}_i \cdot \mathbf{p}_\gamma)^2 \rangle = \langle p_i^2 \rangle p_\gamma^2/3$, and the first two moments become

$$\langle E_f \rangle = E_i + R \tag{4a}$$

$$\langle (E_f)^2 \rangle = (E_i + R)^2 + 2R\langle p_i^2 \rangle/3M \tag{4b}$$

and the dispersion of the distribution is given by

$$\langle E_f^2 \rangle - \langle E_f \rangle^2 = 2R\langle p_i^2 \rangle/3M \tag{4c}$$

From Eq. (4a) we see that the average energy transfer to the lattice is just the free recoil energy R. From Eqs. (4b) and (4c) we see that the "spread" or dispersion of the distribution is simply related to the dispersion of the initial momentum distribution. This spread is just the usual "Doppler broadening."

THE QUANTUM-MECHANICAL PROBLEM

Let us now consider the real quantum-mechanical problem where a momentum $-\mathbf{p}_\gamma$ is transferred suddenly to an atom in a lattice, say by emission of a gamma ray of momentum $\mathbf{p}_\gamma$, and the lattice is initially in a quantum state $|i\rangle$. The probability that the lattice will be in the state $|f\rangle$ after the emission of the gamma ray has been shown to be given by (3) the square of the transition matrix element

$$P_{i \to f} = |\langle f| \exp(-i\mathbf{p}_\gamma \cdot \mathbf{X}_L/\hbar)|i\rangle|^2 \tag{5}$$

where $\mathbf{X}_L$ is the coordinate of the atom emitting the gamma ray.

Let us now consider the energy spectrum $P(E_f)$ for the final lattice state. Since the lattice has a discrete energy spectrum, $P(E_f)$ can differ from zero only for values of E_f corresponding to energy levels of the lattice. $P(E_f)$ is therefore a highly singular function consisting of a set of closely spaced delta functions. (These are smeared out in the gamma ray spectrum, because of the finite line width.) For this reason it is more convenient to treat quantities like the moments and the Fourier transform of $P(E_f)$, rather than $P(E_f)$ itself, particularly if a comparison with corresponding classical problem is desired. The moments are conveniently expressed with the aid of Eq. (5):

$$\langle E_f^n \rangle = \int E_f^n P(E_f)\, dE_f = \sum_f E_f^n P_{i \to f}$$
$$= \sum_f \langle i| \exp(i\mathbf{p}_\gamma \cdot \mathbf{X}_L/\hbar)|f\rangle E_f^n \langle f| \exp(-i\mathbf{p}_\gamma \cdot \mathbf{X}_L/\hbar)|i\rangle \tag{6}$$

If H is the Hamiltonian of the lattice, then E_f is just the eigenvalue of H in the state $|f\rangle$, and Eq. (6) reduces to the form

$$\langle E_f^n \rangle = \langle i\, |\{\exp(i\mathbf{p}_\gamma \cdot \mathbf{X}_L/\hbar)\} H^n \{\exp(-i\mathbf{p}_\gamma \cdot \mathbf{X}_L/\hbar)\}|\, i\rangle \tag{7a}$$

$$= \langle i\, |[\{\exp(i\mathbf{p}_\gamma \cdot \mathbf{X}_L/\hbar)\} H \{\exp(-i\mathbf{p}_\gamma \cdot \mathbf{X}_L/\hbar)\}]^n|\, i\rangle \tag{7b}$$

The expression (7b) can be simplified considerably if the lattice forces are assumed to be velocity independent, as is certainly the case to a very good approximation.[2] Then the only part of the Hamiltonian H which does not commute with the coordinate $\mathbf{X}_L$ is the kinetic energy of the atom $\mathbf{X}_L$; namely $\mathbf{P}_L^2/2M$, where $\mathbf{P}_L$ is the momentum of this atom. Thus

$$\{\exp(i\mathbf{p}_\gamma \cdot \mathbf{X}_L/\hbar)\} \mathbf{P}_L \{\exp(-i\mathbf{p}_\gamma \cdot \mathbf{X}_L/\hbar)\} = \mathbf{P}_L - \mathbf{p}_\gamma \tag{8a}$$

[2] This is true both in the usual phenomenological models of the lattice, where the interatomic forces are taken as approximately harmonic, and in the real lattice where the forces are Coulomb forces between the ions and electrons. The Lorentz force due to the motion of the ion in magnetic fields is certainly negligible.

$$\{\exp(i\mathbf{p}_\gamma\cdot\mathbf{X}_L/h)\}(\mathbf{P}_L{}^2/2M)\{\exp(-i\mathbf{p}_\gamma\cdot\mathbf{X}_L/h)\} = (\mathbf{P}_L - \dot{p}_\gamma)^2/2M$$
$$= P_L{}^2/2M + R - (\mathbf{P}_L\cdot\mathbf{p}_\gamma/M) \tag{8b}$$

and

$$\{\exp(i\mathbf{p}_\gamma\cdot\mathbf{X}_L/\hbar)\}H\{\exp(-i\mathbf{p}_\gamma\cdot\mathbf{X}_L/\hbar)\} = H + R - (\mathbf{P}_L\cdot\mathbf{p}_\gamma)/M \tag{9}$$

Substituting Eq. (9) into Eq. (7b) we obtain

$$\langle E_f{}^n\rangle = \langle i\,|[H + R - (\mathbf{p}_\gamma\cdot\mathbf{P}_L)/M]^n|\,i\rangle \tag{10}$$

Note the similarity between Eq. (10) and the corresponding classical result Eq. (3). The only difference is the appearance of the operator H in (10) instead of the initial energy E_i. However, the operator H, operating on $|\,i\rangle$ either from the left or from the right gives just the energy of the initial state E_i. Thus for $n = 1$ and $n = 2$, we obtain

$$\langle E_f\rangle = E_i + R - \langle i\,|(\mathbf{p}_\gamma\cdot\mathbf{P}_L)/M\,|\,i\rangle \tag{11a}$$

$$\langle E_f{}^2\rangle = \langle i\,|[E_i + R - (\mathbf{p}_\gamma\cdot\mathbf{P}_L)/M]^2|\,i\rangle \tag{11b}$$

These now have exactly the same form as Eq. (3). If we assume an isotropic angular distribution for the momentum $\mathbf{P}_L$, the sum rules (11) reduce to

$$\langle E_f\rangle = E_i + R \tag{12a}$$

$$\langle E_f{}^2\rangle = (E_i + R)^2 + 2R\langle P_L{}^2\rangle/3M \tag{12b}$$

and the dispersion is given by

$$\langle E_f{}^2\rangle - \langle E_f\rangle^2 = 2R\langle P_L{}^2\rangle/3M \tag{12c}$$

For the higher moments there will be at least one factor involving the Hamiltonian H which does not act directly on the states $|\,i\rangle$, neither from the left nor from the right. Because of the binding forces, H does not commute with the operator $\mathbf{P}_L$. By use of the commutation rules for H and $\mathbf{P}_L$, all operators H appearing in (6) can be moved to either the right or left end and then replaced by E_i, thus reducing Eq. (6) to the form

$$\langle E_f{}^n\rangle = \langle i\,|[E_i + R - (\mathbf{p}_\gamma\cdot\mathbf{P}_L)/M]^n|\,i\rangle + \text{terms involving commutators}[3] \tag{13}$$

DISCUSSION

We now note that except for the terms involving commutators in Eq. (13) the expressions (11), (12), and (13) are exactly the same as the corresponding classical expressions (3) and (4). The expressions (11), (12), and the first term in (13) are therefore just the values of the moments of the energy distribution

[3] Similar results have been obtained for neutron scattering (7).

which would be obtained by *classical kinematics from the momentum distribution of the initial state*. They depend only upon the moments $\langle(\mathbf{p}_\gamma\cdot\mathbf{P}_L)^n\rangle$ of the momentum distribution, and are independent of the dynamics of the system (i.e., of the Hamiltonian). We also note that the terms involving commutators in (13) are proportional to h and vanish in the classical limit. We can therefore now draw the following conclusions:

In the classical limit for the lattice, all the moments of the energy distribution are the same as they would be for a gas of free atoms having the same momentum distribution. Thus *there are no effects of the binding on gamma ray spectrum as long as the lattice can be treated classically.* Any effects of the binding must be quantum effects which appear only when the lattice is described by small quantum numbers; i.e., at low temperature.

The first and second moments are always the same as for a gas of free atoms with the same momentum distribution. These are the *mean* energy transfer and the *mean square* energy transfer. The dispersion, Eq. (12c), is therefore also the same. As has been discussed above, this dispersion is just the Doppler broadening, due to the spread in the initial momenta of the gas atoms. This *"Doppler width"* *is not affected by quantum and binding effects.* The only effect of the binding can be a change in the *shape* of the spectrum, without changing either its centroid or its width.

The manner in which quantum effects can produce a large probability of a small or zero energy transfer can be understood as follows. Let us assume that the system has an isotropic initial momentum distribution which, in a gas, would give the energy distribution $P(E_f)$ shown in Fig. 1. It is centered at $(E_i + R)$ in accordance with Eq. (12a), and has a width which is characteristic of the spread in the momentum distribution as given by Eq. (12c). Let us now assume that the system is at zero temperature. This implicitly assumes that the system is quantum-mechanical having zero-point motion at absolute zero. (A classical system would have no velocity at zero temperature and there would be no spread and no width to the momentum distribution nor to the corresponding distribution of $P(E_f)$.)

According to our sum rules, the energy spectrum for the low temperature quantum crystal must have the same mean and the same width as the distribution shown in Fig. 1 for a "gas" having the same momentum distribution.[4] However, *all the area to the left of $E = 0$ in Fig. 1 cannot be present in a system at zero temperature.* The system *cannot lose energy* as there are no available lower states.

Figure 2 shows a distribution which is identical to that of Fig. 1, except that all the area to the left of $E = 0$ has been removed. The curve of Fig. 2 has eliminated.

[4] Such a "gas" would not be in general in thermal equilibrium. It is simply a system of non-interacting particles with a momentum distribution which would probably not be Maxwellian.
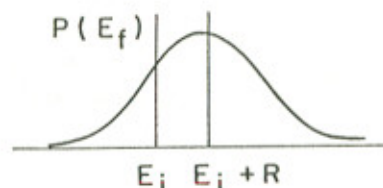
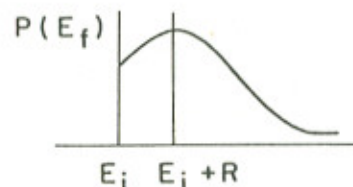FIG. 1. Classical energy spectrum for gaseous source.

FIG. 2. Positive energy transfer portion of Fig. 1.

nated the "nonphysical region" of Fig. 1 for a zero temperature system. However, it does not satisfy the sum rules (11a) and (11b). By removing the area to the left of $E = E_i$ the centroid of the distribution has been shifted to the right, and the width has been decreased. In order to obtain a distribution which has the proper centroid and width, it is necessary to modify Fig. 2 by shifting the centroid to the *left* and by increasing the width.

Let us now attempt to restore the area of the nonphysical region which has been removed in Fig. 2, in such a way that it appears in a physical region and restores the sum rules. It is immediately evident that this is impossible. The best that one can do for the sum rules is to insert this area as a delta function at $E = E_i$, as shown in Fig. 3. However, it is clear by comparing Figs. 1 and 3 that the centroid is still shifted to the right and the width has been reduced. In order to obtain a distribution which satisfies the sum rules and has all its area in a physical region it is necessary to modify Fig. 3 in such a way as to shift its centroid to the *left* and *increase* its width. This can only be done by shifting the distribution between E_i and $E_i + R$ to the left, thereby obtaining a distribution which is peaked around $E = E_i$ perhaps even more than that of Fig. 3.

Although these simple arguments do not show why the form of $P(E_f)$ should necessarily have a sharp narrow peak at $E = E_i$ they indicate why there should be a peaking in this region much greater than expected for a similar momentum distribution in a gas. It is not because the nucleus is "frozen in the crystal and cannot recoil," nor is it because "the Doppler broadening is washed out by the motion in the lattice." *Both the recoil energy loss and the "Doppler" broadening are present with exactly the same magnitude as for a classical gas with the same momentum distribution.* However, the momentum spectrum contains components
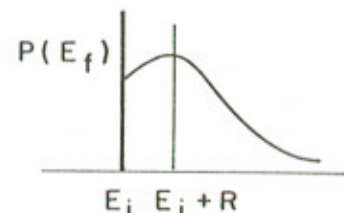
FIG. 3. Spectrum of Fig. 2 with added delta function.

in which the nucleus is moving rapidly in the same direction as that of the emitted gamma ray, and would thus *lose* kinetic energy in the emission process according to classical kinematics. It is these components in the momentum spectrum which produce the nonphysical region in Fig. 1 to the left of $E_f = E_i$. These components "have no place to go" in a low temperature crystal. This is the essential difference between the classical and the quantum case, which leads to the Mössbauer phenomenon.

At zero temperature the spread in the momentum distribution of the system is entirely due to quantum-mechanical zero-point motion. At finite temperature, part of the spread will be due to thermal motion, and some of the area to the left of $E_f = E_i$ in Fig. 1 is allowed for the crystal, as there are energy states available with lower energy than the initial state. However, as long as the contribution of the zero-point motion is appreciable by comparison with the thermal motion, one would expect a "nonphysical region" to be present at the left-hand side of Fig. 1, where the energy loss as calculated by classical kinematics would be too large for a quantum system at low temperatures. The presence of such a "nonphysical region" in the classical curve indicates that the spectrum for a crystal must be different from the classical case and must be peaked around zero energy transfer in order to satisfy the sum rules.

THE MÖSSBAUER PEAK

Using the sum rule (11b) for the second moment of the energy distribution, we shall now see in a simple way how the Mössbauer peak arises; i.e., how there can be a finite and appreciable value for the probability $P(E_i)$ that the lattice energy remains at its initial value E_i after the transition. Let us first assume that the atom is moving in a one-dimensional harmonic oscillator well, with frequency ω, and that it is initially in the nth excited state of the oscillator. Let P_k be the probability that the atom jumps to the $(n + k)$th state of the oscillator after the transition. If we choose the zero of our energy scale such that the initial state energy E_i is zero, then the sum rule (11b) for the second moment tells us that

$$\sum_k P_k (k\hbar\omega)^2 = R^2 + p_\gamma^2 \langle P_L^2 \rangle / M^2 = R^2 + 2R\langle P_L^2 \rangle / M \qquad (14)$$

If we assume that the only appreciable contributions come from $k = 1, 0, -1$; i.e., that jumps of more than one phonon are negligible,[5] Eq. (14) gives us directly the probability P_0 of the Mössbauer peak, since

$$\sum_k P_k (k\hbar\omega)^2 \sim [(\hbar\omega)^2 \cdot (P_1 + P_{-1})] \sim (\hbar\omega)^2 (1 - P_0) \qquad (15a)$$

Equation (15a) is easily generalized to the case where we do not neglect the multiphonon transitions. In this case a lower limit for P_0 is obtained:

$$\sum_k P_k (k\hbar\omega)^2 \geq \sum_{k \neq 0} P_k (\hbar\omega)^2 = (\hbar\omega)^2 (1 - P_0) \qquad (15b)$$

Substituting Eqs. (15) into Eq. (14), we obtain

$$P_0 \geq 1 - 2R\langle P_L^2\rangle / M(\hbar\omega)^2 - R^2/(\hbar\omega)^2 \qquad (16a)$$

$$\geq 1 - p_\gamma^2\langle P_L^2\rangle / M^2(\hbar\omega)^2 - R^2/(\hbar\omega)^2 \qquad (16b)$$

where the equality holds when jumps of more than one phonon are neglected.

The reason why the sum rule gives us a lower limit for P_0 is clear. Because of the quantization of the energy levels of the oscillator, the part of the probability distribution $(1 - P_0)$ which is not at the Mössbauer peak must be at least at a distance $\hbar\omega$ away from it, and must contribute *at least* $(1 - P_0)(\hbar\omega)^2$ to the second moment. The quantity $(1 - P_0)$ is therefore limited *to prevent the "Doppler width" from being too large.* An appreciable probability P_0 for the Mössbauer peak thus follows from the finite separation between the discrete oscillator states and the necessity to conserve the average "Doppler" broadening.

The results (16) can be expressed in more convenient forms by making use of the well-known relations for the mean values of the kinetic and potential energies of a harmonic oscillator,

$$\frac{\langle P_L^2\rangle}{2M} = \frac{M\omega^2\langle X_L^2\rangle}{2} = \frac{1}{2}\left(n + \frac{1}{2}\right)\hbar\omega \qquad (17)$$

Substituting Eq. (17) into Eq. (16) we obtain

$$P_0 \geq 1 - (2n + 1)\frac{R}{\hbar\omega} - \frac{R^2}{(\hbar\omega)^2} \qquad (18a)$$

$$P_0 \geq 1 - \frac{p_\gamma^2\langle X_L^2\rangle}{\hbar^2} - R^2/(\hbar\omega)^2 \qquad (18b)$$

From Eq. (18a) we see that P_0 is appreciable if $(2n + 1)R/\hbar\omega$ is small; i.e., if the oscillator energy level spacing is large compared with the free recoil energy and if the initial excitation is not too high. This fits in with our earlier conclusion that zero-point motion must be appreciable. The energy of zero-point motion is

[5] This approximation is also made in conventional treatments of the effect (1).

just $(\hbar\omega)/2$ and this is significant if R is small compared to $\hbar\omega$ and if n is not too large. Since ω in this simple model can be interpreted as some average phonon frequency for the lattice and $n\hbar\omega$ as the thermal energy, we see that this is also in accord with the usual result that the Mössbauer effect is large if the Debye temperature is larger than the free recoil energy and the temperature is not too high (3).

From Eq. (18b) we obtain an alternative expression of the same conclusion; namely that an appreciable Mössbauer probability is obtained if the mean square deviation of the atom from its equilibrium position, $\langle X_L^2\rangle$, is small with respect to the wavelength $\hbar/p_\gamma$ of the gamma ray. This is suggestive of the expression encountered in x-ray diffraction for the intensity of the scattered beam (the Debye-Waller factor) (6). One obtains an apparently completely different picture of an atom as a "radiating cloud" of extension $\langle X_L^2\rangle$. The intensity of the radiated electromagnetic wave is small if size of the cloud is large compared to the gamma ray wavelength, because of destructive interference between radiation originating at different points of the "cloud."

The relation between this wave picture and our original "billiard-ball" kinematics is just the characteristic complementarity of the quantum theory. The mean square deviation $\langle X_L^2\rangle$ of the atom from its equilibrium position is related by the uncertainty principle to the spread in momentum due to zero-point motion. To say that the size of the radiating cloud must be smaller than the wavelength of the gamma ray is thus the same as saying that the momentum of the zero-point motion must be greater than the momentum of the gamma ray. Thus we return again to our central argument that an essential feature of the Mössbauer effect is a zero-point motion of large momentum which can absorb the momentum transfer involved in the emission of the gamma ray.

The results (18) can be generalized to the case of a crystal lattice in which there are a large number of normal vibrational modes. Because the normal modes are all independent, we may treat each individual mode like the single oscillator model of Eqs. (18). The probability that there is no change in the energy in the lattice is then the probability that there is no change in the energy of the normal modes. Thus from Eq. (18)

$$P_0 = \prod_s (P_0)_s \geq \prod_s [1 - (2n_s + 1)R_s/\hbar\omega_s - R_s^2/(\hbar\omega_s)^2] \qquad (19a)$$

$$\geq \prod_s [1 - (p_s^2\langle x_s^2\rangle/\hbar^2) - R_s^2/(\hbar\omega_s)^2] \qquad (19b)$$

where $(P_0)_s$ is the probability of no energy change in the sth normal mode; ω_s is the frequency, n_s the state of excitation, x_s the coordinate of the sth normal mode; and p_s and R_s are the fraction of the gamma ray momentum and free recoil energy taken up by the sth normal mode.

The well-known approximate result for P_0 is obtained directly from Eq. (19) in

the approximation that the number of normal modes is large and that jumps of more than one phonon *in a single mode* can be neglected. In the latter approximation the relations of Eq. (19) hold as approximate equalities, as well as inequalities. The exact manner in which the momentum of the gamma ray p_γ is divided between the different normal modes is determined by the specific transformation from the particle coordinates to the normal coordinates. However, since this is an orthogonal transformation, the scalar product of the two vectors $\mathbf{p}_\gamma/\hbar$ and $\mathbf{X}_L$ remains invariant; thus

$$\mathbf{p}_\gamma \cdot \mathbf{X}_L/\hbar = \sum_s p_s x_s/\hbar \tag{20}$$

Since the normal modes are independent of one another, the mean values of products $\langle x_s x_t \rangle$ must vanish for $s \neq t$. We thus have for the mean square of Eq. (20),

$$\langle (p_\gamma \cdot X_L)^2/\hbar^2 \rangle = \sum_s p_s^2 \langle x_s^2 \rangle/\hbar^2 \tag{21}$$

Since the left-hand side of Eq. (21) is of order unity, each term in the sum on the right-hand side, being positive definite, must be small if the number of contributing normal modes is large. We thus see that the second term in the square brackets in each of Eqs. (19) is small and the third term, being of the order of the square of the second, is negligible. The product of a large number of factors very close to unity can be approximated well by an exponential (3), to give the well-known results (1-4)

$$P_0 \sim \exp[-\sum_s (2n+1) R/\hbar\omega_s] \tag{22a}$$

$$\sim \exp[-\langle (\mathbf{p}_\gamma \cdot \mathbf{X}_L)^2 \rangle] \tag{22b}$$

ACKNOWLEDGMENT

APPENDIX—THE SUDDENNESS OF THE MOMENTUM TRANSFER

The discussion of the momentum transfer process given in this paper indicates a considerable similarity between the quantum-mechanical treatment and the classical example of an impulsive momentum transfer treated by billiard ball mechanics. The classical treatment describes well the "average" properties of the energy transfer distribution (i.e., the mean and the mean square energy transfer). The deviations of finer details of the distribution from the classical result can be interpreted as typical quantum effects due to the discreteness of lattice energy levels and the presence of zero point kinetic energy even at zero temperature. One may ask whether the process is really described correctly as a sudden momentum transfer with quantum corrections. To investigate this point, we must look more

closely at the quantum-mechanical calculations and see whether the process can in some way be described as "sudden."

Considerable insight is gained by examining the relation (5) that the probability of a transition between two states $|i\rangle$ and $|f\rangle$ is given by the square of the matrix element of the operator $\exp(-i\mathbf{p}_\gamma \cdot \mathbf{X}_L/\hbar)$ between the two states

$$P_{i \to f} = |\langle f | M | i \rangle|^2 = |\langle f | \exp(-i\mathbf{p}_\gamma \cdot \mathbf{X}_L/\hbar) | i \rangle|^2 \tag{5}$$

We note, first of all, that this relation is true regardless of the nature of the binding and even in the absence of binding. The effects of the binding appear only in the form of the initial and final wave functions $|i\rangle$ and $|f\rangle$, but not in the form of the operator. We also note that the probability P_0 for the Mössbauer peak, in which the final and initial states are the same, is the square of the diagonal matrix element of this operator in the initial state. If we write the wave function $|i\rangle$ as a function $\psi_i(X_1, \cdots X_L \cdots X_N)$ of the coordinates of the N atoms in the lattice, then

$$P_0 = \left| \int \psi_i^* \exp(-i\mathbf{p}_\gamma \cdot \mathbf{X}_L/\hbar)\psi_i \, dX_1 \cdots dX_L \cdots dX_N \right|^2$$

Since the operator in the integral depends only upon the coordinate X_L, the integration over all the other coordinates can be carried out independent of the operator, to give the result

$$P_0 = \left| \int \rho_i(\mathbf{X}_L) \exp(-i\mathbf{p}_\gamma \cdot \mathbf{X}_L) \, d\mathbf{X}_L \right|^2$$

where

$$\rho_i(\mathbf{X}_L) = \int \psi_i^* \psi_i \quad \text{(integrated over all coordinates except } \mathbf{X}_L)$$

$\rho_i(\mathbf{X}_L)$ is the spatial probability density for the atom X_L. The Mössbauer probability P_0 is therefore just the Fourier transform of the density distribution for the atom $\mathbf{X}_L$. (For the case where this density is approximated by a gaussian, the Fourier transform is also gaussian and the familiar result (22b) is obtained directly without further assumptions regarding lattice dynamics.)

These relations are all consistent with the picture of a sudden impulsive momentum transfer. The operator appearing in the expression (5) is a purely kinematic operator, unaffected by binding forces, and the probability P_0 depends only upon the spatial density distribution for the atom $\mathbf{X}_L$ in the initial state, independent of the binding effects or of properties of the other states of the system. Let us now investigate the conditions for the validity of these relations to see whether they can be interpreted as a requirement that the transfer be sudden.

All these relations follow directly from Eq. (5), which has the feature that the operator appearing in the expression is independent of binding effects. This is clearly true for any process described by first order perturbation theory, where the operator appearing in the transition matrix element is simply the interaction giving rise to the transition, and the form of the operator is determined uniquely by momentum conservation and Galilean invariance (3).

Equation (5) and its consequences are not *generally* valid, as can be seen by examining a case described by *second order* perturbation theory. The transition matrix element for such a case is

$$\langle f\,|\,M\,|\,i\rangle = \sum_k \frac{\langle f\,|\,H'\,|\,k\rangle\langle k\,|\,H'\,|\,i\rangle}{E_k - E_i} \tag{A.1}$$

where H' is the interaction causing the transition, and the sum is over all intermediate states $|\,k\rangle$. The operator M now depends explicitly on the binding of the system, since the intermediate state wave functions $|\,k\rangle$ and their energy denominators $E_k - E_i$ depend upon the binding. In time-dependent language, one would say that the propagation of the system in the intermediate state is affected by the binding forces.

One can now ask under which conditions the expression (A.1) would still be independent of binding effects. Let us first rewrite the expression (A.1) to separate the lattice variables and those of the internal degrees of freedom of the atom. Let $|\,i_a\rangle$, $|\,k_a\rangle$ and $|\,f_a\rangle$ be the initial, intermediate, and final internal states of the atom and $|\,i_l\rangle$, $|\,k_l\rangle$, and $|\,f_l\rangle$ be the corresponding lattice states. Let $\mathbf{p}_1$ be the momentum emitted in the transition from the initial to the intermediate state and $\mathbf{p}_2$ the momentum emitted in the transition to the final state (this would correspond, for example, to γ-ray scattering described as the absorption of a photon of momentum $-\mathbf{p}_1$ and re-emission of a photon of momentum $\mathbf{p}_2$). The operator H' can be shown (3) to have the form of the product of a factor H_a' depending only upon the internal variables of the atom and a momentum transfer factor $\exp(-i\mathbf{p}\cdot\mathbf{X}_L/\hbar)$. Thus Eq. (A.1) can be rewritten

$$\langle f\,|\,M\,|\,i\rangle$$
$$= \sum_{k_a}\sum_{k_l} \frac{\langle f_a\,|\,H_a'\,|\,k_a\rangle\langle f_l\,|\,e^{(-i\mathbf{p}_2\cdot\mathbf{X}_L/\hbar)}\,|\,k_l\rangle\langle k_a\,|\,H_a'\,|\,i_a\rangle\langle k_l\,|\,e^{(-i\mathbf{p}_1\cdot\mathbf{X})/\hbar}\,|\,i_l\rangle}{E_{k_a} + E_{k_l} - E_{i_a} - E_{i_l}} \tag{A.2}$$

This expression will be independent of binding effects and will become equivalent to Eq. (5) if the energy denominators are large compared to the lattice energies; i.e. if $E_{k_a} - E_{i_a} > E_{k_l} - E_{i_l}$. Then the lattice contribution to the energy denominators can be neglected, the double sum can be broken up into a product, and the sum depending on the lattice can be evaluated by closure.

$$\langle f\,|\,M\,|\,i\rangle \sim \sum_{k_a} \frac{\langle f_a\,|\,H'\,|\,k_a\rangle\langle k_a\,|\,H'\,|\,i_a\rangle}{E_{k_a} - E_{i_a}}$$
$$\cdot \sum_{k_l} \langle f_l\,|\,\exp(-i\mathbf{p}_2\cdot\mathbf{X}_L/\hbar)\,|\,k_l\rangle\langle k_l\,|\,\exp(-i\mathbf{p}_1\cdot\mathbf{X}_L/\hbar)\,|\,i_l\rangle \tag{A.3}$$
$$= \left(\sum_{k_a} \frac{\langle f_a\,|\,H'\,|\,k_a\rangle\langle k_a\,|\,H'\,|\,i_a\rangle}{E_{k_a} - E_{i_a}}\right) \langle f_l\,|\,\exp[-i(\mathbf{p}_2 + \mathbf{p}_1)\cdot\mathbf{X}_l/\hbar]\,|\,i_l\rangle$$

The probability of a transition to a particular final state of the lattice is given by the square of the second factor, and is of the same form as Eq. (5), depending only upon the total momentum transfer $(\mathbf{p}_2 + \mathbf{p}_1)$.

The condition for the validity of this result (A.3), that the lattice energies can be neglected in the energy denominators, can also be stated in time-dependent language. Since the energy denominator expresses the degree in which energy is not conserved in the intermediate state, it is related by the uncertainty principle to the time in which the system can exist in this intermediate state. To state that lattice energies can be neglected in comparison with the energy denominator is thus equivalent to saying that the time the system spends in the intermediate state is short compared to lattice times; and that one can neglect the effect of lattice forces on the propagation of the system in the intermediate state.

Another statement of this result is the following. The momentum is transferred to the system in two pieces, $\mathbf{p}_1$ and $\mathbf{p}_2$. If the time between the two momentum transfers is short compared to lattice times, the binding forces do not have time to act in the intermediate state; i.e., to cause the lattice to adjust to the absorption of $\mathbf{p}_1$ *before* the absorption of $\mathbf{p}_2$. In this case, the lattice behaves exactly the same as if the total momentum $(\mathbf{p}_1 + \mathbf{p}_2)$ were transferred in one piece.

The same kind of argument can be extended to cases of arbitrary order in perturbation theory; there are simply more matrix elements and more energy denominators. The momentum is now transferred in many pieces, rather than in one piece. However, the lattice will still behave as if the momentum were all transferred in one piece if the binding forces do not have time to act in the intermediate states; i.e., if lattice energies can be neglected in all energy denominators.

Our conclusions can be summed up as follows: We define the time characterizing the momentum transfer as the time interval during which the system exists in a state which is *neither the initial state nor the final state*. This is the time during which binding forces can act to modify the momentum transfer process. If this time is short compared to lattice periods, then the momentum transfer can be considered to be *sudden* and the probability of a given lattice transition is given by the exponential recoil factor (5) depending upon the total momentum trans-

fer. If this time is *not short* compared to lattice times, then Eq. (5) is not valid, and a correct treatment requires detailed description of the dynamical effects of the binding forces during the momentum transfer process.

We note that the momentum transfer time defined in this way is always zero in a process described by first order perturbation theory, where the system is never in any state other than the initial or final state. We also note that this time bears no relation to the *lifetime* of the initial state. The apparent contradiction between the "instantaenous" emission of a photon in a process with a finite lifetime is another example of complementarity and wave-particle duality in quantum mechanics. The "photon wave" is an exponentially damped wave with a decay constant characteristic of the lifetime of the nuclear state. This wave has properties of coherence and can produce interference effects over the lifetime. The "photon particle" is indivisible and its "particle-like" properties of energy and momentum can be absorbed only in a single quantum jump, not in pieces. The two are related by the probability interpretation of the wave function; the amplitude of the wave at a given time is the probability amplitude for the photon being "emitted" (i.e., the energy and momentum having been transferred) at that time.

The Mössbauer effect itself gives instructive examples of both sudden and slow processes. The *emission* of the Mössbauer gamma ray is described by first order perturbation theory and is therefore sudden, as we have seen. The *scattering* of a gamma ray is second order, involving an absorption and a re-emission. Rayleigh scattering by atomic electrons is a sudden process; the time in which the atom exists in an intermediate state is short (or the lattice energies can be neglected compared to the energies of atomic excitation appearing in the energy denominators). This leads to the result familiar in x-ray scattering that the scattered intensity is proportional to the Debye-Waller factor which depends only upon the net momentum transfer and therefore upon the scattering angle. Mössbauer scattering, on the other hand, is *not sudden*. The intermediate state lives a time long compared to lattice periods (or there is a resonance having a width small compared to lattice energies, which cannot be neglected in energy denominators). However, the Mössbauer scattering can be considered as two successive independent sudden processes—absorption and re-emission—because the resonant state is so narrow that only a single intermediate lattice state gives an appreciable contribution to the sum (A.2); namely $| k_l \rangle = | i_l \rangle$. The sum therefore reduces to a single product of two independent processes, each of which is first order and must be sudden. The Mössbauer scattering matrix element is thus the product of a diagonal absorption matrix element, depending upon the momentum transfer in absorption, and an emission matrix element, which depends upon the momentum transfer in emission. If no energy measurement is made on the emitted gamma ray, the re-emission probability is summed over all

possible final states of the lattice and gives unity. One is left then with the Debye-Waller factor for the *absorption* alone, which depends only upon the momentum transfer during the absorption process, and is independent of the scattering angle.

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