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Mössbauer sum rules for use with synchrotron sources

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The availability of tunable synchrotron radiation sources with millivolt resolution has opened new prospects for exploring dynamics of complex systems with Mössbauer spectroscopy. Early Mössbauer treatments and moment sum rules are extended to treat inelastic excitations measured in synchrotron experiments, with emphasis on the unique new conditions absent in neutron scattering and arising in resonance scattering: prompt absorption, delayed emission, recoil-free transitions and coherent forward scattering. The first moment sum rule normalizes the inelastic spectrum. New sum rules obtained for higher moments include the third moment proportional to the second derivative of the potential acting on the Mössbauer nucleus and independent of temperature in the the harmonic approximation.

1. Introduction

The recent development of tunable synchrotron radiation sources using the Mössbauer effect provide new tools for investigating properties of complex condensed matter systems. The use of these tunable sources for studying different types of elastic and inelastic transitions in crystals [1–3] has opened a new field of millivolt spectroscopy for investigation of the dynamics of complex systems which are not accessible to other techniques like neutron scattering. For ^{57}Fe at 14.413 keV it has been possible to prepare a monochromatic beam with a 1 meV bandpass, tunable over a few hundred eV [4].

The synchrotron source offers new possibilities beyond the conventional Mössbauer spectroscopy [5] by exciting nuclear resonances with an incident pulse much shorter than the natural lifetime of the resonance. The disappearance of the incident pulse and all prompt background scattered radiation before the detection of the signal leads to both an enormous background suppression and the possibility of observing forward scattered radiation completely separated from the incident beam, not possible with other techniques. Prompt Rayleigh scattering and scattering by other nonresonant atoms give no background. Forward scattering from many different nuclei is coherent by analogy with Bragg scattering, but is essentially independent of the structure of the sample. This allows the study of coherent radiation from many nuclei in a sample, with the interesting time behavior of speedup and quantum beats [5],

simply by looking at forward radiation without the need to choose Bragg angles, and without even the need for an ordered structure.

In addition, there is the well established difference of the Mössbauer technique from other techniques; e.g., neutron scattering, by being sensitive to a particular nucleus like ^{57}Fe in a sample, and having a high cross-section. It, therefore, gives information on the forces and possible localized vibration modes and local forces in the vicinity of the iron or other Mössbauer nuclei in complicated and small samples, and allows investigation of this information as a function of changes in the composition or structure of the system and behavior near phase transitions.

Many of the qualitatively new effects observable in Mössbauer experiments with synchrotron radiation have been discussed in detail by Hannon and Trammell [5]. In this paper we focus on one point not discussed in this excellent review, the information on inelastic excitations produced by hitting nuclei at specific positions in the lattice with a synchrotron pulse. We shall see that sum rules originally derived for moments of the energy spectrum of gamma rays emitted from Mössbauer transitions [6] have now acquired a new significance in data analysis from synchrotron radiation and have already been used in recent experiments [1,2].

A central problem arising in understanding the spectrum of inelastic excitations produced by a synchrotron pulse on a sample is the separation of the elastic and inelastic cross-sections; i.e., the determination of the Debye–Waller or Mössbauer f-factor. Samples used in these experiments must be sufficiently thick so that there is appreciable inelastic absorption from the radiation off resonance. With such thick crystals the radiation at the resonance which is absorbed and scattered elastically is both enhanced by coherent scattering from different nuclei and attenuated by absorption in passing through the sample. The coherent elastic scattering is concentrated into a sharp forward peak to give a very different angular distribution from that of the inelastic scattered radiation. The relative normalization of the elastic and inelastic cross-sections and the value of the Lamb–Mössbauer f-factor are not obtainable from the data alone. The sum rules provide both a method of separating and normalizing the elastic and inelastic data without detailed analysis [2] and of obtaining localized information about forces on and motion of the Mössbauer nucleus.

2. General features of elastic and inelastic transitions

We first summarize some general features of the different types of transitions that occur in the excitation of nuclear resonance levels in a crystal by a pulse of synchrotron radiation which is much shorter than the lifetime of the nuclear state. The nuclei in the crystal will be in a complicated state of excitation after the pulse is over, and the subsequent radiation will be a mixture of several different types of transitions. The absorption and emission processes can both be either elastic or inelastic. In elastic processes a photon is absorbed or emitted by the internal degrees of freedom of the nucleus, with no change in the other degrees of freedom of the system. Inelastic processes involve energy transfer to the other degrees of freedom. In both absorption

and emission, inelastic momentum and energy transfer can occur to the lattice degrees of freedom via nuclear recoil. In emission there is also the possibility of internal conversion with the emission of an electron and subsequent X-rays rather than a γ-ray.

The synchrotron radiation pulse will generally have a broad enough energy spectrum to excite both the elastic and inelastic transitions. There will also be tunable sources within this spectrum to enable separation of different types of elastic and inelastic transitions. The elastic excitation can be coherent over many nuclei in the crystal with a subsequent speedup in the decay lifetime. We can, thus, expect to observe two lifetimes in the detected radiation, the normal lifetime for decays of nuclei produced by inelastic excitation and a speeded up lifetime produced by the decay of the coherent or superradiant state.

The emitted radiation would therefore consist of the following components:

1. Purely inelastic transitions giving photons with the inelastic spectrum and also conversion electrons and X-rays, with the decay lifetime and angular distributions of single nuclear excitations.
2. Purely elastic transitions giving a coherent spectrum with the speeded up lifetime and a broadened natural line width produced by the speedup and a sharply peaked angular distribution in the forward and/or Bragg direction.
3. Inelastic excitation and elastic emission. This will give a photon spectrum with the natural line width and the natural lifetime and the angular distribution of single nuclear excitations.
4. Elastic excitation and inelastic emission. This will give the inelastic spectrum and also conversion electrons and X-rays, with the angular distributions of single nuclear excitations, but with the speeded-up lifetime.

For general orientation we note the very different energy scales arising in synchrotron Mössbauer physics. The natural line widths of nuclear transitions and nuclear hyperfine and quadrupole splittings are in the nanoelectronvolt range. At the other end of relevant energies is rest energy of an ^{57}Fe nucleus, which is in the tens of gigavolts, and differs from the natural line widths by a factor of 10^{18}. In between is the energy of the 14 keV γ-ray emitted by the nuclear transition in ^{57}Fe used in Mössbauer spectroscopy which differs from the rest energy by a factor of order 10^6. This factor is relevant, because the ratio of the gamma energy to the rest energy is also the ratio of the free recoil energy of the nucleus after emission of the γ-ray:

$$R = \frac{E_\gamma^2}{2Mc^2} \approx 10^{-6} \cdot E_\gamma. \tag{2.1}$$

We thus have four energy scales relevant to the Mössbauer transition; namely, tens of nanovolts, millivolts, kilovolts and gigavolts, separated from one another by factors of 10^6. The Mössbauer experiment features two other energies which happen to lie in the same millivolt range as the free recoil energy; namely room temperature and the characteristic temperature or Debye temperature of common crystal lattices. The fact

that room temperature is in this millivolt range provided the original motivation for the experiment to use thermal energy to compensate for the free recoil energy. The surprising result which led to the development of a new field was the result of the fact that crystal phonon energies are also in this energy range.

The sharp natural line width of the Mössbauer line enabled nanovolt spectroscopy to be studied with tunable Doppler-shifted lines from radiative sources and by observing time-dependent quantum beats following an excitation from photons generated by a synchrotron pulse. The new domain of millivolt spectroscopy has now become available with synchrotron radiation sources for the study of lattice phonon spectra. The synchrotron radiation pulse will generally have a broad enough energy spectrum to excite both the elastic and inelastic transitions. The inelastic spectrum in this range has not been experimentally explored in detail.

3. The semiclassical parton model

The original motivation for Mössbauer's experiment was to measure the natural line width of a nuclear transition by using the thermal Doppler broadening of a photon line to overcome the recoil shift and obtain resonance absorption. Measuring the resonance absorption at two different temperatures then gave sufficient information to calculate the natural line width. Mössbauer found that this procedure succeeded when he compared a measurement at room temperature with a measurement when either the source or the absorber was cooled to liquid nitrogen temperature. But when both were cooled to liquid nitrogen temperature, the experiment disagreed with this simple theoretical description. The anticipated Doppler broadening did not give a complete description of the emission and absorption spectra.

In the early days of the Mössbauer effect sum rules were developed for the moments of the Mössbauer emission [7] spectrum with the aim of clarifying how momentum could be transferred to a crystal without energy loss due to recoil. Since then it has become clear that that these sum rules are generally valid for a large number of very different processes in which momentum is transferred to a constituent of a complex bound system by the emission, absorption or scattering of an electroweak boson which can be either a real or virtual photon or a W boson. The momentum and energy transfer is now simply described in the language of Feynman's parton model which did not exist in Mössbauer's time. It is an instantaneous momentum transfer to or from the emitting or absorbing particle, which Feynman called the "active parton" at the instant the transition takes place. In the case of the Mössbauer transition the active parton is the nucleus that emits or absorbs the photon. The kinematics provides an "instantaneous snapshot" of the momentum distribution of the active parton which is assumed to behave like a free particle at the time of the momentum transfer. If one knows the momentum distribution one can calculate the energy spectrum for the boson emission or absorption. This is what Mössbauer assumed in his original experimental program, using the known thermal momentum distributions for room and liquid nitrogen temperatures. If one measures the energy transfer spectrum, one

can calculate the momentum spectrum of the active partons. This is what Feynman initially assumed in showing how the structure of the proton could be determined from data on deep inelastic scattering. Both assumptions turned out to be approximations.

We shall see here that the approximation fails because of quantum mechanics. The momentum distribution does not give a complete description of the initial state of the active parton. It is described by a quantum mechanical wave function in which components in the momentum spectrum with different momenta are coherent and can interfere in the transition process. Furthermore, both the initial and final states of a bound system have discrete energy levels in quantum mechanics, and the energy transfer cannot be determined completely at the instant when the boson is emitted or absorbed; information about the allowed initial and final state energies and their wave functions must somehow be included. All these quantum-mechanical effects can be simply described by the moment sum rules. But the basic assumption that the transition is a sudden single momentum transfer to the initial wave function remains correct. The final wave function $|f\rangle$ differs from the initial wave function $|i\rangle$ only by having all of its momentum components shifted coherently by the momentum transfer

$$|f\rangle = \mathrm{e}^{\mathrm{i}\vec{k}\cdot\vec{r}_\mu}\,|i\rangle\,, \tag{3.1}$$

where $\vec{r}_\mu$ and $\vec{p}_\mu$ denote the coordinate and momentum of the active parton and $\hbar\vec{k}$ is the momentum transfer. The energy spectrum of the final state is obtained by expanding this final wave function in the energy eigenstates of the complex system.

We begin with Feynman's semiclassical model, in which the energy transfer to the complex system is equal to the change in kinetic energy of a free active parton in absorbing a momentum $\hbar\vec{k}$ at the instant when its momentum is initially $\vec{p}_\mu$:

$$E_f - E_i = T\big(\vec{p}_\mu + \vec{k}\,\big) - T\big(\vec{p}_\mu\big) \approx \frac{(\hbar\vec{k})^2 + 2\hbar\vec{p}_\mu\cdot\vec{k}}{2M_\mu} = R + \frac{\hbar\vec{p}_\mu\cdot\vec{k}}{M_\mu}, \tag{3.2}$$

where $T(\vec{p})$ is the kinetic energy of a free active parton with momentum $\vec{p}$, the non-relativistic approximation holds for all cases of nuclei moving in a lattice, and R is the free recoil energy for a nucleus of mass M_μ,

$$R = \frac{(\hbar k)^2}{2M_\mu}. \tag{3.3}$$

We shall see below that this relation between energy and momentum transfers is a semiclassical approximation to the exact quantum-mechanical relation. We now consider the case where the momentum spectrum of the active parton in the initial state of the system is described by a momentum density distribution function $\rho(\vec{p}_\mu)$. The centroid or first moment of the excitation energy spectrum is

$$\langle E_f - E_i\rangle = \int \rho\big(\vec{p}_\mu\big)\mathrm{d}\vec{p}_\mu\left(R + \frac{\hbar\vec{p}_\mu\cdot\vec{k}}{M_\mu}\right) = R, \tag{3.4}$$

where we have assumed that there is no correlation between the directions of $\vec{k}$ and $\vec{p}_\mu$, and therefore that the expectation values of all odd powers of $\vec{p}_\mu \cdot \vec{k}$ must vanish:

$$\left\langle \left(\vec{p}_\mu \cdot \vec{k}\right)^{(2r+1)} \right\rangle = 0. \tag{3.5a}$$

This is generally true in all cases of interest, since it follows from time reversal invariance of the interactions. It is convenient to choose our z-axis in the direction of the photon momentum $\vec{k}$ so that

$$\frac{\hbar\vec{k} \cdot \vec{p}_\mu}{M_\mu} = \frac{\hbar k p_{z\mu}}{M_\mu} = \frac{2R p_{z\mu}}{\hbar k}. \tag{3.5b}$$

The dispersion, or second moment relative to the first moment, is then

$$\left\langle (E_f - E_i - R)^2 \right\rangle = \frac{2R}{M_\mu} \langle p_{z\mu}^2 \rangle = 4R\overline{T}_{z\mu}, \tag{3.6a}$$

where

$$\overline{T}_{z\mu} \equiv \frac{\langle p_{z\mu}^2 \rangle}{2M_\mu} \tag{3.6b}$$

is the mean kinetic energy in the z-direction for nucleus μ.

The general relation for the moments of the excitation energy spectrum is then

$$\left\langle (E_f - E_i - R)^n \right\rangle = \int \rho(\vec{p}_\mu) \mathrm{d}\vec{p}_\mu \left(\frac{\hbar\vec{p}_\mu \cdot \vec{k}}{M_\mu} \right)^n. \tag{3.7a}$$

It is convenient for comparison with the quantum expression to rewrite this expression:

$$\left\langle (E_f - E_i - R)^n \right\rangle = \frac{2R}{M_\mu} \left\langle p_{z\mu} \left(\frac{\hbar k p_{z\mu}}{M_\mu} \right)^{(n-2)} p_{z\mu} \right\rangle. \tag{3.7b}$$

In this semiclassical model we see that the energy excitation spectrum is determined by the initial momentum spectrum distribution of the active parton. This is the model originally used by Mössbauer for his first experiment and used by Feynman in reverse to interpret the experimental data on deep inelastic electron scattering. In both cases this semiclassical approximation breaks down because of quantum mechanics.

4. Quantizing the semiclassical parton model

Moment sum rules have been applied in many areas of physics where a sudden momentum transfer occurs on an effectively point-like constituent in a bound system, from X-ray and neutron scattering [8–10] to lepton-pair emission by heavy quarks bound in hadrons [11]. The general formulation is essentially the same for all processes but the applications to data analyses for individual processes can be very different.

All the physics needed to understand the Mössbauer effect had been published long before Mössbauer's discovery [8–10]. That photons could be scattered by atoms in

a crystal without energy loss due to recoil was basic to all work in X-ray diffraction and crystallography. All the quantitative calculations including the definition and evaluation of the Debye–Waller factor were well known but not interpreted as a probability that a photon could be scattered by an atom in a crystal without energy loss due to recoil. In the wave picture of radiation the Debye–Waller factor written as $\exp(\langle -k^2x^2\rangle)$ described the loss of intensity of coherent radiation because the atoms were not fixed at their equilibrium positions and their motion introduced random phases into the scattered wave.

The relation between Lamb's treatment [8] of neutron capture in crystals and Ott's X-ray treatment [9] was first pointed out by Kaufman [12,13] and reported in detail in a history of these developments [14]. A general formulation including these and other processes of momentum transfer to bound systems is given in the quantum mechanics book [6] which shows the relation of the dual wave–particle descriptions of similar phenomena.

The first article to use the name Mössbauer effect [15] appeared at a time when the physics community either did not believe in the effect or felt that it was not important enough to be called by its discoverer's name. At that time a number of sum rules were derived [7] along with other results [16,17] which remain pedagogically useful today for teaching basic principles of quantum mechanics to graduate students [6]. The general state of confusion on this issue can be seen in the panel discussion which took place at the Second International Mössbauer conference [18]. Further applications of the basic theory [8–10] for the Mössbauer effect and for neutron scattering are reported in [2].

We now quantize the derivation for the moments of the excitation energy spectrum by introducing the quantum description of the transition (3.2):

$$\left\langle (E_f - E_i - R)^n \right\rangle = \sum_f (E_f - E_i - R)^n \left| \langle f | \, \mathrm{e}^{\mathrm{i}\vec{k}\cdot\vec{r}_\mu} \, |i\rangle \right|^2. \tag{4.1}$$

The moments can be rewritten by using closure

$$\left\langle (E_f - E_i - R)^n \right\rangle = \langle i | \, \mathrm{e}^{-\mathrm{i}\vec{k}\cdot\vec{r}_\mu} (H - E_i - R)^n \mathrm{e}^{\mathrm{i}\vec{k}\cdot\vec{r}_\mu} \, |i\rangle \, , \tag{4.2}$$

where H is the Hamiltonian describing the lattice dynamics,

$$H = \sum_{\mu=1}^{N} \frac{\vec{p}_\mu^{\,2}}{2M_\mu} + \sum_{\mu,\nu=1}^{N} V_{\mu\nu}\left(\vec{x}_\mu, \vec{x}_\nu\right); \tag{4.3}$$

N is the mumber of atoms in the lattice, M_μ is the mass of the atom, which may be different from the mass M of the Mössbauer nucleus for other atoms in the lattice, $V_{\mu\nu}(\vec{x}_\mu, \vec{x}_\nu)$ is some interaction potential depending only upon the coordinates $(\vec{x}_\mu, \vec{x}_\nu)$ of the atoms and not on their momenta.

Substituting the Hamiltonian (4.3) into expression (4.2) gives

$$\left\langle (E_f - E_i - R)^n \right\rangle = \langle i| \left(H - E_i + \frac{\hbar \vec{k} \cdot \vec{p}_\mu}{M} \right)^n |i\rangle \,, \tag{4.4a}$$

and we note that

$$\langle i| (H - E_i) = (H - E_i) |i\rangle = 0. \tag{4.4b}$$

Then

$$\left\langle (E_f - E_i - R)^n \right\rangle = - \langle i| \frac{2Rp_{z\mu}}{\hbar k} \left(H - E_i - \frac{\hbar k p_{z\mu}}{M} \right)^{(n-1)} |i\rangle \,, \tag{4.5a}$$

$$\left\langle (E_f - E_i - R)^n \right\rangle = \frac{2R}{M} \langle i| p_{z\mu} \left(H - E_i - \frac{\hbar k p_{z\mu}}{M} \right)^{(n-2)} p_{z\mu} |i\rangle \,. \tag{4.5b}$$

The first and second moments are seen to be exactly the same as those for the semiclassical parton model (3.4) and (3.6) and equal to their values for the case of nuclear transitions in a noninteracting gas. The first moment is again equal to the free recoil energy R (3.3) and is completely independent of the dynamics of the system and the temperature. The second moment is proportional to the mean kinetic energy $\overline{T}_{z\mu}$ and is, thus, a monotonically increasing function of the temperature.

The effects of quantum mechanics in the higher moments can be seen explicitly by comparing the quantum expression (4.5b) for the general moment with the corresponding classical expression (3.7b). They differ only by the presence of the term $(H - E_i)$ in eq. (4.5b), which vanishes by virtue of eq. (4.4b) when acting directly on the initial state $|i\rangle$. The additional quantum contribution results from the commutator $[p_{z\mu}, H]$, which vanishes in the classical limit and also in the quantum case for a noninteracting gas.

5. Basic theory of excitation by synchrotron radiation

We now apply this basic theory to the case of resonance excitation of a single bound nucleus by a broad beam X-ray source [19]. The cross-section for this excitation as a function of the incident gamma ray energy will contain a peak at the resonance energy corresponding to the elastic or no-recoil Mössbauer transition, and a spectrum on both sides of the resonance energy corresponding to inelastic transitions in which the state of the lattice is changed. Consider a transition for photon absorption between some initial lattice state denoted by $|i\rangle$ and a final state denoted by $|f\rangle$. We denote the cross-section for this transition as $\sigma_{i\to f}(E)$ and note that its integral over the entire relevant energy interval can be written

$$\int \sigma_{i\to f}(E)\, \mathrm{d}E = \bar{\sigma} \left| \langle f| \, \mathrm{e}^{\mathrm{i}\vec{k}\cdot\vec{r}_\mu} \, |i\rangle \right|^2, \tag{5.1}$$

where $\vec{k}$ denotes the photon wave number, $\vec{r}_\mu$ is the coordinate in the lattice of the nucleus being excited, and $\bar{\sigma}$ is normalized to give the total integrated cross-section over all final states:

$$\bar{\sigma} = \sum_f \int \sigma_{i\to f}(E)\,\mathrm{d}E. \tag{5.2}$$

In the normal Mössbauer effect, the probability that the transition takes place without any change in the state of the lattice is given exactly by the Debye–Waller factor. In excitation by synchrotron radiation the same Debye–Waller or Mössbauer fraction factor appears in the cross-section for the elastic transition in which the lattice remains in its initial state,

$$\int \sigma_{i\to i}(E)\,\mathrm{d}E = \bar{\sigma}\left|\langle i|\,\mathrm{e}^{\mathrm{i}\vec{k}\cdot\vec{r}_\mu}\,|i\rangle\right|^2. \tag{5.3}$$

Interesting properties of the inelastic transitions are obtainable by generalizing sum rules (4.1) for Mössbauer emission [7] to apply to the moments of the excitation energy spectrum

$$\begin{aligned}\left\langle (E_f - E_i - R)^n \right\rangle &\equiv \sum_f \frac{1}{\bar{\sigma}} \int \mathrm{d}E (E_f - E_i - R)^n \sigma_{i\to f}(E) \\ &= \sum_f (E_f - E_i - R)^n \left|\langle f|\,\mathrm{e}^{\mathrm{i}\vec{k}\cdot\vec{r}_\mu}\,|i\rangle\right|^2,\end{aligned} \tag{5.4}$$

where the centroid of the spectrum is again the free recoil energy R (3.3) for a nucleus of mass M.

6. Sum rules for the third and fourth moments

Higher moments had not previously been considered, since they did not seem to be relevant to feasible experimental tests at the time. Their evaluation also appeared to be more complicated, since the Hamiltonian H appears explicitly in eq. (4.5b) sandwiched between factors $p_{z\mu}$ with which H does not commute. In contrast to the first two moments, which are equal to the values obtained simply from classical billiard-ball kinematics for a non-interacting gas, the higher moments depend upon properties of the dynamics, i.e., upon the values of parameters in the Hamiltonian (4.3) and introduce effects of quantum mechanics, expressed by the explicit appearance of commutators proportional to $\hbar$. These have been shown [19] to provide interesting new information on properties of the lattice.

The relevant commutators needed to evaluate the higher moments are

$$[p_{z\mu}, H] = -\mathrm{i}\hbar \frac{\partial}{\partial z_\mu} \sum_{\rho,\nu=1}^{N} V_{\rho\nu}, \tag{6.1a}$$

$$\big[p_{z\mu},[p_{z\mu},H]\big] = -\hbar^2 \frac{\partial^2}{\partial z_\mu^2} \sum_{\rho,\nu=1}^{N} V_{\rho\nu}. \tag{6.1b}$$

For the case of a harmonic crystal, the potential energy is a polynomial of second order in all coordinates, which can be written

$$\sum_{\rho,\nu=1}^{N} V_{\rho\nu}\big(\vec{x}_\rho,\vec{x}_\nu\big) = V_{\mu\mu}^{zz}(z_\mu)^2 + \cdots, \tag{6.2a}$$

where all the terms beyond the first do not contribute to the double commutator (6.1b). The potential energy can also be expressed in terms of the coordinates ξ_j and the frequencies ω_j of the normal modes,

$$\sum_{\mu,\nu=1}^{N} V_{\mu\nu} = \sum_{j=1}^{3N} \frac{1}{2} M\omega_j^2 \xi_j^2. \tag{6.2b}$$

From the orthonormality of the linear transformation between nucleus coordinates z_μ and the normal coordinates ξ_j we obtain the useful relations

$$\sum_{j=1}^{3N} \left(\frac{\partial \xi_j}{\partial z_\mu}\right)^2 = 1, \tag{6.3a}$$

$$\sum_{\mu=1}^{N} \left(\frac{\partial \xi_j}{\partial x_\mu}\right)^2 + \left(\frac{\partial \xi_j}{\partial y_\mu}\right)^2 + \left(\frac{\partial \xi_j}{\partial z_\mu}\right)^2 = 1. \tag{6.3b}$$

For a harmonic crystal the commutators (6.1) become

$$[p_{z\mu},H] = -\mathrm{i}\hbar \sum_{j=1}^{3N} M\omega_j^2 \xi_j \frac{\partial \xi_j}{\partial z_\mu}, \tag{6.4}$$

$$\big[p_{z\mu},[p_{z\mu},H]\big] = -\hbar^2 \sum_{j=1}^{3N} M\omega_j^2 \left(\frac{\partial \xi_j}{\partial z_\mu}\right)^2, \tag{6.5a}$$

$$\big[p_{z\mu},[p_{z\mu},H]\big] = -\hbar^2 \frac{\partial^2}{\partial z_\mu^2} \sum_{\rho,\nu=1}^{N} V_{\rho\nu} = -2\hbar^2 V_{\mu\mu}^{zz}. \tag{6.5b}$$

Note that the double commutator (6.5) depends only upon the force on the coordinate z_μ which is expressed in terms of normal mode variables as a function of the frequencies ω_j and the expansion coefficients of the coordinate z_μ in the normal coordinates ξ_j. The value of the double commutator for a harmonic lattice thus depends only on the parameters of the Hamiltonian and is completely independent of the state of the lattice and of the temperature. This feature is particularly interesting because

the third moment of the energy spectrum can be seen to be proportional just to this double commutator:

$$\begin{aligned}\left\langle (E_f - E_i - R)^3 \right\rangle &= \frac{R}{M} \langle i| \, [p_{z\mu}, H] p_{z\mu} + p_{z\mu} [H, p_{z\mu}] \, |i\rangle \\ &= -\frac{R}{M} \langle i| \, \left[p_{z\mu}, [p_{z\mu}, H]\right]. \end{aligned} \tag{6.6a}$$

Thus,

$$\left\langle (E_f - E_i - R)^3 \right\rangle = \frac{R}{M} \langle i| \, \hbar^2 \frac{\partial^2}{\partial z_\mu^2} \sum_{\rho,\nu=1}^{N} V_{\rho\nu} \, |i\rangle \, . \tag{6.6b}$$

For a harmonic lattice this becomes

$$\left\langle (E_f - E_i - R)^3 \right\rangle = \hbar^2 R \sum_{j=1}^{3N} \omega_j^2 \left(\frac{\partial \xi_j}{\partial z_\mu} \right)^2 = R \hbar^2 \overline{\omega_z^2}, \tag{6.7a}$$

where

$$\overline{\omega_z^2} \equiv \sum_{j=1}^{3N} \omega_j^2 \left(\frac{\partial \xi_j}{\partial z_\mu} \right)^2 \tag{6.7b}$$

is a weighted mean square average lattice frequency, and the subscript z denotes that it is determined by normal modes with motion in the z-direction. The weighing factors are seen from the normalization relation (6.3a) to be normalized to unity. For a harmonic crystal the third moment can also be expressed in terms of the force on the coordinate z_μ,

$$\left\langle (E_f - E_i - R)^3 \right\rangle = \frac{2\hbar^2 R}{M} V_{\mu\mu}^{zz}. \tag{6.8}$$

This result is independent of the lattice wave function $|i\rangle$ and therefore also of the temperature. For an isotropic crystal this result is a simple function of the characteristic temperature of the lattice, e.g., the Debye or Einstein temperature. For an anisotropic crystal, the result will depend upon the angles between the crystal axes and the photon direction, and can give information about the parameters of the anisotropic lattice. If the crystal is not harmonic, expression (6.6b) depends upon the coordinates of various atoms in the lattice and therefore on the temperature.

The fourth moment can now be evaluated using the same commutators. We immediately discard expectation values of all odd powers of $p_{z\mu}$ and obtain

$$\begin{aligned}\left\langle (E_f - E_i - R)^4 \right\rangle &= \frac{2R}{M} \langle i| \, \frac{2R}{M} p_{z\mu}^4 + [p_{z\mu}, H](H - E_i) p_{z\mu} \, |i\rangle \\ &= \frac{2R}{M} \langle i| \, \frac{2R}{M} p_{z\mu}^4 - [p_{z\mu}, H]^2 \, |i\rangle \\ &= \frac{2R}{M} \langle i| \, \frac{2R}{M} p_{z\mu}^4 + \hbar^2 \left(\frac{\partial}{\partial z_\mu} \sum_{\rho,\nu=1}^{N} V_{\rho\nu} \right)^2 |i\rangle \, . \end{aligned} \tag{6.9a}$$

For a harmonic lattice this becomes

$$\left\langle (E_f - E_i - R)^4 \right\rangle = \frac{2R}{M} \langle i | \frac{2R}{M} p_{z\mu}^4 + \hbar^2 \sum_{j=1}^{3N} M^2 \omega_j^4 \xi_j^2 \left(\frac{\partial \xi_j}{\partial z_\mu} \right)^2 | i \rangle \,. \tag{6.9b}$$

7. Use of sum rules for thick samples with many nuclei

These results are easily generalized to the case where there are many nuclei in the lattice which can be excited by the Mössbauer transition, but the intensity of the incident beam is sufficiently weak so that only one photon is absorbed. Since the single excitation cross-sections for inelastic transitions by individual nuclei are independent, the total rate for inelastic transitions in an experiment is obtained in the usual manner by summing over all nuclei in the target.

The elastic transitions require special attention. Coherent effects [20] like superradiance can enhance the transition matrix element for photon emission [21]. The coherence changes the angular distribution of the radiation and the enhancement produces a corresponding speedup in the lifetime of the excited state. These effects were originally predicted by Trammell [21], further developed [22] theoretically and observed in very beautiful experiments [23,24]. An excellent review of these developments has been given in [5], where the particular coherent state is called a "nuclear exciton".

The speedup of the elastic transition also broadens the line width of the nuclear exciton and therefore affects the integrated total cross-section (5.2). However, this coherence does not affect the inelastic excitation spectrum in a lattice by synchrotron radiation. The moments can still be obtained by the above analysis and eqs. (6.6)–(6.9) but corrections are necessary to the normalization procedure, both because of the enhanced elastic contribution and because radiation in the resonance peak can be attenuated in passing through a sample which is still sufficiently thin to leave radiation off resonance unaffected.

To devise a procedure for data analysis which takes account of these effects at resonance we note that they are all at $(E_f - E_i) = (E_f - E_i)^n = 0$. We therefore define an "experimental moment"

$$\left\langle (E_f - E_i)^n \right\rangle_{\text{ex}} \equiv \sum_f \frac{1}{\bar{\sigma}_{\text{ex}}} \int \mathrm{d}E (E_f - E_i)^n \sigma_{i \to f}(E) = \frac{\langle (E_f - E_i)^n \rangle_1}{K_{\text{en}}}, \tag{7.1a}$$

where $\langle (E_f - E_i)^n \rangle_1$ denotes the moment for the case of a single nucleus (5.4), K_{en} denotes a normalization correction factor which is the same for all moments and $\bar{\sigma}_{\text{ex}}$ denotes a modified total cross-section which takes into account the fact that the cross-section in the region of the elastic peak is not correct.

$$\bar{\sigma}_{\text{ex}} = \sum_f \int_{-\infty}^{E_i - \varepsilon} \sigma_{i \to f}(E)\, \mathrm{d}E + \sum_f \int_{E_i + \varepsilon}^{\infty} \sigma_{i \to f}(E)\, \mathrm{d}E + \sigma_{\text{o}}, \tag{7.1b}$$

where ε is a suitably chosen small energy interval and $\sigma_{\rm o}$ is the measured value of the integrated cross-section in the interval $E_i - \varepsilon \leqslant E \leqslant E_i + \varepsilon$.

The normalization factor $K_{\rm en}$ can be determined experimentally from the first moment and then applied to expressions for the higher moments. Substituting the result for the first moment (3.4) we obtain

$$\big\langle (E_f - E_i) \big\rangle_{\rm ex} = \frac{\langle (E_f - E_i) \rangle_1}{K_{\rm en}} = \frac{R}{K_{\rm en}}. \tag{7.2a}$$

Thus,

$$\big\langle (E_f - E_i)^n \big\rangle_{\rm ex} = \big\langle (E_f - E_i)^n \big\rangle_1 \frac{\langle (E_f - E_i) \rangle_{\rm ex}}{R}. \tag{7.2b}$$

These moments can now be measured by using tunable sources with an energy band width small compared with the free recoil energy R. The moments can be normalized either by integrating over the entire spectrum, or by integrating only over the inelastic spectrum and removing the elastic peak; i.e., by defining the modified total cross-section $\bar{\sigma}_{\rm ex}$ either to include the measured integral over the resonance $\sigma_{\rm o}$ or by setting $\sigma_{\rm o} = 0$. The normalization factor $K_{\rm en}$ will be different in the two cases, but the result (7.2b) applies to both.

The value of the factor $K_{\rm en}$ can be calculated theoretically for samples sufficiently thin so that there is no attenuation of the resonance radiation in passing through the sample, from the values of the speedup factor denoted by $F^{\rm o}_{\rm speed}$ for the superradiant component or nuclear exciton and the Debye–Waller or Mössbauer fraction factor commonly denoted denoted by f. Note, however, that in experiments where the nuclear excitation is detected by the decay of the excitation into a particular decay channel the value of $K_{\rm en}$ can depend upon the branching ratio for the decay into the observed channel.

This is particularly important in the case where the detector sees only the incoherent channels like conversion electrons or X-rays. The speedup factor changes the relative branching ratios for decays into different channels, since the speedup applies only to the Mössbauer fraction of the radiation which is proportional to the Debye–Waller or Mössbauer fraction factor f. The total decay width $\Gamma_{\rm tot}$ for an elastically produced coherent state, i.e., the nuclear exciton, is the sum of the partial widths for coherent γ-ray emission, incoherent γ-ray emission and internal conversion. The partial widths for incoherent γ emission and internal conversion are not enhanced by superradiance. They are the same as for a single excited nucleus and proportional respectively to $1 - f$ and to the internal conversion coefficient α. The coherent component is proportional to f but has an additional speedup factor denoted by $F^{\rm o}_{\rm speed}$. Thus,

$$\Gamma^{\rm ex}_{\rm tot} = \Gamma^{\rm ex}_{\rm coherent} + \Gamma_{\rm incoherent} + \Gamma_{\rm inconv} = \big[F^{\rm o}_{\rm speed} f + (1 - f) + \alpha\big]\Gamma_\gamma, \tag{7.3}$$

where Γ_γ denotes the partial width for gamma decay by a single nucleus. The relative probabilities or branching ratios for incoherent gamma emission and internal conversion, respectively, are reduced:

$$\frac{\Gamma_{\text{incoherent}}}{\Gamma^{\text{ex}}_{\text{tot}}} = \frac{1-f}{F^{\text{o}}_{\text{speed}} f + (1-f) + \alpha}, \tag{7.4a}$$

$$\frac{\Gamma_{\text{inconv}}}{\Gamma^{\text{ex}}_{\text{tot}}} = \frac{\alpha}{F^{\text{o}}_{\text{speed}} f + (1-f) + \alpha}. \tag{7.4b}$$

The loss due to internal conversion is thus reduced, since the probability that a given excited nucleus will emit a photon rather than ejecting an electron has been increased [21,23,24]. The net speedup factor for the decay rate of a nuclear exciton relative to that of a single nucleus is

$$F_{\text{speed}} = \frac{F^{\text{o}}_{\text{speed}} f + (1-f) + \alpha}{1+\alpha}. \tag{7.5}$$

Thus in experiments where the detector sees only the inelastic channels like conversion electrons or X-rays, the branching ratios for these detection modes are seen from eqs. (7.4a) and (7.4b) to be reduced relative to that of the speeded-up coherent forward radiation. This bias must be taken into account in calculating the factor K_{en}.

Since the coherent effects do not change the inelastic excitations, the normalization factor K_{en} should be the same for the coherent case as for a single nucleus if the experimental normalization for the moments is calculated only by integrating over the inelastic spectrum. For this case the integral is just the total inelastic probability for the single nucleus case; namely $1-f$. Thus we obtain

$$K^{\text{inelastic}}_{\text{en}} = \frac{1}{1-f}. \tag{7.6}$$

8. Separating elastic and low-energy inelastic excitations

In most Mössbauer spectra there is a clear distinction between the elastic peak and the inelastic continuum. But there may also be cases where the Lamb–Mössbauer factor commonly denoted by f is small and the contributions of very low energy excitations are appreciable. In this case, one must consider inelastic excitations where the Mössbauer resonance is excited together with the exchanges of phonons whose wavelengths are all very long in comparison with the lattice spacings in the crystal. This can be considered as a kind of nuclear exciton in which the coherence exists over some finite and non-negligible number of nuclei in the crystal. This exciton may then decay with a speeded-up lifetime and a modified angular distribution which will be forward peaked.

In some experiments the excitation is detected by observing the scattered γ-rays in a particular solid angle away from the forward direction, and with a time delay of the order of the Mössbauer lifetime in order to discriminate against prompt radiation.

In such experiments a nuclear exciton with a speeded-up lifetime and a forward-peaked angular distribution would tend to decay too soon and in the wrong direction to be observed at the detector. This could reduce the number of events detected at low excitations when these long wave excitations arise. In a crystal where there are acoustic and optical modes, this could reduce the detection efficiency of acoustic modes relative to optical modes. If the data are interpreted by using the sum rule (7.2a) and eq. (7.6) to obtain the f factor from the first moment of the inelastic excitation spectrum, the value for f obtained should give the probability for low-energy excitations which are missed in the observed inelastic spectrum. Normally this is just the probability of elastic excitation. But here the missed long-wave-phonon excitations would be included in defining the modified total cross-section $\bar{\sigma}_{\rm ex}$, and an "effective" f-factor $f_{\rm eff}$ determined by this procedure would be higher than the real f.

For a simple example let us assume that the initial radiation is incident on a thin plane of nuclei in a direction normal to the plane. If there is any coherence between the excitations of different nuclei the relative phases of the radiation emitted nearly parallel to the plane will be very different and will tend to cancel out. The coherence therefore not only enhances the forward peak, it strongly suppresses the intensity in the direction normal to the incident beam.

For a rough quantitative estimate, let us asssume that there is a sharp difference between excitations which are low enough to produce a nuclear exciton and those which are too high and do not. We then define $f_{\rm low}$ as the probability of producing such a low-energy excitation. This is defined precisely as the ratio of the integral over the low-energy portion of the excitation spectrum to the total integral over the excitation spectrum. We also define a speedup factor for the decay of the nuclear exciton. We can apply the treatment of eqs. (7.3)–(7.5) to this case using $f_{\rm low}$ as the probability of producing the nuclear exciton rather than the normal f which only considers elastic transitions.

The total decay width $\Gamma^{\rm ex}_{\rm tot}$ for the exciton

$$\Gamma^{\rm ex}_{\rm tot} = \left[F^{\rm o}_{\rm speed} f_{\rm low} + (1 - f_{\rm low}) + \alpha\right]\Gamma_\gamma. \tag{8.1a}$$

The relative probabilities or branching ratios for incoherent gamma emission and internal conversion, respectively, are reduced:

$$\frac{\Gamma^{\rm ex}_{\rm incoherent}}{\Gamma^{\rm ex}_{\rm tot}} = \frac{1 - f_{\rm low}}{F^{\rm o}_{\rm speed} f_{\rm low} + (1 - f_{\rm low}) + \alpha}, \tag{8.1b}$$

$$\frac{\Gamma^{\rm ex}_{\rm inconv}}{\Gamma^{\rm ex}_{\rm tot}} = \frac{\alpha}{F^{\rm o}_{\rm speed} f_{\rm low} + (1 - f_{\rm low}) + \alpha}. \tag{8.1c}$$

The net speedup factor for the exciton decay rate relative to that of a single nucleus is

$$F^{\rm ex}_{\rm speed} = \frac{F^{\rm o}_{\rm speed} f_{\rm low}(1 - f_{\rm low}) + (1 - f_{\rm low}) + \alpha}{1 + \alpha}. \tag{8.1d}$$

The effective total width that is measured in a scattering experiment by integrating the observed cross-section over energy is the sum of the true width of the observed

scattering outside the exciton energy range and the measured width of the scattering emitted from the exciton. The width of the excitation outside the exciton range is just $(1 - f_{\rm low})\Gamma_\gamma$. The measured exciton width depends upon experimental conditions like angular and time acceptance. For a rough estimate we assume that the coherent emission from the exciton is lost because of wrong angular and time acceptance and we also neglect internal conversion. We then obtain

$$\frac{\Gamma^{\rm obs}_{\rm tot}}{\Gamma_\gamma} = 1 - f_{\rm low} + f_{\rm low}\frac{\Gamma^{\rm ex}_{\rm incoherent}}{\Gamma^{\rm ex}_{\rm tot}} = (1 - f_{\rm low})\frac{1 + F^{\rm o}_{\rm speed} f_{\rm low}}{1 + (F^{\rm o}_{\rm speed} - 1) f_{\rm low}}. \tag{8.2a}$$

This satisfies the inequality

$$1 - f_{\rm low} \leqslant \frac{\Gamma^{\rm obs}_{\rm tot}}{\Gamma_\gamma} \leqslant 1 - f^2_{\rm low}. \tag{8.2b}$$

Here, the upper bound is for the case of no speedup ($F^{\rm o}_{\rm speed} = 1$). The factor $f_{\rm low}$ appears twice, once for the probability of producing the exciton and once for the probability of coherent decay of the exciton. The lower bound is for the case of very large speedup ($F^{\rm o}_{\rm speed} \gg 1$). Here, the probability of incoherent decay of the exciton is negligible and only the incoherent excitation without exciton production is observed.

9. Conclusions

The development of tunable synchrotron radiation sources in the millivolt range provides the possibility of experimental tests and applications for moment sum rules originally derived for the emission of Mössbauer resonance radiation and hitherto used primarily for pedagogical purposes. These sum rules are shown to be very useful in obtaining crucial information from inelastic resonance scattering data.

The first moment sum rule enables the normalization of the inelastic scattering data and the determination of the Lamb–Mössbauer f-factor. This moment is equal to the free recoil energy of the resonant nuclear transition and is independent of the structure of the bound system, its wave function and the temperature.

The second moment is proportional to the mean kinetic energy of the resonant nucleus and is a function of the temperature and the wave function describing the motion of the nucleus in the bound system.

The third is proportional to the second derivative of the potential acting on the resonant nucleus. This is the force constant seen by this nucleus if the forces are harmonic. For a harmonic system this moment depends only upon the force constants in the Hamiltonian of the system and is independent of the wave function of the system or the Hamiltonian.

The fourth moment is the sum of two terms. One term is proportional to the mean value of the fourth power of the resonant nucleus momentum; the second term is a function of the constants appearing in the system Hamiltonian and of the wave function describing the motion of the resonant nucleus in the bound state. The theoretical value of this moment is easily calculated for any particular model.

These sum rules can be particularly useful for Mössbauer synchrotron experiments performed in cases where inelastic excitations are not accessible to other experimental techniques like neutron scattering. The advantages of the synchrotron Mössbauer technique are discussed in detail in [2], and include the ability to use small samples and thin films, the speed of the measurement with the possibility of investigating short-lived structures and the time development of phase transitions and the ability to focus on a comparatively rare constituent in a sample.

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