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Mössbauer Diffraction. I. Quantum Theory of Gamma-Ray and X-Ray Optics*

J. P. HANNON† AND G. T. TRAMMELL
Physics Department, Rice University, Houston, Texas

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The Green-function techniques of quantum electrodynamics are used to obtain the equations governing the interaction of x rays and γ rays with crystals. In particular, the theory of Mössbauer γ-ray optics for crystals containing the resonant nuclei is developed.

I. INTRODUCTION

THE scattering of Mössbauer γ rays has received relatively little attention from physicists, yet these processes involve features of considerable fundamental interest and of great potential for practical use.

The most extensive experimental work has been carried out by Moon, Black, O'Connor, and co-workers at Birmingham.[1–6] This group first demonstrated the nuclear scattering effect by Bragg reflection of the 14.4-kev Fe^{57} γ ray from enriched iron crystals, and they have examined the interference effects between the electronic and nuclear scattered waves. In addition, Bernstein and Campbell[7] have investigated the effects of the nuclear processes in the critical reflection of Mössbauer γ rays from Fe^{57}-enriched iron. The angular variation of the nuclear scattered wave in the Bragg region has been measured by Major[8] and by the Birmingham group.[9]

For most Mössbauer transitions, the γ-ray wavelength ($\approx$0.1–1 Å) is well suited for diffraction experiments. The linewidths are exceedingly sharp, allowing the easy variation of the phase and amplitude of the resonantly scattered wave by Doppler shifting, with negligible variation in the nonresonant electronically scattered wave. This offers a powerful method for determination of the structure factors for crystals with complicated unit cells which contain the resonant nuclei.[10–14]

Mössbauer scattering may also be very useful in magnetic structure determination. In magnetic crystals, the nuclear ground state and/or excited levels are Zeeman split, and the amplitude and polarization of nuclear scattered waves are strongly dependent upon the magnetic structure. The magnetic spiral structures of rare-earth metals, for example,[15] will result in Mössbauer diffraction patterns which exhibit the spiral structure. This also affords a possible means of determination of a complicated magnetic unit cell containing several unequivalent sites, e.g., yttrium iron garnet (YIG).[16] We discuss these applications to magnetic structure determination more fully in II.[17]

It is our purpose to develop the quantum theory of crystal optics and to treat in particular the quantum optics of Mössbauer γ rays.

Shortly after the discovery of the Mössbauer effect, several workers[1,10,11,18–21] suggested the possibility of the use of the Mössbauer γ rays in performing diffraction studies. In Refs. 18 and 19 it was pointed out that the effective coherent cross section per crystal site for resonant nuclear scattering is

$$\sigma_{\mathrm{coh}}=\tfrac{2}{3}\pi\left(\frac{2j_1+1}{2j_0+1}\right)^2\left(\frac{f\Gamma_\gamma}{\Gamma}\right)^2 F^2\lambda^2\approx 3F^2\times10^4\ \mathrm{b}\quad\text{for}\quad \mathrm{Fe}^{57},$$

where F is the fraction of resonant nuclei in the sample. The Rayleigh scattering from atomic electrons is about 40 b/sr in the forward direction and about an order of magnitude less at a 60° scattering angle. Thus, for appreciable values of F, the nuclear scattering can be made to stand out above the electronic very near resonance.

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† Present address: Laboratory for Electrophysics, The Technical University, Lyngby, Denmark.

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It was also pointed out in Ref. 18 that the nuclear absorption cross section is generally several orders of magnitude greater than the scattering cross section ($\sigma_A \approx 10^6$ b at resonance for Fe^{57}). Thus, under ordinary circumstances, there is very little penetration into an enriched crystal, and appreciable scattering occurs only from the first few thousand crystal layers at resonance. The extraordinary circumstance in which one obtains deep penetration even at resonance is when the incident radiation is very near a Bragg angle.[18,21–23] When a crystal containing resonant nuclei is excited at a Bragg angle, the effective coherent elastic radiative width is enhanced over that of a single nucleus by a factor proportional to the number of crystal layers. This gives a consequent suppression of absorptive and inelastic processes and leads to large reflection and/or transmission amplitudes (III[24]).[25] These modes of excitation correspond to the "super-radiant" emission modes of a gas studied by Dicke.[26–28] To discuss these and other "thick" crystal results, one must of course go beyond the Born and kinematical approximations to the dynamical theory.[24,29]

In this paper we make use of the techniques of modern quantum field theory to develop a relatively simple theory which determines the scattering of x rays and γ rays by crystals.

In Sec. II we give a preliminary discussion of the scattering from a single atom. We then give the general expression for the scattering of a quantum by an arbitrary system in terms of the scattering operator of the system.

In Sec. III we obtain an approximate set of equations determining the scattering amplitude of N scatterers in terms of the single-atom scattering operators by summing a class of ladder diagrams for the photon Green function. This leads to a set of coupled equations of the multiple scattering type studied by Foldy,[30] Lax,[31] and Watson,[32] and indeed formally the same as those derived in the dynamical x-ray theory in a semiclassical manner.[33–35]

In Sec. IV we extend the multiple scattering formalism to include phonon-photon exchange between the scatterers and obtain our fundamental Eqs. (50) and (51).

In Sec. V we give the relevant ensemble averaged equations.

In II we discuss the single-atom scattering operators in terms of which the general theory has been developed. We then discuss the interference between nuclear and electronic scattering, the effects of electronic shielding of the nucleus, polarization effects, and finally we discuss several applications of the Mössbauer diffraction in the Born approximation. In III we use the general formulas to develop the dynamical theory of Mössbauer optics.

II. BASIC EQUATIONS

The quantum theory of crystal optics is most conveniently developed using the Feynman-Schwinger-Dyson Green-function techniques of quantum electrodynamics.[36–38] In Secs. II and III we use the simple intuitive Feynman procedures to obtain equations of optics bearing a close formal relation to those of classical optics.[39]

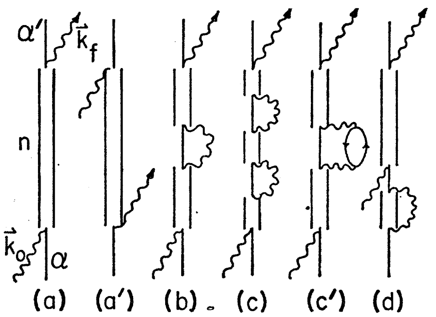

FIG. 1. Feynman diagrams for scattering by a single atom. The light solid lines represent the ground states of the atom and the double lines the excited states. The external wavy lines represent the incident and scattered photons, and the internal lines represent virtual photon emission and absorption. In (c′) the solid lines represent nuclear states and the "bubble" is an excited electron with a hole in a normally filled electronic level.

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At the outset we should emphasize that we shall be concerned with single-photon processes. We are interested primarily in x-ray and γ-ray optics, and for technological reasons it would seem that the day is far off when we will need be concerned with coherent multiple-photon effects in these energy ranges.

Initially, we consider just one atom and for simplicity let it be fixed in space. Then the lowest-order contribution to the scattering is given by the two diagrams of Figs. 1(a) and 1(a′). In Fig. 1 the light solid lines represent the (possibly degenerate) ground states of the atom (nuclear and electronic) and the double lines the excited states. The external wavy lines represent the incident and scattered photons, and the internal wavy lines represent virtual photon emission-absorption. Figures 1(a) and 1(a′) represent of course just the ordinary second-order perturbation expression for the scattering. These processes would suffice if we were only dealing with electronic scattering. However, for the resonant nuclear scattering it will of course be necessary to include a class of diagrams which include radiation reaction, internal conversion, and the effects of electronic shielding of the nucleus. The simplest higher-order diagram is shown in Fig. 1(b). If both excited states are nuclear, the virtual photon emission-absorption gives a radiation reaction correction [similarly in Fig. 1(c)]. If one of the excited states is electronic and the other nuclear, then Fig. 1(b) contributes to the electronic shielding of the nucleus. The effect of internal conversion on the scattering is an e^6 diagram, which we show by the more explicit Fig. 1(c′). Here the double lines represent excited nuclear states, and the "bubble" is an excited electron with a hole in a normally filled electronic level. Diagrams of the type 1(d) with disconnected radiative parts give ignorable radiative corrections to the ground-state energy.

In any case the net scattering amplitude is the sum over the elaboration of the basic diagrams of 1(a), where internal photon lines are inserted in all possible ways. This leads, as is easily shown, to the expression for the S matrix (see Appendix A)[40]:

$$S^{f0}=-(i/\hbar)\iint a_\mu{}^f(x)^* M_{\mu\nu}{}^{f0}(x,y)\,a_\nu{}^0(y)\,d^4x\,d^4y, \tag{1}$$

where

$$M_{\mu\nu}{}^{f0}(x,y)=-(i/\hbar c^2)\langle\phi_f\,|\,T[j_\mu(x)j_\nu(y)]\,|\,\phi_0\rangle. \tag{2}$$

In Eq. (2), ϕ_0 and ϕ_f are the initial and final Heisenberg atomic-state vectors, $j_\mu(x)$ is the Heisenberg current operator, T is the time-ordering operator, and a^0 and a^f are the Feynman potentials representing the initial and final photons,[39]

$$a_\mu{}^0(x)=[4\pi\hbar c^2/2\omega_0]^{1/2}e_\mu{}^0\exp(-i\omega_0 t_x+i\mathbf{k}_0\cdot\mathbf{x}),$$

$$a_\mu{}^f(x)^*=[4\pi\hbar c^2/2\omega_f]^{1/2}e_\mu{}^{f*}\exp(i\omega_f t_x-i\mathbf{k}_f\cdot\mathbf{x}). \tag{3}$$

Although we have motivated our discussion by first considering the scattering by a single fixed atom, Eqs. (1)–(3), as well as the subsequent developments of this section, are valid for an arbitrary scattering system (Appendix A).

It follows from the gauge invariance of the S matrix that

$$\partial_\mu M_{\mu\nu}(x,y)=0 \tag{4}$$

and that the transition current induced by a^0,

$$c^{-1}J_\mu(x)=\int d^4y\,M_{\mu\nu}(x,y)\,a_\nu{}^0(y), \tag{5}$$

is conserved. The Feynman potential for the photon at the space time point z due to the current (5) is (Appendix A)

$$A_\mu{}^s(z)=c^{-1}\int\delta_+(z,x)J_\mu{}^{f0}(x)\,d^4x, \tag{6}$$

where

$$\delta_+(z,x)=-4\pi\int\frac{\exp[-ik(z-x)]}{k^2+i\epsilon}\frac{d^4k}{(2\pi)^4} \tag{7}$$

is the Feynman photon propagator. $A_\mu{}^s$ satisfies the Lorentz gauge condition $\partial_\mu A_\mu=0$. Furthermore, that $J_\mu(x)$ [Eq. (5)] is invariant under the gauge transformation $a_\mu{}^0\rightarrow a_\mu{}^0+\partial_\mu\chi$ follows from $\partial_\mu M_{\mu\nu}(x,y)=0$ and the symmetry of $M_{\mu\nu}$, $M_{\mu\nu}(x,y)=M_{\nu\mu}(y,x)$.

If E_f and E_0 are the energies of the states ϕ_f and ϕ_0, then we obtain from (3) and (5)

$$\langle\phi_f\,|\,J_\mu(\mathbf{x},t_x)\,|\,\phi_0\rangle=J_\mu{}^{f0}(\mathbf{x},\omega_0)\exp[-i(\omega_0+E_0-E_f)t_x], \tag{8}$$

and from (6) and (7)

$$A_\mu{}^s(z)=\exp[-i(\omega_0+E_0-E_f)t_z]c^{-1}\times\int\frac{\exp(ik_f\,|\,\mathbf{z}-\mathbf{x}\,|)}{|\,\mathbf{z}-\mathbf{x}\,|}J_\mu{}^{f0}(\mathbf{x},\omega_0)\,d\mathbf{x}, \tag{9}$$

where

$$k_f=c^{-1}\omega_f=c^{-1}(\omega_0+E_0-E_f).$$

The Feynman potential of the scattered photon (9) due to the steady current (8) is the same as the classical retarded potential due to that current, and this is the basis for the validity of the semiclassical formulas of x-ray diffraction. In fact, in the integral over t_x of Eq. (6), which leads to Eq. (9) for the Feynman potential, the contribution for $t_x<t_z$ represents the amplitude for a photon emitted by the system to be found at z, whereas the contribution from $t_x>t_z$ represents the amplitude that a photon emitted from z is absorbed by the system. If (9) were expressed as the

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[40] We use the four-vector conventions of Ref. 39. x, y are four-vectors $(ct_x,\mathbf{x})$, $(ct_y,\mathbf{y})$. Four-vector contractions are denoted as either $kx=(ck_4t_x-\mathbf{k}\cdot\mathbf{x})$ or by repeated indices $A_\mu B_\mu=A_4B_4-\mathbf{A}\cdot\mathbf{B}$. The four-dimensional gradient operator used later is $\partial_\mu=[(1/c)(\partial/\partial t),-\nabla]$. In intermediate calculations we take $\hbar=c=1$.

sum of these two contributions, then each part would be a complicated function and not be of use, whereas their sum is simple and useful. If $k_f \mid \mathbf{z}-\mathbf{x} \mid$ is large, only $t_x<t_z$ contributes appreciably to (9), and (9) becomes the amplitude of the scattered photon; on the other hand, for multiple scattering processes involving more than one atom, it is (9) which is of direct relevance.

At large distances from the scattering system,

$$A_\mu{}^s(z)=\exp[-i(\omega_0+E_0-E_f)t_z]\frac{\exp(ik_f\mid \mathbf{z}\mid)}{\mid \mathbf{z}\mid}$$

$$\times\int\exp(-i\mathbf{k}_f\cdot\mathbf{x})J_\mu{}^{f0}(\mathbf{x},\omega_0)d\mathbf{x}/c,\qquad(10)$$

which may be used to compute the scattering cross section in the following manner: At large distances from the scatterer the expected energy flux is given by

$$\mathbf{S}=(c/4\pi)\ \mathrm{Re}(\mathbf{E}\times\mathbf{B}^*),\qquad(11)$$

where $\mathbf{E}$ and $\mathbf{B}$ are computed from the potential (10) in the usual manner.[39] The quantum flux is $(\hbar\omega)^{-1}\mathbf{S}$. Dividing by the incident quantum flux, we obtain for the scattering cross section

$$\frac{d\sigma}{d\Omega}=\frac{\omega_f}{\omega_0}\lim_{R\to\infty}R^2A_\mu{}^s(\mathbf{R})^*A_\mu{}^s(\mathbf{R})/(a_\nu{}^{0*}a_\nu{}^0)$$

$$=-\frac{\omega_f}{\omega_0}\lim_{R\to\infty}R^2\mid \mathbf{A}_\perp{}^s(\mathbf{R})\mid^2/(a_\nu{}^{0*}a_\nu{}^0),\qquad(12)$$

or equivalently, substituting (10) into (12),

$$\frac{d\sigma}{d\Omega}=-\frac{\omega_f}{\omega_0}$$

$$\times\left|\frac{1}{c}\int\exp(-i\mathbf{k}_f\cdot\mathbf{x})\mathbf{J}_\perp{}^{f0}(\mathbf{x},\omega_0)d\mathbf{x}\right|^2\bigg/(a_\nu{}^{0*}a_\nu{}^0),\qquad(13)$$

where $\mathbf{J}_\perp$ is the current component perpendicular to $\mathbf{k}_f$.

Our concern will be primarily with coherent scattering in which the initial and final states of the system are the same. In this case $M_{\mu\nu}{}^{f0}(x,y)$ depends only on (t_x-t_y) as is seen from Eq. (2);

$$M_{\mu\nu}{}^{00}(x,y)=M_{\mu\nu}{}^{00}(\mathbf{x},\mathbf{y},t_x-t_y).\qquad(14)$$

We delete the superscripts "0" and we have from Eqs. (5) and (8)

$$J_\mu(\mathbf{x},\omega)=\int M_{\mu\nu}{}^\omega(\mathbf{x},\mathbf{y})a_\nu{}^0(\mathbf{y})d\mathbf{y},\qquad(15)$$

where the superscript ω indicates the Fourier transform. In order to avoid excessive suffices and symbols, we shall delete the symbol ω in $J(\mathbf{x},\omega)$ and $M^\omega(\mathbf{x},\mathbf{y})$; the explicit arguments of space position only can serve to remind us that we are referring to a particular frequency component. Thus, $M^\omega(\mathbf{x},\mathbf{y})\to M(\mathbf{x},\mathbf{y})$. Deleting the time-dependent factor, Eq. (9) becomes

$$A_\mu{}^s(\mathbf{z})=\iint\frac{\exp(ik_0\mid \mathbf{z}-\mathbf{x}\mid)}{\mid \mathbf{z}-\mathbf{x}\mid}M_{\mu\nu}(\mathbf{x},\mathbf{y})A_\nu{}^0(\mathbf{y})d\mathbf{x}d\mathbf{y},\qquad(16)$$

or in obvious matrix notation

$$A^s=\delta^+MA^0.\qquad(17)$$

If z is very large compared to the atomic dimension, Eq. (16) gives for the scattered wave amplitude (replacing $\mathbf{z}$ by $\mathbf{R}$)

$$A_\mu{}^s(\mathbf{R})=\frac{e^{ikR}}{R}\int\exp(-i\mathbf{k}_f\cdot\mathbf{x})M_{\mu\nu}(\mathbf{x},\mathbf{y})A_\nu{}^0(\mathbf{y})d\mathbf{y}d\mathbf{x}.\qquad(18)$$

III. MULTIPLE SCATTERING EQUATIONS

In this and the following sections we shall obtain approximate equations determining the coherently scattered wave from a crystal in terms of the scattering operators of the individual atoms.

We shall regard the crystal as a collection of independent atoms with harmonic forces acting between their c.m.'s. In the absence of radiation we take the Hamiltonian of the crystal to be

$$H_0=\sum_{i=1}^N H^i+\sum_{i=1}^N P_i{}^2/2M_i+V(R_1,\cdots,R_N),\qquad(19)$$

where H^i is the internal Hamiltonian of the ith atom with the electromagnetic effect represented by instantaneous Coulomb interaction among its constituents, $\mathbf{P}_i$ is the total momentum of ith atom, M_i its mass, and V represents the interatomic interaction.[41] In this section we simplify by taking the atoms as fixed in space, so that

$$H_0=\sum_{i=1}^N H^i.$$

We may now develop the expression for the S matrix as a sum of terms each corresponding to a Feynman diagram. In each diagram there will be an external photon line representing the incident photon, another representing the outgoing photon, a number of interatomic lines representing virtual quanta exchanged among the atoms, and finally a number of intra-atomic photon lines representing the atomic radiative reactions.

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[41] In (19) we neglect the effect of correlations among the internal motions of the various atoms and the effect of itinerant electrons, but for x-ray energies these effects are quite negligible. For elastic scattering, the itinerant electrons make a negligible contribution, except in the forward direction, and in this case the correct results are given if we treat all electrons as bound. Magnon effects could be treated in a manner similar to that employed in Sec. IV. However, for γ-ray scattering, the primary effect of the spin correlations is to determine the effective magnetic field at the nucleus and hence to determine the Zeeman splitting, and for our purposes, it is sufficient to treat this effect as a temperature-dependent contribution to H^i.

Calling the interatomic lines, as well as the incident and outgoing photons, "external," we then initially consider the sum of all the diagrams contributing to the coherent elastic scattering from N atoms in which no more than two external photon lines are connected to any given atom. In Figs. 2(a) and 2(b) we give such diagrams. The circles in Figs. 2(a) and 2(b) represent the summed contribution of all possible internal photon lines on the respective atoms. The wavy lines between atoms represent photon exchange, and the singly connected wavy lines represent the incident and scattered photons. Figure 2(c) gives a diagram which is not included in the sum. The time integrations are carried out as shown in Appendix B. We note that since t_i' is not restricted to be greater than t_i, diagrams like Figs. 2(a) and 2(b) contain contributions from multiphoton and multiatomic excitations simultaneously present. These contributions must be included or else spurious R^{-2} interaction terms appear.

The contribution to the amplitude of the coherent scattered wave for the class of graphs summed is easily seen to be given by (Appendix B)

$$(A^s)'=\delta^+M^i[1+\delta^+M^j+\delta^+M^j\delta^+M^k+\cdots]A^0, \quad (20)$$

where summation over all different i, j, k is understood and the matrix notation is that of Eq. (17). The interpretation of the third term in the brackets of (20) is that the incident photon is scattered from the kth atom, it propagates to the jth atom ($j\neq k$), where it is again scattered, and then it propagates to the ith atom $i\neq j\neq k$, where it is finally scattered to an "exterior" point. The effect of the "mirror" terms such as shown in Fig. 2(c) is partially accounted for by letting k also run over i in (20), and we obtain

$$A^s=\delta^+M^i\{A^0+\delta^+M^j[A^0+\delta^+M^kA^0+\cdots]\}, \quad (21)$$

where k is now summed over all values except $k=j$. It is shown in Appendix B that for x-ray and γ-ray scattering this is indeed a very good approximation.

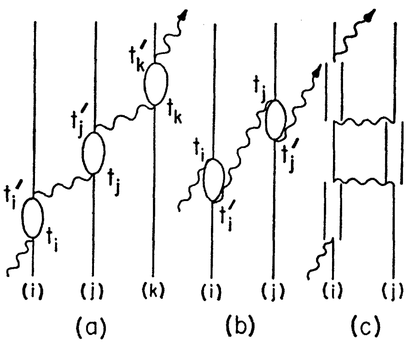

FIG. 2. Feynman diagrams representing contributions to coherent elastic scattering from N atoms. The circles represent the summed contribution of all possible internal photon lines on the respective atoms.

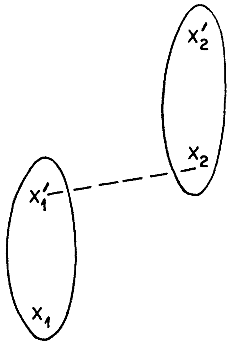

FIG. 3. Schematic diagram representing the two-atom scattering operator $M^{(2,1)}$. The dotted line between the atoms represents the exchange of a photon and an arbitrary number of phonons.

We may rewrite (21) as

$$A^s=\sum_i \delta^+M^iA^i, \quad (22)$$

$$A^i=A^0+\sum_{j\neq i}\delta^+M^jA^j, \quad (23)$$

where (23) gives the equation determining the effective field incident on the ith atom in our approximation.[42]

Except for inaccuracy in accounting for "mirror terms," Eqs. (22) and (23) are the exact single-quantum coherent-scattering equations from a collection of scatterers. A^s is linear in the incident field, and the total field is $A^s(\mathbf{R})+A^0(\mathbf{R})$. We have assumed an incident photon of good energy $\hbar\omega$. However, if the incident wave packet is

$$\int A^0(\omega)e^{-i\omega t}d\omega,$$

then

$$A^s=\sum_i\int\delta^+(\omega)M^i(\omega)A^i(\omega)e^{-i\omega t}d\omega \quad (24)$$

gives the scattered-photon wave packet.

Finally, we write (22) and (23) explicitly:

$$A_\mu{}^s(\mathbf{R})=\sum_i\iint\frac{\exp(ik_0|\mathbf{R}-\mathbf{x}|)}{|\mathbf{R}-\mathbf{x}|}\times M_{\mu\nu}{}^i(\mathbf{x},\mathbf{y})A_\nu{}^i(\mathbf{y})d\mathbf{x}d\mathbf{y}, \quad (25)$$

$$A_\mu{}^i(\mathbf{x})=A_\mu{}^0(\mathbf{x})+\sum_{j\neq i}\iint\frac{\exp(ik_0|\mathbf{x}-\mathbf{y}|)}{|\mathbf{x}-\mathbf{y}|}\times M_{\mu\nu}{}^j(\mathbf{y},\mathbf{z})A_\nu{}^j(\mathbf{z})d\mathbf{y}d\mathbf{z}. \quad (26)$$

IV. CRYSTAL VIBRATIONS AND THE EFFECTIVE FIELD EQUATIONS

In the preceding it was assumed that the atoms were fixed in position; now we wish to consider the effect of the thermal- and zero-point motion on the coherent scattering.

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[42] See Foldy, Lax, and Watson (Refs. 30–32) for similar developments.

Let $\mathbf{R}$ be the operator of the position of the c.m. of an atom and let ξ denote a complete set of internal dynamical variables. Now $j_\mu(\mathbf{x}) = f_\mu(\mathbf{x}-\mathbf{R})$, or we shall simply write $j_\mu(\mathbf{x}) = j_\mu(\mathbf{x}-\mathbf{R})$. $\mathbf{j}(\mathbf{x}-\mathbf{R}) = \mathbf{j}(\xi, \mathbf{x}-\mathbf{R}) + \rho(\xi, \mathbf{x}-\mathbf{R})\mathbf{V}$, but the second term representing the contribution to the current of the c.m. motion is of no importance and we shall neglect it.

Our single scattering operator [Eqs. (1) and (2)] now has the form

$$M_{\mu\nu}^{(1)}(x', x) = -iT[j_\mu(\xi(t'), \mathbf{x}'-\mathbf{R}(t'))j_\nu(\xi(t), \mathbf{x}-\mathbf{R}(t))]. \quad (27)$$

Similarly, our double-scattering operator corresponding to a virtual quantum exchange between atom 1 at x_1' and atom 2 at x_2 (see Fig. 3) is

$$M_{\mu\nu}^{(2,1)}(x_2', x_1) = (-i)^2 \iint T[j_\mu^{(2)}(\xi_2(t_2'), \mathbf{x}_2'-\mathbf{R}_2(t_2'))j_\lambda^{(2)}(\xi_2(t_2), \mathbf{x}_2-\mathbf{R}_2(t_2)) \times\delta_+(x_2x_1')j_\lambda^{(1)}(\xi_1(t_1'), \mathbf{x}_1'-\mathbf{R}_1(t_1'))j_\nu^{(1)}(\xi_1(t_1), \mathbf{x}_1-\mathbf{R}_1(t_1))]dx_2dx_1'. \quad (27')$$

The expression for the multiscattering operator is the straightforward extension of (27′).

We shall take the Hamiltonian of the form [Eq. (19)]

$$H = [\sum_{i=1}^{N} H_i(\xi_i) + H_R(\mathbf{R}, \mathbf{P})],$$

where $H_i(\xi_i)$ refers to the internal Hamiltonian of the ith atom and the ξ_i are its internal dynamical variables, and $H_R(\mathbf{R}, \mathbf{P})$ is the crystal-vibration Hamiltonian, with $\mathbf{R}$ and $\mathbf{P}$ standing for the c.m.'s of the various atoms and their momenta. Under our assumptions the $\xi_i(t)$'s referring to different atoms (and same or different times) commute, and $\xi_i(t)$'s commute with $\mathbf{R}(t')$'s.[43]

It is useful to introduce the double-space Fourier transform of the scattering operators. For $M^{(1)}$ [Eq. (27)] we have

$$M_{\mu\nu}^{(1)}(t', \mathbf{k}_f; t, \mathbf{k}_0) = \int \exp(-i\mathbf{k}_f\cdot\mathbf{x}')M_{\mu\nu}^{(1)}(x', x)\exp(i\mathbf{k}_0\cdot\mathbf{x})d\mathbf{x}d\mathbf{x}', \quad (28)$$

and substituting

$$j_\mu(\xi(t), \mathbf{x}-\mathbf{R}(t)) = \exp(iH_Rt)j_\mu(\xi(t), \mathbf{x}-\mathbf{R})\exp(-iH_Rt)$$

into Eqs. (27) and (28) before doing the space integration, we obtain

$$M_{\mu\nu}^{(1)}(t', \mathbf{k}_f; t, \mathbf{k}_0) = M_{\mu\nu}^{0}(t', \mathbf{k}_f; t, \mathbf{k}_0) \times T[\exp(-i\mathbf{k}_f\cdot\mathbf{R}(t'))\exp(i\mathbf{k}_0\cdot\mathbf{R}(t))], \quad (29)$$

where

$$M_{\mu\nu}^{0}(t', \mathbf{k}_f; t, \mathbf{k}_0) = -i\int \exp(-i\mathbf{k}_f\cdot\mathbf{x}') \times T[j_\mu(\xi(t'), \mathbf{x}')j_\nu(\xi(t), \mathbf{x})]\exp(i\mathbf{k}_0\cdot\mathbf{x})d\mathbf{x}'d\mathbf{x} \quad (30)$$

is the atomic scattering operator for the nucleus fixed at the origin. Similarly, the Fourier transform of $M^{(2,1)}$ is

$$M_{\mu\nu}^{(2,1)}(t_2', \mathbf{k}_f; t_1, \mathbf{k}_0) = \int \exp(-i\mathbf{k}_f\cdot\mathbf{x}_2')M_{\mu\nu}^{(2,1)}(x_2', x_1) \times \exp(i\mathbf{k}_0\cdot\mathbf{x}_1)d\mathbf{x}_1d\mathbf{x}_2', \quad (28')$$

which from (27′) is

$$M_{\mu\nu}^{(2,1)}(t_2', \mathbf{k}_f; t_1, \mathbf{k}_0) = \iint dt_2dt_1' \int d^4k\, M_{\mu\lambda}^{0(2)}(t_2', \mathbf{k}_f; t_2, \mathbf{k})M_{\lambda\nu}^{0(1)}(t_1', \mathbf{k}; t_1, \mathbf{k}_0)\delta_+(k^2) \times \exp(-ik_4(t_2-t_1'))T[\exp(-i\mathbf{k}_f\cdot\mathbf{R}_2(t_2'))\exp(i\mathbf{k}\cdot\mathbf{R}_2(t_2))\exp(-i\mathbf{k}\cdot\mathbf{R}_1(t_1'))\exp(i\mathbf{k}_0\cdot\mathbf{R}_1(t_1))], \quad (29')$$

where $\delta_+(k^2)$ is the Fourier transform of $\delta_+(x)$ [Eq. (7)], $\delta_+(k^2) = -4\pi(2\pi)^{-4}[k^2+i\eta]^{-1}$, $\eta\to 0+$. In (29′) the M^0's carry superscripts 2 and 1, since they may be different for different atoms.

The analysis of (29′) and more complicated processes is simplified by noting that in the time-ordered product t_2 and t_1' may be set equal because during the transit time of the quantum between the two atoms the crystal will not change its configuration (neglecting V/c terms). This can be seen mathematically in the following way. Suppose that the internal current at t_1' is $\exp(-i\omega t_1')$, where ω is an x-ray frequency ($\approx$10 keV). Then the relevant term in (29′) is

$$\int \frac{\exp(-ik_4(t_2-t_1'))}{k_4^2-k^2+i\eta}\{\exp(i\epsilon_nt_2)\exp(-i\epsilon_\beta(t_2-t_1')) \times\exp(-i\epsilon_0t_1')\exp(-i\omega t_1')\langle\chi_n|\exp(i\mathbf{k}\cdot\mathbf{R}_2)|\chi_\beta\rangle \times\langle\chi_\beta|\exp(-i\mathbf{k}\cdot\mathbf{R}_1)|\chi_0\rangle\}dt_1'd^4k.$$

In this expression the matrix element of $\exp[i\mathbf{k}\cdot\mathbf{R}_2(t_2)]\exp[-i\mathbf{k}\cdot\mathbf{R}_1(t_1')]$ has been taken using as bases the stationary vibration states $|\chi_i\rangle$ with energies ϵ_i,

$$H_R|\chi_i\rangle = \epsilon_i|\chi_i\rangle. \quad (31)$$

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[43] It is clear that the small slow crystal vibrations have negligible effect on the internal dynamics of the atom {the $(V/c)^2$ shift of the nuclear splittings discussed by R. V. Pound and G. A. Rebka, Jr. [Phys. Rev. Letters **4**, 274 (1960)] and B. D. Josephson [*ibid.* **4**, 341 (1960)] are of no interest in the present discussion}.

Performing first the t_1' integration, then the d^4k integration, we obtain

$$\int \exp(-i(\omega+\epsilon_0-\epsilon_n)t_2)$$

$$\times\langle\chi_n\,|\,\exp(ik'\mathbf{\Omega}\cdot\mathbf{R}_2)\,|\,\chi_\beta\rangle\langle\chi_\beta\,|\,\exp(-ik'\mathbf{\Omega}\cdot\mathbf{R}_1)\,|\,\chi_0\rangle d\mathbf{\Omega},$$

where $\mathbf{\Omega}$ is a unit directional vector and $k'=\omega-(\epsilon_\beta-\epsilon_0)$. But $(\epsilon_\beta-\epsilon_0)\approx 10^{-2}$ eV and $\omega\approx 10^4$ eV; therefore, the change of wave number of the photon has a negligible effect in the matrix elements (the term depends on R_2-R_1, but for very large R_2-R_1 the phonon exchange is unimportant, in any case). We may then replace k' by ω and replace the sum over β by 1; the result is that of setting $t_2=t_1'$ in the time-ordered brace of Eq. (29′). Making this replacement, Eq. (29′) becomes

$$M_{\mu\nu}{}^{(2,1)}(t_2',\mathbf{k}_f;t_1,\mathbf{k}_0)$$
$$=\iint dt_2dt_1'\int d^4k\; M_{\mu\lambda}{}^{0(2)}(t_2',\mathbf{k}_f;t_2,\mathbf{k})$$
$$\times M_{\lambda\nu}{}^{0(1)}(t_1',\mathbf{k};t_1,\mathbf{k}_0)\delta_+(k^2)$$
$$\times\exp(-ik_4(t_2-t_1'))T\{\exp(-i\mathbf{k}_f\cdot\mathbf{R}_2(t_2'))$$
$$\times\exp[i\mathbf{k}\cdot(\mathbf{R}_2(t_2)-\mathbf{R}_1(t_2))]\exp(i\mathbf{k}_0\cdot\mathbf{R}_1(t_1))\}. \tag{29''}$$

Or equivalently we could replace t_2 by t_1' in the brace.

Rather than further general discussion of (29″), it is convenient first to discuss the single-scattering formula (29).

Again, we are principally interested in coherent scattering for which the initial and final internal atomic state is the same. We denote by $|\,\alpha\rangle$ this initial internal state and by $|\,\chi_0\rangle$ the initial vibration state of the crystal. We now assume that the expectation value of $M_{\mu\nu}{}^0$ [Eq. (30)] in the state $|\,\alpha\rangle$ has been taken and inserted in (29), which then becomes an operator only in the dynamical variable $\mathbf{R}$ (and $\mathbf{P}_R$).

$M_{\mu\nu}{}^0$ is a sum of a very fast electronic part $E_{\mu\nu}{}^0(t'-t)$, for which the primed and unprimed times may be set equal in Eq. (29), and a very slow nuclear part $N_{\mu\nu}{}^0(t'-t)$ (we assume that ω_0 is within a few widths of a nuclear resonance), for which $(t'-t)\approx\tau_n$, the nuclear excited-state lifetime. For Mössbauer transitions τ_n is very long with respect to crystal-vibration times and we can effectively take the primed time infinitely later than the unprimed time in the brace of Eq. (29).[44] The nuclear part $N_{\mu\nu}{}^0$ includes not only the purely nuclear processes such as shown in Fig. 4(a), but all processes which pass through the nucleus, such as the screening processes Figs. 4(b) and 4(c). The electronic part $E_{\mu\nu}{}^0$ includes only purely electronic processes, such as shown in Figs. 4(d) and 4(e), and gives a very broad (frequency-insensitive) contribution. More explicitly (as shown by direct calculation in II[17]), we have

$$M_{\mu\nu}{}^0(t',\mathbf{k}_f;t,\mathbf{k}_0)$$
$$=N_{\mu\nu}{}^0(\mathbf{k}_f,\mathbf{k}_0,t'-t)+E_{\mu\nu}{}^0(\mathbf{k}_f,\mathbf{k}_0,t'-t), \tag{32}$$

where

$$N_{\mu\nu}{}^0(\mathbf{k}_f,\mathbf{k}_0,t'-t)=-i\sum_n N_{\mu\nu}{}^0(\mathbf{k}_f,\mathbf{k}_0,n)$$
$$\times\exp(-i(E_n-E_\alpha-\tfrac{1}{2}i\Gamma_n)(t'-t))1(t'-t) \tag{33}$$

and, sufficient for our purposes,

$$E_{\mu\nu}{}^0(\mathbf{k}_f,\mathbf{k}_0,t'-t)=E_{\mu\nu}{}^0(\mathbf{k}_f,\mathbf{k}_0,\omega_0)\delta(t-t'). \tag{34}$$

In Eq. (33) $E_n-\frac{1}{2}i\Gamma_n$ is the energy of the excited nuclear state $|\,n\rangle$. If we now insert (33) for M^0 in (29), multiply on the right side by $|\,\chi_0\rangle\exp(-i\omega_0t)$, and perform the t integration, we obtain

$$N_{\mu\nu}{}^{(1)}(t',\mathbf{k}_f,\mathbf{k}_0)\,|\,\chi_0\rangle=\sum_{n,\beta}\frac{N_{\mu\nu}{}^0(\mathbf{k}_f,\mathbf{k}_0,n)\exp(-i\omega_0t')\exp(-i\mathbf{k}_f\cdot\mathbf{R}(t'))\,|\,\chi_\beta\rangle\langle\chi_\beta\,|\,\exp(i\mathbf{k}_0\cdot\mathbf{R})\,|\,\chi_0\rangle}{\omega_0-(E_n-E_\alpha)-(\epsilon_\beta-\epsilon_0)+\frac{1}{2}i\Gamma_n}, \tag{35}$$

which becomes for the very slow Mössbauer transition

$$N_{\mu\nu}{}^{(1)}(t',\mathbf{k}_f,\mathbf{k}_0)\,|\,\chi_0\rangle=\exp(-i\omega_0t')\exp(-i\mathbf{k}_f\cdot\mathbf{R}(t'))\,|\,\chi_0\rangle\left(\sum_n\frac{N_{\mu\nu}{}^0(\mathbf{k}_f,\mathbf{k}_0,n)}{\omega_0-(E_n-E_\alpha)+\frac{1}{2}i\Gamma_n}\right)\langle\chi_0\,|\,\exp(i\mathbf{k}_0\cdot\mathbf{R})\,|\,\chi_0\rangle$$
$$\equiv\exp(-i\omega_0t')\exp(-i\mathbf{k}_f\cdot\mathbf{R}(t'))\,|\,\chi_0\rangle N_{\mu\nu}{}^0(\mathbf{k}_f,\mathbf{k}_0)\langle\chi_0\,|\,\exp(i\mathbf{k}_0\cdot\mathbf{R})\,|\,\chi_0\rangle. \tag{36}$$

Similarly, for the fast electronic contribution to $M_{\mu\nu}{}^{(1)}(t',\mathbf{k}_f,\mathbf{k}_0)\,|\,\chi_0\rangle$, we have

$$E_{\mu\nu}{}^{(1)}(t',\mathbf{k}_f,\mathbf{k}_0)\,|\,\chi_0\rangle$$
$$=\exp(-i\omega_0t')\exp(-i(\mathbf{k}_f-\mathbf{k}_0)\cdot\mathbf{R}(t'))\,|\,\chi_0\rangle$$
$$\times E_{\mu\nu}{}^0(\mathbf{k}_f,\mathbf{k}_0,\omega_0). \tag{37}$$

Equations (36) and (37) give the effect of the crystal vibrations on the Mössbauer and x-ray single-scattering operators and have been discussed extensively in the literature. For elastic scattering the final phonon state is $|\,\chi_0\rangle$, and nuclear scattering processes have the phonon factor $\langle\exp(i\mathbf{k}_0\cdot\mathbf{R})\rangle\langle\exp(-i\mathbf{k}_f\cdot\mathbf{R})\rangle$, which is simply the Mössbauer phonon factor (averaging over initial phonon states χ_0). while the purely electronic scattering has the usual Debye-Waller phonon factor $\langle\exp[-i\mathbf{k}_f-\mathbf{k}_0)\cdot\mathbf{R}]\rangle$.

Returning to the multiple-scattering formula (29″), since the most interesting phonon effects are nuclear, we first neglect the electronic part and take M^0 of the

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[44] Phonon frequencies are on the order of $\omega_{ph}\approx 10^{14}$/sec. For the excited $\frac{3}{2}$ state of the Fe^{57} nuclei, $\tau_n\approx 10^{-7}$ sec and $\omega_{ph}\approx 10^7/\tau_n$.

form (33). Inserting (33) for the M^0's in (29″) and multiplying on the right by $\exp(-i\omega_0 t_1)\,|\,\chi_0\rangle$ and performing all integrations except t_2' we obtain

$$\int M_{\mu\nu}{}^{(2,1)}(t_2', \mathbf{k}_f; t_1, \mathbf{k}_0)\exp(-i\omega_0 t_1)\,|\,\chi_0\rangle dt_1$$

$$= \exp(-i\omega_0 t_2')\exp(-i\mathbf{k}_f\cdot\mathbf{R}_2(t_2'))\,|\,\chi_0\rangle$$

$$\times N_{\mu\lambda}{}^{0(2)}(\mathbf{k}_f, \mathbf{k})\left\langle\chi_0\left|\frac{\exp(ik_0\,|\,\mathbf{R}_2-\mathbf{R}_1\,|)}{|\,\mathbf{R}_2-\mathbf{R}_1\,|}\right|\chi_0\right\rangle$$

$$\times N_{\lambda\nu}{}^{0(1)}(\mathbf{k}, \mathbf{k}_0)\langle\chi_0\,|\exp(i\mathbf{k}_0\cdot\mathbf{R}_1)\,|\,\chi_0\rangle, \qquad (38)$$

where we have made the Mössbauer assumption (or the slow-collision time assumption) that

$$|\,\omega_0-(E_n-E_\alpha)\,|\ll k_B\theta_D\approx \text{phonon energies.}$$

The interesting feature of Eq. (38) is that the amplitude for simultaneous photon-phonon exchange between two resonant atoms is given by

$$\langle\chi_0\,|\,\delta_{21}{}^+\,|\,\chi_0\rangle=\left\langle\chi_0\left|\frac{\exp(ik_0\,|\,\mathbf{R}_2-\mathbf{R}_1\,|)}{|\,\mathbf{R}_2-\mathbf{R}_1\,|}\right|\chi_0\right\rangle \qquad (39)$$

(see Fig. 3). We shall discuss this factor in more detail below.

The significance of $\mathbf{k}$ appearing in (38) is that of the momentum operator for the virtual photon exchanged between atoms 1 and 2. Before doing the $d\mathbf{k}$ integration of (29″), there was the photon factor $\exp(i\mathbf{k}\cdot\mathbf{R}_2(t_2))\exp(-i\mathbf{k}\cdot\mathbf{R}_1(t_2))$, and $\mathbf{k}$ also appeared in $N^{0(1)}(\mathbf{k}, \mathbf{k}_0)$ in the form

$$\int\exp(-i\mathbf{k}\cdot\mathbf{x}_1)N^{0(1)}(\mathbf{x}_1, \mathbf{k}_0)d\mathbf{x}_1$$

and in $N^{0(2)}(\mathbf{k}_f, \mathbf{k})$ in the form

$$\int\exp(i\mathbf{k}\cdot\mathbf{x}_2)N^{0(2)}(\mathbf{k}_f, \mathbf{x}_2)d\mathbf{x}_2.$$

We can then replace $i(-\mathbf{k})$ appearing in the $N^{0(1)}(\mathbf{k}, \mathbf{k}_0)$ integration by $\boldsymbol{\nabla}_{\mathbf{R}_1}$ and $i\mathbf{k}$ in the $N^{0(2)}(\mathbf{k}_f, \mathbf{k})$ integration by $\boldsymbol{\nabla}_{\mathbf{R}_2}$. The $d\mathbf{k}$ integration then gives

$$N^{0(2)}(\mathbf{k}_f, -i\overrightarrow{\boldsymbol{\nabla}}_{\mathbf{R}_2})\frac{\exp(ik_0\,|\,\mathbf{R}_2-\mathbf{R}_1\,|)}{|\,\mathbf{R}_2-\mathbf{R}_1\,|}N^{0(1)}(i\overleftarrow{\boldsymbol{\nabla}}_{\mathbf{R}_1}, \mathbf{k}_0),$$

where the arrows indicate the directions the gradient operators are to operate. Since the photon propagator $\delta_{21}{}^+$ is only a function of $\mathbf{R}_2-\mathbf{R}_1$ and $\boldsymbol{\nabla}_{\mathbf{R}_1}=-\boldsymbol{\nabla}_{\mathbf{R}_2}$, employing the same symbol $\mathbf{k}$ in $N^{0(1)}$, $N^{0(2)}$ in Eq. (38) is consistent. If $k_0\,|\,\mathbf{R}_2-\mathbf{R}_1\,|\gg1$, then it is seen that $\mathbf{k}\to\mathbf{k}_{12}=k_0(\mathbf{R}_2-\mathbf{R}_1)/|\,\mathbf{R}_2-\mathbf{R}_1\,|$.

Effective Field Equations

The extension of Eq. (38) to the nuclear multiscattering case is straightforward. Summing up all the diagrams as in Sec. III, we have for the generalization of Eq. (23) for the effective field incident on the nucleus at $\mathbf{R}_i$

$$\langle A^i(\mathbf{R}_i)\rangle=\langle A^0(\mathbf{R}_i)\rangle+\sum_{j\neq i}\left\langle\frac{\exp(ik_0\,|\,\mathbf{R}_i-\mathbf{R}_j\,|)}{|\,\mathbf{R}_i-\mathbf{R}_j\,|}\right\rangle$$

$$\times N^{0(j)}(\mathbf{k}, \mathbf{k}')\langle A^j(\mathbf{R}_j)\rangle \qquad (40)$$

and for the scattered photon potential

$$[A^s(\mathbf{R})]^{f0}\,|\,\chi_f\rangle=\sum_i|\,\chi_f\rangle\left\langle\chi_f\left|\frac{\exp(ik_f\,|\,\mathbf{R}-\mathbf{R}_i\,|)}{|\,\mathbf{R}-\mathbf{R}_i\,|}\right|\chi_0\right\rangle$$

$$\times N^{0(i)}(\mathbf{k}, \mathbf{k}')\langle A^i(\mathbf{R}_i)\rangle. \qquad (41)$$

In the above Eqs. (40) and (41) the angular brackets refer to the expectation value in the initial vibrational state $|\,\chi_0\rangle$. Also in (40) and (41) we have both $\mathbf{k}$ and $\mathbf{k}'$ appearing. The meaning of $N^{0(j)}(\mathbf{k}, \mathbf{k}')$ is that $\mathbf{k}'$ is the momentum that was absorbed by the jth atom and should be replaced by $(-i)\overrightarrow{\boldsymbol{\nabla}}_{\mathbf{R}_j}$, whereas $\mathbf{k}$ is the momentum emitted by the jth atom and should be replaced by $i\overleftarrow{\boldsymbol{\nabla}}_{\mathbf{R}_j}$; therefore, $N^{0(j)}(\mathbf{k}, \mathbf{k}')$ means $N^{0(j)}(i\overleftarrow{\boldsymbol{\nabla}}_{\mathbf{R}_j}, -i\overrightarrow{\boldsymbol{\nabla}}_{\mathbf{R}_j})$. The $\mathbf{R}_i$'s appearing in the above equations are the operators for the c.m. of the various atoms. If we let $\mathbf{R}_i=\mathbf{R}_i{}^0+\mathbf{r}_i$, where $\mathbf{R}_i{}^0$ indicates the equilibrium position of the ith atom, then in Eq. (40), for example, taking $A^0(\mathbf{R}_i)=a^0\exp(i\mathbf{k}_0\cdot\mathbf{R}_i)$, where a^0 is a constant four-vector, we have

$$\langle A^0(\mathbf{R}_i)\rangle=a^0\langle\exp(i\mathbf{k}_0\cdot\mathbf{r}_i)\rangle\exp(i\mathbf{k}_0\cdot\mathbf{R}_i{}^0) \qquad (42)$$

and

$$\langle\delta_{ij}{}^+\rangle=\left\langle\frac{\exp(ik_0\,|\,\mathbf{R}_i-\mathbf{R}_j\,|)}{|\,\mathbf{R}_i-\mathbf{R}_j\,|}\right\rangle$$

$$=\left\langle\frac{\exp(ik_0\,|\,\mathbf{R}_{ij}{}^0+\mathbf{r}_i-\mathbf{r}_j\,|)}{|\,\mathbf{R}_{ij}{}^0+\mathbf{r}_i-\mathbf{r}_j\,|}\right\rangle. \qquad (43)$$

As noted above, $\langle\delta_{ij}{}^+\rangle$ gives the amplitude for simultaneous photon-phonon exchange. By Fourier transformation we have

$$\langle\delta_{ij}{}^+\rangle=\frac{1}{4\pi}\int\frac{\exp(i\mathbf{k}\cdot\mathbf{R}_{ij}{}^0)}{(k^2-k_0{}^2-i\eta)}\langle\exp(i\mathbf{k}\cdot(\mathbf{r}_i-\mathbf{r}_j))\rangle d\mathbf{k}. \qquad (44)$$

Taking account of the fact that in the crystal $\mathbf{r}_i$ and $\mathbf{r}_j$ are the sums of many small independent displacements,[45] we have

$$\langle\exp(i\mathbf{k}\cdot(\mathbf{r}_i-\mathbf{r}_j))\rangle$$

$$=\exp(-\tfrac{1}{2}\langle(\mathbf{k}\cdot\mathbf{r}_i)^2+(\mathbf{k}\cdot\mathbf{r}_j)^2-2(\mathbf{k}\cdot\mathbf{r}_i)(\mathbf{k}\cdot\mathbf{r}_j)\rangle).$$

Therefore, $\langle\delta_{ij}{}^+\rangle$ is given by[46]

$$\langle\delta_{ij}{}^+\rangle=\exp(-\tfrac{1}{2}\langle(\mathbf{k}\cdot\mathbf{r}_i)^2+(\mathbf{k}\cdot\mathbf{r}_j)^2-2(\mathbf{k}\cdot\mathbf{r}_i)(\mathbf{k}\cdot\mathbf{r}_j)\rangle)$$

$$\times[\exp(ik_0R_{ij}{}^0)/R_{ij}{}^0], \qquad (45)$$

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[45] L. Van Hove, Phys. Rev. **95**, 249 (1954).

[46] It is interesting to note from (45) that even if the amplitude of oscillation of each of the atoms were quite large, so that the Mössbauer factor would be quite small, the amplitude for photon exchange could still be quite appreciable if the motions of the two atoms were well correlated $(2\langle(\mathbf{k}\cdot\mathbf{r}_i)(\mathbf{k}\cdot\mathbf{r}_j)\rangle\approx\langle(\mathbf{k}\cdot\mathbf{r}_i)^2+(\mathbf{k}\cdot\mathbf{r}_j)^2\rangle)$.

or, equivalently,

$$\langle\delta_{ij}^{+}\rangle = f_i^{1/2}(\mathbf{k})f_j^{1/2}(\mathbf{k})[1+\xi_{ij}(\mathbf{k})][\exp(ik_0R_{ij}^0)/R_{ij}^0]. \tag{46}$$

In Eqs. (45) and (46), $\mathbf{R}_{ij}^0=(\mathbf{R}_i^0-\mathbf{R}_j^0)$, $\mathbf{k}=-i\nabla_{\mathbf{R}_i^0}$, $f_i(\mathbf{k})=\exp[-\langle(\mathbf{k}\cdot\mathbf{r}_i)^2\rangle]$ is the Mössbauer factor for atom i (when the ensemble average is taken), and

$$\xi_{ij}(\mathbf{k})=\exp\langle(\mathbf{k}\cdot\mathbf{r}_i)(\mathbf{k}\cdot\mathbf{r}_j)\rangle-1 \tag{47}$$

represents the effect of the correlation in the motion of i and j on their amplitude for exchanging a Mössbauer γ ray. The ξ_{ij} correction term to the ordinary $f_i^{1/2}f_j^{1/2}$ Mössbauer factor for quantum exchange is generally very small. In a rough model (Debye, $T\sim\theta$, $R_{ij}/a\gg1$, where a is the lattice constant) it can be shown that ξ_{ij} is of the order $k^2\langle r^2\rangle a/R_{ij}$, and the decrease of $[f_j\xi_{ij}R_{ij}^{-1}\exp(ik_0R_{ij})]$ with R_{ij} will make this correction of the order of the mirror terms discussed in Appendix B and will be similarly negligible.

With the neglect of ξ_{ij}, Eqs. (40) and (41) simplify so that it is now possible, as in the fixed-atom case, to define an effective field which is an ordinary function of space. If in (40) we replace $\langle A^i(\mathbf{R}_i)\rangle$ by $f_i^{1/2}(\mathbf{k})$ $A^i(\mathbf{R}_i^0)$, then (40) leads to the equation

$$A^i(\mathbf{R}_i^0)=A^0(\mathbf{R}_i^0)+\sum_{j\neq i}\frac{\exp(ik_0R_{ij}^0)}{R_{ij}^0}f_j^{1/2}(\mathbf{k}) \times N^{0(j)}(\mathbf{k},\mathbf{k}')f_j^{1/2}(\mathbf{k}')A^j(\mathbf{R}_j^0) \tag{48}$$

and (41) becomes

$$[A^s(\mathbf{R})]^{f0}=\sum_i\frac{\exp(ik_f\,|\mathbf{R}-\mathbf{R}_i^0|)}{|\mathbf{R}-\mathbf{R}_i^0|}\langle\chi_f\,|\exp(-i\mathbf{k}\cdot\mathbf{r}_i)\,|\chi_0\rangle N^{0(i)}(\mathbf{k},\mathbf{k}')f_i^{1/2}(\mathbf{k}')A^i(\mathbf{R}_i^0). \tag{49}$$

The electronic contribution to the coherent scattering may be obtained by similar arguments. Adding the electronic contribution, we obtain for the coherent elastic wave incident on the ith atom

$$A^i(\mathbf{R}_i^0)=A^0(\mathbf{R}_i^0)+\sum_{j\neq i}\frac{\exp(ik_0R_{ij}^0)}{R_{ij}^0}[f_j^{1/2}(\mathbf{k})N^{0(j)}(\mathbf{k},\mathbf{k}')f_j^{1/2}(\mathbf{k}')+f_j^{1/2}(\mathbf{k}-\mathbf{k}')E^{0(j)}(\mathbf{k},\mathbf{k}')]A^j(\mathbf{R}_j^0), \tag{50}$$

and for the coherent scattered wave at $\mathbf{R}$

$$[A^s(\mathbf{R},t)]^{f0}=\sum_j\frac{\exp\big(i(k_f\,|\mathbf{R}-\mathbf{R}_j^0|-\omega_ft)\big)}{|\mathbf{R}-\mathbf{R}_j^0|} \times\langle\chi_f\,|[\exp(-i\mathbf{k}\cdot\mathbf{r}_j)\,|\chi_0\rangle N^{0(j)}(\mathbf{k},\mathbf{k}')f_j^{1/2}(\mathbf{k}')+\exp\big(-i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{r}_j\big)\,|\chi_0\rangle E^{0(j)}(\mathbf{k},\mathbf{k}')]A^j(\mathbf{R}_j^0). \tag{51}$$

In Eqs. (50) and (51), $\mathbf{k}=i\overleftarrow{\nabla}_{\mathbf{R}_j^0}$, $\mathbf{k}'=-i\overrightarrow{\nabla}_{\mathbf{R}_j^0}$. Defining the operator

$$\begin{aligned}M_{\mu\nu}^{f0}(i)&=N_{\mu\nu}^{f0}(i)+E_{\mu\nu}^{f0}(i)\\&=\langle\chi_f\,|\exp(-i\mathbf{k}\cdot\mathbf{r}_i)\,|\chi_0\rangle N_{\mu\nu}^{0(i)}(\mathbf{k},\mathbf{k}')\langle\chi_0\,|\exp(i\mathbf{k}'\cdot\mathbf{r}_i)\,|\chi_0\rangle+\langle\chi_f\,|\exp\big(-i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{r}_i\big)\,|\chi_0\rangle E_{\mu\nu}^{0(i)}(\mathbf{k},\mathbf{k}'),\end{aligned} \tag{52}$$

then Eqs. (50) and (51) can be written in the previous matrix form

$$A^i=A^0+\sum_{j\neq i}\delta_{ij}^{+}(k_0)M^{00}(j)A^j, \tag{50'}$$

$$[A^s(\mathbf{R})]^{f0}=\sum_i\delta_{\mathbf{R},i}^{+}(k_f)M^{f0}(i)A^i, \tag{51'}$$

where $\delta_{ij}^{+}(k_0)=(R_{ij}^0)^{-1}\exp(ik_0R_{ij}^0)$.

Finally, for clarity, we rewrite the equations determining the potentials (50) and (51) more explicitly. We give the expression for the total coherent wave: $A(\mathbf{R})=A^0(\mathbf{R})+A_s^{00}(\mathbf{R})$. If we write

$$\langle f(\mathbf{r}_j)\rangle\equiv\langle\chi_0\,|f(\mathbf{r}_j)\,|\chi_0\rangle=\int\rho_j(\mathbf{r}_j)f(\mathbf{r}_j)\,d\mathbf{r}_j,$$

then

$$A_\mu(\mathbf{R})=A_\mu^0(\mathbf{R})+\sum_j\int d\mathbf{r}_jd\mathbf{x}d\mathbf{r}_j'd\mathbf{y}\,\frac{\exp(ik_0\,|\mathbf{R}-\mathbf{R}_j^0-\mathbf{r}_j-\mathbf{x}|)}{|\mathbf{R}-\mathbf{R}_j^0-\mathbf{r}_j-\mathbf{x}|} \times\rho(\mathbf{r}_j)\{N_{\mu\nu}^{0(j)}(\mathbf{x},\mathbf{y})\rho(\mathbf{r}_j')+E_{\mu\nu}^{0(j)}(\mathbf{x},\mathbf{y})\delta(\mathbf{r}_j-\mathbf{r}_j')\}A_\nu^j(\mathbf{R}_j^0+\mathbf{r}_j'+\mathbf{y}). \tag{53}$$

In (53) the summation is over all of the atoms of the crystal. To obtain $A^i(\mathbf{R})$, we delete the $j=i$ term in (53).

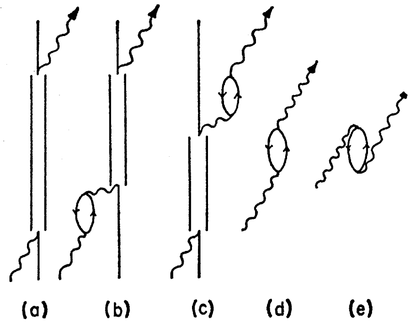

FIG. 4. Contributions to the single-atom scattering operator M^0. The solid lines represent nuclear states, and the "bubbles" represent virtual electronic transitions.

V. ENSEMBLE AVERAGE

Equations (50) and (51) give the coherent fields for the crystal in a well-defined initial state (and a well-defined final state). The fields thus depend upon the initial crystal-vibration state, the initial state of each atom (degenerate ground states for Mössbauer nuclei), and indeed upon which atom occupies a particular site if there is atomic disorder (isotope effect).

We shall never have such precise information, of course, and what is of interest in obtaining the scattering cross sections is the ensemble average $\langle A^i\rangle$ of the incident wave.[30] Taking the ensemble average of Eq. (50′) we have

$$A_c{}^i \equiv \langle A^i\rangle = A^0 + \sum_{j\neq i} \delta_{ij}{}^+(k_0)\langle M^{00}(j)A^j\rangle. \tag{54}$$

If we neglect the effect of "mirror" terms, then Eq. (54) becomes

$$A_c{}^i = A^0 + \sum_{j\neq i} \delta_{ij}{}^+(k_0) M_c(j) A_c{}^j. \tag{55}$$

In Eq. (55) the subscript c referring to the coherent wave means the ensemble average of the quantity. In Eq. (55) we delete the (00) superscript on the scattering operators M [Eq. (52)].

APPENDIX A

Equation (2) for $M_{\mu\nu}$ in terms of the ground-state expectation value of the time-ordered current densities is not quite correct if the electromagnetic-matter interaction Lagrangian contains an $A_\mu A_\mu$ term. The photon propagator (from which the S matrix and the Feynman potential may be obtained) is defined by[47]

$$D_{\mu\nu}(x,y) = -(i/\hbar c)\langle G \mid TA_\mu(x)A_\nu(y) \mid G\rangle, \tag{A1}$$

where G is the exact ground-state Heisenberg state vector of the scattering system, and $A_\mu(x)$ is the electromagnetic potential operator in the Heisenberg representation.

If we write for the interaction Lagrangian density

$$\mathfrak{L}_I = h_\mu A_\mu + g A_\mu A_\mu, \tag{A2}$$

where h and g are operators depending only on the matter variables, then the current density

$$j_\mu = \partial\mathfrak{L}_I/\partial A_\mu = h_\mu + 2gA_\mu \tag{A3}$$

will have an explicit dependence on the potential. The Feynman perturbation expansion for $D_{\mu\nu}$ is obtained in the usual manner, by going to the interaction representation and assuming that the ground state $\mid G\rangle$ evolves from the no-interaction ground state $\mid G_0\rangle$ as the interaction (A2) is slowly switched on.[47] In this case $D_{\mu\nu}$ may be expressed as

$$D_{\mu\nu}(x,y) = -(i/\hbar c) \times \langle G_0 \mid TS\hat{A}_\mu(x)\hat{A}_\nu(y) \mid G_0\rangle / \langle G_0 \mid S \mid G_0\rangle, \tag{A4}$$

with[48,49]

$$S = T\exp\left(\frac{i}{\hbar}\int \mathfrak{L}_I(x)\,dx\right), \tag{A5}$$

where the integration is over all space-time, with $\mathfrak{L}_I$ being slowly switched off as $t\to\pm\infty$. The operators in (A4) and (A5) are in the interaction representation. Expanding S in powers of $\mathfrak{L}_I$ and utilizing Wick's theorem,[50] all of the photon operators may be contracted to give an expansion of $D_{\mu\nu}$, each term of which may be represented by a Feynman graph which may be evaluated by the simple Feynman rules.[38] According to Wick, the contraction of two simple photon factors is given by

$$\begin{aligned}\hat{A}_\mu{}^\bullet(x)\hat{A}_\nu{}^\bullet(y) &\equiv \langle G_0 \mid T\hat{A}_\mu(x)\hat{A}_\nu(y) \mid G_0\rangle \\ &= i\hbar c g_{\mu\nu}\delta_+(x,y) \\ &= i\hbar c D_{\mu\nu}{}^0(x,y),\end{aligned} \tag{A6}$$

where δ_+ is given by Eq. (7). Utilizing

$$\hat{A}_\mu{}^\bullet(x)[(\hat{A}_\nu(y))^n]^\bullet = i\hbar c D_{\mu\nu}{}^0(x,y)\,n[\hat{A}_\nu(y)]^{n-1} \tag{A7}$$

and the form of S [Eq. (A5)], it is very easy to obtain

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[47] M. Gell-Mann and M. L. Goldberger, Phys. Rev. **96**, 398 (1953).

[48] Silvan S. Schweber, *An Introduction to Relativistic Quantum Field Theory* (Harper & Row, New York, 1961), pp. 481–482.

[49] P. T. Mathews, Phys. Rev. **76**, 684(L) (1949); **76**, 1489(E) (1949).

[50] G. C. Wick, Phys. Rev. **80**, 268 (1950).

the relation

$$\langle G_0 | TS\hat{A}_\mu(x)\hat{A}_\nu(y) | G_0\rangle = i\hbar c D_{\mu\nu}{}^0(x,y)\langle G_0 | S | G_0\rangle + (i\hbar c)^2\left(\frac{i}{\hbar}\right)^2 \iint \left\langle G_0 \middle| TS\frac{\partial\mathfrak{L}_I(x')}{\partial A_{\mu'}(x')}\frac{\partial\mathfrak{L}_I(y')}{\partial A_{\nu'}(y')} \middle| G_0\right\rangle D_{\mu\mu'}{}^0(xx')D_{\nu'\nu}{}^0(y'y)\,dx'dy' + (i\hbar c)^2\left(\frac{i}{\hbar}\right)\int \left\langle G_0 \middle| TS\frac{\partial^2\mathfrak{L}_I(x')}{\partial A_{\mu'}(x')\partial A_{\nu'}(x')} \middle| G_0\right\rangle D_{\mu\mu'}{}^0(x,x')D_{\nu'\nu}{}^0(x'y)\,dx'. \tag{A8}$$

Substituting (A8) into (A4) we obtain

$$D_{\mu\nu}(x,y) = D_{\mu\nu}{}^0(x,y) + \iint D_{\mu\mu'}{}^0(x,x')M_{\mu'\nu'}(x',y')D_{\nu'\nu}{}^0(y'y)\,dx'dy', \tag{A9}$$

with $M_{\mu\nu}(x,y)$ given by

$$M_{\mu\nu}(x,y) = -(ic/\hbar)\langle G | Tj_\mu(x)j_\nu(y) | G\rangle - \langle G | 2g(x) | G\rangle\delta(x-y)g_{\mu\nu}, \tag{A10}$$

where j_μ and g are defined in (A3) and (A2).

The second term in (A10) is absent if we are dealing with electromagnetic interaction of normal Dirac particles (for which $\mathfrak{L}_I \sim j_\mu A_\mu$), although a similar term (the Rayleigh-scattering term, see II[17]) arises in the nonrelativistic approximation in this case. This term is present in the case of nuclear scattering due to the electromagnetic interaction with the virtual mesons; however, its effect is quite negligible (being frequency-independent and of the order of nuclear Rayleigh scattering) in the low-energy resonance scattering regions of interest to us. The S matrix is obtained from $D_{\mu\nu}$ [Eq. (A1)] by letting $t_x \rightarrow +\infty$ and $t_y \rightarrow -\infty$, which, if we go over to a momentum rather than a space representation of D, gives Eq. (1). The Feynman potential results from letting $t_y \rightarrow -\infty$ in (A1) and subsequent equations and yields Eq. (6) of the text.

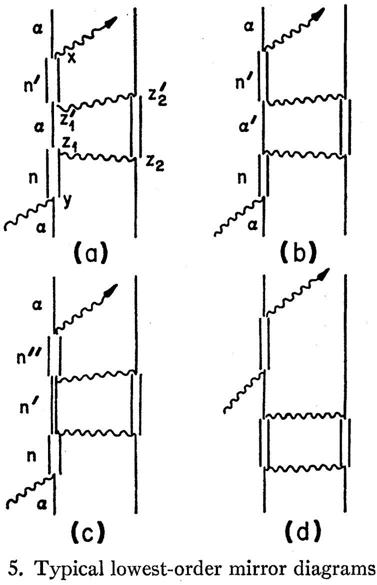

FIG. 5. Typical lowest-order mirror diagrams.

APPENDIX B

In Sec. III we approximated the effect of "mirror terms" and obtained multiple-scattering equations [Eqs. (22) and (23)] of the classical form. In this Appendix we wish to show that the "quantum corrections" to these equations will be quite small for cases of interest. For this purpose we consider the scattering from two atoms in some detail. This example will also serve to illustrate certain interesting features of multi-atom resonant scattering.

Before getting involved in detailed calculations we first note that Eq. (23) for the incident wave on atom i can be written

$$A^i = A^0 + \sum_{j\neq i}\delta_{ij}{}^+M^j[A_0{}^j + \sum_{k\neq i,j}\delta_{jk}{}^+M^kA^k] + \sum_{j\neq i}\delta_{ij}{}^+M^j\delta_{ji}{}^+M^iA^i, \tag{B1}$$

where the last term on the right of (B1) represents the (leading) mirror contribution. The summand of this term is of the order $[f_i\, f_j \exp(2ik_0R_{ij})/(R_{ij})^2]A^i$, where f_i and f_j are the scattering amplitudes. Summing over j, we obtain approximately

$$[-if_i\langle f_j\rangle\lambda_0 \exp(2ik_0a)/a^3]A^i,$$

where a is the lattice constant. For x-ray wavelengths the coefficient of A^i is $\ll 1$. For example, for the Fe^{57} resonance radiation, $f_{\text{nucl}} \approx 6\times10^{-11}$ cm (assuming no Zeeman splitting), $fe \approx 6\times10^{-12}$ cm, $a \approx 2.5\times10^{-8}$ cm, and the contribution from the mirror term will be $\approx 2\times10^{-6}A^i$ and thus quite negligible. The point of our further treatment is now to show that the "quantum corrections" do not change this estimate and, secondly, to show, as a matter of some interest, that for a sharp nuclear resonance the fractional error in our expression for the "elastic" mirror term (see below) is of the order of $\Gamma/\hbar\omega_0$.

For two atoms, typical mirror terms which can occur are shown in Figs. 5(a)–5(c). These terms, and higher-order mirror terms, give the effect on atom i due to the response of atom j (or the surrounding "medium") to the field emitted (scattered) from atom i.

In Fig. 5(a) the state of atom 1 during the time $t_{z_1}\rightarrow t_{z_1'}$ that a photon is being exchanged with atom 2 is the same as the initial ground state $|\alpha(1)\rangle$. As we shall see below, this type of mirror term is correctly accounted for by Eq. (23). We shall call this type of mirror term an "elastic" mirror term.

In Figs. 5(b) and 5(c) atom 1 is in the ground state $|\alpha'(1)\rangle[\neq|\alpha(1)\rangle]$ or an excited state $|n'(1)\rangle$ during the exchange time $t_{z_1}\rightarrow t_{z_1'}$. We shall call these terms "inelastic" mirror terms. It is important to note that for coherent elastic scattering, the final states for atoms 1 and 2 must be the same as the initial states. Thus the transitions $\alpha\rightarrow n\rightarrow\alpha'$, $\alpha\rightarrow n\rightarrow n'$ can only contribute to the coherent elastic scattering through "inelastic" mirror terms, such as shown in Figs. 5(b) and 5(c). These are of course purely quantum processes, whereas the elastic mirror processes have classical analogs. The "inelastic" mirror terms are not accounted for by Eq. (23), but, as we shall see, these contributions have a negligible effect on the equations for the coherent field.

In computing the elastic mirror term contribution, Fig. (5a), the time integrations must be restricted so that (t_y, t_{z_1}) are both less than or both greater than $(t_{z_1'}, t_x)$. The contribution of Fig. 5(a) is thus given by

$$\int' d^4x d^4z_1' d^4z_1 d^4y \int d^4z_2' d^4z_2$$
$$\times a_\mu^f(x)^* M_{\mu\eta}^{(1)}(x, z_1')\delta_+(z_1', z_2')$$
$$\times M_{\eta\lambda}^{(2)}(z_2', z_2)\delta_+(z_2, z_1) M_{\lambda\nu}^{(1)}(z_1, y) a_\nu^0(y), \quad \text{(B2)}$$

where the time integrals involving atom 1 are carried out with the above restrictions. As we discussed at the beginning of this Appendix, $(B2)\propto(f_1)^2f_2$ and will be of most importance in the case that all three scatterings correspond to (sharp) resonance transitions. For this case $M^{(i)}$ is given by

$$N_{\mu\nu}^{(i)}(x, y) = -i\sum_n N_{\mu\nu}^{(i)}(\mathbf{x}, \mathbf{y}, n)\exp\big(-i(E_n - E_\alpha - i\Gamma_n/2)(t_x - t_y)\big)\mathbf{1}(t_x - t_y), \quad \text{(B3)}$$

in correspondence with Eq. (33). Substituting (B3) into (B2), the time integrations for $(t_y, t_{z_1})<(t_{z_1'}, t_x)$ give the factor

$$\frac{2\pi\delta(\omega_f - \omega_0)\exp\big(ik_0(|\mathbf{z}_1' - \mathbf{z}_2'| + |\mathbf{z}_2 - \mathbf{z}_1|)\big)}{(Q(1))^2 Q(2)\,|\mathbf{z}_1' - \mathbf{z}_2'|\,|\mathbf{z}_2 - \mathbf{z}_1|} + \epsilon' \equiv m + \epsilon', \quad \text{(B4)}$$

where

$$\epsilon' = \left(\frac{2\delta(\omega_f - \omega_0)}{(Q(1))^2\,|\mathbf{z}_1' - \mathbf{z}_2'|\,|\mathbf{z}_1 - \mathbf{z}_2|}\right)\int_0^\infty d\sigma\,\frac{[\omega_0\Delta E(2) - \sigma^2]\exp\big(-\sigma(|\mathbf{z}_1' - \mathbf{z}_2'| + |\mathbf{z}_2 - \mathbf{z}_1|)\big)}{[\sigma^2 + (\Delta E(2))^2](\sigma^2 + \omega_0^2)}. \quad \text{(B4')}$$

In Eqs. (B4) and (B4′), $Q(i) = [k_0 - \Delta E(i) + \frac{1}{2}i\Gamma]$ and $\Delta E(i) = E_{n(i)} - E_{\alpha(i)}$. The leading term m in (B4) is the term that would be obtained with no restrictions on the time integrals involving atom 1 (which is equivalent to our approximation for the mirror term), and ϵ' gives the "quantum" correction.[51] The integral in (B4′) is of the order of $[\omega_0 + E(2)]^{-1}F(k_0R_{12})$, where $F(k_0R_{12})\approx 1$ for $k_0R_{12}\ll 1$, and $(k_0R_{12})^{-1}$ for $k_0R_{12}\gg 1$. Thus the relative error (ϵ'/m) is given approximately by

$$\left(\frac{\epsilon'}{m}\right) \approx \left(\frac{Q(2)}{\omega_0 + \Delta E}\right) F(k_0R_{12})$$
$$= \left(\frac{\omega_0 - \Delta E(2) + \frac{1}{2}i\Gamma}{\omega_0 + \Delta E(2)}\right) F(k_0R_{12}). \quad \text{(B5)}$$

The time integrations for $(t_y, t_{z_1}) > (t_{z_1'}, t_x)$ give only a term $\epsilon''\approx(Q(1)/[\omega_0 + E(1)])^2\epsilon'\ll\epsilon'$. Thus near resonance $(\epsilon' + \epsilon'')/m\approx(\Gamma/4\omega_0)F(k_0R_{12})$ and we see that the "quantum corrections" are quite negligible.

The form which we obtain for the "quantum correction" ϵ' can be understood in the following way: The correction arises from the fact that in the integrations over time for processes represented by Fig. 5(a), $(t_{z_1'}, t_x)$ are restricted to occur later than (t_y, t_{z_1}); but if the lifetime of the "mirroring" state of the nearby atom is long, then the main contributions to the mirroring process will occur for $t_{z_1'} - t_{z_1}\approx(\Gamma_{(2)})^{-1}$ and the relative error introduced by formally extending the integrations to $t_{z_1'} < t_{z_1}$ (which yields our approximation for the mirror term) is only of the order of $(\Gamma_{(2)}/\omega_0)$, in accordance with (B5). If the "mirroring" should be due to a nonresonant reflection, e.g., the electronic contribution, the relative error $\approx 1\times F(k_0R_{12})$. For this case the relative error is still quite negligible for $k_0R_{12}\gg 1$, but more importantly the (leading) mirror term itself is proportional to the scattering amplitude of atom 2 and is quite negligible for nonresonant scattering.

We have thus verified that the quantum corrections to the "elastic mirror" term give a negligible correction to our multiple scattering equations (23). Equations (23) do *not* include the effects of inelastic terms [e.g., Figs. 5(b) and 5(c)]; however, it is quite easy to show that generally these terms are no larger than the elastic mirror terms and thus are similarly negligible.

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[51] Actually, radiative corrections such as shown in Fig. 5(d) will contribute terms also of the order of the error term which we computed, but the above suffices for an order-of-magnitude estimate of the error involved.

Resonant Scattering from Two Identical Atoms

We now wish to discuss the resonant scattering from two identical atoms. This problem has been treated in Refs. 18 and 19 (J.P.H., M.A. thesis) and serves to illustrate several interesting features which occur in multiatom resonant scattering (and emission).

For simplicity we shall assume that the Zeeman sublevels of the ground and excited states are sufficiently separated so that for a particular incident frequency, $\omega_0 \approx (E_b - E_a)$, we only need to consider the transitions from $|a\rangle = |J_a, m_a\rangle$ to $|b\rangle = |J_b, m_b\rangle$. Both atoms are assumed to be initially in the state $|a\rangle$.

For two atoms the coherent-field equations (23) are explicitly

$$A^{(1)} = A^0 + \delta_{12}{}^{+} M^{(2)} A^{(2)},$$

$$A^{(2)} = A^0 + \delta_{21}{}^{+} M^{(1)} A^{(1)}, \tag{B6}$$

and, for $k_0 |\mathbf{R} - \mathbf{R}_i| \gg 1$, the elastic scattered wave A^s [Eq. (22)] is given by

$$A_\mu{}^s(\mathbf{R}) = \frac{\exp(ik_0R)}{R} \sum_{i=1}^{2} \exp(-i\mathbf{k}_f \cdot \mathbf{R}_i) \times M_{\mu\nu}{}^{(i)}(\mathbf{k}_f, \mathbf{k}) A_\nu{}^{(i)}(\mathbf{R}_i), \tag{B7}$$

where $\mathbf{k} = -i\vec{\boldsymbol{\nabla}}_{\mathrm{R}_i}$, and

$$\mathbf{k}_f = \lim_{R\to\infty} k_0(\mathbf{R} - \mathbf{R}_i)/|\mathbf{R} - \mathbf{R}_i|.$$

For the near-resonance case being considered, the scattering operator is given by

$$M_{\mu\nu}(\mathbf{k}, \mathbf{k}') = j_\mu{}^{ab}(-\mathbf{k}) j_\nu{}^{ba}(\mathbf{k}') / [k_0 - (E_b - E_a) + \tfrac{1}{2} i\Gamma], \tag{B8}$$

where

$$j_\mu(\pm\mathbf{k}) = \int \exp(\pm i\mathbf{k} \cdot \mathbf{x}) j_\mu(\mathbf{x}) d\mathbf{x}$$

is the Fourier transform of the current density $j_\mu(\mathbf{x})$ and the superscripts $ab(ba)$ indicate the matrix elements of $j_\mu(\pm\mathbf{k})$ between the states $|a\rangle, |b\rangle (b, a)$. Γ is the total width of the excited level b and is equal to $[\Gamma_\alpha + \Gamma_\gamma(b)]$, where Γ_α is the width for inelastic and absorptive processes, such as internal conversion, and $\Gamma_\gamma(b)$ is the radiative width of level b, which is given by

$$\begin{aligned}\tfrac{1}{2}\Gamma_\gamma(b) &= -\operatorname{Im} \sum_{a'} \frac{1}{2\pi^2} \int d\mathbf{k}\, j_\mu{}^{ba'}(\mathbf{k}) j_\mu{}^{a'b}(-\mathbf{k}) \times [k^2 - k_0{}^2 - i\eta]^{-1} \\ &= -\operatorname{Im} \sum_{a'} \iint d\mathbf{x} d\mathbf{y}\, j_\mu{}^{ba'}(\mathbf{x}) \times \frac{\exp(ik_0|\mathbf{x} - \mathbf{y}|)}{|\mathbf{x} - \mathbf{y}|} j_\mu{}^{a'b}(\mathbf{y}).\end{aligned} \tag{B9}$$

From Eqs. (B7) and (B8) we see that the scattered wave $A_\mu{}^s$ is given in terms of the quantities

$$M_{\mu\nu}{}^{(i)}(\mathbf{k}_f, \mathbf{k}) A_\nu{}^{(i)}(\mathbf{R}_i) \equiv j_\mu{}^{ab}(-\mathbf{k}_f) S^{(i)}, \tag{B10}$$

where

$$S^{(i)} = j_\nu{}^{ba}(\mathbf{k}) A_\nu{}^{(i)}(\mathbf{R}_i) / [k_0 - (E_b - E_a) + i\tfrac{1}{2}\Gamma]. \tag{B10$'$}$$

$S^{(i)}$ corresponds intuitively to the amplitude that the atom i is in the excited state $|b\rangle$, and we shall refer to the $S^{(i)}$ as "excitation amplitudes."

It is easier to solve for the scalar excitation amplitudes $S^{(i)}$ than for the four-vectors $A_\nu{}^{(i)}$. Contracting Eqs. (B6) with $j_\mu{}^{ba}(\mathbf{k})$, we obtain the equations determining $S^{(i)}$:

$$[k_0 - (E_b - E_a) + i\tfrac{1}{2}\Gamma] S^{(1)} = j_\mu{}^{ba}(\mathbf{k}) \left[a_\mu{}^0 \exp(i\mathbf{k}_0 \cdot \mathbf{R}_1) + \frac{\exp(ik_0R_{12})}{R_{12}} j_\mu{}^{ab}(-\mathbf{k}) S^{(2)} \right],$$

$$[k_0 - (E_b - E_a) + i\tfrac{1}{2}\Gamma] S^{(2)} = j_\mu{}^{ba}(\mathbf{k}) \left[a_\mu{}^0 \exp(i\mathbf{k}_0 \cdot \mathbf{R}_2) + \frac{\exp(ik_0R_{21})}{R_{21}} j_\mu{}^{ab}(-\mathbf{k}) S^{(1)} \right]. \tag{B11}$$

From (B11) we easily obtain

$$S^{(i)} = j_\mu{}^{ba}(\mathbf{k}_0) a_\mu{}^0 \tfrac{1}{2} \{ [\exp(i\mathbf{k}_0 \cdot \mathbf{R}_i) + \exp(i\mathbf{k}_0 \cdot \mathbf{R}_j)] / Q(+) + [\exp(i\mathbf{k}_0 \cdot \mathbf{R}_i) - \exp(i\mathbf{k}_0 \cdot \mathbf{R}_j)] / Q(-) \}, \tag{B12}$$

where $i = 1, j = 2$ or vice versa, and $Q(\pm)$ is given by

$$\begin{aligned} Q(\pm) &= k_0 - (E_b - E_a) + i\tfrac{1}{2}\Gamma \mp \iint j_\mu{}^{ba}(\mathbf{x}_1) \frac{\exp(ik_0|\mathbf{R}_1 + \mathbf{y}_1 - \mathbf{R}_2 - \mathbf{y}_2|)}{|\mathbf{R}_1 + \mathbf{y}_1 - \mathbf{R}_2 - \mathbf{x}_2|} j_\mu{}^{ba}(\mathbf{x}_2) d\mathbf{x}_1 d\mathbf{x}_2 \\ &= k_0 - (E_b - E_a) + i\tfrac{1}{2}\Gamma \mp j_\mu{}^{ba}(\mathbf{k}) [\exp(ik_0R_{12}) / R_{21}] j_\mu{}^{ab}(-\mathbf{k}). \end{aligned} \tag{B13}$$

In the last line of (B13) $\mathbf{k} = -i\boldsymbol{\nabla}_{\mathrm{R}_1}$. From Eqs. (B12), (B10), and (B7), we obtain the scattered wave

$$\begin{aligned} A_\mu{}^s(\mathbf{R}) &= [\exp(ik_0R)/R] j_\mu{}^{ab}(-\mathbf{k}_f) j_\nu{}^{ba}(\mathbf{k}_0) a_\nu{}^0 \\ &\times \tfrac{1}{2} \{ (Q(+))^{-1} [\exp(i(\mathbf{k}_0 - \mathbf{k}_f) \cdot \mathbf{R}_1) + \exp(i(\mathbf{k}_0 \cdot \mathbf{R}_2 - \mathbf{k}_f \cdot \mathbf{R}_1)) + \exp(i(\mathbf{k}_0 \cdot \mathbf{R}_1 - \mathbf{k}_f \cdot \mathbf{R}_2)) + \exp(i(\mathbf{k}_0 - \mathbf{k}_f) \cdot \mathbf{R}_2)] \\ &+ (Q(-))^{-1} [\exp(i(\mathbf{k}_0 - \mathbf{k}_f) \cdot \mathbf{R}_1) - \exp(i(\mathbf{k}_0 \cdot \mathbf{R}_2 - \mathbf{k}_f \cdot \mathbf{R}_1)) - \exp(i(\mathbf{k}_0 \cdot \mathbf{R}_1 - \mathbf{k}_f \cdot \mathbf{R}_2)) + \exp(i(\mathbf{k}_0 - \mathbf{k}_f) \cdot \mathbf{R}_2)] \}. \end{aligned} \tag{B14}$$

It is convenient for further discussion to define the quantities $\delta\omega$, $E(\pm)$, and $\Gamma_\gamma(\pm)$ as

$$\delta\omega=\iint j_\mu^{ba}(\mathbf{x}_1)\,\frac{\exp(ik_0\,|\,\mathbf{R}_1+\mathbf{x}_1-\mathbf{R}_2-\mathbf{x}_2\,|)}{|\,\mathbf{R}_1+\mathbf{x}_1-\mathbf{R}_2+\mathbf{x}_2\,|}\times j_\mu^{ab}(\mathbf{x}_2)\,d\mathbf{x}_1 d\mathbf{x}_2$$

$$=j_\mu^{ba}(\mathbf{k})[\exp(ik_0R_{12})/R_{12}]j_\mu^{ab}(-\mathbf{k}),\qquad\text{(B15)}$$

$$E(\pm)=E_b\pm\operatorname{Re}(\delta\omega),\qquad\text{(B16)}$$

$$\tfrac{1}{2}\Gamma_\gamma(\pm)=\tfrac{1}{2}\Gamma_\gamma(b,a)\mp\operatorname{Im}(\delta\omega).\qquad\text{(B17)}$$

In (B17) $\Gamma_\gamma(b,\,a)$ is the partial radiative width of level b that is associated with the transition $b\rightarrow a$ [e.g., $\Gamma_\gamma(b,\,a)=C^2(J_aLJ_b;\,m_a,\,m_b-m_a)\Gamma_\gamma(b)$, where C is the Clebsch-Gordan coefficient for transition $b\rightarrow a$]. With $\Gamma_\gamma(\pm)$ and $E(\pm)$ given by (B16) and (B17), $Q(\pm)$ is now given by

$$Q(\pm)=[k_0-(E(\pm)-E_a)+i\tfrac{1}{2}(\Gamma'+\Gamma_\gamma(\pm))],\qquad\text{(B13}')$$

where Γ' represents all contributions to the total width of level b, except the partial width $\Gamma_\gamma(b,\,a)$ [e.g., $\Gamma'=\Gamma_\alpha+\sum_{a'\neq a}C^2(J_{a'}LJ_b;\,m_{a'},\,m_b-m_{a'})\Gamma_\gamma(b)$].

For simplicity of further discussion we assume a pure multipole transition $(L,\,l)$ [$L=l,\,l+1$; $(l,\,l)$ indicates an $M(l)$ and $(l+1,\,l)$ an $E(l+1)$ transition].

As shown explicitly in II,[17] for an $(L,\,l)$ transition, we can utilize (B9) to obtain

$$j_\mu^{ba}(\mathbf{k})j_\mu^{ab}(-\mathbf{k})=-(\Gamma_\gamma(b,\,a)/2k)F_{LM}(\theta).\qquad\text{(B18)}$$

In Eq. (B18)

$$F_{LM}(\theta)=\tfrac{1}{2}[(d_{1M}^{(L)}(\theta))^2+(d_{-1M}^{(L)}(\theta))^2](2L+1),$$

where the notation for the rotation matrices $d_{\lambda M}^{(L)}$ is that of Rose,[52] $M=m_b-m_a$, and θ is the angle between the direction of $\mathbf{k}$ and the quantization axis $\mathbf{z}$. Thus, in the region $k_0R_{12}\gg1$, where we can replace $\mathbf{k}$ by $\mathbf{k}_{12}=k_0(\mathbf{R}_1-\mathbf{R}_2)/|\,\mathbf{R}_1-\mathbf{R}_2\,|$ in Eqs. (B15)-(B17), $E(\pm)$ and Γ_γ are given by

$$E(\pm)=E_b\mp\tfrac{1}{2}\Gamma_\gamma(b,\,a)F_{LM}(\theta)\,\cos(k_0R_{12})/(k_0R_{12}),\qquad\text{(B16}')$$

$$\Gamma_\gamma(\pm)=\Gamma_\gamma(b,\,a)[1\pm F_{LM}(\theta)\,\sin(k_0R_{12})/(k_0R_{12})].\qquad\text{(B17}')$$

To obtain $\Gamma_\gamma(\pm)$ and $E(\pm)$ in the region $k_0R_{12}\ll1$, we first note that we can write $\delta\omega$ (B15) as

$$\delta\omega=\int d\mathbf{k}\,j_\mu^{ba}(\mathbf{k})j_\mu^{ab}(-\mathbf{k})\,\exp(i\mathbf{k}_0\cdot\mathbf{R}_{12})[k^2-k_0^2-i\eta]^{-1}$$

$$=\int d\mathbf{k}\,j_\mu^{ba}(\mathbf{k})j_\mu^{ab}(-\mathbf{k})\times\left\{i\left[(2\pi)^{-1}\delta(k^2-k_0^2)\,\cos(\mathbf{k}\cdot\mathbf{R}_{12})+\frac{PV}{2\pi^2}\frac{\sin(\mathbf{k}\cdot\mathbf{R}_{12})}{k^2-k_0^2}\right]+\left[\frac{PV}{2\pi^2}\frac{\cos(\mathbf{k}\cdot\mathbf{R}_{12})}{k^2-k_0^2}-(2\pi)^{-1}\delta(k^2-k_0^2)\,\sin(\mathbf{k}\cdot\mathbf{R}_{12})\right]\right\}.\qquad\text{(B15}')$$

If the states a and b are states of good parity, then $j_\mu^{ba}(\mathbf{k})j_\mu^{ab}(-\mathbf{k})=j_\mu^{ba}(-\mathbf{k})j_\mu^{ab}(\mathbf{k})$, and the integrations over $\sin(\mathbf{k}\cdot\mathbf{R}_{12})$ in Eq. (B15′) give zero. In the region $k_0R_{12}\ll1$ we expand $\cos(\mathbf{k}\cdot\mathbf{R}_{12})$ in powers of $(\mathbf{k}_0\cdot\mathbf{R}_{12})$ in the imaginary part of (B15′) and utilize Eq. (B18) to obtain

$$\delta\omega=-i(\tfrac{1}{2}\Gamma_\gamma(b,\,a))[(\sin k_0R_{12}/k_0R_{12})+O(k_0R_{12})^2]-(\Gamma_\gamma(b,\,a)/4\pi^2)\int d\mathbf{k}\,F_{LM}(\theta)\,\cos(\mathbf{k}\cdot\mathbf{R}_{12})PV([k(k^2-k_0^2)]^{-1}).\qquad\text{(B15}'')$$

Thus we see from (B15″) that if the two atoms are much less than a wavelength apart, then the (partial) radiative widths $\Gamma_\gamma(\pm)$ are given by

$$\Gamma_\gamma(\pm)=\Gamma_\gamma(b,\,a)\left[1\pm\frac{\sin(k_0R_{12})}{k_0R_{12}}\pm O(k_0R_{12})^2\right],\qquad\text{(B17}'')$$

The $(+)$ and $(-)$ quantities in Eqs. (B12)-(B17″) refer to the symmetric and antisymmetric semistationary excited states, $|\,\pm\rangle=(1/\sqrt{2})[|\,a(1)\rangle\,|\,b(2)\rangle\pm|\,b(1)\rangle\,|\,a(2)\rangle]$, whose virtual excitations are responsible for the scattering. If the separation is small compared to the wavelength ($k_0R_{12}\ll1$), then we see from (B17″) that the (partial) radiative width of the symmetric state, $\Gamma_\gamma(+)$, is twice the single-atom (partial) radiative width $\Gamma_\gamma(b,\,a)$ (corresponding to a multipole moment $\sqrt{2}$ times that of a single atom), whereas $\Gamma_\gamma(-)\approx O(k_0R_{12})^2$ (corresponding to the next higher multipole order). As the separation increases $\Gamma_\gamma(+)$, $\Gamma_\gamma(-)\rightarrow\Gamma_\gamma(b,\,a)$. The energy shifts $(E(\pm)-E_b)$ are large for $k_0R_{12}\ll1$, while for $k_0R_{12}\gg1$, $E(\pm)\rightarrow E_b$.

The intensity of the scattered radiation is proportional to $|\,A^S\,|^2$ [Eq. (B14)], and we see that as the

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[52] M. E. Rose, *Elementary Theory of Angular Momentum* (John Wiley & Sons, Inc., New York, 1957), pp. 32–48.

incident frequency is Doppler-shifted, two scattering peaks will occur—a peak of width $\Gamma'+\Gamma_\gamma(+)$ at the frequency $\omega_0=(E(+)-E_a)$, corresponding to resonance fluorescence from the symmetric state, and a peak of width $\Gamma'+\Gamma_\gamma(-)$ at the frequency $\omega_0=(E(-)-E_a)$, corresponding to resonance fluorescence from the antisymmetric state. The fact that the radiative widths can be broadened or narrowed in multiatom resonant scattering is a characteristic feature of such scattering and has been discussed by several authors.[18,21,22]

We also note from (B12) and (B14) that it is possible to selectively excite the symmetric or antisymmetric state. If $\mathbf{k}_0\cdot\mathbf{R}_{12}=2n\pi$, then we see that only the symmetric mode will be excited, while if $\mathbf{k}_0\cdot\mathbf{R}_{12}=(2n+1)\pi$, then only the antisymmetric mode will be excited. In particular, if $k_0R_{12}\ll 1$, the first term of the bracket in (B14) $\approx 4/Q(+)$, while the second term ≈ 0. Thus if the two atoms are much less than a wavelength apart, the interaction is entirely with the symmetric state. The (partial) radiative width in this case is twice that for a single atom, and the emitted radiation is four times as intense off resonance, and

$$4\left(\frac{\Gamma'+\Gamma_\gamma(b,a)}{\Gamma'+2\Gamma_\gamma(b,a)}\right)^2$$

times as intense at resonance $[\omega_0=E(+)-E_a]$.

The above results are of course intuitively obvious from classical considerations. If two identical multipoles are vibrating in phase with a separation much less than a wavelength, the emitted radiation is of the same multipole order, with field amplitudes twice as large and with radiated intensity four times as great as for a single multipole, and hence the symmetric-state radiative width is $\Gamma_\gamma(+)\approx 2\Gamma_\gamma$. However, if the currents are 180° out of phase, then for $k_0R_{12}\ll 1$ only higher-order multipole radiation is emitted and $\Gamma_\gamma(-)\approx 0$. (For example, two electric dipoles vibrating 180° out of phase become an electric quadrupole current source for $k_0R_{12}\ll 1$). If $\mathbf{k}_0\cdot\mathbf{R}_{12}=2n\pi$, then the currents are driven in phase and only the symmetric state is excited, while if $\mathbf{k}_0\cdot\mathbf{R}_{12}=(2n+1)\pi$, then the currents are driven 180° out of phase and only the antisymmetric state is excited.

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Relation between the *g* Shift and Hyperfine Field in Intermetallic Compounds

D. Davidov and D. Shaltiel
Department of Physics, The Hebrew University, Jerusalem, Israel

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The appreciable variation of the gadolinium hyperfine fields from one compound to another in $\mathrm{Gd}X_2$ (X=Rh, Ir, Mn, Pt, Al) is explained by interaction of the nucleus with the conduction electrons. These electrons are polarized by their exchange interaction with the Gd ion. This interaction was investigated experimentally by measuring the Gd *g* shift by means of electron spin resonance. The *g* shift was found to vary in both magnitude and sign in these compounds. A relation between the Gd hyperfine field and the Gd *g* shift is derived, enabling us to calculate the hyperfine field per spin for 6*s* electrons in $\mathrm{GdPt_2}$ to be 2.8×10^6 G.

INTRODUCTION

In a recent letter, Gegenwarth *et al.*[1] reported on the gadolinium hyperfine fields in the magnetically ordered state for several $\mathrm{Gd}X_2$ cubic Laves phase compounds. They found that the hyperfine fields vary considerably from one compound to another. According to Gegenwarth, the hyperfine fields in $\mathrm{Gd}X_2$ compounds result from two main phenomena: (1) core polarization[2] and (2) interaction with valence electrons.

On the assumption that core polarization remains constant from sample to sample, any variation in the hyperfine fields should be attributed to interaction with the valence electrons. Gegenwarth stressed this point but did not specify the mechanism of the interactions. It is the purpose of this paper to present further experimental results on the $\mathrm{Gd}X_2$ compounds and to explain the origin of these hyperfine fields.

In electron spin resonance (ESR), we measure the exchange interactions between the Gd ion and the conduction electrons. Since these interactions are responsible for the variation in the hyperfine fields (as will be explained later), we believe that ESR measurements are best suited to the above-mentioned purpose.

RESULTS AND DISCUSSION

The ESR of gadolinium in powdered samples of $\mathrm{Gd}X_2$ (X=Rh, Ir, Mn, Pt) and GdN was measured as a function of temperature, from liquid nitrogen to

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[1] R. E. Gegenwarth, J. I. Budnick, S. Skalski, and J. H. Wernick, Phys. Rev. Letters **18**, 9 (1967).

[2] G. T. Rado and H. Suhl, in *Magnetism* (Academic Press Inc., New York, 1965), Vol. AII, p. 237.