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Time-Dependent Displacement Correlations and Inelastic Scattering by Crystals*

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A function is defined which expresses quantum mechanically the correlation of the displacements of pairs of lattice points at different times due to the wave-like nature of crystal excitations. Methods are developed for summing implicitly the effects of multiple emission and absorption of lattice quanta occurring during a scattering process. The inelastic scattering cross sections found thereby are expressed entirely in terms of the time-dependent correlation function defined earlier. The resulting treatment thus emerges as a natural generalization of the static theory of x-ray scattering. The results are discussed in relation to a number of approximation methods.

I. INTRODUCTION

Of the particles whose scattering by crystal lattices is of experimental interest, electrons and photons show the simplest behavior energetically. The energies of these quanta are in general high enough that their exchanges of energy with the lattice system may be ignored and the collisions treated as approximately elastic. For particles as heavy as neutrons, however, the inelasticity is no longer negligible. The energies of neutrons with wavelengths suitable for interference experiments are quite comparable with those of the thermally excited vibrational quanta of the crystal. The absorption or emission of vibrational quanta therefore causes relatively appreciable changes of the neutron's kinetic energy. It is with the generalization of the theory to the treatment of such inelastic processes that the present work is chiefly concerned.

The deviations of a crystal lattice from perfect regularity due to thermal vibrations were first shown by Debye[1] to bring about a reduction in the intensities of the Laue spots formed in x-ray scattering. Later and more explicitly, quantum-theoretical investigations[2] have explained quantitatively the background of diffuse scattering which also results from thermal agitation. In particular, it has been shown that it is the correlation in the displacements of pairs of nearby scattering centers existing at any instant, which brings about the observed distributions of diffuse scattering. These displacement correlations are due to the wave-like nature of the lattice excitations, and may be expected to persist over finite intervals of time as well as distance. The latter fact is especially significant in the treatment of heavy-particle scattering since at the low energies of interest the particle's passage through a crystal cannot be approximated as instantaneous. It is natural then to introduce a function expressing the correlation of displacements of pairs of points in its dependence on intervals of time, as well as position in the lattice. This function is a direct generalization of the instantaneous correlation function associated with the treatment of x-ray scattering. We shall show that it furnishes, in fact, all of the information necessary for expressing the solution of the inelastic scattering problem. Recently, Van Hove has demonstrated the usefulness of defining analogous time-dependent correlation functions for more general types of scattering systems.[3]

The emission and absorption of vibrational quanta by a scattered particle is an intrinsically multiple process. Arbitrary numbers of quanta may be created, and arbitrary numbers absorbed in a single collision with the lattice. Problems of multiple quantum emission bearing considerable analogy to this have long been of interest in field theoretical contexts, and certain of the methods developed to handle them are well suited to the crystal problem. Use will be made of these without appealing to an explicit knowledge of field theory. Using the neutron case as an illustration we shall thereby derive a closed expression for the inelastic scattering cross section which is valid for all relevant initial energies and takes into account all possible quantum transitions. Previous treatments have mainly been confined either to one-quantum processes,[4] and therefore to low energies, or to the asymptotic limit of high energies.[5,6]

Before undertaking the calculation of the scattering it will be useful to discuss the relevant properties of the lattice.

II. THE DISPLACEMENT FIELD

The normal modes of crystal lattices bound by Hooke's-law forces are plane vibrational waves. The elastic energy of the crystal is quadratic in the amplitudes of these waves, which are therefore quantized in the way familiar for harmonic oscillators. The particle coordinates then become operators defined at each point of the lattice. We shall designate these collectively as the displacement field $\mathbf{u}(\mathbf{r}_j,t)$, that is the set of vector displacements at time t of the mass points whose

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* A brief account of this work was presented at the Washington meeting of the American Physical Society, May 1, 1952 [Phys. Rev. **87**, 189 (1952)]. See also Phys. Rev. **94**, 751 (1954).

[1] P. Debye, Ann. Physik **43**, 49 (1914).

[2] I. Waller, Uppsala Dissertation, 1925 (unpublished). For a review of this work and later contributions see M. Born, Repts. Progr. Phys. **9**, 294 (1942–3).

[3] L. Van Hove, Phys. Rev. **95**, 249 (1954); **95**, 1374 (1954).

[4] This work is reviewed by J. M. Cassels, Progr. Nuc. Phys. **1**, 185 (1950); see also reference 5.

[5] A. Akhiezer and I. Pomeranchuk, J. Exptl. Theoret. Phys. U.S.S.R. **17**, 770 (1947).

[6] G. L. Squires, Proc. Roy. Soc. (London) **A212**, 192 (1952).

equilibrium positions are $\mathbf{r}_j$. In discussing this field more explicitly it will greatly simplify notation to specialize to the cases of lattices of identical atoms occupying equivalent positions. The extension to more general lattices is straightforward. Assuming then that there are N atoms in all, each of mass M, the expansion in plane waves of the α component ($\alpha=1, 2, 3$) of the displacement field will be[7]

$$u_\alpha(\mathbf{r},t)=\sum_{\mathbf{k},p} e_\alpha{}^{(p)}\left(\frac{\hbar}{2NM\omega}\right)^{\frac{1}{2}} \times\left(a_{\mathbf{k},p}e^{i(\mathbf{k}\cdot\mathbf{r}-\omega t)}+a_{\mathbf{k},p}{}^{\dagger}e^{-i(\mathbf{k}\cdot\mathbf{r}-\omega t)}\right). \quad (1)$$

Here $\mathbf{e}^{(p)}$ ($p=1, 2, 3$) are the three unit polarization vectors for waves of propagation vector $\mathbf{k}$ and angular frequency $\omega=\omega^{(p)}(\mathbf{k})$.

The amplitudes $a_{\mathbf{k},p}$ and $a_{\mathbf{k},p}{}^{\dagger}$ are the familiar operators of harmonic oscillator quantization. They destroy and create single quanta, respectively, in virtue of their commutation rules:

$$\begin{gathered} a_{\mathbf{k},p}a_{\mathbf{k}',p'}{}^{\dagger}-a_{\mathbf{k}',p'}{}^{\dagger}a_{\mathbf{k},p}=[a_{\mathbf{k},p},a_{\mathbf{k}',p'}{}^{\dagger}]=\delta_{\mathbf{k}\mathbf{k}'}\delta_{pp'}, \\ [a_{\mathbf{k},p},a_{\mathbf{k}',p'}]=0, \quad [a_{\mathbf{k},p}{}^{\dagger},a_{\mathbf{k}',p'}{}^{\dagger}]=0. \end{gathered} \quad (2)$$

We shall later need the expectation values of certain rather general expressions involving these operators. It will be shown, however, that the results may be expressed in terms of those for the two bilinear combinations with nonvanishing expectation values,

$$\langle a_{\mathbf{k},p}{}^{\dagger}a_{\mathbf{k},p}\rangle=n_{\mathbf{k},p}, \quad \langle a_{\mathbf{k},p}a_{\mathbf{k},p}{}^{\dagger}\rangle=n_{\mathbf{k},p}+1, \quad (3)$$

where $n_{\mathbf{k},p}$ is the average number of quanta in the mode specified by $\mathbf{k}$ and p.

As we have already noted, the wave-like nature of crystal excitation causes correlations in the displacements of lattice points many unit cells apart which may also persist over long intervals of time. A measure of the correlations of position is furnished by the expectation values of the products of the displacement components at different points $\mathbf{r}$ and $\mathbf{r}'$, and times t and t'. In the absence of correlation the expectation values vanish. Their evaluation proceeds immediately by use of (3):

$$\langle u_\alpha(\mathbf{r},t)u_\beta(\mathbf{r}',t')\rangle=\sum_{\mathbf{k},p}\frac{\hbar}{2NM\omega}e_\alpha{}^{(p)}e_\beta{}^{(p)} \times\{(n_{\mathbf{k},p}+1)\exp[i(\mathbf{k}\cdot(\mathbf{r}-\mathbf{r}')-\omega(t-t'))] +n_{\mathbf{k},p}\exp[-i(\mathbf{k}\cdot(\mathbf{r}-\mathbf{r}')-\omega(t-t'))]\}. \quad (4)$$

Similarly constructed expectation values, usually called propagation functions, also play a central role in elementary particle theories. There their evaluation is simplified, however, by the vacuum's emptiness, for all practical purposes, of stray quanta. By contrast the background of thermally excited quanta of a lattice forms a Bose-Einstein gas of considerable concentration. The average quantum populations are given by the Planck distribution

$$n_{\mathbf{k},p}=[\exp(\hbar\omega^{(p)}(\mathbf{k})/\kappa T)-1]^{-1}, \quad (5)$$

in which κ is the Boltzmann constant and T the temperature. Expectation values such as (4), averaged over a thermal distribution of quantum states at temperature T, will be denoted by $\langle\ \rangle_T$. Thus the brackets $\langle\ \rangle_0$ which customarily denote the average in a space devoid of quanta, will retain their usual meaning.

The scattering calculations to be undertaken presently will be seen to require only the information about the crystal contained in the expression (4). The summation over propagation vectors may be replaced by an integration of the vector $\mathbf{k}/2\pi$ over a unit cell of the reciprocal lattice. For a given lattice temperature T, we are thus led to define a tensor correlation function

$$C_{\alpha\beta,T}(\mathbf{r}-\mathbf{r}', t-t')=\langle u_\alpha(\mathbf{r},t)u_\beta(\mathbf{r}',t')\rangle_T, \quad (6)$$

for which we find

$$C_{\alpha\beta,T}(\mathbf{r},t)=\frac{V_0\hbar}{16\pi^3M}\sum_p\int e_\alpha{}^{(p)}e_\beta{}^{(p)} \times\left\{e^{i(\mathbf{k}\cdot\mathbf{r}-\omega t)}+\frac{2\cos(\mathbf{k}\cdot\mathbf{r}-\omega t)}{\exp(\hbar\omega/\kappa T)-1}\right\}\frac{d\mathbf{k}}{\omega^{(p)}(\mathbf{k})}, \quad (7)$$

where V_0 is the volume of the unit cell. The first term of the integrand, which is temperature independent, gives the correlation of the zero-point vibrations $C_{\alpha\beta,0}(\mathbf{r},t)$, while the second adds the effect of thermal excitation.

For vanishing time arguments the correlation function is real-valued, which is to be expected since displacement operators evaluated at the same time commute, and their product is hermitian. Evaluated at different times, however, these operators do not in general commute, an expression of the fact that the corresponding position measurements cannot be carried out independently.[8] For finite time differences the correlation function is therefore complex-valued. It obeys the relation

$$C_{\alpha\beta,T}(\mathbf{r},t)=C_{\alpha\beta,T}{}^{*}(-\mathbf{r},-t), \quad (8)$$

the latter expression reducing, for the simple lattices under consideration to $C_{\alpha\beta,T}{}^{*}(\mathbf{r},-t)$.

For the rougher purposes of orientation, the Debye model may be used to evaluate the correlation function.

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[7] Although the plane wave expansion defines a displacement field for all $\mathbf{r}$, only the values at the lattice points are needed, provided the individual scattering centers are translated rigidly.

[8] A sound cone may of course be defined similar to the light cone of electrodynamics, but the analogy is a crude one, since the exact commutation of the displacement operators holds only at equal times. It does not extend to other intervals outside the sound cone because of the impossibility of forming sharp wave packets within the crystal.

The integrations in $\mathbf{k}$-space are then carried out over the volume of a sphere of radius $k_D = (6\pi^2/V_0)^{\frac{1}{3}}$. We may further assume the existence of a unique sound velocity $s = \omega/k$ for all quanta, thereby neglecting certain effects of anisotropy, polarization, etc. The constants s and k_D define the characteristic Debye temperature Θ through the relation $\kappa\Theta = \hbar s k_D$. With these simplications the polarization summation of (6) reduces to a factor of $\delta_{\alpha\beta}$, the unit tensor; orthogonal displacements are uncorrelated. The correlation function then assumes the form

$$C_{\alpha\beta,\,T}(\mathbf{r},t) = \delta_{\alpha\beta} C_T{}^{(D)}(\mathbf{r},t), \tag{9}$$

with

$$C_T{}^{(D)}(\mathbf{r},t) = \frac{3\hbar^2}{8\pi M\kappa\Theta k_D{}^2} \int \left\{ e^{i(\mathbf{k}\cdot\mathbf{r}-skt)} + \frac{2\cos(\mathbf{k}\cdot\mathbf{r}-skt)}{\exp(\Theta k/k_D T)-1} \right\} \frac{d\mathbf{k}}{k}. \tag{10}$$

Evaluated for vanishing intervals of both space and time, the correlation function reduces to the mean-squared value of a displacement component ($\alpha = 1$, 2, or 3).

$$C_T{}^{(D)}(0,0) = \langle u_\alpha{}^2(\mathbf{r},t)\rangle_T = \frac{3\hbar^2}{M\kappa\Theta}\{\tfrac{1}{4} + (T/\Theta)\Phi(\Theta/T)\}. \tag{11}$$

Here Φ is the function introduced by Debye

$$\Phi(x) = \frac{1}{x}\int_0^x \frac{y\,dy}{\exp(y)-1}, \tag{12}$$

which is discussed and tabulated in many references.[9]

At temperature zero the Debye correlation function reduces to elementary form

$$C_0{}^{(D)}(\mathbf{r},t) = \frac{3\hbar^2}{4M\kappa\Theta k_D{}^2 r}\left\{ \frac{1-\exp[ik_D(r-st)]}{r-st} + \frac{1-\exp[-ik_D(r+st)]}{r+st} \right\}. \tag{13}$$

More generally, for $T \ll \Theta$ the temperature-dependent term of the integrand of (8) may be expanded in powers of $\exp[-\Theta k/k_D T]$ and integrated in elementary terms. For high temperatures, $T \gg \Theta$, direct expansion in powers of $\Theta k/k_D T$ is possible, which leads to results expressible in terms of sine integrals.

III. THE POTENTIAL AND ITS TREATMENT

A particle scattered by an ideally rigid crystal would be subject to an exactly periodic potential.[10] We shall represent this function as a summation over the lattice points $\mathbf{r}_j$ of equivalent potentials centered about each of them.

$$V(\mathbf{r}) = \sum_j \mathcal{V}(\mathbf{r}-\mathbf{r}_j). \tag{14}$$

In an elastically bound lattice the scattering centers are at any instant shifted from their equilibrium positions $\mathbf{r}_j$ by an amount given by the displacement field $\mathbf{u}(\mathbf{r}_j,t)$. In the present work we shall assume that the individual potentials are shifted rigidly along with their lattice-points, so that the total potential is represented by

$$V'(\mathbf{r},t) = \sum_j \mathcal{V}(\mathbf{r}-\mathbf{r}_j-\mathbf{u}(\mathbf{r}_j,t)). \tag{15}$$

In the Born approximation the scattering problem reduces to finding the matrix elements of this operator, and summing their squares over the various possible transitions.

Particular mention must be given the case of neutron scattering where the treatment proceeds by means of the Fermi pseudopotential approximation.[11] The short-range potentials between neutrons and nuclei are replaced by point interactions (delta functions) whose magnitudes are adjusted so that the scattering by isolated fixed nuclei is correctly represented by the Born approximation. That is, the interaction between a neutron (mass m) and a nucleus at $\mathbf{r}_j$ is taken to be $(2\pi\hbar^2/m)a_j\delta(\mathbf{r}-\mathbf{r}_j)$, where a_j is the bound scattering length.[12] The use of the Born approximation formalism is then extended to the case in which the nuclei are no longer fixed, so that the effective potential becomes

$$V'_{\text{neut}}(\mathbf{r},t) = (2\pi\hbar^2/m)\sum_j a_j \delta(\mathbf{r}-\mathbf{r}_j-\mathbf{u}(\mathbf{r}_j,t)). \tag{16}$$

Although the problem of finding the matrix elements of operator functions such as (15) has rather a general appearance, it may always be reduced by means of the fourier integral representations of the potentials to the problem of treating exponential functions of the quantized field $\mathbf{u}(\mathbf{r},t)$. The analysis required for these is particularly simple, as has been shown in other field-theoretical contexts.[13] By evaluating the matrix elements of these functions without expanding them in power series, we avoid the need to consider in detail the enormous variety of vibrational transitions the potential operator may induce. In effect the great number of degrees of freedom, which is responsible for this multiplicity, makes possible the use of field-theoretical methods which perform the summations automatically.

We shall require the matrix elements of operators of the form $\exp U$, where U is some linear combination of the components of the displacement field u_α. The only property of U needed for this purpose is that it is a sum of creation and destruction operators for all the

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[9] See for example R. W. James, *Optical Principles of the Diffraction of X-Rays* (G. Bell and Sons, London, 1948).

[10] In the scattering of x-rays the periodic function of interest is, of course, the electronic charge density, rather than a potential. The mathematical analysis is so similar, however, that the methods of the present work carry over with a few simple substitutions.

[11] E. Fermi, Ricerca sci. 7, 13 (1936).

[12] A review of the necessary information on neutron scattering is given in reference 4.

[13] R. J. Glauber, Phys. Rev. 84, 395 (1951).

modes of the system. As the simplest example we write the reduced form of $\exp U$ for the emission or absorption of a single quantum in any mode, assuming that all the modes of the crystal are initially in specified quantum states. This is

$$\langle \exp U\rangle^{(1)} = U\left\langle \frac{d}{dU}\exp U\right\rangle = U\langle \exp U\rangle, \tag{17}$$

in which the expectation values on the right are to be taken in the initial state of the system. In effect (17) corresponds to a separation of a single factor of U, the one which is to perform the real creation or absorption in all possible ways from the terms of the series expansion of $\exp U$, together with the requirement that the remaining operators leave the state unchanged. It is easy to show that the neglect of the commutation rules in thus separating a creation or destruction operator leads to errors which are only of order $1/N$. Since N, the number of lattice points is usually enormous we shall consider (17) as exact. To find the reduced forms for n-quantum transitions an analogous procedure may be used to separate a factor of U^n, which must then be divided by $n!$ since each of the U's may be responsible for any of the transitions

$$\langle \exp U\rangle^{(n)} = \frac{U^n}{n!}\left\langle \frac{d^n}{dU^n}\exp U\right\rangle = (U^n/n!)\langle \exp U\rangle. \tag{18}$$

The occupation numbers of the crystal modes are of course never known precisely and transition probabilities calculated from (18) must be averaged over an ensemble of initial states at some temperature T. This procedure may be simplified by first performing the averaging directly on the expectation value occurring in (18). The eventual error incurred thereby once again vanishes with $1/N$. We therefore define an average reduced form of $\exp U$ for an n-quantum process at temperature T.

$$\langle \exp U\rangle_T{}^{(n)} = (U^n/n!)\langle \exp U\rangle_T. \tag{19}$$

To compute the averaged expectation value $\langle \exp U\rangle_T$ we consider the expression $\langle \exp\lambda U\rangle_T$ as a function of the variable λ. Differentiating, we have

$$\frac{d}{d\lambda}\langle \exp\lambda U\rangle_T = \langle U\exp\lambda U\rangle_T. \tag{20}$$

Since the expression on the right is a sum of diagonal matrix elements, only the one-quantum matrix element of the exponential can contribute to it. Then, replacing the exponential by $\langle \exp\lambda U\rangle_T{}^{(1)} = \lambda U\langle \exp\lambda U\rangle_T$, we obtain the differential equation

$$\frac{d}{d\lambda}\langle \exp\lambda U\rangle_T = \lambda\langle U^2\rangle_T\langle \exp\lambda U\rangle_T, \tag{21}$$

for which the solution sought is[14]

$$\langle \exp\lambda U\rangle_T = \exp(\tfrac{1}{2}\lambda^2\langle U^2\rangle_T). \tag{22}$$

This completes the evaluation of the averaged reduced form (19):

$$\langle \exp U\rangle_T{}^{(n)} = (U^n/n!)\exp(\tfrac{1}{2}\langle U^2\rangle_T). \tag{23}$$

IV. SCATTERING CALCULATIONS

The individual potentials $\mathcal{V}(\mathbf{r})$ of (14), we assume, have the Fourier integral representation

$$\mathcal{V}(\mathbf{r}) = \int F(\mathbf{k})\exp[i\mathbf{k}\cdot\mathbf{r}]d\mathbf{k}, \tag{24}$$

where, in particular for neutron scattering, $F(\mathbf{k}) = \hbar^2 a/(2\pi)^2 m$. The potential acting on the scattered particle is then

$$V'(\mathbf{r},t) = \int F(\mathbf{k})\textstyle\sum_j \exp[i\mathbf{k}\cdot(\mathbf{r}-\mathbf{r}_j-\mathbf{u}(\mathbf{r}_j,t))]d\mathbf{k}. \tag{25}$$

The particle's initial state is represented by a plane wave, $\exp[i(\mathbf{p}\cdot\mathbf{r}-Et)]$, where $\mathbf{p}$ and E are the initial momentum and energy, divided by $\hbar$. Its final state $\exp[i(\mathbf{p}'\cdot\mathbf{r}-E't)]$ has, in general, a momentum differing in magnitude as well as direction. Introducing the differences

$$\Delta\mathbf{p} = \mathbf{p}'-\mathbf{p},\quad \Delta E = E'-E, \tag{26}$$

the time-dependent matrix element for the transition, insofar as the particle variables are concerned, is

$$\begin{aligned} M(t) &= \int V'(\mathbf{r},t)\exp[-i(\Delta\mathbf{p}\cdot\mathbf{r}-\Delta Et)]d\mathbf{r} \\ &= (2\pi)^3 F(\Delta\mathbf{p})\textstyle\sum_j \exp\{-i[\Delta\mathbf{p}\cdot(\mathbf{r}_j+\mathbf{u}(\mathbf{r}_j,t)) \\ &\qquad -\Delta Et]\}. \end{aligned} \tag{27}$$

This expression, however, is still an operator capable of inducing all possible vibrational transitions.

The rules formulated in the preceding section may be applied directly to find the reduced form of (27) for an n-quantum process. We identify the quantity $-i\Delta\mathbf{p}\cdot\mathbf{u}(\mathbf{r}_j,t)$ with U, and note that

$$\begin{aligned} \langle U^2\rangle_T &= -\langle(\Delta\mathbf{p}\cdot\mathbf{u})^2\rangle_T \\ &= -\sum_{\alpha\beta}\Delta p_\alpha\Delta p_\beta\langle u_\alpha(r_j,t)u_\beta(r_j,t)\rangle_T && (28) \\ &= -\sum \Delta p_\alpha\Delta p_\beta C_{\alpha\beta,T}(0,0) && (29) \\ &= -\Delta\mathbf{p}\Delta\mathbf{p}:\mathbf{C}_T(0,0), && (30) \end{aligned}$$

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[14] It may be noted that the present result holds true, whatever are the thermal weightings attached to the various degrees of excitation, i.e., even in nonequilibrium states. A similar theorem, due to F. Bloch [Z. Physik 74, 295 (1932)] which holds for oscillator systems with any number of modes requires explicitly the weightings of thermal equilibrium.

where the second line follows from the definition (6) of the correlation function, and in the third line dyadic notation is used to abbreviate the tensor product.

With the above identification of U, the relation (23) applied to (27) yields the effective transition operator for an n-quantum process:

$$\langle M(t)\rangle_T{}^{(n)}=(2\pi)^3F(\Delta\mathbf{p})\\ \times\left\{\sum_j\frac{1}{n!}(-i\Delta\mathbf{p}\cdot\mathbf{u}(\mathbf{r}_j,t))^n e^{-i\Delta\mathbf{p}\cdot\mathbf{r}_j}\right\}\\ \times\exp[-\tfrac{1}{2}\langle(\Delta\mathbf{p}\cdot\mathbf{u})^2\rangle_T]e^{i\Delta Et}. \quad (31)$$

The features of the elastic scattering which occurs when no quanta are emitted or absorbed are already apparent. For $n=0$ the absolute value, squared, of (31) exhibits Debye's classic result for the Laue-Bragg scattering. The pattern is the same as for a rigid lattice, but modulated in intensity[15] by a factor $\exp[-\langle(\Delta\mathbf{p}\cdot\mathbf{u})^2\rangle_T]$.

To compute the cross sections when quantum transitions do occur, it is convenient once more to develop a procedure which carries out implicitly the summations over the many processes possible. The expression for transition probabilities in the Born approximation may be written in the form

$$w=(2\pi/\hbar^2)\textstyle\sum_f M_{if}{}^{\dagger}M_{fi}\delta(\mathcal{E}_f-\mathcal{E}_i), \quad (32)$$

where the matrix elements, if time-dependent, may be evaluated at any time, and the summation over final states is restricted, as shown, by the conservation of energy. Without this explicit restriction of the summation, (32) could be expressed as the diagonal element of a matrix product. This may be effected by noting that for any conservative system, the time integral of a matrix element contains the conservation condition. Thus, for example, we have

$$\int_{-\infty}^{\infty}M_{if}{}^{\dagger}(t)dt=M_{if}{}^{\dagger}(0)2\pi\delta(\mathcal{E}_f-\mathcal{E}_i),$$

which permits us to write (32) as the expectation value[16]

$$w=\frac{1}{\hbar^2}\left\{\int_{-\infty}^{\infty}M^{\dagger}(t)M(0)dt\right\}_{ii}. \quad (33)$$

The total probability of an n-quantum process, summed over all the forms it may take is found by substituting the matrix element (31). Because the initial state of the system remains unknown the probability must finally be averaged thermally to represent the effects of the real processes. We have then

$$w_n=\frac{1}{\hbar^2}\int_{-\infty}^{\infty}\langle\langle M^{\dagger}(t)\rangle_T{}^{(n)}\langle M(0)\rangle_T{}^{(n)}\rangle_T dt. \quad (34)$$

To find the cross section for scattering accompanied by n-quantum processes w_n must be multiplied by the usual state-density factor for the outgoing particle and divided by its incoming flux. We are led thus to define the n-quantum differential cross section:

$$\sigma_n(\mathbf{p}')=[m^2p'/(2\pi\hbar)^3p]w_n, \quad (35)$$

where the inelasticity leaves the magnitude p' of the final momentum unrestricted. The total cross section for the n-quantum process is obtained by integrating over energy $d(\hbar E')$ and solid angle $d\Omega'$.

$$\sigma_{n,\,\mathrm{tot}}=\int\sigma_n(\mathbf{p}')d(\hbar E')d\Omega'. \quad (36)$$

The only expectation value in (34) which remains to be found is that of the product of the quantized operators in the two factors of $\langle M\rangle_T{}^{(n)}$. It has the form

$$(n!)^{-2}\langle[i\Delta\mathbf{p}\cdot\mathbf{u}(\mathbf{r}_l,t)]^n;[-i\Delta\mathbf{p}\cdot\mathbf{u}(\mathbf{r}_m,0)]^n\rangle_T, \quad (37)$$

in which a semicolon has been placed between the factors as a reminder that the n real transitions induced by the operators to the right of it must be reversed by those to the left.[17] The pairing of the operators on the two sides which effects this takes place in $n!$ ways. Furthermore in the limit of large N the expectation value (37) for each pairing scheme reduces to the product of the expectation values for the corresponding pairs. Thus (37) reduces to the nth power of the correlation function

$$(n!)^{-1}\{\langle[\Delta\mathbf{p}\cdot\mathbf{u}(\mathbf{r}_l,t)][\Delta\mathbf{p}\cdot\mathbf{u}(\mathbf{r}_m,0)]\rangle_T\}^n\\ =(n!)^{-1}\{\sum_{\alpha\beta}\Delta p_\alpha\Delta p_\beta\langle u_\alpha(\mathbf{r}_l,t)u_\beta(\mathbf{r}_m,0)\rangle_T\}^n\\ =(n!)^{-1}\{\Delta\mathbf{p}\Delta\mathbf{p}:\mathbf{C}_T(\mathbf{r}_l-\mathbf{r}_m,t)\}^n. \quad (38)$$

The evaluation of the n-quantum differential cross section now proceeds directly by combining (31), (34), and (38) in (35). In particular we find that all of the knowledge required about lattice vibrations is contained in the time-dependent correlation function $\mathbf{C}_T(\mathbf{r}_l-\mathbf{r}_m,t)$. The summations to be performed over the lattice points $\mathbf{r}_l$ and $\mathbf{r}_m$ may be simplified by noting that only the difference $\mathbf{r}_l-\mathbf{r}_m$ appears in the summand. In the limit of large N the double summation therefore becomes N times the single summation over positions relative to a particular lattice point, chosen as origin. The expression for the n-quantum cross section, thus

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[15] A simple way of viewing this is that $\langle M\rangle_T{}^{(0)}$ is just the matrix element of the thermally averaged potential. The latter, according to (31), may be expressed as $\int K_T(\mathbf{r}-\mathbf{r}')V'(\mathbf{r}')d\mathbf{r}'$, where $K(\mathbf{r})=\langle\delta(\mathbf{r}-\mathbf{u})\rangle_T$ which, in a Debye crystal, is

$$(2\pi\langle u_\alpha{}^2\rangle_T)^{-\frac{3}{2}}\exp[-r^2/2\langle u_\alpha{}^2\rangle_T].$$

[16] This device was first used in a similar context by W. Lamb, Phys. Rev. **55**, 190 (1939).

[17] If, in a single one of the factors of $(\Delta\mathbf{p}\cdot\mathbf{u})^n$ a pair of $\mathbf{u}$'s were used to both emit and reabsorb a quantum in a single mode, the number of real processes carried out would be $n-2$. Virtual processes of this type are already correctly accounted for in (31).

reduced, is

$$\sigma_n(\mathbf{p}')=\frac{(2\pi)^3Nm^2p'}{n!\hbar^5p}|F(\Delta\mathbf{p})|^2\exp[-\langle(\Delta\mathbf{p}\cdot\mathbf{u})^2\rangle_T]\times\sum_j e^{i\Delta\mathbf{p}\cdot\mathbf{r}_j}\int_{-\infty}^{\infty}e^{-i\Delta Et}\{\Delta\mathbf{p}\Delta\mathbf{p}:\mathbf{C}_T(\mathbf{r}_j,t)\}^n dt. \quad (39)$$

The summation over n from zero to infinity to include all possible quantum processes is now immediate, and results in the introduction of the function $\exp[\Delta\mathbf{p}\Delta\mathbf{p}:\mathbf{C}_T(\mathbf{r}_j,t)]$ within the time integration. For purposes of illustration we specialize to the case of neutron scattering, for which we have noted $F(\Delta\mathbf{p})=\hbar^2a/(2\pi)^2m$. Then, defining the differential cross section for all quantum processes $\sigma(\mathbf{p}')=\sum_{(n)}\sigma_n(\mathbf{p}')$, we have

$$\sigma(\mathbf{p}')=\frac{Na^2p'}{2\pi\hbar p}\exp[-\langle(\Delta\mathbf{p}\cdot\mathbf{u})^2\rangle_T]\sum_j e^{i\Delta\mathbf{p}\cdot\mathbf{r}_j}\times\int_{-\infty}^{\infty}\exp[-i\Delta Et+\Delta\mathbf{p}\Delta\mathbf{p}:\mathbf{C}_T(\mathbf{r}_j,t)]dt. \quad (40)$$

Although we have thus far assumed the lattice to consist of identical scatterers, the presence of spin- or isotope-dependent interactions will cause a fluctuation of the scattering length from one nucleus to another. In such cases, with the replacement of a^2 by $(a)_{\mathrm{Av}}^2$, (40) represents the coherent scattering by the lattice. To this must be added the scattering, proportional to $(a^2)_{\mathrm{Av}}-(a)_{\mathrm{Av}}^2$, which results from the disorder of the system. The treatment of this incoherent scattering is the same, in relation to the lattice quanta, as the coherent scattering. The result is similar to (40) but, of course, lacks the interference effects represented by the sum over lattice points $\mathbf{r}_j$.

$$\sigma_{\mathrm{inc}}(\mathbf{p}')=\frac{Np'}{2\pi\hbar p}[(a^2)_{\mathrm{Av}}-(a)_{\mathrm{Av}}^2]\exp[-\langle(\Delta\mathbf{p}\cdot\mathbf{u})^2\rangle_T]\times\int_{-\infty}^{\infty}\exp[-i\Delta Et+\Delta\mathbf{p}\Delta\mathbf{p}:\mathbf{C}_T(0,t)]dt. \quad (41)$$

The incoherent cross section, which is in general also inelastic, is seen to depend only on the difference $\mathbf{C}_T(0,t)-\langle\mathbf{uu}\rangle_T=\mathbf{C}_T(0,t)-\mathbf{C}_T(00)$.

V. COMPARISON WITH APPROXIMATE METHODS

We have derived expressions for the inelastic scattering cross sections which are essentially exact in their treatment of lattice vibrations. In particular, the information required about the lattice is seen to be entirely contained in its characteristic tensor correlation function $C_{\alpha\beta,T}(\mathbf{r},t)$. Unfortunately our knowledge of the vibrational frequency distributions $\omega^{(p)}(\mathbf{k})$ in crystals is still too fragmentary in nearly all cases to permit explicit construction of these functions. It seems reasonable to hope, however, that some of the required data on frequency distributions can be found directly from measurements of the inelastic scattering of slow neutrons.[18] For the present we shall limit ourselves to the discussion of various approximation methods, which correspond to the use of incomplete knowledge of the correct correlation function. Equations (40) and (41) furnish a unified starting point for all such procedures.

One means of evaluating the expressions (40) and (41) proceeds by re-expressing them as the sums of n-quantum partial cross sections. The expansion will converge quite rapidly for small momentum transfers and low temperatures, that is for $(\Delta p)^2\langle u_\alpha^2\rangle_T<1$. In this case not many terms need be retained and the integrals required are only those of the corresponding powers of the correlation function. The one-quantum terms have been extensively investigated in this way,[4,5] and certain estimates made of higher-order effects,[5,6] all on the basis of the Debye model. As an illustration of this method applied to inelastic scattering, without restriction on the number of quanta, we write the cross section for incoherent neutron scattering by a Debye lattice at zero temperature, with energy loss $-\Delta E\leq\kappa\Theta/\hbar$. Direct computation with (41), expanded, yields

$$\sigma_{\mathrm{inc}}(\mathbf{p}')=(Np'/\hbar p)[(a^2)_{\mathrm{Av}}-(a)_{\mathrm{Av}}^2]\times\exp[-(\Delta p)^2\langle u_\alpha^2\rangle_T]H(\Delta\mathbf{p},\Delta E), \quad (42)$$

where

$$H(\Delta p,\Delta E)=\delta(\Delta E)+\frac{1}{|\Delta E|}\sum_{n=1}^{\infty}\frac{1}{n!(2n-1)!}\times\left(\frac{3\hbar^4(\Delta p)^2(\Delta E)^2}{2M(\kappa\Theta)^3}\right)^n. \quad (43)$$

The delta function $\delta(\Delta E)$ evidently represents elastic scattering in the zero-quantum case, and the terms following add the inelastic effects of all other quantum processes.

The scattering of x-rays and electrons by crystals, as we have noted earlier, is usually studied at energies high enough that the gain or loss of lattice quantum energies is relatively insignificant. In cases such as these, the final energies will be in a band so narrow that for any given direction of scattering they may be integrated over without appreciably disturbing the value of $\Delta\mathbf{p}$. Such integrations may be carried out on the cross sections (40) and (41). Letting $p'=p$, and holding $\Delta\mathbf{p}$ fixed, we may extend the limits of the ΔE integration to ∞ and $-\infty$, since it is assumed that only the central region contributes. The integrations over ΔE performed in this way place the delta function $\delta(t)$ within the time integrations which may then be performed directly. The results are seen to contain

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[18] G. Placzek and L. Van Hove, Phys. Rev. **93**, 1207 (1954).

only the correlation function evaluated at time $t=0$.

$$\int \sigma_{\mathrm{coh}}(\mathbf{p}')d(\hbar E')$$

$$=N(a)_{\mathrm{Av}}^2 \exp[-\langle(\Delta\mathbf{p}\cdot\mathbf{u})^2\rangle_T]$$

$$\times\sum_j \exp[i\Delta\mathbf{p}\cdot\mathbf{r}_j+\Delta\mathbf{p}\Delta\mathbf{p}:\mathbf{C}_T(\mathbf{r}_j,0)], \quad (44)$$

$$\int \sigma_{\mathrm{inc}}(\mathbf{p}')d(\hbar E')=N[(a^2)_{\mathrm{Av}}-(a)_{\mathrm{Av}}^2]. \quad (45)$$

These, of course, are just the results of the static treatment usually employed in the study of x-ray diffraction. They may be arrived at somewhat more directly by assuming the lattice vibration frequencies relatively so low that the passage of the particle through the system is effectively instantaneous. This makes it possible to replace the correlation function by its value for vanishing time intervals $C_{\alpha\beta,T}(\mathbf{r},0)$, the scattering being thereby represented as elastic $[\sigma(\mathbf{p}')\sim\delta(\Delta E)]$. A procedure for correcting the angular distributions resulting from the static approximation has been introduced by Placzek.[19] In the present context it corresponds directly to expanding the function $\exp[\Delta\mathbf{p}\Delta\mathbf{p}:\mathbf{C}_T(\mathbf{r},t)]$ in successive powers of t.

Another limit whose discussion is instructive is that of large momentum transfer and/or high crystal temperature, i.e., large values of $\langle(\Delta\mathbf{p}\cdot\mathbf{u})^2\rangle_T$. In such cases a detailed discussion of the coherent cross section shows that the interference effects represented by the lattice points $\mathbf{r}_j\neq 0$ become relatively small. For these points the correlation function is too small to compensate the negative exponent of the Debye-Waller factor. The coherent scattering in this limit comes entirely from the point $\mathbf{r}_j=0$, and is proportional to the incoherent scattering.[20]

The energy dependence of the incoherent scattering may also be found in the same limit, $\langle(\Delta\mathbf{p}\cdot\mathbf{u})^2\rangle_T\gg 1$, and we include it as a further illustration of the time-dependent method. The definition (7) of the correlation function shows that the real part of $C_{\alpha\beta,T}(0,t)$ is stationary at $t=0$, and as we shall see this corresponds to a maximum. Since asymptotically the principal contribution to the time integration will come from near $t=0$, we expand the correlation function:

$$C_{\alpha\beta,T}(0,t)=C_{\alpha\beta,T}(0,0)+tC_{\alpha\beta}^{(1)}+t^2C_{\alpha\beta,T}^{(2)}. \quad (46)$$

The coefficient $C_{\alpha\beta}^{(1)}$ may be obtained from (7):

$$C_{\alpha\beta}^{(1)}=-i(V_0\hbar/16\pi^3M)\sum_p \int e_\alpha^{(p)}e_\beta^{(p)}d\mathbf{k}.$$

Since the vibrational modes for each propagation vector are mutually orthogonal, this reduces to

$$C_{\alpha\beta}^{(1)}=-i(\hbar/2M)\delta_{\alpha\beta}, \quad (47)$$

an expression independent of the lattice structure. If the t^2 term were negligible, substitution of (46) in (41) at this point would yield $\sigma_{\mathrm{inc}}(\mathbf{p}')\sim\delta(\Delta E+(\hbar(\Delta p)^2/M))$. The scattering would in effect be by free particles of mass M.

The Debye approximation may be used to estimate the quadratic term of (46). This is

$$C_{\alpha\beta,T}^{(2)}=-(V_0\hbar/16\pi^3M)\delta_{\alpha\beta}$$

$$\times\int\{\tfrac{1}{2}+[\exp(\hbar\omega/\kappa T)-1]^{-1}\}\omega d\mathbf{k}$$

$$=-[\hbar\mathcal{E}(T)/2M]\delta_{\alpha\beta}, \quad (48)$$

where $\mathcal{E}(T)$ is defined as $\hbar^{-1}$ times the average thermal energy per lattice particle (including zero-point energy). The time integral required, of the exponential of a form quadratic in t may be performed immediately to yield a Gaussian distribution[5] of final energies centered about $\Delta E=-\mathcal{E}_r=-\hbar(\Delta p)^2/2M$, with a dispersion proportional to $[\mathcal{E}_r\mathcal{E}(T)]^{\frac{1}{2}}$. In the limit we have been discussing, the residual effects of interference in the coherent cross section may be estimated by similarly using the maxima of the real part of $C_T^{(D)}(\mathbf{r}_j,t)$ which occur near $t=\pm r_j/s$, where s is the sound velocity. For this purpose, however, it would be desirable to employ a correlation function representing dispersive effects more realistically.

Applications of the time-dependent method to neutron scattering by molecular systems will be discussed in a forthcoming paper.

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[19] G. Placzek, Phys. Rev. **86**, 377 (1952).

[20] A. Akhiezer and I. Pomeranchuk, reference 5, have discussed many quantum processes in the high energy limit, and have stated a form of (40), for the Debye model, retaining, in effect, only the central lattice point $\mathbf{r}_0=0$. The derivation given appears to omit certain terms leading to the Debye-Waller factors when the number of quanta is greater than zero, although these appear in the result stated. The same argument is repeated in their text, A. Akhiezer and I. Pomeranchuk, *Certain Topics in Nuclear Theory* (Moscow, 1950), revised second edition.