ELASTIC REFLECTION OF ATOMS FROM CRYSTALS

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Abstract

The reflection of atoms by a crystal surface is examined by a modification of the Born collision method. The fraction of reflections in which all the normal coordinates of the crystal remain unaltered is found to be approximately

$$U = e^{-3\pi^2(m_A/m_B)(t_A/\Theta)^2(t_B/\Theta)/(1+4\pi d/\lambda)}.$$

m_A, m_B are the masses of the reflected atom A and of the lattice atoms, respectively. The energy of atom A is kt_A. The temperature of the lattice is t_B. Θ is the characteristic temperature of the lattice. d is the distance in which the mutual repulsion between atom A and lattice atoms falls to one e'th its value. λ is the de Broglie wave-length of atom A. For reflection of H atoms on LiF at room temperature, U is estimated to be 0.9. When Θ and t_A are comparable, those normal coordinates are found to be most readily excited which have the lowest frequency.

I. Introduction

RECENT experiments[1] indicate that the majority of light atoms bombarding a crystal may be reflected without an appreciable loss of energy. It is of interest to ask: what fraction of atoms will be perfectly elastically reflected? In the classical theory this fraction is infinitesimal. Some transfer of energy would always occur between lattice and bombarding atom. The situation is not so obvious from the standpoint of the quantum mechanics. Each normal coordinate of the lattice can absorb only quantised amounts of energy. But as the number of atoms in the lattice becomes infinite, the spectrum of the lattice approaches a continuum, so it is not evident that the quantum mechanics should hinder an exchange of energy. The following analysis will show however that this actually is the case.

It will be assumed that the only transitions of the crystal are those of the normal coordinates of the lattice. The excitation of electronic levels by the colliding atoms is considered negligible.

II. Formulation of Problem

Our problem will be stated in an idealised form. (See Figure 1.) Angular reflection difficulties will be avoided by confining the bombarding atom A to one dimension. Its line of motion is taken to be perpendicular to the surface of the lattice, and to pass through the equilibrium position of a definite surface atom B. The interaction energy is considered to be a function only of the distance R between the two atoms A and B, say $V(R)$.

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[1] T. H. Johnson, Phys. Rev. **37**, 847 (1931); J. K. Roberts, Proc. Roy. Soc. **129**, 155 (1930) has discussed the similar implications of the experiments of Stern and his collaborators.

The crystal is to be of simple cubic type, with all the atoms of equal mass, m_B. There are N atoms on an edge, N^3 atoms in all. The three components of the displacement from equilibrium position of the atom with indices (lmn) shall be x_{lmn}, y_{lmn}, z_{lmn}.

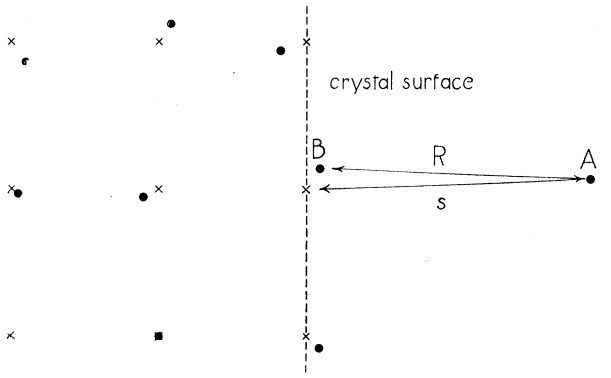

FIG. 1.

If in the lattice we assume the mutual energy of pairs of atoms to be a function only of their interatomic distance, the transformation[2]

$$\begin{aligned} x_{lmn} &= N^{-3/2} \sum_{\alpha\beta\gamma=-N/2}^{N/2} a_{\alpha\beta\gamma} e^{2\pi i(l\alpha+m\beta+n\gamma)/N} \\ y_{lmn} &= N^{-3/2} \sum_{\alpha\beta\gamma=-N/2}^{N/2} b_{\alpha\beta\gamma} e^{2\pi i(l\alpha+m\beta+n\gamma)/N} \\ z_{lmn} &= N^{-3/2} \sum_{\alpha\beta\gamma=-N/2}^{N/2} c_{\alpha\beta\gamma} e^{2\pi i(l\alpha+m\beta+n\gamma)/N} \end{aligned} \tag{1}$$

changes the Hamiltonian of crystal into nearly

$$\begin{aligned} H = \sum_{\alpha\beta\gamma} \{ & m_B/2(|\dot{a}_{\alpha\beta\gamma}|^2 + |\dot{b}_{\alpha\beta\gamma}|^2 + |\dot{c}_{\alpha\beta\gamma}|^2) \\ & + K(\sin^2 \pi\alpha/N + \sin^2 \pi\beta/N + \sin^2 \pi\gamma/N)(|a_{\alpha\beta\gamma}|^2 + |b_{\alpha\beta\gamma}|^2 + |c_{\alpha\beta\gamma}|^2)\}. \end{aligned}$$

The conditions

$$a_{-\alpha-\beta-\gamma} = \overset{*}{a}_{\alpha\beta\gamma}, \text{ etc.}$$

are necessary in order that the displacements be real. The terms that must be added to make this transformed Hamiltonian exact involve only the coordinates of the surface atoms. Our neglect of these terms is equivalent to assuming that the surface atoms behave as if the crystal were of infinite extent.

We are now able to write the wave equation of the system. The center of gravity of the total system is eliminated as usual. Let the mass of the free atom be m_A, and let its distance from the equilibrium position of the lattice

[2] M. Born and T. v. Karman, Phys. Zeits. **13**, 297 (1912).

atom B be s. Let $\xi_{x\alpha\beta\gamma}$, $\eta_{x\alpha\beta\gamma}$ be the real and imaginary parts of $a_{\alpha\beta\gamma}$, respectively. The wave equation is then

$$\Big\{ \sum_{\alpha\beta\gamma} \sum_{xyz} [(h^2/8\pi^2 m_B)(\partial^2/\partial\xi^2{}_{x\alpha\beta\gamma} + \partial^2/\partial\eta^2{}_{x\alpha\beta\gamma}) - \tfrac{1}{2} m_B(2\pi\nu_0)^2(2l/N)^2(\xi^2{}_{x\alpha\beta\gamma} + \eta^2{}_{x\alpha\beta\gamma})] + \frac{h^2}{8\pi^2 m_A}\frac{\partial^2}{\partial s^2} - V(R) + E\Big\}\psi = 0 \tag{2}$$

We have made the usual approximation of the Debye theory of specific heat that

$$K\{\sin^2(\pi\alpha/N) + \sin^2(\pi\beta/N) + \sin^2(\pi\gamma/N)\} = m_B(2\pi\nu_0)^2(2l/N)^2/2$$

where $l^2=\alpha^2+\beta^2+\gamma^2$ with $0<l\leqq N/2$.

Our problem may now be precisely defined. We are to find a solution of (2) which for large values of s satisfies the initial condition that when atom A is moving to the left, it has a definite energy kt_A, and the crystal is in a definite state corresponding to a temperature t_B. The solution is thus to have the asymptotic form

$$\psi \overset{s\to\infty}{=} e^{2\pi i(p_0/h)\cdot s}(p_0/m_A)^{-1/2}\phi_{\tau_0}(X) + \sum_\tau C_\tau e^{-2\pi i(p_\tau/h)\cdot s}(p_\tau/m_A)^{-1/2}\phi_\tau(X). \tag{3}$$

The variables of the crystal are denoted by X. $\Phi_\tau(X)$ is that normalized wave function of the crystal whose ensemble of quantum numbers is denoted by τ. If ϵ_τ is the eigenenergy of the crystal in state τ, then $E_\tau=E-\epsilon_\tau$ is the energy of atom A when the crystal is in state τ. p_τ refers to the corresponding momentum $(2m_AE_\tau)^{1/2}$.

The first term is normalized to represent a unit flux of atoms[3] to the left associated with the crystal in the initial state τ_0. The reflected atoms are represented by the summation. In order that the net flux of atoms across a given point vanish

$$\sum |C_\tau|^2 = 1. \tag{4}$$

In particular, the elastic reflection coefficient U is equal to $|C_{\tau_0}|^2$, or

$$U = 1 - \sum{}' |C_\tau|^2 = 1 - S \tag{5}$$

where the summation is over all states except τ_0, and is denoted by S.

III. Solution

A method previously used by the author[4] for studying the interchange of energy between molecules will be applied to calculate the coefficients of (3). In this method the first approximation to C_{τ_0} is unity, so the elastic reflection probability must be defined by (5) where the first approximations to the C_τ's are used.

[3] Cf. P. Dirac, Principles of Quantum Mechanics, Oxford Press (1930), p. 176.

[4] C. Zener, Phys. Rev. **37**, 556 (1931).

Let the x component of displacement of atom B from its position of equilibrium be denoted by x_B. Since atom A is confined to one dimension, the interaction $V(R)$ must be a function only of one dimension, so we set $R=s-x_B$. Then

$$V(R) = V(s) - x_B V'(s),$$

neglecting higher powers of x_B.

The perturbation scheme starts with the solution of (2) in which $V(s)$ is substituted for $V(R)$. The difference between $V(R)$ and $V(s)$, namely $-x_B \cdot V'(s)$, is taken as the perturbing term that causes transitions. The probability of the transition $\tau_0 \rightarrow \tau$ is given by[5]

$$\gamma^{\tau}_{\tau_0} = \left| (8\pi^2 m_A/h^2) \int \phi_{\tau_0} x_B \phi_\tau dX \int Q_{\tau_0} V'(s) Q_\tau ds \right|^2. \tag{6}$$

$Q_\tau(s)$ is that solution of

$$\{(h^2/8\pi^2 m_A) d^2/ds^2 - V(s) + E_\tau\} Q_\tau(s) = 0 \tag{7}$$

which has the asymptotic behavior

$$Q_\tau(s) \overset{s\to\infty}{=} \frac{\sin((2\pi/h)p_\tau s + \theta_\tau)}{(2\pi p_\tau/h)^{1/2}}.$$

In evaluating the first integral of (6) we replace the index B by the indices $(N/2\ m\ n)$, and use the transformation (1). We see that this integral vanishes except when one and only one normal coordinate changes its quantum number by ± 1. Let that normal coordinate which changes be $\xi_{x\alpha\beta\gamma}$ or $\eta_{x\alpha\beta\gamma}$, and let its initial quantum number be $n_{\alpha\beta\gamma}$. Then the value of $\left|\int \phi_{\tau_0} x_B \phi_\tau dX\right|^2$ averaged over all surface atoms, i.e., over m and n, is

$$N^{-3}\binom{n_{\alpha\beta\gamma}+1}{n_{\alpha\beta\gamma}} h/(4\pi^2 m_B \nu_{\alpha\beta\gamma}).$$

The two quantities in the bracket are to be associated with the transitions ± 1. $\nu_{\alpha\beta\gamma}$ is related to the limiting frequency ν_0 by

$$\nu_{\alpha\beta\gamma} = \nu_0 2l/N.$$

A definite form for $V(s)$ must be assumed in the evaluation of the second integral of (6). This may be taken to be $Ce^{-s/d}$,[6] in which d has the magnitude of about $0.2\times 10.^{-8}$. Then $V'(s) = -V(s)/d$. However, with this potential Eq. (7) is difficult to solve. Hence we substitute a potential with which we can solve this equation. Such a potential is $A/(s-B)^2$, where the constants A and B are so adjusted that the two potentials join smoothly at that value of s for which $V(s) = E_{\tau_0}$, i.e., at the classical closest distance of approach. For ease in integration we shall still replace $V'(s)$ by $-V(s)/d$. These assumptions lead to[7]

[5] Reference 4, Eq. 13.

[6] Reference 4, Section II.

[7] Reference 4 (19). The E'' of this reference has been replaced by E_{τ_0} to facilitate future integrations.

$$\left|(8\pi^2 m_A/h^2)\int_0^\infty Q_{\tau_0}V'(s)Q_\tau ds\right|^2 = (2\pi^2 m_A/h^2)(\epsilon'/\epsilon)^{2d(2\pi p_{\tau_0}/h)}.$$

Here $\epsilon' = E_{\tau_0} - h\nu_{\alpha\beta\gamma}$, $\epsilon = E_{\tau_0}$, or $\epsilon' = E_{\tau_0}$, $\epsilon = E_{\tau_0} + h\nu_{\alpha\beta\gamma}$ according as $n_{\alpha\beta\gamma}$ changes by $+1$ or -1. $\lambda = p_{\tau_0}/h$ is the de Broglie wave-length of atom A before collision. Combining these integrations gives

$$\gamma_{\tau_0}{}^{\tau} = (\pi^2/2N^3)(m_A/m_B)(E_{\tau_0}/h\nu_{\alpha\beta\gamma})(n_{\alpha\beta\gamma} + \tfrac{1}{2} \pm \tfrac{1}{2})\cdot\left(\frac{E_{\tau_0} - (\tfrac{1}{2} \pm \tfrac{1}{2})h\nu}{E_{\tau_0} + (\tfrac{1}{2} \mp \tfrac{1}{2})h\nu}\right)^v$$

where $v = 4\pi d/\lambda$.

The frequency ν_0 is related to the characteristic temperature Θ of the crystal by

$$h\nu_0 = k\Theta.$$

If the temperature of atom A is defined by $E_{\tau_0} = kt_A$, the preceding equation becomes

$$\gamma_{\tau_0}{}^{\tau} = (\pi^2/4lN^2)(m_A/m_B)(t_A/\Theta)(n_{\alpha\beta\gamma} + \tfrac{1}{2} \pm \tfrac{1}{2})\left(\frac{t_A - (1 \pm 1)\Theta l/N}{t_A + (1 \mp 1)\Theta l/N}\right)^V.$$

In forming the summation of $\gamma_{\tau_0}{}^{\tau}$ over all possible transitions, several more approximations will be made. First we replace the summation by the integration

$$3N^3\int_0^1 (2l/N)^2 d(2l/N).$$

Now if $\Theta \ll t_A$,

$$t_A/(t_A + \Theta 2l/N) \backsimeq (t_A - \Theta 2l/N)/t_A.$$

When the inequality is not satisfied, $n_{\alpha\beta\gamma}$ is very small except for those values of l for which the above is nearly valid, provided $t_B \leqq t_A$, which is usual in experiments. We thus have for the sum S of all the transition probabilities approximately

$$S = 3\pi^2(m_A/m_B)(t_A/\Theta)\int_0^1 (2l/N)(n_{\alpha\beta\gamma} + \tfrac{1}{2})(1 - 2l/N\Theta/t_A)^v d(2l/N).$$

If $\Theta > t_A$, the upper limit is to be replaced by t_A/Θ.

When $\Theta\ 2l/N \ll t_B$,

$$n_{\alpha\beta\gamma} + \tfrac{1}{2} = kt_B/h\nu_{\alpha\beta\gamma} = (t_B/\Theta)(N/2l).$$

However, since $(t_A - \Theta\ 2l/N)$ occurs to a fairly large power in the integrand, the major contributions to the integral are associated with small values of $2l/N$. Only a small error will thus be made if we substitute $(N/2l)t_B/\Theta$ for $n_{\alpha\beta\gamma} + 1/2$, provided t_B/Θ is not a very small fraction. We now have

$$S = 3\pi^2(m_A/m_B)(t_A/\theta)(t_B/\theta)\int_0^1 (1 - 2l/N\Theta/t_A)^{4\pi d/\lambda} d(2l/N). \qquad (8)$$

Integration gives

$$S = 3\pi^2(m_A/m_B)(t_A/\Theta)^2(t_B/\Theta)(1 + 4\pi d/\lambda)^{-1}\cdot[1 - (1 - \Theta/t_A)^{4\pi d/\lambda}]. \quad (9)$$

The second term in the last bracket is to be omitted if $\Theta/t_A > 1$.

We must investigate under what conditions we may substitute the S of (9) into (5). S has been obtained by a perturbation scheme which uses as an unperturbed solution that corresponding to an elastic reflection. Hence the method fails unless the unperturbed solution is the major portion of the final solution, which requires that $S \ll 1$. The previous analysis is thus limited to cases of large elastic reflection. However, a simplification is introduced by the large magnitude of the number of normal coordinates of the crystal. Consider a wave packet representing atom A being reflected by the crystal. We have seen that the majority of the transitions in the crystal are associated with an energy change very small in comparison with the energy of the wave packet, kt_A. This preferential weighting is caused by the presence of the factor $(1 - \Theta/t_A\ 2l/N)^{4\pi d/\lambda}$ in the integrand of (8). Moreover, the energy changes associated with various transitions partially cancel each other. Hence the character of the wave packet during collision is not very different from that corresponding to an elastic reflection, obtained by holding the lattice atoms rigidly to their positions of equilibrium.

The preceding discussion shows that in the collision of a wave packet with a crystal, the transition of one normal coordinate does not appreciably effect the probability that a second normal coordinate will suffer a change. Assuming that these transitions are absolutely independent, and defining β_k as the probability that the k'th normal coordinate suffers a transition, then the probability that all normal coordinates remain unchanged during collision is

$$U = \prod_k (1 - \beta_k).$$

Now the β_k's approach zero as N becomes infinite, so we may replace $(1 - \beta_k)$ by $\exp(-\beta_k)$. Thus

$$U = e^{-\Sigma\cdot\beta_k}.$$

To a good approximation the β_k of the wave packet will be equal to the probability calculated by the previous method that the k'th normal coordinate suffer a transition, irrespective of whether S is large or small. Since in that method only one normal coordinate can change during collision, β_k is simply the sum of the $|C_r|^2$'s for which the k'th quantum number changes by ± 1. The sum over the β_k's is thus equal to S. We have finally

$$U = e^{-S}. \quad (10)$$

This expression for U is no longer limited to small values of S, as is (5).

IV. Discussion

The one-dimensional collision of atoms with a crystal has been examined. An expression has been found for the fraction, U, of atoms reflected elasti-

cally. It is to be expected that the general dependence of U upon the parameters of the crystal and bombarding atoms will be approximately valid for actual reflections.

If the conditions $m_B \geqq 7m_A$, $\Theta \geqq 2t_A$, $\Theta \geqq 2t_B$, $d \backsimeq 0.25 \times 10^{-8}$ are satisfied, then $S \leqq 0.15$, and both (5) and (10) give $U \gtrsim 0.75$. Johnson[8] has found the experimental value of U to be as high as 0.5 for H atoms bombarding LiF. Here the above inequalities are valid. Application to other crystals gives consistently larger values for U than found by Johnson. It may be possible that the experimental values of U have been lowered by the presence of adsorbed gases on the crystal surface. The author wishes to acknowledge illuminating discussions with Dr. E. Wigner.

[8] T. H. Johnson, Phys. Rev. **35,** 650 (1930).