

Short Communications

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The relationship between the dynamical theories of electron and X-ray diffraction by periodic lattices.

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The dynamical theories of X-ray and electron diffraction can be expressed in similar Schrödinger wave equation forms. The detailed correspondence between the two phenomena then becomes directly obvious.

Introduction

Although it is well known that the wave-vector dispersion relationship obtained in the dynamical theories of electron and X-ray diffraction are similar, no attempt, to the author's knowledge, has been made to investigate the detailed analogy between the two phenomena (*e.g.* see the remarks of Hirsch, Howie, Nicholson, Pashley & Whelan, 1965). In fact, and perhaps not surprisingly, the X-ray case can be readily expressed in a Schrödinger equation form and compared term by term with the Schrödinger equation appropriate to electron diffraction.

Electron diffraction

The properties of a high-energy electron (~ 100 keV) inside a crystal must satisfy the Schrödinger equation:

$$\nabla^2 \psi + (2m/\hbar^2) [E - V] \psi = 0, \quad (1)$$

where the symbols have their usual meaning. The total energy of the electron, E , remains unchanged during its interaction with the crystal since elastic scattering only is being considered. The potential energy V inside the crystal is a periodic function of the lattice:

$$-V(\mathbf{r}) = \sum_{\mathbf{g}} V_{\mathbf{g}} \exp 2\pi i \mathbf{g} \cdot \mathbf{r}, \quad (2)$$

where \mathbf{g} are reciprocal lattice vectors of the crystal, \mathbf{r} is a point in the crystal and the $V_{\mathbf{g}}$ are Fourier coefficients of potential.

X-ray diffraction

It is assumed (James, 1958) that the diffracting crystal is electrically neutral and that the X-ray frequency is sufficiently high for the crystal to behave as an insulator. The Maxwell equations for an insulator may be developed to give (*e.g.*, Ditchburn, 1963):

$$\nabla^2 \boldsymbol{\varepsilon} = \frac{\eta}{c^2} \frac{\partial^2 \boldsymbol{\varepsilon}}{\partial t^2}, \quad (3)$$

where $\boldsymbol{\varepsilon}$ is the electric field of the radiation and η is the dynamic dielectric constant. Thus, inserting $\boldsymbol{\varepsilon} = \boldsymbol{\varepsilon}_0 \exp(i\omega t)$, where ω is the angular frequency of the radiation, gives the wave equation:

$$\nabla^2 \boldsymbol{\varepsilon} + \eta \omega^2 \boldsymbol{\varepsilon} / c^2 = 0. \quad (4)$$

Now if \mathbf{P} is the polarization of the medium, then:

$$\begin{aligned} 4\pi \mathbf{P} &= (\eta - 1) \boldsymbol{\varepsilon} \\ &= 4\pi \rho e^2 \boldsymbol{\varepsilon} / m\omega^2, \end{aligned}$$

where ρ is the crystal electron density and e and m are the charge and mass of the electron. This expression is valid as long as ω is remote from any absorption frequency of the crystal atoms; therefore, equation (4) yields:

$$\nabla^2 \boldsymbol{\varepsilon} + c^{-2} [\omega^2 - 4\pi \rho e^2 / m] \boldsymbol{\varepsilon} = 0. \quad (5)$$

But the mass of the photon is $\tilde{m} = \hbar\omega/c^2$, so that (5) can be written as:

$$\nabla^2 \boldsymbol{\varepsilon} + (\tilde{m}/\hbar^2) [\hbar\omega - 4\pi \rho e^2 \hbar / m\omega] \boldsymbol{\varepsilon} = 0, \quad (6)$$

which is closely analogous to the Schrödinger equation (1) for electron diffraction. In (6), however, the mass $2m$ for the electron is replaced by the relativistic photon mass \tilde{m} , and the total energy E is replaced by the photon energy in vacuum $\hbar\omega$. The 'potential energy' of the photon, $4\pi \rho e^2 \hbar / m\omega$, is the fraction of the total energy $\hbar\omega$ which is stored in the medium. This arises because *in vacuo* the energy in an electromagnetic wave is proportional to $|\boldsymbol{\varepsilon}|$ and the energy stored in the medium is proportional to $-\mathbf{P} \cdot \boldsymbol{\varepsilon}$. Therefore, the energy per photon stored in the medium is:

$$\begin{aligned} V &= -\hbar\omega \mathbf{P} \cdot \boldsymbol{\varepsilon} / |\boldsymbol{\varepsilon}|^2 \\ &= -\hbar\omega(\eta - 1) \\ &= 4\pi \rho e^2 \hbar / m\omega, \end{aligned}$$

which is the potential energy term of equation (6).

In a crystal, the electron density is:

$$\rho(\mathbf{r}) = \sum_{\mathbf{g}} \rho_{\mathbf{g}} \exp 2\pi i \mathbf{g} \cdot \mathbf{r},$$

where $\rho(\mathbf{r})$ is the electron density at point \mathbf{r} and the $\rho_{\mathbf{g}}$ are Fourier coefficients associated with reciprocal lattice points \mathbf{g} of the crystal.

Dispersion equations

The solution of (1) and (6) are Bloch waves of the form:

$$\psi(\mathbf{k}) = \sum_{\mathbf{g}} \exp 2\pi i (\mathbf{k} + \mathbf{g}) \cdot \mathbf{r}.$$

Solutions for the coefficients $C_{\mathbf{g}}$ can only be found if the wave vectors \mathbf{k} in the crystal satisfy the dispersion equations (Hirsch *et al.*, 1965):

$$[K^2 - (\mathbf{k} + \mathbf{g})^2] C_{\mathbf{g}}(\mathbf{k}) + \sum_{\mathbf{h} \neq 0} U_{\mathbf{h}} C_{\mathbf{g}-\mathbf{h}}(\mathbf{k}) = 0, \quad (7)$$

where for the electron case:

$$K^2 = (2m/h^2) [E + V_0]$$

$$U_g = (2m/h^2) V_g,$$

and for the X-ray case:

$$K^2 = c^{-2} [v^2 - 4\pi Q_0 e^2 / m\pi] \quad (8)$$

$$U_g = -e^2 Q_g / (\pi m c^2).$$

Since in the X-ray case η is only very slightly greater than unity, \mathbf{D} can replace ϵ in (6) with negligible error. The solutions of (7), therefore, give the allowed values of the wave vector \mathbf{k} for each Bloch wave excited in the crystal.

Discussion

The above treatment of dynamical theory gives explicitly the close relation between X-ray and electron scattering by crystals and shows in detail why the dispersion equations for the two phenomena have a similar form. The usual treatment of X-ray dynamical theory, following Laue (1931) and James (1958) assumes that the 'polarizability', $(1 - 1/\eta)$, is a periodic function of the lattice and then Bloch wave solutions are inserted into the basic Maxwell equations. As

shown above, however, manipulation of the Maxwell equations gives a 'single photon Schrödinger equation' in which the potential energy term is the fraction of the photon energy stored in the polarized lattice. The Bloch wave solutions and dispersion relationships then follow because of the periodic electron density in the lattice. The mathematical formalism is, thus, somewhat simplified, and the analogy to electron diffraction by a periodic potential is made obvious.

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A note on Cerrini's paper 'Tensor analysis of the harmonic vibrations of atoms in crystals'. By D. W. J. CRUICKSHANK, *Chemistry Department, University of Manchester Institute of Science and Technology, Manchester M60 1QD, England*

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Comments are made on papers by Cerrini, Cruickshank and Scheringer on representations of the harmonic vibration tensor \mathbf{U} with respect to different bases.

The paper by Cerrini (1971) on anisotropic harmonic vibrations in affine (triclinic) coordinate systems is very helpful in clarifying my paper (Cruickshank, 1956) and its relation to the apparently contradictory analysis of Scheringer (1966). The 1956 paper was less explicit than it should have been, and it would have been much better if it had used, as Cerrini has used, the upper- and lower-suffix notation for contravariant and covariant tensor components. The attempt in 1956 to keep the notation simple has led to some confusion, and an indication now of what should have been added to the 1956 paper and of its relation to a 1961 paper may be helpful.

Cerrini uses the following symbols for base axes: \mathbf{a}_i ($i=1,2,3$) are the direct axes, and \mathbf{a}^i are the corresponding reciprocal axes ($\mathbf{a}_i \cdot \mathbf{a}^j = \delta_i^j$). These are called the frame $(\mathbf{a}_i, \mathbf{a}^i)$, and $(\mathbf{e}_i, \mathbf{e}^i)$ is the frame for which \mathbf{e}_i are unit vectors parallel to \mathbf{a}_i ; the \mathbf{e}^i are parallel to \mathbf{a}^i , but are not of unit length for general triclinic direct axes. $(\mathbf{f}_i, \mathbf{f}^i)$ is the frame for which \mathbf{f}^i are unit vectors parallel to \mathbf{a}^i ; the \mathbf{f}_i are parallel to \mathbf{a}_i , but are not of unit length for general triclinic direct axes. Sets $\mathbf{e}_i, \mathbf{e}^i, \mathbf{f}_i, \mathbf{f}^i$ are identical and of unit lengths only when \mathbf{a}_i (hence also \mathbf{a}^i) are an orthogonal set. [The reader should beware of the misprint in the third line of the third paragraph of Cerrini's 'Introduction' where the direct axes are printed \mathbf{a}^i in error for \mathbf{a}_i . A misprint also occurs in the middle of the left-hand column of p. 132 where $U_{ii}(\cos \theta_i)^2$ should read $U^{ii}(\cos \theta_i)^2$.]

A confusion in notation that can occur is that the symbol \mathbf{x} may be used to denote either a vector or a set of vector components. Of itself, the vector has no algebraic form, but when a frame $(\mathbf{a}_i, \mathbf{a}^i)$ is defined, we write

$$\mathbf{x} = x^1 \mathbf{a}_1 + x^2 \mathbf{a}_2 + x^3 \mathbf{a}_3$$

$$= x_1 \mathbf{a}^1 + x_2 \mathbf{a}^2 + x_3 \mathbf{a}^3.$$

The point to be watched comes if the component array (x^1, x^2, x^3) is called \mathbf{x} . In tensor language both (x^1, x^2, x^3) and (x_1, x_2, x_3) , together with an infinity of arrays for other frames, are all representations of the vector \mathbf{x} . Similarly, symbol \mathbf{U} , according to context, may denote either the vibration tensor \mathbf{U} or one of the 3×3 matrix arrays U^{ij} and U_{ij} , which are the contravariant and covariant representations of the tensor with respect to the frame $(\mathbf{a}_i, \mathbf{a}^i)$.

Cerrini's discussion shows that in equations (1.5)–(1.7) and the Appendix of my 1956 paper symbols \mathbf{x} and \mathbf{U} are the contravariant arrays x^i and U^{ij} , and the 1956 symbols ' x_i ' and ' U_{ij} ' are also these contravariant arrays, while the symbols s and s_i are the covariant array s_i . The 1956 symbol \mathbf{U}^{-1} is Cerrini's covariant array V_{ij} . With these interpretations, equations (1.5)–(1.7) and the Appendix are true for any frame $(\mathbf{a}_i, \mathbf{a}^i)$.

In equations (2.1) and (2.2), a particular choice of reciprocal base is implicit in the exponential term

$$\exp [-2\pi^2 (h^2 a^{*2c} U_{11} + \dots)].$$