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A Density-Matrix Approach to Coherence in High-Energy Electron Diffraction

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Abstract

It is shown that a density-matrix formalism may be used to analyse various aspects of coherence in high-energy electron diffraction theory. This approach is demonstrated by two examples: an analysis of the coherence between two Bloch waves generated by diffuse scattering as a function of crystal thickness (the dependent-to-independent Bloch-wave 'transition') and an analysis of the coherence between electrons which are diffusely scattered in different directions and their contribution to high-resolution images.

1. Introduction

Using density-matrix theory one can fully describe a quantum or statistical system even if one cannot construct the exact wave function for the system (*e.g.* Blum, 1981). To quote Ziman (1969), 'we cannot learn more than is given by the density matrix; it is all we know and all we need to know about the "state" of the system'. One important feature of the density matrix is that it contains information about the correlation or coherence between the states of a quantum system; this is manifested in the off-diagonal elements of the relevant density matrix. The effects of interactions on the system are described by the Liouville equation which governs the evolution of the density matrix. Physical observables are then readily found by operating on the resulting matrix.

There are many different kinds of scattering experiments where a density-matrix description provides a convenient framework in which to describe the coherence among the states involved in the scattering. These include photon (*e.g.* Loudon, 1983), electron (*e.g.* Blum, 1981) and neutron (*e.g.* Balcar & Lovesey, 1989) scattering. The question of coherence arises in several contexts in high-energy electron diffraction theory. One obvious case is in high-resolution imaging, where the coherently diffracted beams are reconstructed (albeit with the effects of lens aberrations) to form an image. A more difficult question concerns the role of diffusely scattered electrons in high-resolution imaging (Cowley, 1988). Do these simply provide a uniform background, or do they also contribute to form a 'background' lattice image? The answer must lie in the degree of coherence between electrons which have been diffusely scattered to different points in the diffraction plane. A second area where coherence has been widely discussed is in the detailed mechanism of inelastic and diffuse scattering processes. A number of questions arise here, such as whether diffusely and inelastically scattered electrons preserve diffraction image contrast (*e.g.* Howie, 1963; Rez, Humphreys & Whelan, 1977) and whether dependent or independent Bloch-wave models provide the most appropriate description (*e.g.* Cherns, Howie & Jacobs, 1973; Wright & Bird, 1989, and references therein). There has been some confusion about what exactly is meant by coherence in this case: what precisely is coherent (or otherwise) with what? Our aim in this paper is to show that a density-matrix approach provides a unifying description which encompasses all these areas where coherence is the issue. The use of density matrices is not new in diffraction and channelling theory. Rez (1977) and Dudarev & Ryazanov (1988) set up a formalism to analyse multiple elastic and inelastic scattering but they do not attempt to analyse detailed questions of coherence. Kagan & Kononets (1973, 1974) discuss the use of density matrices in the theory of particle channelling and analyse the damping of the off-diagonal elements of the matrix (see below) due to inelastic scattering. However, they do not discuss aspects of the theory which are specific to high-energy electron scattering. The results we derive are not new and can be found without density-matrix theory. Nevertheless, our analysis shows how correlation and coherence can be discussed in a rigorous

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quantum-mechanical theory, leading to a better understanding of how different forms of coherence are related to each other.

In § 2 an outline of density-matrix theory is presented which sets up the formal framework and gives the basic results which can be used in any particular case. We concentrate on thermal diffuse scattering (TDS) in crystals, and in §§ 3 and 4 discuss two examples of coherency in TDS. § 3 concerns the coherence between Bloch waves generated by diffuse scattering events which is observed in the form of subsidiary fringes on Kikuchi bands which disappear with increasing crystal thickness. This is an example of the dependent-to-independent Bloch-wave 'transition' which is observed in many cases of inelastic scattering (Wright & Bird, 1989). In § 4 we discuss the contribution of diffusely scattered electrons to high-resolution images. The analysis shows that, regardless of dynamical diffraction effects, *any* two points in the diffraction plane which are separated by a reciprocal-lattice vector will be coherent with one another and are therefore capable of giving rise to lattice fringes. Concluding remarks are made in § 5.

2. Basics of density-matrix theory

There are several books which give a thorough exposition of density-matrix theory, for example that by Blum (1981). Here, we give a brief outline to introduce the notation that will be used later. Consider a collection of states $\{|\psi_n\rangle\}$, not necessarily orthogonal to one another. W_n is the probability that the system is in the state $|\psi_n\rangle$. The density matrix is defined by

$$\rho = \sum_n W_n |\psi_n\rangle\langle\psi_n|. \qquad (1)$$

We assume that each state $|\psi_n\rangle$ can be expanded in terms of an orthonormal set of basis states $\{|\varphi_m\rangle\}$

$$|\psi_n\rangle = \sum_m a^n_m |\varphi_m\rangle, \qquad (2)$$

in which case the density matrix becomes

$$\rho = \sum_{n,m,m'} W_n a^n_{m'} a^{n*}_m |\varphi_{m'}\rangle\langle\varphi_m| \qquad (3)$$

and its individual elements in the $\{|\varphi_m\rangle\}$ representation are

$$\rho_{m'm} = \langle\varphi_{m'}|\rho|\varphi_m\rangle = \sum_n W_n a^n_{m'} a^{n*}_m. \qquad (4)$$

The diagonal elements, ρ_{mm}, of ρ give the probability of finding the system in state $|\varphi_m\rangle$, while the off-diagonal elements, $\rho_{m'm}$, represent the degree of correlation between basis states $|\varphi_m\rangle$ and $|\varphi_{m'}\rangle$. Physical observables are described in terms of the expectation value of an operator, $\hat{O}$, averaged appropriately over the system. For the mixture of states that make up the system,

$$\begin{aligned}\bar{O} &= \sum_n W_n \langle\psi_n|\hat{O}|\psi_n\rangle \\ &= \sum_{nmm'} W_n a^n_{m'} a^{n*}_m \langle\varphi_m|\hat{O}|\varphi_{m'}\rangle \\ &= \sum_{mm'} \langle\varphi_{m'}|\rho|\varphi_m\rangle\langle\varphi_m|\hat{O}|\varphi_{m'}\rangle = \mathrm{tr}\,(\rho\hat{O}),\end{aligned} \qquad (5)$$

where tr represents the trace of the matrix product. In this way the value of any physical quantity can be extracted from the density matrix.

The wave function of the system varies with time according to the time-dependent Schrödinger equation (TDSE)

$$i\hbar[\partial|\psi(t)\rangle/\partial t] = H(t)|\psi(t)\rangle. \qquad (6)$$

From this one can derive the Liouville equation which governs the evolution of the density matrix (*e.g.* Blum, 1981)

$$i\hbar[\partial\rho(t)/\partial t] = [H(t), \rho(t)], \qquad (7)$$

where [,] is the commutator. Let the Hamiltonian be separated as

$$H(t) = H_0 + V(t), \qquad (8)$$

where the eigenvalues, E_n, and eigenvectors, $|\varphi_n\rangle$, of H_0 are known. In terms of the $\{|\varphi_n\rangle\}$ states the Liouville equation becomes

$$\begin{aligned}i\hbar(\partial\rho_{m'm}/\partial t) &= (E_{m'} - E_m)\rho_{m'm} \\ &\quad + \sum_n (V_{m'n}\rho_{nm} - \rho_{m'n}V_{nm}),\end{aligned} \qquad (9)$$

where $V_{nm} = \langle\varphi_n|V|\varphi_m\rangle$. This can be transformed using

$$\rho_{m'm} = \tilde{\rho}_{m'm} \exp[-it(E_{m'} - E_m)/\hbar] \qquad (10)$$

to give

$$i\hbar(\partial\tilde{\rho}_{m'm}/\partial t) = \sum_n (\tilde{V}_{m'n}\tilde{\rho}_{nm} - \tilde{\rho}_{m'n}\tilde{V}_{nm}) \qquad (11)$$

with

$$\tilde{V}_{nm} = V_{nm} \exp[it(E_n - E_m)/\hbar]. \qquad (12)$$

This is the form we will use in subsequent calculations. The division between the known Hamiltonian H_0 and the perturbation V is chosen according to the problem in hand.

We use an iterative method to solve (11), similar to a perturbation expansion in conventional quantum mechanics. V is rewritten as λV and the density matrix is expressed as a power series in λ

$$\tilde{\rho} = \tilde{\rho}^{(0)} + \lambda\tilde{\rho}^{(1)} + \lambda^2\tilde{\rho}^{(2)} + \ldots. \qquad (13)$$

This is substituted into (11) and powers of λ are equated. We obtain

$$i\hbar(\partial\tilde{\rho}^{(1)}/\partial t) = \tilde{\mathbf{V}}\tilde{\rho}^{(0)} - \tilde{\rho}^{(0)}\tilde{\mathbf{V}}, \qquad (14a)$$

$$i\hbar(\partial\tilde{\rho}^{(2)}/\partial t) = \tilde{\mathbf{V}}\tilde{\rho}^{(1)} - \tilde{\rho}^{(1)}\tilde{\mathbf{V}}, \qquad (14b)$$

and so on for the higher $\rho^{(n)}$. In (14), $\tilde{\mathbf{V}}$ is the matrix of the $\tilde{V}_{nm}$ and $\rho^{(0)}$ is the initial density matrix at $t=0$. Finally, we set $\lambda=1$ in (13). In this way the density matrix is expanded essentially as a Born series, with each term including a higher power of the perturbing potential, V.

In both examples to be discussed later there are three basis states ($\varphi_0, \varphi_1, \varphi_2$) and ρ_{mn} is therefore a 3×3 matrix. In both cases the initial conditions give $\tilde{\rho}^{(0)}_{00}=1$, with all other elements of $\tilde{\rho}^{(0)}$ being zero. In this case it is straightforward to integrate (14a) and (14b) and to second order in V the elements of $\tilde{\rho}$ which refer to states φ_1 and φ_2 become

$$\begin{aligned}
\hbar^2\tilde{\rho}_{11}(t) &= \left[\int_0^t \mathrm{d}t_1\, \tilde{V}_{10}(t_1)\right] \times \left[\int_0^t \mathrm{d}t_2\, \tilde{V}_{01}(t_2)\right],\\
\hbar^2\tilde{\rho}_{12}(t) &= \left[\int_0^t \mathrm{d}t_1\, \tilde{V}_{10}(t_1)\right] \times \left[\int_0^t \mathrm{d}t_2\, \tilde{V}_{02}(t_2)\right],\\
\hbar^2\tilde{\rho}_{21}(t) &= \left[\int_0^t \mathrm{d}t_1\, \tilde{V}_{20}(t_1)\right] \times \left[\int_0^t \mathrm{d}t_2\, \tilde{V}_{01}(t_2)\right],\\
\hbar^2\tilde{\rho}_{22}(t) &= \left[\int_0^t \mathrm{d}t_1\, \tilde{V}_{20}(t_1)\right] \times \left[\int_0^t \mathrm{d}t_2\, \tilde{V}_{02}(t_2)\right].
\end{aligned} \qquad (15)$$

The reason for singling out these elements will be discussed later. In any analysis of scattering the basis states will correspond to various scattered waves and V will represent a scattering potential. It follows that $\tilde{\rho}_{11}$ and $\tilde{\rho}_{22}$ basically give the 'intensities' of states φ_1 and φ_2, while $\tilde{\rho}_{12}$ and $\tilde{\rho}_{21}$ describe the coherence between φ_1 and φ_2. It is important to realize that these second-order expressions refer to *single* scattering in the perturbing potential V. The reason is that ρ is constructed from pairs of amplitudes and for scattering to occur both parts must change. In this paper we consider only the single-scattering expressions given by (15) and so we are limited to crystal thicknesses smaller than the relevant scattering lengths. However, the same formalism can in principle be used to analyse multiple scattering in V; this is done by including higher-order iterations of (13) and (14).

How are these results applied to high-energy electron diffraction? In principle, of course, electron diffraction is governed by the Schrödinger equation and so all the above analysis applies. However, in this paper we concentrate on the case of thermal diffuse scattering in which any energy loss or gain is not resolved and so, in effect, there is no energy transferred between the fast electron and the crystal. In this case, each fast electron 'sees' an instantaneous frozen arrangement of atoms and the scattering from these different potentials are averaged in the appropriate way at the end of the calculation (*e.g.* Dederichs, 1972). As we shall see, the question of coherence arises when these thermal averages are made. When analysing TDS, therefore, the true time dependence of the Schrödinger equation vanishes, and we may use the standard approach to elastic diffraction theory [*e.g.* Bird (1989), whose notation we follow]. In the forward-scattering approximation, the fast-electron wavefunction, $\Phi(\mathbf{r})$, is governed by the equation

$$[-\nabla^2_{\mathbf{R}} + U(\mathbf{r})]\Phi(\mathbf{r}) = 2ik(\partial\Phi/\partial z). \qquad (16)$$

Here, k is the fast-electron wavevector, $U(\mathbf{r})$ represents the (instantaneous) crystal potential felt by the electrons (it is $2m/\hbar^2$ times the actual potential, where m is the relativistic electron mass) and $\nabla^2_{\mathbf{R}}$ acts only on the transverse component of $\mathbf{r}$. We use the convention that any vector $\mathbf{v}$ (in either real or reciprocal space) is separated into transverse and z components as $\mathbf{v}\equiv(\mathbf{V}, v_z)$. The three-dimensional position vector $\mathbf{r}$ then becomes $(\mathbf{R}, z)$. The crystal surfaces lie in the planes $z=0$ and $z=t$ (where t is the crystal thickness) and the fast electrons are incident close to the z axis. The relationship with the above density-matrix theory emerges when we observe that (16) has the same form as the Schrödinger equation (6), with the correspondence

$$r\rightarrow\mathbf{R}, \quad t\rightarrow z, \quad \hbar(\partial/\partial t)\rightarrow 2k(\partial/\partial z). \qquad (17)$$

It follows that the depth through the crystal, z, takes the place of time in the TDSE, and the three spatial dimensions of the TDSE have been replaced by the planar coordinate, $\mathbf{R}$. By analogy with (11), the Liouville equation in high-energy electron diffraction then becomes

$$2ik(\partial\tilde{\rho}_{m'm}/\partial z) = \sum_n (\widetilde{\delta U}_{m'n}\tilde{\rho}_{nm} - \tilde{\rho}_{m'n}\widetilde{\delta U}_{nm}) \qquad (18)$$

with

$$\widetilde{\delta U}_{nm} = \delta U_{nm} \exp\,[iz(s_n - s_m)/2k] \qquad (19a)$$

and

$$\begin{aligned}
\delta U_{nm} &= \langle\varphi_n|\delta U|\varphi_m\rangle\\
&= \int \mathrm{d}\mathbf{R}\, \varphi^*_n(\mathbf{R})\delta U(\mathbf{R}, z)\varphi_m(\mathbf{R}).
\end{aligned} \qquad (19b)$$

Here, δU is the part of the potential taken to be the perturbation, and φ_m and s_m are the eigenvectors and eigenvalues respectively of the unperturbed Hamiltonian $\nabla^2_{\mathbf{R}} + U_0(\mathbf{R})$. It is assumed that U_0 represents some kind of average potential which is not z dependent and is not affected by thermal averaging. Any thermal fluctuations will be included in the perturbation δU.

The solution of (18) and the extraction of physical observables proceeds in much the same way as described above. There is one significant difference, however, which concerns the thermal averages implicit in our analysis of TDS. In effect, we want the *thermal average* of ρ (which we write as $\langle\rho\rangle$) rather than ρ itself. Each electron passing through the instantaneously distorted crystal suffers only elastic scattering. Of interest are the properties built up by the passage of many electrons. It follows from (5) that $\langle\rho\rangle$ must be the important quantity because the average of any observable is $\langle\mathrm{tr}\,(\rho\hat{O})\rangle$ and, provided $\hat{O}$ itself does not depend on the thermal fluctuations, this reduces to $\mathrm{tr}\,(\langle\rho\rangle\hat{O})$. In practice $\langle\rho\rangle$ is found by averaging (13) term by term and so, for example, the second-order results (15) become

$$\begin{aligned}
4k^2\langle\tilde{\rho}_{11}(z)\rangle &= \left\langle\left[\int_0^z \mathrm{d}z_1\,\widetilde{\delta U}_{10}(z_1)\right]\left[\int_0^z \mathrm{d}z_2\,\widetilde{\delta U}_{01}(z_2)\right]\right\rangle,\\
4k^2\langle\tilde{\rho}_{12}(z)\rangle &= \left\langle\left[\int_0^z \mathrm{d}z_1\,\widetilde{\delta U}_{10}(z_1)\right]\left[\int_0^z \mathrm{d}z_2\,\widetilde{\delta U}_{02}(z_2)\right]\right\rangle,\\
4k^2\langle\tilde{\rho}_{21}(z)\rangle &= \left\langle\left[\int_0^z \mathrm{d}z_1\,\widetilde{\delta U}_{20}(z_1)\right]\left[\int_0^z \mathrm{d}z_2\,\widetilde{\delta U}_{01}(z_2)\right]\right\rangle,\\
4k^2\langle\tilde{\rho}_{22}(z)\rangle &= \left\langle\left[\int_0^z \mathrm{d}z_1\,\widetilde{\delta U}_{20}(z_1)\right]\left[\int_0^z \mathrm{d}z_2\,\widetilde{\delta U}_{02}(z_2)\right]\right\rangle.
\end{aligned}\tag{20}$$

It is important to note that we cannot use (18) to obtain an equation for $\langle\rho\rangle$ directly because on the right-hand side both $\tilde{\rho}$ and $\widetilde{\delta U}$ depend on the instantaneous configuration and we cannot split the combined average, $\langle\tilde{\rho}\widetilde{\delta U}\rangle$.

To summarize, (18) represents the basic equation of our theory. The second-order solutions (which, as discussed above, correspond to *single* thermal diffuse scattering) for the relevant elements of the density matrix are given by (20). Physical observables are calculated from $\langle\rho\rangle$ using (5) with the appropriate operator $\hat{O}$.

3. Coherence between diffusely scattered Bloch waves

The first example of the use of density-matrix theory concerns the coherence between the electron waves which contribute to thermal diffuse scattering in a particular direction in the diffraction pattern. The scattered distribution is observed in the form of a Kikuchi pattern and the question of coherence arises in the visibility of the subsidiary fringes which surround Kikuchi bands in relatively thin crystals (Wright & Bird, 1989, and references therein). We shall take the simplest case of a single plane wave entering the crystal and being diffusely scattered into a direction where only two Bloch waves are significantly excited.

The full instantaneous scattering potential, $U(\mathbf{r})$, is divided into its thermal average, $\langle U(\mathbf{r})\rangle$, and the fluctuation, $\delta U(\mathbf{r})$, so

$$U(\mathbf{r}) = \langle U(\mathbf{r})\rangle + \delta U(\mathbf{r}). \tag{21}$$

The unperturbed Hamiltonian is

$$H_0 = -\nabla^2_{\mathbf{R}} + U_0(\mathbf{R}), \tag{22}$$

where the two-dimensional potential $U_0(\mathbf{R})$ has replaced $\langle U\rangle$, that is, we have made the standard *projection approximation* of high-energy electron diffraction theory (*e.g.* Bird, 1989). The eigenstates, $\varphi_n(\mathbf{R})$, with 'energy' s_n form the basis of our density-matrix representation. Three states are used to describe the incoming and outgoing waves. We assume for simplicity that the incident plane wave, $\exp\,(i\mathbf{K}\cdot\mathbf{R})$, is undiffracted by the average potential. It is then scattered by the fluctuating potential into a direction, $\mathbf{K}'$, where two Bloch waves of U_0 are excited. The three states are then

$$\begin{aligned}
\varphi_0 &= \exp\,(i\mathbf{K}\cdot\mathbf{R}),\\
\varphi_1 &= \exp\,(i\mathbf{K}'\cdot\mathbf{R})[C_{\mathbf{0}}^{(1)} + C_{\mathbf{G}}^{(1)}\exp\,(i\mathbf{G}\cdot\mathbf{R})],\\
\varphi_2 &= \exp\,(i\mathbf{K}'\cdot\mathbf{R})[C_{\mathbf{0}}^{(2)} + C_{\mathbf{G}}^{(2)}\exp\,(i\mathbf{G}\cdot\mathbf{R})],
\end{aligned}\tag{23}$$

with eigenvalues $s_0(=K^2)$, $s_1(\mathbf{K}')$ and $s_2(\mathbf{K}')$. $\mathbf{G}$ is the diffracting reciprocal-lattice vector of the two-beam geometry. Explicit expressions for the Bloch-wave coefficients $C_{\mathbf{0},\mathbf{G}}^{(1,2)}$ and eigenvalues can be found in two-beam theory (*e.g.* Hirsch, Howie, Nicholson, Pashley & Whelan, 1977; Bird & Wright, 1989), but we are not interested in those details here.

The observable we wish to calculate is the intensity scattered in the $\mathbf{K}'$ direction. This is extracted by multiplying ρ by an observable matrix, $\hat{O}_{\mathbf{K}'}$, and taking the trace (5). The $\hat{O}_{\mathbf{K}'}$ operator simply projects out the $\exp\,(i\mathbf{K}'\cdot\mathbf{R})$ part of the state it operates on, and so

$$\hat{O}_{\mathbf{K}'} = \begin{pmatrix} 0 & 0 & 0\\ 0 & C_{\mathbf{0}}^{(1)*}C_{\mathbf{0}}^{(1)} & C_{\mathbf{0}}^{(1)*}C_{\mathbf{0}}^{(2)}\\ 0 & C_{\mathbf{0}}^{(2)*}C_{\mathbf{0}}^{(1)} & C_{\mathbf{0}}^{(2)*}C_{\mathbf{0}}^{(2)} \end{pmatrix}. \tag{24}$$

The intensity scattered into the $\mathbf{K}'$ direction from a crystal of thickness t then becomes

$$\begin{aligned}
I_{\mathbf{K}'} &= \langle\mathrm{tr}\,(\rho\hat{O}_{\mathbf{K}'})\rangle\\
&= \sum_{i=1,2}\sum_{j=1,2}\langle\tilde{\rho}_{ij}(t)\rangle C_{\mathbf{0}}^{(j)*}C_{\mathbf{0}}^{(i)}\exp\,[-it(s_i-s_j)/2k].
\end{aligned}\tag{25}$$

It follows that only four elements of the density matrix control this intensity, and the second-order expressions for these are given by (20).

The problem now reduces to one of calculating the density-matrix elements of (20). These are evaluated in the Appendix, using the Einstein approximation for the atomic vibrations. By combining (20), (23), (25), (*A*9) and (*A*10) one can show that $I_{\mathbf{K}'}$ reduces (as it must) to the standard expression for the TDS intensity in single-scattering theory (*e.g.* Bird & Wright, 1989, and references therein). However, a re-derivation of these results is not the point of our analysis. The density-matrix formalism also enables us to discuss the correlation between the states involved in the scattering, in this case the coherence of Bloch waves φ_1 and φ_2, which is reflected in the relative sizes of the diagonal and off-diagonal elements of ρ. In turn, these are essentially determined by the magnitude of the thickness integral term (*A*10).

For the diagonal elements ρ_{11} and ρ_{22} the $(q_{1z}-q_{2z})$ factor is zero, while for ρ_{12} and ρ_{21} it has magnitude $|[s_1(\mathbf{K}')-s_2(\mathbf{K}')]/2k|$. Only ρ_{12} and ρ_{21} are therefore thickness dependent and the coherence they represent between Bloch waves 1 and 2 is manifested in the Kikuchi-band fringes discussed by Wright & Bird (1989). As t increases, however, the off-diagonal components reduce in size relative to the diagonal elements which indicates that the coherence between Bloch waves 1 and 2 is gradually lost. Wright & Bird (1989) showed how this leads to the visibility of the Kikuchi band fringes decreasing with increasing thickness. The physical origin of the coherence loss is clear from ($A9$) and ($A10$). It arises from the sum (integral) over the crystal thickness, which corresponds physically to a sum over different *sources* for the diffusely scattered waves. If there were only one source, the waves generated from it would be perfectly coherent [*i.e.* the limit as t goes to zero in ($A10$)]. However, the waves generated by a number of sources spread throughout the crystal thickness steadily become incoherent with one another. This is analogous to the situation in optics where a point monochromatic source produces coherent light, but the coherence volume is reduced as the source size increases. In that case, the coherence loss is observed, for example, as a reduction of fringe visibility in a Young's slits experiment.

The loss of coherence between Bloch waves generated throughout the finite thickness of a crystal is a common feature of many diffuse and inelastic scattering experiments, and is often referred to as a 'transition' between dependent (*i.e.* coherent) and independent (incoherent) Bloch waves (Wright & Bird, 1989, and references therein). It can be seen that the density-matrix formalism provides a rigorous framework in which to analyse the degree of coherence which exists. Although we have discussed only single scattering here it is clear that higher-order iterations of (14) could in principle be used to analyse multiple diffuse scattering and the coherence of the waves involved would still be manifested in the relative sizes of the diagonal and off-diagonal elements of ρ.

4. Coherence of electrons diffusely scattered in different directions

Our first example concerned the coherence between two states of an electron travelling in a given direction in a crystal. We now address the question of whether electrons travelling in different directions after being diffusely scattered are coherent with one another. The significance of this arises in the context of high-resolution imaging and the extent to which the diffusely scattered electrons contribute to a lattice image (Cowley, 1988). Again, we find that the density-matrix formalism developed in § 2 is directly applicable here.

To keep the analysis as simple as possible we ignore all diffraction on the incoming and outgoing waves, in which case the basis states become plane waves. There are again three states:

$$\begin{aligned}\varphi_0&=\exp(i\mathbf{K}_0\cdot\mathbf{R}), & s_0&=K_0^2,\\ \varphi_1&=\exp(i\mathbf{K}_1\cdot\mathbf{R}), & s_1&=K_1^2,\\ \varphi_2&=\exp(i\mathbf{K}_2\cdot\mathbf{R}), & s_2&=K_2^2,\end{aligned}\tag{26}$$

where $\mathbf{K}_0$, $\mathbf{K}_1$ and $\mathbf{K}_2$ are the transverse wavevectors of the incoming wave and two outgoing waves respectively. The diffuse scattering potential will again be taken to be the δU of (21), so all the analysis in § 2 and the Appendix still applies. For example, the density-matrix elements of (20) become

$$\begin{aligned}\tilde{\rho}_{ij}&=(4k^2)^{-1}u(\mathbf{q}_1)u^*(\mathbf{q}_2)S(\mathbf{q}_1,-\mathbf{q}_2)\\ &\quad\times\sum_{\mathbf{l}}\exp[i(\mathbf{q}_2-\mathbf{q}_1)\cdot\mathbf{l}]\end{aligned}\tag{27}$$

where the relevant values of $\mathbf{q}_1$ and $\mathbf{q}_2$ are

for ρ_{11}:

$$\begin{aligned}\mathbf{q}_1&=[\mathbf{K}_1-\mathbf{K}_0,(K_0^2-K_1^2)/2k],\\ \mathbf{q}_2&=[\mathbf{K}_1-\mathbf{K}_0,(K_0^2-K_1^2)/2k];\end{aligned}\tag{28a}$$

for ρ_{12}:

$$\begin{aligned}\mathbf{q}_1&=[\mathbf{K}_1-\mathbf{K}_0,(K_0^2-K_1^2)/2k],\\ \mathbf{q}_2&=[\mathbf{K}_2-\mathbf{K}_0,(K_0^2-K_2^2)/2k];\end{aligned}\tag{28b}$$

for ρ_{21}:

$$\begin{aligned}\mathbf{q}_1&=[\mathbf{K}_2-\mathbf{K}_0,(K_0^2-K_2^2)/2k],\\ \mathbf{q}_2&=[\mathbf{K}_1-\mathbf{K}_0,(K_0^2-K_1^2)/2k];\end{aligned}\tag{28c}$$

for ρ_{22}:

$$\begin{aligned}\mathbf{q}_1&=[\mathbf{K}_2-\mathbf{K}_0,(K_0^2-K_2^2)/2k],\\ \mathbf{q}_2&=[\mathbf{K}_2-\mathbf{K}_0,(K_0^2-K_2^2)/2k].\end{aligned}\tag{28d}$$

If we are just interested in the intensity scattered into $\mathbf{K}_1$ and $\mathbf{K}_2$ then only ρ_{11} and ρ_{22} are relevant and, as expected, we recover the standard kinematic results for the TDS intensity (*e.g.* Cowley, 1981). The correlation between the scattered waves is carried by ρ_{12} and ρ_{21}.

To be specific we consider forming an image from just the $\mathbf{K}_1$ and $\mathbf{K}_2$ waves, which could be realized by placing a pair of small apertures at the appropriate points in the diffraction plane. If, at the exit surface of the crystal, these have amplitudes A_1 and A_2 respectively, the image intensity becomes

$$\begin{aligned}I(\mathbf{R})&=\langle|A_1\exp(i\mathbf{K}_1\cdot\mathbf{R})+A_2\exp(i\mathbf{K}_2\cdot\mathbf{R})|^2\rangle\\ &=\langle|A_1|^2\rangle+\langle|A_2|^2\rangle+2\langle|A_1A_2^*|\rangle\\ &\quad\times\cos[(\mathbf{K}_1-\mathbf{K}_2)\cdot\mathbf{R}+\theta],\end{aligned}\tag{29}$$

where θ is the phase of $\langle A_1A_2^*\rangle$ and $\langle\,\rangle$ again indicates that a thermal average has been taken. Equation (29) shows that fringes are formed with period $2\pi/|\mathbf{K}_1-\mathbf{K}_2|$; the phase θ is an unimportant origin shift. The amplitude combinations which appear in (29) are just the elements of the averaged density matrix [see (4)] and the visibility of the fringes is therefore given by

$$\begin{aligned} V &= (\max-\min)/(\max+\min) \\ &= 2|\langle\rho_{12}\rangle|/(\langle\rho_{11}\rangle+\langle\rho_{22}\rangle). \end{aligned} \tag{30}$$

The fringe visibility is therefore directly controlled by the size of the off-diagonal terms of the density matrix.

As in § 3 the relative size of the diagonal and off-diagonal terms is controlled by the lattice sums in (27). We first note that $\mathbf{Q}_1$ and $\mathbf{Q}_2$ can differ only by a $\mathbf{G}$ vector, so no fringes will be observed unless $\mathbf{K}_1$ and $\mathbf{K}_2$ are separated by a $\mathbf{G}$ vector. Assuming this is the case, we write $\mathbf{K}_2=\mathbf{K}_1+\mathbf{G}$, in which the contribution from (*A*10) to the visibility becomes

$$\begin{aligned} \mathbf{V} &\sim \sin[(2\mathbf{K}_1\cdot\mathbf{G}+\mathbf{G}^2)t/2k] \\ &\quad\times[(2\mathbf{K}_1\cdot\mathbf{G}+\mathbf{G}^2)t/2k]^{-1}. \end{aligned} \tag{31}$$

The visibility therefore varies considerably, depending both on the thickness and on the positions of the two scattered waves in the diffraction plane. Interestingly, (31) shows that waves on either side of the $\mathbf{G}$ Kikuchi band (so $2\mathbf{K}_1\cdot\mathbf{G}+\mathbf{G}^2=0$) are perfectly coherent. This result must break down in dynamical theory because these orientations correspond exactly to the Bragg condition for the outgoing waves. However, there does seem to be a considerable degree of coherence between the diffusely scattered waves. It must be emphasized that this is not related to diffraction of the outgoing waves - it arises purely from consideration of the source of the scattered waves and the extent to which the source is localized or extended. Although these results indicate that the TDS background could contribute to a lattice image, it is clearly necessary to extend the work here to include the interactions between all the scattered waves and to include the effects of dynamical diffraction (Bird & Wright, 1992).

5. Concluding remarks

The most rigorous way to analyse coherence and correlation in scattering theory is through the use of density matrices. We have shown how this approach can be used in thermal diffuse scattering to produce expressions for the thermally averaged density matrix. The examples demonstrate that, as well as being very general, the formalism is also highly flexible and can be used to tackle questions of coherence in a variety of contexts. In this paper we have attempted only to discuss the framework of the theory. However, there are a number of extensions of the examples discussed here which will be the subject of a forthcoming paper (Bird & Wright, 1992). One is the extent to which multiple diffuse scattering preserves or destroys the coherence between Bloch waves found in § 3. This can be analysed by extending the perturbation expansion (13) of ρ to higher terms and investigating the effect on the off-diagonal terms. The second is to continue the analysis of § 4 to look at the full TDS contribution to a lattice image, including the effects of all the scattered waves and their dynamical interactions.

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APPENDIX

In this Appendix we evaluate the matrix elements of the thermally fluctuating potential. In both examples discussed in the paper the second-order expressions for the density-matrix elements (20) contain integrals of the form

$$\begin{aligned} \mathcal{I} &= \langle[\textstyle\int \mathrm{d}\mathbf{R}_1\,\mathrm{d}z_1 f_1(\mathbf{R}_1,z_1)\delta U(\mathbf{R}_1,z_1)] \\ &\quad\times[\textstyle\int \mathrm{d}\mathbf{R}_2\,\mathrm{d}z_2 f_2(\mathbf{R}_2,z_2)\delta U(\mathbf{R}_2,z_2)]\rangle, \end{aligned} \tag{A1}$$

where f_1 and f_2 represent the functions which appear in (19*a*) and (19*b*). In (20) the z_1 and z_2 integrals are over the thickness of the crystal, but as δU goes to zero outside the crystal they can be extended to be over all space. Only δU (and not f) is thermally fluctuating, so it follows that the important quantity is [using (21)]

$$\begin{aligned} &\langle\delta U(\mathbf{r}_1)\delta U(\mathbf{r}_2)\rangle \\ &\quad= \langle U(\mathbf{r}_1)U(\mathbf{r}_2)\rangle-\langle U(\mathbf{r}_1)\rangle\langle U(\mathbf{r}_2)\rangle, \end{aligned} \tag{A2}$$

which can then be integrated as in (*A*1). We take the simplest case of a crystal with one atom per unit cell and write $U(\mathbf{r})$ as a sum over atomic potentials u situated at the lattice sites $\mathbf{l}$:

$$U(\mathbf{r})=\sum_{\mathbf{l}} u(\mathbf{r}-\mathbf{l}-\boldsymbol{\Delta}_{\mathbf{l}}). \tag{A3}$$

$\boldsymbol{\Delta}_{\mathbf{l}}$ is the displacement of the atom at site $\mathbf{l}$. It is convenient to rewrite (*A*3) in a Fourier representation

$$\begin{aligned} U(\mathbf{r}) &= (2\pi)^{-3}\sum_{\mathbf{l}}\int \mathrm{d}\mathbf{k}\exp(i\mathbf{k}\cdot\mathbf{r})u(\mathbf{k}) \\ &\quad\times\exp(-i\mathbf{k}\cdot\mathbf{l})\exp(-i\mathbf{k}\cdot\boldsymbol{\Delta}_{\mathbf{l}}), \end{aligned} \tag{A4}$$

where $u(\mathbf{k})$ is the Fourier transform of $u(\mathbf{r})$. We use the Einstein approximation for the atomic vibrations, in which case the motion of the atom at $\mathbf{l}$ is correlated only with itself, and

$$\langle\boldsymbol{\Delta}_{\mathbf{l}}\boldsymbol{\Delta}_{\mathbf{l}'}\rangle=2M\delta_{\mathbf{l},\mathbf{l}'}, \tag{A5}$$

where M is the usual temperature factor and δ is the Kroneker delta function. Equation (*A*2) then becomes

$$\langle \delta U(\mathbf{r}_1)\delta U(\mathbf{r}_2)\rangle = (2\pi)^{-6}\iint d\mathbf{k}_1\, d\mathbf{k}_2 \exp(i\mathbf{k}_1\cdot\mathbf{r}_1)\exp(i\mathbf{k}_2\cdot\mathbf{r}_2) \times u(\mathbf{k}_1)u(\mathbf{k}_2)S(\mathbf{k}_1,\mathbf{k}_2)\sum_{\mathbf{l}}\exp[-i(\mathbf{k}_1+\mathbf{k}_2)\cdot\mathbf{l}], \quad (A6)$$

where the correlation function S is given by

$$S(\mathbf{k}_1,\mathbf{k}_2) = \exp[-M(\mathbf{k}_1+\mathbf{k}_2)^2] - \exp(-Mk_1^2)\exp(-Mk_2^2). \quad (A7)$$

In both examples discussed in the paper the f functions of ($A1$) take the form of plane waves and so we write

$$f_1(\mathbf{r}_1) = \exp(-i\mathbf{q}_1\cdot\mathbf{r}_1),\quad f_2(\mathbf{r}_2) = \exp(i\mathbf{q}_2\cdot\mathbf{r}_2). \quad (A8)$$

When ($A6$) is substituted into ($A1$) we obtain

$$\mathcal{I} = u(\mathbf{q}_1)u^*(\mathbf{q}_2)S(\mathbf{q}_1-\mathbf{q}_2)\sum_{\mathbf{l}}\exp[i(\mathbf{q}_2-\mathbf{q}_1)\cdot\mathbf{l}] \quad (A9)$$

which is the basic result for the matrix elements. It only remains to look at the sum in ($A9$), which covers all lattice sites in the crystal. It follows that the transverse parts, $\mathbf{Q}_1$ and $\mathbf{Q}_2$, of $\mathbf{q}_1$ and $\mathbf{q}_2$ must be equal to within a two-dimensional reciprocal-lattice vector, $\mathbf{G}$. The sum in the z direction is however only over the finite thickness of the crystal. Provided $(q_2)_z-(q_1)_z$ is small (as it is in practice) the sum can be replaced by an integral to yield

$$(1/l_z)\int_0^t dz \exp[i(q_{2z}-q_{1z})z] = (t/l_z)\exp[i(q_{2z}-q_{1z})t/2] \times \sin[(q_{2z}-q_{1z})t/2]/[(q_{2z}-q_{1z})t/2], \quad (A10)$$

where l_z is the repeat distance in the z direction. It is this oscillatory thickness-dependent factor which controls the degree of coherence between different states. If $q_{1z}=q_{2z}$, ($A10$) gives a contribution which increases linearly with t. However, if q_{1z} and q_{2z} are different the $(\sin x)/x$ factor in ($A10$) falls off with increasing thickness, which indicates a reduction in the off-diagonal elements of the density matrix and a correspondingly weaker coherence.

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Orientational Parameters of *n*-Dimensional Symmetry Operations

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Abstract

The number of orientational parameters is evaluated for a general point-symmetry operation in n dimensions. When the operation contains orthogonal identical crypto-components some of the parameters become free and this phenomenon is investigated.

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