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Correlations in space and time and dynamical diffraction of high-energy electrons by crystals

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The problem of scattering of high-energy electrons by solids is formulated on the basis of a kinetic equation (KE) for the one-particle density matrix. This equation provides a general treatment of spatial and temporal coherence of electrons and takes account of both elastic and inelastic scattering for arbitrary geometry of diffraction. Formulating the KE, we prove that if the energy of an electron is sufficiently high ($E \sim 100$ keV), the problem of multiple elastic and inelastic scattering by a solid is entirely determined by two universal functions, namely, the Coulomb potential averaged over the motion of the crystal particles and the mixed dynamic form factor of inelastic excitations, which is related to the time-dependent correlation function of the positions of electrons and nuclei in a solid. We show that in all the diffraction experiments the scattering cross section contains information about both these functions and discuss the possibility of their separate determination. The KE method generalizes previous theoretical approaches to the description of multiple inelastic scattering of high-energy electrons, and in the case of single inelastic interactions the solution of the KE reduces to the distorted-wave approximation. As an illustration, we consider an application of the KE to the problem of multiple scattering of high-energy electrons by collective electronic excitations of a crystal. Numerical solution of the KE is shown to be consistent with experimental observations, and evidence is found for the existence of a mechanism of damping of coherence by small-angle inelastic scattering of high-energy electrons by a crystal.

I. INTRODUCTION

High-energy electron diffraction (HEED) and electron microscopy are commonly accepted now as one of the main analytical tools for materials science and its technological applications. This is primarily because HEED methods are based upon a clear physical understanding of the interaction of the electron with matter via Coulomb forces acting between the electron and the particles of a solid. However, the problem of the unambiguous interpretation of experimental observations is in many respects far from complete. The basic difficulty comes from the multiplicity of interactions of high-energy electrons with nuclei and electrons in a solid. Even for a crystal with a periodic distribution of atoms the observed diffraction pattern seldom has the form of a set of discrete spots following Bragg's law, but rather the scattering exhibits a continuous background over the whole solid angle of 4π. This background comes primarily from inelastic scattering of the high-energy electron arising from excitations of the vibrational and electronic subsystems of the crystal. The intensity of sharp Bragg diffraction spots results from elastic scattering of the electron, thereby providing information about the geometrical arrangement of atoms in the solid,[1] while the analysis of angular and energy spectra of inelastically scattered electrons forms a basis for many analytical techniques[2] and makes it possible to study the transitions between different eigenstates of the crystal, in particular, to locate impurities in the lattice[3] as well as to determine the local chemical state of particular atoms.[4] Generally, the recording of the double differential cross section of scattering of high-energy electrons $d^2\sigma/dodE$ (where do is the element of solid angle and E is the energy) makes it possible to investigate two basic properties of a substance, namely, its static equilibrium characteristics, i.e., the parameters which are relevant to the time-averaged distribution of particles, and its dynamic properties, i.e., the parameters characterizing the motion of electrons and nuclei.

In spite of the clear significance of a theoretical method which would enable the evaluation of the cross section, taking account of both elastic and inelastic scattering, the basic equations of the theory are yet to be formulated. A treatment of the problem was given by Yoshioka,[5] who considered a system of coupled differential equations for the amplitudes of elastically and inelastically scattered electrons. Howie[6] showed how to solve these equations and discussed the problem of multiple bulk plasmon excitations in transmission diffraction geometry. Howie's result was extended by Cundy, Howie, and Valdré,[7] Humphreys and Whelan,[8] Rez, Humphreys, and Whelan,[9] Rossouw and Whelan,[10] and Allen and Rossouw[11] to the cases of phonon and electron-hole excitation.

An alternative approach was proposed by Høier[12] who showed how to combine the method of treating the effects of diffuse scattering developed by Gjønnes[13] with Moliére's multiple scattering theory.[14] Furthermore, a kinetic equation governing the time evolution of the one-particle density matrix has been derived by Kagan and Kononets.[15] They developed a consistent quantum-mechanical theory of channeling of nonrelativistic protons in single crystals. Similar equations were considered later by Rez[16] and Dudarev and Ryazanov[17] in the theory of multiple inelastic scattering of high-energy electrons propagating through thin crystals. A multislice method which takes inelastic interactions into account has been proposed recently by Wang.[18,19] In summary, all the theoretical approaches quoted above[6–18] were developed for the transmission diffraction geometry.

A theory which treats the high-angle backscattering of incident electrons from bulk single crystals was formulated by Hirsch and Humphreys.[20] Further progress was made by Spencer and Humphreys[21] who applied the methods of transport theory to the problem of the evaluation of the contrast of electron channeling patterns. However, the transport equation in Ref. 21 was postulated rather than derived, and the question remains of how to incorporate consistently the diffraction effects into the theory based on the time-independent Boltzmann equation. As a recent illustration, here we may quote the problem of the quantitative interpretation of electron channeling images of dislocations[22,23] obtained by scanning transmission electron microscopy (STEM) with an inclined incident beam using a detector without energy filtering.

All of the known theoretical approaches to the problem of diffraction and inelastic scattering of high-energy electrons by solids have been developed in forms which are suitable for various diffraction geometries, but a unified principle concerning all geometrical situations has not yet been discussed. The importance of a unified approach arises from the following question, which attracted much attention in recent years (see, e.g., Refs. 24–27 and references therein). If we consider HEED as an analytical tool for determination of the structure of a solid, then how many independent functions characterizing the substance can be obtained from diffraction measurements and what is the origin of these functions? Within the framework of kinematic (i.e., single scattering) theory the answer to this question was given by Van Hove[28] who demonstrated that it is the so-called dynamic form factor $S(\mathbf{q},\omega)$ which contains all the information about the time-averaged $[S(\mathbf{q},\omega=0)]$ and the dynamic $[S(\mathbf{q},\omega\neq 0)]$ properties of the system. Cowley[29] has recently discussed this point in connection with the influence of time-dependent perturbations on electron micrographs, but the ultimate solution to the problem was not given. The present study aims to generalize the Van Hove theory[28] to the case of multiple scattering of the high-energy electrons by a solid.

We develop a unified theory which accounts both for elastic diffraction by the time-averaged distribution of atoms and inelastic scattering by excitations of the solid using a method which is similar to the approach previously developed for evaluation of the conductivity of alloys[30] and for the study of wave scattering and propagation in a randomly inhomogeneous medium.[31] An application of this method to the problem of multiple incoherent scattering of waves in a crystal was made by Dudarev[32] who found an exact solution to the problem of Kikuchi pattern formation in the geometry of backscattering from a lattice of pointlike scatterers. Gorodnichev and Dudarev[33] used the same model and considered qualitatively the effect of multiple energy losses on the angular distribution of backscattered electrons.

In the present paper we derive the basic relationships describing multiple scattering of high-energy electrons in a solid and discuss the approximate methods of solving these equations. The main entity in the theory is the one-particle density matrix $\rho(\mathbf{r},\mathbf{r}',E)$ which describes the mutual coherence of the wave field of the high-energy electron at the points $\mathbf{r}$ and $\mathbf{r}'$. The kinetic equation (KE) discussed below determines the evolution of $\rho(\mathbf{r},\mathbf{r}',E)$ in the problem of multiple elastic and inelastic scattering. We prove that if the energy of the electron is sufficiently high, then there are two and only two separate functions accounting for the static and dynamic properties of a substance relevant to the electron-crystal interaction. These are the time-averaged Coulomb potential and the mixed dynamic form factor of inelastic excitations, and they are the only two quantities which affect the cross section of scattering of the high-energy electron by a solid.

We show how previous theoretical approaches to inelastic scattering in HEED can be deduced from our equations, and then consider an application of the KE method to the problem of multiple small-angle inelastic scattering of the high-energy electrons by collective electronic excitations in a crystal. We evaluate numerically of the cross section of multiple inelastic scattering, and compare the results with experimentally observed intensity distributions. Reasonable agreement is obtained between computed profiles and experimental data, and evidence is found for the strong effect of the small-angle inelastic scattering on the coherence of high-energy electrons propagating through thin crystals.

II. KINETIC EQUATION

For brevity, in this section we formulate the basic equations of the theory in the form of a theorem, the proof of which is given in Appendixes A and B. We then discuss the approximations involved, avoiding long mathematical derivations. Our goal is to establish how the previous approaches can be unified, and the advantages and limitations of the new method.

In order to define the meaning of the basic entity of the theory we first consider the following simple example. Let $\Psi(\mathbf{r},t)$ be the wave function of an electron propagating in the medium occupied by moving classical particles. This wave function depends on the coordinates of the particles $\{\mathbf{R}_1(t_1),\mathbf{R}_2(t_2),\ldots\mathbf{R}_M(t_M)\}$, taken at the preceding moments of time $t_1 < t$, $t_2 < t$, $\ldots t_M < t$. Experimentally, a bilinear combination of the wave functions $\rho(\mathbf{r},\mathbf{r}',t,t') = \Psi(\mathbf{r},t)\Psi^*(\mathbf{r}',t')$ can be observed. Provided that the medium is in its thermodynamic equilibrium, and assuming steady state conditions of illumination with fast electrons, we may express $\rho(\mathbf{r},\mathbf{r}',t,t')$ as $\rho(\mathbf{r},\mathbf{r}',t-t')$. We introduce the *spectral one-particle density matrix* $\rho(\mathbf{r},\mathbf{r}',E)$ by the Fourier transformation

$$\rho(\mathbf{r},\mathbf{r}',E) = \frac{1}{2\pi\hbar}\int_{-\infty}^{\infty} d(t-t')\exp\Big(i\frac{E}{\hbar}(t-t')\Big) \times\rho(\mathbf{r},\mathbf{r}',t-t'). \qquad (1)$$

In the simplest case where the interaction potential does not depend on time we write

$$\Psi(\mathbf{r},t) = \Psi_\nu(\mathbf{r}) \exp\Big(-i\frac{E_\nu}{\hbar}t\Big),$$

where $\Psi_\nu(\mathbf{r})$ is a wave function of the continuous spectrum, and then we obtain

$$\rho(\mathbf{r},\mathbf{r}',E) = \Psi_\nu(\mathbf{r})\Psi^*_\nu(\mathbf{r}')\delta\Big(E - E_\nu\Big). \tag{2}$$

The spectral one-particle density matrix $\rho(\mathbf{r},\mathbf{r}',E)$ describes the mutual coherence of the wave field of high-energy electrons at the points $\mathbf{r}$ and $\mathbf{r}'$, and, as this example shows, its diagonal elements $\rho(\mathbf{r},\mathbf{r},E)$ are proportional to the probability of finding the electron with energy E at the point $\mathbf{r}$. The kinetic equation considered below describes the evolution of $\rho(\mathbf{r},\mathbf{r}',E)$ due to processes of multiple elastic and inelastic scattering. The distribution of electrons over a solid angle and energy is related to the Fourier transform of $\rho(\mathbf{r},\mathbf{r}',E)$ over the coordinates $\mathbf{r}$ and $\mathbf{r}'$ [see Ref. 34 and equation (14) of the present paper].

As is shown below, there are two functions which determine the elastic and inelastic scattering of the high-energy electron, namely, the time-averaged Coulomb potential of the interaction between the incident electron and the nuclei and electrons of the substance and the mixed dynamic form factor of inelastic excitations. We first define these two quantities.

Let $H'(\mathbf{r},\mathbf{r}_1,\mathbf{r}_2,...,\mathbf{r}_M)$ be the Coulomb interaction between the primary electron (coordinate $\mathbf{r}$) and the crystal particles (coordinates $\mathbf{r}_1,\mathbf{r}_2,...,\mathbf{r}_M$ in the generalized sense). If we denote a particular state of the crystal by $|n\rangle$ (the corresponding eigenvalue of the crystal Hamiltonian is ϵ_n), then we can define a transition matrix element as $H'_{n_1,n}(\mathbf{r}) = \langle n_1|H'(\mathbf{r},\mathbf{r}_1,\mathbf{r}_2,...,\mathbf{r}_M)|n\rangle$. The time-averaged Coulomb interaction potential is defined as

$$\langle H'(\mathbf{r})\rangle = \frac{1}{\mathcal{Z}}\sum_n \exp(-\epsilon_n/k_BT)H'_{nn}(\mathbf{r}), \tag{3}$$

where $\mathcal{Z} = \sum_n \exp(-\epsilon_n/k_BT)$ is the partition function, T is the absolute temperature, and k_B is Boltzmann's constant. $\langle H'(\mathbf{r})\rangle$ describes the averaged potential field acting on the high-energy electron in the crystal provided that polarization of the medium can be neglected.

The difference between the transition matrix element $H'_{n_1,n}(\mathbf{r})$ and the matrix element of the averaged potential (3) represents the fluctuating part of the interaction,

$$\delta H'_{n_1,n}(\mathbf{r}) = H'_{n_1,n}(\mathbf{r}) - \delta_{n_1,n}\langle H'(\mathbf{r})\rangle. \tag{4}$$

Notice that the matrix element defined by Eq. (4) vanishes after averaging over the equilibrium,

$$\sum_n \exp(-\epsilon_n/k_BT)\delta H'_{n,n}(\mathbf{r}) = 0. \tag{5}$$

The quantity which characterizes the influence of fluctuations of the interaction potential on the state of the high-energy electron is expressed in terms of a bilinear combination of matrix elements (4), namely,

$$\overline{s}(\mathbf{r},\mathbf{r}',\omega) = \frac{1}{\mathcal{Z}}\sum_{n,n_1} \exp(-\epsilon_n/k_BT)\delta H'_{n,n_1}(\mathbf{r})\delta H'_{n_1,n}(\mathbf{r}') \times\delta\Big(\omega - \frac{\epsilon_{n_1}-\epsilon_n}{\hbar}\Big). \tag{6}$$

The double Fourier transform of (6),

$$S(\mathbf{q},\mathbf{q}',\omega) = \frac{q^2q'^2}{(4\pi e^2)^2}\int d^3r d^3r' \exp(-i\mathbf{q}\cdot\mathbf{r} + i\mathbf{q}'\cdot\mathbf{r}') \times\overline{s}(\mathbf{r},\mathbf{r}',\omega), \tag{7}$$

where e denotes the electron charge, is known as the mixed dynamic form factor,[35] and in what follows we will use this term both for (7) as well as for (6). The proof given by Van Hove[28] shows that the functions (6) and (7) contain all the information about time-dependent correlations in the positions of the crystal particles as well as about spectrum of excitations of the substance. The mixed dynamic form factor (7) is proportional to the Fourier transform of the equilibrium correlation function of charge density fluctuations,

$$S(\mathbf{q},\mathbf{q}',\omega) = \frac{1}{\mathcal{Z}}\sum_n \exp(-\epsilon_n/k_BT)\int\frac{dt}{2\pi}\exp(i\omega t)\langle n|\delta\hat{P}_{\mathbf{q}}(t)\delta\hat{P}_{-\mathbf{q}'}(0)|n\rangle\ , \tag{8}$$

where $\hat{P}_{\mathbf{q}}(t)$ denotes the Fourier component of the Heisenberg operator of the total charge density, namely,

$$\hat{P}(\mathbf{r},t) = \sum_\alpha Z_\alpha\delta(\mathbf{r} - \hat{\mathbf{R}}_\alpha(t))$$

and

$$\hat{P}_{\mathbf{q}}(t) = \sum_\alpha Z_\alpha \exp\big[-i\mathbf{q}\cdot\hat{\mathbf{R}}_\alpha(t)\big].$$

As follows from the above discussion, various eigenstates of the medium contribute to the form factor (8) independently, i.e., in the form of a simple summation over n, each term being weighted with a factor of $\mathcal{Z}^{-1}\exp(-\epsilon_n/k_BT)$. This means that the excitation of various eigenstates takes place incoherently, and this arises as a corollary of the assumption of the crystal being in thermal equilibrium.

We proceed now to the formulation of the equations of the theory of multiple scattering. There are three equations, the solutions of which need to be known in order to evaluate the double differential cross section of scattering of the high-energy electron by a solid. The first equation

$$\left[E + \frac{\hbar^2}{2m}\nabla^2 - \langle H'(\mathbf{r})\rangle\right] G_0(\mathbf{r},\mathbf{r}',E) = \delta(\mathbf{r}-\mathbf{r}') \qquad (9)$$

determines the wave amplitude $G_0(\mathbf{r},\mathbf{r}',E)$ (Green's function) at $\mathbf{r}$ due to a point source of electrons at $\mathbf{r}'$ in the averaged potential field $\langle H'(\mathbf{r})\rangle$. The solution to the second equation (see Appendix A for a derivation)

$$\left[E + \frac{\hbar^2}{2m}\nabla^2 - \langle H'(\mathbf{r})\rangle\right] G(\mathbf{r},\mathbf{r}',E) - \int d^3x \int d\omega\ \bar{s}(\mathbf{r},\mathbf{x},\omega) G_0(\mathbf{r},\mathbf{x},E-\hbar\omega) G(\mathbf{x},\mathbf{r}',E) = \delta(\mathbf{r}-\mathbf{r}') \qquad (10)$$

is a similar Green's function, but unlike Eq. (9), Eq. (10) takes into account the influence of the fluctuating part of the interaction on the motion of the electron from $\mathbf{r}'$ to $\mathbf{r}$. The effective non-local potential term in Eq. (10) coincides with that derived by Dederichs[36] based on a single inelastic scattering approximation. He proved that this form of the effective potential takes into account in a unified manner both the vibrational and electronic excitations of a substance. He also showed that the appearance of the nonlocal potential term in Eq. (10) gives rise to the absorption of the fast electrons.

The third equation is an integral equation, the derivation of which is given in Appendix B, viz.,

$$\rho(\mathbf{r},\mathbf{r}',E) = \rho_0(\mathbf{r},\mathbf{r}',E) + \int d^3x d^3x' G(\mathbf{r},\mathbf{x},E) G^*(\mathbf{r}',\mathbf{x}',E) \left[\int d\omega\ \bar{s}(\mathbf{x}',\mathbf{x},\omega)\rho(\mathbf{x},\mathbf{x}',E+\hbar\omega)\right], \qquad (11)$$

and is the basic relationship of the theory, and in what follows it will be referred to as the kinetic equation (KE). This equation describes the evolution of the one-particle density matrix of the electron in the process of multiple elastic and inelastic scattering in a solid. It shows simply that $\rho(\mathbf{r},\mathbf{r}',E)$ is a sum of the "coherent" wave $\rho_0(\mathbf{r},\mathbf{r}',E)$ (which includes the incident wave and associated elastic scattering) and waves inelastically scattered at $(\mathbf{x},\mathbf{x}')$, the propagation of which from $(\mathbf{x},\mathbf{x}')$ to $(\mathbf{r},\mathbf{r}')$ is described by the product of two Green's functions $G(\mathbf{r},\mathbf{x},E)G^*(\mathbf{r}',\mathbf{x}',E)$. Equation (11) is similar to the integral form of the transport equation,[37] so that we can term the second term on the right-hand side of expression (11) as the integral of inelastic collisions. Notice that this quantity as well as the nonlocal term in the effective interaction potential in Eq. (10) depends on the mixed dynamic form factor (6).

One of the basic problems of diffraction physics is the problem of scattering of a well-collimated beam of the high-energy electrons of energy E_0 by the crystal. To consider this problem in more detail, we adapt Eqs. (9)–(11) to this particular case which formally corresponds to the incidence of a plane wave. Let $\mathbf{k}_0$ be the wave vector of the incident electron, $\hbar^2\mathbf{k}_0^2/2m = E_0$; then the wave function $\Psi_{\mathbf{k}_0}(\mathbf{r})$ describing the elastic scattering obeys the equation [for $T = 0$ this equation coincides with Eq. (11) of Yoshioka's paper[5]]

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + \langle H'(\mathbf{r})\rangle\right]\Psi_{\mathbf{k}_0}(\mathbf{r}) + \int d^3x \int d\omega\ \bar{s}(\mathbf{r},\mathbf{x},\omega) G_0(\mathbf{r},\mathbf{x},E-\hbar\omega)\Psi_{\mathbf{k}_0}(\mathbf{x}) = \frac{\hbar^2\mathbf{k}_0^2}{2m}\Psi_{\mathbf{k}_0}(\mathbf{r}). \qquad (12)$$

At infinity $\Psi_{\mathbf{k}_0}(\mathbf{r})$ is a superposition of the incident plane wave $\exp(i\mathbf{k}_0\mathbf{r})$ and waves elastically scattered by a crystal. If the solution to (12), satisfying the appropriate boundary conditions, is found, then the KE (11) takes the form

$$\rho(\mathbf{r},\mathbf{r}',E) = \Psi_{\mathbf{k}_0}(\mathbf{r})\Psi^*_{\mathbf{k}_0}(\mathbf{r}')\delta\left(E - \frac{\hbar^2\mathbf{k}_0^2}{2m}\right) + \int d^3x d^3x' G(\mathbf{r},\mathbf{x},E) G^*(\mathbf{r}',\mathbf{x}',E) \int d\omega\ \bar{s}(\mathbf{x}',\mathbf{x},\omega)\rho(\mathbf{x},\mathbf{x}',E+\hbar\omega). \qquad (13)$$

Equation (13) provides a complete description to the quantum-mechanical multiple scattering problem and, in particular, by solving Eq. (13), one can find the density of high-energy electrons $\rho(\mathbf{r},\mathbf{r},E)$ at any point $\mathbf{r}$. Choosing an arbitrary Cartesian system of coordinates and evaluating the current density at a distant point, we can express the double differential scattering cross section as

$$\frac{d^2\sigma}{dodE} = \frac{k}{k_0}\left(\frac{k\cos\theta}{2\pi}\right)^2 \lim_{z\to\pm\infty} \int d^2R d^2R' \exp(-i\mathbf{q}_\perp\cdot\mathbf{R} + i\mathbf{q}_\perp\cdot\mathbf{R}')\rho(\mathbf{R},z,\mathbf{R}',z,E), \qquad (14)$$

where $k = \sqrt{2mE/\hbar^2}$, θ is the angle between the wave vector $\mathbf{k}$ of the scattered electron and the z axis of the chosen system of coordinates, $\mathbf{R} = (x,y)$, and $\mathbf{q}_\perp = \mathbf{k}_{x,y}$ is a two-dimensional vector lying in a plane perpendicular to the z axis, $\mathbf{q}_\perp = (k\sin\theta\cos\phi, k\sin\theta\sin\phi, 0)$. The choice of a sign (plus or minus) in expression (14) depends on whether the electron is scattered into the forward (+) or the backward (−) hemisphere.

The general equations (9)–(11) as well as the more particular relationships (12) and (13) make it possible to evaluate the angular and energy distributions in high-energy electron diffraction. Our formulation, therefore, shows that there are two and only two universal functions which determine the double differential scattering cross section (14), namely, the averaged Coulomb interaction potential $\langle H'(\mathbf{r})\rangle$ [Eq. (3)] and the mixed dynamic form factor $\overline{s}(\mathbf{r},\mathbf{r}',\omega)$ [Eq. (6)]. We can conclude, therefore, that only these two quantities can in principle be retrieved from the diffraction data by solving the inverse scattering problem. As follows from the above equations, both $\langle H'(\mathbf{r})\rangle$ and $\overline{s}(\mathbf{r},\mathbf{r}',\omega)$ always enter the diffraction data simultaneously, and any formulation of the inverse problem must include the procedure for the separation of these two functions. In other words, inelastic vibrational and electronic excitations affect the intensities of Bragg reflections, while elastic scattering by the averaged crystal potential influences the cross section of inelastic scattering. We discuss this in more details in the next section.

It is important to notice that Eqs. (9)–(13) do not assume the structure of a solid to be periodic. This makes it possible to use these equations to take account of not only the well-known electron and phonon excitations in a perfect crystal,[6,9,10] but also surface, interface, and other types of localized excitations which exist in a non-periodic system. The above formulation demonstrates that in any geometry of diffraction combinations of the coordinates $\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_M$ of the particles of the system, apart from $\langle H'(\mathbf{r})\rangle$ and $\overline{s}(\mathbf{r},\mathbf{r}',\omega)$, do not affect the results of an experimental observation.

In summary, in this section we have formulated the kinetic equation (11), the solution of which determines the magnitude of the one-particle density matrix $\rho(\mathbf{r},\mathbf{r}',E)$ everywhere in space and which makes it possible to evaluate the cross section of inelastic scattering for arbitrary geometry of diffraction. Equation (11) is an integral equation and in general the problem of solving it may require substantial computational effort. However, it has already been shown that in some cases the exact analytical solutions of Eq. (11) may be found[32,33,37] and, as demonstrated below, the KE approach appears to be useful for analysis of such effects like evolution of the coherence of the wave field of high-energy electrons in their multiple scattering by electronic excitations in a crystal.

In the following section we discuss the approximations involved in the theory as well as its advantages and limitations, and establish the correspondence between the present formulation and the earlier approaches to the problem of inelastic scattering in HEED.

III. CONDITIONS OF VALIDITY AND APPROXIMATE RELATIONSHIPS

We start from a brief description of the basic idea involved in the KE method (for more details see Appendixes A and B). Basically, Eqs. (9)–(13) can be derived if we represent the propagation amplitude of the high-energy electron in the form of an infinite series in the fluctuating part $\delta\hat{H}'$ of the interaction potential, the matrix element of which is determined by the expression (4), and then perform averaging of this amplitude over the thermodynamic equilibrium, conserving only terms quadratic in $\delta\hat{H}'$. The same procedure of averaging is applied to $\rho(\mathbf{r},\mathbf{r}',E)$.

The approximation just described was first developed in the theory of wave scattering and propagation in a random medium (see, e.g., the review in Ref. 31). A similar approach to the problem of inelastic scattering in crystals was developed by Kagan and Kononets.[15] Recent studies have shown that the first nontrivial correction to this approximation coming from higher-order terms gives rise to an effect which is similar to the *coherent backscattering* of light. This phenomenon was studied in detail by Gorodnichev *et al.*, [38] and it was found that the magnitude of this effect in the case of HEED is fairly small. The approximation which is quadratic in $\delta\hat{H}'$ means that in the treatment of multiple inelastic scattering, each successive inelastic interaction is described by the single inelastic scattering approximation. We must emphasize, however, that this approximation is not equivalent to the ordinary Born formula for scattering of a high-energy electron by an atom. It is only the fluctuating part of the Coulomb interaction $\delta\hat{H}'$ which is considered as a perturbation and is assumed to be sufficiently weak. In other words, the present treatment of inelastic scattering can be considered as a *multiple scattering distorted wave approximation*, insofar as we are interested in the propagation and inelastic interactions of the high-energy electron in the averaged potential field $\langle H'(\mathbf{r})\rangle$.

As is now well established, the process of inelastic scattering cannot be attributed to a particular atom of a solid. In most cases one has to deal with collective excitations of the phonon and electron subsystems of the solid. Therefore it is not very obvious how to formulate the precise conditions of validity of Eqs. (9)–(13). In order to proceed to a more quantitative discussion, we introduce the effective correlation radius of excitations, which we denote by r_c. We define r_c as a characteristic distance between two arguments $\mathbf{r}$ and $\mathbf{r}'$ of the mixed dynamic form factor $\overline{s}(\mathbf{r},\mathbf{r}',\omega)$ which determines the range over which this factor is appreciable. In some cases this definition leads to difficulties, such as, for example, the dynamic form factor of collective electronic excitations in the bulk crystal behaving at large distances like $|\mathbf{r}-\mathbf{r}'|^{-1}$. In this case the formulation of the Born condition may require some additional consideration similar to that known in the quantum-mechanical problem of scattering by the Coulomb field.[39,40] However, the use of r_c makes it convenient to estimate different terms entering Eqs. (9)–(13).

Let the effective strength of the fluctuating part of the interaction $\delta\hat{H}'$ be $\delta\overline{H}'$. Then the condition of validity of the distorted-wave approximation for inelastic scattering can be formulated as[39,40]

$$\frac{\hbar^2}{mr_c^2} \gg |\delta\overline{H}'|, \tag{15}$$

where m is the electron mass. In the case where the energy of the electron is high, i.e., $kr_c \gg 1$, a weaker inequality can be used instead of (15),

$$kr_c\frac{\hbar^2}{mr_c^2} \gg \left|\delta\overline{H}'\right|. \tag{16}$$

The latter condition can be interpreted as follows. The combination $\hbar^2 k/m|\delta\overline{H}'|$ has dimensions of length. If we denote this length by L and consider the electron moving in a uniform potential field $\delta\overline{H}'$, the wave function acquires an additional phase of the order of π over a path length of the order of L. Therefore the inequality (16) requires that the fluctuating part of the interaction must be sufficiently weak for no dynamical diffraction effects to develop over a path length of the order of the correlation radius r_c. Employing an optical analogy, we may say that every inelastic perturbation associated with $\delta\hat{H}'$ must be transparent for the electron, although the entire crystal may be turbid. For a further discussion of the meaning of inequalities (15) and (16) see Ref. 41.

Having formulated the kinetic equation and defined the conditions of its validity, we proceed to a discussion of how the scattering cross section (14) can be evaluated in practice. We demonstrate that the Fourier transform of the density matrix in (14) can be evaluated analytically, and that this result leads to a very simple and useful expression for the scattering cross section, which is suitable both for making analytical estimates and numerical computations.

First we notice that the right-hand side of Eq. (13) is a sum of two terms. The first term is proportional to the product of two wave functions, each of them is a solution to the elastic scattering problem (12). The second term on the right-hand side of (13) results from the processes involving at least one inelastic collision. Therefore we may represent the total cross section (14) in the form of a sum of elastic scattering cross section and a term which describes single, double, etc., inelastic interactions in a substance,

$$\frac{d^2\sigma}{dodE} = \delta(E-E_0)\frac{d\sigma_{\rm el}}{do} + \frac{d^2\sigma_{\rm inel}}{dodE}. \tag{17}$$

The problem of evaluation of the elastic scattering cross section reduces to solving the Schrödinger equation (12), and this problem has been widely discussed in the literature (for a review see Ref. 1 and Ref. 36). In what follows we concentrate on the second term in (17). Comparing (17) and (14) we see that in order to find the inelastic scattering cross section one needs to calculate the Fourier transform of the Green's function $G(\mathbf{r},\mathbf{x},E)$. For brevity, we quote here only the result (for details of the derivation see Appendix C)

$$\int d^2R\, G(\mathbf{R},z,\mathbf{x},E)\exp(-i\mathbf{q}_\perp.\mathbf{R}) = -\frac{im}{\hbar^2 k|\cos\theta|}\exp(ikz\cos\theta)\Psi_{-\mathbf{k}}(\mathbf{x}), \tag{18}$$

where $\mathbf{k} = (q_{\perp x}, q_{\perp y}, k\cos\theta)$ is the wave vector of the scattered electron, and the Cartesian system of coordinates coincides with that one chosen for evaluation of the cross section (14). Substituting (18) into (14) we obtain

$$\frac{d^2\sigma_{\rm inel}}{dodE} = \frac{k}{k_0}\left(\frac{m}{2\pi\hbar^2}\right)^2\int d^3x d^3x'\Psi_{-\mathbf{k}}(\mathbf{x})\Psi^*_{-\mathbf{k}}(\mathbf{x}') \times\int d\omega\;\overline{s}(\mathbf{x}',\mathbf{x},\omega) \times\rho(\mathbf{x},\mathbf{x}',E+\hbar\omega). \tag{19}$$

If the contribution of double, triple, etc., inelastic interactions to the cross section (19) is small, we can put [see (13)]

$$\rho(\mathbf{r},\mathbf{r}',E)\approx\Psi_{\mathbf{k}_0}(\mathbf{r})\Psi^*_{\mathbf{k}_0}(\mathbf{r}')\delta\Big(E-\frac{\hbar^2\mathbf{k}_0^2}{2m}\Big). \tag{20}$$

Substituting this into the right-hand side of (19), we arrive at a simple result

$$\frac{d^2\sigma_{\rm inel}}{dodE} = \frac{k}{k_0}\left(\frac{m}{2\pi\hbar^2}\right)^2\frac{1}{\hbar}\int d^3xd^3x'\Psi_{-\mathbf{k}}(\mathbf{x})\Psi^*_{-\mathbf{k}}(\mathbf{x}')\overline{s}\left(\mathbf{x}',\mathbf{x},\frac{\hbar\mathbf{k}_0^2}{2m}-\frac{\hbar\mathbf{k}^2}{2m}\right)\Psi_{\mathbf{k}_0}(\mathbf{x})\Psi^*_{\mathbf{k}_0}(\mathbf{x}'), \tag{21}$$

which provides a general form of a *single inelastic scattering approximation.* In (21) we used the notation $E = \hbar^2\mathbf{k}^2/2m$. A formula which is similar to (21) was used by Kainuma[42] in his theory of Kikuchi patterns as early as in 1955. However, a single inelastic scattering approximation in its final form (21) has been formulated only recently.[43] Equation (21) shows that provided the contribution of multiple inelastic collisions is small, the double differential cross section of inelastic scattering of high-energy electrons by a crystal can be easily computed analytically or numerically by integrating the product of two wave functions of the incident electron and two "reciprocal" wave functions (in the sense used by Kainuma[42]) of the scattered electron times the mixed dynamic form factor of inelastic excitations. Formula (21) is particularly suitable for backscattering or reflection diffraction geometries, where the problem of finding the wave function of an elastically scattered electron may require considerable numerical computation.[44,45,46]

We take account of multiple inelastic interactions by iterating Eq. (13) and obtain

$$\frac{d^2\sigma_{\rm inel}}{dodE} = \frac{k}{k_0}\left(\frac{m}{2\pi\hbar^2}\right)^2\frac{1}{\hbar}\int d^3xd^3x'd^3x_1d^3x_1'\Psi_{-\mathbf{k}}(\mathbf{x})\Psi^*_{-\mathbf{k}}(\mathbf{x}')\Sigma\Big(\mathbf{x},\mathbf{x}',\frac{\hbar^2\mathbf{k}^2}{2m}\,\Big|\,\mathbf{x}_1,\mathbf{x}_1',\frac{\hbar^2\mathbf{k}_0^2}{2m}\Big)\Psi_{\mathbf{k}_0}(\mathbf{x}_1)\Psi^*_{\mathbf{k}_0}(\mathbf{x}_1'), \tag{22}$$

where the operator $\hat{\Sigma}$ denotes the sum of the following series:

$$\begin{aligned}
&\Sigma\Big(\mathbf{x},\mathbf{x}',E\Big|\mathbf{x}_1,\mathbf{x}_1',E+\hbar\omega\Big)\\
&\quad=\overline{s}(\mathbf{x}',\mathbf{x},\omega)\delta(\mathbf{x}-\mathbf{x}_1)\delta(\mathbf{x}'-\mathbf{x}_1')\\
&\qquad+\int d\omega_0 d\omega_1\overline{s}(\mathbf{x}',\mathbf{x},\omega_0)G(\mathbf{x},\mathbf{x}_1,E+\hbar\omega_0)G^*(\mathbf{x}',\mathbf{x}_1',E+\hbar\omega_0)\overline{s}(\mathbf{x}_1',\mathbf{x}_1,\omega_1)\delta(\omega_0+\omega_1-\omega)\\
&\qquad+\int d\omega_0 d\omega_1 d\omega_2\overline{s}(\mathbf{x}',\mathbf{x},\omega_0)\int d^3x_2 d^3x_2' G(\mathbf{x},\mathbf{x}_2,E+\hbar\omega_0)G^*(\mathbf{x}',\mathbf{x}_2',E+\hbar\omega_0)\overline{s}(\mathbf{x}_2',\mathbf{x}_2,\omega_1)\\
&\qquad\times G(\mathbf{x}_2,\mathbf{x}_1,E+\hbar\omega_0+\hbar\omega_1)G^*(\mathbf{x}_2',\mathbf{x}_1',E+\hbar\omega_0+\hbar\omega_1)\overline{s}(\mathbf{x}_1',\mathbf{x}_1,\omega_2)\delta(\omega_0+\omega_1+\omega_2-\omega)\\
&\qquad+\cdots\,.
\end{aligned} \tag{23}$$

The meaning of expressions (22) and (23) becomes clear if we represent the successive terms in the expansion (23) in graphical form. Three terms corresponding to a single, double, and triple inelastic interactions [the first, the second, and the third terms on the right-hand side of (23), respectively] are shown in Fig. 1. The straight lines represent schematically the propagation in real space of two amplitudes of the high-energy electron, and the size of the circles is proportional to the correlation radius of inelastic interactions r_c (which may differ for various types of inelastic excitations), the dashed lines representing the atomic planes of the crystal. The incoming and outgoing lines in Fig. 1 describe the incident and emerging waves, respectively. The directions of these lines, $\mathbf{k}_0$ and $\mathbf{k}$, are fixed by the geometry of the experiment (i.e., by the positions of the source of electrons and the detector). The directions of intermediate lines connecting two circles in case of double, triple, etc., scattering are determined by the scattering process itself, and they are not influenced by the experimental arrangement. It is important to emphasize that the definition of the propagation amplitudes $G(\mathbf{r},\mathbf{x},E)$ shown schematically by the straight lines in Fig. 1 actually includes the effect of the averaged crystal potential on the motion of the electron between two points $\mathbf{x}$ and $\mathbf{r}$. The elastic scattering cross section in this notation would correspond to a single pair of straight lines (not shown in Fig. 1).

Equations (21) and (22) demonstrate that the problem of the determination of static and dynamic properties of a solid by HEED is far more complicated than a simple inversion of the kinematical formula given by Van Hove.[28] Even in the case of single inelastic scattering in (21) the transition takes place between exact solutions of the elastic scattering problem (*distorted*-wave approximation) rather than between plane waves. In general, we can say that the determination of static and dynamic properties of a solid by HEED always includes two stages. At the first stage the elastic scattering cross section is analyzed in order to retrieve the averaged crystal potential $\langle H'(\mathbf{r})\rangle$. The effects of inelastic scattering [i.e., the influence of the nonlocal term involved in Eq. (12)] can at this stage be included by making use of a simple approximate expression for $\overline{s}(\mathbf{r},\mathbf{r}',\omega)$ or by introducing some effective adjustable absorption parameters.[47] After the averaged potential $\langle H'(\mathbf{r})\rangle$ and the explicit form of the wave function $\Psi_{\mathbf{k}}(\mathbf{r})$ are known, expressions (21) and (22) can be considered as integral equations for $\overline{s}(\mathbf{r},\mathbf{r}',\omega)$, the left-hand side of which is a quantity known from experimental observations. Therefore, the determination of crystal structure by HEED turns out to be a more complicated problem than simple restoration of $S(\mathbf{q},\omega)$ from the kine-

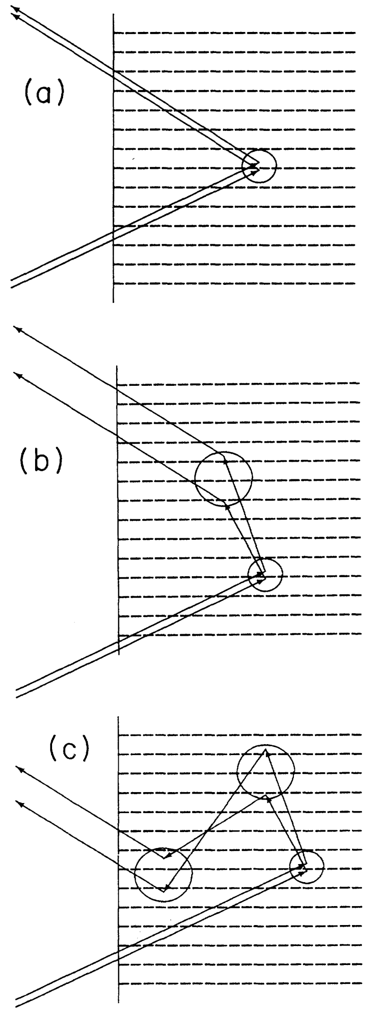

FIG. 1. A schematic representation of the scattering processes involved in the kinetic equation: (a) single inelastic scattering, (b) double inelastic scattering; and (c) triple inelastic scattering.

matic scattering cross section.[28] However, the technique of HEED, being nonkinematical, has the advantage of making it possible to find the *mixed* dynamic form factor of inelastic excitations $S(\mathbf{q},\mathbf{q}',\omega)$ for $\mathbf{q} \neq \mathbf{q}'$, which contains information about excitations in a spatially inhomogeneous system.

We now discuss approximate methods of solving Eqs. (9)–(13). In these equations an explicit form of the averaged potential $\langle H'(\mathbf{r})\rangle$ has not been defined so far. Therefore Eqs. (9) and (10) are valid for an arbitrary distribution of atoms in a solid provided that the correlation radius of inelastic excitations r_c satisfies the condition (15) or (16). In practice, however, in order to find a solution to (13) one must first solve Eqs. (9) and (10) and evaluate the Green's functions $G_0(\mathbf{r},\mathbf{r}',E)$ and $G(\mathbf{r},\mathbf{r}',E)$, and it is this point which turns out to be difficult in most cases.

For some particular situations there exist useful analytical expressions which we quote below. When $\langle H'(\mathbf{r})\rangle$ is zero, the Green's function (9) has the form

$$G_0(\mathbf{r},\mathbf{r}',E) = -\frac{m}{2\pi\hbar^2}\frac{1}{|\mathbf{r}-\mathbf{r}'|}\exp\Big(i\sqrt{\frac{2mE}{\hbar^2}}|\mathbf{r}-\mathbf{r}'|\Big). \tag{24}$$

Another expression corresponds to the transmission geometry of diffraction,

$$\begin{aligned} G_0(\mathbf{R},z,\mathbf{R}',z',E) &= G_0(z-z',\mathbf{R},\mathbf{R}',E) \\ &= -\frac{im}{\hbar^2 k}\Theta(z-z')\exp[ik(z-z')]\sum_j\int_{\mathrm{BZ}}\frac{d^2q}{(2\pi)^2}\exp\Big(-i\frac{mE_j(\mathbf{q})}{\hbar^2 k}(z-z')\Big)b_j(\mathbf{R},\mathbf{q})b_j^*(\mathbf{R}',\mathbf{q}), \end{aligned} \tag{25}$$

where $k = \sqrt{2mE/\hbar^2}$ is the wave vector of the fast electron, the summation is performed over different branches j of the dispersion surface, the z axis is along the inward directed surface normal, and the integral is over $\mathbf{q}$ vectors in the first two-dimensional Brillouin zone (BZ). In Eq. (25), $b_j(\mathbf{R},\mathbf{q}) = b_j(x,y,\mathbf{q})$ denotes a transverse Bloch wave function of an electron in the projected two-dimensional periodic crystal potential $\langle H'(x,y)\rangle$, which satisfies a "transverse" Schrödinger equation with transverse energy $E_j(\mathbf{q})$,

$$\Big[-\frac{\hbar^2}{2m}\nabla^2 + \langle H'(\mathbf{R})\rangle\Big]b_j(\mathbf{R},\mathbf{q}) = E_j(\mathbf{q})b_j(\mathbf{R},\mathbf{q}). \tag{26}$$

In the expression (25) it is assumed that the electron propagates along the positive direction of z axis, so that $\Theta(\zeta) = 1$ for positive and $\Theta(\zeta) = 0$ for negative arguments. In the limiting "empty lattice" case where $\langle H'(x,y)\rangle \to 0$ formula (25) reduces to the well-known propagator of the multislice method,

$$\begin{aligned} G_0(\mathbf{r},\mathbf{r}',E) = &-\frac{m}{2\pi\hbar^2}\frac{1}{(z-z')}\Theta(z-z') \\ &\times\exp\Big(ik(z-z') + i\frac{k}{2}\frac{(\mathbf{R}-\mathbf{R}')^2}{(z-z')}\Big). \end{aligned} \tag{27}$$

Formula (27) also follows from (24) provided that $k(\mathbf{R}-\mathbf{R}')^2 \ll (z-z')$. It is important to emphasize that expression (27) can also be used as a propagator of the high-energy electron in the nonzero potential field $\langle H'(\mathbf{R})\rangle$ if the angle between the wave vector of the electron and the zone axis is many times the Bragg angle.

Using expressions (24), (25), and (27), we can classify previous approaches to the theory of multiple inelastic scattering of high-energy electrons by crystals.[12,16–20,32,33] Primarily, most of these formulations differ in the choice of a form of the Green's function describing the propagation of an electron between successive inelastic collisions inside the medium. For instance, solutions found by Høier[12] and by Dudarev and Ryazanov[17] result from the choice of the Green's function in the form (27), provided that absorption effects are taken into account. The treatments of backscattering developed by Spencer and Humphreys,[21] by Dudarev,[32] and by Gorodnichev and Dudarev[33] are actually based upon expression (24). The equations derived by Rez[16] are equivalent to the choice of the Green's function in the form (25). A multislice approach developed by Wang,[18,19] although being based upon a different formalism, is in accordance with expression (25) as well.

It must be emphasized, however, that a more recent version of the multislice formulation proposed by Wang[48–50] includes an additional approximation, which restricts the range of validity of his method. The approximation made in Refs. 48–50 can be understood as follows. If one neglects the derivatives of the Green's function over x, y in Eq. (9), provided that the electron propagates along the positive direction of z axis, the solution to (9) can be found analytically in the eikonal approximation [51]

$$G_0(\mathbf{R},z,\mathbf{R}',z',E) = -\frac{im}{\hbar^2 k}\Theta(z-z')\delta(\mathbf{R}-\mathbf{R}')\exp\Big(ik(z-z') - i\frac{m}{\hbar^2 k}\int_{z'}^{z}d\zeta\langle H'(\mathbf{R},\zeta)\rangle\Big). \tag{28}$$

As is well known (see, for example, Ref. 39, p. 162), this form of the solution can be used only if $|z - z'| \ll kb^2$, where b characterizes the scale of variation of the potential $\langle H'(\mathbf{r})\rangle$ in real space. For $b \sim 1$ Å and energy $E \sim 100$ keV the magnitude of kb^2 does not exceed 100 Å. The original approximation used in Refs. 48–50 is somewhat more sophisticated than (28). However, it can be shown that the method[48--50] is subject to the same restriction $|z - z'| \ll kb^2$ and the thickness of the crystal $\mathcal{L}$ for the approach formulated in Refs. 48–50 to be valid must not exceed the value of $kb^2 \sim 100$ Å for $E \sim 100$ keV.

In order to formulate the principle which determines the choice of an approximate form of the Green's function in Eqs. (11) and (13), it is useful to consider qualitatively the process of motion of the electron from $(\mathbf{x}, \mathbf{x}')$ to $(\mathbf{r}, \mathbf{r}')$ as a propagation of a set of plane waves with slowly varying amplitudes. The amplitude of each wave is affected by the averaged potential $\langle H'(\mathbf{r})\rangle$, and the choice between (24), (25), and (27) depends on the magnitude of this effect within the range of phase space of final states of a single inelastic collision. Given the value of the correlation radius of inelastic excitations r_c is many times the electron wavelength; then the mean angle of scattering of the high-energy electron in a single inelastic interaction equals $\theta_0 \sim (kr_c)^{-1}$. In order to estimate the influence of the averaged potential on the propagation of the electron from one inelastic collision to another, we compare θ_0 with the angular width of the Kikuchi lines which are visible in the diffraction pattern and which are known to result from diffraction of inelastically scattered electrons. The angular width θ_K of Kikuchi lines can be estimated from two-beam dynamical diffraction theory, as[17] $\theta_K \sim m|\langle \overline{H}'\rangle|/\hbar^2 k|\mathbf{G}|$, where $\mathbf{G}$ is a reciprocal lattice vector. Comparing the magnitudes of θ_0 and θ_K we may say that if $\theta_0 \gg \theta_K$, then most of inelastically scattered electrons propagate between $(\mathbf{x}, \mathbf{x}')$ and $(\mathbf{r}, \mathbf{r}')$ with their momenta lying far from the Bragg condition. Therefore the inequality $\theta_0 \gg \theta_K$ makes it possible to employ the approximate forms of the Green's function (24) and (27), disregarding the influence of the averaged potential $\langle H'(\mathbf{r})\rangle$ on the propagation of the electron between successive inelastic collisions. Equation (22) shows that in this case one needs to take diffraction effects into account only for the incident and emerging electrons, i.e., before the first and after the last inelastic interaction. On the other hand, when $\theta_0 \ll \theta_K$, diffraction effects influence strongly the amplitude of propagation of the high-energy electron between successive inelastic collisions in a crystal. To our knowledge, however, no realistic model of excitations results in the latter inequality $\theta_0 \ll \theta_K$.

The third case to be discussed here cannot be reduced to either of the inequalities $\theta_0 \ll \theta_K$ or $\theta_0 \gg \theta_K$. This case concerns collective excitations of the electronic subsystem of the crystal, the cross section of which is

$$\frac{d\sigma}{do} \sim \frac{1}{\theta^2 + \theta_E^2}, \tag{29}$$

and for which the mean scattering angle θ_0 depends on the choice of the upper limit of integration $\theta_c = q_c/k$, where q_c is the plasmon cutoff vector.[52] The lack of a well-defined value of the mean angle of inelastic scattering by collective excitations of electronic subsystem of a solid was one of the main reasons which gave rise to intensive discussion of the role of electron-electron scattering in the diffraction contrast preservation[6–8,10] (for a recent review see Reimer[53]). The problem of the mutual influence of diffraction and multiple inelastic scattering by collective electronic excitations is considered below.

In summary, in this section we have discussed the conditions for the KE method to be applicable to the description of multiple elastic and inelastic scattering of the high-energy electron by a solid and the relation between the present formulation and previous theoretical approaches to the same problem. In what follows we discuss a particular application of the KE to the problem of multiple inelastic scattering in the transmission geometry of diffraction. We show how in the case of small-angle elastic and inelastic scattering, the equations previously formulated by Kagan and Kononets[15] and by Rez[16] can be derived from the general form of the KE (11) or (13). We find that scattering by collective electronic excitations of a crystal results in a rapid damping of coherence of the wave field of the high-energy electron propagating through a single crystal. We obtain numerical solutions of the KE with emphasis on the influence of multiple small-angle inelastic scattering on the contrast of convergent-beam electron diffraction (CBED) patterns, and then compare simulated intensity profiles with experimental data. The reasonable agreement between simulations and observed intensity distributions shows that the KE method provides a useful technique for quantitative analysis of the effects of inelastic scattering on electron diffraction patterns.

IV. MULTIPLE INELASTIC SCATTERING BY DELOCALIZED ELECTRONIC EXCITATIONS

In the preceding sections we formulated the kinetic equation approach to the problem of diffraction and multiple inelastic scattering of high-energy electrons by a crystal, and established the conditions determining the range of validity of this method. In the present section we consider an application of the above developed formulation to the problem of multiple scattering of fast electrons by collective excitations of the electronic subsystem of a solid.

The cross section of inelastic scattering by plasmon and valence electron excitations (29) is strongly peaked in the forward direction. This circumstance was explicitly employed in previous approaches to the problem (see, e.g., Refs. 6 and 54), where the inelastic scattering was considered to be effectively at zero angle, leading to retention of the diffraction contrast by the inelastically scattered electrons. Qualitatively this approximation is in a good agreement with experimental observations performed for thin crystals.[55] However, the contrast degrades rapidly for second- and higher-order losses.[56] We notice here that although the effect of energy loss can in principle be eliminated from the diffraction pattern by energy filtering, there are some cases where it is not desirable[22,23] or even possible, for example, the production of characteristic x-ray or Auger electron emission.[57] This complicates the interpretation of experimental observations, because the image contrast depends on the finite angular divergence of the beam resulting from multiple small-angle inelastic scattering. For single inelastic scattering Metherell[58] showed that such a dependence existed.

In order to apply the KE method to study of the effect of inelastic scattering of the high-energy electrons by collective electron excitations of the crystal we first need to evaluate the relevant mixed dynamic form factor (7), which can be expressed in terms of the matrix of inverse dielectric constant[35] as

$$S_{\mathrm{el}}(\mathbf{q},\mathbf{q}',\omega)=\frac{i\hbar}{8\pi^2e^2}[1-\exp(-\hbar\omega/k_BT)]^{-1}\times\{q^2\varepsilon^{-1}(\mathbf{q},\mathbf{q}',\omega)-q'^2[\varepsilon^{-1}(\mathbf{q}',\mathbf{q},\omega)]^*\}. \tag{30}$$

Collective electronic excitations in most crystals are usually considered not to be sensitive to the periodicity of the lattice (for observations of weak anisotropy of the dispersion law of bulk plasmons see Refs. 59 and 60). This makes it possible to simplify (30) as follows:

$$S_{\mathrm{el}}(\mathbf{q},\mathbf{q}',\omega)=(2\pi)^3\delta(\mathbf{q}-\mathbf{q}')S_{\mathrm{el}}(\mathbf{q},\omega), \tag{31}$$

where

$$S_{\mathrm{el}}(\mathbf{q},\omega)=-\frac{\hbar q^2}{4\pi^2e^2}\frac{1}{1-\exp(-\hbar\omega/k_BT)}\mathrm{Im}\Big[\frac{1}{\varepsilon(\mathbf{q},\omega)}\Big]. \tag{32}$$

In accordance with (7), the kernel of the integral equations (11) and (13) can be obtained by making use of the Fourier transform of (32),

$$\bar{s}_{\mathrm{el}}(\mathbf{r},\mathbf{r}',\omega)=-\frac{4\hbar e^2}{1-\exp(-\hbar\omega/k_BT)}\times\int\frac{d^3q}{(2\pi)^3}\frac{1}{q^2}\exp[i\mathbf{q}\cdot(\mathbf{r}-\mathbf{r}')]\mathrm{Im}\Big[\frac{1}{\varepsilon(\mathbf{q},\omega)}\Big]. \tag{33}$$

Neglecting the dependence of the dielectric function on the wave vector $\mathbf{q}$ [this approximation is valid for small $|\mathbf{q}|<q_c$ in the frequency range where the value of $\hbar\omega$ does not exceed several tens eV, this region of $(\mathbf{q},\omega)$ corresponding primarily to collective excitations of the electron subsystem of a solid) we arrive at an explicit expression for $\bar{s}_{\mathrm{el}}(\mathbf{r},\mathbf{r}',\omega)$,

$$\bar{s}_{\mathrm{el}}(\mathbf{r},\mathbf{r}',\omega)=-\frac{\hbar e^2}{\pi}\frac{1}{|\mathbf{r}-\mathbf{r}'|}\frac{1}{1-\exp(-\hbar\omega/k_BT)}\times\mathrm{Im}\Big[\frac{1}{\varepsilon(\omega)}\Big]. \tag{34}$$

The above relationship (34) is valid for $|\mathbf{r}-\mathbf{r}'|>q_c^{-1}$, and it determines the long-range behavior of the dynamic form factor of electronic excitations in the crystal bulk. There is no dimensional parameter in the expression (34) which could be interpreted as an effective radius r_c of collective electronic excitations. This complicates the definition of the mean angle of single inelastic scattering, θ_0, and a more careful consideration is required[52] in order to estimate the effect of collective electronic excitations on the propagation of high-energy electrons through a crystal.

Using (34) and neglecting the exponential term in the denominator, we can write Eq. (13) in the form

$$\begin{aligned}\rho(\mathbf{R},\mathbf{R}',z,z',E)={}&\Psi_{\mathbf{k}_0}(\mathbf{R},z)\Psi^*_{\mathbf{k}_0}(\mathbf{R}',z')\delta\Big(E-\frac{\hbar^2\mathbf{k}_0^2}{2m}\Big)\\&-\frac{\hbar e^2}{\pi}\int d\omega\mathrm{Im}\Big[\frac{1}{\varepsilon(\omega)}\Big]\int d\zeta d\zeta'\int d^2u d^2u' G(z-\zeta,\mathbf{R},\mathbf{u},E)G^*(z'-\zeta',\mathbf{R}',\mathbf{u}',E)\\&\times\frac{1}{\sqrt{(\zeta-\zeta')^2+(\mathbf{u}-\mathbf{u}')^2}}\rho(\mathbf{u},\mathbf{u}',\zeta,\zeta',E+\hbar\omega).\end{aligned} \tag{35}$$

As follows from (10), the Green's function $G(z-z',\mathbf{R},\mathbf{R}',E)$ is so defined as to take absorption effects into account, and an explicit expression for this function can be obtained from Eq. (25) by making use of a standard substitution

$$E_j(\mathbf{q})\to E_j(\mathbf{q})-i\mu_j(\mathbf{q})-i\mu_{\mathrm{el}}, \tag{36}$$

where $\mu_j(\mathbf{q})$ results from localized (e.g., phonon and core-electron) excitations, and μ_{el} comes from inelastic scattering by collective excitations of electronic subsystem of a solid, namely,

$$\mu_{\mathrm{el}}=-\frac{me^2}{\pi\hbar k}\int d\omega\mathrm{Im}\Big[\frac{1}{\varepsilon(\omega)}\Big]\ln\Big(\frac{\hbar kq_c}{m\omega}\Big). \tag{37}$$

Substituting (36) into (25) we arrive at

$$\begin{aligned}G(z-z',\mathbf{R},\mathbf{R}',E)={}&-\frac{im}{\hbar^2k}\Theta(z-z')\exp[ik(z-z')]\sum_j\int_{\mathrm{BZ}}\frac{d^2q}{(2\pi)^2}\exp\Big(-i\frac{mE_j(\mathbf{q})}{\hbar^2k}(z-z')\Big)\\&\times b_j(\mathbf{R},\mathbf{q})b_j^*(\mathbf{R}',\mathbf{q})\exp\Big(-\frac{\mu_j(\mathbf{q})}{\hbar v}(z-z')\Big)\exp\Big(-\frac{\mu_{\mathrm{el}}}{\hbar v}(z-z')\Big).\end{aligned} \tag{38}$$

The density matrix of electrons scattered through small angles can be represented in the form of a linear combination of Bloch waves with slowly varying amplitudes,

$$\rho(\mathbf{R},\mathbf{R}',z,z',E)=\sum_{j,j'}\int_{\mathrm{BZ}}\frac{d^2q}{(2\pi)^2}\bar{\rho}_{jj'}(\mathbf{q},z,z',E)b_j(\mathbf{R},\mathbf{q})b^*_{j'}(\mathbf{R},\mathbf{q})\exp\left[ik(z-z')\right]$$
$$\times\exp\Big(-i\frac{z}{\hbar v}E_j(\mathbf{q})+i\frac{z'}{\hbar v}E_{j'}(\mathbf{q})\Big)\exp\Big(-\frac{z}{\hbar v}\mu_j(\mathbf{q})-\frac{z'}{\hbar v}\mu_{j'}(\mathbf{q})-\frac{\mu_{\mathrm{el}}}{\hbar v}(z+z')\Big),\qquad(39)$$

where $v=\hbar k/m$ is the velocity of an electron, the summation is performed over different branches j, j' of the dispersion surface, the z axis is along the inward directed surface normal, and the integral is over $\mathbf{q}$ vectors in the first two-dimensional Brillouin zone (BZ). In Eq. (39) the coefficients $\mu_j(\mathbf{q})$ and $\mu_{j'}(\mathbf{q})$ account for the attenuation of the flux of electrons scattered through small angles as a result of large-angle scattering by localized excitations. The inhomogeneous term in Eq. (35) has a standard form[1]

$$\Psi_{\mathbf{k}_0}(\mathbf{r})=\sum_j C^*_{0j}(\mathbf{q}_0)b_j(\mathbf{R},\mathbf{q}_0)\exp\Big(-i\frac{E_j(\mathbf{q}_0)z}{\hbar v}-\frac{\mu_{\mathrm{el}}z}{\hbar v}-\frac{\mu_j(\mathbf{q}_0)z}{\hbar v}\Big),\qquad(40)$$

where $\mathbf{q}_0=(\mathbf{k}_0)_{x,y}$ and $\{C_{0j}(\mathbf{q}_0)\}$ are the coefficients of expansion of the Bloch wave in the plane wave basis,

$$b_j(\mathbf{R},\mathbf{q}_0)=\sum_h C_{hj}(\mathbf{q}_0)\exp[i(\mathbf{q}_0+\mathbf{G}_h)\cdot\mathbf{R}].\qquad(41)$$

Using (39) and (38), we arrive at

$$\bar{\rho}_{jj'}(\mathbf{q},z,z',E)=(2\pi)^2\delta(\mathbf{q}-\mathbf{q}_0)\delta\Big(E-\frac{\hbar^2\mathbf{k}_0^2}{2m}\Big)C^*_{0j}(\mathbf{q}_0)C_{0j'}(\mathbf{q}_0)$$
$$-\frac{2\hbar e^2}{k^2}\Big(\frac{m}{2\pi\hbar^2}\Big)^2\int d\omega\,\mathrm{Im}\Big[\frac{1}{\varepsilon(\omega)}\Big]\int_0^z d\zeta\int_0^{z'}d\zeta'\int_{|\mathbf{Q}_\perp|<q_c}\frac{d^2Q_\perp}{|\mathbf{Q}_\perp|}$$
$$\times\exp(-|\mathbf{Q}_\perp||\zeta-\zeta'|)\sum_{JJ'}M_{Jj}(\mathbf{q}+\mathbf{Q}_\perp,\mathbf{q})M^*_{J'j'}(\mathbf{q}+\mathbf{Q}_\perp,\mathbf{q})\bar{\rho}_{JJ'}(\mathbf{q}+\mathbf{Q}_\perp,\zeta,\zeta',E+\hbar\omega)$$
$$\times\exp\Big(i\frac{\omega}{v}(\zeta-\zeta')\Big)\exp\Big(i\frac{\zeta}{\hbar v}[E_j(\mathbf{q})-E_J(\mathbf{q}+\mathbf{Q}_\perp)]\Big)\exp\Big(-i\frac{\zeta'}{\hbar v}[E_{j'}(\mathbf{q})-E_{J'}(\mathbf{q}+\mathbf{Q}_\perp)]\Big)$$
$$\times\exp\Big(\frac{\zeta}{\hbar v}[\mu_j(\mathbf{q})-\mu_J(\mathbf{q}+\mathbf{Q}_\perp)]\Big)\exp\Big(\frac{\zeta'}{\hbar v}[\mu_{j'}(\mathbf{q})-\mu_{J'}(\mathbf{q}+\mathbf{Q}_\perp)]\Big),\qquad(42)$$

where the following notation is introduced:

$$M_{Jj}(\mathbf{q}+\mathbf{Q}_\perp,\mathbf{q})=\sum_h C_{hJ}(\mathbf{q}+\mathbf{Q}_\perp)C^*_{hj}(\mathbf{q}).\qquad(43)$$

The probability of finding the electron at a particular point $\mathbf{r}$ is proportional to the diagonal elements of the density matrix $\rho(\mathbf{R},\mathbf{R},z,z,E)$. Evaluation of this quantity may be greatly simplified if we rewrite (42) in the form of a closed equation for $\bar{\rho}(\mathbf{q},z,E)=\bar{\rho}(\mathbf{q},z,z',E)\big|_{z=z'}$. Introducing two variables $\eta=\zeta-\zeta'$ and $\xi=(\zeta+\zeta')/2$, performing the integration over η, and neglecting the terms which do not increase with increasing z, we obtain

$$\bar{\rho}_{jj'}(\mathbf{q},z,E)=(2\pi)^2\delta(\mathbf{q}-\mathbf{q}_0)\delta\Big(E-\frac{\hbar^2\mathbf{k}_0^2}{2m}\Big)C^*_{0j}(\mathbf{q}_0)C_{0j'}(\mathbf{q}_0)$$
$$-\frac{e^2}{\pi^2\hbar v^2}\int d\omega\,\mathrm{Im}\Big[\frac{1}{\varepsilon(\omega)}\Big]\int_0^z d\xi\int_{Q_\perp<q_c}\frac{d^2Q_\perp}{Q_\perp^2+(\omega/v)^2}$$
$$\times\sum_{JJ'}M_{Jj}(\mathbf{q}+\mathbf{Q}_\perp,\mathbf{q})M^*_{J'j'}(\mathbf{q}+\mathbf{Q}_\perp,\mathbf{q})\bar{\rho}_{JJ'}(\mathbf{q}+\mathbf{Q}_\perp,\xi,E+\hbar\omega)$$
$$\times\exp\Big(i\frac{\xi}{\hbar v}[E_j(\mathbf{q})-E_J(\mathbf{q}+\mathbf{Q}_\perp)]\Big)\exp\Big(-i\frac{\xi}{\hbar v}[E_{j'}(\mathbf{q})-E_{J'}(\mathbf{q}+\mathbf{Q}_\perp)]\Big)$$
$$\times\exp\Big(\frac{\xi}{\hbar v}[\mu_j(\mathbf{q})-\mu_J(\mathbf{q}+\mathbf{Q}_\perp)]\Big)\exp\Big(\frac{\xi}{\hbar v}[\mu_{j'}(\mathbf{q})-\mu_{J'}(\mathbf{q}+\mathbf{Q}_\perp)]\Big).\qquad(44)$$

The kinetic equation (44) describes the evolution of the density matrix of the high-energy electron $\bar{\rho}_{jj'}(\mathbf{q},z,E)$ along the path length followed by collective excitations of electronic subsystem of the crystal. The matrix element (43) satisfies the condition

$$\lim_{\mathbf{Q}_\perp \to 0} M_{Jj}(\mathbf{q}+\mathbf{Q}_\perp,\mathbf{q}) = \begin{cases} 1 \text{ if } J = j \\ 0 \text{ if } J \neq j, \end{cases} \tag{45}$$

which means that for small transverse momentum transfers the probability of *intrabranch* $(J = j)$ transitions is many times the probability of *interbranch* $(J \neq j)$ transitions. This was first pointed out by Howie.[6] The use of the *intrabranch* scattering approximation $M_{Jj}(\mathbf{q}+\mathbf{Q}_\perp,\mathbf{q}) \approx \delta_{Jj}$, simplifies Eq. (44) as follows:

$$\begin{aligned} \bar{\rho}_{jj'}(\mathbf{q},z,E) = {} & (2\pi)^2\delta(\mathbf{q}-\mathbf{q}_0)\delta\Big(E - \frac{\hbar^2\mathbf{k}_0^2}{2m}\Big)C^*_{0j}(\mathbf{q}_0)C_{0j'}(\mathbf{q}_0) \\ & - \frac{e^2}{\pi^2\hbar v^2}\int d\omega \mathrm{Im}\Big[\frac{1}{\varepsilon(\omega)}\Big]\int_0^z d\xi \int_{Q_\perp<q_c}\frac{d^2Q_\perp}{Q_\perp^2+(\omega/v)^2}\bar{\rho}_{jj'}(\mathbf{q}+\mathbf{Q}_\perp,\xi,E+\hbar\omega) \\ & \times \exp\Big(i\frac{\xi}{\hbar v}[E_j(\mathbf{q})-E_j(\mathbf{q}+\mathbf{Q}_\perp)]\Big)\exp\Big(-i\frac{\xi}{\hbar v}[E_{j'}(\mathbf{q})-E_{j'}(\mathbf{q}+\mathbf{Q}_\perp)]\Big) \\ & \times \exp\Big(\frac{\xi}{\hbar v}[\mu_j(\mathbf{q})-\mu_j(\mathbf{q}+\mathbf{Q}_\perp)]\Big)\exp\Big(\frac{\xi}{\hbar v}[\mu_{j'}(\mathbf{q})-\mu_{j'}(\mathbf{q}+\mathbf{Q}_\perp)]\Big). \end{aligned} \tag{46}$$

Differentiating (46) with respect to z, we obtain a matrix relationship

$$\begin{aligned} \frac{\partial}{\partial z}\rho_{jj'}(\mathbf{q},z,E) = {} & -\frac{2\mu_{\mathrm{el}}}{\hbar v}\rho_{jj'}(\mathbf{q},z,E) - \frac{\mu_j(\mathbf{q})+\mu_{j'}(\mathbf{q})}{\hbar v}\rho_{jj'}(\mathbf{q},z,E) \\ & - \frac{e^2}{\pi^2\hbar v^2}\int d\omega \mathrm{Im}\Big[\frac{1}{\varepsilon(\omega)}\Big]\int_{Q_\perp<q_c}\frac{d^2Q_\perp}{Q_\perp^2+(\omega/v)^2}\rho_{jj'}(\mathbf{q}+\mathbf{Q}_\perp,z,E+\hbar\omega) \\ & \times \exp\Big(i\frac{z}{\hbar v}[E_j(\mathbf{q})-E_j(\mathbf{q}+\mathbf{Q}_\perp)]\Big)\exp\Big(-i\frac{z}{\hbar v}[E_{j'}(\mathbf{q})-E_{j'}(\mathbf{q}+\mathbf{Q}_\perp)]\Big), \end{aligned} \tag{47}$$

which for *intrabranch* inelastic scattering is equivalent to Eqs. (2.6) and (2.7) of Kagan and Kononets[15] and to Eq. (13) of Rez.[16] The diagonal elements of (47) coincide with the Boltzmann transport equation

$$\begin{aligned} \frac{\partial}{\partial z}\rho_{jj}(\mathbf{q},z,E) = {} & -\frac{2\mu_{\mathrm{el}}}{\hbar v}\rho_{jj}(\mathbf{q},z,E) - \frac{2\mu_j(\mathbf{q})}{\hbar v}\rho_{jj}(\mathbf{q},z,E) \\ & - \frac{e^2}{\pi^2\hbar v^2}\int d\omega \mathrm{Im}\Big[\frac{1}{\varepsilon(\omega)}\Big]\int_{Q_\perp<q_c} d^2Q_\perp \frac{\rho_{jj}(\mathbf{q}+\mathbf{Q}_\perp,z,E+\hbar\omega)}{Q_\perp^2+(\omega/v)^2}. \end{aligned} \tag{48}$$

In Eqs. (47) and (48) we have used the notation

$$\rho_{jj'}(\mathbf{q},z,E) = \bar{\rho}_{jj'}(\mathbf{q},z,E)\exp\Big(-\frac{2\mu_{\mathrm{el}}}{\hbar v}z\Big)\exp\Big(-\frac{[\mu_j(\mathbf{q})+\mu_{j'}(\mathbf{q})]}{\hbar v}z\Big). \tag{49}$$

Provided the solution to the kinetic equation (47) is known, we can find the localization probability $P(\mathbf{r})|_{\text{small angle}}$ for the electron, multiply scattered through small angles at a particular point $\mathbf{r}$, as

$$P(\mathbf{r})|_{\text{small angle}} = \sum_{j,j'}\int_{\mathrm{BZ}}\frac{d^2q}{(2\pi)^2}\int dE\ \rho_{jj'}(\mathbf{q},z,E)b_j(\mathbf{R},\mathbf{q})b^*_{j'}(\mathbf{R},\mathbf{q})\exp\Big(-i\frac{z}{\hbar v}[E_j(\mathbf{q})-E_{j'}(\mathbf{q})]\Big). \tag{50}$$

We see that this quantity decreases with increasing crystal thickness. This results from localized inelastic interactions giving rise to large-angle scattering. The contribution to the localization probability coming from the electrons scattered through large angles can be evaluated as follows:[61,62]

$$P(\mathbf{r})|_{\text{large angle}} = 1 - \sum_j \int_{\mathrm{BZ}}\frac{d^2q}{(2\pi)^2}\int dE\ \rho_{jj}(\mathbf{q},z,E). \tag{51}$$

The sum of (50) and (51) gives rise to the total localization probability $P(\mathbf{r})$, the quantity which at low temperatures determines the rate of x-ray production and high-angle backscattering from thin crystal films.[61,62]

Therefore, for thin crystals the problem of calculating the cross section of multiple inelastic scattering through small angles or high-angle backscattering reduces to the problem of solving the kinetic equation (44) or its simplified form (47). This equation includes both the diagonal and off-diagonal elements of the density matrix $\rho_{jj'}(\mathbf{q},z,E)$. The diagonal elements $\rho_{jj}(\mathbf{q},z,E)$ of this matrix can be interpreted as the probabilities of finding the electron in a particular Bloch state $b_j(\mathbf{R},\mathbf{q})$. The off-diagonal elements of $\rho_{jj'}(\mathbf{q},z,E)$ for $j \neq j'$ describe the coherence between the states of the electron on different branches of the dispersion surface,[17,63] j and j'. As was shown by Kagan and Kononets,[15] the off-diagonal elements of the density matrix $\hat{\rho}_{jj'}$ attenuate along the path length, and it was found that the distance characterizing the damping of the off-diagonal elements of the density matrix of nonrelativistic protons under conditions of channeling is many times the inelastic mean free path. Their result can be qualitatively understood as follows: After the first inelastic interaction the wave function of the fast electron can be represented in the form of a set of waves propagating along slightly different directions and therefore having slightly different excitation parameters. Although the difference between the excitation errors of two particular waves may be small, the phase difference between them increases linearly with the path length. Successive inelastic rescattering of scattered waves gives rise to a convolution of their amplitudes with the differential cross section of inelastic collisions as in Eq. (47). This results in averaging out the phase factors which describe the interference between the states of the high-energy electron propagating through a thin crystal, and causes a loss of diffraction contrast in a transmission electron microscope image.[7] In the following section we consider this problem more quantitatively. We show that in light elements such as silicon, the inelastic scattering by delocalized electronic excitations provides the basic mechanism destroying the coherence between different Bloch states in the two-dimensional periodic projected potential. Since such excitations give rise to a major part of the inelastic scattering cross section, they are found to affect strongly the contrast of electron diffraction patterns, and this statement is verified below by a straightforward comparison of simulated intensity profiles with experimentally observed distributions.

V. DAMPING OF COHERENCE AND EFFECT OF SMALL-ANGLE SCATTERING ON DIFFRACTION PATTERNS

In this section we develop methods of solving the kinetic equation for multiple small-angle inelastic scattering in a crystal. First, we consider an approximate analytical approach, and then study numerically the evolution of the density matrix with increasing crystal thickness. Finally, we compare the results of theoretical simulations with experimental data on the intensity distribution in energy-unfiltered convergent-beam electron diffraction (CBED) patterns.

In order to study analytically solutions of the kinetic equation (47), we consider the case where the cross section for small-angle inelastic scattering is many times the cross section of localized excitations, so that the effect of the latter may be neglected. As follows from the data given by Radi,[64] this condition holds well for light elements such as silicon. Integrating Eq. (48) for the diagonal elements of the density matrix over $\mathbf{q}$ and E, and summing over the branches j of the dispersion surface, we arrive at

$$\sum_j \int_{\mathrm{BZ}} \frac{d^2q}{(2\pi)^2} \int dE\, \rho_{jj}(\mathbf{q}, z, E) = \text{const.} \tag{52}$$

This equation represents the condition of conservation of the total probability in the process of multiple scattering. There is no similar condition for the off-diagonal elements of the density matrix $\rho_{jj'}(\mathbf{q}, z, E)$. The off-diagonal elements describe the coherence between Bloch states of the high-energy electron on different branches j and j' of the dispersion surface.[65] These elements attenuate when the electron penetrates into the crystal since the coherence between different Bloch states gradually disappears. In order to evaluate the rate of attenuation of the off-diagonal elements of the density matrix, we expand the exponents in Eq. (47) in the power series in $\mathbf{Q}_\perp$,

$$\frac{\partial}{\partial z}\rho_{jj'}(\mathbf{q}, z, E) = -\frac{e^2}{\pi^2 \hbar v^2} \int d\omega\, \mathrm{Im}\Big[\frac{1}{\varepsilon(\omega)}\Big] \int_{Q_\perp < q_c} \frac{d^2Q_\perp}{Q_\perp^2 + (\omega/v)^2}$$
$$\times \Big\{ \rho_{jj'}(\mathbf{q} + \mathbf{Q}_\perp, z, E + \hbar\omega) \exp\Big(i\frac{z}{\hbar v} \mathbf{Q}_\perp \frac{\partial}{\partial \mathbf{q}} \big[E_{j'}(\mathbf{q}) - E_j(\mathbf{q})\big]\Big) - \rho_{jj'}(\mathbf{q}, z, E) \Big\}\ . \tag{53}$$

The last term in curly brackets on the right-hand side of (53), when taken with the integral over $\mathbf{Q}_\perp$ and ω, is by (37) the same as the first term on the right of (47). In the region of relatively small z the quantity $\rho_{jj'}(\mathbf{q}, z, E)$, regarded as a function of $\mathbf{q}$, exhibits a pronounced peak near $\mathbf{q}_0$, so that we can approximate the derivative $\frac{\partial}{\partial \mathbf{q}}\big[E_{j'}(\mathbf{q}) - E_j(\mathbf{q})\big]$ by its value at $\mathbf{q} = \mathbf{q}_0$. Then the solution of (53) can be found by making use of the two-dimensional Fourier transform over $\mathbf{q}$, which results in

$$\int \frac{d^2q}{(2\pi)^2} \int dE\, \rho_{jj'}(\mathbf{q}, z, E) = C_{0j}^*(\mathbf{q}_0) C_{0j'}(\mathbf{q}_0) \exp\Big[-\Omega(0) z + \int_0^z d\xi\, \Omega\Big(\frac{\xi}{\hbar v} \frac{\partial}{\partial \mathbf{q}} \{E_{j'}(\mathbf{q}) - E_j(\mathbf{q})\}\Big|_{\mathbf{q}_0} \Big) \Big], \tag{54}$$

where

$$\Omega(\mathbf{R}) = -\frac{2e^2}{\pi \hbar v^2} \int d\omega \mathrm{Im}\Big[\frac{1}{\varepsilon(\omega)}\Big] K_0\Big(\frac{\omega}{v}\sqrt{\mathbf{R}^2 + q_c^{-2}}\Big), \tag{55}$$

and $K_0(x)$ is the modified Bessel function.[66] For small arguments $x \ll 1$ this function can be approximated as follows:

$$K_0(x) \approx -\Big\{ \ln\Big(\frac{x}{2}\Big) + 0.577216... \Big\}, \tag{56}$$

which makes it possible to perform integration over z in (54) analytically. This results in

$$\int \frac{d^2q}{(2\pi)^2} \int dE\ \rho_{jj'}(\mathbf{q},z,E) = C^*_{0j}(\mathbf{q}_0)C_{0j'}(\mathbf{q}_0)\exp\Big(-\frac{2e^2}{\pi\hbar v^2}\Big\{\int d\omega \mathrm{Im}\Big[\frac{1}{\varepsilon(\omega)}\Big]\Big\}$$
$$\times\Big\{-z\ln\sqrt{1+\left(\frac{q_c z}{\hbar v}\frac{\partial}{\partial\mathbf{q}}\{E_{j'}(\mathbf{q})-E_j(\mathbf{q})\}\Big|_{\mathbf{q}_0}\right)^2}+z$$
$$-\frac{\hbar v}{q_c\left|\frac{\partial}{\partial\mathbf{q}}\{E_{j'}(\mathbf{q})-E_j(\mathbf{q})\}\big|_{\mathbf{q}_0}\right|}\arctan\Big(\frac{zq_c}{\hbar v}\Big|\frac{\partial}{\partial\mathbf{q}}\{E_{j'}(\mathbf{q})-E_j(\mathbf{q})\}\big|_{\mathbf{q}_0}\Big|\Big)\Big\}\Big). \tag{57}$$

For small z, $z \ll \hbar v\left|q_c\frac{\partial}{\partial\mathbf{q}}\{E_{j'}(\mathbf{q})-E_j(\mathbf{q})\}\big|_{\mathbf{q}_0}\right|^{-1}$, the rate of attenuation of the off-diagonal elements of the density matrix follows the law[67] $\hat{\rho}_{jj'} \sim \exp(-\mathrm{const}\ \times z^3)$, namely,

$$\int \frac{d^2q}{(2\pi)^2} \int dE\ \rho_{jj'}(\mathbf{q},z,E) = C^*_{0j}(\mathbf{q}_0)C_{0j'}(\mathbf{q}_0)\exp\Big(z^3\frac{e^2}{3\pi\hbar v^2}\Big\{\int d\omega\ \mathrm{Im}\Big[\frac{1}{\varepsilon(\omega)}\Big]\Big\}\Big[\frac{q_c}{\hbar v}\Big|\frac{\partial}{\partial\mathbf{q}}\{E_{j'}(\mathbf{q})-E_j(\mathbf{q})\}\big|_{\mathbf{q}_0}\Big|\Big]\Big). \tag{58}$$

For larger depths $z \gg \hbar v\left|q_c\frac{\partial}{\partial\mathbf{q}}\{E_{j'}(\mathbf{q})-E_j(\mathbf{q})\}\big|_{\mathbf{q}_0}\right|^{-1}$ the coherence between Bloch states decays exponentially,

$$\int \frac{d^2q}{(2\pi)^2} \int dE\ \rho_{jj'}(\mathbf{q},z,E) = C^*_{0j}(\mathbf{q}_0)C_{0j'}(\mathbf{q}_0)\exp\Bigg(-\frac{2e^2}{\pi\hbar v^2}\Big\{\int d\omega\ \mathrm{Im}\Big[\frac{1}{\varepsilon(\omega)}\Big]\Big\}$$
$$\times\Bigg\{z\ln\left[\frac{zq_c\left|\frac{\partial}{\partial\mathbf{q}}\{E_{j'}(\mathbf{q})-E_j(\mathbf{q})\}\big|_{\mathbf{q}_0}\right|}{2.71\hbar v}\right]+\frac{\pi\hbar v}{2q_c\left|\frac{\partial}{\partial\mathbf{q}}\{E_{j'}(\mathbf{q})-E_j(\mathbf{q})\}\big|_{\mathbf{q}_0}\right|}\Bigg\}\Bigg). \tag{59}$$

In accordance with Eqs. (58) and (59), the rate of attenuation of the off-diagonal elements of the density matrix depends on how different are the dispersion laws $E_j(\mathbf{q})$ and $E_{j'}(\mathbf{q})$ for different branches j and j' of the two-dimensional Bloch wave dispersion surface. If most of the branches involved in the scattering are nearly flat, i.e., $E_j(\mathbf{q}) \approx$const, as is the case for fast protons,[67] the distance characterizing the rate of attenuation of the off-diagonal elements of the density matrix is many times the inelastic mean free path. For high-energy electrons, however, any two functions $E_j(\mathbf{q})$ and $E_{j'}(\mathbf{q})$ $(j \neq j')$ differ considerably, and therefore one may expect that the effective distance of attenuation of the off-diagonal elements is comparable with the inelastic mean free path.[68]

In order to investigate more accurately the effect of damping of coherence of high-energy electrons in inelastic scattering by crystals, we develop a numerical approach for solving the kinetic equation. As has been noticed by Rez,[16] the integral term in (47) may be approximated by a summation over a finite number of points in the Brillouin zone. Further simplification may be introduced if we consider the so-called systematic diffraction case where the energy of a particular Bloch state can be expressed as $E_j(\mathbf{q}) = E_j(q_x) + \hbar^2q_y^2/2m$ and $\mu_j(\mathbf{q}) = \mu_j(q_x)$, where the x axis is in the direction of the systematic row of reciprocal lattice points. In this case we can integrate Eq. (48) over q_y and E, and obtain a one-dimensional kinetic equation of the form

$$\frac{\partial}{\partial z}\rho_{jj'}(q_x,z) = -\frac{2\mu_{\mathrm{el}}}{\hbar v}\rho_{jj'}(q_x,z) - \frac{\mu_j(q_x)+\mu_{j'}(q_x)}{\hbar v}\rho_{jj'}(q_x,z)$$
$$-\frac{e^2}{\pi^2\hbar v^2}\int d\omega\mathrm{Im}\Big[\frac{1}{\varepsilon(\omega)}\Big]\int_{Q_x<q_c}\frac{dQ_x}{\sqrt{Q_\perp^2+(\omega/v)^2}}\rho_{jj'}(q_x+Q_x,z)$$
$$\times\exp\Big(i\frac{z}{\hbar v}[E_j(q_x)-E_j(q_x+Q_x)]\Big)\exp\Big(-i\frac{z}{\hbar v}[E_{j'}(q_x)-E_{j'}(q_x+Q_x)]\Big), \tag{60}$$

where

$$\rho_{jj'}(q_x,z) = \int_0^{E_{\max}} dE \int \frac{dq_y}{2\pi}\rho_{jj'}(\mathbf{q},z,E). \tag{61}$$

Representing the integral of inelastic collisions in Eq. (60) in the form of a finite summation over 100 points in the Brillouin zone, we arrive at the numerical problem of solving a set of 200 coupled linear differential equations for the real part and for the imaginary part of each of the elements of the density matrix $\rho(q_x,z)$. These equations were integrated numerically by the Runge-Kutta-Merson method using an Elonex 386SX computer, each run from $z = 0$ Å to $z = 4000$ Å taking about 10 h of CPU time. In the computation we used measured values of the electron-electron scattering cross section obtained by Kamiya *et al.*,[69] and assumed that ω under the square root sign in Eq. (60) is equal to the plasmon frequency; i.e., for silicon[70] $\hbar\omega = 16.9$ eV.

Experimental observations of the energy-unfiltered CBED patterns were made using a Philips CM20 analytical electron microscope at an accelerating voltage of 80 kV. The silicon single crystal sample was cooled to 100 K in order to reduce thermal diffuse scattering. The intensity distributions were recorded on a photographic film, and precautions were made to ensure that the optical density of the negative is proportional to the exposure. The (110) systematic row of reciprocal lattice vectors of the Si single crystal specimen was chosen for observations, and the relevant CBED disk of the (220) reflection is shown in Fig. 2. Observations were made varying the thickness of the crystal, and for each thickness the distribution of intensity across the (220) disk was digitized by making use of a charge coupled device (CCD) camera and a microdensitometer. Both methods resulted in similar profiles. The thickness of the crystal was determined from the positions of the maxima and minima, and for the case shown in Fig. 2 the thickness was found to be 2860 ± 20 Å.

Three densitometer traces across the (220) CBED disk corresponding to three different thicknesses of the crystal are shown by solid lines in Fig. 3. The profile in Fig. 3(b) corresponds to the CBED pattern of Fig. 2. The dotted lines in Fig. 3 represent the results of theoretical simulations of the dark-field rocking curves based on the classical formulation of dynamical diffraction theory,[1] where the effects of inelastic scattering are taken into account as an effective absorption of electrons. It is seen that this approach results in highly symmetrical profiles even for very thick crystals. The dashed curves represent the dark-field intensity profiles evaluated by numerical integration of the kinetic equation for the density matrix (60). As is evident from Fig. 3, the kinetic equation approach provides a better quantitative description of the experimental data than does the standard dynamical theory, and in particular, it reproduces correctly the asymmetry of the profiles which was first noticed by Howie[6] and by Metherell.[58] The difference between the dashed and solid curves in Fig. 3 is probably attributable to the use of the *intrabranch* scattering approximation in (47) and neglect of the coupling between different matrix elements of $\hat{\rho}$ in Eq. (42) (i.e., neglect of *interbranch* transitions), the incorporation of which into the numerical procedure leads to considerable computational difficulties. However, the agreement between the theory and the experimental data is encouraging since, for the first time, it demonstrates the possibility of quantitative simulation of energy-unfiltered diffraction patterns using the kinetic

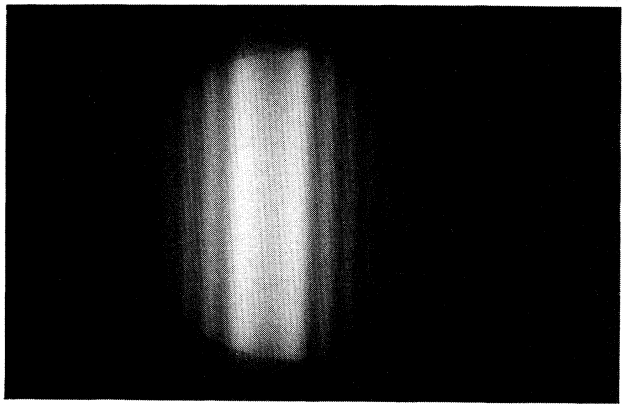

FIG. 2. Energy-unfiltered convergent-beam electron diffraction pattern of the Si(220) reflection taken in transmission diffraction geometry. The thickness of the crystal is 2860±20 Å , the absolute temperature is $T \approx 100$ K, and the energy is 80 keV.

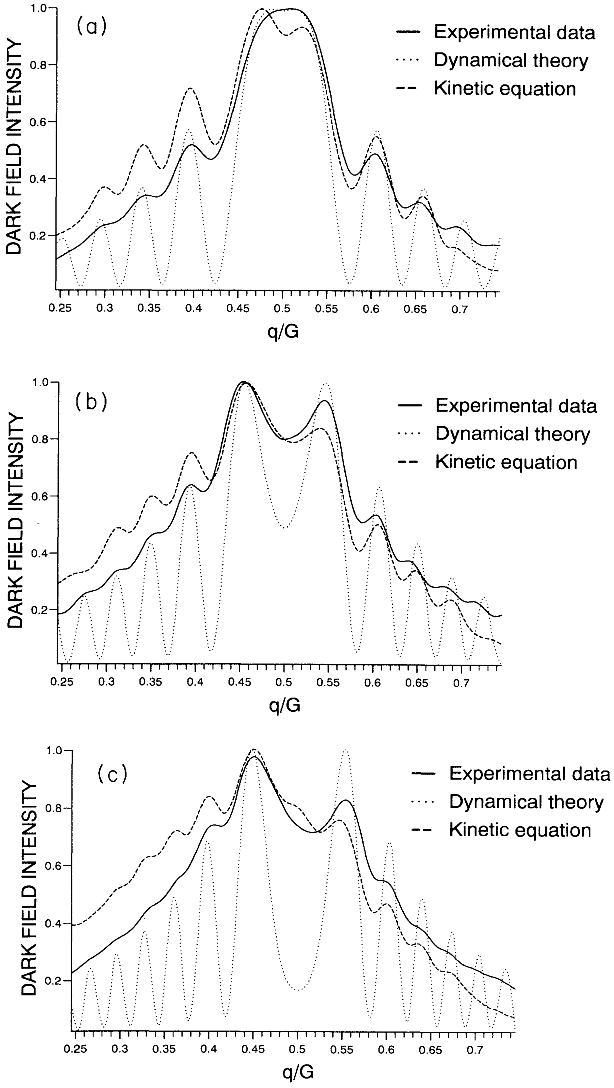

FIG. 3. Experimentally observed (solid curves) and theoretically simulated intensity profiles of the dark-field CBED pattern of the Si(220) reflection. Dotted curves calculated using an 11-beam approximation of dynamical diffraction theory. Dashed curve calculated by numerical solution of the kinetic equation. Crystal thickness: (a) 2340 ± 20 Å, (b) 2860 ± 20 Å, and (c) 3420 ± 20 Å.

equation for the density matrix. It also confirms the existence of the damping of coherence of high-energy electrons due to small-angle inelastic scattering as described analytically by Eqs. (53)–(59), and the effective distance characterizing the rate of attenuation of the off-diagonal elements of the density matrix is found to be comparable with the mean free path for inelastic electron-electron scattering.

VI. CONCLUSIONS

In this paper we have formulated a self-consistent approach to the problem of high-energy electron diffraction by solids. Equations have been derived which take into acccount both the elastic scattering of electrons by the time-averaged distribution of atoms, and the inelastic scattering due to excitations of the vibrational and electronic subsystems of the crystal. In formulating the approach, we proved that in the general case of multiple elastic and inelastic scattering there are only two basic quantities which describe elastic and inelastic interactions. They are respectively the Coulomb interaction potential averaged over the motion of the crystal particles, and the mixed dynamic form factor of inelastic excitations. It was shown that if the energy of the electron is sufficiently high, no other quantity is required to evaluate the double differential scattering cross section. We discussed how these two quantities can be retrieved from the experimental measurements, and concentrated on the analysis of the effects of multiple inelastic scattering of high-energy electrons in crystals. We showed how our formulation generalizes previous approaches to the problem, and discussed the conditions of validity of the approximations in those approaches.

We have studied the effect of multiple small-angle inelastic scattering by collective electronic excitations on the coherence of high-energy electrons propagating in a single crystal. The distance characterizing the damping of coherence of the electron wave field was found to be comparable with the mean free path of inelastic electron-electron scattering. A numerical method of solving the kinetic equation was developed and reasonable agreement between the theory and experiment was achieved, demonstrating the possibility of quantitative simulation of energy-unfiltered electron micrographs of crystalline materials.

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APPENDIX A

In this appendix we derive Eq. (10) for the Green's function of the high-energy electron. We are interested in the evaluation of the amplitude of propagation of the electron from point $\mathbf{r}'$ to $\mathbf{r}$ provided that initial and final states of the crystal coincide. This was first considered by Yoshioka[5] in 1957. In his treatment Yoshioka analyzed how inelastic excitations affect the amplitude of the elastic wave. He considered the $\delta\hat{H}'$ term (in our notation) as a perturbation and found that, within the approximation which is quadratic in $\delta\hat{H}'$, the effect of inelastic transitions may be accounted for by adding a nonlocal term to the effective potential in the Schrödinger equation governing the evolution of the elastic wave propagating through the crystal. In this section we follow the same idea. However, we use a somewhat more suitable Green's function technique and consider a more general case of $T \neq 0$. For the case $T = 0$ our results are equivalent to those by Yoshioka[5], and in particular, our Eq. (12) at $T = 0$ coincides with Eq. (11) from Ref. 5.

First we represent the Hamiltonian of the system in the form of a sum

$$\hat{H} = \hat{H}_{\rm cr} + \hat{H}_{\rm el} + \delta\hat{H}', \tag{A1}$$

of the crystal Hamiltonian, the Hamiltonian of the fast electron which includes the averaged interaction potential

$$\hat{H}_{\rm el} = -\frac{\hbar^2}{2m}\nabla^2 + \langle\hat{H}'\rangle, \tag{A2}$$

and the fluctuating part of the interaction $\delta\hat{H}'$, the matrix element of which is defined by Eq. (4). It is important to emphasize that $\hat{H}_{\rm el}$ has no off-diagonal matrix elements between eigenstates of the crystal. If we neglect the $\delta\hat{H}'$ term, then the time-dependent Green's function of the system obeys the equation

$$i\hbar\frac{\partial}{\partial t}\hat{\Gamma}(t,t_0) = (\hat{H}_{\rm cr} + \hat{H}_{\rm el})\hat{\Gamma}(t,t_0) + \delta(t-t_0), \tag{A3}$$

the solution of which is

$$\hat{\Gamma}(t,t_0) = -\frac{i}{\hbar}\Theta(t-t_0)\exp\Big(-\frac{i}{\hbar}(\hat{H}_{\rm el} + \hat{H}_{\rm cr})(t-t_0)\Big), \tag{A4}$$

describing the independent evolution of the states of both the electron and the crystal. Extracting from (A4) the factor which is responsible for the time evolution of the crystal, $\exp[-\{i/\hbar\}\hat{H}_{\rm cr}(t-t_0)]$, we obtain, for the remaining part of the Green's function (A4),

$$\hat{G}_0(t,t_0) = \hat{G}_0(t-t_0) = -\frac{i}{\hbar}\Theta(t-t_0)\exp\Big(-\frac{i}{\hbar}\hat{H}_{\rm el}(t-t_0)\Big). \tag{A5}$$

The latter quantity is the Green's function of the high-energy electron propagating in the averaged potential field $\langle\hat{H}'\rangle$. The Fourier transform of this function,

$$\hat{G}_0(E) = \int_{-\infty}^{\infty} dt\exp\Big(i\frac{E}{\hbar}t\Big)\hat{G}_0(t) = \frac{1}{E - \hat{H}_{\rm el} + i0}, \tag{A6}$$

obeys Eq. (9), i.e.,

$$(E - \hat{H}_{\rm el})\hat{G}_0(E) = \hat{1}. \tag{A7}$$

If we take into account the fluctuating part of the interaction $\delta\hat{H}'$, then

$$i\hbar\frac{\partial}{\partial t}\hat{\Gamma}(t,t_0) = (\hat{H}_{\mathrm{cr}} + \hat{H}_{\mathrm{el}} + \delta\hat{H}')\hat{\Gamma}(t,t_0) + \delta(t-t_0). \tag{A8}$$

Writing

$$\hat{\gamma}(t,t_0) = \exp\Big(\frac{i}{\hbar}\hat{H}_{\mathrm{cr}}(t-t_0)\Big)\hat{\Gamma}(t,t_0), \tag{A9}$$

we obtain from (A8)

$$i\hbar\frac{\partial}{\partial t}\hat{\gamma}(t,t_0) = [\hat{H}_{\mathrm{el}} + \delta\hat{H}'(t-t_0)]\hat{\gamma}(t,t_0) + \delta(t-t_0), \tag{A10}$$

where

$$\delta\hat{H}'(t) = \exp\Big(\frac{i}{\hbar}\hat{H}_{\mathrm{cr}}t\Big)\delta\hat{H}'\exp\Big(-\frac{i}{\hbar}\hat{H}_{\mathrm{cr}}t\Big) \tag{A11}$$

is the Heisenberg operator of the fluctuating part of the interaction. It is interesting to notice that the Heisenberg form of $\langle\hat{H}'\rangle$ does not depend on time, and this makes it possible to interpret $\langle\hat{H}'\rangle$ as a static part of the interaction.

In what follows we will be interested in the propagation amplitude averaged over the thermodynamical equilibrium,

$$\hat{G}(t,t_0) = \frac{1}{\mathcal{Z}}\sum_n \exp(-\epsilon_n/k_BT)\langle n|\hat{\gamma}(t,t_0)|n\rangle. \tag{A12}$$

In order to perform averaging, we obtain an integral form of Eq. (A10),

$$\hat{\gamma}(t) = \hat{\gamma}(t,0) = \hat{G}_0(t) + \int_0^t d\tau\hat{G}_0(t-\tau)\delta\hat{H}'(\tau)\hat{\gamma}(\tau). \tag{A13}$$

Because $\hat{G}_0(t-\tau) = 0$ for $\tau > t$ and $\hat{\gamma}(\tau) = 0$ for $\tau < 0$ we can represent (A13) as follows:

$$\hat{\gamma}(t) = \hat{G}_0(t) + \int_{-\infty}^{\infty} d\tau\hat{G}_0(t-\tau)\delta\hat{H}'(\tau)\hat{\gamma}(\tau). \tag{A14}$$

For convenience we may rewrite (A14) in a symbolic form

$$\hat{\gamma} = \hat{G}_0 + \hat{G}_0\delta\hat{H}'\hat{\gamma}.$$

Iterating this equation and conserving only terms quadratic in $\delta\hat{H}'$, we obtain after averaging

$$\begin{aligned}\langle\hat{\gamma}\rangle &= \hat{G}_0 + \hat{G}_0\langle\delta\hat{H}'\hat{G}_0\delta\hat{H}'\rangle\hat{G}_0 + \hat{G}_0\langle\delta\hat{H}'\hat{G}_0\delta\hat{H}'\rangle\hat{G}_0\langle\delta\hat{H}'\hat{G}_0\delta\hat{H}'\rangle\hat{G}_0 + \cdots\\ &= \hat{G}_0 + \hat{G}_0\langle\delta\hat{H}'\hat{G}_0\delta\hat{H}'\rangle\langle\hat{\gamma}\rangle\end{aligned}$$

or, explicitly,

$$\hat{G}(t) = \hat{G}_0(t) + \int_{-\infty}^{\infty}\int_{-\infty}^{\infty} d\tau_1 d\tau_2\hat{G}_0(t-\tau_1)\langle\delta\hat{H}'(\tau_1)\hat{G}_0(\tau_1-\tau_2)\delta\hat{H}'(\tau_2)\rangle\hat{G}(\tau_2), \tag{A15}$$

where the sign $\langle\cdots\rangle$ denotes the averaging of an operator over the thermal ensemble,

$$\langle\cdots\rangle = \frac{1}{\mathcal{Z}}\sum_n \exp(-\epsilon_n/k_BT)\langle n|\cdots|n\rangle. \tag{A16}$$

Consider the combination $\langle\delta\hat{H}'(\tau_1)\delta\hat{H}'(\tau_2)\rangle$. Writing the coordinates $\mathbf{x}_1$ and $\mathbf{x}_2$ in an explicit form, we obtain

$$\begin{aligned}\langle\delta\hat{H}'(\mathbf{x}_1,\tau_1)\delta\hat{H}'(\mathbf{x}_2,\tau_2)\rangle &= \frac{1}{\mathcal{Z}}\sum_{n,n'}\exp(-\epsilon_n/k_BT)\langle n|\delta\hat{H}'(\mathbf{x}_1,\tau_1)|n'\rangle\langle n'|\delta\hat{H}'(\mathbf{x}_2,\tau_2)|n\rangle\\ &= \frac{1}{\mathcal{Z}}\sum_{n,n'}\exp(-\epsilon_n/k_BT)\langle n|\delta\hat{H}'(\mathbf{x}_1)|n'\rangle\langle n'|\delta\hat{H}'(\mathbf{x}_2)|n\rangle\exp\Big(i\frac{\epsilon_n-\epsilon_{n'}}{\hbar}(\tau_1-\tau_2)\Big),\end{aligned} \tag{A17}$$

where $\delta\hat{H}'(\mathbf{x})$ is the Schrödinger operator of the fluctuating part of the interaction. Comparing (A17) with (6) we see that

$$\langle\delta\hat{H}'(\mathbf{x}_1,\tau_1)\delta\hat{H}'(\mathbf{x}_2,\tau_2)\rangle = \bar{s}_t(\mathbf{x}_1,\mathbf{x}_2,\tau_1-\tau_2), \tag{A18}$$

where

$$\bar{s}_t(\mathbf{x}_1,\mathbf{x}_2,\tau) = \int d\omega\,\bar{s}(\mathbf{x}_1,\mathbf{x}_2,\omega)\exp(-i\omega\tau). \tag{A19}$$

Therefore, Eq. (A15) takes the form

$$G(\mathbf{r},\mathbf{r}',t) = G_0(\mathbf{r},\mathbf{r}',t) + \int_{-\infty}^{\infty} d\tau_1 \int_{-\infty}^{\infty} d\tau_2 \int d^3x_1 \int d^3x_2 G_0(\mathbf{r},\mathbf{x}_1,t-\tau_1)G_0(\mathbf{x}_1,\mathbf{x}_2,\tau_1-\tau_2) \times \bar{s}_t(\mathbf{x}_1,\mathbf{x}_2,\tau_1-\tau_2)G(\mathbf{x}_2,\mathbf{r}',\tau_2). \tag{A20}$$

Performing the Fourier transform

$$G(\mathbf{r},\mathbf{r}',E) = \int_{-\infty}^{\infty} \exp\Big(i\frac{E}{\hbar}t\Big)G(\mathbf{r},\mathbf{r}',t) \tag{A21}$$

and noticing that

$$\bar{s}(\mathbf{x}_1,\mathbf{x}_2,\omega) = \int \frac{dt}{2\pi}\exp(i\omega t)\bar{s}_t(\mathbf{x}_1,\mathbf{x}_2,t), \tag{A22}$$

we arrive at

$$G(\mathbf{r},\mathbf{r}',E) = G_0(\mathbf{r},\mathbf{r}',E) + \int d^3x_1 G_0(\mathbf{r},\mathbf{x}_1,E)\int d\omega \int d^3x_2 G_0(\mathbf{x}_1,\mathbf{x}_2,E-\hbar\omega)\bar{s}(\mathbf{x}_1,\mathbf{x}_2,\omega)G(\mathbf{x}_2,\mathbf{r}',E). \tag{A23}$$

Acting on this equation by the inverse Green's function operator

$$\hat{G}_0^{-1} = \left(E + \frac{\hbar^2}{2m}\nabla^2 - \langle \hat{H}'\rangle\right) ,$$

we obtain expression (10).

APPENDIX B

In order to derive an equation which governs the evolution of a bilinear combination of wave functions of the high-energy electron we start from Eq. (A14). It is convenient to rewrite this as follows:

$$\hat{\gamma}(\mathbf{r},t|\mathbf{r}_0,t_0) = \hat{G}_0(\mathbf{r},t|\mathbf{r}_0,t_0) + \int_{-\infty}^{\infty} d\tau \int d^3x \hat{G}_0(\mathbf{r},t|\mathbf{x},\tau)\delta\hat{H}'(\mathbf{x},\tau)\hat{\gamma}(\mathbf{x},\tau|\mathbf{r}_0,t_0). \tag{B1}$$

We define the propagation operator of a bilinear combination of wave functions of the high-energy electron by the equality

$$K(\mathbf{r},t;\mathbf{r}',t'|\mathbf{r}_0,t_0;\mathbf{r}_0',t_0') = \frac{1}{\mathcal{Z}}\sum_{n,n'}\exp(-\epsilon_{n'}/k_BT)\langle n|\hat{\gamma}(\mathbf{r},t|\mathbf{r}_0,t_0)|n\rangle\Big(\langle n|\hat{\gamma}(\mathbf{r}',t'|\mathbf{r}_0',t_0')|n'\rangle\Big)^*. \tag{B2}$$

This definition is analogous to the standard rule of summation over final and averaging over initial states of a target in evaluating the quantum-mechanical scattering cross section.

We may rewrite (B2) in a symbolic form as

$$\hat{K} = \langle\hat{\gamma}^\dagger\hat{\gamma}\rangle,$$

and expand $\hat{\gamma}$ in a power series in $\delta\hat{H}'$,

$$\hat{\gamma} = \hat{G}_0 + \hat{G}_0\delta\hat{H}'\hat{G}_0 + \hat{G}_0\delta\hat{H}'\hat{G}_0\delta\hat{H}'\hat{G}_0 + \cdots .$$

ie proceed now to a step-by-step averaging of the product $\hat{\gamma}^\dagger\hat{\gamma}$, i.e.,

$$\hat{\gamma}^\dagger\hat{\gamma} = \{\hat{G}_0^\dagger + \hat{G}_0^\dagger\delta\hat{H}'^\dagger\hat{G}_0^\dagger + \hat{G}_0^\dagger\delta\hat{H}'^\dagger\hat{G}_0^\dagger\delta\hat{H}'^\dagger\hat{G}_0^\dagger + \cdots\}\{\hat{G}_0 + \hat{G}_0\delta\hat{H}'\hat{G}_0 + \hat{G}_0\delta\hat{H}'\hat{G}_0\delta\hat{H}'\hat{G}_0 + \cdots\}. \tag{B3}$$

Our basic idea is to collect the terms in (B3) which are quadratic in $\delta\hat{H}'$ and which describe *successive*[31,37] inelastic interactions. In order to simplify the derivation, in what follows we will distinguish between $\delta\hat{H}'^\dagger$ and $\delta\hat{H}'$, although, of course, the interaction is Hermitian and these two terms coincide.

We first perform averaging of (B3), neglecting the coupling between the terms $\delta\hat{H}'^\dagger$ and $\delta\hat{H}'$ belonging to $\hat{\gamma}^\dagger$ and $\hat{\gamma}$, respectively. This results in

$$\hat{K} = \langle\hat{\gamma}^\dagger\hat{\gamma}\rangle = \hat{G}^\dagger\hat{G} + \cdots . \tag{B4}$$

What we have to do next is to join up the terms $\delta\hat{H}'^\dagger$ and $\delta\hat{H}'$ belonging to the first and to the second series in (B3), respectively. The first term arising from this coupling is

$$\hat G_0^\dagger\langle\delta\hat H'^\dagger\hat G_0^\dagger\hat G_0\delta\hat H'\rangle\hat G_0.$$

Carrying on averaging, we arrive at

$$\hat K=\langle\hat\gamma^\dagger\hat\gamma\rangle=\hat G^\dagger\hat G+\hat G_0^\dagger\langle\ \delta\hat H'^\dagger\underline{\{\hat G_0^\dagger+\hat G_0^\dagger\langle\delta\hat H'^\dagger\hat G_0^\dagger\delta\hat H'^\dagger\rangle\hat G_0^\dagger+\hat G_0^\dagger\langle\delta\hat H'^\dagger\hat G_0^\dagger\delta\hat H'^\dagger\rangle\hat G_0^\dagger\langle\delta\hat H'^\dagger\hat G_0^\dagger\delta\hat H'^\dagger\rangle\hat G_0^\dagger+\cdots\}}$$

$$\times\underline{\{\hat G_0+\hat G_0\langle\delta\hat H'\hat G_0\delta\hat H'\rangle\hat G_0+\hat G_0\langle\delta\hat H'\hat G_0\delta\hat H'\rangle\hat G_0\langle\delta\hat H'\hat G_0\delta\hat H'\rangle\hat G_0+\cdots\}}\delta\hat H'\rangle\hat G_0,$$

where the underlined terms coincide with $\hat G^\dagger$ and $\hat G$ from (A15), respectively. This gives rise to an additional contribution to (B4), namely,

$$\hat K=\langle\hat\gamma^\dagger\hat\gamma\rangle=\hat G^\dagger\hat G+\hat G_0^\dagger\langle\delta\hat H'^\dagger\hat G^\dagger\hat G\delta\hat H'\rangle\hat G_0+\cdots\ . \tag{B5}$$

The next step is to join up two or more pairs of operators $\delta\hat H'^\dagger$ and $\delta\hat H'$ belonging to expansions of $\hat\gamma^\dagger$ and $\hat\gamma$ from (B3). We obtain

$$\hat K=\langle\hat\gamma^\dagger\hat\gamma\rangle=\hat G^\dagger\hat G+\hat G_0^\dagger\langle\delta\hat H'^\dagger\hat G^\dagger\hat G\delta\hat H'\rangle\hat G_0+\hat G_0^\dagger\langle\delta\hat H'^\dagger\hat G^\dagger\langle\delta\hat H'^\dagger\hat G^\dagger\hat G\delta\hat H'\rangle\hat G\delta\hat H'\rangle\hat G_0+\cdot \tag{B6}$$

At this stage, there are as yet some more terms to be taken into account. Indeed, in choosing pairs of operators $\delta\hat H'^\dagger$ and $\delta\hat H'$ in (B4)–(B6), we started from the outer terms of (B3). However, we can, for example, join up the third term $\delta\hat H'^\dagger$ from the left-hand side, and the first term $\delta\hat H'$ from the right-hand side, and this results in the following contribution to (B6):

$$\hat G_0^\dagger\langle\delta\hat H'^\dagger\hat G_0^\dagger\delta\hat H'^\dagger\rangle\hat G_0^\dagger\langle\delta\hat H'^\dagger\hat G^\dagger\hat G\delta\hat H'\rangle\hat G_0.$$

Another similar term arises if we join up the first operator $\delta\hat H'^\dagger$ from the right-hand side and the third operator $\delta\hat H'$ from the left-hand side. This gives

$$\hat G_0^\dagger\langle\delta\hat H'^\dagger\hat G^\dagger\hat G\delta\hat H'\rangle\hat G_0\langle\delta\hat H'\hat G_0\delta\hat H'\rangle\hat G_0.$$

Carrying on, we obtain

$$\begin{aligned}\hat K=\langle\hat\gamma^\dagger\hat\gamma\rangle&=\hat G^\dagger\hat G+\underline{(\hat G_0^\dagger+\hat G_0^\dagger\langle\delta\hat H'^\dagger\hat G_0^\dagger\delta\hat H'^\dagger\rangle\hat G_0^\dagger+\hat G_0^\dagger\langle\delta\hat H'^\dagger\hat G_0^\dagger\delta\hat H'^\dagger\rangle\hat G_0^\dagger\langle\delta\hat H'^\dagger\hat G_0^\dagger\delta\hat H'^\dagger\rangle\hat G_0^\dagger+\cdots)}\\&\qquad\times\{\langle\delta\hat H'^\dagger\hat G^\dagger\hat G\delta\hat H'\rangle+\langle\delta\hat H'^\dagger\hat G^\dagger\langle\delta\hat H'^\dagger\hat G^\dagger\hat G\delta\hat H'\rangle\hat G\delta\hat H'\rangle+\cdots\}\\&\qquad\times\underline{(\hat G_0+\hat G_0\langle\delta\hat H'\hat G_0\delta\hat H'\rangle\hat G_0+\hat G_0\langle\delta\hat H'\hat G_0\delta\hat H'\rangle\hat G_0\langle\delta\hat H'\hat G_0\delta\hat H'\rangle\hat G_0+\cdots)}\\&=\hat G^\dagger\hat G+\hat G^\dagger\{\langle\delta\hat H'^\dagger\hat G^\dagger\hat G\delta\hat H'\rangle+\langle\delta\hat H'^\dagger\hat G^\dagger\langle\delta\hat H'^\dagger\hat G^\dagger\hat G\delta\hat H'\rangle\hat G\delta\hat H'\rangle+\cdots\}\hat G\\&=\hat G^\dagger\hat G+\hat G^\dagger\langle\delta\hat H'^\dagger\hat K\delta\hat H'\rangle\hat G,\end{aligned} \tag{B7}$$

where we have underlined the expansions of the Green's functions $\hat G^\dagger$ and $\hat G$. Within the framework of the diagram technique, Eq. (B7) corresponds to the ladder approximation,[30,32,37,38,41] and, in particular, it coincides with Eq. (4.36) from Ref. 31. The symbolic equation (B7) may be rewritten in an explicit form as follows:

$$\begin{aligned}K(\mathbf r,t;\mathbf r',t'|\mathbf r_0,t_0;\mathbf r_0',t_0')&=G(\mathbf r,t|\mathbf r_0,t_0)G^*(\mathbf r',t'|\mathbf r_0',t_0')\ +\int_{-\infty}^{\infty}d\tau\int_{-\infty}^{\infty}d\tau'\int d^3xd^3x'G(\mathbf r,t|\mathbf x,\tau)G^*(\mathbf r',t'|\mathbf x',\tau')\\&\times\frac{1}{\mathcal Z}\sum_{n,n'}\exp(-\epsilon_{n'}/k_BT)\langle n|\delta\hat H'(\mathbf x,\tau)|n'\rangle\Big(\langle n|\delta\hat H'(\mathbf x',\tau')|n'\rangle\Big)^*K(\mathbf x,\tau;\mathbf x',\tau'|\mathbf r_0,t_0;\mathbf r_0',t_0').\end{aligned} \tag{B8}$$

Noticing that

$$\frac{1}{\mathcal Z}\sum_{n,n'}\exp(-\epsilon_{n'}/k_BT)\langle n|\delta\hat H'(\mathbf x,\tau)|n'\rangle\Big(\langle n|\delta\hat H'(\mathbf x',\tau')|n'\rangle\Big)^*=\bar s_t(\mathbf x',\mathbf x,\tau'-\tau), \tag{B9}$$

we obtain

$$\begin{aligned}K(\mathbf r,t;\mathbf r',t'|\mathbf r_0,t_0;\mathbf r_0',t_0')&=G(\mathbf r,t|\mathbf r_0,t_0)G^*(\mathbf r',t'|\mathbf r_0',t_0')\\&\quad+\int_{-\infty}^{\infty}d\tau\int_{-\infty}^{\infty}d\tau'\int d^3xd^3x'G(\mathbf r,t|\mathbf x,\tau)G^*(\mathbf r',t'|\mathbf x',\tau')\bar s_t(\mathbf x',\mathbf x,\tau'-\tau)\\&\quad\times K(\mathbf x,\tau;\mathbf x',\tau'|\mathbf r_0,t_0;\mathbf r_0',t_0').\end{aligned} \tag{B10}$$

According to the definition of the operator $K(\mathbf{x},\tau;\mathbf{x}',\tau'|\mathbf{r}_0,t_0;\mathbf{r}_0',t_0')$, an integral of this function multiplied by a source function $I(\mathbf{r}_0,t_0;\mathbf{r}_0',t_0')$ results in a bilinear combination of wave functions of the high-energy electrons at $(\mathbf{x},\tau;\mathbf{x}',\tau')$, namely,

$$\rho(\mathbf{x},\tau;\mathbf{x}',\tau') = \int dt_0 \int dt_0' \int d^3r_0 \int d^3r_0' K(\mathbf{x},\tau;\mathbf{x}',\tau'|\mathbf{r}_0,t_0;\mathbf{r}_0',t_0') I(\mathbf{r}_0,t_0;\mathbf{r}_0',t_0'). \tag{B11}$$

Performing the convolution (B11), we obtain from (B10)

$$\rho(\mathbf{r},t;\mathbf{r}',t') = \rho_0(\mathbf{r},t;\mathbf{r}',t') + \int_{-\infty}^{\infty} d\tau \int_{-\infty}^{\infty} d\tau' \int d^3x d^3x' G(\mathbf{r},t|\mathbf{x},\tau) G^*(\mathbf{r}',t'|\mathbf{x}',\tau') \overline{s}_t(\mathbf{x}',\mathbf{x},\tau'-\tau) \rho(\mathbf{x},\tau;\mathbf{x}',\tau'). \tag{B12}$$

The Fourier transform of (B12),

$$\rho(\mathbf{r},E;\mathbf{r}',E') = \int dt' \int dt \exp\Big(i\frac{E}{\hbar}t - i\frac{E'}{\hbar}t\Big) \rho(\mathbf{r},t;\mathbf{r}',t'), \tag{B13}$$

obeys the equation

$$\begin{aligned}\rho(\mathbf{r},E;\mathbf{r}',E') &= \rho_0(\mathbf{r},E;\mathbf{r}',E') \\ &\quad + \int_{-\infty}^{\infty} d\tau' \int d^3x d^3x' G(\mathbf{r},t|\mathbf{x},E) G^*(\mathbf{r}',t'|\mathbf{x}',E') \int d\omega\, \overline{s}(\mathbf{x}',\mathbf{x},\omega) \rho(\mathbf{x},E+\hbar\omega;\mathbf{x}',E'+\hbar\omega).\end{aligned} \tag{B14}$$

Assuming conditions of permanent illumination of the system by an external source of electrons, and introducing the definition

$$\rho(\mathbf{r},\mathbf{r}',E) = \frac{1}{2\pi\hbar\mathcal{T}} \rho(\mathbf{r},E;\mathbf{r}',E), \tag{B15}$$

where $\mathcal{T}$ is the time of observation, we arrive at Eq. (11). The latter definition is in accordance with Eq. (1).

APPENDIX C

As follows from (14), in order to evaluate the scattering cross section, one needs first to calculate the Fourier transform of the Green's function (18),

$$\int d^2R\, G(\mathbf{R},z,\mathbf{x},E) \exp(-i\mathbf{q}_\perp \cdot \mathbf{R}) = G(\mathbf{q}_\perp,z,\mathbf{x},E). \tag{C1}$$

To perform this, we first notice that for arbitrary $\mathbf{r}$ and $\mathbf{x}$ the Green's function obeys the reciprocity relation

$$G(\mathbf{r},\mathbf{x},E) = G(\mathbf{x},\mathbf{r},E). \tag{C2}$$

Considering the second argument of the Green's function as a coordinate of a source of the electrons, and the first argument as a coordinate of point of observation, and assuming $\mathbf{x}$ to be inside, and $\mathbf{r}$ outside the medium, we write

$$G(\mathbf{r},\mathbf{x},E) = -\frac{m}{2\pi\hbar^2} \frac{1}{|\mathbf{x}-\mathbf{r}|} \exp(ik|\mathbf{x}-\mathbf{r}|) + G_s(\mathbf{x},\mathbf{r},E), \tag{C3}$$

where $G_s(\mathbf{x},\mathbf{r},E)$ represents waves scattered by the medium. Let us first consider the geometry where $(\mathbf{r})_z = z > (\mathbf{x})_z = \zeta$. In this case

$$\begin{aligned}&\int d^2R \Big[-\frac{m}{2\pi\hbar^2} \frac{1}{|\mathbf{x}-\mathbf{r}|} \exp(ik|\mathbf{x}-\mathbf{r}|)\Big] \exp(-i\mathbf{q}_\perp \cdot \mathbf{R}) \\ &\quad = -\frac{im}{\hbar^2\sqrt{k^2-\mathbf{q}_\perp^2}} \exp(-i\mathbf{q}_\perp \cdot \mathbf{x}_\perp) \\ &\qquad \times \exp[i\sqrt{k^2-\mathbf{q}_\perp^2}(z-\zeta)].\end{aligned} \tag{C4}$$

Noticing that $\mathbf{k}_{x,y} = \mathbf{q}_\perp$ and $\mathbf{k}_z = \sqrt{k^2-\mathbf{q}_\perp^2} = k\cos\theta$, we obtain

$$\begin{aligned}&\int d^2R\, G(\mathbf{R},z,\mathbf{x},E) \exp(-i\mathbf{q}_\perp \cdot \mathbf{R}) \\ &\quad = -\frac{im}{\hbar^2\sqrt{k^2-\mathbf{q}_\perp^2}} \exp(-i\mathbf{q}_\perp \cdot \mathbf{x}_\perp) \exp\big[ik(z-\zeta)\cos\theta\big] \\ &\qquad + \int d^2R\, G_s(\mathbf{R},z,\mathbf{x},E) \exp(-i\mathbf{q}_\perp \cdot \mathbf{R}).\end{aligned} \tag{C5}$$

Considering the right-hand side of Eq. (C5) as a function of $\mathbf{x}$, we can say that the second term represents the waves scattered by the medium provided that the incident wave has the form

$$\Psi_{\rm inc}(\mathbf{x}) = -\frac{im}{\hbar^2 k\cos\theta} \exp(-i\mathbf{k}\cdot\mathbf{x}) \exp(ikz\cos\theta). \tag{C6}$$

By definition the solution of quantum-mechanical problem of scattering which corresponds to the incident wave of the form (C6) is

$$-\frac{im}{\hbar^2 k\cos\theta} \exp(ikz\cos\theta) \Psi_{-\mathbf{k}}(\mathbf{x}),$$

and this quantity actually equals the right-hand side of (C1),

$$\int d^2R\, G(\mathbf{R}, z, \mathbf{x}, E) \exp(-i\mathbf{q}_\perp \cdot \mathbf{R})$$

$$= -\frac{im}{\hbar^2 k \cos\theta} \exp(ikz\cos\theta)\Psi_{-\mathbf{k}}(\mathbf{x}). \quad \text{(C7)}$$

Repeating our arguments in the case where $z < \zeta$, we arrive at a general result

$$\int d^2R\, G(\mathbf{R}, z, \mathbf{x}, E) \exp(-i\mathbf{q}_\perp \cdot \mathbf{R})$$

$$= -\frac{im}{\hbar^2 k |\cos\theta|} \exp(ikz\cos\theta)\Psi_{-\mathbf{k}}(\mathbf{x}), \quad \text{(C8)}$$

which is the result stated in (18).

[1] P. Hirsch, A. Howie, R. B. Nicholson, D. W. Pashley, and M. J. Whelan, *Electron Microscopy of Thin Crystals* (Krieger, New York, 1977).

[2] J. A. Venables, D. R. Batchelor, M. Handbücken, C. J. Harland, and G. W. Jones, Philos. Trans. R. Soc. London A **318**, 243 (1986); J. A. Venables, D. J. Smith, and J. M. Cowley, Surf. Sci. **181**, 235 (1987).

[3] J. Taftø and J. C. H. Spence, Science **218**, 49 (1982).

[4] P. Rez, in *Transmission Electron Energy Loss Spectroscopy in Materials Science*, edited by M. M. Disko, C. C. Ahn, and B. Fultz (The Minerals, Metals & Materials Society, Seattle, 1992), p. 107.

[5] H. Yoshioka, Phys. Soc. Jpn. **12**, 618 (1957).

[6] A. Howie, Proc. R. Soc. London A **271**, 268 (1963).

[7] S. L. Cundy, A. Howie, and U. Valdré, Philos. Mag. **20**, 147 (1969).

[8] C. J. Humphreys and M. J. Whelan, Philos. Mag. **20**, 165 (1969).

[9] P. Rez, C. J. Humphreys, and M. J. Whelan, Philos. Mag. **35**, 81 (1977).

[10] C. J. Rossouw and M. J. Whelan, Ultramicroscopy **6**, 53 (1981).

[11] L. J. Allen and C. J. Rossouw, Phys. Rev. B **39**, 8313 (1989).

[12] R. Høier, Acta Crystallogr. A **29**, 663 (1973).

[13] J. Gjønnes, Acta Crystallogr. A **20**, 240 (1966).

[14] G. Moliére, Z. Naturforsch. Teil A **3**, 78 (1948).

[15] Yu. Kagan and Yu. V. Kononets, Zh. Eksp. Teor. Fiz. **64**, 1042 (1973) [Sov. Phys. JETP **37**, 530 (1973)].

[16] P. Rez, in *Electron Diffraction 1927-1977*, edited by P. J. Dobson, J. B. Pendry, and C. J. Humphreys (IOP Conference Proc. No. 41 (Institute of Physics, London, 1978), p. 61.

[17] S. L. Dudarev and M. I. Ryazanov, Acta Crystallogr. A **44**, 51 (1988).

[18] Z. L. Wang, Acta Crystallogr. A **45**, 636 (1989).

[19] Z. L. Wang, Phys. Rev. B **41**, 12818 (1990).

[20] P. B. Hirsch and C. J. Humphreys, in *Scanning Electron Microscopy*, Proceedings of the 3rd Annual Symposium, Chicago, 1970, edited by O. Johari (IIT Research Institute, Chicago, 1970), p. 451.

[21] J. P. Spencer and C. J. Humphreys, Philos. Mag. A **42**, 433 (1980).

[22] J. T. Czernuszka, N. J. Long, E. D. Boyes, and P. B. Hirsch, Philos. Mag. Lett. **62**, 227 (1990).

[23] A. J. Wilkinson, G. R. Anstis, J. T. Czernuszka, N. J. Long, and P. B. Hirsch, Philos. Mag. A **68**, 59 (1993).

[24] J. C. H. Spence, in *Electron Diffraction Techniques*, edited by J. M. Cowley (Oxford University Press, New York, 1992), Vol. 1, pp. 360–438.

[25] D. M. Bird and M. Saunders, Acta Crystallogr. A **48**, 555 (1992).

[26] S. J. Pennycook and D. E. Jesson, Ultramicroscopy **37**, 14 (1991).

[27] H. Nakahara and A. Ichimiya, Surf. Sci. **241**, 124 (1991); **242**, 162 (1991).

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

[29] J. M. Cowley, Acta Crystallogr. A **44**, 847 (1988).

[30] A. A. Abrikosov, L. P. Gorkov, and I. E. Dzyaloshinskii, *Methods of Quantum Field Theory in Statistical Physics* (Prentice-Hall, Englewood Cliffs, 1963), pp. 325–334.

[31] U. Frisch, in *Probabilistic Methods in Applied Mathematics*, edited by A. T. Bharucha-Reid (Academic Press, New York, 1968), p. 75.

[32] S. L. Dudarev, Zh. Eksp. Teor. Fiz. **94**(11), 289 (1988) [Sov. Phys. JETP **67**, 2338 (1988)].

[33] E. E. Gorodnichev and S. L. Dudarev, Fiz. Tverd. Tela (Leningrad) **32**, 1068 (1990) [Sov. Phys. Solid State **32**, 628 (1990)].

[34] S. L. Dudarev, L.-M. Peng, and M. I. Ryazanov, Acta Crystallogr. A **47**, 170 (1991).

[35] H. Kohl and H. Rose, in *Advances in Electronics and Electron Physics*, edited by P. W. Hawkes (Academic Press, Orlando, 1985), Vol. 65, p. 173.

[36] P. H. Dederichs, in *Solid State Physics*, edited by H. Ehrenreich, F. Seitz, and D. Turnbull (Academic Press, New York, 1972), Vol. 27, p. 135 (see pp. 193–197).

[37] E. E. Gorodnichev, S. L. Dudarev, D. B. Rogozkin, and M. I. Ryazanov, Zh. Eksp. Teor. Fiz. **93**, 1642 (1987) [Sov. Phys. JETP **66**, 938 (1987)], and references therein.

[38] E. E. Gorodnichev, S. L. Dudarev, D. B. Rogozkin, and M. I. Ryazanov, Zh. Eksp. Teor. Fiz. **96**, 1801 (1989) [Sov. Phys. JETP **69**, 1017 (1989)]; **97**, 1511 (1990) [**70**, 853 (1990)]; Phys. Lett. A **144**, 411 (1990).

[39] L. D. Landau and E. M. Lifshitz, *Quantum Mechanics, Non-Relativistic Theory*, 3rd ed. (Pergamon Press, Oxford, 1977).

[40] N. F. Mott and H. S. W. Massey, *The Theory of Atomic Collisions*, 3rd ed. (Clarendon Press, Oxford, 1965), p. 110.

[41] S. L. Dudarev, Kristallografiya **35**, 1332 (1991) [Sov. Phys. Crystallogr. **35**, 785 (1990)].

[42] Y. Kainuma, Acta Crystallogr. **8**, 247 (1955).

[43] S. L. Dudarev, L.-M. Peng, and M. J. Whelan, Proc. R. Soc. London A **440**, 567 (1993).

[44] P. A. Maksym and J. L. Beeby, Surf. Sci. **110**, 423 (1981).

[45] A. Ichimiya, Jpn. J. Appl. Phys. **22**, 176 (1983).

[46] G. Meyer-Ehmsen, Surf. Sci. **219**, 177 (1989).

[47] J. M. Zuo, J. C. H. Spence, and M. O'Keeffe, Phys. Rev. Lett. **61**, 353 (1988).

[48] Z. L. Wang, Acta Crystallogr. A **47**, 686 (1991).

[49] Z. L. Wang, Acta Crystallogr. A **48**, 674 (1992).
[50] Z. L. Wang, Philos. Mag. B **65**, 559 (1992).
[51] M. Goldberger and K. M. Watson, *Collision Theory* (Wiley, New York, 1967).
[52] R. F. Egerton, Philos. Mag. **34**, 49 (1976).
[53] L. Reimer, in *Advances in Electronics and Electron Physics*, edited by P. W. Hawkes (Academic Press, Boston, 1991), Vol. 81, p. 43.
[54] V. P. Artem'ev, V. V. Makarov, N. N. Petrov, and O. A. Podsvirov, Fiz. Tverd. Tela (Leningrad) **25**, 684 (1983) [Sov. Phys. Solid State **25**, 390 (1983)].
[55] N. Ajika, H. Hashimoto, K. Yamaguchi, and H. Endoh, Jpn. J. Appl. Phys. **24**, L41 (1985).
[56] A. Bakenfelder, I. Fromm, L. Reimer, and R. Rennekamp, J. Microsc. **159**, 161 (1990).
[57] M. V. Gomoyunova, S. L. Dudarev, and I. I. Pronin, Surf. Sci. **235**, 156 (1990).
[58] A. J. F. Metherell, Philos. Mag. **15**, 763 (1967).
[59] K. Zeppenfeld, Z. Phys. **211**, 391 (1968).
[60] I. Fromm, L. Reimer, and R. Rennekamp, J. Microsc. **166**, 257 (1992).
[61] D. Cherns, A. Howie, and M. H. Jacobs, Z. Naturforsch. Teil A **28**, 565 (1973).
[62] S. K. Andersen and A. Howie, Surf. Sci. **50**, 197 (1975).
[63] A. G. Wright and D. M. Bird, Acta Crystallogr. A **48**, 215 (1992).
[64] G. Radi, Acta Crystallogr. A **26**, 41 (1970).
[65] K. Blum, *Density Matrix: Theory and Applications* (Plenum, New York, 1981).
[66] G. N. Watson, *A Treatise on the Theory of Bessel Functions* (Cambridge University Press, Cambridge, 1966).
[67] Yu. Kagan and Yu. V. Kononets, Kurchatov Institute of Atomic Energy Report No. IAE-2249 (Moscow, 1972).
[68] S. L. Dudarev, L.-M. Peng, and M. J. Whelan, Phys. Lett. **170**, 111 (1992); A **175**, 465 (1993).
[69] Y. Kamiya, Y. Nakai, and E. Masuda, Acta Crystallogr. A **37**, 485 (1981).
[70] H. Raether, *Excitation of Plasmons and Interband Transitions by Electrons* (Springer, Berlin, 1980), p. 52.

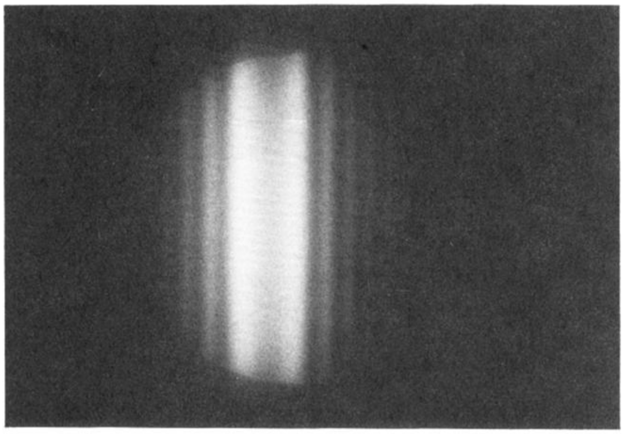

FIG. 2. Energy-unfiltered convergent-beam electron diffraction pattern of the Si(220) reflection taken in transmission diffraction geometry. The thickness of the crystal is 2860±20 Å , the absolute temperature is $T \approx 100$ K, and the energy is 80 keV.