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Interference between resonance and potential scattering of high energy electrons from crystal surfaces

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Abstract

A solution of the tight-binding model of resonance diffraction of high-energy electrons from a crystal surface is found which describes the behaviour of the reflectivity in the vicinity of the intersection of a resonance parabola and a horizontal Kikuchi line. A simple analytical formula is obtained which makes it possible to evaluate the wave function for the case where both resonance *and* potential contributions to the reflectivity are of the same order of magnitude. The intensity of the specular reflection is shown to be directly related to the effective displacement Δ of the beam in the direction parallel to the surface, and a general formula suitable for evaluation of Δ from calculated RHEED rocking curves is derived.

Keywords: Electron–solid interactions, scattering, diffraction; Reflection electron microscopy (REM); Reflection high-energy electron diffraction (RHEED)

1. Introduction

The phenomenon of the resonance diffraction of high-energy electrons from surfaces, discovered by Kikuchi and Nakagawa in 1933 [1], has remained a subject of discussion for more than 60 years [2–16]. The term "resonance diffraction" is used to describe the enhancement of the surface reflectivity which occurs in the vicinity of the orientation where one of the diffracted beams propagates nearly parallel to the surface of the crystal (see Fig. 1). The existing theoretical models of resonance scattering of electrons have been reviewed by McRae [17] and by Echenique and Pendry [18] with particular emphasis on the applications of the theory to low-energy electron diffraction (LEED).

One of the main reasons for studying resonance scattering in LEED was the idea that provided that this channel of scattering is associated with trapping of electrons by surface states, it might be used for obtaining information about the form of the interaction potential in the surface transition layer between vacuum and the crystal bulk [18]. In the case of diffraction of high-energy electrons (RHEED) the interest in the phenomenon of resonance scattering was largely stimulated by the widespread application of the "resonance" orientation

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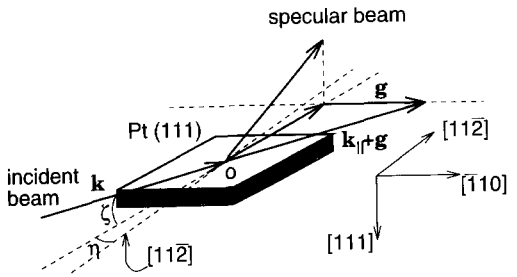

Fig. 1. Schematic representation of the diffraction process leading to the resonance enhancement of the intensity of the specular reflection.

(similar to that shown in Fig. 1) to electron microscope imaging of surface structures [19,20] and to the study of surface excitations [21,22]. Experimental studies of the phenomenon of the resonance diffraction of high-energy electrons performed by Bleloch et al. [11], and theoretical analyses carried out by Zuo and Liu [14] and Zhao and Tong [15], have shown that the explanation of the origin of this effect in terms of a process involving surface states seemed less probable than in the case of LEED. This has stimulated the study of an alternative model which was proposed by Kambe [23]. In this model the process of scattering involves virtual trapping of electrons by the bulk states localized in the potentials of the adjacent atomic planes parallel to the surface. The analytical solution which has been found recently using this model [24,25] agrees well with the results of numerical simulations performed for the (111) surface of Pt, and this has confirmed that resonance scattering of high-energy electrons is a dynamical diffraction phenomenon involving coherent interaction of the incident particle with many atomic planes parallel to the surface of the crystal.

As was noted by Dudarev and Whelan [25], the problem of resonance diffraction of electrons shows some formal similarity with the problem of diffraction of waves by a periodic array of point-like resonance scattering centres which was intensively studied in the past with reference to the interaction of neutrons and Mössbauer quanta with bulk crystals. In a series of papers published in the 1960s, Afanas'ev and Kagan [26–28] showed that dynamical diffraction of resonance radiation by crystals follows laws which differ from those known for dynamical diffraction of electrons or X-rays. The main difference between the resonance scattering of neutrons by a nucleus and the potential (i.e. non-resonance) scattering of electrons by an atom consists in the fact that in the latter case the real part of the scattering amplitude is many times the imaginary part, while in the former case the situation is the reverse. Smirnov et al. [29] showed that the patterns of standing waves formed in the crystal as a result of dynamical scattering are quite different in the two cases.

According to the unified theory of nuclear reactions developed by Feshbach [30], the appearance of resonance poles of the amplitude of scattering is associated with bound states revealing themselves as poles of the relevant Green's function. The situation becomes more complicated when we analyse resonance scattering by an *ensemble* of scatterers where the effects of multiple scattering make it impossible to attribute any particular peak in the cross-section to an individual bound state, and more sophisticated theoretical consideration is required. For the case of scattering of resonance neutrons and Mössbauer quanta by crystals the appropriate formulation of dynamical theory valid both for the case of resonance and potential scattering of radiation by nuclei has been developed by Afanas'ev and Kagan [26–28].

An important feature distinguishing diffraction of resonance neutrons and Mössbauer quanta by crystals from "resonance" scattering of electrons by crystal surfaces considered below, is the fact that in the former case the parameter which determines the magnitude of the resonance part of the amplitude of scattering (i.e. the part of the amplitude associated with scattering via a bound state [30]) is the *energy* of the particle, while in the latter case it is the *orientation of the incident beam*, i.e. the polar and the azimuthal *angles of incidence*. The solution of the tight-binding model of the resonance diffraction which has been obtained recently [24,25], demonstrates that in the geometry of scattering shown in Fig. 1 the parameter which determines the magnitude

of the resonance contribution to the reflectivity (i.e. the part of the reflectivity associated with diffraction via bound states) is the azimuthal angle η. In the absence of momentum transfer in the direction parallel to the surface the reflectivity depends only on the glancing angle ζ (in this case bound states are not involved in the process of scattering and the relevant part of the reflectivity is called "potential" [30]). The solution described in Refs. [24,25] corresponds to the case where the potential contribution to the reflectivity is small and can be neglected.

However, for many applications of the resonance scattering of high-energy electrons, which have advanced particularly strongly in recent years [20,31,32], a more general form of the solution is required which does not assume the potential contribution to the reflectivity to be small. Experimentally this corresponds to the orientation of the incident beam in which the specular reflection lies in the vicinity of the intersection of one of the resonance parabolas and one of the horizontal Kikuchi lines [14,20,31]. In this paper we describe a solution of the tight-binding model of the resonance diffraction which corresponds to this experimental situation and which is valid for the case where both resonance and potential contributions to the reflectivity are of the same order of magnitude. In the following section we describe a general approach and arrive at a formal solution to the problem, and then in the next section we consider some approximations which can be made to carry out a qualitative analysis of the problem and we compare the resulting solution with numerical simulations.

One of the important questions which we address in this paper is the relation between the reflectivity and other parameters which can be used to characterize the process of scattering, namely the effective distance of penetration of the incident electrons in the crystal bulk l_{eff} and the displacement Δ of the beam in the direction parallel to the surface. The appearance of the latter represents a purely quantum-mechanical effect associated with the dispersion of the phase of the reflected wave, and in this paper we derive a simple formula for Δ which is very convenient for evaluation of this parameter from the results of many-beam RHEED calculations.

2. The solution

In this section we consider a solution of the tight-binding model of resonance scattering. We use the technique developed recently by Dudarev and Whelan [24,25] and consider a more general case than that analysed there. The solution found below describes the two-dimensional distribution of intensity in the diffraction pattern, i.e. the dependence of the surface reflectivity on both the azimuthal and polar angles of incidence in the vicinity of the resonance condition.

Our treatment is based on a model which assumes that the atoms form a regular lattice filling the half-space $z > 0$, so that the optical potential $U(\boldsymbol{r}) = U'(\boldsymbol{r}) + \mathrm{i}U''(\boldsymbol{r})$, which is a sum of potentials of separate atoms, is a periodic function within any plane parallel to the surface $z = 0$,

$$U(\boldsymbol{r}) = \sum_{\boldsymbol{g}} U_{\boldsymbol{g}}(z)\exp(\mathrm{i}\boldsymbol{g}\cdot\boldsymbol{R}), \tag{1}$$

where $\boldsymbol{R} = (x, y)$ is a two-dimensional vector parallel to the surface of the crystal and $\boldsymbol{g}$ is a reciprocal lattice vector of the two-dimensional lattice. The wave function of the scattering problem which corresponds to the plane wave $\exp(\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r})$ incident on the surface from the half-space $z < 0$, can be represented in the form

$$\Psi(\boldsymbol{r}) = \sum_{\boldsymbol{g}} \Phi_{\boldsymbol{g}}(z)\exp[\mathrm{i}(\boldsymbol{k}_{\parallel} + \boldsymbol{g})\cdot\boldsymbol{R}], \tag{2}$$

where $\boldsymbol{k}_{\parallel} = (k_x, k_y)$ is the projection of the wave vector of the incident electron on the x, y-plane, $\boldsymbol{k} = (\boldsymbol{k}_{\parallel}, k_z)$, and $\Phi_{\boldsymbol{g}}(z)$ for $z \to -\infty$ satisfies the asymptotic condition

$$\Phi_{\boldsymbol{g}}(z) = \delta_{\boldsymbol{g}\boldsymbol{0}}\exp(\mathrm{i}K_0 z) + R_{\boldsymbol{g}}\exp(-\mathrm{i}K_{\boldsymbol{g}} z), \tag{3}$$

where $K_g^2 = \boldsymbol{k}^2 - (\boldsymbol{k}_\parallel + \boldsymbol{g})^2 = k_z^2 - 2(\boldsymbol{k}_\parallel \cdot \boldsymbol{g}) - \boldsymbol{g}^2$ and $K_0^2 = k_z^2$. The quantity $|R_0|^2$ is proportional to the intensity of the specular reflection, and our goal is to determine how this depends on the orientation of the wave vector $\boldsymbol{k}$ of the incident electrons.

The functions $\Phi_g(z)$ satisfy the system of integral equations [24,25]

$$\Phi_0(z) = \Phi_{K_0}^{(+)}(z) + \int \mathrm{d}z'\, G\left(z, z', \frac{\hbar^2 K_0^2}{2m}\right) U_{-g}(z')\Phi_g(z'),$$

$$\Phi_g(z) = \int \mathrm{d}z'\, G\left(z, z', \frac{\hbar^2 K_g^2}{2m}\right) U_g(z')\Phi_0(z'), \tag{4}$$

where $\Phi_{K_0}^{(+)}(z)$ is the solution of the one-dimensional scattering problem

$$-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial z^2}\Phi_{K_0}^{(+)}(z) + U_0(z)\Phi_{K_0}^{(+)}(z) = \frac{\hbar^2 K_0^2}{2m}\Phi_{K_0}^{(+)}(z) \tag{5}$$

satisfying the asymptotic condition at $z \to -\infty$

$$\Phi_{K_0}^{(+)}(z) = \exp(\mathrm{i}K_0 z) + R_0^{(\mathrm{pot})}\exp(-\mathrm{i}K_0 z), \tag{6}$$

and $G(z, z', E)$ is the Green's function satisfying the Schrödinger equation of the form

$$\left[E - \left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial z^2} + U_0(z)\right)\right] G(z, z', E) = \delta(z - z'). \tag{7}$$

The treatment developed in Refs. [24,25] shows that the resonance contribution to R_0 comes from the integral terms on the right-hand side of Eq. (4) (i.e. from processes of scattering involving momentum transfer $\hbar\boldsymbol{g}$ in the direction parallel to the surface). This explains the meaning of the notation $R_0^{(\mathrm{pot})}$ used in Eq. (6), where the "potential" (i.e. non-resonance) contribution to the reflectivity results from ordinary one-dimensional Bragg reflection of electrons from atomic planes parallel to the surface.

In what follows we consider the case in which the quantity $\hbar^2 K_g^2/2m$ is close to the energy ϵ_0 of one of the (identical) bound states localized in the potentials of the adjacent atomic planes parallel to the surface. As was shown in Refs. [24,25], this tight-binding model provides a good quantitative description of scattering of electrons from the Pt(111) surface. The Green's function $G(z, z', \hbar^2 K_g^2/2m)$ can then be represented in the form

$$G\left(z, z', \frac{\hbar^2 K_g^2}{2m}\right) = \sum_{n=0}^{\infty} \frac{\phi_n(z)\phi_n(z')}{(\hbar^2 K_g^2/2m) - \epsilon_0 + \mathrm{i}(\Gamma/2)}, \tag{8}$$

where the summation in Eq. (8) ranges over potential wells centered at $z_n = nd$ and Γ is the inelastic width parameter. Each function $\phi_n(z)$ represents the ground state for the relevant well and is assumed to be real.

Substituting Eq. (8) into Eq. (4) we see that the function $\Phi_g(z)$ has the form of a sum of localized orbitals [33]

$$\Phi_g(z) = \sum_n \alpha_n \phi_n(z), \tag{9}$$

where α_n are some numerical coefficients satisfying the equation

$$\alpha_n = \frac{1}{(\hbar^2 K_g^2/2m) - \epsilon_0 + \mathrm{i}(\Gamma/2)}\left[\int \mathrm{d}z'\, \phi_n(z')U_g(z')\Phi_{K_0}^{(+)}(z')\right.$$

$$+\sum_{l=0}^{\infty}\alpha_l\int\int \mathrm{d}z'\,\mathrm{d}z''\,\phi_n(z')U_g(z')G\left(z',z'',\frac{\hbar^2K_0^2}{2m}\right)U_{-g}(z'')\phi_l(z'')\Bigg]. \tag{10}$$

The one-dimensional Green's function entering Eq. (10) can be represented in the form (see Appendix A for more detail)

$$G\left(z',z'',\frac{\hbar^2K_0^2}{2m}\right)=-\frac{\mathrm{i}m}{\hbar^2K_0}\begin{cases}\Phi_{K_0}^{(+)}(z')\Phi_{K_0}^{(-)}(z''), & \text{when } z'>z'',\\ \Phi_{K_0}^{(-)}(z')\Phi_{K_0}^{(+)}(z''), & \text{when } z'<z'',\end{cases} \tag{11}$$

where $\Phi_{K_0}^{(+)}(z)$ and $\Phi_{K_0}^{(-)}(z)$ are two independent solutions of the same equation (5) satisfying different boundary conditions at $z=\pm\infty$, namely

$$\Phi_{K_0}^{(+)}(z)=\begin{cases}\exp(\mathrm{i}K_0z)+R_0^{(\mathrm{pot})}\exp(-\mathrm{i}K_0z), & \text{when } z\to-\infty,\\ \tau b(z,\kappa), & \text{when } z\to\infty,\end{cases} \tag{12}$$

and

$$\Phi_{K_0}^{(-)}(z)=\begin{cases}\exp(-\mathrm{i}K_0z), & \text{when } z\to-\infty,\\ \upsilon b(z,-\kappa)+\rho b(z,\kappa), & \text{when } z\to\infty,\end{cases} \tag{13}$$

In Eqs. (12) and (13) the quantities $b(z,\kappa)$ and $b(z,-\kappa)$ are two Bloch functions corresponding to the same energy $\hbar^2K_0^2/2m$ and propagating in opposite directions, and τ, υ and ρ are some numerical constants which depend on the form of the potential in the transition surface layer and in the crystal bulk. These coefficients can be found by solving the one-dimensional Schrödinger equation (5) (an example of how this can be done in practice is considered in the following section).

Substituting Eqs. (11)–(13) into Eq. (10) and using the translation property of the Bloch functions $b(z+d,\kappa)=\exp(\mathrm{i}\kappa d)b(z,\kappa)$ and $b(z+d,-\kappa)=\exp(-\mathrm{i}\kappa d)b(z,-\kappa)$, where d is the distance between centres of the neighbouring atomic planes parallel to the surface of the crystal, we arrive at

$$\alpha_n=\frac{\Lambda\tau}{(\hbar^2K_g^2/2m)-\epsilon_0-M_{00}-(\mathrm{i}m/\hbar^2K_0)\tau\upsilon\Lambda^2+\mathrm{i}(\Gamma/2)}$$
$$\times\left\{\exp(\mathrm{i}\kappa nd)-\frac{\mathrm{i}m}{\hbar^2K_0}\Lambda\sum_{l=0}^{\infty}\left[\upsilon\exp(\mathrm{i}\kappa d|n-l|)+\rho\exp(\mathrm{i}\kappa d(n+l))\right]\alpha_l\right\}, \tag{14}$$

where we have assumed that the potential of each atomic plane is a symmetrical function, and have introduced the notation

$$\Lambda=\int \mathrm{d}z\,\phi_0(z)U_g(z)b(z,\kappa)=\int \mathrm{d}z\,\phi_0(z)U_g(z)b(z,-\kappa),$$

and

$$M_{00}=M_{nn}=\int\int \mathrm{d}z'\,\mathrm{d}z''\,\phi_n(z')U_g(z')G\left(z',z'',\frac{\hbar^2K_0^2}{2m}\right)U_{-g}(z'')\phi_n(z'').$$

In the case $\tau=\upsilon=1$ and $\rho=0$ the solution of Eq. (14) is known [24,25]. In what follows we consider how the approach developed in Refs. [24,25] can be generalized to obtain the solution valid for arbitrary values of the constants τ, υ and ρ from Eqs. (12) and (13).

Firstly, combining Eqs. (4), (8) and (11), we find that the resonance contribution to the reflectivity can be evaluated using the formula

$$R_0^{(\mathrm{res})} = -\frac{\mathrm{i}m}{\hbar^2 K_0}\int \mathrm{d}z'\,\Phi_{K_0}^{(+)}(z')U_{-g}(z')\Phi_g(z') = -\frac{\mathrm{i}m}{\hbar^2 K_0}\Lambda\tau\sum_{n=0}^{\infty}\alpha_n \exp(\mathrm{i}\kappa n d), \tag{15}$$

which shows that in order to determine the resonance part of R_0, it is *sufficient* to know the solution of Eq. (14).

Secondly, it can be proved that the solution of Eq. (14) is related to the appropriate solution of the Schrödinger equation of the form

$$-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2}{\mathrm{d}z^2}\Psi(z) + V\Theta(-z)\Psi(z) + U\sum_{l=0}^{\infty}\delta(z-ld)\Psi(z) = \frac{\hbar^2\kappa^2}{2m}\Psi(z), \tag{16}$$

where $\Theta(z)$ is the step function ($\Theta'(z) = \delta(z)$), and V and U are arbitrary parameters. Indeed, the integral form of Eq. (16) for $z \geq 0$ leads to

$$\Psi(z) = J\exp(\mathrm{i}\kappa z) - \frac{\mathrm{i}m}{\hbar^2\kappa}U\sum_{l=0}^{\infty}\left\{\exp[\mathrm{i}\kappa|z-ld|] + \left(\frac{\kappa-q}{\kappa+q}\right)\exp[\mathrm{i}\kappa(z+ld)]\right\}\Psi(ld), \tag{17}$$

where J is an arbitrary constant and $q^2 = \kappa^2 - 2mV/\hbar^2$. Comparing Eqs. (17) and (14), we see that for $z = nd$ by the choice of parameters

$$J = \Lambda\tau\left(\frac{\hbar^2 K_g^2}{2m} - \epsilon_0 - M_{00} - \frac{\mathrm{i}m}{\hbar^2 K_0}\tau v\Lambda^2 + \mathrm{i}\frac{\Gamma}{2}\right)^{-1}, \tag{18}$$

$$U = \frac{\kappa}{K_0}\Lambda^2 v\tau\left(\frac{\hbar^2 K_g^2}{2m} - \epsilon_0 - M_{00} - \frac{\mathrm{i}m}{\hbar^2 K_0}\tau v\Lambda^2 + \mathrm{i}\frac{\Gamma}{2}\right)^{-1}, \tag{19}$$

and

$$V = \frac{\hbar^2\kappa^2}{2m}\cdot\frac{4v\rho}{(v+\rho)^2}, \tag{20}$$

Eq. (17) can be made identical to Eq. (14). The fact that the system of equations (4) can be reduced to a one-dimensional Schrödinger equation with non-Hermition δ-function potentials shows that there exists a similarity between the problem of resonance diffraction of high-energy electrons and the problem of scattering of resonance neutrons and Mössbauer quanta by crystals [26–28]. Employing the equivalence of Eqs. (16) and (14), and taking account of the fact that Eq. (16) can be solved exactly using the transfer-matrix technique [25], the details of which will not be repeated here, we obtain after some algebra

$$\alpha_n = J\frac{(\kappa+q)}{q(1+R)+\kappa(1-R)}(1+R)\left(1-\frac{r}{R}\right)^n\frac{1}{t^n}\exp(-\mathrm{i}\kappa n d), \tag{21}$$

where

$$R = \exp(-\mathrm{i}\kappa d)\frac{Z-1}{Z+1}, \tag{22}$$

$$Z = \left\{\frac{[r+\exp(-\mathrm{i}\kappa d)]^2 - t^2}{[r-\exp(-\mathrm{i}\kappa d)]^2 - t^2}\right\}^{1/2},$$

and

$$r = t - 1 = -\mathrm{i}\frac{m\Lambda^2}{\hbar^2 K_0}v\tau\left(\frac{\hbar^2 K_g^2}{2m} - \epsilon_0 - M_{00} + \mathrm{i}\frac{\Gamma}{2}\right)^{-1}. \tag{23}$$

r and t are the reflection and transmission coefficients of a single δ-function potential $U\delta(z)$ (see Ref. [25] for details). It is interesting to note that both the width and the position of the resonance feature characterizing the *reflectivity* of a single layer of atoms (23) are different from the same parameters entering the effective *potential* of a single layer (formula (19)). This is a manifestation of the phenomenon associated with multiple scattering in a periodic ensemble of scattering centres discovered by Kagan and Afanas'ev [27], who found that the parameters (the width and the position of the resonance on the energy scale) describing the interaction of resonance neutrons with a large array of periodically distributed nuclei are different from those characterizing the interaction of neutrons with an individual nucleus (see also formula (14) of Ref. [34]).

Substituting Eq. (21) into Eq. (15), we arrive at

$$R_0^{(\mathrm{res})} = -\mathrm{i}\frac{m}{\hbar^2 K_0}\Lambda\tau\left[\frac{(\kappa+q)}{q(1+R)+\kappa(1-R)}\right]\frac{t}{r}R, \tag{24}$$

from which, using definitions (18), (19), (20) and (23), we obtain the final result

$$R_0^{(\mathrm{res})} = \frac{\tau R}{\upsilon - \rho R}. \tag{25}$$

In the limiting case $\tau = \upsilon = 1$ and $\rho = 0$, Eq. (25) coincides with Eq. (10) of Ref. [24] and Eq. (35) of Ref. [25]. Note that according to Eq. (25) $R_0^{(\mathrm{res})}$ depends on the coefficients τ, υ and ρ via the ratios υ/τ and ρ/τ. This is a consequence of the fact that $R_0^{(\mathrm{res})}$ must be independent of the choice of normalization of the Bloch functions $b(z,\kappa)$ and $b(z,-\kappa)$ used in Eqs. (12) and (13).

3. Discussion

In this section we consider some approximate forms of Eq. (25) and compare the results of our analytical study with numerical calculations. As we noted above, most reflection electron microscope observations of surface structures have been performed using the orientation of the incident beam for which the specular reflection lies in the vicinity of the intersection of the resonance parabola (i.e. the curve defined by the equation $\hbar^2 K_g^2/2m \approx \epsilon_0$) and one of the horizontal Kikuchi lines. It is well known that the horizontal Kikuchi lines appear as a result of one-dimensional Bragg diffraction of electrons from the atomic planes parallel to the surface of the crystal. The contrast of these lines can be evaluated using the so-called two-beam approximation, in which the potential of the crystal is represented by the sum of two terms $U_0(z) = U_0 + 2U_1\cos(Gz)$ and $|U_1|$ is assumed to satisfy the condition $|U_1| \ll \hbar^2 G^2/2m$. If the origin of coordinates is chosen to be at an atomic centre of symmetry, U_0 and U_1 have in practice negative real parts. Defining

$$u_{0,1} = U_{0,1}/(\hbar^2 G^2/2m),$$

and

$$\omega = [(K_0 - G)^2 - K_0^2]/G^2,$$

a solution of the wave equation exists, known as the Darwin solution (see Ref. [36]), which gives

$$R_0^{(\mathrm{pot})} = -\frac{2u_1}{\omega + 2u_0 - \sqrt{(\omega+2u_0)^2 - 4u_1^2}}. \tag{26}$$

We have adopted the convention that the square root of a complex number $Z = |Z|\exp(\mathrm{i}\phi)$ $(0 \le \phi \le 2\pi)$ is given by $Z^{1/2} = |Z|^{1/2}\exp(\mathrm{i}\phi/2)$. In the two-beam approximation the crystal wave vector κ is given by

$$\kappa = \frac{G}{2}[1 + \sqrt{(\omega+2u_0)^2 - 4u_1^2}], \tag{27}$$

and for the three coefficients entering Eq. (25) we find

$$\tau = 1, \qquad \upsilon = \frac{1}{1 - [R_0^{(\mathrm{pot})}]^2}, \qquad \rho = -\frac{R_0^{(\mathrm{pot})}}{1 - [R_0^{(\mathrm{pot})}]^2}. \tag{28}$$

Substituting this into Eq. (25), we arrive at [35]

$$R_0^{(\mathrm{tot})} = R_0^{(\mathrm{pot})} + R_0^{(\mathrm{res})} = \frac{R_0^{(\mathrm{pot})} + R}{1 + R_0^{(\mathrm{pot})} R}, \tag{29}$$

where R is defined by Eq. (22). It is important to note that in formula (29) R is not an independent quantity because the coefficients τ, υ and ρ entering its definition (22) depend on $R_0^{(\mathrm{pot})}$ via Eqs. (28). It is also interesting to note (see Appendix B) that in fact Eq. (29) follows from the requirement of T-invariance of the amplitude of scattering, and remains valid beyond the limits of the two-beam approximation.

Formulae (25) and (29) make it possible to evaluate the reflectivity of the surface as a function of the two angles of incidence, namely the glancing angle ζ and the azimuthal angle η. The direction of the wave vector of incident electrons is related to these two angles via $\boldsymbol{k} = |\boldsymbol{k}|(\cos\zeta\cos\eta, \cos\zeta\sin\eta, \sin\zeta)$. Experimentally, this dependence of $|R_0(\zeta,\eta)|^2$ can be observed using the so-called convergent-beam electron diffraction (CBED) technique [37,38] in which the crystal is illuminated by a convergent beam of incident electrons. The distribution of intensity in the CBED pattern can be calculated by solving Eqs. (4) (usually the differential form of (4) is used for numerical study [13]). The distribution of intensity calculated numerically in the vicinity of the point of intersection of the (666) horizontal Kikuchi line and the resonance parabola associated with the $(\bar{2}20)$ side reflection is shown in Fig. 2 for the Pt(111) surface. The form of the distribution of intensity shown in Fig. 2 is familiar from the results of experimental studies of resonance diffraction (see, e.g., Ref. [14]), and the pattern shown in Fig. 2 corresponds to the orientation which is most often used for electron microscope observations of surface structures [20,31].

The distribution of the CBED intensity shown in Fig. 2 is also similar to a pattern often observed using transmission electron diffraction in the vicinity of the point of intersection of two Kikuchi lines [39]. The difference between the process of resonance diffraction described in this paper and the mechanism resulting in the appearance of the so-called "two-beam features" [39] lies in the fact that in the latter case the observed distribution of intensity results from interaction between two *propagating* waves while in the former case one of the two Bloch functions is a superposition of many states tightly bound by the potential of the atomic planes.

Fig. 3 shows the distribution of the CBED intensity for the same region of angles ζ and η as in Fig. 2, but calculated *analytically* using formula (29). In this case no solution of the differential equations was required, and the form of the distribution shown in Fig. 3 is entirely determined by the magnitude of the Fourier coefficients of the crystal potential U_{666} and U_{000}, and the values of two constants, Λ and Γ, which are proportional to the elastic and inelastic widths of the resonance, respectively.

The advantage of the analytical formulae (25) and (29) lies in the fact that they are suitable for evaluation of other parameters (besides the reflectivity $|R_0(\zeta,\eta)|^2$ itself) characterizing the process of scattering which would otherwise be difficult to find from numerical consideration. One of the parameters which is important for applications of resonance diffraction to energy loss spectroscopy [11,32] is the effective penetration depth l_{eff} characterizing the rate of attenuation of the wave function in the bulk of the crystal. This penetration depth is given by

$$l_{\mathrm{eff}} = -d\left[\mathrm{Re}\ln(\alpha_{n+1}/\alpha_n)\right]^{-1} = \left\{\mathrm{Im}\left[\kappa - \mathrm{i}\frac{1}{d}\ln\left(1 - \frac{r}{R}\right) + \mathrm{i}\frac{1}{d}\ln t\right]\right\}^{-1}. \tag{30}$$

In the vicinity of the point of intersection of the resonance parabola with one of the Kikuchi lines this quantity depends on the two angles of incidence ζ and η as shown in Fig. 4. As follows from examination

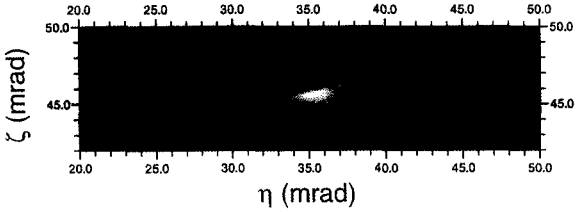

Fig. 2. The distribution of intensity in the convergent beam diffraction pattern in the vicinity of the point of intersection of the (666) horizontal Kikuchi line and the $(\bar{2}20)$ resonance parabola calculated numerically for the Pt(111) surface using the differential form of Eqs. (4). The azimuth $\eta = 0$ corresponds to the $|11\bar{2}|$ direction, and the energy of the electrons is 100 keV. The Doyle–Turner coefficients used in the calculations have been taken from Ref. [25].

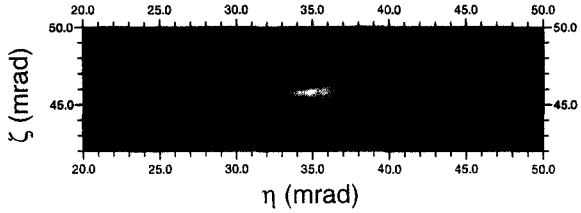

Fig. 3. The distribution of intensity in the convergent beam diffraction pattern in the vicinity of the point of intersection of the (666) horizontal Kikuchi line and the $(\bar{2}20)$ resonance parabola calculated analytically for the Pt(111) surface using formula (29). The azimuth $\eta = 0$ corresponds to the $|11\bar{2}|$ direction, and the energy of the electrons is 100 keV. The following numerical values of the parameters have been used in the calculations $U_{666} = -0.66 - i0.28$ eV, $U_{(00)} = -34.34 - i1.98$ eV, $\Gamma = 18.9$ eV and $\epsilon_0 = -65.72$ eV.

of the data shown in this figure, the effective penetration depth is almost insensitive to the potential channel of scattering, so the magnitude of l_{eff} is mainly determined by the distance from the resonance parabola. In particular, this quantity remains relatively large ($l_{\text{eff}} \sim 6$ Å, i.e. four times its minimal value $l_{\text{eff}} \sim 1.5$ Å) in the vicinity of the point $\zeta_0 = 45.8$ mrad, $\eta_0 = 34.4$ mrad corresponding to the peak value of surface reflectivity $|R_0(\zeta_0, \eta_0)|^2 = 0.73$.

Another important parameter characterizing the process of resonance diffraction is the effective displacement Δ of the electron beam in the direction *parallel* to the surface. This distance determines the splitting of electron microscope images [40] obtained at grazing incidence. Wang [9] has considered how Δ can be estimated using the results of multislice simulations. An analytical formula for Δ can be obtained by considering the time delay t_Δ associated with the interaction of the incident wave packet with the potential of the crystal [41]. After some algebra described in detail in Appendix C we arrive at the following equation for Δ

$$\Delta = \frac{1}{k \sin\zeta} \frac{\partial}{\partial \zeta} \left\{ \mathrm{Im} \left[\ln R_0(\zeta, \eta) \right] \right\}, \tag{31}$$

which states that the effective displacement of the beam in the direction parallel to the crystal surface is proportional to the derivative of the phase of the coefficient of reflection with respect to the glancing angle ζ. As shown in Appendix C, Eq. (31) is equivalent to formula (1) from Ref. [40]. The range of applicability of Eq. (31) to the determination of barrier interaction time in tunnelling phenomena has recently been discussed by Landauer and Martin [42]. They found that Eq. (31) often fails to produce a meaningful result, and in particular, in many cases the value of Δ calculated using formula (31) is *negative*. It should be emphasized that Eq. (31), although being formally equivalent to the results obtained earlier by other authors [45,40], is far more convenient for doing practical calculations. Indeed, in most cases the amplitude of the specular beam R_0 is known from many-beam RHEED calculations as a function of the two angles of incidence, and therefore evaluation of Δ is in fact equivalent to simple differentiation of this function with respect to the grazing angle ζ, or in other words it requires differentiating a calculated rocking curve. The derivative can be expressed in terms of the real and imaginary part of the amplitude of the specular beam as

$$\frac{\partial}{\partial \zeta} \left\{ \mathrm{Im} \left[\ln R_0(\zeta, \eta) \right] \right\} = \frac{1}{|R_0(\zeta, \eta)|^2} \left[\mathrm{Re} R_0(\zeta, \eta) \frac{\partial}{\partial \zeta} \left\{ \mathrm{Im}\, R_0(\zeta, \eta) \right\} - \mathrm{Im}\, R_0(\zeta, \eta) \frac{\partial}{\partial \zeta} \left\{ \mathrm{Re} R_0(\zeta, \eta) \right\} \right]. \tag{32}$$

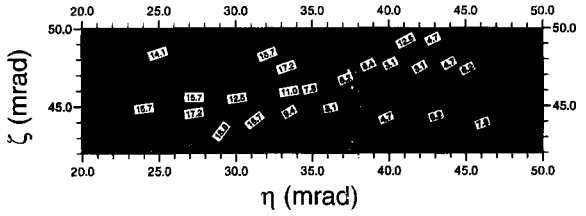

Fig. 4. The dependence of the effective depth of penetration l_{eff} on the two angles of incidence ζ and η calculated using formula (30) for the Pt(111) surface and 100 keV electrons. The boxes represent the values of l_{eff} (Å) at contour lines.

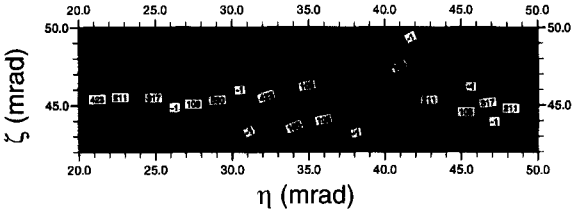

Fig. 5. The dependence of the distance Δ of propagation of the electron parallel to the surface (formula (31)) on the two angles of incidence ζ and η. The boxes represent the values of Δ (Å) at contour lines. Note that the orientation corresponding to the maximum of the surface reflectivity almost coincides with the orientation of the incident beam giving rise to the largest value of Δ.

Fig. 5 is the contour map showing the dependence of Δ on the angles of incidence in the vicinity of the (666) Bragg / $(\bar{2}20)$ resonance conditions calculated analytically using formulae (29) and (31). As follows from comparison of the results shown in Fig. 5 with Figs. 2 and 3, the maximum of Δ nearly coincides with the maximum of the surface reflectivity $|R_0(\zeta_0, \eta_0)|^2$, indicating that the peak of the reflectivity is indeed associated with the trapping of electrons by the "resonance" state and the associated process of travelling a long distance parallel to the surface, in accordance with the idea proposed by Cowley [46] (note that Δ is a manifestation of a purely quantum-mechanical effect and that it vanishes in the classical limit). It also follows from our analysis that there exists no direct relation between the reflectivity of the surface $|R_0|^2$ and the depth of penetration of the electrons in the crystal bulk, indicating that resonance diffraction of high-energy electrons from crystal surfaces is a collective process involving interaction with many bulk atomic planes, in agreement with the results of numerical studies [9,14,15].

4. Conclusions

In this paper we have found an analytical solution of the problem of resonance diffraction of high-energy electrons from a crystal surface using the tight-binding model and making no assumption regarding the relative magnitude of the resonance and the potential contributions to the amplitude of the specular beam. This solution is shown to agree well with the results of numerical simulations of the resonance scattering of electrons from the Pt(111) surface. It is found that the maximum of the surface reflectivity does not correspond to the minimum of penetration of electrons in the crystal bulk, but it is associated with the maximum distance of propagation in the direction parallel to the surface.

Appendix A.

A solution of Eq. (7) satisfying the appropriate boundary conditions at $z = \pm\infty$ has the form

$$G\left(z', z'', \frac{\hbar^2 K_0^2}{2m}\right) = \begin{cases} A(z'')\Phi_{K_0}^{(+)}(z'), & \text{when } z' > z'', \\ B(z'')\Phi_{K_0}^{(-)}(z'), & \text{when } z' < z'', \end{cases} \tag{A.1}$$

where $A(z'')$ and $B(z'')$ are two arbitrary functions. These functions can be found using the condition of continuity of the Green's function at $z' = z''$

$$G\left(z''+0,z'',\frac{\hbar^2K_0^2}{2m}\right)=G\left(z''-0,z'',\frac{\hbar^2K_0^2}{2m}\right), \tag{A.2}$$

which using Eq. (A.1) leads to

$$A(z'')=C\Phi_{K_0}^{(-)}(z''),\qquad B(z'')=C\Phi_{K_0}^{(+)}(z''). \tag{A.3}$$

The constant C is determined by the condition on the derivative of the Green's function following from Eq. (7) by integration over a small interval of z' containing $\delta(z'-z'')$

$$\frac{\hbar^2}{2m}\left[\frac{\partial}{\partial z'}G\left(z',z'',\frac{\hbar^2K_0^2}{2m}\right)\Big|_{z'=z''+0}-\frac{\partial}{\partial z'}G\left(z',z'',\frac{\hbar^2K_0^2}{2m}\right)\Big|_{z'=z''-0}\right]=1. \tag{A.4}$$

Noting that the following combination of the functions $\Phi_{K_0}^{(+)}(z')$ and $\Phi_{K_0}^{(-)}(z')$

$$W\left[\Phi_{K_0}^{(-)}(z');\Phi_{K_0}^{(+)}(z')\right]=\Phi_{K_0}^{(-)}(z')\frac{\mathrm{d}}{\mathrm{d}z'}\Phi_{K_0}^{(+)}(z')-\Phi_{K_0}^{(+)}(z')\frac{\mathrm{d}}{\mathrm{d}z'}\Phi_{K_0}^{(-)}(z')$$

is the Wronskian (which, since Eq. (7) does not contain a first-order derivative, is independent of z' [43] and can be evaluated at any point z', for example, at $z'=-\infty$), and using the appropriate expressions from Eqs. (12) and (13) for $z'\to-\infty$, we find that $W=2\mathrm{i}K_0$, and hence from Eq. (A.4) that $C=-\mathrm{i}m/\hbar^2K_0$. With Eqs. (A.3) and (A.1) this leads to Eq. (11).

Appendix B.

In this appendix we show that Eq. (29) can be derived from Eq. (25) under fairly general assumptions using the condition of T-invariance of the amplitude of scattering [44]. Reversing the directions of propagation of waves in Eq. (12) we obtain

$$\Phi_{-K_0}^{(+)}(z)=\begin{cases}\exp(-\mathrm{i}K_0z)+R_0^{(\mathrm{pot})}\exp(\mathrm{i}K_0z), & \text{when } z\to-\infty,\\ \tau b(z,-\kappa), & \text{when } z\to\infty.\end{cases} \tag{B.1}$$

Considering the asymptotic behaviour of the linear combination of functions $\Phi_{-K_0}^{(+)}(z)-R_0^{(\mathrm{pot})}\Phi_{K_0}^{(+)}(z)$ we arrive at

$$\Phi_{-K_0}^{(+)}(z)-R_0^{(\mathrm{pot})}\Phi_{K_0}^{(+)}(z)=\begin{cases}\exp(-\mathrm{i}K_0z)\left(1-\left[R_0^{(\mathrm{pot})}\right]^2\right), & \text{when } z\to-\infty,\\ \tau\left[b(z,-\kappa)-R_0^{(\mathrm{pot})}b(z,\kappa)\right], & \text{when } z\to\infty.\end{cases} \tag{B.2}$$

Comparing Eq. (B.2) with Eq. (13) we obtain

$$\frac{v}{\tau}=\frac{1}{1-[R_0^{(\mathrm{pot})}]^2},\qquad \frac{\rho}{\tau}=-\frac{R_0^{(\mathrm{pot})}}{1-[R_0^{(\mathrm{pot})}]^2}. \tag{B.3}$$

Combining Eqs. (B.3) and (25) we arrive at Eq. (29).

Appendix C.

In this appendix we present two derivations of Eq. (31). The first derivation is based on the time-independent treatment of the diffraction problem and is similar to that given by Artmann [45]. The second derivation uses

a time-dependent picture, and in our opinion is more interesting. Both derivations lead to the same result (31) for Δ.

Consider the time-independent approach first. Let us represent the incident wave as a linear combination of plane waves

$$\Psi_{\mathrm{inc}}(\boldsymbol{r}) = \int \mathrm{d}q_x\,\mathrm{d}q_y\, A(\boldsymbol{q}-\boldsymbol{q}_0)\exp\left(\mathrm{i}\boldsymbol{q}\cdot\boldsymbol{R}+\mathrm{i}\sqrt{k^2-\boldsymbol{q}^2}z\right), \tag{C.1}$$

where the function $A(\boldsymbol{q}-\boldsymbol{q}_0) = A(q_x-[\boldsymbol{q}_0]_x, q_y-[\boldsymbol{q}_0]_y)$ is assumed to be sharply peaked at $\boldsymbol{q}=\boldsymbol{q}_0$. Then according to Eq. (3) the solution of the problem of scattering in the half-space $z<0$ is

$$\begin{aligned}\Psi(\boldsymbol{r}) = \int \mathrm{d}q_x\,\mathrm{d}q_y\, A(\boldsymbol{q}-\boldsymbol{q}_0)\Big[&\exp\left(\mathrm{i}\boldsymbol{q}\cdot\boldsymbol{R}+\mathrm{i}\sqrt{k^2-\boldsymbol{q}^2}z\right)\\ &+\sum_{\boldsymbol{g}} R_{\boldsymbol{g}}(\boldsymbol{q})\exp\left(\mathrm{i}\{\boldsymbol{q}+\boldsymbol{g}\}\cdot\boldsymbol{R}-\mathrm{i}\sqrt{k^2-\{\boldsymbol{q}+\boldsymbol{g}\}^2}z\right)\Big].\end{aligned} \tag{C.2}$$

Expanding the arguments of the exponents as a power series in $\boldsymbol{q}-\boldsymbol{q}_0$, writing $R_{\boldsymbol{g}} = |R_{\boldsymbol{g}}|\exp[\mathrm{i}\phi_{\boldsymbol{g}}(\boldsymbol{q})]$ and retaining only linear terms, we arrive at

$$\begin{aligned}\Psi(\boldsymbol{r}) =& \exp(\mathrm{i}\boldsymbol{q}_0\cdot\boldsymbol{R})\int \mathrm{d}q_x\,\mathrm{d}q_y\, A(\boldsymbol{q}-\boldsymbol{q}_0)\exp\left(\mathrm{i}[\boldsymbol{q}-\boldsymbol{q}_0]\cdot\boldsymbol{R}+\mathrm{i}\sqrt{k^2-\boldsymbol{q}^2}z\right)\\ &+\sum_{\boldsymbol{g}}|R_{\boldsymbol{g}}(\boldsymbol{q}_0)|\exp(\mathrm{i}\phi_{\boldsymbol{g}}(\boldsymbol{q}_0))\exp(\mathrm{i}[\boldsymbol{q}_0+\boldsymbol{g}]\cdot\boldsymbol{R})\\ &\times\int \mathrm{d}q_x\,\mathrm{d}q_y\, A(\boldsymbol{q}-\boldsymbol{q}_0)\exp\left(\mathrm{i}\left\{\frac{\partial}{\partial\boldsymbol{q}}\phi_{\boldsymbol{g}}(\boldsymbol{q})|_{\boldsymbol{q}_0}+\boldsymbol{R}\right\}\cdot[\boldsymbol{q}-\boldsymbol{q}_0]-\mathrm{i}\sqrt{k^2-\{\boldsymbol{q}+\boldsymbol{g}\}^2}z\right).\end{aligned} \tag{C.3}$$

As follows from Eq. (C.3), at $z=0$ each of the reflected beams is displaced in the direction parallel to the surface, and the magnitude of the displacement is given by

$$\boldsymbol{R}_0 = -\frac{\partial}{\partial\boldsymbol{q}}\phi_{\boldsymbol{g}}(\boldsymbol{q})|_{\boldsymbol{q}_0}. \tag{C.4}$$

This result is equivalent to Eq. (2.6) from Ref. [45] and Eq. (8) from Ref. [40]. To make the result (C.4) more suitable for practical use, instead of (q_x, q_y) we introduce angular variables (ζ,η) as

$$\begin{cases} q_x = k\cos\zeta\cos\eta,\\ q_y = k\cos\zeta\sin\eta,\\ q_z = k\sin\zeta. \end{cases} \tag{C.5}$$

In the transformation defined by Eq. (C.5), q_x and q_y are independent variables, and q_z is a function of q_x and q_y. Noting that for any function $\phi_{\boldsymbol{g}}(q_x, q_y)$

$$\begin{cases} \dfrac{\partial\phi_{\boldsymbol{g}}}{\partial\zeta} = -k\sin\zeta\cos\eta\dfrac{\partial\phi_{\boldsymbol{g}}}{\partial q_x} - k\sin\zeta\sin\eta\dfrac{\partial\phi_{\boldsymbol{g}}}{\partial q_y},\\ \dfrac{\partial\phi_{\boldsymbol{g}}}{\partial\eta} = -k\cos\zeta\sin\eta\dfrac{\partial\phi_{\boldsymbol{g}}}{\partial q_x} + k\cos\zeta\cos\eta\dfrac{\partial\phi_{\boldsymbol{g}}}{\partial q_y}, \end{cases} \tag{C.6}$$

we find

$$\begin{cases} \dfrac{\partial\phi_{\boldsymbol{g}}}{\partial q_x} = -\dfrac{1}{k}\dfrac{\cos\eta}{\sin\zeta}\dfrac{\partial\phi_{\boldsymbol{g}}}{\partial\zeta} - \dfrac{1}{k}\dfrac{\sin\eta}{\cos\zeta}\dfrac{\partial\phi_{\boldsymbol{g}}}{\partial\eta},\\ \dfrac{\partial\phi_{\boldsymbol{g}}}{\partial q_y} = -\dfrac{1}{k}\dfrac{\sin\eta}{\sin\zeta}\dfrac{\partial\phi_{\boldsymbol{g}}}{\partial\zeta} + \dfrac{1}{k}\dfrac{\cos\eta}{\cos\zeta}\dfrac{\partial\phi_{\boldsymbol{g}}}{\partial\eta}. \end{cases} \tag{C.7}$$

Defining Δ as the projection of $\boldsymbol{R}_0$ on the direction of the incident beam, we arrive at

$$\Delta = (\boldsymbol{R}_0)_x \cos\eta + (\boldsymbol{R}_0)_y \sin\eta = -\cos\eta \frac{\partial \phi_g(\boldsymbol{q})}{\partial q_x} - \sin\eta \frac{\partial \phi_g(\boldsymbol{q})}{\partial q_y}, \tag{C.8}$$

and using formulae (C.7) we obtain for the effective displacement of the specular beam

$$\Delta = \frac{1}{k \sin\zeta} \frac{\partial \phi_0}{\partial \zeta}, \tag{C.9}$$

where ϕ_0 is now considered as a function of two angles ζ and η, and k is a constant. Formula (C.9) is equivalent to Eq. (31).

It is instructive to consider how the lateral displacement of the specular beam (C.9) can be evaluated using a time-dependent formalism. Although the use of the time-dependent formalism does not simplify the problem of evaluation of Δ, it is more appealing for an understanding of the physical contents of the problem of scattering, and it also enables an estimate to be made of the time delay t_Δ associated with the interaction between the incident electron and the crystal. In the time-dependent formalism we use *three* independent variables (q_x, q_y, q_z) and represent the wave function for $z < 0$ as

$$\Psi(\boldsymbol{r}, t) = \int \mathrm{d}q_x \, \mathrm{d}q_y \, \mathrm{d}q_z \, B(\boldsymbol{q} - \boldsymbol{q}_0) \exp(-\mathrm{i}\epsilon_{\boldsymbol{q}} t/\hbar) \left[\exp\left(\mathrm{i}\boldsymbol{q} \cdot \boldsymbol{R} + \mathrm{i}\sqrt{k^2 - \boldsymbol{q}^2} z \right) + \sum_{\boldsymbol{g}} R_{\boldsymbol{g}} \exp\left(\mathrm{i}\{\boldsymbol{q} + \boldsymbol{g}\} \cdot \boldsymbol{R} - \mathrm{i}\sqrt{k^2 - \{\boldsymbol{q} + \boldsymbol{g}\}^2} z \right) \right], \tag{C.10}$$

where $B(\boldsymbol{q} - \boldsymbol{q}_0) = B(q_x - [\boldsymbol{q}_0]_x, q_y - [\boldsymbol{q}_0]_y, q_z - [\boldsymbol{q}_0]_z)$. Using the expansion

$$\epsilon_{\boldsymbol{q}} = \epsilon_{\boldsymbol{q}_0} + \frac{\partial \epsilon_{\boldsymbol{q}}}{\partial \boldsymbol{q}}\Big|_{\boldsymbol{q}_0} \cdot (\boldsymbol{q} - \boldsymbol{q}_0) = \epsilon_{\boldsymbol{q}_0} + \hbar \boldsymbol{v}_0 \cdot (\boldsymbol{q} - \boldsymbol{q}_0), \tag{C.11}$$

we find that the incident wave represents an electron moving with velocity $\boldsymbol{v}_0$

$$\Psi_{\mathrm{inc}}(\boldsymbol{r}, t) \sim B(\boldsymbol{r} - \boldsymbol{v}_0 t), \tag{C.12}$$

which enters the crystal at the point $\boldsymbol{R} = 0$ at time $t = 0$. The remaining terms in Eq. (C.10) describe wave packets reflected from the surface. Expanding the arguments of the exponential functions as a power series in $\boldsymbol{q} - \boldsymbol{q}_0$, and performing integration over $\boldsymbol{q}$, we arrive at

$$\begin{aligned} \Psi(\boldsymbol{r}, t) = {} & \exp(-\mathrm{i}\epsilon_{\boldsymbol{q}_0} t/\hbar) \exp(\mathrm{i}\boldsymbol{q}_0 \cdot \boldsymbol{r}) B(\boldsymbol{r} - \boldsymbol{v}_0 t) \\ & + \sum_{\boldsymbol{g}} |R_{\boldsymbol{g}}(\boldsymbol{q}_0)| \exp(-\mathrm{i}\epsilon_{\boldsymbol{q}_0} t/\hbar) \exp(\mathrm{i}\phi_{\boldsymbol{g}}(\boldsymbol{q}_0) - \mathrm{i}K_{\boldsymbol{g}}(\boldsymbol{q}_0) z + \mathrm{i}[\boldsymbol{q}_{0\|} + \boldsymbol{g}] \cdot \boldsymbol{R}) \\ & \times B\left(\boldsymbol{R} - \frac{\partial K_{\boldsymbol{g}}}{\partial \boldsymbol{q}}\Big|_{\boldsymbol{q}_0} z + \frac{\partial \phi_{\boldsymbol{g}}}{\partial \boldsymbol{q}}\Big|_{\boldsymbol{q}_0} - \boldsymbol{v}_0 t \right), \end{aligned} \tag{C.13}$$

where $K_{\boldsymbol{g}}(\boldsymbol{q}) = \sqrt{\boldsymbol{q}^2 - (\boldsymbol{q}_{\|} + \boldsymbol{g})^2}$ and the subscript $\|$ denotes the surface parallel component of the three-dimensional $\boldsymbol{q}$ vector. Using the explicit expression for the derivative

$$\frac{\partial K_{\boldsymbol{g}}}{\partial \boldsymbol{q}} = \frac{1}{K_{\boldsymbol{g}}} (q_z \boldsymbol{e}_z - \boldsymbol{g}), \tag{C.14}$$

where $\boldsymbol{e}_z$ is a unit vector along z, we find that the coordinate $\boldsymbol{r}_0(t) = (\boldsymbol{R}_0(t), z_0(t))$ of the centre of the wave packet associated with the reciprocal lattice rod $\boldsymbol{g}$ satisfies the equation

$$\boldsymbol{R}_0(t) - \frac{1}{K_g}(q_{0z}\boldsymbol{e}_z - \boldsymbol{g})z_0(t) + \frac{\partial\phi_g}{\partial\boldsymbol{q}}|_{q_0} - \frac{\hbar\boldsymbol{q}_0}{m}t = 0. \tag{C.15}$$

The solution of Eq. (C.15) describes a particle moving along a straight line

$$\begin{cases} \boldsymbol{R}_0(t) = \boldsymbol{R}_0 + (\hbar/m)(\boldsymbol{q}_{0\|} + \boldsymbol{g})(t - t_\Delta), \\ z_0(t) = -(\hbar/m)K_g(t - t_\Delta), \end{cases} \tag{C.16}$$

where

$$\begin{cases} \boldsymbol{R}_{0x} = -\dfrac{\partial\phi_g}{\partial q_x} + \dfrac{q_x}{q_z}\dfrac{\partial\phi_g}{\partial q_z}, \\ \boldsymbol{R}_{0y} = -\dfrac{\partial\phi_g}{\partial q_y} + \dfrac{q_y}{q_z}\dfrac{\partial\phi_g}{\partial q_z}, \\ t_\Delta = \dfrac{m}{\hbar q_z}\dfrac{\partial\phi_g}{\partial q_z}. \end{cases} \tag{C.17}$$

According to Eq. (C.16) the reflected wave packet is delayed, and it emerges from the surface at a point which is displaced from the point where the electron entered the crystal. It should be noted that formally the equation for $\boldsymbol{R}_0$ following from Eq. (C.17) differs from Eq. (C.4), and this difference results from the fact that in the present consideration we have used *three* independent variables instead of the two which are required for the analysis of the time-independent problem of scattering. Introducing three new variables (ζ, η, q)

$$\begin{cases} q_x = q\cos\zeta\cos\eta, \\ q_y = q\cos\zeta\sin\eta, \\ q_z = q\sin\zeta, \end{cases} \tag{C.18}$$

we obtain

$$\begin{cases} \dfrac{\partial\phi_g}{\partial\zeta} = -q\sin\zeta\cos\eta\dfrac{\partial\phi_g}{\partial q_x} - q\sin\zeta\sin\eta\dfrac{\partial\phi_g}{\partial q_y} + q\cos\zeta\dfrac{\partial\phi_g}{\partial q_z}, \\ \dfrac{\partial\phi_g}{\partial\eta} = -q\cos\zeta\sin\eta\dfrac{\partial\phi_g}{\partial q_x} + q\cos\zeta\cos\eta\dfrac{\partial\phi_g}{\partial q_y}, \\ \dfrac{\partial\phi_g}{\partial q} = \cos\zeta\cos\eta\dfrac{\partial\phi_g}{\partial q_x} + \cos\zeta\sin\eta\dfrac{\partial\phi_g}{\partial q_y} + \sin\zeta\dfrac{\partial\phi_g}{\partial q_z}. \end{cases} \tag{C.19}$$

From Eq. (C.19) it follows that

$$\begin{cases} \dfrac{\partial\phi_g}{\partial q_x} = \cos\zeta\cos\eta\dfrac{\partial\phi_g}{\partial q} - \dfrac{\sin\zeta\cos\eta}{q}\dfrac{\partial\phi_g}{\partial\zeta} - \dfrac{\sin\eta}{q\cos\zeta}\dfrac{\partial\phi_g}{\partial\eta}, \\ \dfrac{\partial\phi_g}{\partial q_y} = \cos\zeta\sin\eta\dfrac{\partial\phi_g}{\partial q} - \dfrac{\sin\zeta\sin\eta}{q}\dfrac{\partial\phi_g}{\partial\zeta} + \dfrac{\cos\eta}{q\cos\zeta}\dfrac{\partial\phi_g}{\partial\eta}, \\ \dfrac{\partial\phi_g}{\partial q_z} = \sin\zeta\dfrac{\partial\phi_g}{\partial q} + \dfrac{\cos\zeta}{q}\dfrac{\partial\phi_g}{\partial\zeta}. \end{cases} \tag{C.20}$$

Substituting Eq. (C.20) into Eq. (C.17) we obtain

$$\begin{cases} \boldsymbol{R}_{0x} = \dfrac{\cos\eta}{q\sin\zeta}\dfrac{\partial\phi_g}{\partial\zeta} + \dfrac{\sin\eta}{q\cos\zeta}\dfrac{\partial\phi_g}{\partial\eta}, \\ \boldsymbol{R}_{0y} = \dfrac{\sin\eta}{q\sin\zeta}\dfrac{\partial\phi_g}{\partial\zeta} - \dfrac{\cos\eta}{q\cos\zeta}\dfrac{\partial\phi_g}{\partial\eta}, \end{cases} \tag{C.21}$$

the substitution of which into Eq. (C.8) for $\boldsymbol{g} = 0$ results in

$$\Delta = \frac{1}{q\sin\zeta}\frac{\partial\phi_0}{\partial\zeta}, \tag{C.22}$$

which is equivalent to Eqs. (C.9) and (31). Substituting the expression for $\partial\phi_0/\partial q_z$ of Eq. (C.20) in the equation for t_Δ of Eq. (C.17), we obtain for the time delay of the specularly reflected wave packet

$$t_\Delta = \hbar\frac{\partial\phi_0}{\partial E} + \frac{\hbar}{2E}\frac{\cos\zeta}{\sin\zeta}\frac{\partial\phi_0}{\partial\zeta}, \tag{C.23}$$

where $E = \hbar^2q^2/2m$ and $\partial\phi_0/\partial E = (m/\hbar^2q)\partial\phi_0/\partial q$. Comparison of Eqs. (C.22) and (C.23) shows that while the effective displacement Δ of the beam in the direction parallel to the surface can be evaluated from the calculated dependence of the phase of the reflected beam as a function of the grazing angle of incidence ζ (the rocking curve), the evaluation of time delay t_Δ requires additional information concerning the dependence of the phase of the reflected beam on the energy of the incident electron beam.

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