450

Corrections to Atomic Scattering Factors for High-Energy Electrons Arising from Atomic Vibrations

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Abstract

Thermal vibrations of the atoms of a crystal result in loss of coherence of a fast electron when it enters the crystal. The scattering of the coherent part of the wave may be modelled by introducing a correction to the time-averaged electrostatic potential of the crystal. The correction involves both a real part and an imaginary part. The real part is not usually considered in calculations of diffracted intensities but for strong scatterers such as Au atoms it is sufficiently large that it should be measurable by convergent-beam diffraction.

1. Introduction

Atomic vibrations have significant effects on the degree of coherence of high-energy electrons that have passed through a thin foil. Coherent scattering is determined by the interaction of the fast electron with the time average of the electrostatic potential of the foil. Atomic vibrations lead to the introduction of a complex correction potential. The amplitude of the wave that remains coherent with the incident wave is determined by the imaginary part of this potential.

Theoretical estimates of the absorption potential are based on the Born approximation of scattering (Hall & Hirsch, 1965), which fails for atoms of high atomic number. This paper provides estimates of the correction potentials, which are based on the Molière or eikonal approximation for the scattering of high-energy electrons (Newton, 1966; Cowley, 1981). The use of this scattering approximation leads not only to an imaginary correction but also to a real correction to the scattering function of an atom.

The paper is organized as follows. In the next section, we derive a formula for the correction potential. Since the formula is based on the Molière approximation, we give the results of some numerical calculations in order to justify the use of this approximation. In §3, we present estimates of the correction potential based on the derived formula for 10, 100 and 300 keV electrons. We show that our results are in agreement with previously published figures for light elements but are significantly different for heavy elements. We point out that the differences should be detectable by quantitative analysis of convergent-beam diffraction patterns. In the final section, we show how multislice programs that are used for calculating scattering by long-period structures can be modified to include the correction potentials without requiring a separate program or table of values.

2. The effect of thermal motion on the atomic scattering function

When a fast electron, initially travelling in the z direction, is scattered by a single atom, the wave function at a point $\mathbf{R} \equiv (x, y)$ in the plane infinitely beyond the atom is given, to some reasonable approximation, by (Newton, 1966; Cowley, 1981)

$$\Psi(\mathbf{R}) = \exp\left[i\sigma \int_{-\infty}^{+\infty} \varphi(\mathbf{R}, z) \, dz \right] \Psi_0(\mathbf{R}). \qquad (1)$$

In this equation, $\varphi(\mathbf{R}, z)$ is the electrostatic potential due to an atom and

$$\sigma = 2\pi me / (h^2 k_z) \qquad (2)$$

is the interaction constant for high-energy electrons. It depends on the relativistic mass m and on the z component of the wave vector $\mathbf{k}$, the magnitude of which is the reciprocal of the relativistic wavelength λ. $\Psi_0(\mathbf{R})$ is the incident wave function on a plane an infinite distance in front of the atom. Equation (1) has been estimated to be a good approximation provided there is no significant scattering of electrons through angles greater than about 10°, although Newton (1966) has argued that it is accurate for a much wider range of angles. We have attempted to estimate the errors associated with using (1) and with the numerical methods used to evaluate the integral in (1) by making use of the analytical solution that is available for scattering by a point charge (Newton, 1966). In that case, it is found that the amplitude of scattering through an angle θ is just that predicted by the Born approximation but that there is a phase variation, depending on the charge and on σ, which is not included in the Born approximation. Unfortunately, we cannot make direct use of this analytic solution since the integral in that equation does not exist for a potential that falls off with distance as $1/r$, so we consider a modified potential for which the angular variation of scattering amplitude

can be estimated on physical grounds. This potential has Fourier components given by

$$\Phi(u) = Z[1 - \exp(-Cu^2)]/u^2. \quad (3)$$

Here, $\mathbf{u}$ is a reciprocal-space vector and C is a large number. Z is the number of elementary charges. The potential is that due to a positive point charge at the origin and an equal amount of negative charge distributed according to a Gaussian distribution with half-width proportional to $C^{1/2}$. It is reasonable to expect that the scattering amplitude at high angles will depend only on the positive point charge for which it is known that the first Born approximation is sufficient. The variation of the phase with scattering angle depends on the long-range part of the potential and an analytical expression is not available.

Since our numerical calculations, which are described in more detail in §§3 and 4, are based on Fourier techniques, we necessarily consider scattering by a periodic array of centres. If the periodicity of the array is 4 Å, $C = 100 \text{ Å}^2$ and the sampling is based on a 512×512 grid then, for 100 keV electrons, for a scattering centre of 14 elementary charges, the calculation of the amplitude using (1) is accurate out to angles of 25°. If a 1024×1024 grid is used, the calculation of amplitudes is good out to 45°. For scattering by 79 elementary charges, *i.e.* for a gold nucleus, the 512×512 calculation is accurate out to about 7°. It overestimates the scattering between 7 and 25° by up to 20% and then underestimates the scattering at higher angles. The 1024×1024 calculation is good to about 20°. For higher angles, there are variations in amplitude of up to 20% from the exact values. The conclusion to be drawn from these preliminary calculations is that (1) is adequate for calculating the scattering amplitudes except for the case of large-angle scattering by heavy elements but even then the error in using (1) is no more than about 20% of relatively small amplitudes.

We shall write

$$\bar{\varphi}(\mathbf{R}) = \int_{-\infty}^{+\infty} \varphi(\mathbf{R}, z) \, dz \quad (4)$$

for the projected atomic potential.

Consider now an assembly of atoms at positions $(\mathbf{R}_n^{(j)}, z_n) \equiv (x_n^{(j)}, y_n^{(j)}, z_n)$. z_n is the z coordinate of the nth layer and $z_n < z_{n+1}$. The wave function $\Psi_n(\mathbf{R})$ on a plane between z_n and z_{n+1} may be calculated using an approach similar to the multislice algorithm of Cowley & Moodie (Cowley, 1981). Given the wave function on a plane before the nth plane, the potential due to the nth plane and the free-electron propagator $p_n(\mathbf{R})$, which describes the propagation of a wave through a distance $z_n - z_{n-1}$, we may write

$$\Psi_n(\mathbf{R}) = \exp[i\sigma\bar{v}_n(\mathbf{R})] \int p_n(\mathbf{R} - \mathbf{R}')\Psi_{n-1}(\mathbf{R}') \, d\mathbf{R}'. \quad (5)$$

The propagator is given by

$$p_n(\mathbf{R}) = [ik/(z_n - z_{n-1})] \exp[ikR^2/(z_n - z_{n-1})] \quad (6)$$

and the potential function due to the nth plane of atoms is

$$\bar{v}_n(\mathbf{R}) = \sum_j \bar{\varphi}(\mathbf{R} - \mathbf{R}_n^{(j)}). \quad (7)$$

The exact multislice algorithm of Cowley & Moodie requires that the potential be divided into slices of thickness Δz. The wave function is found by calculating the scattering due to a potential slice followed by propagation to the next slice and then scattering by that slice and so on. The exact wave function is obtained by allowing the slice thickness to approach zero. The calculation described by (5) is an approximation to the exact multislice algorithm since it does not involve taking the limit of zero slice thickness. However, it is expected to be adequate provided that the range of the atomic potentials in the z direction is sufficiently small so that the potential between the atomic planes is effectively zero.

It is useful to note for later work that we may write the scattering function for the nth layer in terms of the atomic scattering functions as follows.

$$\exp[i\sigma\bar{v}_n(\mathbf{R})] = \prod_j \exp[i\sigma\bar{\varphi}(\mathbf{R} - \mathbf{R}_n^{(j)})]. \quad (8)$$

If the foil through which the electrons pass consists of N planes of atoms, the wave function $\Psi_N(\mathbf{R})$ can be used to calculate the image intensity and the intensity of the diffraction pattern. The image intensity at position $\mathbf{R}$ in the image plane is given by

$$i(\mathbf{R}) = \left| \int t_{\varepsilon,C_s}(\mathbf{R} - \mathbf{R}')\Psi_N(\mathbf{R}') \, d\mathbf{R}' \right|^2, \quad (9)$$

where $t_{\varepsilon,C_s}(\mathbf{R})$ describes the effects of the objective lens with coefficient of spherical aberration C_s and defocused by an amount ε.

If we label points within the diffraction pattern by two-dimensional reciprocal-space vectors $\mathbf{U}$, the intensity of the diffracted wave at $\mathbf{U}$ is obtained by the Fourier transform of the wave function $\Psi_N(\mathbf{R})$.

$$I(\mathbf{U}) = \left| \int \exp(2\pi i\mathbf{U} \cdot \mathbf{R})\Psi_N(\mathbf{R}) \, d\mathbf{R} \right|^2. \quad (10)$$

In the calculation of both the image intensity by using (9) and the intensity in the diffraction pattern by using (10), the product of all terms involving either the position of layer n or the position of atom j in layer n is

$$p_{n+1}(\mathbf{R}'_{n+1} - \mathbf{R}'_n) \exp[i\sigma\bar{\varphi}(\mathbf{R}'_n - \mathbf{R}_n^{(j)})]$$
$$\times p_n(\mathbf{R}'_n - \mathbf{R}'_{n-1})p_{n+1}^*(\mathbf{R}''_{n+1} - \mathbf{R}''_n)$$
$$\times \exp[-i\sigma\bar{\varphi}(\mathbf{R}''_n - \mathbf{R}_n^{(j)})]p_n^*(\mathbf{R}''_n - \mathbf{R}''_{n-1}), \quad (11)$$

where we have used (5) and (8) to obtain this expression.

The observed image and diffracted intensities are weighted averages of intensities arising from all possible positions of the atoms. The weightings depend on the amplitudes of atomic vibrations, which in turn depend on the temperature. It will be assumed that each atom vibrates independently of all other atoms and the distribution of deviations of position from the mean is given by the Gaussian distribution

$$d(r) = (1/2\pi\Delta^2)^{3/2} \exp(-r^2/2\Delta^2). \qquad (12)$$

r is a three-dimensional radial coordinate and Δ is the mean square displacement of an atom in any given direction. With this distribution, we can calculate the average of the function given in (11) for all values of $\mathbf{R}_n^{(j)}$ and all values of z_n. Thus, we include the effects of fluctuations in the separation of atomic planes. We shall work with Fourier transforms.

Let $\Phi(\mathbf{U})$ be the Fourier transform of $\exp[i\sigma\bar{\varphi}(\mathbf{R})]$, i.e. the atomic scattering function in the eikonal approximation for a stationary atom, and let $\exp(-\frac{1}{4}Bu^2)$ be the Fourier transform of the distribution function $d(r)$. $\mathbf{u}$ is a three-dimensional reciprocal-space vector and

$$B = 8\pi^2\Delta^2 \qquad (13)$$

is the standard thermal parameter of crystallography. The Fourier transform of the propagator $p_n(\mathbf{R})$ is

$$p_n(\mathbf{U}) = \exp[-i\pi\lambda U^2(z_n - z_{n-1})]. \qquad (14)$$

The average of (11) is found by convoluting it with the Gaussian distribution (12). Making use of the convolution theorem for Fourier transforms and with further details given in Appendix A, we obtain

$$p_{n+1}(\mathbf{R}'_{n+1} - \mathbf{R}'_n) \int d\mathbf{U}' \exp[-2\pi i\mathbf{U}' \cdot (\mathbf{R}' - \mathbf{R}_{eq}^{(j)})]$$
$$\times \Phi(U')p_n(\mathbf{R}'_n - \mathbf{R}'_{n-1})p_{n+1}^*(\mathbf{R}''_{n+1} - \mathbf{R}''_n)$$
$$\times \int d\mathbf{U}'' \exp[2\pi i\mathbf{U}'' \cdot (\mathbf{R}'' - \mathbf{R}_{eq}^{(j)})]\Phi^*(U'')$$
$$\times p_n^*(\mathbf{R}''_n - \mathbf{R}''_{n-1}) \exp\{-\frac{1}{4}B(\mathbf{U}' - \mathbf{U}'')^2$$
$$\times [1 + \frac{1}{4}\lambda^2(\mathbf{U}'^2 - \mathbf{U}''^2)^2]\}. \qquad (15)$$

We have introduced the mean coordinates $\mathbf{R}_{eq}^{(j)} \equiv (x_{eq}^{(j)}, y_{eq}^{(j)})$ of atom j. The usual Debye–Waller factor $\exp(-\frac{1}{4}BU^2)$ appears in modified form with an additional factor $(1 + \frac{1}{4}\lambda^2U^2)$, which is related to the surface of the Ewald sphere. This factor gives a good approximation to the Ewald sphere provided U is not too large. It arises as a result of variations in the z direction of an atom with mean position z_n and is just the convolution of the Gaussian distribution (12) with the Fourier transform of the propagator (14).

By consideration of the last exponential term in (15), it can be seen that factors such as $\exp(\frac{1}{2}B\mathbf{U}' \cdot \mathbf{U}'')$ are present. By expanding this term in powers of B, we

obtain an expression for the total scattering in terms of contributions from thermal scattering of all orders. The nth-order thermal scattering refers to a multiscattering process in which the electron interacts with the crystal and causes n changes to the vibrational state of the crystal. Electrons that have undergone thermal scattering of a certain order are incoherent with electrons that have undergone thermal scattering of a different order so that the total intensity is a sum of intensities of electrons associated with each order of scattering. Here, we restrict our considerations to the calculation of the scattering of electrons that remain coherent with the incident wave (zeroth-order scattering). The expansion of this exponential term in powers of B is then approximated by unity so that (15) factorizes into a function of $\mathbf{U}'$ and a function of $\mathbf{U}''$. Equation (15) is approximated by

$$p_{n+1}(\mathbf{R}'_{n+1} - \mathbf{R}'_n) \int d\mathbf{U}' \exp[-2\pi i\mathbf{U}' \cdot (\mathbf{R}' - \mathbf{R}_{eq}^{(j)})]$$
$$\times \Phi(U') \exp[-\frac{1}{4}BU'^2(1 + \frac{1}{4}\lambda^2U'^2)]$$
$$\times p_n(\mathbf{R}'_n - \mathbf{R}'_{n-1})p_{n+1}^*(\mathbf{R}''_{n+1} - \mathbf{R}''_n)$$
$$\times \int d\mathbf{U}'' \exp[2\pi i\mathbf{U}'' \cdot (\mathbf{R}'' - \mathbf{R}_{eq}^{(j)})]\Phi^*(U'')$$
$$\times p_n^*(\mathbf{R}''_n - \mathbf{R}''_{n-1}) \exp[-\frac{1}{4}BU''^2(1 + \frac{1}{4}\lambda^2U''^2)]. \qquad (16)$$

Taking the inverse Fourier transform of the function of U', say, we obtain a function of $\mathbf{R}'_n - \mathbf{R}_{eq}^{(j)}$, which we write as

$$\langle\exp[i\sigma\bar{\varphi}(\mathbf{R}'_n - \mathbf{R}_{eq}^{(j)})]\rangle p_n(\mathbf{R}'_n - \mathbf{R}'_{n-1}), \qquad (17)$$

where

$$\langle\exp[i\sigma\bar{\varphi}(\mathbf{R})]\rangle = \int d\mathbf{U} \exp(-2\pi i\mathbf{U} \cdot \mathbf{R})\Phi(U)$$
$$\times \exp[-\frac{1}{4}BU^2(1 + \frac{1}{4}\lambda^2U'^2)]. \qquad (18)$$

The angular brackets define a type of thermal average. It is an average for a single atom within a crystal, the interplanar distances of which are fluctuating due to thermal vibrations.

This thermally averaged atomic scattering function can be expressed in terms of $\langle\bar{\varphi}(\mathbf{R})\rangle$, the thermal average of the projected atomic potential, by introducing a correction potential $i\mu(\mathbf{R})$ (Cowley, 1981).

$$\langle\exp[i\sigma\bar{\varphi}(\mathbf{R})]\rangle = \exp\{i\sigma[\langle\bar{\varphi}(\mathbf{R})\rangle + i\mu(\mathbf{R})]\}. \qquad (19)$$

The relationship between $\mu(\mathbf{R})$ and the normally employed corrections to the real scattering function can be seen by expanding (19) to second order in σ. We find

$$\mu(\mathbf{R}) = \frac{1}{2}\sigma[\langle\bar{\varphi}(\mathbf{R})^2\rangle - \langle\bar{\varphi}(\mathbf{R})\rangle^2]. \qquad (20)$$

The Fourier transform of this function is

$$M(\mathbf{U}) = \frac{1}{2}\sigma \int d\mathbf{U}' V(\mathbf{U} - \mathbf{U}')V(\mathbf{U}')$$
$$\times \left(\exp[-\frac{1}{4}BU^2(1 + \frac{1}{4}\lambda^2U^2)]\right.$$
$$- \exp\{-\frac{1}{4}B(\mathbf{U} - \mathbf{U}')^2[1 + \frac{1}{4}\lambda^2(\mathbf{U} - \mathbf{U}')^2]\}$$
$$\left.\times \exp[-\frac{1}{4}BU'^2(1 + \frac{1}{4}\lambda^2U'^2)]\right), \qquad (21)$$

where $V(\mathbf{U})$ is the Fourier coefficient of the atomic potential. Equation (21) is similar to the expression used by Hall & Hirsch (1965) and other authors, including most recently Bird & King (1990) and Dudarev, Peng & Whelan (1995) to calculate corrections to the real scattering function that arise from thermal vibrations. The difference between the previous expression and ours is that the range of integration in (21) is over a plane in reciprocal space, whereas in the earlier expression the range is the surface of the Ewald sphere. We have partly accounted for the Ewald sphere as we explained after (15), but in (21) the Fourier coefficients of the potential are evaluated at points on a plane rather than on the Ewald sphere. The difference arises because we have assumed that all scattering by an atom has occurred over an infinitesimally small distance in the direction of the electron beam. Alternatively, we may say that the scattering function of a single atom in reciprocal space varies infinitesimally slowly with u in the direction perpendicular to the U_xU_y plane.

Equation (19) includes corrections to the mean potential in addition to that given by (20). We could choose to expand (19) to higher orders in σ to see under what situations further corrections may be significant but we will choose instead to work numerically and some results are given in the next section.

If (19) is solved for $\mu(\mathbf{R})$, we obtain

$$\mu(\mathbf{R}) = -(1/\sigma)\ln\langle\exp[i\sigma\bar{\varphi}(\mathbf{R})]\rangle + i\langle\bar{\varphi}(\mathbf{R})\rangle. \quad (22)$$

$\mu(\mathbf{R})$ is a complex function. Its real part is related to the reduction in amplitude of the scattered wave that is coherent with the incident wave. The imaginary part is related to phase changes in the coherent part of the electron beam brought about by the vibrations of the atom. It arises from thermal scattering of thermally scattered electrons and such scattering is neglected in previous studies. Rigorous derivations of previous expressions for the correction potential (e.g. Yoshioka & Kainuma, 1962) have been based on the work of Yoshioka (1957), who makes explicit his assumption that the contributions of double inelastic scattering is negligible. In this work, we have taken account of such scattering events but our calculations are restricted by the assumption that the atomic potential has a very small range in the direction of the incident beam. A rigorous derivation of the correction potential is desirable. It could be achieved through an extension of Yoshioka's work or by a consideration of the multislice method. In the latter case, the derivation will be necessarily restricted to small-angle scattering.

3. Numerical estimates of the correction potential

We use (22) to calculate corrections to the Fourier coefficients of the potential of several crystalline materials. The atomic scattering factors $\Phi(\mathbf{U})$ are calculated using

Table 1. *Corrections to the Fourier components of the potential of crystalline aluminium as determined by the present theory and by Bird & King (1990)*

Values are in V. $\Delta^2 = 0.0105 \text{ Å}^2$

G	Present	Bird & King
000	0.015 + i0.162	i0.164
111	0.014 + i0.144	i0.145
400	0.010 + i0.097	i0.097
444	0.005 + i0.042	i0.042
933	0.002 + i0.011	i0.011

Table 2. *Corrections to the potential of crystalline gold*

Values are in V. $\Delta^2 = 0.0074 \text{ Å}^2$.

G	Present	Bird & King
000	2.11 + i1.05	i2.859
111	1.01 + i1.96	i2.683
400	0.84 + i1.48	i2.087
444	0.54 + i0.82	i1.209
933	0.26 + i0.35	i0.534

the parameters for scattering of X-rays given by Doyle & Turner (1968). The parameters given by Doyle & Turner apply only in the range $s \equiv \sin(\theta)/\lambda \leq 2 \text{ Å}^{-1}$. Fox, O'Keefe & Tabbernor (1989) give parameters for the range $2 \leq s \leq 6 \text{ Å}^{-1}$. For larger values of s, it is assumed that there is no significant scattering of X-rays. The electron scattering factors are then calculated using Mott's formula:

$$f^e(s) = (me^2/2h^2)(1/s)^2[Z - f^x(s)]. \quad (23)$$

Table 1 shows the corrections, in V, to the Fourier coefficients of the time-averaged potential of crystalline aluminium for 100 keV electrons. The calculations were performed by constructing atomic scattering functions from Fourier coefficients $V(\mathbf{U})$ with $U < 21 \text{ Å}^{-1}$. It was found that doubling the maximum value of U did not change the results significantly. The results of Bird & King (1990) are also given in Table 1.

Table 1 shows that the results of the present method are essentially identical to those calculated assuming the first Born approximation as far as the imaginary part of the correction potential is concerned. There is a small correction of a few parts in a thousand to the real part of the potential.

Table 2 shows that for a heavy element, gold, the corrections to the real part of the potential are a few parts in a hundred and that there are significant differences in the imaginary potential between the results of the present calculations and those of Bird & King. These differences arises from higher-order terms in the Born series for scattering.

In Table 3, we show the effects of changing the energy of the electrons on the correction potential for silicon. 10 keV is a typical energy used in RHEED

Table 3. *Corrections to the potential of crystalline silicon for three values of energy*

Values are in V. $\Delta^2 = 0.0058\ \text{Å}^2$.

G	10 keV	100 keV	300 keV
000	$0.06 + i0.30$	$0.010 + i0.111$	$0.005 + i0.079$
111	$0.04 + i0.20$	$0.007 + i0.075$	$0.003 + i0.053$
400	$0.05 + i0.23$	$0.009 + i0.088$	$0.004 + i0.062$
444	$0.04 + i0.17$	$0.007 + i0.063$	$0.003 + i0.045$
933	$0.02 + i0.07$	$0.004 + i0.028$	$0.002 + i0.020$

experiments and 300 keV is often used in convergent-beam electron diffraction for precise estimates of the Fourier coefficients of potential (Spence & Zuo, 1994).

Table 3 shows that at 10 keV the correction to the real part amounts to a few parts in a hundred while at 300 keV it is a few parts in a thousand. This is similar to the precision claimed for measurements of Fourier coefficients of the potential by convergent-beam electron diffraction (Saunders, Bird, Midgley & Vincent, 1994), so it should be possible to measure the correction terms predicted in this paper. Any such measurement would have to take into account corrections to the real potential due to the excitation of single electrons by the fast electron. Rez (1978), using a formula of Yoshioka (1957), has calculated these corrections to the low-order Fourier coefficients of crystals of silicon, copper and germanium to be of the order of a few parts in a thousand.

4. Inclusion of thermal effects in multislice calculations

We showed in the previous section that to a good approximation the atomic scattering function, $\langle \exp[i\sigma\bar\varphi(\mathbf{R})]\rangle$, can be obtained from the discrete Fourier transform of the projected atomic potential $\bar\varphi$ evaluated on a two-dimensional grid of points in reciprocal space. The transform is then multiplied by the temperature factor $\exp[-\tfrac{1}{4}BU^2(1 + \tfrac{1}{4}\lambda^2 U^2)]$ and the inverse transform found. These are the types of operation performed in standard algorithms for calculating the potential. To calculate the scattering due to a layer when there are atoms at positions $\mathbf{R}^{(j)}$ within the layer, it is necessary to shift the scattering function to be centred on each atomic position. The scattering due to a layer, *viz*

$$\prod_j \langle \exp[i\sigma\bar\varphi(\mathbf{R} - \mathbf{R}^{(j)}_{\text{eq}})]\rangle, \qquad (24)$$

is then the input into a standard multislice algorithm for the scattering. There is then no need to specifically make use of a separate program for calculating corrections to the real potential.

In conclusion, the effects of thermal vibrations can be readily calculated by the techniques used in the multislice method. The resulting corrections to the scattering potential depend on the energy of the electrons and this dependence on energy should be measurable by convergent-beam diffraction at least for heavy elements.

APPENDIX A

Equation (11) is derived from (5) and (8). Equation (5) implies

$$\Psi_{n+1}(\mathbf{R}) = \exp[i\sigma\bar v_{n+1}(\mathbf{R})] \int d\mathbf{R}'\, p_{n+1}(\mathbf{R} - \mathbf{R}')$$
$$\times \exp[i\sigma\bar v_n(\mathbf{R}')] \int d\mathbf{R}''\, p_n(\mathbf{R}' - \mathbf{R}'')$$
$$\times \Psi_{n-1}(\mathbf{R}''). \qquad (25)$$

Using (8) and retaining only those terms involving $\mathbf{R}_n^{(j)}$ and z_n, we are led to consider

$$\int d\mathbf{R}'\, p_{n+1}(\mathbf{R} - \mathbf{R}') \exp[i\sigma\bar\varphi(\mathbf{R}' - \mathbf{R}_n^{(j)})]$$
$$\times \int d\mathbf{R}''\, p_n(\mathbf{R}' - \mathbf{R}'')\Psi_{n-1}(\mathbf{R}''). \qquad (26)$$

Introducing $\Phi(U)$, the Fourier transform of $\exp[i\sigma\bar\varphi(\mathbf{R})]$, we can express (26) as

$$\int d\mathbf{R}' \int d\mathbf{U}' \exp[-2\pi i\mathbf{U}' \cdot (\mathbf{R} - \mathbf{R}')]P_{n+1}(\mathbf{U}')$$
$$\times \int d\mathbf{V}' \exp[-2\pi i\mathbf{V}' \cdot (\mathbf{R}' - \mathbf{R}_n^{(j)})]\Phi(\mathbf{V}')$$
$$\times \int d\mathbf{R}'' \int d\mathbf{W}' \exp[-2\pi i\mathbf{W}' \cdot (\mathbf{R}' - \mathbf{R}'')]P_n(\mathbf{W}'). \qquad (27)$$

The integration with respect to $\mathbf{R}'$ produces a δ function $\delta(\mathbf{U}' - \mathbf{V}' - \mathbf{W}')$. Integration with respect to $\mathbf{U}'$ and using (14) for the Fourier transform of the propagator gives

$$\int d\mathbf{V}' \int d\mathbf{W}' \exp[-2\pi i(\mathbf{V}' + \mathbf{W}') \cdot \mathbf{R}]$$
$$\times \exp[-i\pi\lambda(\mathbf{V}' + \mathbf{W}')^2(z_{n+1} - z_n)]$$
$$\times \exp(2\pi i\mathbf{V}' \cdot \mathbf{R}_n^{(j)})\Phi(\mathbf{V}') \exp(2\pi i\mathbf{W}' \cdot \mathbf{R}'')$$
$$\times \exp[-i\pi\lambda W'^2(z_n - z_{n-1})]. \qquad (28)$$

We are interested in determining the intensity of the electron wave and so we multiply the above expression by a similar one involving complex conjugates. There are two new integration variables $\mathbf{V}''$ and $\mathbf{W}''$ in the resulting expression. The weighted average of this expression, considered as a function of $\mathbf{R}_n^{(j)}$ and z_n, is obtained by performing a convolution with the distribution (12), which descibes the probability of an atom being displaced a certain distance from its equilibrium position.

Averaging first over the values of $\mathbf{R}_n^{(j)}$ and making use of the convolution theorem for Fourier transforms, we obtain the terms

$$\exp[-\tfrac{1}{4}B(\mathbf{V}' - \mathbf{V}'')^2] \exp[-i\pi\lambda(\mathbf{V}' + \mathbf{W}')^2(z_{n+1} - z_n)]$$
$$\times \exp(2\pi i \mathbf{V}' \cdot \mathbf{R}_{\mathrm{eq}}^{(j)})\Phi(\mathbf{V}') \exp[-i\pi\lambda W'^2(z_n - z_{n-1})]$$
$$\times \exp[i\pi\lambda(\mathbf{V}'' + \mathbf{W}'')^2(z_{n+1} - z_n)]$$
$$\times \exp(-2\pi i \mathbf{V}'' \cdot \mathbf{R}_{\mathrm{eq}}^{(j)})\Phi^*(\mathbf{V}'')$$
$$\times \exp[i\pi\lambda W''^2(z_n - z_{n-1})], \tag{29}$$

where $\mathbf{R}_{\mathrm{eq}}^{(j)}$ is the mean position of atom j in layer n.

Then, averaging over all values of z_n, we obtain the terms

$$\exp[-\tfrac{1}{4}B(\mathbf{V}' - \mathbf{V}'')^2] \exp(2\pi i \mathbf{V}' \cdot \mathbf{R}_{\mathrm{eq}}^{(j)})\Phi(\mathbf{V}')$$
$$\times \exp(-2\pi i \mathbf{V}'' \cdot \mathbf{R}_{\mathrm{eq}}^{(j)})\Phi^*(\mathbf{V}'') \exp\{-\tfrac{1}{16}B\lambda^2$$
$$\times [(\mathbf{V}' + \mathbf{W}')^2 - W'^2 - (\mathbf{V}'' + \mathbf{W}'')^2 + W''^2]^2\}$$
$$\times P_{n+1}(\mathbf{V}' + \mathbf{W}')P_n(\mathbf{W}')P_{n+1}^*(\mathbf{V}'' + \mathbf{W}'')P_n^*(\mathbf{W}'').$$
$$\tag{30}$$

We can write the first exponential in (30) as a sum of products of $\mathbf{V}'$ and of $\mathbf{V}''$ by expanding the term $\exp(\tfrac{1}{2}B\mathbf{V}' \cdot \mathbf{V}'')$, which comes from the first exponential in the equation, as a power series in B. In a similar way, we can express the last exponential in (30) as a sum of products of functions of $\mathbf{V}'$, $\mathbf{V}''$, $\mathbf{V}' \cdot \mathbf{W}'$ and $\mathbf{V}'' \cdot \mathbf{W}''$. In the resulting expression, B occurs either as part of the Debye–Waller factor or as an integral power of B. The term in which B occurs only in the Debye–Waller factor is a contribution to the intensity from the wave that is coherent with the incident beam. The next term in which B also occurs raised to the power one represents the contribution from single thermal diffuse scattering. The term in which it is raised to the power two involves diffuse scattering of diffuse scattering and so on. The contributions are added incoherently.

Here, we consider only the contribution to the total scattering from the coherent or elastically scattered wave and obtain

$$\int d\mathbf{V}' \int d\mathbf{W}' \exp[-2\pi i(\mathbf{V}' + \mathbf{W}') \cdot \mathbf{R}]P_{n+1}(\mathbf{V}' + \mathbf{W}')$$
$$\times \exp(-\tfrac{1}{16}B\lambda^2\mathbf{V}'^4) \exp(2\pi i \mathbf{V}' \cdot \mathbf{R}_{\mathrm{eq}}^{(j)})\Phi(\mathbf{V}')$$
$$\times \exp(-\tfrac{1}{4}BV'^2) \exp(2\pi i \mathbf{W}' \cdot \mathbf{R}'')P_n(\mathbf{W}') \tag{31}$$

and a similar expression involving complex conjugates.

Equation (31) is of the same form as (28) and we can reverse the steps leading to the derivation of this equation from (25) to obtain an expression for $\Psi_n^{(\mathrm{el})}(\mathbf{R})$, the wave function of the coherent (elastically scattered) electrons at layer n in terms of the wave function at layer $n - 1$:

$$\Psi_n^{(\mathrm{el})}(\mathbf{R}) = \prod_j \langle \exp[i\sigma\bar{\varphi}(\mathbf{R} - \mathbf{R}_{\mathrm{eq}}^{(j)})]\rangle$$
$$\times \int d\mathbf{R}' p_n(\mathbf{R} - \mathbf{R}')\Psi_{n-1}^{(\mathrm{el})}(\mathbf{R}'), \tag{32}$$

where $\langle\,\rangle$ indicates the average defined by (18).

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