

Dynamical Diffraction of High Energy Electrons by Light-Atom Structures: A Multiple Forward Scattering Interpretation

TARIK R. DREVON,^{a,b} DAVID G. WATERMAN^{a,b} AND EUGENE KRISSINEL^{a,b*}

^a *STFC, Rutherford Appleton Laboratory, Didcot OX11 0FA, United Kingdom , and*

^b *CCP4, Research Complex at Harwell, Rutherford Appleton Laboratory, Didcot
OX11 0FA, United Kingdom . E-mail: eugene.krissinel@stfc.ac.uk*

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Abstract

Due to the strong electron-atom interaction, the kinematic theory of diffraction cannot be used to describe the scattering of electrons by an assembly of atoms due to the strong dynamical diffraction that needs to be taken into account. In this paper, the scattering of high energy electrons by a regular array of light atoms is solved exactly by applying the T-matrix formalism to the corresponding Schrödinger's equation in spherical coordinates. We use the independent atom model, where each atom is represented by a sphere with an effective constant potential. The validity of the forward scattering approximation and the phase grating approximation, assumed by the popular multislice method, are discussed, and an alternative interpretation of multiple scattering is proposed and compared with existing interpretations.

1. Introduction

1.1. Motivation

The theory of dynamical diffraction was first developed in 1928 (Bethe, 1928; Cowley, 1975), very shortly after the first experimental demonstration of electron diffraction. Over the 20th century, several theories of electron diffraction have been extensively applied in various areas of solid state physics. In particular, the theory of multiple scattering (Korringa, 1947; Kohn & Rostoker, 1954; Korringa, 1994; Dederichs, 1971) has proven to be efficient while also providing an intuitive picture of dynamical diffraction. Other attempts at an intuitive depiction of dynamical diffraction have been proposed to explain electron channelling in crystals, for example in VanDyck (1996).

Dynamical diffraction must be taken into account when considering electron-atom interactions, since even at the very high electron energies commonly used in modern transmission electron microscopes, the interaction is so strong that, theoretically, the kinematic approximation is not valid for ideal crystals thicker than 10-15 nm (Glaeser & Downing, 1993; Subramanian *et al.*, 2015). In practice, crystal growth cannot be controlled to such a degree of accuracy and, usually, nanocrystals of organic compounds have a size on the order of hundreds of nanometers. This is a challenging aspect of high energy electron diffraction in crystallography, as it significantly complicates the structure determination process. However, structures have been successfully determined from ED data using the standard kinematic theory (Gemmi *et al.*, 2019; Nannenga *et al.*, 2014; Nannenga & Gonen, 2019),

which suggests that dynamical diffraction

does not affect the diffraction intensities as much as the theory predicts. Although dynamical refinement (Palatinus *et al.*, 2013) usually leads to better intensity predictions (Gemmi *et al.*, 2019), the agreement between theory and experiment is still

significantly worse than that obtained for X-ray data (Oleynikov *et al.*, 2007), (Klar *et al.*, 2021).

Therefore, more accurate theoretical models are needed for getting better results from electron diffraction experiments.

1.2. State of the art

The multislice (MS) (Cowley & Moodie, 1957) and Blochwave (BW) (Bethe, 1928) approaches are the most popular methods for simulating high-energy electron scattering in crystals. MS is particularly well suited for solving large problems as it involves successive convolutions, which can be very efficiently computed with the Fast Fourier Transform (FFT) (Ishizuka & Uyeda, 1977). However, in order to avoid aliasing, transverse periodic boundary conditions must be met, which is only possible for orthogonal cells in zone axis orientations. Although a small beam tilt can also be used (Ishizuka, 1982; Chen *et al.*, 1997), simulations with arbitrary orientations can be performed only by considering a full crystal with added zero padding. This can quickly become computationally intractable.

On the contrary, the BW method can simulate ED for structures in arbitrary orientations but does not scale well with the structure size. Although a few rather efficient BW implementations (Zuo & Weickenmeier, 1995) have been proposed to include a large number of beams, BW can hardly be applied to very large structures since the scattering matrix becomes prohibitively large. Due to the unfavourable $O(N^3)$ complexity of matrix diagonalization, where N is the number of beams, the method is not applicable to macromolecular structures. Non-periodic structures, defects and solvent scattering are also hard to model with this method.

A few very efficient multislice implementations have been reported to date (Ophus, 2017). Some of them are targeted at convergent beam electron diffraction (CBED),

while others have special features such as inclusion of inelastic scattering (Allen *et al.*, 2015). Yet, an approach combining full modelling capabilities with an acceptable computational efficiency, designed specifically for the continuous rotation electron diffraction of large organic structures, does not seem to be available yet. Such an approach would indeed be of a significant value for macromolecular structure determination from ED data.

1.3. Contribution and outline

The purpose of this paper is to develop a new approach to the scattering of fast electrons by light-atom structures, based on the T-matrix formalism. This approach has been extensively applied to problems in various areas of physics including electromagnetics (Hamid *et al.*, 1990b; Hamid *et al.*, 1990a; Eremin *et al.*, 1995), optics (Moine & Stout, 2005) and acoustics (Silva *et al.*, 2012; Godin, 2011). Although it does not compete with MS from a computational standpoint, this approach benefits from providing an exact solution to Schrödinger’s equation for an ensemble of spherically-symmetric atomic potentials in the independent atom model approximation (IAM). We further present an intuitive picture of multiple scattering in the forward scattering approximation and make a comparison with other interpretations. In addition, we discuss the validity of the forward scattering approximation and the phase grating approximation used in the multislice approach. Finally, we draw conclusions and outline extensions of the proposed approach in order to account for incoherent inelastic electron scattering.

2. Theory

The scattering of fast electrons by an atomic structure is described by the wave function Ψ , obeying the following Schrödinger’s equation (Kirkland, 2019):

$$\left[-\frac{\hbar^2}{2m_e} \nabla_{\mathbf{r}}^2 - eV(\mathbf{r}) \right] \Psi = E\Psi \quad (1)$$

where $\hbar$ is Planck's constant, m_e the mass of the electron, e the elementary charge, $V(\mathbf{r})$ is the spatially-varying electrostatic potential created by the atoms, and E the electron eigen energy.

In an ED experiment, $E \gg V(r \rightarrow \infty) = 0$, which corresponds to the continuum, non-quantized state of the system (Chuang, 1996). Therefore, we solve (1) with E as a parameter, equal to the energy of incident electrons.

The wave function is sought as the sum of the incident wave $\Psi^{(i)}$ and the scattered wave $\Psi^{(s)}$. From a partial differential equation perspective, the incident wave must be seen as a boundary condition.

2.1. *T-matrix formulation*

In its standard form, the T-matrix approach solves for the case where the incident wave is described by a plane wave of wavenumber $k_0 = 2\pi/\lambda$ (optics convention), and the electrostatic potential is modelled by a uniform constant inside non-overlapping spheres. The constant potential and radius of the spheres depend on the atom type.

Although this is not an accurate representation of the actual potential profile $V(r)$, using an appropriate amplitude for the constant potential V_0 should provide a faithful depiction of the extent of multiple scattering in the structures of interest.

The setup is shown in Figure 1. This formulation is well established (Hamid *et al.*, 1990b; Hamid *et al.*, 1990a; Eremin *et al.*, 1995) and the theory is outlined here for the purpose of introducing the forward multiple scattering approximation. In the T-matrix approach, the electrostatic potential is assumed constant inside different regions of the 3D space. In each region, the problem is reduced to the Helmholtz equation in spherical

coordinates:

$$\begin{aligned}\nabla_{\mathbf{r}_p}^2 \Psi + k_p^2 \Psi &= 0 \\ k_p &= k_0 n_p \\ k_0 &= \sqrt{\frac{2m_e E}{\hbar^2}} \\ n_p &= \sqrt{1 + \frac{V_p}{E}}\end{aligned}$$

where $V_p \geq 0$ is the constant attractive potential inside sphere p of radius a_p centered at $\mathbf{d}_p$, k_p the wave number inside the sphere and n_p can be referred to as the refractive index by analogy with optics. The scattered wave function inside and outside of sphere p can then be expressed as :

$$\Psi_p^{(in)}(\mathbf{r}_p) = \sum_{l=0}^{\infty} j_l(k_p r_p) \sum_{m=-l}^{m=l} a_{p;lm} Y_l^m(\theta_p, \phi_p) \quad (2)$$

$$\Psi_p^{(out)}(\mathbf{r}_p) = \sum_{l=0}^{\infty} h_l^{(1)}(k_0 r_p) \sum_{m=-l}^{m=l} b_{p;lm} Y_l^m(\theta_p, \phi_p) \quad (3)$$

$$(4)$$

where $p = 1..N$, j_l and $h_l^{(1)}$ are the spherical Bessel and Hankel functions of the first kind, Y_l^m are the spherical harmonics of order l and azimuthal order m . Note that these equations are expressed in the reference frame of each sphere p , hence the use of variable $\mathbf{r}_p$.

The unknown coefficients $a_{p;lm}$, $b_{p;lm}$ are found by imposing the continuity of the wave function and its radial derivative at the surface of each sphere p . After some mathematical manipulations (see appendix A), this results in the following linear system of equations:

$$(\mathbf{I} - \mathbf{T})\mathbf{A} = \mathbf{L} \quad (5)$$

where $\mathbf{I}$ is the identity matrix, $\mathbf{A}$ is the unknown vector of coefficients, $\mathbf{L}$ the incident wave right hand side and $\mathbf{T}$ is the cross-coupling matrix.

2.2. Far field and scattering cross section

In electron crystallography, diffraction patterns are recorded that correspond to the intensity of the scattering amplitude profile $|f(\theta, \phi)|^2$ for various crystal orientations. A diffraction pattern is obtained in the far field diffraction regime, which arises when the shape of the angular radiation scattering amplitude $f(\theta, \phi)$ no longer depends on the distance to the scattering specimen. Using the asymptotic behaviour $h_l^{(1)}(k_0 r_p) \approx (-j)^{l+1} \frac{e^{jk_0 r_p}}{k_0 r_p}$ and since $\theta_p \approx \theta$, $\phi_p \approx \phi$ the far field scattering amplitude $f_p(\theta, \phi)$ from each individual sphere p can be written as:

$$f_p(\theta, \phi) = \sum_{l=0}^{\infty} \sum_{m=-l}^l (-j)^{l+1} b_{p;lm} Y_l^m(\theta, \phi) \quad (6)$$

The total far field scattering amplitude is the sum of the contributions from all individual spheres. Since in the far field, $r_p \approx r - \mathbf{d}_p \cdot \mathbf{e}_r$:

$$f(\theta, \phi) = \sum_{p=1}^N f_p(\theta, \phi) e^{-jk_0 \mathbf{e}_r \cdot \mathbf{d}_p} \quad (7)$$

The normalized differential scattering cross section can be obtained as :

$$\frac{\sigma(\theta, \phi)}{\pi a_p^2} = \frac{4\pi r^2}{\pi a_p^2} \left\| \frac{\Psi^{(s)}(r, \theta, \phi)}{\Psi^{(i)}(r, \theta, \phi)} \right\|^2 = \frac{4|f(\theta, \phi)|^2}{(k_0 a_p)^2} \quad (8)$$

where we have used $\Psi^{(s)}(r, \theta, \phi) \underset{r \rightarrow \infty}{\approx} \frac{e^{jk_0 r}}{k_0 r} f(\theta, \phi)$.

3. Real space forward multiple scattering picture

3.1. T-matrix forward multiple scattering approximations

Eq. (5) is a convenient way to represent the system as it readily identifies $\mathbf{L}$ as the solution to the uncoupled ($\mathbf{T} = 0$) problem. If $\mathbf{T} = 0$, the system can be broken down separately into the scattering problems for each individual sphere, for which the solutions are immediately identified as $a_{p;lm} = c_{lm} u_{p;l}$, $b_{p;lm} = c_{lm} v_{p;l}$. These are indeed the well known analytical solutions of Mie scattering by a soft sphere (Balanis, 1989).

The cross-coupling matrix $\mathbf{T}$ accounts for multiple scattering effects. If $\mathbf{A}$ is written as $\mathbf{A} = (...a_{p;lm}, b_{p;lm}...)^T$, then $\mathbf{T}$ is a matrix with only off-diagonal block components:

$$\mathbf{T} = \begin{bmatrix} \mathbf{0} & .. & \mathbf{T}_{1q} & .. & .. & \mathbf{T}_{1p} & .. & \mathbf{T}_{1N} \\ \mathbf{T}_{q1} & .. & \mathbf{0} & .. & .. & \mathbf{T}_{qp} & .. & \mathbf{T}_{qN} \\ \mathbf{T}_{p1} & .. & \mathbf{T}_{pq} & .. & .. & \mathbf{0} & .. & \mathbf{T}_{pN} \\ \mathbf{T}_{N1} & .. & \mathbf{T}_{Nq} & .. & .. & \mathbf{T}_{Np} & .. & \mathbf{0} \end{bmatrix}$$

where $\mathbf{T}_{pq}$ represents the scattering from sphere p due to the scattering from sphere q . By taking into account all blocks, we assume that the scattering from sphere p affects scattering from sphere q and vice versa. Therefore, solution of Eq. (5) requires matrix inversion, which is computationally expensive.

However, as detailed below in section 4.2, backscattering can be neglected for very fast electrons, which is known as the forward scattering approximation. This results in $\mathbf{T}$ being lower triangular if the spheres are sorted in ascending order along $\mathbf{e}_z$. In that case, matrix inversion is not necessary and calculations can be performed sequentially one atom after another.

Since $\mathbf{A}_0 = \mathbf{L}$ represents single scattering, we can establish that $\mathbf{A}_1 = \mathbf{T}\mathbf{A}_0$ accounts for secondary scattering. Similarly, outward scattering amplitudes from sphere p can be written:

$$\begin{aligned} \mathbf{b}_p &= \mathbf{b}_p^{(0)} + \sum_{q, z_q < z_p} \mathbf{T}_{pq} \mathbf{b}_q^{(0)} \\ &\quad + \mathbf{T}_{pq} \sum_{q, z_q < z_p} \mathbf{T}_{qr} \sum_{r, z_r < z_q} \mathbf{b}_r^{(0)} + .. \\ &= \sum_{n=0} \mathbf{T}^n \mathbf{b}_p^{(0)} = \sum_{n=1} \mathbf{b}_p^{(n)} \end{aligned} \tag{9}$$

where the first term accounts for kinematic scattering, the second term for secondary scattering, the third term for tertiary scattering and so on. This is a development similar to the Korringa-Kohn-Rostoker (KKR) theory of multiple scattering (Korringa, 1947; Kohn & Rostoker, 1954; Korringa, 1994). This forward multiple scattering picture is illustrated in Figure 2 for the case of a two-atom system. From a computational point of view, Eq. (9) may offer an advantage over the full forward

scattering approximation if only a few n-time scattering terms are necessary. Indeed, since each term in the expansion depends on precomputed coefficients $b_{p;lm}^{(0)}$, computing of the $b_{p;lm}^{(n)}$ coefficients for the n^{th} scattering term can be massively parallelized for each atom.

3.2. Scattering probabilities

The probability of an electron to be scattered elastically n times can be estimated classically from ballistic arguments using a continuous model of matter. It can be established (Egerton, 2011) that the probability of an electron to be elastically scattered n times after passing through an amorphous sample of thickness z follows a Poisson distribution $P_e^n = \frac{1}{n!}(z/l_e)^n e^{-z/l_e}$ where l_e is the elastic mean free path.

Alternatively, using a wave-like description, the probability of an electron to undergo a scattering event can be determined from the scattering cross section as follows. Let S be the area over which the specimen is illuminated.

Let z be the thickness of the specimen. The incident electron plane wave can be normalized by $|A|^2 = 1/Sz$ so that it integrates over the interaction volume $V = Sz$ to a single electron. Then, the flow of electrons per unit time per unit area (Vainshtein, 1964) is defined as $J_0 = \hbar k_0/m|A|^2 = v_0/Sz$ where v_0 is the speed of the incident electrons.

By definition of the cross section, $J_0\sigma$ is the probability of an electron to be scattered every second. Since it takes a time $\Delta t = z/v_0$ for an electron to pass through the specimen, the overall probability of a single electron to be scattered is therefore $P_{scat} = \sigma J_0 \Delta t$. Therefore, after injecting the expressions for J_0 and Δt :

$$P_{scat} = \frac{\sigma}{S}$$

where S can for example be the area of the aperture in selected area electron diffraction (SAED). When performing a multislice simulation, S is the area of the simulated

domain (transverse super cell if performing a periodic simulation).

Here, we define f_n as the scattering amplitudes obtained by considering scattering from the wave being scattered n times. It can readily be established that:

$$\begin{aligned} f(\theta) &= \sum_{n=1}^N f_n(\theta) \\ \sigma &= \sum_{n=1}^N \sigma_n \\ \sigma_n &= |f_n|^2 + 2\Re \left(f_n \sum_{m>n}^N f_m^* \right) \end{aligned} \tag{10}$$

We can then define $P_n = \sigma_n/S$ as the probability of an electron to be scattered n times. A consistent picture of multiple scattering should ensure that the total cross section be larger as more n-times scattering terms are being taken into account. The above definition for n-times scattering cross sections satisfies this condition.

The probability of an electron not being scattered is naturally $P_{coh} = 1 - P_{scat}$, where $P_{scat} = \sum_n P_n$. Note that since S is large compared to σ , the probability of scattering is necessarily less than 1.

For a very large number of scatterers, N , regularly spaced by distance dz , we can define the average cross section $\sigma_a = \sigma/N$. The corresponding scattering probability is then $P(dz) = \sigma_a \rho dz = dz/l_e$ where $\rho = 1/Sdz$ is the density (since Sdz contains only one scatterer) and $l_e = 1/\sigma_a \rho$ is the mean free path. This is consistent with the definition used in (Latychevskaia & Abrahams, 2019).

3.3. First Born approximation and kinematic scattering

Let us assume normal incidence with $\theta_i = 0$, so that $e_p = e^{jk_0 d_p}$, and note that the Ewald sphere can be represented by $\mathbf{q} = K(\sin \theta \cos \phi, \sin \theta \sin \phi, 1 - \cos \theta)$ in reciprocal space (or transfer vector momentum space), with $K = 1/\lambda$ being the wave number in crystallographic convention. Keeping only the kinematic term in Eq. (9)

and injecting in the far field in Eq. (7) gives:

$$f(\theta, \phi) = \sum_{p=1}^N f_p^{(e)} e^{2j\pi \mathbf{q} \cdot \mathbf{d}_p} \quad (11)$$

where $f_p^{(e)}$ is the scattering amplitude of sphere p in the First Born approximation, also known as the form factor. Eq. (11) corresponds to the standard kinematic formula for the structure factor traditionally used in crystallography. Note that the kinematic approximation is nothing else than the first Born approximation applied to the whole assembly of atoms.

It will be shown in section 4.2 that the first Born approximation holds in case of single scatterers, but fails in application to multi-atom systems. This means that the kinematic approximation is not generally valid.

3.4. Multiple scattering in multislice approach

In multislice, the forward scattering approximation is used and the potential discretized in slices. The wave function is propagated from one slice to the other using a Fresnel propagator.

A multiple scattering interpretation of the multislice approach has been proposed (Cowley & Moodie, 1957), which, albeit analogous to the one presented above, differs in that it is stated in reciprocal space. More details on the differences between the two interpretations can be found in appendix B.

4. Application and Results

Very efficient open source packages exist for T-matrix calculations, but they are targeted at applications in electromagnetics (Egel *et al.*, 2017; Kottke, 2020). Therefore, a package adapted specifically to Schrödinger's equation (1), has been developed Ref. (Drevon, 2021).

4.1. Validity of the implementation

In practice, the size of the matrix in Eq.(5)

has to be truncated to a maximum integer order ν_{max} . A rule for obtaining accurate results is to use $\nu_{max} > ka_{max}$, i.e. an integer slightly larger than the maximum value of ka .

Besides, the translational addition theorem (Dufva *et al.*, 2008) used for expressing the scattered field of any sphere in the reference frame of another sphere, results in an approximation of the translated spherical Hankel functions. The accuracy of this translation decreases from the center at which this expansion is written, analogous to a Taylor's expansion. Therefore, the distances between the spheres do not affect the accuracy of this translation operation and should not affect the choice of ν_{max} . Once again, the radius of the spheres drive the choice of ν_{max} . This is illustrated in Figure 3a, where the error between $h_l^{(1)}Y_{42}$, computed at the origin, using the translational addition theorem with $\mathbf{d}_p = (0, 3, 5)$ and $\nu_{max} = 10$, is displayed in logscale.

The criteria for a sufficiently large choice of ν_{max} is best evaluated by assessing the continuity of the wave functions at the sphere boundaries as shown in Figure 3b for $N = 4$ and $ka_{max} = 4$. This is also used to validate the correctness of the implementation since it can be seen that machine accuracy can be reached when increasing the order of the expansion.

4.2. Validity of forward scattering and phase grating approximations for light atoms

In the case of very fast electrons typically used in transmission electron microscopes, $E = 50 - 300 keV$. Inclusion of relativistic effects results in $\lambda = 0.025 \text{\AA}$ at $200 keV$, which will be assumed from now on unless stated otherwise.

In the IAM, the Coulomb potential is created by the charge of the nucleus and its

electron cloud. It is typically fitted with a sum of three screened Coulomb potential and three Gaussian terms (Kirkland, 2019) which results in the potential shown in Figure 4a.

The solution to Schrödinger's equation in such a potential can only be solved perturbatively (Müller, 1965) and is beyond the scope of this study. However, indicative values for k_p and ka_p can be used with a multi-shell representation as shown in form of blue patches in Figure 4a. Although the range of the screened Coulomb potential is theoretically infinite, it can be truncated to radius ka for most practical purposes. In Figure 4b, the multi-shell scattering amplitudes in the Born approximation are shown for increasing values of truncation radius. The Figure only shows a satisfactory agreement with the electron diffraction scattering factors for normalized radius as large as $ka = 400$. This is necessary to account for the proper low angle representation, i.e. small values of q , even though $V(r)$ is extremely small at such radius.

As mentioned above, ED simulations based on the T-matrix approach are very expensive computationally at such large truncation radii, because higher-order terms of series in Eqs. (2,3) would need to be included. However, the medium truncation range should be sufficient for providing a reasonable picture of dynamical scattering. Figure 5a shows the total scattering cross section of a single sphere with increasing radius for a range of values of effective refractive index n_p . The dark blue curve shows the locations of the spherical shell for carbon. It becomes almost flat for the parameter set ($ka = 30$, $n_p = 1.001$),

from which it keeps increasing very slightly to reach the asymptotic value $\sigma \approx 0.0035$. This value is almost identical to the average elastic cross section for real carbon in the Born approximation (Latychevskaia & Abrahams, 2019) which confirms that ($ka = 30$, $n_p = 1.001$) captures the strength of incident electron Carbon interaction. Figure 5b shows the shape of the far field amplitudes for 2 sets ka , n_p values.

The first is for the extreme value of $ka = 3$ and $n_p = 1.1$ while the second corresponds to one of the carbon shells. While differences are obvious for the first case, the Born approximation is very accurate for the carbon shells, although some minor differences appear at low angles where the phase grating approximation provides some improvements too.

Figures 5a and 5b show that for a two body problem, the error in a (ka, n_p) map in computing the coefficients :

$$err(b_{p;l,m}) = \sum_{p;l,m} |b_{p;l,m} - b_{p;l,m}^{\text{approx}}| \quad (12)$$

as a result of using the kinematic and forward approximations respectively. For this case, a value of $kd = 3ka$ is used, which should represent inter-atomic distances. Overall, it is clear that the forward scattering approximation is very accurate over all range of parameter sets for carbon, which is expected since there is very little backscattering beyond 90° . On the other hand, the kinematic approximation does not appear quite as good, even for this, a mere two-atom problem. Although not shown here, both the kinematic and forward scattering approximations tend to work slightly better with increasing distances kd , since coupling between the spheres gets reduced, and, therefore, is less likely to affect scattering from the other spheres. The low values of n_p result in an overall good approximation of both the uncoupled and forward scattering approximation. This is an anticipated result, since for weak potentials, the kinematic approximation works better. The uncoupled approximation improves with decreasing radii, since a small ka results in a small scattering cross section. On the other hand, the forward scattering approximation improves with larger values of ka , which make backward scattering less likely.

Figure 7a shows the scattering coefficients $b_{p;l,m}$ in complex space for the given two-body problem where $n_p = 1.01$, $kd = 3ka$, while increasing radius ka (up to $ka = 15$) for a selected set of orders l . Only the coefficients for sphere $p = 2$ are shown since

it is the sphere most affected by the approximations. Only $m = 0$ coefficients are used, because under planar illumination this configuration has azimuthal symmetry. The coefficients are computed using the full T-matrix, the forward scattering approximation and the kinematic approximation. In order to get this picture, reminiscent of a spiral galaxy, the coefficients were divided by the phase factor at sphere p , i.e. $b_{p;lm}e^{jkd}$. The arms of the galaxy are rotated by $\pi/2$ from one order to the other as a result of the j^l factor in the spherical expansion of the incident plane wave. All the coefficients increase with ka as a result of the increasing scattering cross section with ka . For a given ka , the strongest contributing orders terms are around $l = ka$ as a direct manifestation of the convergence behaviour presented above. It can be observed that the kinematic approximation error increases with the radius while the forward approximation is very accurate across all radii.

Figure 7b shows a comparison of the computed far field scattering amplitudes for $N = 2$, $ka = 30$, $n_p = 1.01$, $kd = 2ka$ using the full T-matrix, the forward approximation and the kinematic approximation. The peaks and valleys are both due to the single scattering profile of the constant sphere and the interferometric path length e^{jkd} . It is already possible to notice that the coupled problem has a slight averaging effect over the kinematic pattern, a well known feature of dynamical diffraction.

4.3. Successive multiple scattering approximations

Finally, we consider an array of N identical scatterers regularly spaced by $kd = 3ka$ which is typical of bond lengths in molecules.

Under normal illumination, we consider the successive multiple scattering approach. This is an extreme case where strong dynamical scattering is expected.

Figure 8a and 8b show the evolution of the error Eq.(12) on scattering amplitude coefficients for an increasing number of spheres while also varying the number of

successive approximations for fixed parameters $ka = 7$, $kdka = 3$.

The forward scattering approximation becomes worse for increasing numbers of spheres as a result of accumulated errors. This is a limitation of a forward scheme such as the one used in the multislice approach, which is only accurate up to a certain value of the simulation thickness parameter. Overall, the successive approximation schemes naturally converge to the forward approximation for sufficiently large n . However, higher-order terms need to be included in Eqs. (2,3) as the number of spheres (or thickness of the sample) increases. This result is similar to other multiple scattering approaches. For example, in the case of a two beam configuration, it was shown (Cowley & Moodie, 1957) that the scattered beam could be expressed using expansion (15), considering only the scattering terms of the primary beam $n = 1, 3, 5...$ The famous two-beam analytical scattering expression is obtained as the sum of the infinite series.

Figure 9a) shows the scattering probabilities of n -times scattering for $ka = 7, n_p = 1.01, ka = 3kd$ with increasing N . The dynamic scattering probability $P_{dyn} = \sum_{n>1} P_n$ and the kinematic as well as the total scattering probabilities are shown. It seems that all multiple scattering terms increase with number of spheres, in contrast to the ballistic picture of the Poisson distribution (Egerton, 2011), also shown as dashed-dotted lines using the average scattering cross section. The main reason for this is that the ballistic picture ignores the effect of interference, which drastically affects the overall scattering process.

Figure 9b) shows the scattering amplitudes f_n , associated with n times scattering for $ka = 7, n_p = 1.01$ and $N = 15$. The scattering amplitudes have similar shapes, which mostly contributes to constructive interference, although slight peak misalignments can be seen.

5. Conclusion and perspective

An alternative approach, based on the T-matrix formalism, has been applied to the scattering of fast electrons by light-atom structures. The validity of important approximations, used in the multislice approach, has been discussed, and a multiple scattering approximation framework has been proposed and compared to other existing interpretations.

Although the spherically symmetric effective potential does not model the real potential very accurately, it was shown that the proposed multiple scattering interpretation should equally apply to the more accurate case of a screened Coulomb potential. Such a potential would naturally be included by using a basis of radial function solutions to the homogeneous Schrödinger's equation, which are available numerically. In fact, since the T-matrix approach mainly relies on the spherical symmetry of the individual scatterers, it can be adapted to any family of radial functions, provided translational coefficients (13,14) can be computed numerically.

For periodic structures, the Green's functions (GF) could be used as basis functions. All GF would be solutions to Schrodinger's equation in a periodic potential, expressed as an expansion upon the lattice vectors of the crystal under consideration. They would automatically satisfy the boundary conditions imposed by the Bloch theorem in crystals. This is the starting point of the Kohn-Rostoker method (Kohn & Rostoker, 1954).

The ultimate limitation of both T-matrix and multislice approaches lies in the use of the independent atom model, which by definition ignores the effect of bonding. While the multislice approach can be adapted, at a computational cost, to bonding models such as Transferable Aspherical Atom Model (TAAM), the T-matrix approach, presented in this paper cannot, as the spheres are treated as non overlapping. Such bonding could in theory be included (Natoli *et al.*, 1986). However, it is still an open

question whether effects of such bonding play an important role in structure determination of organic structures.

The advantage of the multiple scattering approximation, presented in this paper, is that it offers both the possibility of a massively parallel computation of dynamical diffraction with the possible inclusion of incoherent inelastic scattering. The latter could, for example, be included in a stochastic fashion. It is anticipated that inelastic scattering may have a significant effect in the mitigation of dynamical diffraction, even when energy filters are used. This aspect is currently under investigation.

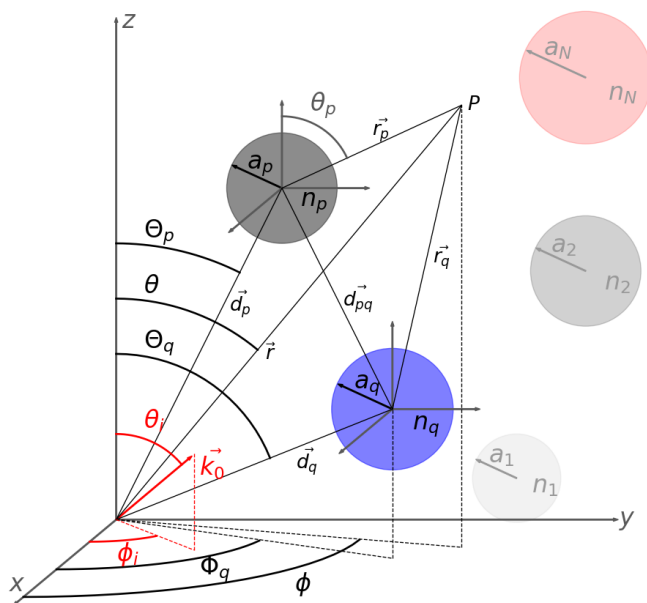


Fig. 1. Setup and conventions for the scattering problem solved with the T-matrix approach. A plane wave with a wave vector $\mathbf{k}_0$ with incident angles (θ_i, ϕ_i) interacts with N spherical atoms, each with individual location (for example, atom p at $\mathbf{d}_p$), radius (a_p) and electrostatic potential of refractive index (n_p). The scattered wave is observed at observation point P at $\mathbf{r}$ in the global reference frame and at individual distances in the local reference frame of the spheres (for example, $|\mathbf{r}_p|$). See discussion in the text for additional details.

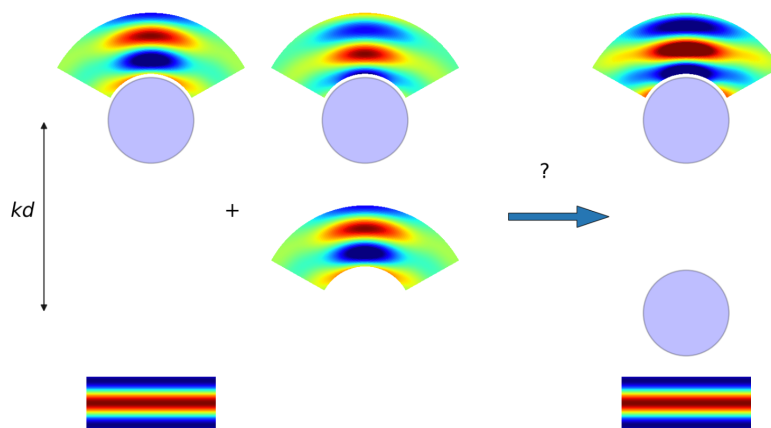


Fig. 2. Two-level forward scattering approximation using the T-matrix approach. By neglecting backscattering, the scattering from the top scatterer located at distance kd from the bottom scatterer can be approximated by the sum of 1) the kinematic scattering to the incident plane wave beam and 2) the secondary scattering in response to the kinematic scattering from the bottom scatterer.

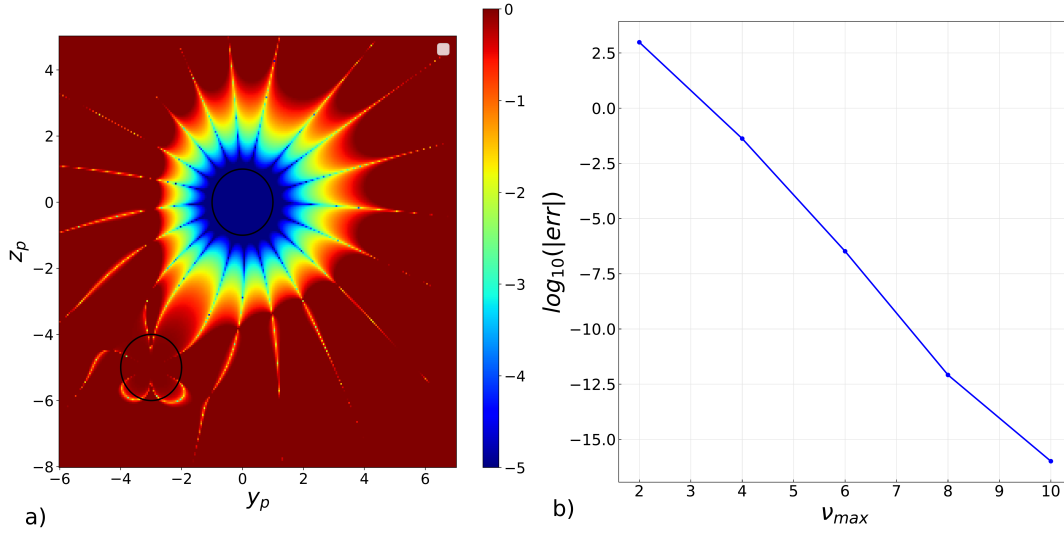


Fig. 3. a) Error difference in evaluating $h_2^{(1)}Y_{42}$ using 1) the standard product of the radial Hankel function $h_2^{(1)}$ and spherical harmonic Y_{42} and 2) using the translational addition theorem (13,14) at a distance $\mathbf{d}_p = (0, 3, 5)$ from the origin with expansion order $\nu_{max} = 10$. The circle represent spheres of radius 1. Color axis in logscale. b) Continuity error at the sphere boundaries (i.e. difference between the solution computed at the boundary using Eqs. (2) and (3), integrated over the sphere boundary). For this example, $N = 4$ and $ka_{max} = 4$. The error reaches machine accuracy at expansion order $\nu_{max} = 10$.

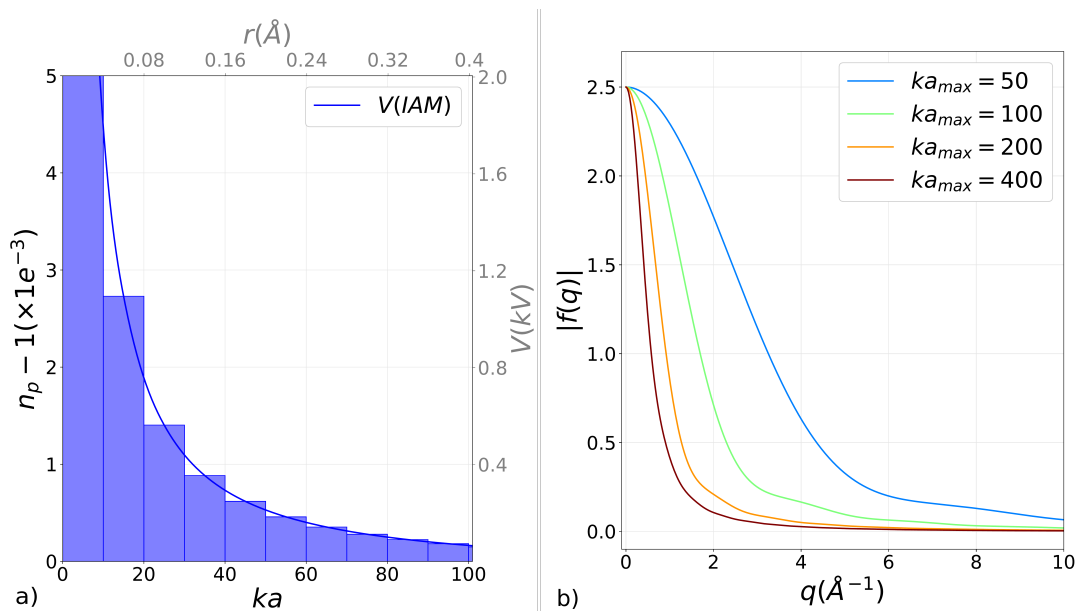


Fig. 4. a) Electrostatic potential, created by an atom of carbon in the independent atom model IAM (blue solid line).

The blue patches show a multi-shell approximation model, which can be used to represent the potential using a T-matrix approach.

b) Scattering amplitude in the Born approximation for the multi-shell model with increasing truncation radius ka_{max} .

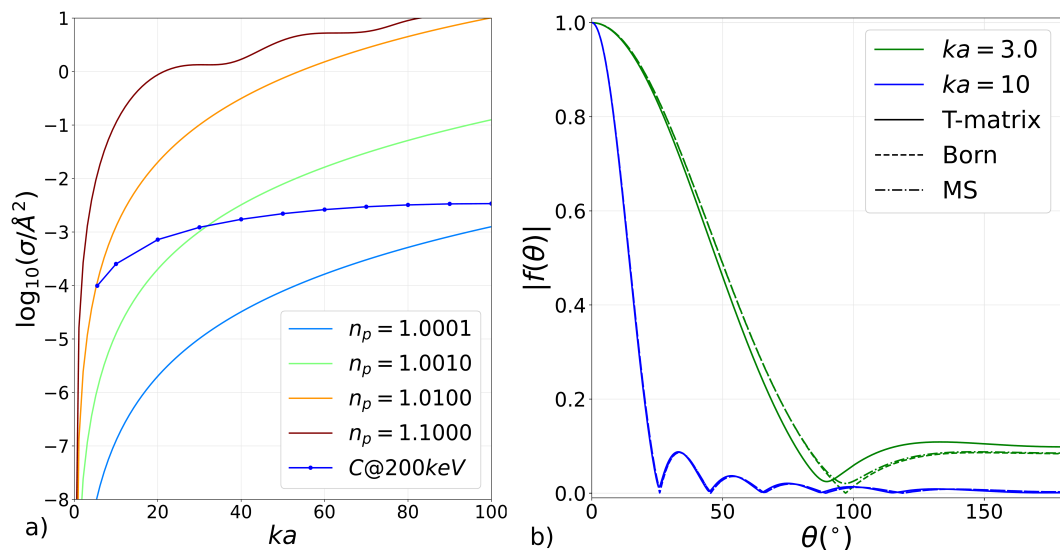


Fig. 5. a) Total scattering cross section σ at 200keV for a few values of n_p over a range of normalized radii ka . The dark blue curve shows the location of the carbon spherical shells. b) Shape of the scattering amplitude for normalized radius $ka = 3$ and refractive index $n_p = 1.1$ (blue). The values $ka = 10$, $n_p = 1.02$ (green) is indicative of data points used for carbon shells. Also shown, the Born approximation (dashed lines) and the phase grating approximation used in multislice (dash-dotted lines). The Born approximation is very good for the carbon data point used.

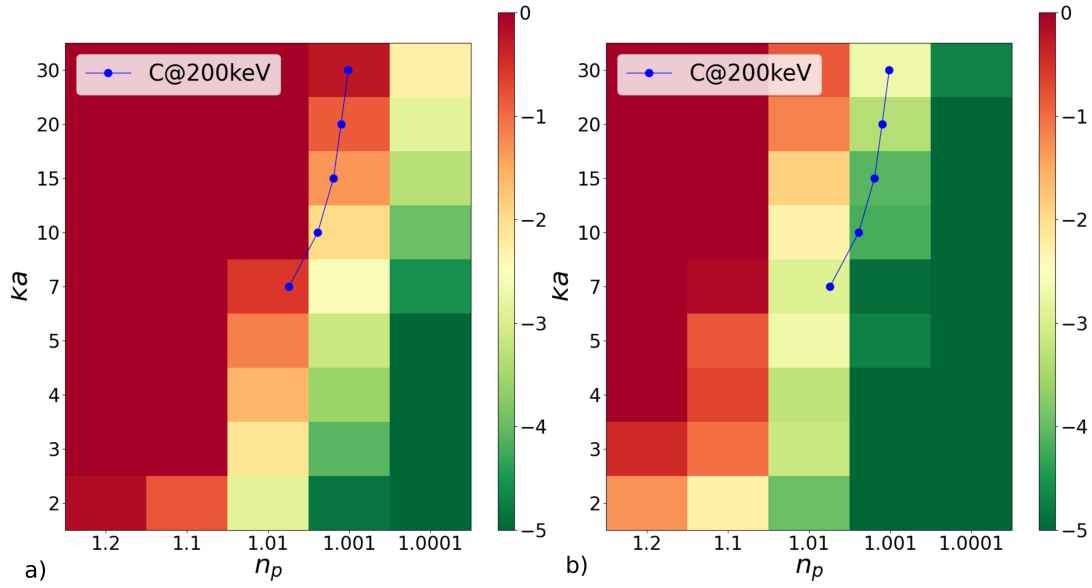


Fig. 6. Error of $b_{p,lm}$ Eq.(12) in (ka, k_p) space(color axis in logscale) of the for a two scatterer system using the a) Kinematic scattering approximation. b) Forward scattering approximation. The blue dots correspond to the location of the spherical shells of a carbon atom at $E = 200keV$.

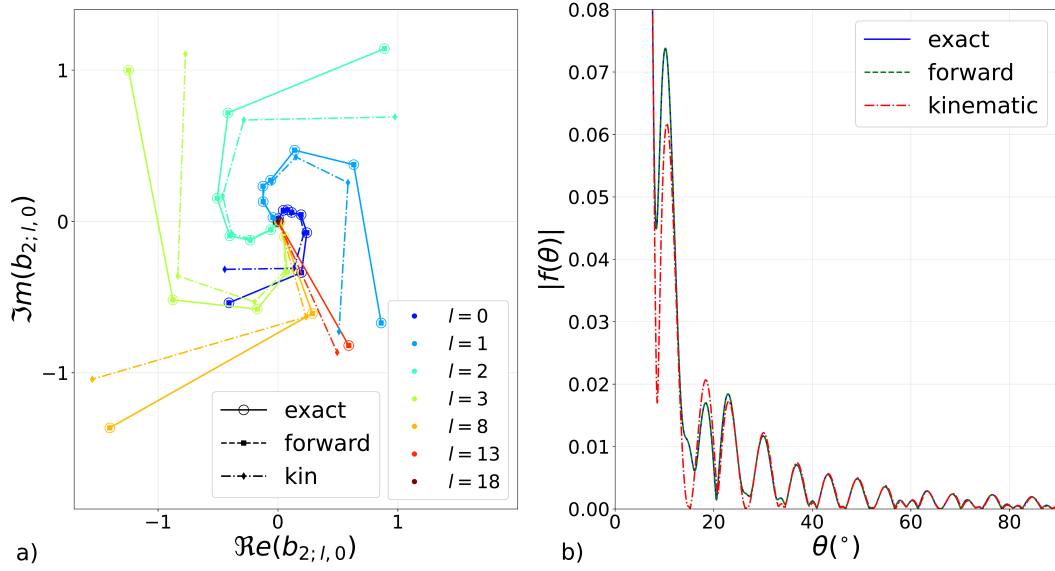


Fig. 7. a) Complex space scattering coefficients $b_{p;l,m}$ for a two body problem for $n_p = 1.01$, $kd = 3ka$ with increasing radius ka . Only the coefficients for sphere $p = 2$ and $m = 0$ are shown. The coefficients were computed from full T-matrix (open circles), the forward scattering approximation (squares) and the kinematic approximation (diamonds).

b) Comparison of far field scattering amplitudes for $N = 2$, $ka = 30$, $n_p = 1.01$, $kd = 2ka$ using full T-matrix (solid blue), forward approximation (green dashed) and kinematic approximation (red dashed-dotted). The forward approximation is indistinguishable from the exact solution in this case.

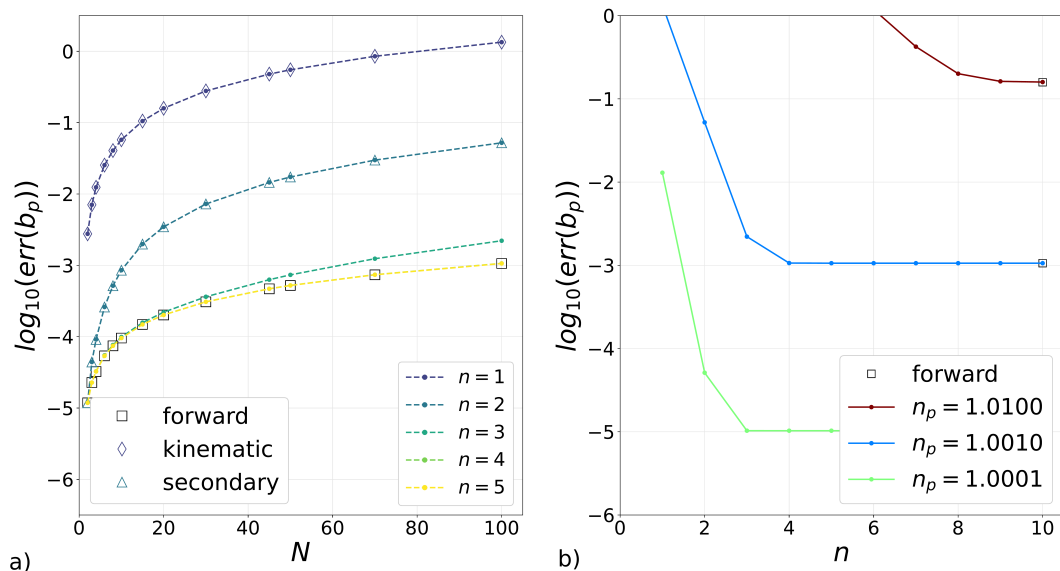


Fig. 8. a) Error Eq.(12) on the scattering amplitudes coefficients with increasing number of spheres N for $ka = 7$, $n_p = 1.001$, $kdka = 3$.

The forward (squares), kinematic(diamonds) and secondary (triangles) approximations are shown as well as the successive n times multiple scattering approximations (colored dashed lines). b) Error on the scattering amplitudes coefficients with increasing successive approximations for $ka = 7$, $kdka = 3$ and $N = 100$ spheres while varying n_p .

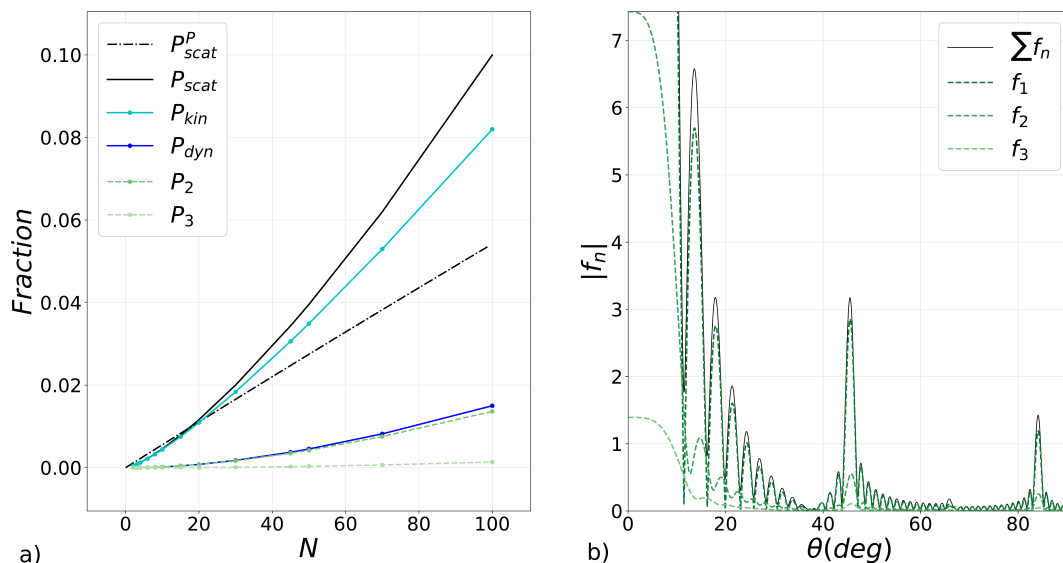


Fig. 9. a) Scattering probabilities (dashed colored lines) of n times scattering, kinematic(cyan solid line), dynamic scattering(blue solid line) and total scattering (black solid) probabilities. The total scattering probability following the Poisson distribution using the average scattering cross section is shown as dashed-dotted line. Probabilities have been integrated over angular distribution using $ka = 7$, $n_p = 1.01$ and $ka = 3kd$. b) Scattering amplitudes f_n , associated with n times scattering for $ka = 7$, $n_p = 1.01$ and $N = 15$. The total scattering amplitude $f = \sum_n f_n$ is shown in solid black.

6. Licensing

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Appendix A

T-matrix

The unknown coefficients $a_{p;lm}$, $b_{p;lm}$ are found by imposing the continuity of the wave function and its radial derivative at the surface of each sphere p :

$$\begin{aligned} \left(\sum_{q=1}^N \Psi_q^{(out)} + \Psi^{(i)} \right) \Big|_{r_p=a_p} &= \left(\Psi_p^{(in)} \right) \Big|_{r_p=a_p} \\ \partial_{r_p} \left(\sum_{q=1}^N \Psi_q^{(out)} + \Psi^{(i)} \right) \Big|_{r_p=a_p} &= \partial_{r_p} \left(\Psi_p^{(in)} \right) \Big|_{r_p=a_p} \end{aligned}$$

where $f^{(i)}$ is the incident electron wavefunction and a_p the radius of sphere p .

Using the orthogonality of the spherical harmonics

the following linear system yields the unknown coefficients :

$$\begin{aligned} a_{p;lm} &= u_{p;l} c_{lm} + u_{p;l} \sum_{q \neq p}^N \\ &\quad \sum_{\nu=0}^{\infty} \sum_{\mu=-\nu}^{\mu=\nu} a_{\nu,\mu;l,m}^{(out-in)}(\mathbf{d}_{pq}) b_{q;\nu\mu} \end{aligned} \quad (13)$$

$$\begin{aligned} b_{p;lm} &= v_{p;l} c_{lm} + v_{p;l} \sum_{q \neq p}^N \\ &\quad \sum_{\nu=0}^{\infty} \sum_{\mu=-\nu}^{\mu=\nu} a_{\nu,\mu;l,m}^{(out-in)}(\mathbf{d}_{pq}) b_{q;\nu\mu} \end{aligned} \quad (14)$$

where the translational addition theorem (Dufva *et al.*, 2008) has been used to express the field scattered by sphere q in the reference frame of sphere p , formally written as $f_q^{(out)}(\mathbf{r}_p)$. This operation involves the coupling coefficients $a_{\nu,\mu;l,m}^{(out-in)}(\mathbf{d}_{pq})$ where $\mathbf{d}_{pq} = \mathbf{d}_q - \mathbf{d}_p$.

The coefficients c_{lm} are related to the incident wave. In the case of a plane wave $e^{j\mathbf{k}_0 \cdot \mathbf{r}}$, $j = \sqrt{-1}$, the addition theorem is used to expand the plane wave on the Spherical Bessel solutions basis set:

$$\begin{aligned}
c_{lm} &= 4\pi j^l Y_l^{m*}(\theta_i, \phi_a) e_p \\
e_p &= e^{jk_0 d_p \zeta_p} \\
\zeta_p &= \sin(\Theta_p) \sin(\Phi_p) \sin(\theta_i) + \cos(\Theta_p) \cos(\theta_i)
\end{aligned}$$

where d_p, Θ_p, Φ_p are the spherical coordinates of the centre of sphere p in the global coordinate system, $0 \leq \theta_i \leq \pi$ is the angle of incidence with respect to the $\mathbf{e}_z$ axis, $\phi_i = \pi/2$ since the propagation is in the (y, z) plane and e_p is the phase offset at sphere p . The different notations are illustrated in Fig. 1.

The coefficients $u_{p;l}$ and $v_{p;l}$ are expressed as:

$$\begin{aligned}
u_{p;l} &= \frac{h'_l(k_0 a_p) j_l(k_0 a_p) - h_l(k_0 a_p) j'_l(k_0 a_p)}{j_l(k_p a_p) h'_l(k_0 a_p) - n_p j'_l(k_p a_p) h_l(k_0 a_p)} \\
v_{p;l} &= \frac{n_p j'_l(k_p a_p) j_l(k_0 a_p) - j_l(k_p a_p) j'_l(k_0 a_p)}{j_l(k_p a_p) h'_l(k_0 a_p) - n_p j'_l(k_p a_p) h_l(k_0 a_p)}
\end{aligned}$$

where $z'_l = \partial_\rho z_l(\rho)$.

Eqs. (13,14) can then be written in the matrix form (5) .

Appendix B

Multiple Scattering picture of Multislice Approach

The expression for the scattering amplitude $f(h, k)$ of beam h, k is proportional to

the following expression :

$$\begin{aligned}
 f(h, k) \propto & \sum_l \sum_{h_1} \sum_{k_1} \sum_{l_1} \dots \sum_{h_{N-1}} \sum_{k_{N-1}} \sum_{l_{N-1}} Q_{h_1, k_1, l_1} \dots \\
 & Q_{h_{N-1}, k_{N-1}, l_{N-1}} Q(h - h_u, k - k_v, l - l_w) \\
 & e^{-2\pi j (H\zeta - \Delta z \sum_{n=1}^{N-1} \zeta_n)}
 \end{aligned} \tag{15}$$

where $h = \sum_{n=1}^N h_n$, $k = \sum_{n=1}^N k_n$, $h_u = \sum_{n=1}^{N-1} h_n$, $k_v = \sum_{n=1}^{N-1} k_n$, $l_w = \sum_{n=1}^{N-1} l_n$, $H = N\Delta z$ is the total thickness of the sample, N the number of slices of thickness Δz , $Q_{h,k,l} = -j/\Delta z \delta_{h,k} e^{-2j\pi l_n z_n/c} + \sigma F_{h,k,l}$, $F_{h,k,l}$ is the structure factor, $\sigma = 2\pi m_e h/\lambda$ the interaction parameter, ζ the excitation error of beam (h, k, l) and ζ_n is the excitation error of beam $(\sum_{r=1}^n h_r, \sum_{r=1}^n k_r, \sum_{r=1}^n l_r)$. The excitation error is expressed as :

$$\zeta = \frac{1}{2K} \left(\frac{h}{a^2} + \frac{k}{b^2} \right) - \frac{l}{c} \tag{16}$$

where a , b and c are the lattice constants of the crystal and $K = 1/\lambda$ the wave number. Eq. (16) is the longitudinal distance of beam (h, k, l) to the paraboloid shown in figure B1a. This paraboloid is a very accurate representation of the Ewald sphere for large wave number K . Therefore, ζ is very close to the excitation error commonly defined in crystallography.

From Eq. (15) it is possible to gather terms in powers of $Q_{0,0,0}^{N-n}$ into $f_{h,k}^{(n)}$, which corresponds to the incident beam scattered n times before contribution to reflection h, k . The term $Q_{0,0,0}^N$ only appears for $h = k = 0$ and corresponds to the unscattered direct beam. There are N terms involving the factor $Q_{0,0,0}^{N-1}$ depending on which slice the single scattering event took place. There are $N(N-1)/2$ terms involving the factor $Q_{0,0,0}^{N-2}$ depending on which pair of slices the two-level scattering process is considered, and so on for the higher order multiple scattering terms (Cowley & Moodie, 1957). This multiple scattering picture is illustrated in 2D in figure B1b for a case with $N = 3$ and using only beams in the zero order Laue zone (ZOLZ) $l_i = 0$.

Using only ZOLZ beams, $f_{h,k}^{(1)}$, $(h, k) \neq (0, 0)$ is expanded as :

$$f_{h,k}^{(1)} \propto F_{h,k,0} \sum_{m=1}^N e^{-2j\pi m \Delta z \zeta} \quad (17)$$

which is the well known kinematic scattering regime, where the sum converges to the standard Ewald sphere curvature factor $\sin(\pi \zeta H) / \pi \zeta$ for infinitely thick slices $N \rightarrow \infty, \Delta z \rightarrow 0, N \Delta z = H$

For a two level scattering using only ZOLZ beams, $f_h^{(2)}$ would expanded as (written in 2D here) :

$$f_h^{(2)} \propto \sum_{h_1} F_{h_1,0} F_{h-h_1,0} \sum_{m_1=1}^N \sum_{m_2 > m_1}^N e^{-2j\pi \Delta z (m_1 \zeta_1 + m_2 (\zeta - \zeta_1))} \quad (18)$$

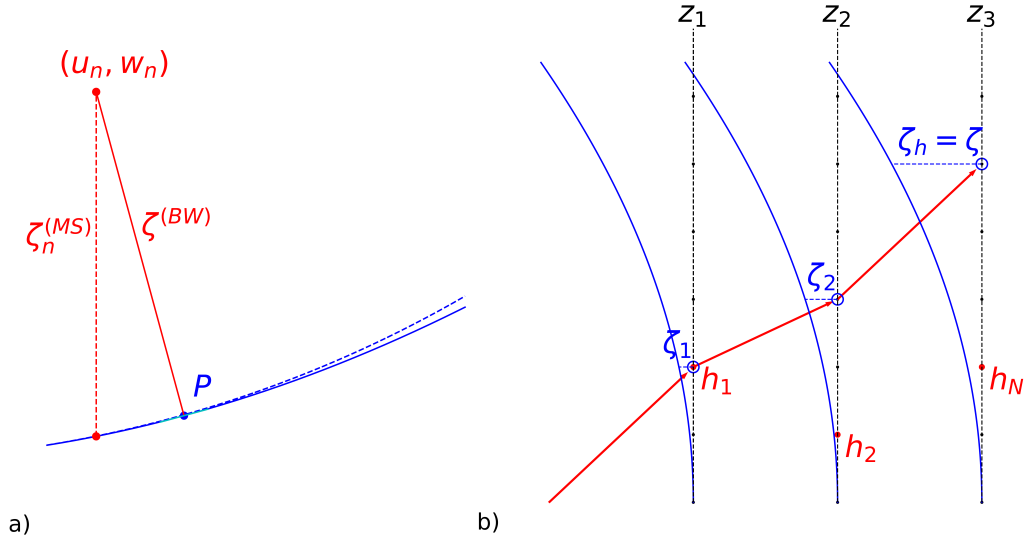


Fig. B1. Multiple scattering in multislice. a) Distance $\zeta_n^{(MS)}$ to the Ewald paraboloid (solid curve) as represented by multislice and distance $\zeta^{(BW)}$ to the Ewald sphere (dashed curve), known as the excitation error in the Blochwave theory. Point P is the projection of reciprocal point (u_n, w_n) onto the Ewald paraboloid. b) Multiple scattering in reciprocal space for $N = 3$ slices located at z_1, z_2, z_3 . In this example, the beam is scattered in the first slice at z_1 in direction $(h_1, 0) = (2, 0)$. Then, at slice z_2 it is scattering in direction $(h_2, 0) = (1, 0)$, which results in an overall scattering of the original beam in $(h_1 + h_2, 0) = (3, 0)$. Finally, at the last slice $z_N = z_3$, deflection is in $(h_N, 0) = (2, 0)$. Therefore, the overall scattering for this example corresponds to a contribution to reflection $(h_1 + h_2 + h_3, 0) = (5, 0)$ in the diffraction pattern. The open blue circles show how to interpret the successive excitation errors ζ_i .

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Synopsis

The T-matrix is used to compute the scattering of fast electrons by a regular array of effective spherical potential wells. An assessment of the forward scattering approximation and a real space multiple scattering interpretation are provided.
