

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

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## Abstract

Due to the strong electron-atom interaction, the kinematic theory of diffraction can not be used to describe the scattering of electrons by an assembly of atoms. Dynamical diffraction need to be taken into account by solving Schrödinger's equation. In this paper, the scattering of high energy electrons by a regular array of light atoms is solved exactly using the T-matrix in spherical coordinates. Using the independent atom model, 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. An interpretation of multiple scattering is proposed and compared with existing interpretations.

*Keywords:* High Energy Electron Diffraction, T-matrix

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## 1. Introduction

### 1.1. Motivation

Since the first experimental demonstration of electron diffraction in 1928, theory of dynamical diffraction has been developed [1, 2]. Besides, multiple scattering [3, 4, 5, 6] has also extensively been studied in solid state physics over the 20th century. In fact, even at very high electron energies commonly used in modern transmission electron microscopes, the electron-atom interaction is very strong and the kinematic theory of diffraction is not theoretically valid for crystals thicker than a few nm [7, 8]. In practice, crystal growth cannot be controlled to such a degree of accuracy and nano-crystals of organic compounds are usually on the order of tens to hundreds of nanometers. This is known as a challenging aspect of high energy electron diffraction (HEED) as it should significantly complicate the structure determination process. However, successful structure determination based on the standard kinematic theory used in X-ray diffraction have regularly been demonstrated over the past 10 years [9, 10] suggesting that dynamical diffraction may not affect the diffraction intensities as much as the theory suggests. Although, dynamical refinement based structure determination [11] usually leads to better intensity predictions [12], the agreement between theory and experiment is still significantly worse than those obtained for X-rays [13]. It is therefore crucial to develop more accurate models of electron diffraction by crystals.

### 1.2. state of the art

The multislice (MS) [14] and Blochwave (BW) [1] approaches are the most popular methods for simulating scattering of high energy electrons in crystals. The MS is particularly well suited for solving large structures as it involves successive convolutions which can be very efficiently computed with the Fast Fourier Transform (FFT) [15]. To avoid aliasing transverse periodic boundary conditions must be met which is only possible for orthorhombic structures in zone axis orientations. Although small beam tilt can also be used [16, 17], simulations with arbitrary orientations must be performed by simulating a full crystal with added zero padding. This can quickly become computationally challenging.

On the other hand, BW method can simulate small structures in any arbitrary orientations. Although some efficient implementation [18] can simulate moderately large structures, BW cannot be applied to large structures due to the unfavorable scaling behaviour of the matrix diagonalization involved. Non periodic structures, defects and solvent scattering cannot be modelled either.

Both approach can handle coherent inelastic scattering through the use of a imaginary part of the potential. This however does not account for the loss of coherency induced by inelastic scattering which may have dramatic impact on the dynamical diffraction [19].

### 1.3. Contribution and outline

The purpose of this paper is to propose an alternative real space approach to the scattering of fast electrons by light-atom structures based on the T-matrix formalism. The T-matrix has been extensively applied to various areas of physics including electromagnetics [20, 21, 22],

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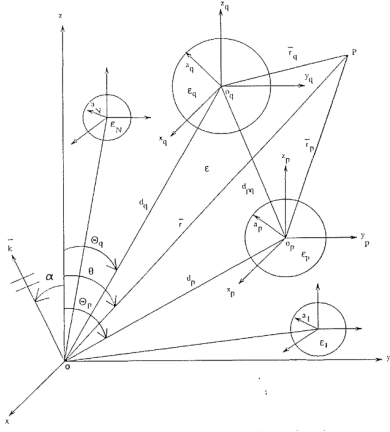


Figure 1: The problem solved by the T-matrix

optics [23] and acoustics [24, 25]. Although not computationally competitive with multislice for large systems, this approach provides an exact solution to Schrödinger's equation for an assemble of spherically symmetric effective atomic potentials in the independent atom model (IAM). An intuitive understanding of multiple scattering in the forward scattering approximation is presented and compared with existing interpretations. The validity of the forward scattering approximation and the phase grating approximation used by multislice are then discussed. Conclusions are drawn and extensions of this approach to account for incoherent inelastic scattering are outlined.

## 2. Theory

The problem of the scattering of fast electrons by an assembly of atoms is found by solving Schrödinger's equation :

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

where  $\hbar$  is plank'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 energy of the incident electrons. The wave function is sought as a sum of an incident wave  $\Psi^{(i)}$  and a scattered wave  $\Psi^{(s)}$ .

### 2.1. T-matrix formulation

In its standard form, the T-matrix solves for the case where the electrostatic potential is uniform constant inside non overlapping spheres and the incident wave is described by a plane wave of wavenumber  $k_0 = 2\pi/\lambda$  (optics convention). The setup shown in figure 1. The formulation is well established and the theory is outlined for the purpose of introducing the forward multiple scattering approximation picture.

In each domain, the problem is reduced to Helmholtz's 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 :

$$\begin{aligned} \Psi_p^{(in)}(\mathbf{r}_p) &= \sum_{l=0}^{\infty} j_l(k_p r_p) \sum_{m=-l}^{m=l} a_{p;lm} Y_l^m(\theta_p, \phi_p) \\ \Psi_p^{(out)}(\mathbf{r}_p) &= \sum_{l=0}^{\infty} h_l^{(1)}(k_0 r_p) \sum_{m=-l}^{m=l} b_{p;lm} Y_l^m(\theta_p, \phi_p) \end{aligned}$$

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  $p$  :

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

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 :

$$\begin{aligned} a_{p;lm} &= u_{p;l} c_{lm} + u_{p;l} \sum_{q \neq p}^N \sum_{\nu=0}^{\infty} \sum_{\mu=-\nu}^{\mu=\nu} a_{\nu,\mu;l,m}^{(out-in)}(\mathbf{d}_{pq}) b_{q;\nu\mu} \end{aligned} \quad (2)$$

$$\begin{aligned} b_{p;lm} &= v_{p;l} c_{lm} + v_{p;l} \sum_{q \neq p}^N \sum_{\nu=0}^{\infty} \sum_{\mu=-\nu}^{\mu=\nu} a_{\nu,\mu;l,m}^{(out-in)}(\mathbf{d}_{pq}) b_{q;\nu\mu} \end{aligned} \quad (3)$$

where the translational addition theorem[26] 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 coefficient  $c_{lm}$  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 family basis of Spherical Bessel solutions :

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

where  $d_p, \Theta_p, \Phi_p$  being the spherical coordinates of the centre of sphere  $p$  in the global coordinate system,  $0 \leq \alpha_i \leq \pi$  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 as illustrated on figure 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  $z'_l = \partial_\rho z_l(\rho)$ .

Equations (2,3) can be written in a matrix notation :

$$(\mathbf{I} - \mathbf{T})\mathbf{A} = \mathbf{L} \quad (4)$$

where  $\mathbf{I}$  is the identity matrix,  $\mathbf{A}$  is the unknown vector 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, the diffraction pattern of particular interest which is recorded in the far field. 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 sphere  $p$  can be written as :

$$f_p(\theta, \phi) = \sum_{l=0}^{\infty} \sum_{m=-l}^l (-j)^{l+1} b_{p;lm} Y_l^m(\theta, \phi) \quad (5)$$

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

$$f(\theta, \phi) = \sum_{p=1}^N f_p(\theta, \phi) e^{-j\mathbf{k}_0 \cdot \mathbf{r}_p} \quad (6)$$

The normalized differential scattering cross section is defined as :

$$\frac{\sigma(\theta, \phi)}{\pi a_p^2} = \frac{4\pi r^2}{\pi a_p^2} \left\| \frac{\Psi^{(s)}(r, \theta, \phi)}{\Psi^{(i)}(r, \theta, \phi)} \right\|^2 = \frac{4|f(\theta, \phi)|^2}{(k_0 a_p)^2} \quad (7)$$

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

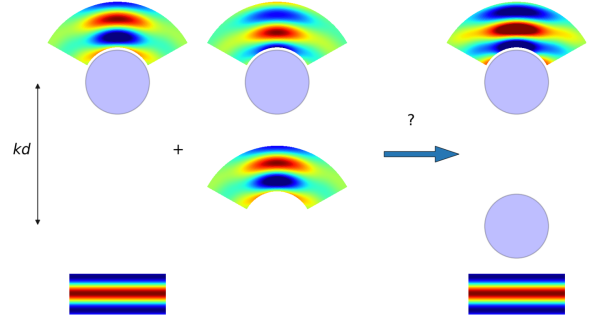


Figure 2: Two-level forward scattering approximation using the T-matrix approach. Neglecting backscattering, scattering from the second scatterer located at distance  $kd$  from the first scatterer can be approximated by the sum of 1) the kinematic scattering to the incident beam and 2) the secondary scattering in response to the kinematic scattering from the first scatterer.

### 3. Forward scattering and multiple scattering approximations

#### 3.1. T-matrix

Expression (4) is a convenient way to write the system as it readily identifies  $\mathbf{L}$  as the solution to the uncoupled problem. Indeed,  $a_{p;lm} = c_{lm} u_{p;l}$ ,  $b_{p;lm} = c_{lm} v_{p;l}$  are then well known analytical solutions of Mie scattering by a soft sphere.

The cross-coupling matrix  $\mathbf{T}$  accounts for multiple scattering effects. If  $\mathbf{A}$  is written  $\mathbf{A} = (..a_{p;lm}, b_{p;lm}..)^T$ ,  $\square^T$  denoting transposition, then  $\mathbf{T}$  is block diagonal :

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

where  $\mathbf{T}_{pq}$  represents the scattering from sphere  $p$  due to the scattering from sphere  $q$ . If the problem is fully coupled, the scattering from sphere  $p$  affects scattering from sphere  $q$  and vice versa which therefore requires inversion of the system.

As detailed further down below, backscattering can be neglected for very fast electrons which is known as forward scattering approximation. This results in  $\mathbf{T}$  being lower triangular if the spheres are sorted in ascending order along  $\mathbf{e}_z$ . Inversion is therefore no longer necessary and calculations can be performed sequentially.

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 :

$$\begin{aligned} b_{p;lm} &= b_{p;lm}^{(0)} + \sum_{q, z_q < z_p} T_{pq} b_{q;lm}^{(0)} \\ &+ T_{pq} \sum_{q, z_q < z_p} T_{qr} \sum_{r, z_r < z_q} b_{r;lm}^{(0)} + .. \end{aligned} \quad (8)$$

where the first term accounts for kinematic scattering, the second term for secondary scattering, the third term three time scattering and so on. This is a similar development to the Korringa-Kohn-Rostoker (KKR) theory of multiple scattering [3, 4, 5]. The forward multiple scattering approximation in the case of 2 scatterers is illustrated in figure 2.

### 3.2. First Born approximation and kinematic scattering

Assuming normal incidence  $\alpha_i = 0$  so that  $e_p = e^{jk_0 d_p \cos \Theta_p}$  and noting that the Ewald sphere can be represented by  $\mathbf{q} = K(\sin \theta \cos \phi, \sin \theta \sin \phi, 1 - \cos \theta)$  in transfer vector momentum space,  $K = 1/\lambda$  being the wave number in crystallographic convention, keeping only the kinematic term in (8) and injecting in the far field (6) gives :

$$f(\theta, \phi) = \sum_{p=1}^N f_p^{(e)} e^{2j\pi \mathbf{q} \cdot \mathbf{d}_p} \quad (9)$$

where  $f_p^{(e)}$  is the scattering amplitude of sphere  $p$  in the First Born approximation also known as the form fac-

tor. Equation (9) does correspond to the standard kinematic formula for the structure factor traditionally used in crystallography. Note that the kinematic approximation is nothing less than the first Born approximation applied to the whole assembly of atoms. It will be seen further down below that it is possible for the first Born approximation to hold at the scatterer level while being invalid at the assembly level.

### 3.3. Multiple scattering in multislice

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

A multiple scattering interpretation by the multislice has been proposed [14] which, although analogous to the one presented above, differs in that it is stated in reciprocal space. The expression for the scattering amplitude  $f(h, k)$  of beam  $h, k$  is proportional to the following expression :

$$f(h, k) \propto \sum_l \sum_{h_1} \sum_{k_1} \sum_{l_1} \dots \sum_{h_{N-1}} \sum_{k_{N-1}} \sum_{l_{N-1}} Q_{h_1, k_1, l_1} \dots Q_{h_{N-1}, k_{N-1}, l_{N-1}} \\ Q\left(h - \sum_n^{N-1} h_n, k - \sum_n^{N-1} k_n, l - \sum_n^{N-1} l_n\right) e^{-2\pi j \left( H\zeta - \Delta z \sum_{n=1}^{N-1} \zeta_n \right)} \quad (10)$$

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

$$\zeta = \frac{1}{2K} \left( \frac{h}{a^2} + \frac{k}{b^2} \right) - \frac{l}{c} \quad (11)$$

where  $a, b$  and  $c$  are the lattice constants of the crystal and  $K = 1/\lambda$  the wave number. Equation (11) is the longitudinal distance of beam  $(h, k, l)$  to the paraboloid shown in figure 3a. This paraboloid is a very accurate representation of the Ewald sphere for large wave number  $K$ .  $\zeta$  is therefore very close to the excitation error commonly defined in crystallography.

From equation (10) 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 contributing 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  $Q_{0,0,0}^{N-1}$  depending on which slice the single scattering event took place. There are  $N(N-1)/2$  terms

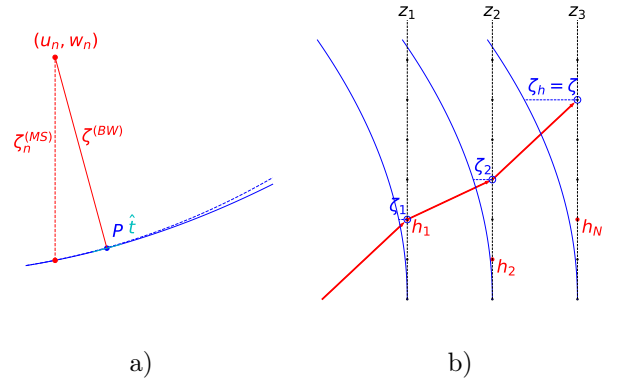


Figure 3: Multiple scattering in multislice. a) Distance  $\zeta^{(MS)}$  to the Ewald paraboloid (solid curve) as approximated by multislice and distance  $\zeta^{(BW)}$  to the Ewald sphere (dashed curve) known as the excitation error in the Blochwave theory. Point P is the projection of reciprocal point  $(u_n, w_n)$  onto the Ewald paraboloid. b) Multiple scattering in reciprocal space for  $N = 3$  slices located at  $z_1, z_2, z_3$ . The beam is scattered by  $(h_1, 0)$ , then  $(h_2, 0)$  and then  $(h_N, 0)$  which results in an overall contribution to reflection  $h$  on the diffraction pattern. The open blue circles show the subsequent excitation errors  $\zeta^{(i)}$ .

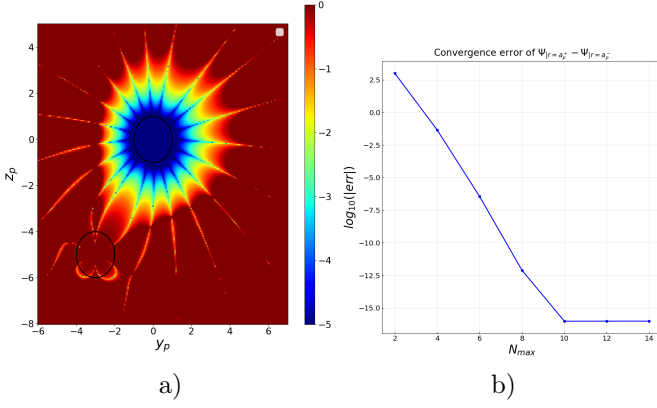


Figure 4: a) Error between  $h_l^{(1)}Y_{lm}$  for  $l = 4$  and  $m = 2$  computed at the origin and using the translational addition theorem  $\mathbf{d}_p = (0, 3, 5)$  with  $\nu_{max} = 10$ . The circle represent spheres of radius 1. Color axis in logscale. b) Continuity error at the sphere boundaries in the T-matrix with increasing order. For this example  $N = 4$  and  $ka_{max} = 4$ .

involving  $Q_{0,0,0}^{N-2}$  depending on which pair of slices are considered the two level scattering process and so on. This multiple scattering picture is illustrated in 2D in 3b 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 :

$$f_{h,k}^{(1)} \propto F_{h,k,0} \sum_{m=1}^N e^{-2j\pi m \Delta z \zeta} \quad (12)$$

which is the well known kinematic scattering regime.

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

$$f_h^{(2)} \propto \sum_{h_1} F_{h_1,0} F_{h-h_1,0} \sum_{m_1=1}^N \sum_{m_2>m_1}^N e^{-2j\pi \Delta z (m_1 \zeta_1 + m_2 (\zeta - \zeta_1))} \quad (13)$$

## 4. Application and Results

Although very efficient open source implementations are available for electromagnetics [27, 28], an implementation suited for solving Schrödinger's equation has been made available [29].

In practice, the sums over (2,3) have to be truncated to a maximum integer order  $l_{max}$ . A rule to obtain accurate results is to take  $l_{max}$  a few integer above the maximum value of  $ka$  since the spherical Bessel functions of order  $l$  have enough ripples to capture the periodicity of the incident wave in the vicinity of the sphere. Moreover, the translational addition theorem provides an approximation of the spherical Hankel functions with decreasing accuracy from the center at which it is written similarly to a Taylor's expansion. This is illustrated in figure 4a where the

error between  $h_l^{(1)}Y_{lm}$  for  $l = 4$  and  $m = 2$  computed at the origin and using the translational addition theorem with  $\mathbf{d}_p = (0, 3, 5)$  and  $\nu_{max} = 10$  is displayed in logscale. This allows for distances between spheres to be arbitrarily large. The criteria for selecting  $l_{max}$  is best evaluated by assessing the continuity of the wave functions at the sphere boundaries as shown in figure 4b 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.

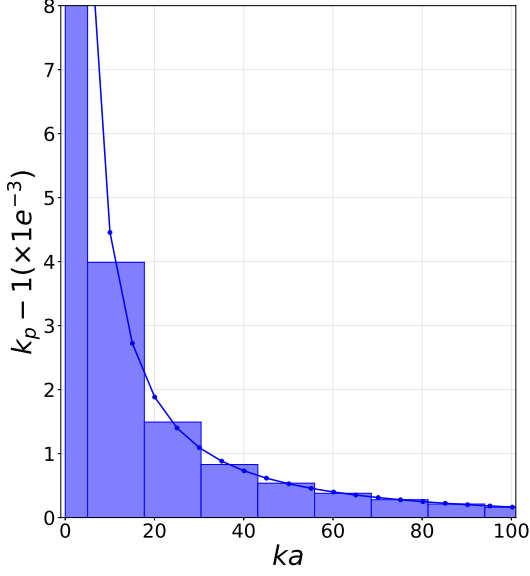
### 4.1. Validity of forward scattering and phase grating approximations for light atoms

In the case of very fast electrons typically used in transmission electron microscopes  $E = 50 - 300 \text{ keV}$ . Inclusion of relativistic effects result in  $\lambda = 0.025 \text{ @ } 200 \text{ keV}$  which will be assumed from now on unless stated otherwise. In the IAM, the potential is the sum of the Coulomb potential created by the charge of the nucleus and the electron cloud. It can be approximated with a sum of screened Coulomb potential and Gaussian terms [30]. For typical light atoms such as commonly found in organic compounds, a single screened Coulomb potential term can be a pretty good approximation as shown in figure 5a. The solution to Schrödinger's equation in such a potential can only be solved perturbatively [31] and is beyond the scope of this document. However, orders of magnitude for  $k_p$  and  $ka_p$  can be estimated by a multi-shell representation as shown in figure 5a. Although the range of the potential is theoretically infinite, it can reliably be truncated to radius  $ka$  by using the Born approximation. In figure ??b the multi-shell scattering amplitudes are shown for increasing values of truncation radius. A satisfactory agreement with the electron diffraction scattering factors is obtained for normalized radius as large as  $ka = 350$  to account for the proper low angle representation although the potential is very small at such radius.

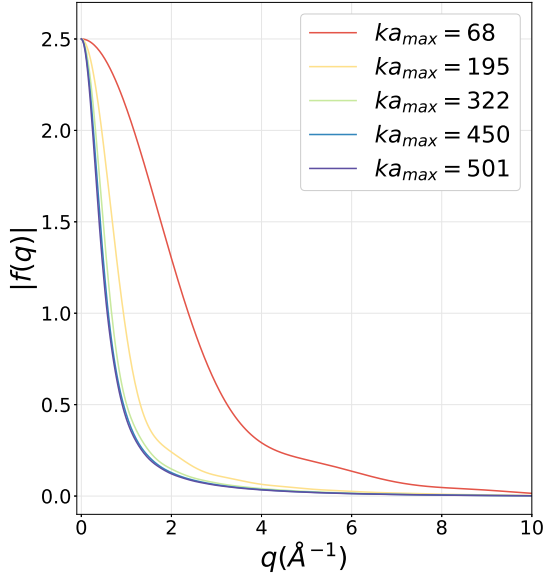
As mentionned above, such a large radius would be quite hard to simulate with the T-matrix due to the large orders to be included. However, it can be argued that at very large radius, the refractive index is so small that the Born approximation is most certainly valid. Figure 6 shows the far field amplitudes for 2 indicative parameter set of  $ka, n_p$ . It is clear that for the  $ka = 60$ ,  $n_p = 1.001$  the Born approximation is extremely accurate. Therefore, the medium to low radius shells with appreciable refractive index are mostly responsible for dynamical diffraction encountered in actual light-atom structures.

For the more extreme value of  $ka = 10$ ,  $n_p = 1.05$ , the Born approximation is very accurate although the phase grating approximation provide some improvement. Overall it is very clear that the forward scattering approximation is very over all range of parameter set as there is very little back backscattering beyond  $90^\circ$ .

It is noted that in the weak scattering regime  $n_p \approx 1$  and for a sphere not too large, the shape of the diffraction



a)



b)

Figure 5: a) Electrostatic potential created by an atom of carbone with the IAM (blue solid line), fitted single screened coulomb potential (blue dashed line), fitted Coulomb potential with offset (red dashed 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  $ka_{max}$ . The electron form factors factors is shown as dashed line.

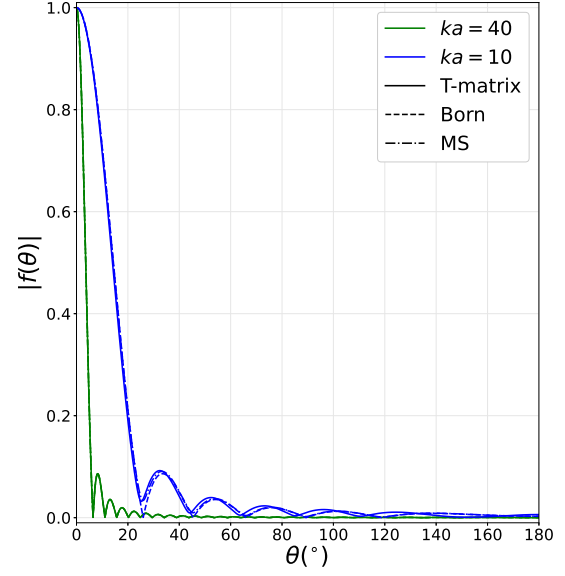


Figure 6: a) Shape of the scattering amplitude for normalized radius  $ka = 5$ ,  $n_p = 1.05$  (blue) and  $ka = 15$ ,  $n_p = 1.001$  (green). Also shown, the Born approximation (dashed lines) and the phase grating approximation used in multislice (dash-dotted lines).

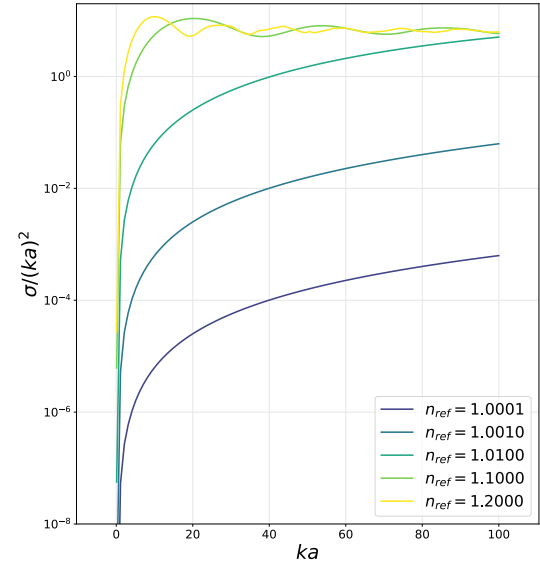


Figure 7: b) Normalized scattering cross section in  $\sigma$  in log for a few values of  $k_p$  over a range of normalized radius  $ka$ .

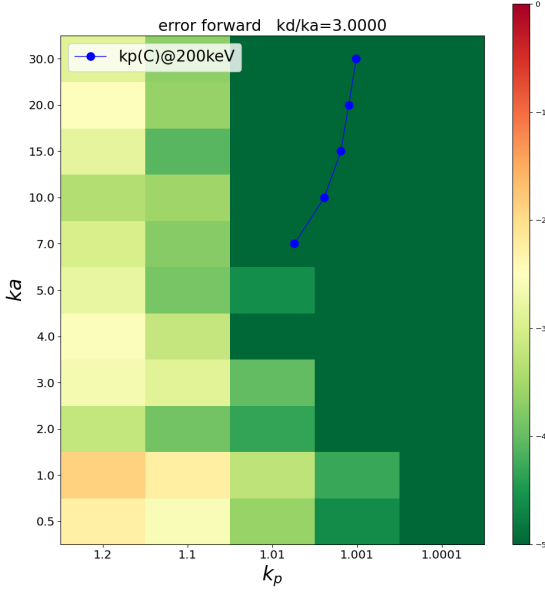


Figure 8:  $(ka, k_p)$  map (color axis in logscale) of the error of  $b_{p;lm}$  using the forward scattering approximation. The blue dot correspond to the location of the spherical shells of Carbone atom at  $E = 200\text{keV}$ .

pattern is identical to the Born approximation. Only the amplitude of the scattering cross section increases with radius.

Both the uncoupled and forward scattering approximation work better with increasing distances  $kd$  since scattering from the spheres reduces with distance. It is therefore less likely to affect scattering from the other spheres. The low values of  $k_p$  result in overall good approximation of both the uncoupled and forward scattering approximation. This is an anticipated result since for weak potentials, the kinematic approximation is more valid. The uncoupled approximation improves with small radii since Small  $ka$  result in small scattering cross section, On the other hand the forward scattering approximation improves with larger values of  $ka$  since backward scattering is less likely for large  $ka$ .

#### 4.2. Multiple scattering approximations

Both the uncoupled and forward scattering approximation work better with increasing distances  $kd$  since scattering from the spheres reduces with distance. It is therefore less likely to affect scattering from the other spheres. The low values of  $k_p$  result in overall good approximation of both the uncoupled and forward scattering approximation. This is an anticipated result since for weak potentials, the kinematic approximation is more valid. The uncoupled approximation improves with small radii since Small  $ka$  result in small scattering cross section, On the other hand the forward scattering approximation improves with larger values of  $ka$  since backward scattering is less likely for large  $ka$ .

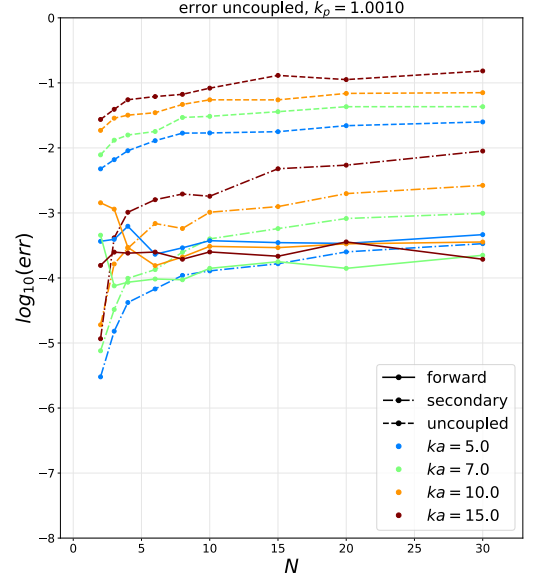


Figure 9:  $\log_{10} \text{err}(b_{p;lm})$  the scattering amplitudes coefficients with increasing number of spheres for a few normalised radius  $ka$  using  $k_p = 1.01$ .

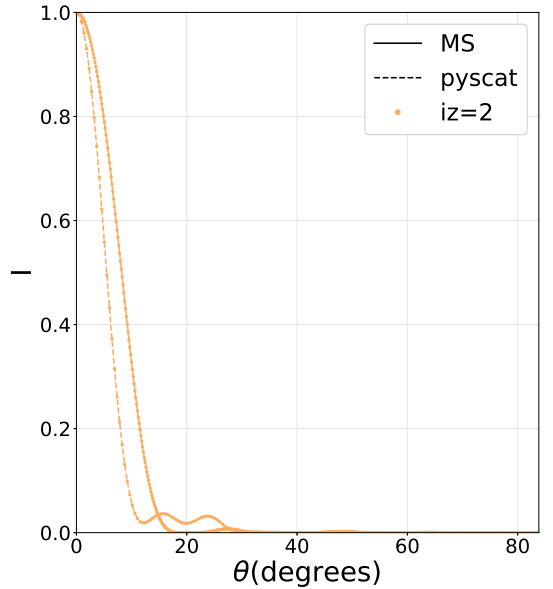


Figure 10: Comparison of multislice and Tmatrix for increasing number of spheres  $N$ .  $\text{keV} = 50$ ,  $ka = 11$ ,  $kd = 3ka$ ,  $k_p = 1.001$ .



## 5. Discussion and Conclusion

An alternative approach based on the T-matrix has been applied to the scattering of fast electrons by light-atom structures. The validity of important approximations used in multislice 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 accurately model the potential used in atoms, it was shown that the multiple scattering interpretation should equally apply to the more accurate case of a screened Coulomb potential. A possible inclusion of such a potential could be performed by using a basis of radial functions solutions the Schrödinger's equation in a Yukawa potential such as produced by a variational or other numerical approach. Since the T-matrix mainly relies on the spherical symmetry of the individual scatterers, it can be adapted to any radial family of functions provided translational coefficients can be computed numerically. The main ultimate limitation of both this approach and the traditional multislice lies in the use of the independent atom model which by definition ignores the effect of bonding. While the multislice can be adapted at a computational cost to bonding models such as Transferrable Aspherical Atom Model (TAAM), the T-matrix presented here certainly cannot. However, it is still an open question whether such bonding play an important role in HEED structure determination of organic structures.

The advantage of a multiple scattering approximation approach is that it offers both the possibility of a massively parallel computation of dynamical diffraction while including incoherent inelastic scattering with a stochastic approach. It is indeed strongly anticipated that inelastic scattering has a dramatic mitigation effect of dynamical diffraction even when energy filters are used. This aspect is currently under investigation.

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