Influence of wavelength and pulse duration on single-shot x-ray diffraction patterns from nonspherical nanoparticles

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Received 15 May 2015, revised 14 July 2015
Accepted for publication 4 August 2015
Published 16 September 2015

Abstract

We introduce a complex scaling discrete dipole approximation (CSDDA) method and study single-shot x-ray diffraction patterns from non-spherical, absorbing nanotargets in the limit of linear response. The convergence of the employed Born series-based iterative solution of the discrete dipole approximation problem via optimal complex mixing turns out to be substantially faster than the original approach with real-valued mixing coefficients, without additional numerical effort per iteration. The CSDDA method is employed to calculate soft x-ray diffraction patterns from large icosahedral silver nanoparticles with diameters up to about 250 nm. Our analysis confirms the requirement of relatively long wavelengths to map truly 3D structure information to the experimentally accessible regions of 2D scattering images. On the other hand, we show that short wavelengths are preferable to retain visibility of fine structures such as interference fringes in the scattering patterns when using ultrashort x-ray pulses in the attosecond domain. A simple model is presented to estimate the minimal pulse duration below which the fringe contrast vanishes. Knowledge of the impact of the bandwidth of short pulses on the diffraction images is important to extract information on ultrafast dynamical processes from time-resolved x-ray diffractive imaging experiments on free nanoparticles, in particular at long wavelengths.

Keywords: x-ray diffraction, single-shot nanoparticle imaging, discrete dipole approximation

(Some figures may appear in colour only in the online journal)

1. Introduction

The combination of high photon flux and short pulse duration of short-wavelength free electron lasers (FELs)\cite{2, 9, 11, 12, 15, 27} has enabled high-resolution single-shot x-ray diffraction experiments to study the structure of single nanoparticles, as demonstrated for free particles such as viruses\cite{28}, soot particles\cite{18}, rare-gas clusters\cite{5, 25}, and doped helium nanodroplets\cite{13} as well as for nanoparticles deposited on surfaces\cite{29, 32}, embedded in liquids\cite{16} or solids\cite{19}. If particles of interest can be immobilized by deposition or embedding, there are well-established other methods to analyze their structure and shape, e.g., the ice embedding method utilizing transmission electron microscopy\cite{1}. A key advantage of single-shot x-ray imaging, however, is the possibility to study unsupported nanosystems, thus, in the following study the main focus lies on the imaging of free nanoparticles. Two of the main challenges of single-shot x-ray imaging are the analysis of ultrafast dynamical processes\cite{22} and the resolution of truly three-dimensional (3D) structural information. In a recent soft x-ray
wide-angle scattering experiment on large free silver clusters, the simultaneous identification of both particle orientation and shape from single scattering images has been demonstrated by Barke et al [3]. Key to the 3D sensitivity in this experiment was the usage of relatively long-wavelength FEL pulses (\(\lambda = 13.5 \text{ nm}\)) to resolve the scattering signal under large angles. In order to adequately describe the scattering process in this wavelength regime, absorption in the target has to be taken into account as it is typically non-negligible. Hence, the first Born approximation [4], whose validity is assumed in most conventional reconstruction methods, becomes inapplicable. A convenient alternative is then the reconstruction via a forward fit of the measured scattering pattern with numerically simulated diffraction patterns of parameterized model shapes [3].

An ideal dynamic x-ray imaging experiment should enable the extraction of 3D structural information with maximal time resolution. Despite the requirement of long wavelengths for capturing the wide-angle scattering signal needed for 3D sensitivity, short wavelengths are preferential for achieving high time resolution. The latter conclusion results from the fact that a short pulse length induces a loss of image contrast due to the finite bandwidth. In first order approximation, this loss of contrast scales linearly with the relative pulse bandwidth and is thus proportional to the central wavelength of a Fourier limited pulse of a given duration. The analysis of the intertwined impact of scattering wavelength and pulse duration on single-shot x-ray scattering images for realistic targets defines the scientific focus of the current work. To investigate this relationship we study the scattering pattern of large icosahedral silver clusters for similar parameters as in the work of Barke et al [3]. For clarity and simplicity, we consider only the linear target response and neglect both nonlinear polarization effects and transient changes of optical properties due to excitation or destruction of the target during the scattering process [20].

The above objective requires scattering simulations that enable the description of arbitrarily shaped, opaque targets. As a conceptually attractive method we use the discrete dipole approximation (DDA) which was originally introduced by Purcell and Pennypacker [23] and is widely used in various areas of science for analyzing the optical properties of nanostructures [8, 30], the plasmonic response of nanoparticles [17, 26], and Raman scattering intensities [33]. The DDA method considers the stationary scattering problem for an ensemble of electromagnetically coupled classical point dipoles for a given wavelength. As a result, a spectral decomposition of the scattered fields is required to treat finite pulses. The discrete nature of the scatterers in principle enables scattering simulations with atomic resolution to describe simultaneously Bragg reflections due to the local crystal structure and Mie-like scattering features due to the particle shape. Further, as the DDA concept does not require a grid, it provides access to the scattered fields at any place, including near and far fields. Despite these conceptual advantages over grid-based continuum methods, such as the finite difference time domain (FDTD) technique, the numerical effort to solve the gridless DDA problem is substantial. In their original work, Purcell and Pennypacker [23] proposed a transparent and intuitive iterative approach based on a Born series expansion that relies on the mixing of the fields from a new Born step to the old approximate solution from the previous step. The real-valued mixing parameter was chosen ad hoc and such that the solution converges.

After reconsidering this original approach, we found that there is an optimal value of the mixing parameter that leads to the best possible reduction of the average residual fields in a given iteration. We show that this optimal mixing parameter can be determined for each iteration, without additional computational effort. Two unique values for the mixing parameter can be specified, depending on whether it should be real-valued or is allowed to be complex-valued. We find that the convergence using the optimal complex-valued mixing parameter is significantly faster than that with the optimal real-valued one. The resulting complex scaling discrete dipole approximation method (CSDDA) might thus be of general interest also for applications in other scientific fields. A comparison to available benchmark results shows that the CSDDA scheme is almost as efficient as highly sophisticated approaches such as the Krylov subspace methods [7, 10, 24, 34]. Further, in difference to such state-of-the-art approaches, the complex scaling scheme is simple, easily accessible, easy to implement, and can be parallelized to a high degree.

Our analysis of the far-field diffraction patterns from icosahedral silver clusters yields the following main results. First, our comparison of single-frequency scattering patterns of \(R = 120 \text{ nm}\) clusters shows that 3D sensitivity, indicated by non-point symmetric features, emerges only at long wavelengths. While such features are hardly measurable at \(\lambda = 1.24 \text{ nm} (\hbar \omega = 1 \text{ keV})\), they become very pronounced at \(\lambda = 13.5 \text{ nm} (\hbar \omega = 92 \text{ eV})\). The details of the scattering pattern in the latter case are strongly influenced by absorption. The two main signatures from absorption are a blurring of the interference fringes and a decreased decay of the scattering signal with scattering angle. Second, we investigate the scattering pattern for a smaller icosahedral silver cluster as a function of pulse duration, assuming bandwidth-limited Gaussian pulses. We find that for soft x-ray pulses with durations in the attosecond domain the fine structure, analyzed in terms of the contrast of interference fringes, vanishes. Still, the distinct non-point symmetric streak signatures that encode the particle orientation remain robust. We show that the critical pulse duration for the loss of fine structures, when taking the fringe contrast as a reference, can reasonably be estimated with a simple model. Our analysis further allows to estimate for which pulse duration regime single-frequency scattering simulations are sufficient for an accurate description of scattering patterns.

2. Methods

In this section we recall the basic idea of the DDA and introduce the notation used throughout the manuscript. We derive the iterative method for solving the DDA problem.
with optimal mixing of intermediate solutions. Finally, we perform benchmark calculations for strongly absorbing silver spheres and compare the resolution-dependent results to Mie calculations.

2.1. Theoretical framework of the DDA approach

Within the DDA, the scattering object is represented by an electromagnetically coupled set of discrete classical point dipoles located at positions \( \mathbf{r}_j \) with strictly linear polarizability. Considering a monochromatic incident wave described by the complex electric field \( \mathbf{E}_{\text{inc}}(\mathbf{r}, t) = \mathbf{E}_{\text{inc}}(\mathbf{r}) e^{-i \omega t} \) with angular frequency \( \omega \), the trivial time dependence \( e^{-i \omega t} \) can be separated from all complex fields \( \mathbf{E}(\mathbf{r}, t) = \mathbf{E}(\mathbf{r}) e^{-i \omega t} \) due to the linearity of Maxwell’s equations. Hence, only the complex spatial amplitudes \( \mathbf{E}(\mathbf{r}) \) have to be considered. Each dipole experiences a local electric field \( \mathbf{E}_{\text{loc}} \) that induces a complex dipole moment \( \mathbf{p}_j = \alpha_j(\omega) \mathbf{E}_{\text{loc}}(\mathbf{r}_j) \) where \( \alpha_j(\omega) \) is the complex dynamic polarizability of the \( j \)th dipole. If a dipole represents an atom, the polarizability can be expressed relative to that of a free electron via the atomic scattering factor \( f^0 \) with

\[
\alpha_j = -\int_0^\infty \frac{e^2}{m_e \omega^2} \,
\]

where \( e \) and \( m_e \) are the elementary charge and the electron mass. At a given observation point \( \mathbf{r} \), the scattered field created by the polarization of the \( j \)th dipole reads

\[
\mathbf{E}_{\text{scat}}(\mathbf{r}, \mathbf{r}_j) = -\frac{\mu_0}{m_e} \int \mathbf{G}(\mathbf{r} - \mathbf{r}_j) \mathbf{E}_{\text{inc}}(\mathbf{r}_j) d^3r,
\]

where \( \mu_0 \) is the vacuum permeability and \( \mathbf{G}(\mathbf{r} - \mathbf{r}_j) \) is the dyadic Green’s function in free space

\[
\mathbf{G}(\mathbf{R}) = \frac{e^{i k \mathbf{R}}}{4 \pi R} \left[ 1 \right. \frac{1 + i k R - 1}{k^2 R^2} \mathbf{I} \\
+ \left. \frac{3 - 3 i k R - k^2 R^2}{k^2 R^2} \right] \mathbf{R} \otimes \mathbf{R} / R^2.
\]

Note that the singularity at \( R = 0 \) has been omitted. Here \( \mathbf{I} \) is the unit dyad. The local field experienced by the \( j \)th dipole can now be constructed from the sum of the incident field and the scattered fields from all other dipoles via

\[
\mathbf{E}_{\text{loc}}(\mathbf{r}_j) = \mathbf{E}_{\text{inc}}(\mathbf{r}_j) + \sum_{k \neq j} \mathbf{E}_{\text{scat}}(\mathbf{r}_j, \mathbf{r}_k) + \sum_{k \neq j} \mathbf{E}_{\text{scat,sum}}(\mathbf{r}_j) \mathbf{E}_{\text{loc}}(\mathbf{r}_k).
\]

The solution of this self-consistent set of Dyson-type equations is the central task of the DDA approach. If all local fields fulfill the above equation, the scattering problem is solved. The resulting local field felt by a test charge can then be calculated by including all dipoles in the summation on the rhs of equation (4).

For weak scattering, the local fields deviate only weakly from the incident external field \( \mathbf{E}_{\text{inc}}(\mathbf{r}_j) \), such that the pure incident field can be used as the local field on the rhs of equation (4) to a good approximation (single scattering or first order Born approximation). In general, however, multiple scattering to high order must be included. Expressed in matrix form, the full DDA problem for an \( N \)-particle system has \( 3N \) variables (three field components for each particle) and a fully populated matrix. The direct solution via matrix algebra is possible but technically inconvenient, or often just not feasible for large particle numbers because of the large size of the matrix (\( 9N^2 \) matrix elements). For the largest number of scatterers considered in the present work the coupling matrix has more than \( 10^{14} \) elements, illustrating the inability to store the full matrix with typical present computer hardware. Instead, iterative solutions are used in practice.

2.2. Iterative solution via mixing

The most intuitive strategy for the iterative solution of the self-consistent DDA problem is to start with an initial guess \( (i = 0) \) for the local electric field \( \mathbf{E}_{\text{loc}}^0(\mathbf{r}_j) = \mathbf{E}_{\text{inc}}(\mathbf{r}_j) \). The scattered fields in the \( i \)th iteration are then given by

\[
\mathbf{E}_{\text{scat,sum}}^i(\mathbf{r}_j) = \sum_{k \neq j} \mathbf{G}(\mathbf{r}_j - \mathbf{r}_k) \mathbf{E}_{\text{loc}}^i(\mathbf{r}_k)
\]

and are used to construct an improved solution for the local fields

\[
\mathbf{E}_{\text{loc}}^{i+1}(\mathbf{r}_j) = \mathbf{E}_{\text{inc}}(\mathbf{r}_j) + \mathbf{E}_{\text{scat,sum}}^i(\mathbf{r}_j)
\]

by evaluating equation (4). This procedure is equivalent to the standard Born series expansion and may be repeated until self-consistency is reached. In practice, the difference between old and new solutions should fall below a certain limit. However, the Born series diverges for most cases as has been already realized by Purcell and Pennypacker [23]. They found that convergence can be improved by applying a mixing scheme where the new solution for the local electric field, computed by a Born step, is mixed to the old values of the local fields via

\[
\mathbf{E}_{\text{loc}}^{i+1}(\mathbf{r}_j) = g_i \mathbf{E}_{\text{loc}}(\mathbf{r}_j) + e^{i+1}_\text{scat,sum}(\mathbf{r}_j) + (1 - g_i) \mathbf{E}_{\text{loc}}^i(\mathbf{r}_j).
\]

Here \( i \) denotes the iteration number and \( g_i \) the corresponding mixing parameter. The standard Born step is recovered for \( g_i = 1 \). In the original scheme by Purcell and Pennypacker the mixing parameter was set ad hoc to a real-valued constant that turned out to be sufficient to reach convergence for the considered scenarios [23]. An optimal value for \( g_i \), similar to the optimal Kalman gain in Kalman filtering, is thus desirable.

The main methodical idea of our current work is to improve the mixing scheme by using an optimal mixing parameter that results in the best possible minimization of the residuum in each iteration. Therefore, we depart from the local and scattered fields \( \mathbf{E}_{\text{loc}}(\mathbf{r}_j) \) and \( \mathbf{E}_{\text{scat,sum}}(\mathbf{r}_j) \) of the \( i \)th iteration and consider the error in the (\( i + 1 \))th iteration, i.e. after performing a mixing step with mixing parameter \( g_i \),
by the root-mean-square residuum of the individual local fields from equation (4) via

$$R^{i+1} = \sqrt{\frac{1}{N} \sum_j \left| E_{\text{loc}}(\mathbf{r}_j) + E_{\text{scat,sum}}^{i+1}(\mathbf{r}_j) - E_{\text{inc}}^{i+1}(\mathbf{r}_j) \right|^2}.$$  (8)

Obviously, the residuum vanishes for the correct solution. In order to determine the mixing parameter that yields the lowest error, the new local fields, given by equation (7), and the corresponding new scattered fields are inserted. Rearranging terms yields a simple expression for the residuum as a function of the mixing parameter

$$R^{i+1} = \sqrt{\frac{1}{N} \sum_j \left| \mathbf{X}_j^i + \mathbf{Y}_j^i \right|^2},$$  (9)

where

$$\mathbf{X}_j^i = E_{\text{loc}}(\mathbf{r}_j) - E_{\text{inc}}(\mathbf{r}_j) - 2E_{\text{scat,sum}}(\mathbf{r}_j) + \sum_{k=1}^{N} G_{jk} \left[ E_{\text{inc}}(\mathbf{r}_k) + E_{\text{scat,sum}}(\mathbf{r}_k) \right],$$

$$\mathbf{Y}_j^i = -E_{\text{loc}}(\mathbf{r}_j) + E_{\text{inc}}(\mathbf{r}_j) + E_{\text{scat,sum}}(\mathbf{r}_j).$$

Because of the basic structure of equation (9), it is now straightforward to analytically solve the optimization problem for the optimal mixing parameter. Two different cases can be considered. Requiring the mixing parameter to be a real number yields an optimal value of

$$g_{\text{opt,real}}^i = -\frac{\sum_j \left[ (\mathbf{X}_j^i) \mathbf{Y}_j^i + \mathbf{X}_j^i (\mathbf{Y}_j^i)^* \right]}{2 \sum_j |\mathbf{X}_j^i|^2}.$$  (11)

When allowing the mixing parameter to be complex, one finds

$$g_{\text{opt,complex}}^i = -\frac{\sum_j \left[ (\mathbf{X}_j^i) \mathbf{Y}_j^i \right]}{\sum_j |\mathbf{X}_j^i|^2}.$$  (12)

It should be emphasized that the determination of the optimized mixing parameter does not increase the computational effort. Note that only the terms $Z_j^{i+1}$, given by the summation in the third term on the rhs of equation (10), are unknown. Their calculation is numerically expensive (in total an $N^2$-operation) but equivalent to the calculation needed for a full Born step that has to be evaluated anyway. Though being needed only for the determination of the mixing parameter $g_{\text{opt}}^i$ in the $i$th iteration, the calculation of $Z_j^{i+1}$ already specifies the scattered field in the next iteration

$$E_{\text{scat,sum}}^{i+1}(\mathbf{r}_j) = g^i Z_j^{i+1} + (1 - g^i) E_{\text{scat,sum}}^i(\mathbf{r}_j).$$  (13)

In order to illustrate the effect of the mixing schemes with real and complex optimized mixing parameters, we study a simple test scenario. To that end, we consider two identical scatterers ($f = 30$) that are placed at $x = \pm 1$ nm ($y = z = 0$) and an incident plane wave propagating along the $z$-direction with $E_{\text{inc}}(\mathbf{r}) = E_{\text{inc}} \exp(ikz) \mathbf{e}_z$. Here $E_{\text{inc}}$ is the field amplitude and $k = 1$ nm$^{-1}$ is the considered wave number. The corresponding setup is depicted in figure 1(a).

![Figure 1](image)

For symmetry reasons, the local fields experienced by the two scatterers are identical. Figure 1(b) shows their evolution in the complex plane for a series of iteration steps performed with the real (red) and complex (blue) mixing parameters in comparison to the Born series result ($g^i = 1$, green), respectively. The results show that the standard Born series diverges. The run with the optimal real-valued mixing parameter converges slowly to the analytic solution, but does not reach convergence within 150 iterations. In contrast to that, the solution with a complex mixing parameter converges after a single iteration. This demonstrates the substantial potential of the complex mixing method, which we named the CSDDA, for DDA applications where the numerical effort is critical.

2.3. Super-particles and benchmark against the Mie solution for spherical targets

In general, the numerical effort for one iteration scales as $9N^2$, as the Green’s matrix has to be computed for each dipole–dipole interaction. Slight improvements are possible by
exploiting the symmetry of the Green’s matrix, see equation (3). However, as the quadratic scaling remains, the explicit consideration of each atom is only feasible for moderate particle numbers. Even with massively parallel computations one is limited to \( N \lesssim 10^7 \) scatterers. A convenient way to enable the effective treatment of larger systems is provided by the super-particle concept, where several actual atoms are merged to super-atoms. This approach is only applicable if atomic resolution is not needed and as long the typical dipole–dipole distance remains small enough to resolve all length scales of interest. The actual scales depend on the specific scenario and are mainly defined by the wavelength of the scattering light, the skin depth, and the characteristic geometry of the scattering object. To account for the reduced density of scatterers, the scattering factor has to be rescaled. For super-particles representing a given number of atoms, the effective scattering factor of a super-dipole is given by \( f^0 = N_{\text{at}}/N f^0 \), where \( N \) is the number of super-particles and \( N_{\text{at}} \) the number of actual atoms. The atomic scattering factor \( f^0 \) can be obtained from the complex refractive index \( n(\omega) \) via the Clausius–Mosotti relation

\[
f^0(\omega) = \frac{3m_\omega^2 e^2}{n_\omega e^2} \left( \frac{1 - n(\omega)^2}{n(\omega)^2 + 2} \right) \tag{14}\]

where \( n_\omega \) is the atomic number density in the considered region and \( \varepsilon_0 \) is the vacuum permittivity.

In the following we analyze the effect of the super-particle representation on the accuracy of the calculated scattering pattern. To this end, we consider the scattering of a plane wave (\( \lambda = 13.5 \) nm), polarized along the \( x \)-direction and propagating along the \( z \)-direction, by a silver sphere of radius \( R = 30 \) nm at solid density (atoms on a fcc grid with Wigner–Seitz radius \( r_s = 1.59 \) Å) and compare the results to the Mie solution. The atomic scattering factor from equation (14) yields \( f^0 = 23.00 - 16.52i \) for the given wavelength [14]. The resulting scattered light intensity, measured here by the scattered fraction, is analyzed in the \( x = 0 \) plane to remove trivial polarization effects and shown in figure 2(a) for varying particle numbers up to full atomic resolution. The numbers in brackets in the legend specifies the in-medium wavelength in units of the interatomic distance \( \tilde{\lambda} = \lambda/|n|d \) and provides a measure for the spatial resolution. Here \( d \) is the average dipole–dipole distance for a given super-particle sampling and \( n \) is the refractive index. The following conclusions can be drawn from the results. First, at full atomic resolution (\( \tilde{N}_{\text{at}} = 6.7 \times 10^6 \)) the CSDDA results perfectly match the Mie results, demonstrating the capability of the CSDDA method to model light scattering for strongly absorbing materials with atomic resolution. Second, sufficient accuracy for all considered scattering angles can be obtained.
down to particle numbers that resolve the wavelength with about 15 points, see orange curve in figure 2(a). Third, for even smaller particle numbers the CSDDA results begin to deviate significantly from the Mie solution, with the most pronounced errors occurring under large scattering angles. As the scattering signal under large angles is mainly determined by small-scale characteristics, it is most strongly affected by a too coarse grained super-particle representation. To quantify the effect of the super-particle sampling, we calculated the residual approach to reach a residuum below $10^{-5}$ with the quasi-minimal residual approach [34] and 90 iterations with our method. The presented mixing approach is very appealing as it is easy to implement, can be explained within the physical picture of multiple scattering and can by parallelized to a high degree. Nevertheless, it should be noted that the CSDDA method does not always converge—a problem that is common to iterative DDA methods.

3. Results and discussion

In the following we present CSDDA results for single shot x-ray imaging of nonspherical icosahedral silver clusters in the hard- and soft-x-ray regime. These systems are of particular interest due to an uneven number of symmetry axes, which leads to non-point symmetric scattering patterns. In the first part we will show that real 3D information, such as shape and orientation of the clusters, can only be mapped to the scattering images in the soft x-ray regime, where large-angle scattering contributions are experimentally accessible. In the second part we investigate the time-resolution limits of imaging of dynamic processes with ultrashort pulses. In particular we evaluate the influence of the spectral bandwidth required for a given pulse duration on the visibility of characteristic features in the scattering images and present a simple analytic estimation for the critical pulse lengths.

3.1. Influence of the x-ray wavelength

As a first application we investigate the scattering of hard x-ray light ($\lambda = 1.24$ nm) by a large $R = 120$ nm icosahedral

![Figure 3.](image-url)
silver cluster \((N = 6.7 \times 10^5)\). The corresponding simulation setup is sketched in figure 3(a). Note that the scattered fields are calculated on a spherical detector to achieve a scattering-geometry independent representation. The resulting 2D scattering image is shown in figure 3(b) depicting the relative scattered fraction as a function of the components \((q_x, q_y)\) of the transfer momentum. The modulus of the latter is given by \(q = \frac{4\pi}{\lambda} \sin \frac{\theta}{2}\). While the calculations can predict the scattered signal with arbitrarily high resolution, the accessibility of scattering data in experiments is limited to a given dynamic range, e.g., due to limited x-ray peak intensity, limited detection efficiency, noise, and photon statistics. To account for such practical constraints, we consider that an effective dynamic range of five orders of magnitude can be resolved, see color bar in figure 3(b). According to Porod’s law the envelope of the scattering intensity decreases with \(q^{-4}\), hence, the scattering signal is only visible in a limited range of transfer momenta. In the limit of short wavelength radiation this corresponds to small scattering angles, where the scattering pattern is essentially determined by the projection of the scattering object onto the plane perpendicular to the propagation direction of the x-ray light and exhibits point-symmetry [3]. As a result, no 3D information can be inferred from such images. The data shown in figure 3(b) strongly supports this conclusion. For very small scattering angles, in the center of the image, a spherical Mie-like pattern is observed that slowly transforms into a ten-fold symmetry with increasing angle. Only in the outermost visible regions, the development of a five-fold symmetry is discernable. To access the thus far hidden wide-angle scattering signal, its intensity needs to be drastically increased. Because of Porod’s law, the scattering signal can be measured only up to a critical transfer momentum \(q_{\text{crit}}\). As the corresponding critical scattering angle scales roughly as \(\Theta_{\text{crit}} \propto \lambda q_{\text{crit}}\), a moderate increase of the wavelength makes wider angles accessible. Figures 4(a) and (b) show the scattering patterns for the same scenario for a wavelength of \(\lambda = 13.5\) nm as predicted within the first Born approximation and with full CSDDA including absorption. In contrast to the short wavelength results, the scattering images show a clear five-fold symmetry with five pronounced streaks. This additional information can be utilized to extract important properties such as cluster size, shape and orientation in a corresponding single-shot FEL experiment by comparison to theoretical calculations [3]. Note that internal structures (e.g. core–shell systems, voids) can only be resolved if these structures create significant signatures in the scattering pattern.

Besides element-specific resonances, absorption is typically much larger in the soft x-ray regime, precluding a meaningful description within the first Born approximation. The importance of absorption is substantiated by the comparison of the calculated patterns in figures 4(a) and (b). Though the overall patterns are similar in both cases, three major differences can be identified. First, the fine structure between the streaks is strongly modified. Second, the slope of the intensity decay with increasing scattering angle is smaller in the full calculation and leads to a relative amplification of the signal at higher scattering orders. Third, the fringes on the streaks show substantial blurring. Figure 4(c) shows an experimental single-shot scattering image obtained by Barke et al at FLASH [3]. The image corresponds to a silver cluster of similar size \((R \approx 120\) nm\) and has been taken with a pulse of central wavelength \(\lambda = 13.5\) nm and pulse duration \(\tau \approx 100\) fs. To compare the experimental data, which has been obtained on a flat detector with distance \(D\) to the scattering object, with the simulation data computed on a spherical detector the scattering intensity was scaled by a factor of...
The determined fine structure, the pronounced streaks, and the blurring of the fringes on the radial streaks are very similar to the full CSDDA calculation image (figure 4(b)). Remaining discrepancies in the fine structure are attributed to a non-perfect icosahedral shape of the particle in the experiment. The Born approximation result, on the other hand, fails qualitatively to describe the experimental pattern, highlighting the necessity to include absorption in the theoretical modeling of scattering images. Most importantly, the blurring of the fringes can be explained by absorption and is not necessarily a marker for transient target expansion.

3.2. Influence of a finite spectral bandwidth

A major long-term goal of FEL science is to analyze fast processes with single-shot x-ray imaging methods, for example, to better understand the functionality of large biomolecules. In principle, even the visualization of ultrafast processes has been considered, such as laser induced plasma expansion or attosecond nonlinear plasma waves [22, 31]. To achieve the necessary time resolution, ultrashort x-ray pulses with durations in the attosecond range would have to be applied. The downside of such pulses is the corresponding large spectral bandwidth, as the contributions from different frequencies will overlap and probably hide characteristic features in the scattering images. In the following we analyze the effect of the pulse duration on the visibility of such features systematically.

In the limit of linear response, the scattering image produced by a broadband pulse can be obtained by summing the intensities of the frequency dependent scattering images according to their spectral weight. For each spectral component, the corresponding wavelength-dependent atomic scattering factors have to be applied. Here we consider bandwidth-limited Gaussian pulses and measure the duration as the full-width-half-maximum of the intensity envelope. Figure 5 shows calculated two-dimensional scattering images for an icosahedral silver cluster (\(R = 64.5 \text{ nm}\)) for selected pulse durations at a center wavelength of \(\lambda = 13.5 \text{ nm}\). The images are plotted as a function of the scattering angle. The indicated components of the momentum transfer correspond to the center wavelength. The continuous-wave solution shown in figure 5(a) serves as a reference scenario providing the best possible contrast for the given center wavelength. Comparing it to the result obtained for a pulse of duration \(\tau = 1 \text{ fs}\) shows no noticeable variations (see figures 5(a) and (b)). For even shorter pulse widths the fine structure in the scattering image, such as the Mie-like fringes, start to blur and vanish completely for pulse durations of the order of \(\tau = 50\) as for the considered scenario (see figure 5(d)). However, the general shape of the diffraction pattern remains unchanged even for the shortest pulse. As a result, while the general shape and orientation of the particle are likely to be accessible even with extremely short pulses, fine details required for example for the quantitative analysis of the particle size are not.

To analyze the effects of the pulse length on the visibility of the fine structure systematically, the blurring effect needs to be quantified. Therefore, we define a simple measure as the ratio of the signal intensities at scattering angles corresponding to the maximum (\(\Theta_{s\text{ max}}\)) and preceding minimum (\(\Theta_{s\text{ min}}\)) of a certain Mie order \(s\); the two angles are taken from the cw-solution. As a result, for a given pulse duration \(\tau\) the fringe contrast \(\gamma_s(\tau)\) is defined by

\[
\gamma_s(\tau) = \frac{I_s(\Theta_{s\text{ max}})}{I_s(\Theta_{s\text{ min}})}.
\]

The determination of the fringe contrast is illustrated in figure 6(a) for the example of an icosahedral silver cluster imaged by a \(\tau = 100\) as pulse (\(\lambda = 5 \text{ nm}\) and \(kR = 20\)). Note that in our definition a fringe contrast of unity corresponds to equal signal under the angles for which the fringe minimum and maximum are expected and therefore marks the pulse length for which fringes can no longer be easily resolved.

In figure 6(b) the pulse length dependence of the fringe contrast is analyzed systematically for two different wavelengths (\(\lambda_1 = 5 \text{ nm}\) and \(\lambda_2 = 13.5 \text{ nm}\)). Here icosahedral silver clusters with \(kR = 20\) are considered. The following conclusions can be drawn from the analysis. (i) Application of
shorter wavelengths, i.e. higher photon energies, provides significantly higher contrast for all considered pulse lengths. This can be mainly attributed to the additional blurring introduced by the stronger absorption at longer wavelengths. Therefore, as long as no resonances are encountered, a higher contrast can be expected for higher photon energies. (ii) The contrast decreases with higher scattering orders, independent of the applied wavelength. (iii) The presented data reveals that the maximum contrast is already reached for pulse durations of the order of 1 fs. As a consequence, it is sufficient to consider the cw-solution for pulses longer than that. (iv) The critical pulse durations, where \( kR = 20 \) and the respective minima are not visible any longer, increase with wavelengths. This trend reflects the increase of the relative spectral bandwidth with wavelength at fixed pulse duration and suggests that higher photon energies have to be applied in order to resolve fine scattering features with high temporal resolution. This, however, is not always desirable as it simultaneously limits the accessible scattering angles, see discussion in section 3.1. To facilitate the search for a satisfactory trade-off between resolution and angular range, we present a simple analytic estimate for the critical pulse length.

In the limit of vanishing absorption the position of the \( s \)th maximum in the Mie scattering pattern is approximately given by

\[
qR = \pi(s + 1).
\]

To obtain the corresponding scattering angles, we assume that \( \Theta \ll 2\pi \) which leads to

\[
\theta^c_{\text{max}} = \frac{\pi(s + 1)}{kR},
\]

where \( k \) is the wave number corresponding to the center of the frequency spectrum. Different parts of the spectrum will generate fringes at different positions, e.g. for higher frequencies the maxima will be shifted to smaller angles and vice versa. As the criterion for vanishing contrast we now define the point where the maximal signal of scattering order \( s \) generated by the high-frequency component of the spectrum \((k + \Delta k/2)\) overlaps with the maximum of order \( s - 1 \) generated by the low-frequency component of the spectrum \((k - \Delta k/2)\), i.e. where they occur under the same scattering angle. This definition yields the relation

\[
\frac{k}{\Delta k} = s + \frac{1}{2}.
\]

Note that the left-hand side is the inverse of the relative spectral bandwidth. This shows that a higher absolute bandwidth, and thus shorter pulses, are affordable at high photon energy. The pulse width is connected to the spectral bandwidth via

\[
\frac{\Delta \omega}{2\pi} \tau = \text{TBP} = \frac{c\Delta k}{2\pi} \tau,
\]

where the time-bandwidth product TBP accounts for the specific pulse shape. Inserting equation (19) into (18) yields the final expression for the critical pulse duration at which the fringe contrast of a certain scattering order will be lost

\[
\tau_{\text{crit}} = \frac{\lambda}{c} \text{TBP} \left( s + \frac{1}{2} \right).
\]

This simple estimate correctly reproduces the trends observed from the full CSDDA calculations, i.e. that the critical pulse duration increases for longer wavelengths and higher

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Figure 6. (a) Cuts through scattering patterns of icosahedral silver cluster with \( kR = 20 \) (same orientation as in figure 5) at central wavelength \( \lambda = 5 \) nm. The data is sampled in the \( y = 0 \) plane (along a streak, see figure 5) and compares the cw solution with the result for a short pulse with \( \tau = 100 \) as. Colored symbols indicate the angles used for the calculation of the fringe contrast for scattering order \( s = 4 \). (b) Evolution of fringe contrast, measured as in (a), as a function of pulse duration for two different central wavelengths (\( \lambda = 5 \) and 13.5 nm) and selected scattering orders (as indicated). The employed wavelength-dependent atomic scattering factors were taken from [14].
scattering orders. Estimated critical pulse durations for bandwidth limited Gaussian pulses (TPB = 0.4413) are indicated by arrows in figure 6(b) for each scattering order. Though the exact shape of the considered clusters is not taken into account, the simple model shows reasonable agreement with the trends observed in the full CSDDA results, justifying its applicability for a rough estimate.

4. Conclusion

In conclusion, we were able to implement an improved optimized mixing scheme to solve the DDA problem. This CSDDA is very intuitive, efficient and can be parallelized to a high degree. In the investigated regime, the convergent speed is comparable to Krylov subspace methods. We applied our approach to better understand the influence of imaging pulse wavelength and pulse duration on the diffraction pattern obtained in single-shot x-ray imaging experiments. With respect to wavelength, the numerical results revealed that 3D information about the target can only be retrieved from the scattering image for radiation in the soft x-ray regime. In addition to that, we could show that agreement with the experiment can only be found when including absorption, and that a blurring of the interference structure results from absorption and not necessarily from an expansion of the cluster due to the interaction with the laser. Regarding the pulse duration, we found that for durations above 1 fs the scattering image converges to the continuous-wave limit. For extremely short pulse durations below 100 as, the overlap of characteristic interference features from the different components of the wide pulse spectrum destroys the visibility of detailed structures in the scattering image. In summary, high photon energies show a better fringe contrast for all pulse durations, and therefore are preferable for ultrafast dynamic imaging. On the other hand, higher photon energies narrow down the range of accessible scattering angles, thus making it more difficult to extract 3D information from the target. A simple analytical estimate is given to determine the best trade-off between these two competing effects. It should be noted that the assumption of linear response in the current study becomes increasingly critical for ultrashort pulses assuming a fixed pulse fluence. In fact, indications for dynamical changes of the optical properties due to nonlinearities have been reported in diffraction experiments on Xe clusters [6]. A rigorous treatment of nonlinear effects requires the explicit description of the scattering process in the time domain, which is possible with appropriate numerical models, e.g. the microscopic particle-in-cell approach [21, 31]. However, for clarity and comparability the current study is restricted to the linear response regime. The full inclusion of nonlinear effects therefore remains a challenging topic for future studies.

Acknowledgments

We thank Ingo Barke for stimulating discussions. Financial support from the Deutsche Forschungsgemeinschaft within SFB 652/3 and computer time provided by the North-German Supercomputing Alliance (HLRN) within projects mvp00004 and mvp00009 are gratefully acknowledged.

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