The T-Matrix method in electron energy loss and cathodoluminescence spectroscopy calculations for metallic nano-particles

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Abstract
In this paper, we present the application of the T-Matrix method (TMM) for the calculation of Electron Energy Loss Spectra (EELS), cathodoluminescence spectra (CLS) and far-field patterns produced by metallic nano-particles. Being frequently used in electromagnetic scattering calculations, the TMM provides an efficient tool for EELS calculations as well and can be employed, e.g. for the investigation of nano-antennas.

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1. Introduction
Electron Energy Loss Spectroscopy (EELS) has recently been used to study the electromagnetic excitations of single metallic nano-particles and systems thereof [1]. Typically, these experiments are carried out in a Transmission Electron Microscope [2], where fast electrons (50–300 keV kinetic energy) are directed at the target particle in a tightly focused beam. The incident electrons cause charge oscillations in the particle, leading to the excitations of surface plasmons. This induced field acts back onto the electrons, which leads to characteristic losses in the order of several electron volt. A part of these induced fields may be re-radiated in the form of propagating electromagnetic waves, a process termed cathodoluminescence (CL) [3,4]. Here, not only the total amount of radiation, but also the angular distribution of the emission is of interest and can be measured in experiments [5]. In Electron Energy Gain Spectroscopy experiments [6], an additional light pulse can be used to excite the particle leading to an increased electron energy. This technique was shown to have an improved energy resolution as compared to conventional EELS experiments [7]. We will, however, focus on EELS and CL in the following. The interpretation of EEL and CL spectra requires the computation of the induced near-field and also the scattered far-field. The T-Matrix method (Transition-Matrix method, TMM) is well suited for these calculations and provides an efficient tool, not only to calculate the spectra of single particles of almost arbitrary shape, but also systems thereof.

We will describe the TMM in Section 2 before showing how the EEL spectra can be calculated in Section 3. Next, the method will be applied to a single spherical particle in Section 4.1. Then, we will simulate EEL spectra, CL spectra and far-field patterns for a prolate spheroidal particle in Section 4.2 and for a sphere dimer in Section 4.4 before concluding the paper.

2. T-Matrix method
The T-Matrix method (TMM) is an exact semi-analytical method for solving the problem of light scattering by small particles. The theory of the method was introduced by Waterman [8] and outlined many times. A detailed review and study can be found in the books by Mishchenko [9] and Doicu et al. [10] and also in the reviews by Mishchenko et al. [11,12].

The TMM solves the boundary-transmission problem for a scatterer occupying the volume $V$ illuminated by a monochromatic electromagnetic wave. The incident field $E_{\text{inc}}$ (illumination) and scattered field $E_{\text{scat}}$ (perturbation of illumination caused by the scatterer) are expanded into spherical vector wave functions (SVWF) [10]

\[ E_{\text{inc}} = \sum_{n=1}^{\infty} \sum_{m=-n}^{n} a_{nm} M_n^m(k_r r) + b_{nm} N_n^m(k_r r), \]

where $M_n^m$ and $N_n^m$ are the complex spherical vector wave functions, $k_r$ is the wave number of the incident light, and $r$ is the position vector.

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The surface fields in (10) are expressed in suitable basis functions, e.g., conventionally, these are regular SVWF
\[ E_{scat}(r) = \sum_{n=1}^{\infty} \sum_{m=-n}^{n} p_{nm}M_{nm}(kr) + q_{nm}N_{nm}(kr). \]

Applying the field expansion in (1) and the Green function expansion in terms of SVWF yields two linear systems binding the coefficients \(a_{nm}, b_{nm}\) and \(f_{nm}, C_{nm}\). The TM is computed from these equations. For spherical particles, the solution of the NFM is well-known and converges to the Mie solution [15] as demonstrated by Hill and Barber [16].

The computation of the EEL spectra of spherical particles was already studied using the Mie theory [17]. Particularly, the expansion coefficients for the electric field of a moving electron were obtained. Adapted to our set of basis functions, which differs from the one used by García de Abajo [17], they read as

\[ a_{nm} = -4\pi ikv \frac{mA_{nm}}{n(n+1)} K_0 \left( \frac{r}{\alpha} \right), \]
\[ b_{nm} = -2n \frac{B_{nm}}{c} \left( \frac{r}{\alpha} \right)^2, \]
\[ A_{nm} = \sqrt{\frac{2n+1}{\pi}} \frac{A_{nm}}{n(n+1)} \frac{m!}{(m+1)!}, \]
\[ B_{nm} = \left( \frac{C_{nm}}{r} \right) \left( \frac{C_{nm+1}}{r} \right), \]

with \(v = 1/\sqrt{1-u^2/c^2}\), the modified Bessel function \(K_0\), the impact parameter \(b\) and \(C_{nm+1/2}\) being the Gegenbauer polynomial, cf. Appendix C of Ref. [1]. This enables us to use the moving electron as an excitation within the TMM formalism, as long as the electron trajectory remains outside the smallest sphere circumscribing the scatterer.

Taking into account recent extensions of the method mentioned in [18], the TMM allows us to treat isotropic/anisotropic solid/layered/inhomogeneous particles of almost arbitrary shape. Strongly elongated particles can accurately be treated using the null-field method with discrete sources (NFM-DS) [18], where several SVWF expansions with different origins are used for the representation of the internal and surface fields (11). Using a multiple-scattering approach, the TM of a system of particles can be calculated from the TMs of the individual particles, cf. Section 4.4. With all these capabilities, the method allows us to treat the particle shapes typically used in EELS experiments like nano-rods and spheres [19], rounded triangles [20] or dimers of layered spheres [21], and makes the TMM extremely well suited for the simulation of such EEL and CL spectra.

3. Calculating the EEL and CL spectrum

We assume a single electron with charge q moving in the z-direction along the trajectory \(r(t) = r_0 + vt\) as depicted in Fig. 1. On approaching the target particle, it will interact with the particle's electrons, which will cause an induced electric field. As in the Mie theory, we will term this induced field \(E_{scat}\).

This field acts back onto the incident electron and leads to an energy loss that is given by the work done against the induced field. Defining the probability that the electron loses a certain amount of energy \(he\) as \(P(\omega)\), we can also express the loss as
The density of states projected in the direction of the trajectory [22], solution of this problem possible in the first place, is well established in EELS simulations [1]. Also, it can be related to the photonic local density of states projected in the direction of the trajectory [22], albeit not necessarily in a straightforward manner [23].

The evaluation of \( P(\omega) \) for a given frequency \( \omega \) is now done by plugging in the SVWF expansion of the scattered field (2) into (14). The scattered field coefficients can be calculated from the incident field coefficients using the TM according to (9). We therefore arrive at the central expression for our analysis

\[
P(\omega) = \frac{q}{\pi \hbar \omega} \sum_{n=1}^{\infty} \sum_{m=-n}^{n} \Re \left[ f_{mn}^{\text{M}} Y_{mn}^{\text{M}} + \tilde{g}_{mn} Y_{mn}^{\text{N}} \right],
\]

with

\[
f_{mn}^{X} = \int_{-\infty}^{+\infty} dt \, e^{-i k t} \cdot X_{mn}^{X}(kr, t),
\]

where \( X \) is either \( \mathbf{M} \) or \( \mathbf{N} \). The above integrals can be evaluated analytically and yield expressions similar to those in Eqs. (12).

The probability for the emission of a photon from the scatterer, called cathodoluminescence (CL), can be calculated by integrating the time-averaged Poynting vector over a closed surface around the scatterer. This evaluates to [17]

\[
P_{\text{rad}}(\omega) = \frac{1}{4 \pi^2 k} \sum_{n=0}^{\infty} \sum_{m=-n}^{n} n(n+1) |f_{mn}|^2 + |g_{mn}|^2.
\]

4. Results

In this section, we will present EEL and CL spectra (denoted as EELP and CLS, respectively) obtained for different particle shapes using the TMM. The permittivity of the target particle is described by a Drude model

\[
\varepsilon(\omega) = 1 - \left( \frac{\omega_p^2}{\omega(\omega + i \gamma)} \right),
\]

with a plasma energy of \( \hbar \omega_p = 9.073 \text{ eV} \) and a damping constant \( \gamma = 0.071 \text{ eV} \), which approximates the permittivity of gold.
The incident electron travels along the z-direction at \( v = 0.29c \) (corresponding to 50 keV initial kinetic energy). Being a frequency-domain method, the TMM could also handle arbitrary frequency dependent permittivities, like experimental values. Using the Drude model, we are able to compare the results with those obtained from a time-domain method, specifically we have employed the discontinuous Galerkin time-domain method (DGTD) [24] for comparison and have seen a good agreement.

4.1. Spherical particle

In the case of spherical particles, the T-Matrix is diagonal in the sense that

\[
T_{11}^{mn, mr} = T_{n}^{1} \delta_{mn} \delta_{mr},
\]

\[
T_{22}^{mn, mr} = T_{n}^{2} \delta_{mn} \delta_{mr},
\]

and of course, \( T_{n}^{1} \) and \( T_{n}^{2} \) are the coefficients encountered in the Mie theory. We calculate the EELP (14) and CLS (17) for a spherical particle of 10 nm radius and the permittivity given in Eq. (18). The impact parameter is \( b = 10.5 \) nm. The basic setup is sketched in Fig. 1.

Fig. 2 shows the EELP and CL spectra for several maximum expansion orders \( N_{r} \). Due to the low damping, i.e. the small value of \( \gamma \) in (18), the first few multipole contributions to the EELP are well separated and already small values of the maximum expansion order \( N_{r} \) suffice for convergence. The higher order multipoles are closely spaced and give rise to a broad peak at the end of the spectrum. Here, increasing the maximum expansion order \( N_{r} \) does not give any further information in terms of peak positions, etc. In contrast to the CL spectrum, that is dominated by the dipole contribution, the EEL spectrum has contributions from several multipoles that do not emit radiation, but are bound to the sphere surface.

4.2. Spheroid

We now choose the target particle to be a prolate spheroid with an aspect ratio of 1:1.5 and the axes are chosen such that the spheroid has the same volume as a 15 nm sphere. This results in semi-axes \( r_{x} = 19.66 \) nm, \( r_{y} = r_{z} = 13.10 \) nm and the impact...
parameter is \( b = 20.16 \, \text{nm} \), which are lateral extends similar to those of the dimer in the next section. The spheroid possesses axial symmetry, which means that the integrals (10) reduce to line integrals over the generatrix of the spheroid. As a consequence, in its local coordinate system, the TM of an axial particle is diagonal in the sense that

\[ T_{m,r,0}^{ij} = T_{mn,0}^{ij}, \quad (20) \]

which additionally reduces the computational cost. Once generated, the particle TM can be rotated arbitrarily by using the transformation properties of the SVWF under rotations [10]. This procedure allows for an efficient treatment of arbitrarily aligned particles with axial symmetry as the prolate spheroid. Note that particles of more general shape can also be treated by evaluating the surface integrals in (10) numerically using triangular surface patches. Fig. 3 shows results for the prolate spheroid as sketched in Fig. 1. To check for convergence, we show spectra for different maximum SVWF expansion orders \( N_r \). We see that increasing \( N_r \) beyond 15 only leads to changes at the high-frequency end of the EEL spectrum, while the other peaks have converged. The CL spectrum indicates that for the spheroid, the signal also has significant contributions from the higher order multipoles. To further understand the spectra, we will now calculate the far-field patterns of the excited modes.

4.3. Far-field pattern—directive emission

EEL spectra have been measured in experiments for a lot of different particles and recently also an angle-resolved CL measurement was reported by Coenen et al. [5]. Thinking of these particles as electron-driven nano-antennas raises the question of the far-field pattern of the emitted radiation \( \mathbf{E}_{\nu,\omega}(\theta, \phi) \). Using the TMM, these patterns can readily be calculated by using the far-field expressions of the SVWFs in expansion (2). Fig. 4 shows selected patterns for the prolate spheroid at frequencies indicated in Fig. 3 along with a sketch of the particle geometry and orientation in the coordinate system.

Pattern 4(b) exhibits the characteristics of a dipole with moment along the x-axis, i.e. the long axis of the spheroid. Pattern 4(d) resembles a dipole being aligned along the z-axis, i.e. the short axis parallel to the electron beam and is located at a higher frequency than 4(b). This behaviour is well known for spheroids in optical spectroscopy where the two different resonances can be addressed with light that is linearly polarized parallel to their corresponding axes. While pattern 4(b) is almost symmetric, the asymmetry is more pronounced in pattern 4(d) with more radiation being emitted to the far side of the spheroid in the negative x-direction and in the positive z-direction. This indicates a directivity of the spheroid nano-antenna and is due to the asymmetric excitation by the electron.

Pattern 4(c) has, as suggested by the CL spectrum in Fig. 3, contributions from peak (c) of dipolar characteristic. In addition, pattern 4(c) shows that there are also quadrupolar contributions that are preferably emitted to the far side of the spheroid.

4.4. Sphere dimer as a nano-antenna

In antenna technology, several components can be combined to increase the directivity of an antenna system, and this idea was also discussed in Ref. [5]. In this section, we want to discuss one of the most basic systems of antennas – a sphere dimer – using the TMM. The TM of a particle given in a certain coordinate system can be transformed to another coordinate system by considering the addition theorem for the SVWF, cf. Appendix B of Ref. [10]. Combining the translation of the particle TMs with a multiple scattering formalism, we are able to construct the TM of a system of particles from those of the individual particles, see also Ref. [25]. This enables us to construct the TM for the sphere dimer. In their local coordinate system, the TMs of the spheres are diagonal and can be obtained analytically as described above. Using the translation technique, we can shift the local coordinate systems along the x-axis by a distance of \( d = \pm 10.5 \, \text{nm} \) to obtain the shifted matrices \( T_x \) and \( T_y \). Then, the TM of the particle system in the global coordinate system is obtained using multiple scattering theory and evaluates to

\[
T_0 = T_{0x} + (T_{-1} - T_{1})^\dagger T_z (T_{-1} + T_{1})^{-1} + T_{10} + T_{-10}^\dagger T_{12} T_{-12}^{-1} + T_{21} T_{-21}^{-1} T_{13} T_{-13}^{-1},
\]

where \( T_{abc} \) are the matrices translating the regular and radiating SVWFs, respectively, from coordinate system \( i \) to \( j \) as described in Ref. [10]. Finally, we obtained the T-Matrix of a dimer consisting of spheres with a radius \( r = 10 \, \text{nm} \) and a gap of \( d = 1 \, \text{nm} \).

Fig. 5 shows the EEL and CL spectrum for the dimer for different SVWF expansion orders \( N_r \). Due to the coupling between the two spheres, we now observe a resonance at approx. 0.41 \( \omega_p \), that is lower than the dipole resonance of the single sphere at approx. 0.56 \( \omega_p \). This behaviour is well known for dimers [21]. With regard to the CL spectrum, we have a significant signal in the frequency range [0.5 \( \omega_p , 0.65 \omega_p \)], whereas this is not present in the case of the single sphere. For the spheroid, we have seen some CL yield in that range, cf. Fig. 5, however, the peak amplitudes were small compared to the dipole peak. For the sphere dimer, the peaks in that range show an amplitude comparable to that of the dipole peak. To gain more insight, Fig. 6 shows the far-field patterns at the frequencies marked in Fig. 5.

The patterns 6(b) and 6(c) show a dipolar characteristic with the dipole moment being aligned parallel to the x-axis. Pattern 6(d) also resembles a dipole field with dipole moment parallel to the z-axis and a slight preference for emission towards the excitation side in the x-direction. Pattern 6(e) shows a high directivity towards the positive x- and positive y-direction and also has the largest maximum amplitude of the patterns. Pattern 6(f) has a dipolar characteristic with moment tilted 40° to the z-axis and preferred emission to the far side of the dimer, however at a relatively low maximum amplitude.
We have seen patterns similar to those in Fig. 6 already for the spheroid in Fig. 4. However, in the latter case, the far-field was dominated by the dipole resonance of the spheroid. For the dimer, the patterns have a similar contribution to the far-field, however, the pattern with high directivity $\gamma(e)$ also possesses the largest maximum amplitude. Therefore, the sphere dimer can be considered as a nano-antenna with increased directivity at the frequency $\omega = 0.601\omega_p$.

5. On efficiency and computation time

Before concluding, we shortly want to comment on the efficiency of our approach, especially in comparison to other methods. One of the most frequently encountered methods for EELS simulations is the boundary element method (BEM) [26]. It transforms Maxwell’s equations into a self-consistent set of integral equations over the particle surface involving the scalar and vector potential both outside and inside the particle. Discretizing the particle surface with $N$ surface patches, one arrives at $8N$ unknowns to solve for, either directly or iteratively. As $N$ can be as high as several 1000’s, the method can be computationally demanding.

Another method that was adapted to EELS is the Discrete Dipole Approximation (DDA) [27]. It approximates the scatterer by an array of coupled dipoles (i.e. SVWF expansion of order $N_r = 1$) and for a given external field calculates a self-consistent arrangement of the dipole moments. Especially for metallic nanoparticles, a huge number of dipoles has to be used in order to get an accurate solution. This renders the method rather inefficient.

To determine the T-Matrix for a given expansion order $N_r$, two matrices of dimension $2N_r(2+N_r)$ have to be constructed, the elements of both are given by integrals over the particle surface involving SVWFs. Finally, one of the matrices has to be inverted...
and the product of these two matrices is the T-Matrix. As an example, for $N_r = 12$ the size of the matrices is only $336 \times 336$.

On a 2.4 GHz desktop computer with 4-core CPU, the calculation of the entire spectrum for the sphere took 0.02 s. Exploiting the axial symmetry, the spheroid calculation with $N_r = 15$ required 0.8 s per frequency including the rotation of the SVWFs. In the case of the dimer, the TMs are easily calculated, however, the translation matrices have to be calculated and the multiple scattering problem has to be solved for each frequency. For a large number of SVWFs, e.g. $N_r = 12$, this sums up to 1.6 s per frequency. The computation time for particles discretized with triangular surface patches is longer but remains in the order of 30 s per frequency. Thus, we consider the method to be extremely efficient.

6. Conclusion and outlook

We have presented an implementation of the T-Matrix method that was used to obtain EEL and CL spectra and also emission patterns for metallic nano-particles. The method is fast and versatile as it can handle particles of almost arbitrary shape, including strongly elongated ones. For particles with axial symmetry, it is particularly efficient. This suggests that the method can be used in optimization of structures for specific properties. Furthermore, the TMs can be stored and re-used for different excitation fields and unlike time-domain methods, the TMM is not restricted to permittivities of analytical form. The inclusion of a substrate is possible within the TM formalism and together with the capabilities outlined in Section 2, the TMM might be of value in the interpretation of EELS and CLS experiments. Improving the method's applicability concerning the allowed trajectories will be the future work.

Finally, using the T-Matrix method, we have shown that a dimer of nano-spheres can act as an electron-driven nano-antenna having studied the far-field patterns of the emitted radiation.

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