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

Christian Matyssek [a,c,*], Vladimir Schmidt [b], Wolfram Hergert [c], Thomas Wriedt [d]

[a] Max Planck Institute of Microstructure Physics, Weinberg 2, 06120 Halle, Germany
[b] University of Bremen, Process and Chemical Engineering, Badgasteiner Str. 3, 28359 Bremen, Germany
[c] Martin Luther University, Institute of Physics, von-Seckendorff-Platz 1, 06120 Halle (Saale), Germany
[d] Institut für Werkstofftechnik, Badgasteiner Str. 3, 28359 Bremen, Germany

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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.

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 $\mathbf{E}_{inc}$ (illumination) and scattered field $\mathbf{E}_{scat}$ (perturbation of illumination caused by the scatterer) are expanded into spherical vector wave functions (SVWF) [10]

$$\mathbf{E}_{inc} = \sum_{n=1}^{\infty} \sum_{m=-n}^{n} a_{mn}\mathbf{M}^1_{mn}(k_s\mathbf{r}) + b_{mn}\mathbf{N}^1_{mn}(k_s\mathbf{r}), \quad (1)$$

* Corresponding author at: Max Planck Institute of Microstructure Physics, Weinberg 2, 06120 Halle, Germany.
E-mail address: matyssek@mpi-halle.de (C. Matyssek).

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$$\mathbf{E}_{scat} = \sum_{n=1}^{\infty}\sum_{m=-n}^{n} f_{mn}\mathbf{M}^3_{mn}(k_s\mathbf{r}) + g_{mn}\mathbf{N}^3_{mn}(k_s\mathbf{r}), \tag{2}$$

where

$$\mathbf{M}^{1,3}_{nm}(k\mathbf{r}) = \frac{1}{\sqrt{2n(n+1)}}\nabla u^{1,3}_{nm}(k\mathbf{r}) \times \mathbf{r}, \tag{3}$$

$$\mathbf{N}^{1,3}_{nm}(k\mathbf{r}) = \frac{1}{k}\nabla \times \mathbf{M}^{1,3}_{nm}(k\mathbf{r}), \tag{4}$$

$$u^{1,3}_{nm}(k\mathbf{r}) = z^{1,3}_n(kr)P^{|m|}_n(\cos\theta)e^{jm\phi}, \tag{5}$$

$$z^{1,3}_n(kr) = \begin{cases} j_n(kr) & \text{for } z^1_n(kr), \\ h^{(1)}_n(kr) & \text{for } z^3_n(kr), \end{cases} \tag{6}$$

$$P^m_n(\cos\theta) = \sqrt{\frac{2n+1}{2}\frac{(n-m)!}{(n+m)!}}\hat{P}^m_n(\cos\theta), \tag{7}$$

$$\hat{P}^m_n(x) = \frac{1}{2^n n!}(1-x)^{m/2}\frac{\partial^{n+m}}{\partial x^{n+m}}(x^2-1)^n, \tag{8}$$

where $k_s = \sqrt{\epsilon_s}\omega/c$ is the wave number in the ambient medium, j_n and h_n are the spherical Bessel and Hankel functions; a_{mn}, b_{mn} and f_{mn}, g_{mn} are the expansion coefficients of the incident and scattered field, respectively. The superscript '1' denotes regular and the superscript '3' radiating fundamental solutions of Maxwell's equations in $\Re^3\backslash\{0\}$. Note that $u^{1,3}_{nm}(k\mathbf{r})$ are the fundamental solutions of the scalar Helmholtz equation. In actual calculations, the sum over the index n has to be truncated by the number N_r, whose value depends on the desired accuracy. The expansion coefficients are related by the T-Matrix (Transition-Matrix, TM)

$$\begin{pmatrix} f_{mn} \\ g_{mn} \end{pmatrix} = \underline{\mathbf{T}}\begin{pmatrix} a_{mn} \\ b_{mn} \end{pmatrix} = \begin{pmatrix} \underline{\mathbf{T}}^{1,1} & \underline{\mathbf{T}}^{1,2} \\ \underline{\mathbf{T}}^{2,1} & \underline{\mathbf{T}}^{2,2} \end{pmatrix}\begin{pmatrix} a_{mn} \\ b_{mn} \end{pmatrix}. \tag{9}$$

The TM contains the whole information about the scattering process except the incident wave. Once calculated, it can be reused for different excitation fields at the same frequency. Special properties of the SVWF also enable us to recompute the TM for the shifted or rotated scatterer, cf. Appendix B of Ref. [10]. The method works correctly as long as the field expansion in (2) is valid. At least, this is true outside the smallest sphere circumscribing the scatterer and here, we will obey this restriction. However, extensions of the method exist to overcome this limitation by expanding the near-field within the circumscribed sphere in both regular and radiating SVWF [13].

The null-field method (NFM), sometimes called the extended boundary condition method (EBCM), is the standard approach to compute the TM. It is based on the Stratton–Chu representation theorem [14] for the electromagnetic fields. Let '+' and '−' denote the areas outside and inside the scattering volume, then, for the fields $\mathbf{E}_{\pm}$, the Stratton–Chu equations combined with the boundary condition $\mathbf{n}\times\mathbf{E}_+ = \mathbf{n}\times\mathbf{E}_-$ yield

$$\begin{aligned} &\nabla\times\int_{\partial V}\mathbf{n}\times\mathbf{E}_-(\mathbf{r}')\cdot g(k_s,\mathbf{r},\mathbf{r}')\,dS(\mathbf{r}') \\ &\quad+\frac{j}{k_0\epsilon_s}\nabla\times\nabla\times\int_{\partial V}\mathbf{n}\times\mathbf{H}_-(\mathbf{r}')\cdot g(k_s,\mathbf{r},\mathbf{r}')\,dS(\mathbf{r}') \\ &\quad=\begin{cases} -\mathbf{E}_{inc}, & \mathbf{r}\in V \\ \mathbf{E}_{scat}, & \mathbf{r}\in\Re^3\backslash V, \end{cases} \end{aligned} \tag{10}$$

where $g(k_s,\mathbf{r},\mathbf{r}')$ is the Green function of the Helmholtz equation. For the case $\mathbf{r}\in V$, Eq. (10) is known as null-field equation, and enables us to obtain the surface fields $\mathbf{n}\times\mathbf{E}_-$ and $\mathbf{n}\times\mathbf{H}_-$ from the excitation field $\mathbf{E}_{inc}$. For the other case, Eq. (10) expresses the scattered field $\mathbf{E}_{scat}$ in terms of the surface fields. This equation is known as the Huygens principle.

The surface fields in (10) are expressed in suitable basis functions, e.g. conventionally, these are regular SVWF

$$\mathbf{E}_-(\mathbf{r}') = \sum_{n=1}^{\infty}\sum_{m=-n}^{n} p_{mn}\mathbf{M}^1_{mn}(k_i\mathbf{r}') + q_{mn}\mathbf{N}^1_{mn}(k_i\mathbf{r}'). \tag{11}$$

Applying the field expansion in (1) and the Green function expansion in terms of SVWF yields two linear systems binding the coefficients $\{a_{mn},b_{mn}\}\Leftrightarrow\{p_{mn},q_{mn}\}$ and $\{f_{mn},g_{mn}\}\Leftrightarrow\{p_{mn},q_{mn}\}$. The TM is computed from these equations. For spherical particles, the solution of the NFM is well-known and corresponds 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

$$a_{mn} = \frac{-4\pi ik\nu}{c^2}\frac{mA^+_{mn}}{n(n+1)}K_m\left(\frac{\omega b}{\nu\gamma}\right), \tag{12a}$$

$$b_{mn} = \frac{-2\pi ik}{c\gamma}\frac{B^+_{mn}}{n(n+1)}K_m\left(\frac{\omega b}{\nu\gamma}\right), \tag{12b}$$

$$\begin{aligned} A^+_{mn} = &\sqrt{\frac{2n+1}{\pi}\frac{(n-|m|)!}{(n+|m|)!}}(2|m|-1)!! \\ &\times\frac{i^{|m|}}{\nu}\left(\frac{c}{\nu\gamma}\right)^{|m|}C^{(|m|+1/2)}_{n-|m|}\left(\frac{c}{\nu}\right), \end{aligned} \tag{12c}$$

$$\begin{aligned} B^+_{mn} = &A^+_{m+1,n}\sqrt{(n+m+1)(n-m)} \\ &-A^+_{m-1,n}\sqrt{(n-m-1)(n+m)}, \end{aligned} \tag{12d}$$

with $\gamma = 1/\sqrt{1-v^2/c^2}$, the modified Bessel function K_m, the impact parameter b and $C^{(m+1/2)}_{n-m}$ 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 $\mathbf{r}_e(t) = \mathbf{r}_0 + \mathbf{v}t$ 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 $\mathbf{E}_{scat}$. 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 $\hbar\omega$ as $P(\omega)$, we can also express the loss as