Simulating Electron Energy-Loss Spectroscopy and Cathodoluminescence for Particles in Arbitrary Host Medium Using the Discrete Dipole Approximation

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**ABSTRACT:** Electron energy-loss spectroscopy (EELS) and cathodoluminescence (CL) are widely used experimental techniques for characterization of nanoparticles. The discrete dipole approximation (DDA) is a numerically exact method for simulating the interaction of electromagnetic waves with particles of arbitrary shape and internal structure. In this work, we extend the DDA to simulate EELS and CL for particles embedded into arbitrary (even absorbing) unbounded host medium. The latter includes the case of the dense medium, supporting the Cherenkov radiation of the electron, which has never been considered in EELS simulations before. We build a rigorous theoretical framework based on the volume integral equation, final expressions from which are implemented in the open-source software package ADDA. This implementation agrees with both the Lorenz–Mie theory and the boundary-element method for spheres in vacuum and moderately dense host medium. And it successfully reproduces the published experiments for particles encapsulated in finite substrates. The latter is shown for both moderately dense and Cherenkov cases—a gold nanorod in SiO$_2$ and a silver sphere in SiN$_x$, respectively. For the nanorod, we successfully reproduced the EELS plasmon maps (scans across the particle cross section), although the developed theory is not fully rigorous for electron trajectories intersecting a particle.

**INTRODUCTION**

Optical excitations of small objects have been gaining interest over the past decades. The quest for the highest possible space and energy resolution is unachievable by purely optical methods due to the diffraction limit. This limit can be overcome using fast electrons as a probe instead of light—the corresponding experimental technique is called electron energy-loss spectroscopy (EELS). EELS is a well-developed extension of the standard electron microscope, where a particle under study is exposed to a beam of relativistic electrons with the same kinetic energies of the order of 100 keV. The energies of transmitted electrons are measured leading to the energy-loss spectrum (EELS spectrum). Currently, EELS provides information about excitations with sub-Å and few-meV space and energy resolution. While exposed to an electron beam, the particle emits photons—this phenomenon, called cathodoluminescence (CL), also provides information about photonic properties. To accurately interpret the results of an EELS or CL experiment, it is necessary to have a theoretical description of particle interaction with the electromagnetic field of a fast electron, complemented by a simulation method.

There are many methods capable of simulating EELS, from the analytical Lorenz–Mie theory for spheres to surface-discretization boundary-element method (BEM) and volume discretization methods, such as finite-difference time-domain (FDTD), finite-element method (FEM), and the discrete dipole approximation (DDA). While a theoretical description of EELS can be developed in a general setting of a particle placed in arbitrary infinite host medium, most of the numerical methods apply only to vacuum environment. The notable exception is MNPBEM, which seems to support arbitrary infinite host medium by its internal parameters. However, this option is poorly documented and the corresponding simulations have been performed only for the case of nonabsorbing medium with relatively low density.

Thus, the simulation capabilities do not fully support the experimental conditions, where the particle is always placed on or inside a substrate, or require discretizing a large chunk of substrate in addition to the particle itself. The presence of a substrate affects the EELS/CL spectra, e.g., by red-shifting localized surface plasmon resonances (LSPRs) with increasing host-medium refractive index. Although the development of very thin substrates has made the experimental results close to vacuum simulations, some experimental studies intentionally consider particles inside a substrate. Importantly, sufficiently dense host medium may slow down the light below the electron speed, leading to a qualitatively different case of the Cherenkov radiation. This case may become more

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common with increasing electron energy, but has never been considered in numerical simulations of EELS.

The goal of this paper is to enhance the capabilities of EELS/CL simulations using the DDA—a numerically exact method for simulating the interaction of electromagnetic waves with particles of arbitrary shape and internal structure,²⁹ based on the volume integral equation (VIE) in the frequency domain.²⁰ The popularity of the DDA is based on conceptual simplicity, combined with the availability of two open-source highly optimized codes: DDSCAT²⁰ and ADDA.²¹ Initially designed for simulating the interaction of particles with plane waves,²¹ the DDA is applicable to arbitrary electromagnetic fields,²⁹ including the field of a fast electron. The latter has been exemplified by two specialized codes: DDEELS²² and e-DDA,²³ which, however, assume the vacuum surrounding. Moreover, the underlying VIE-based theory of EELS is available only for this case.²⁴

In this paper, we, first, construct a general theoretical framework of EELS and CL for particles in arbitrary host medium, based on the VIE and energy budget considerations.²⁴ When the host medium is absorbing or incurs the Cherenkov radiation, particle-induced energy losses are accompanied by free-space ones. We discuss the feasibility of separating these two losses in experimental signals. Moreover, we extend the scale invariance rule of electromagnetics to EELS simulations, expanding the applicability domain of existing vacuum-based codes.

Second, we implement the obtained general expressions in the ADDA code together with a dedicated Python library, allowing a wide range of EELS and CL simulations in arbitrary host medium out of the box. The developed theory has certain limitations, when the electron beam penetrates a particle, but the presented library circumvents them to produce meaningful plasmon maps (Section S5). Next, we demonstrate the high accuracy of this implementation in comparison with the Lorenz—Mie theory and MNPBEM for a test sphere in vacuum and various nonabsorbing host media. The latter comparison highlights the limitations of MNPBEM in the Cherenkov case. Several illustrative examples of absorbing host medium are presented in Section S8. Finally, we demonstrate the practical applicability of the updated ADDA code by accurately reproducing experimental EELS data for a silver nanosphere encapsulated in a nonabsorbing Cherenkov host medium²⁵ and for a nanowire placed inside a glass substrate.²⁶ We use SI units throughout the paper, and preliminary results of this paper were presented in refs 25, 26.

### THEORY

#### Energy Budget for Time-Harmonic Sources.

This section is based on refs 20, 24, 27. Let us define the current density of time-harmonic external sources \( \mathbf{J}_\text{s}(\mathbf{r}) \) to be independent of the resulting electromagnetic field and consider nonmagnetic (\( \mu = \mu_0 \)) isotropic host medium with dielectric permittivity \( \varepsilon_h = m_h^2 \varepsilon_0 \) (\( m_h \) is its refractive index). The incident (or ‘source-generated’) electromagnetic field must satisfy the Maxwell equations in \( \mathbb{R}^3 \):

\[
\nabla \times \mathbf{E}_\text{inc}(\mathbf{r}) = i \omega \mu_0 \mathbf{H}_\text{inc}(\mathbf{r})
\]

\[
\nabla \times \mathbf{H}_\text{inc}(\mathbf{r}) = -i\omega\varepsilon_h \mathbf{E}_\text{inc}(\mathbf{r}) + \mathbf{J}_\text{s}(\mathbf{r})
\]  

(1)

Below we consider the cases of nonabsorbing (\( \varepsilon_h \in \mathbb{R} \)) and absorbing (\( \varepsilon_h \in \mathbb{C} \)) host media. In both cases, we assume \( 0 \leq \arg \varepsilon_h < \pi \) (passive medium) and therefore \( 0 \leq \arg m_h < \pi/2 \), where \( \arg \) is the complex argument, for which we assume the range \(-\pi, \pi\).

A particle is a nonmagnetic object with finite volume \( V_\text{int} \) and complex isotropic permittivity distribution \( \varepsilon_p(\mathbf{r}) = m_p^2(\mathbf{r})\varepsilon_0 \) (\( m_p(\mathbf{r}) \) is the particle’s refractive index). Then, the dielectric permittivity function in the whole space is

\[
\varepsilon(\mathbf{r}) \overset{\text{def}}{=} \begin{cases} 
\varepsilon_h, & \mathbf{r} \in V_{\text{ext}}, \\
\varepsilon_h(m_p^2(\mathbf{r}) - 1) & \mathbf{r} \in V_{\text{int}}
\end{cases}
\]  

(2)

where \( V_{\text{ext}} = \mathbb{R}^{3}\backslash V_{\text{int}} \) and \( m(\mathbf{r}) \) is the refractive index relative to the host medium: \( m(\mathbf{r}) = m_p(\mathbf{r})/m_h \).

The presence of the particle changes the electromagnetic field in the whole space, composed of the particle’s volume \( V_{\text{int}} \) and the external volume \( V_{\text{ext}} \). This field must satisfy the following Maxwell’s equations

\[
\nabla \times \mathbf{E}(\mathbf{r}) = i\omega\mu_0\mathbf{H}(\mathbf{r})
\]

\[
\nabla \times \mathbf{H}(\mathbf{r}) = -i\omega\varepsilon(\mathbf{r})\mathbf{E}(\mathbf{r}) + \mathbf{J}(\mathbf{r})
\]  

and boundary conditions at the particle interface. These equations are equivalent to the following volume integral equation (VIE) for the electric field \( \mathbf{E}(\mathbf{r}) \)

\[
\mathbf{E}(\mathbf{r}) = \mathbf{E}_{\text{inc}}(\mathbf{r}) + \frac{k^2}{\varepsilon_h} \lim_{\varepsilon \to 0} \int_{V_{\text{ext}}} d^3r (|\mathbf{m}(\mathbf{r}') - 1|\mathbf{G}(\mathbf{r},\mathbf{r}') \cdot \mathbf{E}(\mathbf{r}'))
\]

\[
- \frac{m^2(\mathbf{r}) - 1}{3} \mathbf{E}(\mathbf{r})
\]  

(3)

where \( V_0 \) is a sphere centered at \( \mathbf{r} \) to exclude the singularity, \( k = \omega/\sqrt{\varepsilon_h\mu_0} = m_h k_0 \) is the wavenumber in the host medium (\( c \) is the speed of light in vacuum, and \( k_0 = \omega/\varepsilon \) is the vacuum wavenumber), and \( \mathbf{G}(\mathbf{r},\mathbf{r}') \) is the free-space Green’s tensor, defined as

\[
\mathbf{G}(\mathbf{r},\mathbf{r}') \overset{\text{def}}{=} \left[ \mathbf{I} + \frac{V_{\text{ext}} \otimes V_{\text{int}}}{k^2} \right] \exp\left(i k |\mathbf{r} - \mathbf{r}'| / 4\pi |\mathbf{r} - \mathbf{r}'| \right)
\]  

(4)

where \( \mathbf{I} \) is the identity tensor and \( \otimes \) denotes dyadic (tensor) product.

Incident electric field can be expressed in terms of \( \mathbf{J}_s(\mathbf{r}) \) as

\[
\mathbf{E}_{\text{inc}}(\mathbf{r}) = i\omega\mu_0 \lim_{\varepsilon \to 0} \int_{V_{\text{ext}}} d^3r' \mathbf{G}(\mathbf{r},\mathbf{r}') \cdot \mathbf{J}_s(\mathbf{r}') - \frac{i}{3} \frac{\mathbf{J}_s(\mathbf{r})}{\varepsilon_h}
\]  

(5)

where \( V_0 \) is the volume enclosing the sources, and the exclusion of the singularity in the volume \( V_0 \) makes the expression valid in the whole \( \mathbb{R}^3 \). In this work, we assume that the sources are outside of the particle: \( V_0 \cap V_{\text{int}} = \emptyset \) (unless noted otherwise). Let us further define the polarization density of the particle as

\[
\mathbf{P}(\mathbf{r}) = (\varepsilon(\mathbf{r}) - \varepsilon_h) \mathbf{E}(\mathbf{r})
\]  

(6)

then the scattered electric field is expressed as

\[
\mathbf{E}_{\text{scat}}(\mathbf{r}) \overset{\text{def}}{=} \mathbf{E}(\mathbf{r}) - \mathbf{E}_{\text{inc}}(\mathbf{r})
\]

\[
= \omega^2 \mu_0 \lim_{\varepsilon \to 0} \int_{V_{\text{int}}} d^3r' \mathbf{G}(\mathbf{r},\mathbf{r}') \cdot \mathbf{P}(\mathbf{r}') - \frac{\mathbf{P}(\mathbf{r})}{3\varepsilon_h}
\]  

(7)

Time-averaged electromagnetic-energy transfer per unit area is given by the Poynting vector²³
Integrating it over the closed surface \( \mathcal{A} \) results in the power generated or lost in the volume inside the surface (according to the Poynting theorem)

\[
W = \oint_{\mathcal{A}} \mathbf{dA} \cdot \mathbf{S}(\mathbf{r})
\]

(10)

where \( \mathbf{dA} = \mathbf{n} \mathbf{dr} \), \( \mathbf{n} \) is the vector normal to the surface, and the sign is chosen such that \( W \) is positive when energy goes outside the surface. Using the divergence theorem, the surface integral is transformed into the volume integral

\[
W = -\frac{\alpha}{2} \int_{V_{\mathcal{A}}} d^3\mathbf{r} |\mathbf{E}(\mathbf{r})|^2 \text{Im}[\varepsilon(\mathbf{r})]
\]

\[
-\frac{1}{2} \int_{V_{\mathcal{A}}} d^3\mathbf{r} \text{Re}[\mathbf{E}(\mathbf{r}) \cdot \mathbf{J}^*(\mathbf{r})]
\]

(11)

where \( V_{\mathcal{A}} \) is the volume inside the closed surface \( \mathcal{A} \). This expression is valid only if \( \mathbf{E}(\mathbf{r}) \) and \( \mathbf{J}(\mathbf{r}) \) are square-integrable inside \( V_{\mathcal{A}} \). Note that the dot product of two vectors does not imply conjugation of the second operand. This is consistent with the definition of action of tensor on the vector, as used above. In other words, this dot product is not a proper inner product of two complex vectors.

For the case of nonabsorbing host medium \( (m_h \in \mathbb{R}) \), let us apply eq 11 to \( V_{\mathcal{A}} \) in the absence of the particle. Substituting \( \mathbf{E}_{\text{inc}}(\mathbf{r}) \) for \( \mathbf{E}(\mathbf{r}) \) gives us the free-space energy loss power \( W_0 \). The first component of eq 11 equals zero, and the second one can be rewritten as

\[
W_0 = \frac{\alpha \mu_0}{2} \int_{V_{\mathcal{A}}} d^3\mathbf{r} d^3\mathbf{r}^* \mathbf{G}(\mathbf{r},\mathbf{r}^*) \cdot \mathbf{J}(\mathbf{r})
\]

(12)

where we use the notation

\[
\mathbf{G}(\mathbf{r},\mathbf{r}^*) = \frac{1}{2i} \{ \mathbf{G}(\mathbf{r},\mathbf{r}^*) - [\mathbf{G}(\mathbf{r},\mathbf{r}^*)]^\dagger \}
\]

(13)

which is a symmetric (self-adjoint) operator kernel, and \( H \) denotes the Hermitian (conjugate) transpose of a tensor (matrix). In isotropic medium

\[
\mathbf{G}(\mathbf{r},\mathbf{r}^*) = \text{Im}[\mathbf{G}(\mathbf{r},\mathbf{r}^*)]
\]

(14)

and in nonabsorbing medium \( \mathbf{G}(\mathbf{r},\mathbf{r}^*) \) is always finite, \(^{24} \) in particular

\[
\lim_{\mathbf{r} \to \mathbf{r}^*} \mathbf{G}(\mathbf{r},\mathbf{r}^*) = \frac{k I}{6\pi}
\]

(15)

Then, as explained in ref 24, eq 12 is continuous versus \( \mathbf{J}(\mathbf{r}) \), whenever the latter is integrable. Thus, it is also valid for delta functions although they are not square-integrable.

By applying eq 11 to \( V_{\mathcal{A}} \) and \( \mathbf{E}_{\text{inc}} \) in a similar manner, we obtain the particle-induced energy loss power \( W_{\text{enh}} \) while the integral over \( V_{\text{inc}} \) gives the extinction power \( W_{\text{ext}} \) (a standard quantity in light scattering problems) \(^{24} \)

\[
W_{\text{enh}} \overset{\text{def}}{=} -\frac{\alpha \mu_0}{2} \int_{V_{\text{inc}}} d^3\mathbf{r} \text{Re}[\mathbf{E}_{\text{inc}}(\mathbf{r}) \cdot \mathbf{J}^*(\mathbf{r})]
\]

\[
= -\frac{\alpha \mu_0}{2} \int_{V_{\text{inc}}} d^3\mathbf{r} \int_{V_{\text{ext}}} d^3\mathbf{r}^* \text{Re}[\mathbf{J}^*(\mathbf{r}) \cdot \mathbf{G}(\mathbf{r},\mathbf{r}^*) \cdot \mathbf{P}(\mathbf{r})]
\]

(16)

Interestingly, eqs 16–18 can also be used in the case of absorbing host medium, but their physical meaning is ambiguous. Absorption by the host medium significantly changes the whole energy budget, particularly positions of the contours in Figure 1 cannot be freely moved around the particle and the sources. This problem does not have a fully satisfactory solution even for the interpretation of \( W_{\text{ext}} \) in the standard scattering problem for the plane electromagnetic waves. \(^{29,30} \) A similar ambiguity appears if the source is placed inside the particle, i.e., \( V_{\text{inc}} \) and \( V_{\text{int}} \) overlap. We leave a rigorous analysis of this case for future research, but it must include certain assumption that sources and the medium are physically separated, i.e., \( V_{\text{inc}} \) is effectively excluded from \( V_{\text{int}} \). In the case of a delta-function source (point, line, or surface), this will additionally incur a small exclusion volume, similar to that used in eq 8, but with the shape corresponding to that of the source (spherical, cylindrical, or planar). Moreover, if the medium around the sources is absorbing, some of the results may depend on the width of this exclusion volume, not having a bounded zero limit. The corresponding problem of defining \( W_{\text{enh}} \) in absorbing host medium is discussed in the Free-Space Energy Losses section.

It is worth mentioning that cross sections \( C \) (extinction, absorption, scattering) are commonly used in scattering problems for plane waves. They are expressed in terms of the corresponding power \( W \) and the intensity of the incident wave \( I_0 \)

\[
C = \frac{W_X}{I_0}, \quad I_0 \overset{\text{def}}{=} m_{h} \frac{E_0}{2} e_0^2
\]

(19)
where $X$ is a subscript of any power from Figure 1, $m'_0$ is the real part of $m_0$, and $E_0$ is the amplitude of the incident wave. $E_0$ has physical meaning for the plane waves and can be meaningfully defined for some other shaped beams. Moreover, postulating any constant instead of $E_0$, e.g., unity multiplied by appropriate unit, allows one to define all cross sections for the moving electron as well. This can be convenient since they are expressed in units of area and, thus, can be trivially converted between different systems of units.

Electric Field of a Relativistic Electron. We consider a relativistic electron as a point charge $q$ moving with the speed $v$ in the positive direction of the $z$-axis. At the time $t = 0$, the charge has coordinates $r_0 = (x_0, y_0, z_0)$. The corresponding current density is

$$J(r,t) = q\delta(x-x_0)\delta(y-y_0)\delta(z-z_0-ut)e_z \quad (20)$$

where $e_z$ is a unit vector along the $z$-axis. After applying the Fourier transform (defined as eq S1), we obtain the current density in the frequency domain

$$\hat{J}(r) = q\delta(x-x_0)\delta(y-y_0)e^{i\omega(z-z_0)}e_z \quad (21)$$

To find the incident electric field, we substitute eq 21 into eq 6 for arbitrary host medium ($m_h \in \mathbb{C}$), dependence on which through $k$ is implicit in the Green’s tensor

$$E_{inc}(r) = \frac{q\omega}{2\pi\epsilon_0 m_h^2} \int d^3r \frac{\exp[ikr-r^1]}{4\pi\sqrt{r^1}} \hat{J}(r^1)$$

$$= \frac{q\omega}{2\pi} \exp[i\omega(z-z_0)] \frac{K_0(\omega b)}{\gamma_h^0} \quad (22)$$

where changing the order of integration and differentiation eliminates the second term in eq 6 and makes the singularity of the kernel integrable (the exclusion volume is then redundant).27 The remaining integral is evaluated in Section S3

$$I_1(r) \equiv \int d^3r \frac{\exp[ikr-r^1]}{4\pi\sqrt{r^1}} \hat{J}(r)$$

$$= \frac{q}{2\pi} \exp[i\omega(z-z_0)] \frac{K_0(\omega b)}{\gamma_h^0} \quad (23)$$

where we introduced $b \equiv \sqrt{(x-x_0)^2 + (y-y_0)^2}$ and the notation analogous to the one used in the special relativity theory

$$\beta_h \equiv \frac{v}{c} m_h, \quad \gamma_h \equiv \sqrt{1 - \beta_h^2} \quad (24)$$

The principal branch for the square-root function is chosen such that it continuously depends on $e_\theta$ when $0 \leq \arg e_\theta < \pi$ (or, equivalently, $0 \leq \arg m_h < \pi/2$, which we assumed in the Energy Budget for Time-Harmonic Sources section), except for the singularity at $\beta_h = 1$. Then, $\gamma_h$ lies in the first quadrant of the complex plane ($0 \leq \arg \gamma_h \leq \pi/2$) excluding the interval $[0,1)$. Specifically, $\beta_h < 1$ and $\beta_h > 1$ lead to real ($\gamma_h > 1$) and imaginary ($\Im \gamma_h > 0$) $\gamma_h$, respectively, corresponding to relatively less and more dense nonabsorbing host media. In the case of vacuum, we always have $\beta_h < 1$.

We substitute eq 23 into eq 22 and obtain

$$E_{inc}(r) = \frac{q\omega}{2\pi\epsilon_0 m_h^2} \exp[i\omega(z-z_0)] \frac{1}{\sqrt{-b^2}} K_0(\omega b) \quad (25)$$

where we used $K_0'(z) = -K_0(z)$ (eq 10.29.3 in ref 32). The behavior of the incident field is mostly determined by $\gamma_h$. When it has a positive real part ($\Re \gamma_h > 0$), the field decays exponentially with $b$ (eq. 10.25.3 in ref 32). By contrast, when $\gamma_h$ is purely imaginary (corresponding to $\beta_h > 1$), the field oscillates and decays as $1/\sqrt{b}$ similar to the field of a line source.

To conclude, we derived the field in the most general case of an arbitrary host medium ($m_h \in \mathbb{C}$). This expression includes the case of nonabsorbing host medium ($m_h \in \mathbb{R}$) or vacuum as special cases, and allows straightforward quasi-static limit. In all cases, the final results match the ones described in the literature.33 However, the latter were derived using different approaches for solving the Maxwell equations for different classes of the host media. By contrast, we used a single VIE framework with only technical differences in evaluating integrals. The observed agreement, thus, supports the universal applicability of this framework, which we further use to evaluate the interaction of the electron field with a nanoparticle.

Free-Space Energy Losses. To find the free-space energy losses of a relativistic electron moving in an infinite nonabsorbing host medium ($m_h \in \mathbb{R}$), we substitute eq 21 into eq 12

$$W_0 = \frac{\alpha\mu_0 q^2}{8\pi} \int_{-\infty}^{\infty} dz' \exp[i\omega(z' - z)]$$

$$ \times \left(1 + \frac{1}{k^2} \frac{\partial^2}{\partial z'^2} \sin[k(z' - z)] \right) \Rightarrow \frac{\partial^2 W_0}{\partial z'^2} = \frac{\alpha\mu_0 q^2}{8\pi} I_2(\beta_h) \quad (26)$$

where we used $k \in \mathbb{R}$ in evaluating $\hat{G}(r,r')$, expressed the loss power per unit distance, and denoted the remaining one-dimensional integral as $I_2(\beta_h)$. To calculate it, we replace $z$ with $z'$ in the derivative and substitute $u \equiv \omega(z' - z)/\nu$

$$I_2(\beta_h) \equiv \int_{-\infty}^{\infty} du \exp(iu) \left(1 + \frac{1}{\beta_h^2} \frac{\partial^2}{\partial u^2} \sin(\beta_h u) \right)$$

$$= \left(1 - \frac{1}{\beta_h^2} \right) \int_{-\infty}^{\infty} du \exp(iu) \sin(\beta_h u) \quad (27)$$

$$= \frac{\Im}{\beta_h^2} \int_{0}^{\infty} \frac{du}{u} \left[\sin((\beta_h - 1)u) + \sin((\beta_h + 1)u)\right]$$

$$= \frac{\pi}{2\beta_h^2} \left[\text{sgn}(\beta_h - 1) + 1\right]$$

where we integrated by parts twice and used the known limit for the sine integral. Note that the integrals converge at infinity due to the oscillating kernel (since $\beta_h \neq 1$) decreasing as $1/u$. 

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and the integrand is regular at zero (together with its derivatives).

By substituting the result for \( I_1 \) into eq 26, we obtain that in vacuum or in a medium with \( \beta_h < 1 \), the free-space energy loss power is

\[
W_0 = 0
\]

which is a known fact: a charge moving slower than the speed of light in the medium does not lose energy. For \( \beta_h > 1 \), when the speed of charge exceeds the speed of light in the medium

\[
\frac{dW_0}{dz} = \frac{\mu_0}{8} d^2 \left( 1 - \frac{\beta^2}{\beta_h^2} \right)
\]

which vanishes when \( \beta_h \rightarrow 1 \). Hence, the validity of eqs 28 and 29 can be extended by continuity to \( \beta_h \leq 1 \) and \( \beta_h \geq 1 \), respectively. Finally, the free-space energy loss per unit distance, given by eq 6, is

\[
\frac{\partial W_0}{\partial z} \Delta E_0 = \frac{\mu_0}{4\pi} d^2 \int_{\beta_1(\omega) > 1} d\omega \alpha \left( 1 - \frac{\beta^2}{\beta_h^2} \right)
\]

Thus, we obtained the well-known Frank–Tamm formula for the Cherenkov radiation in any nonabsorbing host medium, which again shows the versatility of our theoretical framework.

In an infinite absorbing host medium \( (m_h \in \mathbb{C}) \), the integral in the expression for \( W_0 \) (eq 12) will become singular due to the divergence of \( G_l^1(\mathbf{r}, \mathbf{r}') \) for \( r \rightarrow r' \). As discussed in the Energy Budget for Time-Harmonic Sources section, the possible workaround is to assume a finite exclusion volume in the host medium around the electron trajectory, which is equivalent to assuming a finite electron size or a cutoff of momentum transfer. In principle, it provides practically usable expressions, but we do not discuss it in this paper.

Note, however, that, conceptually, this singularity indicates the limitation of macroscopic Maxwell’s equations (specifically, of macroscopic permittivity). Since the latter are obtained by averaging microscopic ones over the size of several atomic scales, they are not expected to be accurate at smaller scales. And it is exactly the latter scales that become important for electron losses in absorbing medium. Microscopically, the electron is always moving in the vacuum under the influence of the induced fields due to surrounding atoms; thus, the losses (per unit of length) are always finite. This also follows from quantum analysis. However, a quantitatively correct simulation of these losses requires one to tune at least one parameter in addition to the permittivity.

**Particle-Induced Energy Losses.** To express particle-induced energy losses, we start from eq 16 considering the most general host medium \( (m_h \in \mathbb{C}) \). We use the general property of tensor transposition

\[
\forall \mathbf{a}, \mathbf{b} : \mathbf{a} \cdot \mathbf{b} = \mathbf{b} \cdot \mathbf{a}^T = \mathbf{a}^T \cdot \mathbf{b}
\]

and Green’s tensor’s symmetry (reciprocity) \( \mathbf{G}(\mathbf{r}, \mathbf{r}') = \mathbf{G}(\mathbf{r}', \mathbf{r}) \) to change the order of integration:

\[
W_{\text{enh}} = -\frac{\alpha}{2} \int_{\text{vol}} d^3\mathbf{r} \text{Im}[E_x(\mathbf{r}) \cdot P(\mathbf{r})]
\]

where we introduced the auxiliary electric field \( E_x(\mathbf{r}) \) equal to the incident field from conjugate sources [cf. eq 22]

\[
\begin{align*}
E_x(\mathbf{r}) &= \text{def} \ i\omega \mu_0 \lim_{\gamma_0 \to 0} \int_{\text{vol}} d^3\mathbf{r}' \mathbf{G}(\mathbf{r}, \mathbf{r}') \cdot \mathbf{J}_h^b(\mathbf{r}') - i\mathbf{e}_x(\mathbf{r}) \frac{3\omega}{3\omega_h}
\end{align*}
\]

(33)

To calculate this field, we note that the conjugation of \( \mathbf{J}_h \) (eq 21) is equivalent to the inversion of sign of \( z - z_0 \) which leads to the same inversion in eq 23 when combined with the inversion of the sign of \( z' \). Therefore, analogously to eq 25, we obtain

\[
\begin{align*}
E_x(\mathbf{r}) &= \frac{-q\omega}{2\pi\epsilon_0 m_h^2 \nu} \exp \left[ -i\frac{\omega}{\nu} (z - z_0) \right] \frac{y - \nu}{\nu} K_0 \left( \frac{\omega b}{\nu} \right) - i \frac{1}{\nu} K_0 \left( \frac{\omega b}{\nu} \right) \left( \frac{\omega b}{\nu} \right) \\
&= -E_{\text{inc,a}}(\mathbf{r}) \exp \left[ -2i\frac{\omega}{\nu} (z - z_0) \right] \left( \frac{\omega b}{\nu} \right)
\end{align*}
\]

(34)

where the additional minus arises from each derivative with respect to \( z \).

Equation 32 is very convenient since the integration is performed over the volume of the particle (rather than that of sources), \( E_x(\mathbf{r}) \) is easily obtained from the known \( E_{\text{inc}}(\mathbf{r}) \), and \( P(\mathbf{r}) \) is efficiently calculated in the DDA. Moreover, the resulting expression (eq 32) for \( W_{\text{enh}} \) is very similar to the expression (eq 17) for \( W_{\text{ext}} \) and can be calculated in a similar way.

Previously, the particle-induced energy losses, expressed as an integral over the volume of the particle, were known only for the specific case of vacuum as a host medium, for which it is known that \( W_{\text{enh}} = W_{\text{ext}} \). In our general approach, the equality of eqs 32 and 17 follows from the fact that \( E_x(\mathbf{r}) = -E^*_x(\mathbf{r}) \), which is true if and only if \( \gamma_h \in \mathbb{R} \) (i.e., when \( \beta_h < 1 \)). Alternatively, the same can be obtained from the total energy budget (Figure 1) using \( W_0 = 0 \) and \( W_{\text{eq}} = W_{\text{ext}} \), where the latter follows from the possibility of extending the integration surface for \( W_{\text{eq}} \) to infinity and the exponential decay of \( E_{\text{inc}}(\mathbf{r}) \). The rapid decay of \( E_{\text{inc}}(\mathbf{r}) \) is actually required for any excitation that has \( W_0 = 0 \) since \( W_0 \) can also be computed as the far-field integral.

The major novelty of eq 32 is its applicability to the arbitrary passive host medium \( (m_h \in \mathbb{C}) \) and the Cherenkov case \( \beta_h > 1 \), when \( W_{\text{enh}} \neq W_{\text{ext}} \). Although in this case \( W_0 \) is not zero and may even be effectively infinite (see the Free-Space Energy Losses section), the expression for (additional) particle-induced energy losses is well defined. However, the equality \( E_x(\mathbf{r}) = -E^*_x(\mathbf{r}) \) also remains approximately valid in the quasistatic case [cf. eq S15], especially when \( \beta_h \approx 1 \). Thus, to notice new effects, predicted by the rigorous theory of this section for the Cherenkov case, one needs to consider relatively large particles and \( \beta_h \) significantly larger than 1.

**Electron Energy-Loss Probability.** Total energy loss for the electron will be the sum of free-space and particle-induced energy losses. To find it, we apply eq 56 to \( W_{\text{enh}} \) and \( W_0 \).
\[ \Delta E = \Delta E_0 + \Delta E_{\text{enh}} = \frac{2}{\pi} \int_0^\infty d\omega (W_0 + W_{\text{enh}}) \]

\[ = \int_0^\infty d(\hbar\omega) \Gamma_{\text{EELS}}(\hbar\omega) \hbar\omega \]

(35)

where we introduced the electron energy-loss probability density function

\[ \Gamma_{\text{EELS}}(\hbar\omega) = \frac{2}{\pi} \frac{W_0 + W_{\text{enh}}}{\hbar^2 \omega} \]

(36)

of the random variable \( h\omega \) such that \( \Delta E \) is the expected value of this variable.

Strictly speaking, the purely classical theory is deterministic, i.e., each electron should lose exactly \( \Delta E \) given by eq 35. By contrast, the quantum description of EELS predicts that each electron loses energy in quanta \( (0 \text{ or some natural number of them}) \), and each of them is chosen randomly from some probability distribution. However, it has been shown that the phenomenological introduction of probability density by eq 36 allows the classical theory to correctly reproduce the quantum result in the single-loss (weak-coupling) regime, i.e., when at most one energy quanta is assumed to be lost (also called the Born approximation). This regime is commonly satisfied in EELS experiments, although the strong-coupling regime to remain valid. The latter requirement can potentially be added, but rather need to be convoluted as functions of \( \omega \) (including the zero-loss peak for normalization). We thus are not aware of the existing rigorous analysis of such an option.

In any case, \( W_0 \) is fully determined by the outer boundaries of the host medium (with respect to the electron beam) and is independent of the particle. By contrast, the focus of this paper is on calculating the particle-induced energy losses \( W_{\text{enh}} \) for which one generally needs to employ the DDA or other numerical method. To avoid confusion, we define the corresponding particle-induced loss probability as \( P_{\text{EELS}} \) and aim to compute only this part. When \( W_0 = 0 \), it is exactly the measurable quantity \( \Gamma_{\text{EELS}} \), otherwise, it is a first step in obtaining \( \Gamma_{\text{EELS}} \) with the second step consisting of a separate calculation of \( W_0 \). In the case of a weak-coupling regime for the whole system (particle + slab of host medium), \( P_{\text{EELS}} \) is equal to the difference between the losses in this system and the losses in the same system without a particle (both of which are potentially measurable). The same approach is commonly used, e.g., when defining cross sections for light scattering by particles in absorbing host medium.\(^{43,44}\) Importantly, if separately measured \( W_0 \) is removed from the total \( \Gamma_{\text{EELS}} \) (either by subtraction or deconvolution), it will also remove the ambiguity of the definition of \( W_0 \) in absorbing host medium. Thus, the particle-induced losses can be calculated fully rigorously even in this case, unless the electron beam intersects the particle.

The explicit expression for \( P_{\text{EELS}} \) follows from eq 36

\[ P_{\text{EELS}}(\hbar\omega) = \frac{2}{\pi} \frac{W_{\text{enh}}}{\hbar^2 \omega} \]

(37)

where we defined the enhancement cross section

\[ C_{\text{enh}} = -\frac{k_0}{m_0^2 e_0^2} \int_{V_m} d^3r \text{Im}[E_A(r') \cdot P(r')] \]

(38)

analogously to \( C_{\text{ext}} \) \([\text{cf. eqs } 17 \text{ and } 19]\). In the case of \( \beta_h < 1 \), we have \( C_{\text{enh}} = C_{\text{ext}} \) and eqs 37 and 38 simplify to a previously known expression for the electron energy-loss probability.\(^9\) Usually, energy losses \( \delta E = h\omega \) are expressed in the units of eV, then \( P_{\text{EELS}} \) is in the units of eV\(^{-1}\).

**Cathodoluminescence Probability.** As discussed in the Particle-Induced Energy Losses section, in vacuum (or more generally when \( \beta_h < 1 \)) the radiation from the particle-electron system \( W_{\text{rad}} \) is only the one produced by induced currents in the particle (\( W_{\text{abs}} \)). In an arbitrary nonabsorbing host medium, the radiated energy is the energy lost by the electron minus the energy absorbed by the particle

\[ \Delta E = \Delta E_0 + \Delta E_{\text{enh}} - \Delta E_{\text{abs}} \]

\[ = \frac{2}{\pi} \int_0^\infty d\omega (W_0 + W_{\text{enh}} - W_{\text{abs}}) \]

\[ = \int_0^\infty d(\hbar\omega) \Gamma_{\text{CL}}^{\text{tot}}(\hbar\omega) \hbar\omega \]

(39)

where, by analogy to \( \Gamma_{\text{EELS}}(\hbar\omega) \), we introduce the total light-emission probability density

\[ \Gamma_{\text{CL}}^{\text{tot}}(\hbar\omega) = \frac{2}{\pi} \frac{W_0 + W_{\text{enh}} - W_{\text{abs}}}{\hbar^2 \omega} \]

(40)

As discussed in the Electron Energy-Loss Probability section, \( W_0 \) is potentially problematic, but the computationally intensive method is only needed to calculate the particle-related contribution to \( \Gamma_{\text{CL}}^{\text{tot}} \) which we further denote as \( P_{\text{CL}}^{\text{tot}}(\hbar\omega) \)

\[ P_{\text{CL}}^{\text{tot}}(\hbar\omega) = \frac{2}{\pi} \frac{W_{\text{rad}} - W_0}{\hbar^2 \omega} = \frac{m_0^2 e_0^2}{\pi \hbar^2 k_0} (C_{\text{enh}} - C_{\text{abs}}) \]

\[ = \frac{m_0^2 e_0^2}{\pi \hbar^2 k_0} (C_{\text{enh}} - C_{\text{ext}} + C_{\text{sc}}) \]

(41)

where the second part prevents the loss of precision when \( C_{\text{enh}} \) and \( C_{\text{abs}} \) are equal within a few decimal places, which is often the case for metallic nanoparticles. In the latter case, one may calculate \( C_{\text{sc}} \) by integrating the far field instead of using the relation \( C_{\text{sc}} = -C_{\text{ext}} - C_{\text{abs}} \).

The above definition of \( P_{\text{CL}}^{\text{tot}} \) is fundamentally the most natural since it accounts for the total outgoing radiation in all directions (denoted by superscript "tot"). However, all existing measurement modalities for CL collect light only in the upper
hemisphere when the electron moves downward; this always excludes the Cherenkov cone (directed in the lower hemisphere). To be more accurate, one should consider a large but finite chunk of the host medium and draw the Cherenkov cone from each point of the electron trajectory inside the host medium. First, this solves the problem with potential unboundedness of $W_{0}$ since it does not contribute to the measured signal if we neglect the reflection of the Cherenkov radiation from the bottom boundary of the host medium. Second, the interference of $E_{\text{inc}}$ and $E_{\text{reb}}$ in the far field (also concentrated in the direction of the Cherenkov cone) is irrelevant to the measurements as well. But this interference is exactly the one that leads to the difference between $W_{\text{ext}}$ and $W_{\text{reb}}$. Thus, to exactly reproduce the experimental signal one should integrate $|E_{\text{inc}}|^2$ over the detector collection angle, which is often not known. However, if one aims to have a simple approximation, the integral of the scattered intensity over the whole solid angle (proportional to $C_{\text{sca}}$) is a reasonable option, at least for particles smaller than the wavelength. For the latter case, the angular dependence of $|E_{\text{inc}}|^2$ is relatively weak, thus the ratio between the integral over the detector collection angle and $C_{\text{sca}}$ is expected to weakly depend on the loss energy (frequency). Then, the simulated spectrum will reproduce the measured one semiquantitatively up to a constant factor. Therefore, we postulate the CL probability to be

$$P_{\text{CL}}(\omega) \equiv \frac{2}{\pi} \frac{W_{\text{sca}}}{h} = \frac{m_{0}^{2} E_{0}^{2}}{\pi h^{2} k_{0} C_{\text{sca}}}$$

which agrees with the ones used in other simulation methods (Lorenz–Mie, BEM). Naturally, we also have $P_{\text{CL}} = P_{\text{CL}}^{\text{tot}}$ for $\beta_{h} < 1$. Finally, we stress once again that in the case of $\beta_{h} > 1$ the difference between $W_{\text{ext}}$ and $W_{\text{reb}}$ is important for the electron energy losses (Electron Energy-Loss Probability section) but is not visible in existing CL measurement configurations.

The definition of $P_{\text{CL}}$ becomes even more problematic in the case of absorbing host medium since the absorption of the scattered radiation is generally significant. To accurately reproduce the signal at a detector, one should account for the variation of optical path in the host medium with the scattering angle. The corresponding attenuation will depend on the variation of $\text{Im} m_{h}$ with $\omega$. Still, we can expect eq 42 to qualitatively reproduce the measured CL spectra. Fortunately, the far limit of the incident electron field, which is not negligible for $\text{Re} \beta_{h} > 1$, has the same behavior as the attenuated Cherenkov radiation. Thus, its contribution to detector signal can also be usually neglected. By contrast, $P_{\text{CL}}^{\text{tot}}$ has no practical relevance at all in this case since all underlying components of the energy balance depend on the outer boundary of the host medium and the far-field powers cannot be computed as integrals over the particle volume.

Finally, we stress that neither $P_{\text{EELS}}$ nor $P_{\text{CL}}^{\text{tot}}$ is generally guaranteed to be positive. While the relations $W_{\text{abs}} \geq 0$ and $W_{\text{sca}} > 0$ (hence, $P_{\text{CL}} > 0$) always hold, see eq 18 and ref 24, only in the case $\beta_{h} < 1$, the probabilities $P_{\text{EELS}}$ and $P_{\text{CL}}$ are proportional to $W_{\text{abs}} + W_{\text{sca}}$ and $W_{\text{sca}}$, respectively, and hence are strictly positive. Negative probabilities that may be obtained in absorbing or Cherenkov host medium are analogous to the phenomenon of negative extinction.\(^3\) Note, however, that $W_{\text{ext}} > 0$ holds in any nonabsorbing medium, including the case $\beta_{h} > 1$.

Scale Invariance. To account for the host medium in the DDA, the Green’s tensor, the incident electric field, and the particle refractive index must be modified according to $m_{h}$. For the electromagnetic codes that do not natively support refractive index of the host medium as an input parameter, this can be done by scaling other input parameters. For the case of the plane-wave excitation and $m_{h} > 0$, it is sufficient to divide both $m_{0}$ and the vacuum wavelength $\lambda$ by $m_{h}$, resulting in the correct values of $m(r)$ and $k$.\(^3\) All computed values are then correct, except for scaling of cross sections since $I_{0}$ scales with $m_{0}$ when $E_{0}$ is fixed (eq 19).

In the case of electron excitation, additional care is required to keep the incident field (eq 25) the same up to a constant factor. Relativistic factors $\beta_{h}$ and $r_{h}$ need to be the same since they differently affect the fields along the transverse and longitudinal coordinates, leading to the scaling $\nu \rightarrow \eta \nu$. Obviously, this applies only to the case of not very dense host medium ($\beta_{h} < 1$)—this derivation additionally illustrates that this case is fully analogous to the case of vacuum. The scaling of $\nu$ is compensated by changed $\omega_{0}$ corresponding to the above scaling of $\lambda$. The resulting $E_{\text{inc}}(r)$ in vacuum is then $m_{h}$ times the correct field in the host medium.

Let us generalize this analysis to arbitrary scaling of refractive index by $\eta \in \mathbb{R}$ combined with scaling of all lengths by $\xi \in \mathbb{R}$ (and inverse scaling of $k$). The latter corresponds to the classical scale invariance rule in electromagnetic scattering.\(^4\) Formally, we have

$$\nu \rightarrow \eta \nu, \quad r \rightarrow r/\xi, \quad r_{0} \rightarrow r_{0}/\xi, \quad k \rightarrow \xi k$$

which, after straightforward algebraic analysis (eqs 7, 17–19, 25, 26, 32, 37, and 41), leads to

$$\omega \rightarrow \eta \omega, \quad E_{\text{inc}} \rightarrow \eta E_{\text{inc}}, \quad E \rightarrow \eta E, \quad P \rightarrow \rho \eta/P, \quad G \rightarrow \xi \xi G$$

$$I_{0} \rightarrow I_{0}/\eta, \quad \frac{\partial W_{0}}{\partial x} \rightarrow \frac{\xi}{\partial \xi} \frac{\partial W_{0}}{\partial \xi}, \quad W_{\nu} \rightarrow \eta W_{\nu}, \quad C_{\nu} \rightarrow \eta^{2} C_{\nu}$$

$$P_{\text{EELS},\text{CL}} \rightarrow P_{\text{EELS},\text{CL}}/\xi^{2}, \quad \Delta E_{\nu} \rightarrow \eta^{2} \Delta E_{\nu}$$

(44)

where $X$ is a subscript of any power (enh, ext, abs) and $E_{0}, \nu, h_{0}$ and $\mu_{0}$ are kept intact. Note that the scaling of powers and cross sections is different from the case of plane-wave excitation due to the additional scaling of the incident field.

Coming back to simulating EELS and CL in the host medium with $\beta_{h} < 1$ using any vacuum-based code, one has two options. The first one, described above, corresponds to the case of not very dense host medium ($\beta_{h} < 1$)—this derivation additionally illustrates that this case is fully analogous to the case of vacuum. The scaling of $\nu$ is compensated by changed $\omega_{0}$ corresponding to the above scaling of $\lambda$. The resulting $E_{\text{inc}}(r)$ in vacuum is then $m_{h}$ times the correct field in the host medium.

Note that the values of both $m_{s}$ and $m_{h}$ correspond to the original frequency rather than to the scaled one. Thus, both $P_{\text{EELS}}$ and $P_{\text{CL}}$ computed with vacuum code for energy loss $m_{h} \omega$ are exactly the sought probabilities for energy loss $\omega$ in the host medium. The second option keeps $\omega$ and $\lambda$ intact at the cost of additional geometrical scaling, i.e., $\eta = m_{h} = 1/\xi$. Thus, both particle dimensions and electron position need to be additionally multiplied by $m_{h}$.

\[^{3}\text{Note that the values of both } m_{s} \text{ and } m_{h} \text{ correspond to the original frequency rather than to the scaled one. Thus, both } P_{\text{EELS}} \text{ and } P_{\text{CL}} \text{ computed with vacuum code for energy loss } m_{h} \omega \text{ are exactly the sought probabilities for energy loss } \omega \text{ in the host medium. The second option keeps } \omega \text{ and } \lambda \text{ intact at the cost of additional geometrical scaling, i.e., } \eta = m_{h} = 1/\xi. \]
\[ P_{\text{EELS, CL}} = \frac{m_h P_{\text{EELS, CL}}}{m_e} \]

In this case, the probability density computed by the vacuum code needs to be further divided by \( m_e \). Finally, note that the scaling \( v \rightarrow m_e v \) corresponds to the following scaling of electron kinetic energy \( E \)

\[ E = E_0 \left( \frac{\sqrt{E_0^2 - (k_0^2 - 1)E(2E_0 + E)}}{E_0} - 1 \right) \]

where \( E_0 = m_e c^2 \) is the electron rest mass energy.

Naturally, the proposed scaling cannot transform the Cherenkov case into a vacuum one, but an alternative approximate scaling for the case \( \beta_0 > 1 \) is described in Section S4.

**Software Implementation.** To perform EELS and CL simulations according to the developed general theory, we modified the open-source software ADDA. A single run of ADDA performs a simulation for a single set of parameters (\( \lambda \), beam position, etc.). To simulate a loss spectrum or to scan a particle’s cross section with the beam, it is necessary to run ADDA multiple times varying the desired parameters. For instance, to simulate the EELS and CL spectra, one needs to vary \( \lambda \) and the corresponding \( m \). We developed a Python wrapper, named ADDAWrapper, to automate this process.

The wrapper is designed to work as a Python library, so one only has to fill the example preset file with the simulation parameters, and call high-level functions from this file to perform the corresponding set of simulations (spectrum, loss probability scan over the cross section of the particle, etc.), collect the data from these simulations, and plot it in various formats. Ready-to-use examples are distributed with ADDA in the folder /examples/.

ADDAwrapper supports multithreading to speed up the simulation up to an order of physical processor cores. Apart from that, the examples use an optimized set of simulation parameters, which allows the wrapper to perform EELS and CL simulations with ADDA up to an order of magnitude faster than that with the default code settings. More details are given in Section S5. In particular, it discusses the possibility of electron beam intersecting the particle, although no rigorous theory is available for this case.

### RESULTS AND DISCUSSION

**Comparison to the Lorenz–Mie Theory in Vacuum.**

The classical Lorenz–Mie theory presents a solution of light scattering by a homogeneous sphere. This solution was extended for calculation of the EELS and CL by Garcia de Abajo et al., who also implemented it in the online simulation tool, which we used to obtain the reference solutions.

In Figure 2, we present the EELS and CL spectra simulated with ADDA and the Lorenz–Mie theory. In vacuum, an electron with kinetic energy \( E = 100 \) keV passes at a distance of 100 nm from the center of a silver 75 nm-radius sphere. Optical data for silver are taken from ref 50 since it is available as a built-in option in the Lorenz–Mie simulation tool, and 128 dipoles along the x-axis (\( n_x = 128 \)) are used for volume discretization. A step size of 0.05 eV is used for all simulations of spectra.

The spectra feature dipole, quadrupole, and octupole resonances and a dip at around 3.9 eV analogously to that for the plane-waver excitation. Simulated spectra are close to the exact solution but can be further improved by increasing \( n_x \) (refining discretization) at the expense of extra computational resources. A more efficient approach is to employ the Richardson extrapolation. Although it is a semiempirical method, it was successfully used in various applications and was especially efficient for nanoparticles. In particular, we used the guidelines from ref 52, performing simulations for a set of \( n_x = 128, 108, 91, 76, 64, 54, 45, 38, \) and 32 and extrapolating the dependence on the dipole size to \( d = 0 \) using the quadratic function (see Figure 3 for an example). The errors of data points were assumed to scale as \( d^3 \), and the standard error of fitted value at \( d = 0 \) was multiplied by 2 to obtain nominal 95% confidence interval.

In Figure 4, the same Richardson extrapolation applied to the whole spectrum leads to almost perfect match with the exact solution. The extrapolation is performed automatically by ADDAWrapper both for a single \( \delta E \) and for the whole spectrum.

**Comparison to the BEM in a Nonabsorbing Host Medium.**

Next, we consider particles embedded in a host medium. In Figure 5, we show how EELS spectrum changes when the same sphere is placed inside a nonabsorbing host medium, in comparison to the simulation for vacuum (\( m_e = 1 \)). In host media, the peaks shift to the lower energies and their
magnitudes decrease. Moreover, the separation between quadrupole and octupole peaks becomes more pronounced, while a hexapole peak appears for \( m_h = 2 \). We also performed scaling of separate DDA simulations for a particle in vacuum according to the Scale Invariance section—both approaches there (eqs 45 and 46) lead to identical results (only one of them is shown). The approximate scaling for \( m_h = 2 \) is also close to the latter curves at high energies in contrast to the true \( P_{\text{CL}} \) values, which are significantly larger over the whole energy range albeit having a similar shape. The latter is related to the use of \( P_{\text{CL}} \) instead of \( P_{\text{CL}} \) and is discussed below in this section.

We further compare our results with that of the BEM, as implemented in the MNPBEM17 code, as it seems to support arbitrary host medium. We limit ourselves to EELS in this section, presenting the corresponding CL results in the Supporting Information (Figures S2–S4). First, we reproduce the EELS data from Figure 4. As shown in Figure 7, the BEM agrees with the DDA and the Lorenz–Mie theory except for the lowest loss energies (<1.4 eV). We used 1024 surface points for all BEM simulations, and further mesh refinement converges to other curves after 3.9 eV. By contrast, the true \( P_{\text{EELS}} \) is much smaller and the dip almost disappears. We leave a detailed analysis of the ultrarelativistic scaling for future research, presenting only some preliminary data in Section S6.

The evolution of the CL peaks with increasing \( m_h \), depicted in Figure 6, is similar to that of EELS, but with large suppression of octupole and hexapole peaks. For \( m_h = 1.5 \), the scaling works perfectly, and the results for high energies are almost the same as in vacuum (much more so than for EELS). The approximate scaling for \( m_h = 2 \) is also close to the latter curves at high energies in contrast to the true \( P_{\text{CL}} \) values, which are significantly larger over the whole energy range albeit having a similar shape. The latter is related to the use of \( P_{\text{CL}} \) instead of \( P_{\text{CL}} \) and is discussed below in this section.

We further compare our results with that of the BEM, as implemented in the MNPBEM17 code, as it seems to support arbitrary host medium. We limit ourselves to EELS in this section, presenting the corresponding CL results in the Supporting Information (Figures S2–S4). First, we reproduce the EELS data from Figure 4. As shown in Figure 7, the BEM agrees with the DDA and the Lorenz–Mie theory except for the lowest loss energies (<1.4 eV). We used 1024 surface points for all BEM simulations, and further mesh refinement

Figure 4. EELS and CL spectra simulated with the Lorenz–Mie theory and ADDA (\( n_x = 128 \) with the extrapolation); 95% confidence interval is shown for the extrapolated values. The parameters of the problem are shown in the inset (the same as in Figure 2).

Figure 5. EELS spectra for a sphere in an infinite nonabsorbing host medium simulated with ADDA (\( n_x = 128 \)), either directly or through scaling of simulations in vacuum (see the text for details). The problem parameters are shown in the inset. In the host medium with \( m_h = 2 \), the electron is faster than light, causing the Cherenkov radiation.

Figure 6. Same as Figure 5, but for the CL.

Figure 7. EELS spectra simulated with the Lorenz–Mie theory, ADDA (\( n_x = 128 \) with the extrapolation), and the BEM. The parameters of the problem are shown in the inset (the same as in Figure 4).
did not improve the accuracy for such energies. We hypothesize that it is related to large \( \ln | \theta | > 7 \) in this range, but it is not important for further discussion. Note also that CL results for BEM do not have this artifact (Figure S2). Since the online tool\(^9\) does not allow manual specification of a dielectric function (which is used below), we further use the Lorenz–Mie theory built into MNPBEM. However, we tested that they produce identical results for the case of Figure 7 (data not shown).

Next, we set \( m_h = 1.5 \) in both MNPBEM and ADDA and compare the results with the Lorenz–Mie theory, scaled according to eq 45. The results in Figure 8 show that all three methods agree. The visible inaccuracy of the DDA at the peak value at 3.0 eV disappears with further grid refinement to \( n_g = 192 \) with the extrapolation (data not shown). The CL results also agree, but only if the MNPBEM results are additionally multiplied by \( m_h \) (Figure S3).

The situation is markedly different for \( m_h = 2 \) (Cherenkov case), as shown in Figure 9 featuring a huge difference between the DDA and BEM. To investigate this issue, let us formally define the extinction probability \( P_{\text{ext}} \) by analogy to \( P_{\text{EELS}} \) (eq 37) as

\[
P_{\text{ext}}(\hbar \omega) = \frac{2 W_{\text{ext}}}{\pi \hbar^2 \omega} m_h^2 E_{\text{CL}}^2 C_{\text{ext}}
\]  

Figure 9. EELS and extinction probabilities simulated with the DDA \( (n_g = 128 \) with the extrapolation) compared to EELS spectrum simulated with the BEM. The parameters of the problem are shown in the inset (a subset of that in Figure S).

As discussed in the Electron Energy-Loss Probability section, \( P_{\text{ext}} \) is identical to \( P_{\text{EELS}} \) for \( \hbar < 1 \), which we explicitly tested for the case of \( m_h = 1.5 \) (data not shown). However, they are different for \( m_h = 2 \), as shown in Figure 9. And, surprisingly, the spectrum simulated with the BEM turns out to be matching \( P_{\text{ext}} \) values instead of \( P_{\text{EELS}} \) (the remaining difference at 2.45 eV can be removed by increasing \( n_g \) data not shown). Thus, we conclude that MNPBEM works fine for \( \hbar < 1 \), but is incorrect for the Cherenkov case. It uses the correct incident field in the latter case but seems to use incorrect expression for \( P_{\text{EELS}} \) based on the equivalence of \( W_{\text{ext}} \) and \( W_{\text{anh}} \) that no longer holds. The latter equivalence is also implicitly used in other DDA codes for EELS simulations: e-DDA\(^{40}\) and DDEELS.\(^3\) By contrast, the results of \( P_{\text{CL}} \) computed with MNPBEM for \( m_h = 2 \) agree with the DDA after multiplication by \( m_h \) (Figure S4). This is expected since the definition of \( P_{\text{CL}} \) is not affected by the difference between \( W_{\text{ext}} \) and \( W_{\text{anh}} \) (in contrast to \( P_{\text{EELS}} \)), as discussed in the Cathodoluminescence Probability section.

To finalize this section, let us summarize the effect of the Cherenkov radiation on the EELS and CL spectra. The position and widths of the peaks are due to LSPRs, which are fully determined by the particle and \( m_h \). However, their magnitudes are determined by the coupling of these inherent resonances to the incident field and to the measured signal (either electron energy loss or far-field radiation). The Cherenkov radiation principally affects these couplings, but not the peak positions. This explains the success of simple scaling in Figures 5 and 6 in reproducing the peak positions, but a similar estimate is possible even if one excites the same system with plane waves.

Based on a single example above, the characteristic feature of the Cherenkov-case EELS is much smaller values at high energies (to the right of plasmon peaks) and lack of the 3.9 eV dip, which is related to the use of the properly defined \( P_{\text{EELS}} \) instead of \( P_{\text{ext}} \). Thus, in addition to directly interacting with an electron, the particle destructively interferes with the Cherenkov radiation decreasing the probability of corresponding electron energy loss. The resulting \( P_{\text{EELS}} \) may even become negative (see Figure S8). Similar behavior is observed for \( P_{\text{CL}} \), while the practically measurable \( P_{\text{CL}} \) retains the overall shape but significantly increases with \( m_h \) beyond the Cherenkov threshold. A plausible explanation is that the particle converts some of the Cherenkov radiation (from the corresponding cone) into other (measurable) scattering angles. More specifically, the decay of \( E_{\text{int}} \) with \( b \) (eq 25) in the Cherenkov case is inverse-square-root rather than exponential, leading to overall stronger excitation of the particle (larger \( | \mathbf{P}(r) | \)), especially for higher energies that imply larger arguments of functions \( K_0 \) and \( K_1 \). The same reasoning explains the increase of \( P_{\text{ext}} \) into the Cherenkov case (see Section S6) and suggests that the differences will decrease with particle size. Overall, \( P_{\text{CL}} \) and \( P_{\text{CL}} \) behave similarly to \( P_{\text{EELS}} \) and \( P_{\text{ext}} \), respectively, which has been suggested in the Cathodoluminescence Probability section.

Therefore, the original design goals of both EELS and CL to probe the LSPRs, i.e., to retrieve the peak positions and visualize the plasmons, are not hampered by the Cherenkov radiation (if the host-medium signal can be filtered out). However, rigorous consideration of the field produced by an electron in a dense medium is imperative for quantitative
agreement with experiments, unless the particle is very small. The distinction between the qualitative and quantitative agreements is naturally vague, e.g., negligible coupling is known to cause disappearance of so-called dark modes in optical extinction spectra.\(^2\) Studying the cases where the Cherenkov radiation may lead to similarly drastic differences (i.e., disappearance of some peaks) is outside the scope of this paper, although a single intriguing example is presented in Figure S8.

We have analyzed above only nonabsorbing host medium since that is where alternative simulation methods and experimental data (see the next section) are available. However, the developed theory and simulation capabilities are fully ready for the absorbing host medium, which we illustrate by a number of examples in Section S8.

**Comparison to the Experiments.** In EELS experiments, a particle is usually placed on or inside a substrate. Raza et al.\(^{13}\) investigated silver nanospheres encapsulated in silicon nitride, which fixes them in place and prevents silver oxidation. In that paper, both experimental and simulated spectra are shown for an encapsulated nanosphere with a radius of 9.2 nm and an electron passing at different impact parameters. The simulations were performed for a full system geometry, discretizing the finite chunk of the silicon nitride layer.

By contrast, we try to reproduce these experimental data by simulations for a particle in an infinite host medium. Specifically, Figure 10 shows the simulated spectrum for the same silver nanosphere along with the experimental data from ref 13 for an impact parameter of 12.4 nm. The problem parameters are in the inset. Experimental data are taken from ref 13, simulation is done with ADDA using \(n_s = 128\) (blue line) and convoluted with Gaussian PSF with FWHM of 0.15 eV (purple line).

**Figure 10.** Experimental and simulated EELS spectra for a silver sphere encapsulated in silicon nitride, normalized to the maximum value. The problem parameters are in the inset. Experimental data are taken from ref 13, simulation is done with ADDA using \(n_s = 128\) (blue line) and convoluted with Gaussian PSF with FWHM of 0.15 eV (purple line).

We also extended the scale invariance rule to EELS, allowing one to apply any existing vacuum-based code to the case of a moderately dense nonabsorbing host medium. The presented framework for a homogeneous medium is derived using the free-space tensor \(\mathbf{G}\), but it can be further generalized to the cases of layered media, such as a semi-infinite or thin substrate, by employing the corresponding Green’s tensors.

For a test case of a sphere in vacuum, the DDA results (with extrapolation of the computed values versus the dipole size) almost match the exact Lorenz–Mie solution, exceeding the accuracy of the BEM. The same agreement between the three methods holds for a host medium with no intrinsic electron losses, but the results of the Lorenz–Mie theory need to be scaled (as mentioned above) since only vacuum implementations of this theory are available. For the Cherenkov (sufficiently dense) host medium, the DDA results for EELS probability disagreed with that of BEM (as implemented in the MNPBEM code) since the latter code ignores the interference values at larger loss energies to systematically lie below zero. While such negative values are not impossible when \(\beta_h > 1\), they are not observed in simulations for the specific problem parameters.

In another work, Kobylko et al.\(^{14}\) investigated gold nanoparticles placed inside a glass substrate. One of them was a 92.6 nm-long gold nanowire with a 7.8 nm radius, investigated by electrons with \(E = 100\) keV. We modeled this nanowire as a perfect cylinder with hemispheres at both ends with a computational grid of \(16 \times 16 \times 190\) dipoles and placed it in an infinite medium with \(m_p = 1.45\) (corresponding to \(\beta_h = 0.79\)); optical data for gold is taken from ref 57. We compare the results of the DDA simulations with the experimental data from ref 14 in Figure 11. The experimental data include EELS spectrum averaged over the cross section of the nanowire (Figure 11a), as well as plasmon maps for four observed resonant energies (Figure 11b–e): 0.86, 1.27, 1.66, and 2.4 eV.

The simulation results include the same cross-section-averaged spectrum (Figure 11f) and the plasmon maps for resonant energies of the simulated spectrum (Figure 11g–i): 0.7, 1.2, 1.55, and 2.4 eV, which are slightly different from the experimental ones. The latter is probably caused by imperfect cylindrical geometry of the particle in the experiment. Apart from that and expected broadening of the experimental peaks, simulations reproduce the experimental data both for EELS spectrum and plasmon maps. This verifies the empirical procedure of setting the electron trajectory in the middle between the dipole centers in the DDA (discussed in Section S5).

## CONCLUSIONS

We derived all of the quantities necessary to simulate EELS and CL in the DDA in the energy budget framework based on the volume integral equation. This framework has shown its versatility in calculating the incident electric field, free-space energy losses, and particle-induced energy losses of a current source, as well as scattered power corresponding to CL. The obtained expressions either coincide with those known from the literature (derived by several other methods) or appear for the first time. In particular, a volume integral expression for particle-induced energy losses of arbitrary source (eq 32) can be efficiently calculated in the DDA. This expression remains valid for an arbitrary (even absorbing or Cherenkov) host medium, and it reduces to the known one in the case of vacuum.\(^{9,10,38}\) We also extended the scale invariance rule to EELS, allowing one to apply any existing vacuum-based code to the case of a moderately dense nonabsorbing host medium. The presented framework for a homogeneous medium is derived using the free-space tensor \(\mathbf{G}\), but it can be further generalized to the cases of layered media, such as a semi-infinite or thin substrate, by employing the corresponding Green’s tensors.

For a test case of a sphere in vacuum, the DDA results (with extrapolation of the computed values versus the dipole size) almost match the exact Lorenz–Mie solution, exceeding the accuracy of the BEM. The same agreement between the three methods holds for a host medium with no intrinsic electron losses, but the results of the Lorenz–Mie theory need to be scaled (as mentioned above) since only vacuum implementations of this theory are available. For the Cherenkov (sufficiently dense) host medium, the DDA results for EELS probability disagreed with that of BEM (as implemented in the MNPBEM code) since the latter code ignores the interference
of the Cherenkov and particle-induced radiations (effectively assuming that EELS probability is proportional to the extinction power). The CL spectra agree between the DDA and BEM in all considered cases up to the overall scale of MNPBEM results (it needed to be additionally multiplied by $m_h$).

Rigorously accounting for the host medium is important for the corresponding experimental conditions, i.e., when particles or voids are considered in larger homogeneous slabs, since LSPRs strongly depend on the dielectric properties of this medium. The implementation of the developed theory in the open-source ADDA code, augmented with a comprehensive Python wrapper, makes any such simulations easily available to practitioners. To illustrate these novel capabilities, we simulated actual EELS experiments for nanospheres encapsulated in silicon nitride and nanowires inside glass. For the former experiment, the electrons were faster than the speed of light in the substrate (Cherenkov case), and the DDA perfectly reproduced the EELS spectrum in terms of a peak position. For the nanorod inside glass, the DDA reproduced the EELS spectrum, as well as the plasmon maps for all four plasmon resonances determined in the experiment.

Theoretical simulations of EELS and CL spectrum in Cherenkov and/or absorbing host medium show interesting features, including the Fano-like deformation of some of the peaks. Their experimental verification is an important topic for future research. Another such topic is a rigorous simulation of electron trajectories intersecting a particle, including the bulk losses in absorbing material of the particle, since, currently, calculated spectra and plasmon maps for such trajectories are only qualitatively correct.

### ASSOCIATED CONTENT

#### Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpcc.2c06813.

- Fourier transform, energy transfer for sources with general time dependence, electric field derivation, ultrarelativistic scaling, code implementation, transition of EELS probabilities into the Cherenkov case, comparison of cathodoluminescence in a nonabsorbing host medium with the BEM, and simulations with absorbing host medium (PDF)

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