Helmholtz decomposition analysis of electron energy loss: Differentiating resonances on polarization and radiation eigenmodes

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Helmholtz decomposition is a powerful mathematical tool for investigation and analysis of vector fields, particularly in electrodynamic systems. In this paper, we apply it to electron energy loss spectroscopy of magnetically inactive structures to get insight into field composition of energy losses. The obtained results show that losses are incurred through two pathways – excitation of transverse/longitudinal fields by solenoidal/conservative currents. Separation of these processes gives us important information about the fields and the type of eigenmodes (polarization or radiation) being in resonance with the electron beam. Capabilities of such analysis are demonstrated in the study case of metal nanofilms and nanodisks, where we perform differentiation of the resonances occurred on plasmons (polarization eigenmodes) and plasmon polaritons (radiation eigenmodes).

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1. INTRODUCTION

Electron energy loss spectroscopy (EELS) is known as an efficient diagnostic instrument [1–3]. In EELS, a structure under the study is exposed to a relativistic electron beam with a narrow range of kinetic energies. Some of the electrons undergo inelastic scattering, characterized by an energy loss incurred due to their interaction with the sample. The amount of energy loss can be measured via an electron spectrometer and interpreted in terms of physical processes causing that loss. Inelastic interactions include inter- and intra-band transitions, ionization processes, and excitation of electromagnetic eigenmodes. The latter caused recently a huge interest amongst the optics community [3] for ability of EELS to excite a much wider range of eigenmodes compared to the standard optical instruments [4, 5].

Experimental interpretations of EELS spectra, however, have certain limitations, such as inability to distinguish resonances on different eigenmodes due to nonexistence of universal fitting functions. The most popular technique used in EELS for separation of eigenmode resonances is deconvolution with Lorentzians [6, 7]. This technique utilizes the model of zero-dimensional harmonic oscillators [7] that obviously has limited applicability for real resonances on three-dimensional eigenoscillations. Another issue in interpretation of eigenmodes is their ambiguous classification. Taking plasmons and plasmon polaritons as an example, they are commonly viewed either as localized and propagating eigenmodes [3, 8] or as non-retarded and retarded eigenoscillations [3, 9] or as longitudinal and transverse eigenoscillations [10, 11]. Eventually, such contradictory definitions cause massive confusion of plasmons and plasmon polaritons in the field of plasmonics.

To clarify the physics behind various eigenmodes and enhance their analysis in EELS, herein, we develop a theoretical framework based on Helmholtz decomposition of the fields excited in a sample by an electron beam. We classify all eigenmodes of Maxwell’s equation in magnetically inactive electromagnetic systems into two groups of radiation and polarization eigenmodes, based on their ability to transfer electromagnetic energy and polarize the sample (see Fig. 1). This classification is identical to the division into retarded/non-retarded eigenmodes, but brings more clarity to their physics. According to Helmholtz decomposition, these groups appear to have distinct fields – polarization eigenmodes such as phonons, plasmons, and excitons exhibit pure longitudinal (conservative) fields, while radiation eigenmodes such as photons and polaritons possess either transverse (solenoidal) fields or hybrid fields composed of transverse and longitudinal components.

The distinct field structures of the radiation and polarization eigenmodes make their differentiation straightforward by performing Helmholtz analysis of electron energy losses. The proposed framework enables such analysis and complements EELS measurements for characterization of eigenmodes in com-
plex electrodynamic structures. Capabilities of this framework are demonstrated in the numerical study of metal nanofilms and nanodiscs.

2. MAXWELL’S EQUATIONS

In the classical electrodynamics, propagation of electromagnetic fields in a magnetically inactive medium is described by the macroscopic Maxwell’s equations,

\[ \nabla \times \mathbf{H}(t, r) = \varepsilon_0 \frac{\partial \mathbf{E}(t, r)}{\partial t} + \mathbf{J}^p(t, r) + \mathbf{J}(t, r), \]

\[ \nabla \times \mathbf{E}(t, r) = -\mu_0 \frac{\partial \mathbf{H}(t, r)}{\partial t}, \]

where \( \varepsilon_0 = 8.8541872 \cdot 10^{-12} \text{ F/m} \) and \( \mu_0 = 4\pi \cdot 10^{-7} \text{ H/m} \) are the electric and magnetic constants; \( \mathbf{E}(t, r) \) and \( \mathbf{H}(t, r) \) are the macroscopic electric and magnetic fields; \( \mathbf{J}(t, r) \) is the macroscopic density of the external current that excites the electromagnetic fields; \( \mathbf{J}^p(t, r) \) is the the macroscopic density of the polarization currents induced in the medium. Within the linear response approach, the medium polarization is assumed linear to electric fields with the temporal dispersion of \( \mathbf{J}^p(t, r) \) given by [11]

\[ \mathbf{J}^p(t, r) = \int_0^{\infty} \hat{\mathbf{J}}(\tau, r) \mathbf{E}(t - \tau, r) \, d\tau, \]

where \( \hat{\mathbf{J}}(\tau, r) \) is the space-dependent operator of differential conductivity describing strength of the polarization dependence on electric fields excited at all preceding times according to the causality principle. In general, \( \hat{\mathbf{J}}(\tau, r) \) is a linear operator given by an anisotropic tensor \( \sigma_{ij}(\tau, r) \) of differential conductivity [11]. By performing the Fourier transform of all fields and current densities to the frequency space, integro-differential equations (1) and (2) reduce to pure differential equations

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

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

where \( \omega \) is the angular frequency, and \( \mathbf{D}(\omega, r) = \varepsilon_0 \hat{\mathbf{D}}(\omega, r) \mathbf{E}(\omega, r) \) is the displacement field defined through the operator of dielectric permittivity

\[ \hat{\varepsilon}(\omega, r) = 1 + \frac{i}{\varepsilon_0 \omega} \int_0^{\infty} \hat{\mathbf{J}}(\tau, r) \mathbf{e}^{i\omega \tau} \, d\tau. \]

The operator of dielectric permittivity \( \hat{\varepsilon}(\omega, r) \) provides complete description of local response to external electromagnetic excitations for any magnetically inactive linear system with temporal dispersion.

3. HELMHOLTZ DECOMPOSITION OF ELECTROMAGNETIC FIELD

To understand how external currents generate electromagnetic fields, we do Helmholtz decomposition for all vector fields in Eqs. (4) and (5). Recall, Helmholtz decomposition is the fundamental theorem of vector calculus [12, 13]. According to it, any physical field \( \mathbf{F}(r) \) can be uniquely decomposed into transverse (solenoidal) \( \mathbf{F}_t(r) \) and longitudinal (conservative) \( \mathbf{F}_l(r) \) components

\[ \mathbf{F}(r) = \mathbf{F}_t(r) + \mathbf{F}_l(r), \]

which feature

\[ \nabla \cdot \mathbf{F}_l(r) = 0, \quad \nabla \times \mathbf{F}_l(r) = 0. \]

This decomposition is universal and geometry-unrelated, in contrast to other numerous expansions over geometry-related harmonics [11]. The transverse and longitudinal components are orthogonal in the sense of their integral relation

\[ \int_0^{\infty} \mathbf{F}_l(r) \cdot \mathbf{F}(r) \, dr = 0, \]

and can be obtained from \( \mathbf{F}(r) \) as follows

\[ \mathbf{F}_l(r) = \frac{1}{4\pi} \nabla \times \int_0^{\infty} \nabla' \times \mathbf{F}(r') \, dr', \]

\[ \mathbf{F}_l(r) = -\frac{1}{4\pi} \nabla \int_0^{\infty} \nabla' \cdot \mathbf{F}(r') \, dr', \]

where \( \nabla' = \partial / \partial r' \).

Decomposing all vector fields in Eqs. (4) and (5), we get four coupled equations that describe excitation of transverse and longitudinal fields by two currents with densities \( \mathbf{J}_t(\omega, r) \) and \( \mathbf{J}_l(\omega, r) \),

\[ \nabla \times \mathbf{H}_t(\omega, r) = -i\omega \mathbf{D}_t(\omega, r) + \mathbf{J}_t(\omega, r), \]

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

\[ -i\omega \mathbf{D}_l(\omega, r) + \mathbf{J}_l(\omega, r) = 0, \]

\[ i\omega \mu_0 \mathbf{H}_l(\omega, r) = 0, \]

where \( \mathbf{D}_l(\omega, r) \) and \( \mathbf{D}_t(\omega, r) \) can be split into two parts,

\[ \mathbf{D}_l(\omega, r) = \varepsilon_0 \hat{\mathbf{D}}_l(\omega, r) \mathbf{E}(\omega, r) + \hat{\mathbf{e}}_l(\omega, r) \mathbf{E}(\omega, r), \]

\[ \mathbf{D}_t(\omega, r) = \varepsilon_0 \hat{\mathbf{D}}_t(\omega, r) \mathbf{E}(\omega, r) + \hat{\mathbf{e}}_l(\omega, r) \mathbf{E}(\omega, r), \]

with \( \hat{\mathbf{e}}_l(\omega, r) \), \( \hat{\mathbf{e}}_l(\omega, r) \), \( \hat{\mathbf{e}}_l(\omega, r) \), \( \hat{\mathbf{e}}_l(\omega, r) \), and \( \hat{\mathbf{e}}_l(\omega, r) \) describing the individual contributions of \( \mathbf{E}(\omega, r) \) and \( \mathbf{E}(\omega, r) \) fields to \( \mathbf{D}_l(\omega, r) \) and \( \mathbf{D}_t(\omega, r) \). As follows from these equations, the transverse and longitudinal fields possess different magnetic fields:

\[ \mathbf{H}_t(\omega, r) = -i(\omega \mu_0)^{-1} \nabla \times \mathbf{E}_l(\omega, r) \neq 0, \]

\[ \mathbf{H}_l(\omega, r) = 0, \]

regardless of the structure and excited currents. This is a universal feature of transverse and longitudinal fields caused by their distinct behaviors. Transverse fields are given by so-called retarded solutions of Maxwell’s equations, while longitudinal fields are non-retarded ones. It can be seen, for instance, from their power fluxes \( \mathbf{E}(\omega, r) \times \mathbf{H}(\omega, r) \). As any longitudinal fields do not possess magnetic fields, they cannot transfer energy along; radiation becomes possible only with addition of transverse fields that bring nonzero magnetic field \( \mathbf{H}(\omega, r) \).

4. RESONANCES ON POLARIZATION AND RADIATION EIGENMODES

The main differences in excitation of two groups of fields are associated with peculiarities of transverse and longitudinal currents: following the continuity equation,

\[ \frac{\partial \mathbf{J}(t, r)}{\partial t} + \nabla \cdot [\mathbf{J}^p(t, r) + \mathbf{J}(t, r)] = 0, \]
only longitudinal currents accompany charge density \( \rho \) variation,

\[
\frac{\partial \rho(t, \mathbf{r})}{\partial t} = -\nabla \cdot \left[ \mathbf{J}_\rho^\dagger(t, \mathbf{r}) + \mathbf{J}_\rho(t, \mathbf{r}) \right], \tag{18}
\]

and, thus, participate in the medium polarization. As a result, transverse and longitudinal currents interact with matter differently. For instance, excitation of transverse and longitudinal fields in a homogeneous isotropic medium with \( \rho(\omega, \mathbf{r}) = \epsilon_t(\omega, \mathbf{r}) = \epsilon_l(\omega, \mathbf{r}) = \epsilon(\omega) \) and \( \epsilon_l(\omega, \mathbf{r}) = \epsilon_l(0, \mathbf{r}) = 0 \) is completely decoupled,

\[
\mathbf{E}_l(\omega, \mathbf{r}) = -\frac{i}{\omega \epsilon_0} \hat{\mathbf{G}}_l(\omega, \mathbf{r}) \mathbf{J}_l(\omega, \mathbf{r}), \tag{19}
\]

\[
\mathbf{E}_t(\omega, \mathbf{r}) = -\frac{i}{\omega \epsilon_0} \hat{\mathbf{G}}_t(\omega, \mathbf{r}) \mathbf{J}_t(\omega, \mathbf{r}), \tag{20}
\]

where \( \hat{\mathbf{G}}_t(\omega, \mathbf{r}) = [k_0^2 \nabla^2 + \epsilon \omega^2]^{-1} \) and \( \hat{\mathbf{G}}_l(\omega, \mathbf{r}) = \epsilon^{-1}(\omega) \) with \( k_0 = \omega / \sqrt{\epsilon_0 \mu_0} \). These fields clearly demonstrate different dynamics: the excitation of \( \mathbf{E}_l(\omega, \mathbf{r}) \) and \( \mathbf{H}_l(\omega, \mathbf{r}) \) by \( \mathbf{J}_l(\omega, \mathbf{r}) \) is nonlocal (retarded), while the dependence of \( \mathbf{E}_t(\omega, \mathbf{r}) \) on \( \mathbf{J}_0(\omega, \mathbf{r}) \) is strictly local (non-retarded). In addition, they exhibit resonances on different eigenmodes of the homogeneous system. Transverse electric fields resonate on transverse eigenmodes given by the dispersion relation

\[
\ker[k_0^2 \nabla^2 + \epsilon \omega^2] = 0, \tag{21}
\]

while longitudinal fields have resonances on longitudinal eigenmodes given by the relation

\[
\ker[\epsilon \omega^2] = 0. \tag{22}
\]

The longitudinal eigenmodes of a homogeneous isotropic medium represent the elementary polarization excitations known in the solid-state physics as phonons, plasmons, and excitons, depending on the nature of polarization (see Fig. 1). Phonons appear as a response of crystal lattice, plasmons are caused by polarization of conduction electrons, and excitons are given by polarization of bound electrons. They all are characterized with nonzero polarization of intrinsic charges and absent energy transfer. In contrast to them, the transverse eigenmodes of a homogeneous isotropic medium are the composite radiation eigenoscillations known as polaritons, which are the coupled states of the elementary polarization (phonons, plasmons, and excitons) and elementary radiation (photons) excitations, as shown schematically in Fig. 1. In solid-state physics, radiation eigenmodes are also known as transverse electromagnetic (TEM) waves and classified as phonon polaritons, plasmon polaritons, exciton polaritons, photon-plasmon polaritons, photon-exciton polaritons, plasmon-exciton polaritons, and phonon-plasmon-exciton polaritons, depending on the coupling type of the elementary eigenmodes. In a homogeneous isotropic medium, they all exhibit nonzero power flux with absent polarization of intrinsic charges.

In an inhomogeneous structure, excitation of longitudinal and transverse fields by \( \mathbf{J}_1(\omega, \mathbf{r}) \) and \( \mathbf{J}_0(\omega, \mathbf{r}) \) is generally coupled, given by

\[
\mathbf{E}_l(\omega, \mathbf{r}) = -\frac{i}{\omega \epsilon_0} \hat{\mathbf{G}}_l(\omega, \mathbf{r}) \mathbf{J}_l(\omega, \mathbf{r}) - \epsilon_l(\omega, \mathbf{r}) F^{-1}_l(\omega, \mathbf{r}) \mathbf{J}_l(\omega, \mathbf{r})], \tag{23}
\]

\[
\mathbf{E}_t(\omega, \mathbf{r}) = -\frac{i}{\omega \epsilon_0} \hat{\mathbf{G}}_t(\omega, \mathbf{r}) \mathbf{J}_t(\omega, \mathbf{r}) - \epsilon_t(\omega, \mathbf{r}) F^{-1}_t(\omega, \mathbf{r}) \mathbf{J}_t(\omega, \mathbf{r})], \tag{24}
\]

where \( F^{-1}_l(\omega, \mathbf{r}) = \frac{1}{\epsilon_l(\omega, \mathbf{r})} \mathbf{J}_l(\omega, \mathbf{r}) \).

\begin{table}[h]
\begin{tabular}{|c|c|c|c|}
\hline
Eigenmode type & Field type & Power flux & Polarization charge \\
\hline
\hline
Polarization & L & \( \equiv 0 \) & \( \neq 0 \) \\
\hline
Radiation & T & \( \equiv 0 \) & \( \equiv 0 \) \\
T+L & \( \equiv 0 \) & \( \neq 0 \) \\
\hline
\end{tabular}
\end{table}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig1.png}
\caption{General classification of Maxwell’s equation eigenmodes in magnetically inactive electrodynamic systems. The labels refer to the type of eigenmode fields: L – longitudinal, T – transverse, and T+L – hybrid. The dotted line depicts eigenmodes of a general system containing all tree types of currents.}
\end{figure}
where the operators $\hat{G}_l(\omega, r)$ and $\hat{G}_r(\omega, r)$ have more complicated forms compared to the case of a homogeneous isotropic medium,

$$
\hat{G}_l(\omega, r) = [\hat{F}_l(\omega, r) - \hat{\varepsilon}_{ll}(\omega, r)\hat{F}_r^{-1}(\omega, r)\hat{\varepsilon}_{rl}(\omega, r)]^{-1},
\hat{G}_r(\omega, r) = [\hat{F}_l(\omega, r) - \hat{\varepsilon}_{rl}(\omega, r)\hat{F}_r^{-1}(\omega, r)\hat{\varepsilon}_{ll}(\omega, r)]^{-1},
$$

with $\hat{F}_l(\omega, r) = k_0^2 \nabla^2 + \hat{\varepsilon}_{ll}(\omega, r)$ and $\hat{F}_r(\omega, r) = \hat{\varepsilon}_{rl}(\omega, r)$. Now, the excitation is generally nonlocal for both groups of fields [until $\hat{\varepsilon}_{ll}(\omega, r)$ and $\hat{\varepsilon}_{rl}(\omega, r)$ are nonzero] with the resonance conditions given by

$$
\ker[\hat{F}_l(\omega, r) - \hat{\varepsilon}_{ll}(\omega, r)\hat{F}_r^{-1}(\omega, r)\hat{\varepsilon}_{rl}(\omega, r)] = 0, \quad (25)
\ker[\hat{F}_l(\omega, r) - \hat{\varepsilon}_{rl}(\omega, r)\hat{F}_r^{-1}(\omega, r)\hat{\varepsilon}_{ll}(\omega, r)] = 0 \quad (26)
$$

for transverse and longitudinal fields respectively.

Note that Eqs. (25) and (26) contain the common solutions given by

$$
\ker[\hat{\varepsilon}_{ll}^{-1}(\omega, r)\hat{F}_l(\omega, r)\hat{\varepsilon}_{rl}^{-1}(\omega, r)\hat{F}_r(\omega, r) - 1] = 0. \quad (27)
$$

These solutions correspond to the radiation eigenmodes composed by both $E_l(\omega, r)$ and $E_r(\omega, r)$ fields. In the literature, they are known as (i) transverse magnetic (TM or E) polaritons, with no magnetic field in the direction of propagation, and (ii) hybrid polaritons, with nonzero electric and magnetic fields in the direction of propagation. For every structure, there is a variety of TM and hybrid polaritons; they all exhibit unique field distributions and frequency dependences defined by material and geometrical composition of the structure. Their common features are nonzero power flux together with nonlinear polarization.

In addition to polaritons that possess both $E_l(\omega, r)$ and $E_r(\omega, r)$, there exist pure eigenmodes that have either $E_l(\omega, r)$ or $E_r(\omega, r)$, given by non-coincident solutions of Eqs. (25) and (26). These are (iii) radiation excitations known as transverse electric (TE or H) polaritons, with $E_l(\omega, r) = 0$ and $E_r(\omega, r)$ being perpendicular to the direction of propagation, and (iv) composite system polarization eigenmodes, with $E_l(\omega, r) = 0$ and $E_r(\omega, r) \neq 0$. The pure system eigenmodes are similar to transverse and longitudinal eigenmodes of a homogeneous isotropic medium though their polarization nature is usually more complex. The transverse system radiation eigenmodes feature nonzero power flux together with zero charge density, while the system polarization eigenmodes exhibit zero power flux with nonzero intrinsic charge density.

Eventually, all the realm of system radiation (i)–(iii) and system polarization (iv) eigenmodes can be observed through resonant effects accompanying excitation of electromagnetic fields by external currents. In particular, they can be detected with electron energy loss spectroscopy.

**5. HELMHOLTZ DECOMPOSITION OF ENERGY LOSS**

Although the excitation of longitudinal and transverse fields by $J_l$ and $J_r$ is generally coupled in inhomogeneous structures, the total power $P(\omega)$ spent for their excitation splits into two independent parts, $P_l(\omega)$ and $P_r(\omega)$,

$$
P(\omega) = -\frac{1}{2} \text{Re} \int_0^\infty \mathbf{J}^*(\omega, r) \cdot \mathbf{E}(\omega, r) \, dr = -\frac{1}{2} \text{Re} \int_0^\infty \mathbf{J}_l^*(\omega, r) \cdot \mathbf{E}_l(\omega, r) \, dr + -\frac{1}{2} \text{Re} \int_0^\infty \mathbf{J}_r^*(\omega, r) \cdot \mathbf{E}_r(\omega, r) \, dr = P_l(\omega) + P_r(\omega), \quad (28)
$$

following the orthogonality of transverse and longitudinal components,

$$
\int_0^\infty \mathbf{J}_l(\omega, r) \cdot \mathbf{E}_l(\omega, r) \, dr = \int_0^\infty \mathbf{J}_l(\omega, r) \cdot \mathbf{E}_r(\omega, r) \, dr = 0. \quad (29)
$$

Here, $P_l(\omega)$ and $P_r(\omega)$ are the powers spend by the traverse and longitudinal external currents for the excitation of respective fields. According to the separation of total power, the energy loss probability in EELS [3, 14–26],

$$
\Gamma_l(\omega) = -\frac{1}{2\hbar\omega} \text{Re} \int_0^\infty \mathbf{J}_l^*(\omega, r) \cdot \mathbf{E}(\omega, r) \, dr \quad (30)
$$

can also be split into two parts $\Gamma_l(\omega) = \Gamma_{ll}(\omega) + \Gamma_{lr}(\omega)$, with

$$
\Gamma_{ll}(\omega) = -\frac{1}{2\hbar\omega} \text{Re} \int_0^\infty \mathbf{J}_{ll}^*(\omega, r) \cdot \mathbf{E}_{ll}(\omega, r) \, dr \quad (31)
$$

being the EELS rates caused by excitation of transverse and longitudinal fields, respectively. Obviously, these rates exhibit the eigenmode resonances following the poles of either $E_l(\omega, r)$ or $E_r(\omega, r)$.

To get the $\Gamma_{ll}(\omega)$ rates, we should solve Maxwell's equations for the excited fields. For this, we use COMSOL Multiphysics with external current density $J(\omega, r)$ defined for the monenergetic electron beam [see Appendix A]. Then, we can apply Helmholtz decomposition to $\mathbf{E}(\omega, r)$ and $\mathbf{J}(\omega, r)$ and calculate $\Gamma_{ll}(\omega)$ with Eq. (31). Alternatively, we can decompose either $\mathbf{E}(\omega, r)$ or $\mathbf{J}(\omega, r)$ owing to the orthogonality of transverse and longitudinal vector fields given by Eq. (29). The calculation based on decomposed current density $J(\omega, r)$,

$$
\Gamma_{ll}(\omega) = -\frac{1}{2\hbar\omega} \text{Re} \int_0^\infty \mathbf{J}_{ll}^*(\omega, r) \cdot \mathbf{E}(\omega, r) \, dr. \quad (32)
$$

is preferred, as it does not require to repeat the decomposition every time we get a new distribution of electric field for a changed position of the beam.

**6. RESONANCE ANALYSIS**

A. Differentiation of resonances on radiation and polarization eigenmodes

Separation of the energy loss probability into two independent components $\Gamma_{ij}(\omega)$ is particularly useful in analysis of sample's eigenmodes, as it allows us to distinguish eigenmode resonances by their field type. Resonances on polarization eigenmodes exhibit maxima in $\Gamma_l(\omega)$ rates only, while resonances on radiation...
Fig. 2. Field decomposition of energy loss probability of an 80 keV electron beam passing through (a) Al, Ag, and Au films and (b), (c) Al, Ag, and Au nanodiscs. The thickness of the films and discs is fixed to 15 nm, the radii of the discs are (b) 100 nm and (c) 50 nm. In the case of discs, the electron beam passes through the center of nanostructures. The olive and stone shadows depict the energy ranges of resonances on plasmon polaritons and plasmons, respectively.

eigenmodes feature maxima either in Γl(ω) (for TE polaritons) or in both Γl(ω) and Γr(ω) (for TM and hybrid polaritons).

As an example, the loss decomposition shown in Fig. 2(a) demonstrates pronounced longitudinal resonances on plasmons in Al and Ag films with small contributions of transverse resonance on plasmon polaritons to overall losses. It is in contrast to Au film, where the losses are dominated by eigenmodes with hybrid fields (TM surface plasmon polaritons), as can been seen from coincident peaks in Γl(ω) and Γr(ω), with a weak contribution of plasmons. Similar loss spectra are shown in Figs. 2(b)–(c) for the electron beam passing through the center of metal discs. They demonstrate the same plasmon resonances as in the case of films for Al and Ag nanodiscs with multiple hybrid-field resonances that correspond to surface plasmon polaritons of metal discs. Note, the number of detected surface plasmon polaritons increases with the size of nanodiscs following the less dense packaging of low-order radiation eigenmodes in the complex frequency space [11].

B. Differentiation of resonances on system and subsystem eigenmodes

Note that not all resonances observed in EELS spectra are given by conditions (25) and (26). Those conditions define only resonances that occur on system eigenmodes which should be distinguished from resonances contributed by locally enhanced fields. As can be seen from Eqs. (23) and (24), the fields excited at a system eigenmode resonance are enhanced (compared to the off-resonance fields) in the entire r space. In contrast to them, the fields excited at resonances on subsystem eigenmodes are enhanced only in a certain part of space [27–30]. For instance, at any points r’ where

\[ \hat{\varepsilon}_{ll}(\omega, r') \hat{F}_l^{-1}(\omega, r') \hat{\varepsilon}_{ll}(\omega, r') E_l(\omega, r') = 0, \]  

\[ \hat{\varepsilon}_{ll}(\omega, r') \hat{F}_l^{-1}(\omega, r') \hat{\varepsilon}_{ll}(\omega, r') E_l(\omega, r') = 0, \]  
The excited fields

\[ E_l(\omega, r') = -\frac{i}{\omega\varepsilon_0} \hat{J}_l^{-1}(\omega, r') J_l(\omega, r') - \hat{\varepsilon}_{ll}(\omega, r') \hat{F}_l^{-1}(\omega, r') \hat{J}_l(\omega, r'), \]  

\[ E_l(\omega, r') = -\frac{i}{\omega\varepsilon_0} \hat{J}_l^{-1}(\omega, r') J_l(\omega, r') - \hat{\varepsilon}_{ll}(\omega, r') \hat{F}_l^{-1}(\omega, r') \hat{J}_l(\omega, r'), \]  

are locally enhanced on transverse and longitudinal subsystem eigenmodes given by \( \text{ker}[\Gamma_l(\omega)] = 0 \) and \( \text{ker}[\Gamma_r(\omega)] = 0 \). These are resonances on subsystem radiation and polarization eigenmodes similar to those given by Eqs. (21) and (22) for a bulk homogeneous isotropic medium but with locally defined \( \hat{\varepsilon}_{ll}(\omega) = \hat{\varepsilon}_{ll}(\omega, r') \) and \( \hat{\varepsilon}_{ll}(\omega) = \hat{\varepsilon}_{ll}(\omega, r') \).

Depending on geometry and composition of the structure, subsystem eigenmode resonances may give quite strong contributions to \( \Gamma(\omega) \). For metal nanostructures, it is dominated by subsystem plasmon resonances of the nanostructure material (so-called bulk plasmon resonance). At any points r’, where \( \hat{\varepsilon}_{ll}(\omega, r') = 0 \), the longitudinal fields are excited locally,

\[ E_l(\omega, r') = -\frac{i}{\omega\varepsilon_0} \hat{J}_l^{-1}(\omega, r') J_l(\omega, r'). \]

Contribution of such points to the rate \( \Gamma_l(\omega) \),

\[ \Gamma_l^{loc}(\omega) = -\frac{1}{2\hbar\varepsilon_0\omega^2} \text{Im} \int J_l^*(\omega, r') \cdot \hat{\varepsilon}_{ll}^{-1}(\omega, r') J_l(\omega, r') dr', \]

is resonant with respect to the local plasmons at r’ given by the condition \( \text{ker}[\hat{\varepsilon}_{ll}(\omega, r')] = 0 \). Its effect can be seen in Figs. 2(a)–(c) for Al structures with a pronounced bulk plasmon resonance of Al at \( \hbar\omega = 15 \text{ eV} \). For Ag and Au films those contributions are not obvious due to their weakness compared to the resonances on system eigenmodes. Nonetheless, they can also be
seen, if we compare two EELS probabilities for electron beams with slightly different positions. To distinguish the effect of bulk plasmon resonances contributed by materials, we consider electron beam passing at the edge of discs. This is the extreme case when a small deviation in the beam position drastically changes EELS spectra: for the beam passing through the disc, $\Gamma_{loc}^\omega(\omega)$ contributes a nonzero value, while for the beam passing by, $\Gamma_{loc}^\omega(\omega)$ is zero. This difference is clearly seen for Al discs, whose EELS spectra are shown in Figs. 3(a) and (b). For Ag and Au, the bulk plasmon resonance of metal becomes evident by calculating the difference $\Delta \Gamma_{l}(\omega)$ for two EELS spectra. It is shown in Figs. 3(c) that reveal the plasmon resonances of bulk Ag and Au materials which were hidden in spectra shown in Figs. 2(b) for the pass-through scenario.

7. CONCLUSION

In this contribution, we have presented a new theoretical framework based on Helmholtz field decomposition for characterization of electromagnetic eigenmodes of magnetically inactive structures. We have introduced the classification of electromagnetic eigenmodes based on their ability to transfer energy and to polarize the structure. We have demonstrated that according to Helmholtz decomposition, polarization and radiation eigenmodes appear to have distinct fields that makes their differentiation straightforward with the field analysis of the electron energy losses. The proposed framework has been shown to provide an advanced analysis of loss spectra that complements EELS measurements for accurate eigenmode characterization.

A. HELMHOLTZ DECOMPOSITION OF ELECTRON BEAM CURRENT DENSITY

Electron beam in EELS is conventionally modeled as a monoenergetic flow of particles with constant velocity $[3, 14–26]$. This model is validated [31] by the average energy loss negligible compared to the initial energy of electrons, as well as by small change of the beam momentum during its interaction with a thin sample. If the beam propagates in the $z$ direction with a velocity $\mathbf{u}$ and exhibits the axial symmetry with the radial profile $G(\omega, r)$,

$$J(\omega, r) = e_z G(\omega, r) e^{i\omega z / u},$$

where $r, z$ are the radial and axial coordinates with respect to the beam axis, then its transverse and longitudinal current densities can be calculated with Eqs. (9) and (10) and written with the use of the modified cylindrical Bessel functions of the first and second kinds, $I_m(\rho)$ and $K_m(\rho)$, as follows

$$J_l = -e_z i k_z^2 \left[ f_1 I_l(k_z r) - f_2 K_l(k_z r) \right] e^{i k_z z} + e_x \left\{ G - k_z^2 \left[ f_1 I_0(k_z r) + f_2 K_0(k_z r) \right] \right\} e^{i k_z z},$$

$$J_l = -e_z i k_z^2 \left[ f_1 I_l(k_z r) - f_2 K_l(k_z r) \right] e^{i k_z z} + e_x k_z^2 \left[ f_1 I_0(k_z r) + f_2 K_0(k_z r) \right] e^{i k_z z}.$$  \(38\)

Here, $k_z = \omega / u$ is the wavenumber in the $z$ direction governed by the beam velocity $u$ and the functions $f_{1,2}$ are the integrals of $G(\omega, r)$,

$$f_1 = f_1(\omega, r) = \int_r^{\infty} G(\omega, r') K_0(k_z(\omega) r') \, dr',$$

$$f_2 = f_2(\omega, r) = \int_0^r G(\omega, r') I_0(k_z(\omega) r') \, dr'.$$  \(40\)

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All calculations in the paper are done for a cylindrical electron beam with the radius $a = 5 \AA$ and
\[ G(\omega, r) = -e/(\pi a^2) \Theta(a - r), \]  
(42)
where $-e$ is the electron charge and $\Theta(\rho)$ is the Heaviside step function.

REFERENCES