

Geometro-optical depolarization manifold as an organizing principle for plasmonic transitions

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Using differential calculus, we derive an exact dipolar condition for the extinction peak position of a nanocrystal, reducing the problem of locating the extinction maximum to a differentiable state equation. This leads to a characteristic polynomial for the plasmon frequency whose coefficients are set by the dielectric function, environment, particle volume, static depolarization factor, and an effective retardation scale. After calibrating this scale with electrodynamic simulations, we construct geometro-optical depolarization manifolds that offer a compact space for tracking plasmonic changes during growth, reshaping, or etching. The resulting polynomials accurately reproduce 56 experimental wavelengths of Au spheres, rods, and bipyramids in an aqueous solution, and two experimental plasmonic transitions, from rods to spheres and from bipyramids to spheres. In addition to providing a general organizing principle for plasmonic transitions, this framework enables accurate variational analyses of extinction peaks, facilitates the inference of nanoparticle morphology from optical responses through data-driven approaches, and provides a robust characterization of plasmonic systems and experiments even in the presence of spurious or nonideal effects that are difficult to capture analytically.

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I. INTRODUCTION

To predict localized surface plasmon resonance (LSPR) frequencies from compact analytical formulas remains a challenging step toward comprehensive plasmonic design, especially for nonspherical nanocrystals evolving by growth, reshaping, or etching. Application-driven design (label-free biosensing [1], near-infrared photothermal therapy [2], visible-light plasmonic catalysis [3], thermoplasmonic self-oscillations [4], etc.) requires the simultaneous optimization of particle dimensions, morphology, the surrounding medium, and surface chemistry [5,6]. This motivates the

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development of closed analytical relations capable of predicting the dipolar LSPR throughout shape and parameter evolutions. Starting from the quasistatic polarizability, long-wavelength expansions of Mie or T -matrix solutions [7] yield a k^2 dynamic-depolarization correction and a k^3 radiation term (k = wave number in the host medium) [8–10]. These elements underlie the modified long-wavelength approximation (MLWA) and related T -matrix or eigenmode expansions [11,12], which provide useful frameworks for describing how the LSPR wavelength, linewidth, and near-field enhancement vary with particle size, while retaining an intuitive oscillator-like interpretation of the mechanisms governing the optical response [13]. Yet, for realistic shapes, the needed corrections are typically mode-specific and high-dimensional.

In its canonical form, the l th multipole T -matrix entry for a sphere is a rational function, $T_l \sim iR_l/(F_l + D_l - iR_l)$, where F_l is a size-independent Fröhlich term, $R_l \sim x^{2l+1}$ is the radiative reaction, and $D_l \sim x^2$ is the dynamic depolarization term ($x \equiv kR$; R = spherical radius). A one-parameter freedom in the choice of D_l that preserves agreement with Mie theory can be defined up to second order, matching the optical response of metallic spheres (Ag, Au, Al, Mg) for size parameters approaching or exceeding $x \approx 1$ and higher-order multipoles [11,12]. Different members of this family may be related to approximations to the internal-field profile, such as uniform and k^2 -modulated distributions. Nevertheless, D_l remains a representation-dependent correction.

Finite-size treatments were introduced for both homogeneous spheres and more complex configurations. Radiatively corrected formulas were developed for nanospheres and nanoshells [8,14], whereas approximate T -matrix and improved electrostatic formulations were applied to spheroids and absorbing or otherwise complex host media [10,12]. Hybrid modal-expansion and dipole-equivalence models have further extended analytical descriptions to coated anisotropic particles [15,16]. In the spheroidal formulations, the finite-size corrections are principal-axis dependent. In the modal descriptions, each optical mode is assigned its own x^2 coefficient, and where retained, additional higher-order terms in x , derived from T -matrix expansions or numerically computed fields. Coatings and host losses are embodied through complex dielectric functions and multilayer boundary conditions. Although accurate, these approaches generally require several parameters for each relevant mode or axis and can get high-dimensional when realistic results are needed.

A complementary roadmap is that of the eigenmode theory. In the quasistatic regime, the polarizability can be decomposed into surface modes with shape-dependent depolarization eigenvalues and coupling weights, separating geometric features from material dispersion [17]. Consistent with Bergman-Milton-type spectral analyses, the optical response was expressed by a set of real, mode-specific geometric parameters, including electric eigenvalues, coupling strengths, and retardation terms [18], allowing extinction spectra and near-field enhancements to be calculated for a number of geometries. More recently, a dipolar approximation based on a Cartesian projection of the Neumann-Poincaré operator was proposed to estimate geometry-dependent eigenvalues and optical responses for arbitrary shapes at low computational cost

[19]. The polarizability concept was likewise generalized to induced dipoles depending explicitly on the excitation phase [9]. Other low-dimensional representations employed global geometric descriptors, such as an ad hoc plasmon length, defined as the characteristic distance over which dipolar charge oscillations develop, and with which plasmon energy and linewidth are expected to scale [20]. The relevance of a reliable single-particle description extends to disordered and assembled systems. Large-scale simulations indicate that the collective optical response of disordered nanoparticle fluids and gels is determined by the distribution of effective single-particle resonance frequencies within the assembly [21]. Structural disorder broadens this profile, while particles with similarly shifted resonances can participate in collectively resonant clusters. A compact analytical description of the individual-particle response can therefore provide a useful building block for theories of interacting and disordered ensembles.

A number of analytical works identify the LSPR with the zero of the real part of a quasistatic, or MLWA, or multipolar polarizability denominator (modal eigenfrequencies with damping adjustments), or use that denominator to interpret or fit the numerically obtained extinction peaks [22]. Formulas based on the Drude-Rayleigh-Fröhlich picture were derived for hierarchies of plasmonic nanostructures [23]. Nevertheless, for accurate analytical treatments under any circumstance, Fröhlich-type equations may prove inadequate, as shown by the error functions evaluated for various shapes of Au nanoparticles (see Supplemental Material, SM [24]). Here we instead state the peak-position problem directly at the extinction observable level, coarse-graining retardation into a single effective dynamic-depolarization descriptor and locating the extinction peak by the rigorous differential calculus. This construction is thereby the first to retain explicitly, within the extinction-maximum condition, the integrodifferential interplay among dynamic depolarization, radiative reaction, Ohmic losses, and the host response, while remaining applicable to arbitrary metals, particle shapes, and dielectric environments. It identifies a resonance hypersurface in a selected geometro-optical manifold, enabling the application of implicit-function theorems, differential sensitivity analysis, and constrained optimization to investigate parameter dependencies and variational extrema.

We generally proceed according to the following points. (i) The particle is represented by a dipolar MLWA polarizability, where the quasistatic response is corrected by dynamic depolarization and radiative reaction. (ii) The extinction peak is defined operationally as the maximum of the extinction cross section (σ_{ext}), not as a Fröhlich pole. (iii) The first and second derivatives of σ_{ext} are evaluated analytically, yielding a characteristic polynomial in the frequency (ω). (iv) The other parameters (here, a retardation scale a_{eff}) are calibrated from electrodynamic simulations for each shape family. (v) Such relations define a geometro-optical space connecting depolarization and geometric variables, where size, shape, and environmental changes can be tracked as trajectories. The reproducibility of this approach is ensured by detailed Supplemental Material [24]. Definitions of the observables, extremum condition, and manifold are given below.

II. CONSTRUCTION OF A NEW FAMILY OF PLASMONIC POLYNOMIALS

A. Polarizability with an effective retardation scale

For each configuration (geometry, metal, host), and a specific illumination or internal field distribution, the MLWA polarizability can be written as

$$\alpha = \frac{\alpha_0}{1 - D_{\text{eff}} - iR_1}, \quad (1)$$

where α_0 is quasistatic, the radiative damping term R_1 ensures energy conservation, and D_{eff} includes an effective retardation scale parameter. The depolarization self-field associated with the MLWA dipolar polarization is expressible in terms of three dyadics: static depolarization $\mathbf{L}$ (k^0), dynamic depolarization tensor $\mathbf{D}$ (k^2), and radiative damping $\mathbf{I}$ (k^3) [30]. For homogeneous bodies, with a common principal axis for $\mathbf{L}$ and $\mathbf{D}$, the first two dyadics can be diagonalized, yielding constant principal eigenvalues L_j and D_j/a_j . For a dominant mode (i), we parametrize the k^2 correction by an effective retardation scale parameter a_{eff} (a length), replacing the ratio a_i/D_i . This is equivalent to introducing a dynamic phase-variation length (ℓ_{eff}), reflecting that the induced polarization can no longer stay perfectly in phase throughout a finite volume. In the former polarizability equation, we therefore employ $D_{\text{eff}} = k^2 \alpha_0 D_i / (4\pi a_i \epsilon_0)$ and express the quasistatic response in the ellipsoidal Clausius-Mossotti (or Lorentz-Lorenz) form [31]

$$\alpha_0 = \epsilon_0 V_p \frac{\epsilon(\omega)/\epsilon_h - 1}{L_{\text{eff}}[\epsilon(\omega)/\epsilon_h - 1] + 1}, \quad (2)$$

ϵ_0 and ϵ_h being the vacuum and the relative host permittivities, V_p the particle volume, and L_{eff} encoding the static depolarization factor for the optical direction i . For nonuniform fields, modeling L_{eff} via the principal electrostatic eigenvalue (spherical degree $l = 1$, azimuth order $m = 0$) is more appropriate in the quasistatic, local, homogeneous regime. We adopted this strategy for rods [18] and bipyramids (SM Secs. 1.4 and 1.5 (Biconical Model Approximation) [24]) because their principal eigenvalues $L_{x=y}$, L_z (SM Sec. 4.2 [24]) yielded unphysical results in meaningful geometry domains ($a_{\text{eff}} < 0$). What stays approximate, however, is the truncation to a single eigenmode when rebuilding the full response. A measure for the dynamic phase-variation length, along the cross-sectional area perpendicular to the direction i , instead follows from the expression for D_{eff} as $\ell_{\text{eff}\perp}^2 \approx V_p / (4\pi a_{\text{eff}})$. It should generally increase monotonically with the particle diameter, remain bounded by it, and vanish as the diameter approaches zero. We have consistently evaluated these constraints for the spherical case and compared $\ell_{\text{eff}\perp}$ with the theoretical prediction [30] (SM Sec. 1.7 [24]). Finally, to complete the polarizability law, the standard radiative-reaction term $R_1 = k^3 \alpha_0 / (6\pi \epsilon_0)$ is included.

B. Optical-theorem prefactor in the extinction-peak condition

We define the wavelength λ_{res} operationally, from the frequency at which the extinction cross section is maximal: $(\partial \sigma_{\text{ext}} / \partial \omega) = 0$ with $(\partial^2 \sigma_{\text{ext}} / \partial \omega^2) < 0$, and not from the ze-

ros of a Fröhlich-like denominator (SM Sec. 1.6 [24]) or as an undamped electrostatic eigenfrequency. This distinction is important because our approach follows the experimentally observed spectral peak, including the frequency-dependent optical-theorem prefactor and damping terms, whereas a Fröhlich-type condition evaluates an underlying pole of the response. The extinction cross section can be derived either from near-field work-rate calculations or via the optical theorem, from the forward scattering amplitude [32]. In dipole-dominated regimes, this reduces to the dipolar form of the optical theorem [31]

$$\sigma_{\text{ext}} = \frac{k}{\epsilon_0} \text{Im}[\alpha], \quad (3)$$

where the next-order quadrupole contribution, proportional to k^2 inside the brackets, is neglected [33]. Given Eq. (3), it is legitimate to formulate the extremum problem for σ_{ext} , but a few remarks are in order. For very small nanoparticles, the extinction and absorption cross sections tend to coincide, but we will not study either absorption or scattering maxima here. They form distinct spectral observables, with dipolar cross sections containing distinct frequency-dependent factors and thereby requiring separate extremum conditions [31,34]. As absorption and scattering processes are not the subject of the present derivation, to avoid complications that would not provide relevant additional insight, they will not be discussed in detail. In particular, the fundamental limits on the optical response of absorbing media, independent of the geometry for both absorption and scattering rates per unit volume, and imposed by intrinsic metal losses [35], will be assumed to be inherently fulfilled through the differential derivation. Another point to discuss is how to treat the vacuum wavelength in Eq. (3) $k = 2\pi \sqrt{\epsilon_h} / \lambda$, which is the prefactor specific to extinction. This term is not optional since it is fixed by energy conservation for a dipole and must be varied when the experimentally observed extinction maximum is sought. Excluding k from the differentiation would shift the calculation toward a Fröhlich-like scheme in which the pole of α defines the response through the real and imaginary parts of its denominator. This is one of the key distinctions between our extinction-peak condition and a Fröhlich-like pole analysis, where the prefactor multiplying the dipolar response is not varied. To fix the ideas, consider a meaningful example. If we apply the extremum condition [Eq. (4)] to the Rayleigh-Drude model in a vacuum ($\epsilon_h = 1$), with a given plasma frequency (ω_p) and electron damping (γ_D), but without varying the prefactor, for $G_D = \gamma_D / \omega_p \ll 1$ we obtain at second order $\omega_{\text{res}} / \omega_p = \sqrt{L_{\text{eff}}} - G_D^2 / (8\sqrt{L_{\text{eff}}})$. The extinction peak slightly redshifts with metal losses, as it must, because we are basically studying the pole of the dipolar response. This can be ascertained directly with the corresponding Fröhlich constraint (albeit with different second-order coefficient $-\frac{1}{2}$). If we also vary k , the peak undergoes a slight blueshift, and this effect exactly compensates the $\sim G_D^2$ redshift due to damping: the maximum falls at $\omega_{\text{res}} = \sqrt{L_{\text{eff}}} \omega_p$ irrespective of losses (γ_D). Such a property remains valid for an arbitrary medium ($\epsilon_h > 1$), but it does not imply that the material can be optically lossless. Within this description, when $G_D \rightarrow 0^+$, the extinction peak amplitude is undefined (Sec. IV). In summary, the optical-theorem prefactor is not a neglected uncertainty

source, but an explicit contribution to the state equation. If it is not varied, which may appear legitimate because the polarizability contains the physical system parameters, the extremum condition tends to a Fröhlich's result and the peak shifts by damping terms. If it is varied along with α , the location of the extinction maximum is modified by $(\frac{\partial k}{\partial \omega})\text{Im}[\alpha]$.

C. Full characteristic equation

Developing the extremal condition is tedious, but it can be reduced to a more compact notation. A convenient setting is suggested by rewriting the polarizability equation as $\alpha^{-1} = \alpha_0^{-1} - \beta$, with $\text{Re}[\beta] = k^2/(4\pi a_{\text{eff}}\epsilon_0)$, $\text{Im}[\beta] = k^3/(6\pi\epsilon_0)$ and by defining $\varphi_A = \text{Im}[\beta\alpha_0]$, $\varphi_B = 1 - \text{Re}[\beta\alpha_0]$, $\varphi_+ = \text{Im}[\alpha_0 + \beta|\alpha_0|^2]$, $\varphi_- = \text{Re}[\alpha_0 - \beta|\alpha_0|^2]$, and $\Xi = |1 - \beta\alpha_0|^2$, linking the real and imaginary parts of the quasistatic response to the wavelength corrections. In this way, one has

$$\frac{c\epsilon_0}{\sqrt{\epsilon_h}} \Xi^2 \left(\frac{\partial \sigma_{\text{ext}}}{\partial \omega} \right) = \omega \Psi(\varphi_A, \varphi_B, \varphi_+, \varphi_-) + \varphi_+ \Xi, \quad (4)$$

where the variation is taken at fixed dielectric and depolarization parameters, and

$$\begin{aligned} \Psi = & 2\varphi_A\varphi_B \left(\frac{\partial \text{Re}[\alpha_0]}{\partial \omega} \right) + (\varphi_B^2 - \varphi_A^2) \left(\frac{\partial \text{Im}[\alpha_0]}{\partial \omega} \right) \\ & + 2\varphi_+\varphi_- \left(\frac{\partial \text{Re}[\beta]}{\partial \omega} \right) + [(\varphi_B^2 + \varphi_A^2)|\alpha_0|^2 - 2\varphi_+^2] \\ & \times \left(\frac{\partial \text{Im}[\beta]}{\partial \omega} \right) \quad (\text{generalized Fröhlich function}). \end{aligned} \quad (5)$$

The compact term $\varphi_+ \Xi$ in Eq. (4) stems from differentiating the optical-theorem prefactor. In fact, setting this equation to zero yields $\omega \Psi = -\varphi_+ \Xi$, where ω_{res} (or λ_{res}) comes from a polynomial condition with odd coefficients, i.e.,

$$P_n(\omega; \epsilon_h, L_{\text{eff}}, a_{\text{eff}}, \{\epsilon\}, V_p) \equiv \sum_{i \in 2\mathbb{N}+1}^n p_i \omega^i, \quad (6)$$

with $n = 25$

$$P_{25}(\lambda_{\text{res}}) = 0. \quad (7)$$

The symbol $\{\epsilon\}$ denotes the set of parameters in the Drude-Lorentz dielectric-function model (SM Sec. 1.1 [24]), including the damping constants that reproduce a line-shape behavior fully consistent with most plasmonic materials [31], with V_p , L_{eff} , ϵ_h , and a_{eff} encoding the geometry and environment. To ensure reproducibility, the complete coefficients p_i and their version for arbitrarily shaped Au nanoparticles are reported in machine-readable files (SM Sec. 2 [24]). The physical solution of Eq. (7) is the real root lying within the fitted spectral window and ensuring that σ_{ext} is locally concave downward at that point. In the Drude limit, this picture reduces to the driven-oscillator model, with L_{eff} setting the restoring force, ik^3 the (radiative) damping, and the k^2 term renormalizing the inertial response [13]. The full polynomial instead retains all the coupled contributions needed for quantitative accuracy.

Recall that the polynomial in Eq. (6) should not be used for absorption or scattering maxima. Such observables include distinct frequency-dependent prefactors, leading to distinct characteristic equations. For example, still in the dipolar picture, $\sigma_{\text{sca}} \propto k^4|\alpha|^2$, and the scattering-peak constraint would contain a factor $\propto k^3(\frac{\partial k}{\partial \omega})|\alpha|^2$, in addition to the derivative of $|\alpha|^2$. This is why scattering (or absorption) spectra need a separate polynomial closure, while our study focuses on the extinction observable measured and used for validation.

D. Polynomial calibration

The present method does not rely on an extensive numerical peak search. Once the polynomial is determined analytically, metallic nanoparticle boundary element method (MNPBEM) simulations are needed only to calibrate a_{eff} . This thorough work can be found in the SM [24] (1.3 to 1.5) for each shape family. All numerical calculations are performed with an SI-based scaled system of units. Lengths are expressed in nanometers, while angular frequencies and frequencies are in petahertz (1 PHz = 10^{15} Hz). For example, the light speed has dimensions $[c] = \text{nm PHz}$. No Gaussian or electrostatic unit system is applied. The vacuum permittivity cancels out in the expression for the extinction cross section after the optical-theorem normalization, so that no additional unit conversion related to ϵ_0 is required. This rescaled SI-based convention turns out to be necessary for numerical stability. When the same polynomials are evaluated in unscaled SI units, the very large powers of frequency and length gave rise to coefficients and values exceeding the floating-point range of our computational tools (matlab), where numbers larger than $\sim 10^{308}$ are treated as infinity. The use of nm and PHz thereby preserves the physical SI scaling while keeping the numerical values within a stable computational range.

In short, we compute reference extinction-peak positions of spheres, rods, and bipyramids over a wide range of dimensions, and insert the corresponding frequencies, with the Drude-Lorentz dielectric parameters ϵ_h , V_p , and L_{eff} , into Eq. (6). The polynomial then becomes a quadratic equation for a_{eff} , and the physical branch is selected by the concavity condition $(\partial^2 \sigma_{\text{ext}}/\partial \omega^2) < 0$. This implies an equation of the form $a_{\text{eff}} = a_{\text{eff}}(V_p, L_{\text{eff}})$, which can be reduced to a dependence on geometric parameters alone. After calibration, no new electrodynamic simulation is required to evaluate the peak position: one can use the shape-specific L_{eff} , V_p , and a_{eff} relationships in the same characteristic polynomial. The equations for L_{eff} and a_{eff} are validated in the SM [24] (1.3 to 1.5; 1.8), but the complete information needed to implement the model is self-contained in Table I. Combining the relations in this table with Eq. (6) yields parameter-free predictions of remarkable precision. We note that the effective retardation length is retained in dimensional form, with units of length; consequently, the numerical coefficients in the third row of Table I are not necessarily dimensionless and may have distinct geometric dimensions. Recasting a_{eff} entirely in homogeneous coordinates is a nontrivial task that would require substantial additional numerical analysis and lies beyond the scope of the present study.

TABLE I. Effective depolarization factor L_{eff} and retardation scale parameter a_{eff} inferred for three nanoparticle shapes. Spheres are defined by their radius (R), rods by their diameter and length (d_1, d_2). Bipyramids are described under the excellent approximation of an equivalent bicone model [43], with width (W), tip-to-tip length (L_n), tip radius (r), and biconical length (L^*), which define the dimensionless ratios $x = 2r/W$ and $y = L^*/W$. All geometric dimensions herein reported (R, d_k, r, W, L^*, L_n) are expressed in nm. The physical dimensions of the numerical coefficients in the bottom row follow from defining a_{eff} as a length. For greater clarity, coefficients with units of nm^{-1} are underlined; those dimensioned to nm are overlined.

	Sphere	Rod	Bipyramid
V_p	$\frac{4\pi}{3} R^3$	$\frac{\pi}{6} d_1^3 + \frac{\pi}{4} d_1^2 (d_2 - d_1)$	$\frac{\pi}{12} W^3 \left[\left(2 - \frac{y^2+2}{\sqrt{1+y^2}} \right) x^3 + y \right]$
L_{eff}^{-1}	3	$1.296 + 1.73 \left(\frac{d_2}{d_1} \right)^{1.45}$	$-2.744 + 5.208x + 5.684y + 26.71x^2 - 14.55xy + 0.3536y^2 - 30.61x^3 + 9.8x^2y - 0.3784xy^2 - 0.00185y^3$
a_{eff}	$0.0113\overline{R^2} + 1.205\overline{R} - \overline{5.011}$	$\overline{-7.3387} + 0.7617d_1 + 0.1563d_2$	$(1.342\overline{W} - \overline{13.3}) + (-\underline{0.05008}\overline{W} - 0.02773)r + (-\underline{0.007569}\overline{W} + 0.3377)L_n$

E. Damping, semiclassical, and quantum effects

Damping enters the extremum condition through the empirical dielectric function whose parameters are fitted to optical data, and is differentiated through the polarizability. For the nanoparticles regarded here, the characteristic size is not smaller than $\langle s \rangle \approx 10$ nm, so that quantum-size corrections can be neglected in the present implementation. When the particle size becomes comparable to the electronic mean-free path, electron-boundary scattering may increase the effective collision rate and enhance plasmon damping [36]. This semiclassical effect is geometry dependent, but it is commonly represented by adding to the bulk Drude damping a surface-scattering contribution $\Delta\gamma_D = Av_F/\langle s \rangle$, where v_F is the Fermi velocity and A is a dimensionless phenomenological surface-scattering coefficient accounting for boundary-scattering details, such as specularity, and particle shape [37,38]. If needed, such residual finite-size contributions could be absorbed into a normalized damping coefficient (G_D^{eff}), but this additional step is unnecessary here. We are not refining linewidths or peak intensities, and this substitution would only change the dielectric parameters entering the polynomial, without altering the differential structure of Eq. (4). Moreover, the semiclassical correction comprises a heuristic surface-scattering coefficient typically of order $A \sim 10^{-1}-10^0$ [37,38] that here would need an independent linewidth-oriented calibration. Geometry-dependent electrodynamic effects relevant to the extinction maximum are already incorporated into a calibrated manifold, while small residual perturbations in geometry, retardation, damping, or local optical environment are renormalized into the effective retardation scale a_{eff} .

We also verified that these corrections remain very small. As a conservative numerical check, we extended the spherical test down to $R = 5$ nm and varied the surface-scattering parameter. For radii within $R = (5-50)$ nm, the absolute correction to the extinction-peak wavelength ranges from $\Delta\lambda_{\text{res}} = 48.5$ pm to 0.728 nm, with the corresponding relative error, defined as $|\lambda_{\text{res}} - \lambda_{\text{corr}}|/\lambda_{\text{res}}$, ranging from 9.3×10^{-5} to 1.4×10^{-3} . Upon further size reduction, e.g., below ~ 5 nm, the bulk dielectric function itself may become inadequate because confinement and surface effects can modify the electronic structure and relaxation pathways. In that quantum-size regime [39], the same peak-finding logic would still apply, but

the dielectric response entering the quasistatic polarizability α_0 would have to be reformulated from the allowed intra and interband transitions, with $\text{Re}[\epsilon(\omega)]$ obtained consistently from $\text{Im}[\epsilon(\omega)]$ via the Kramers-Krönig relations. Accordingly, the present implementation should not be interpreted as a quantum theory for clusters below a few nanometers.

III. PLASMONIC PATHS

A. Geometro-optical depolarization manifold

The former construction turns each nanoparticle geometry into a point of the state space, e.g., $(L_{\text{eff}}, V_p, a_{\text{eff}})$ or $(L_{\text{eff}}, V_p, \lambda_{\text{res}})$. This is what we call geometro-optical depolarization manifold. It offers an overview of how the dipolar depolarization properties vary across a family of shapes. Figure 1 develops this concept for spheres, rods, and bipyramids of various sizes, while Fig. 2 arranges representative transitions into a closed path between the three geometric branches. It is an organizing construction, indicating how forward and reverse growth or etching routes can be confronted (SM 3.1–2 [24]). The static component of the response, quantified by L_{eff} , measures the electrostatic rigidity of the polarization, while the dynamic part, quantified by a_{eff} and therefore $\ell_{\text{eff}\perp}$, captures the degree of phase retardation in the induced polarization. Accordingly, a surface path such as $a_{\text{eff}} = a_{\text{eff}}(L_{\text{eff}}, V_p)$ or $\lambda_{\text{res}} = \lambda_{\text{res}}(L_{\text{eff}}, V_p)$ can reveal how size and shape drive the plasmonic transition. This provides a compact framework for following spectral fingerprints during growth or oxidative etching and checking whether and how the final nanoparticle structure reaches the intended morphological target [40–43]. For example, if the path evolves mainly along V_p at nearly constant L_{eff} , the transition is approximately a homothetic rescaling, whereas changes in L_{eff} at nearly fixed V_p denote reshaping. Elongation of a particle along its optically dominant axis generally improves longitudinal polarization (lower L_{eff}) and worsens retardation (larger $\ell_{\text{eff}\perp}$), while environmental changes shift λ_{res} at nearly fixed (V_p, L_{eff}) . When both depolarization and volume vary, the local slopes indicate whether growth or reshaping prevails. These representations also give a controlled way to analyze inverse trends. A single extinction peak is normally insufficient to reconstruct a unique morphology, but a sequence of nearby states, can be interpreted as a manifold path. A detailed study

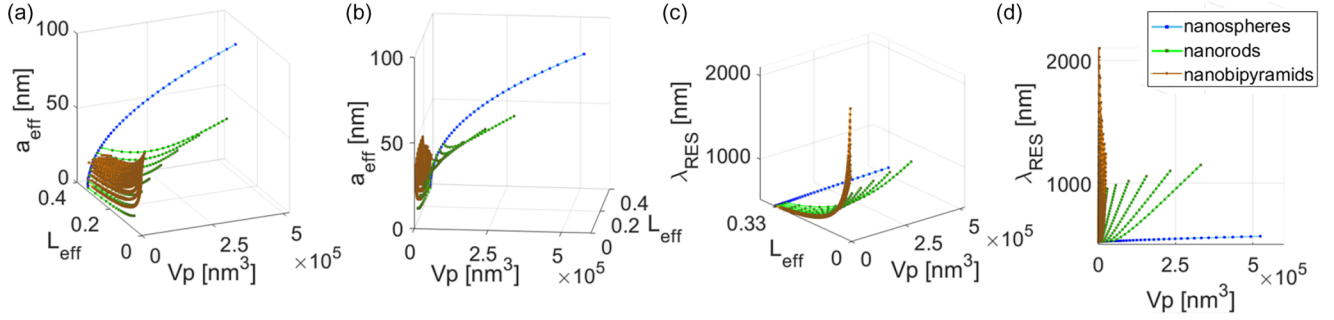


FIG. 1. Shape transition paths of spheres (blue), rods (green), and bipyramids in the biconical approximation (orange) in two geometro-optical manifolds: $\{a_{\text{eff}}, V_p, L_{\text{eff}}\}$ (a), (b) and $\{\lambda_{\text{res}}, V_p, L_{\text{eff}}\}$ (c), (d). Plots in (b) and (d) reproduce those in (a) and (c), respectively, from a different angle. For spheres, the radius increases from $R = 5$ nm to 50 nm. For rods, eight curves are shown, each corresponding to a particular value of d_1 . The parameter d_1 increases from 10 nm (lowest trajectory) to 45 nm (trajectory with the highest a_{eff}) in eight equal steps. For each d_1 , d_2 takes 51 values ranging from d_1 to 10, d_1 . For bicones, seven curves are shown, each associated with one value of W (from 10 nm to 25 nm). L^* takes 21 values (from 30 nm to 150 nm), and r takes 15 values (from 1 nm to $L_n/2$). Bipyramids that do not satisfy the biconical existence condition $\frac{2r}{W} < \cos[\arctan(\frac{W}{L^*})]$ [43] are excluded.

of evolutionary perturbations (local path derivatives) across these manifolds can indicate not only whether the dominant change is volume growth, reshaping, or environmental variation, but is also promising for inferring the geometric features of nanoparticles from their optical response. Contributing to this challenging inverse problem would reduce the need for costly imaging techniques (transmission electron microscopy, TEM), saving time and financial resources.

B. Experimental spectra and shape transitions

To prove the efficacy of the present method, we accurately describe two representative experimental contexts: the extinction-peak wavelength and plasmonic shape transitions of Au nanocrystals. In both cases, we use high-quality

ultraviolet–visible–near-infrared (UV-Vis-NIR) extinction spectra of Au nanospheres, nanorods, and nanobipyramids dispersed in water, all stabilized with cationic surfactant (cetyltrimethylammonium bromide/chloride, CTAB/C). All nanoparticle solutions in these tests are synthesized according to published protocols: spherical particles were produced according to the recipe of Zheng *et al.* [44], nanorods by the methods of Sánchez-Iglesias *et al.* [45] and Ye *et al.* [46]. Bipyramids were synthesized based on our recent investigation [6]. The datasets of experimental spectra, for spheres, rods, and bipyramids, totaled $14 + 22 + 20 = 56$ entries, respectively. They were normalized at the maximum of the extinction peak. Figure 3 reports the corresponding predictions, proving that our state equation reliably reproduces the extinction-peak wavelengths measured in all particle shapes. Then we tested our model on two oxidative shape transitions, rod-to-sphere and bipyramid-to-sphere, where nanoparticles were subjected to well-documented chemical etching processes [43]. Figure 4 shows that these plasmonic transitions can also be accurately represented as geometro-optical manifold paths. All details are collected in the SM [24].

C. Redshift and blueshift refinements

MNPBEM computations cannot fully reproduce experimental measurements, as spectra may include shifts ascribed, e.g., to ligand shells, local dielectric screening, or excess charge. Such effects do not vary the extremum construction, but can be embodied either by recalibrating the effective optical parameters with experiments, or by adding explicit perturbative corrections. Two routes are generally possible: scaling the plasmonic polynomial to the measurements of interest, thus absorbing systematic nonideal effects, or explicitly correcting the dominant physical perturbations. An example of the latter arises from surfactant stabilization (CTAB/C), as it locally increases the effective permittivity and normally redshifts the extinction peak [47]. However, spectral measurements in our laboratory show systematic blueshifts, consistent with electrostatic interface and excess-charge effects [42]. It implies an effective increase in the plasma

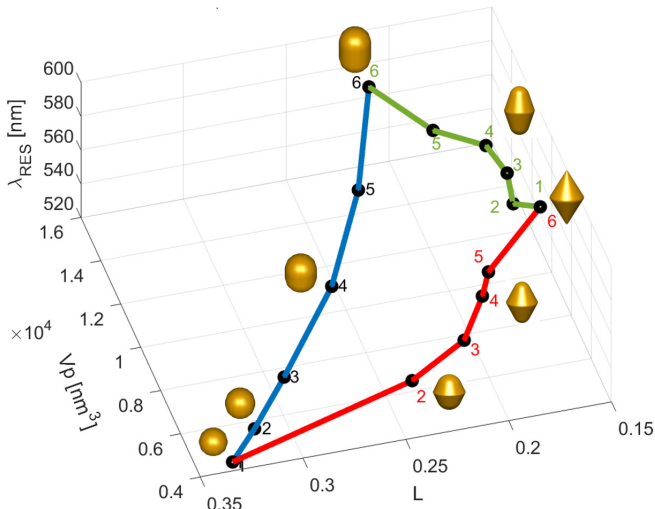


FIG. 2. Numerical transition paths in the $\{\lambda_{\text{res}}, V_p, L_{\text{eff}}\}$ manifold representative of nanoparticle growth or etching phenomena (according to the traversal directions): from a sphere to a nanorod (blue curve); from a sphere to a bicone (red); from a nanobicone to a nanorod (green). The radius of the sphere is $R = 10$ nm. The largest nanorod has $d_1 = 25$ nm and $d_2 = 40$ nm. The sharpest nanobicone corresponds to $W = 25$ nm, $L_n = 40$ nm, and $r = 2$ nm. All the evolutionary geometric steps are in the SM [24].

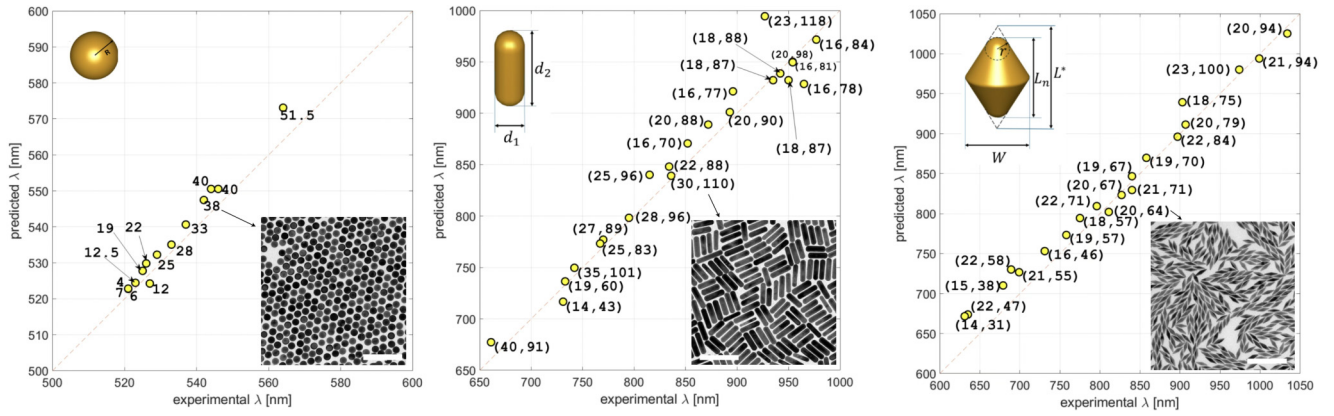


FIG. 3. Theory vs experiment for spheres (L), rods (M), and bipyramids in the biconical approximation (R) [43]. The numbers near the data points indicate the geometric quantities introduced in Table I and reported in the top-left insets. The bottom-right insets show micrographs of representative experimental Au nanoparticles (scale bar = 200 nm). The tip radius behaves as $r = 0.5 \text{ nm} - 0.024L_n + 0.213W$ [5]. All details are in SM [24]. Normalized root-mean-square deviation (NRMSD) relative to the measurements are 0.66% (L), 2.7% (M), and 2.4% (R).

frequency, inversely proportional to the specific surface area of nanoparticles, and thus to an increase in the plasmon oscillator stiffness.

To quantify the antagonism between these trends, the extinction spectra for spheres, rods, and bicones were generally computed for different coating thicknesses ($t = 0, 3.5, 7 \text{ nm}$) and relative plasma-frequency shifts ($s = \delta\omega_p/\omega_p = 0, 0.1, 0.2$) (SM [24]). We assume $\epsilon_c = 2.25$, representative of most

coatings [48], while CTAB/C molecules are typically believed to form bilayers with $t \approx (3.0\text{--}4.0) \text{ nm}$ around sufficiently large nanoparticles [49]. Regardless of particle shape, the introduction of a coating produces a progressive redshift and a peak amplitude increase of extinction spectra, whereas increasing the effective surface-charge term blueshifts the response, accompanied by a slight amplitude decrease. The resulting red- and blue-shift proportions are summarized by a

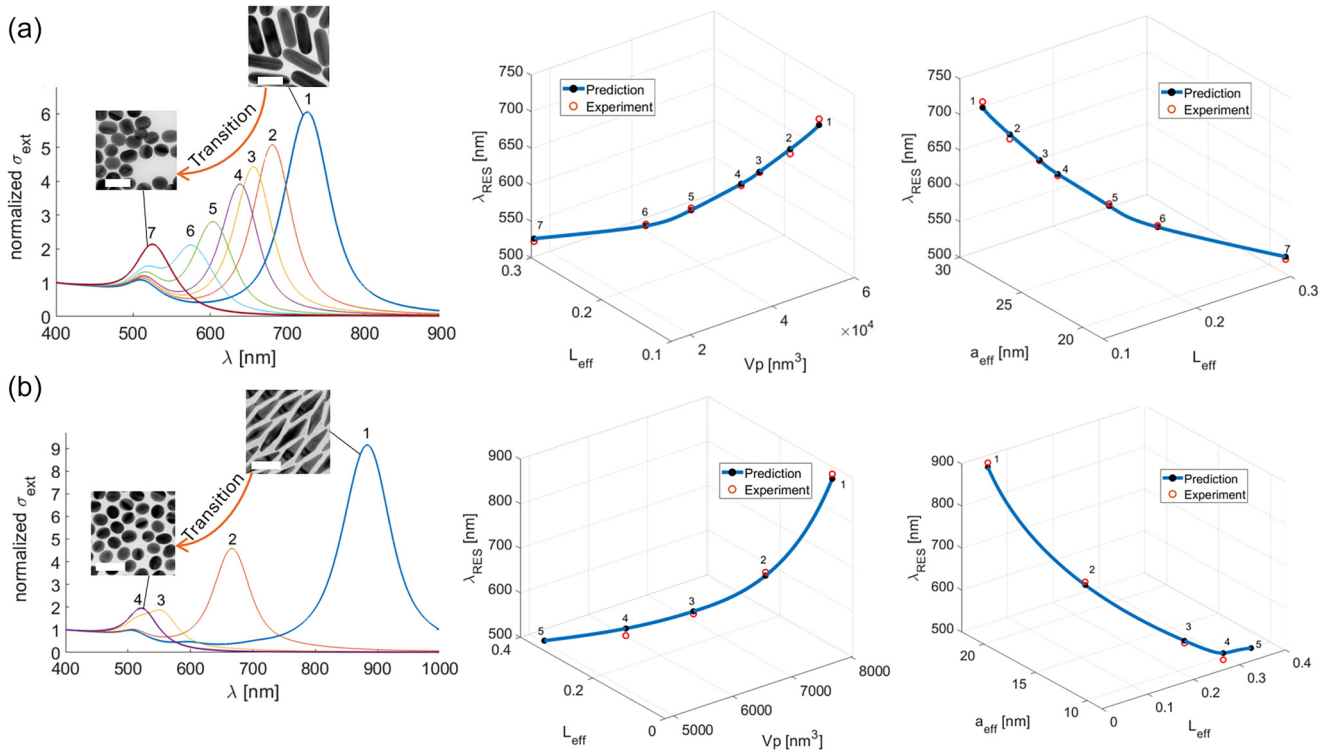


FIG. 4. Experimental plasmonic transitions: (a) rod-to-sphere and (b) bipyramid-to-sphere whose extinction-peak wavelengths are modeled using the characteristic polynomial. In (a), the stages corresponding to the TEM micrographs, extinction spectra, and points in the geometro-optical manifold are labeled by the indices 1 to 7. In (b), the stages are labeled by indices 1 to 4, where we add a sphere of $R = 10.5 \text{ nm}$ at the extrapolated stage 5. All spectra are normalized to the value of σ_{ext} at 400 nm. The white bar in the bottom-left images is 50-nm long, and the red arrow indicates decreasing anisotropy in the transition. In the geometro-optical manifolds in the center and right, NRMSD relative to the measurements are (a) 0.71% and (b) 1.6%. All details are in the SM [24].

second-order relation for the plasmon shift, $\Sigma_{\pm} \equiv \delta\lambda_{\text{res}}/\lambda_{\text{res}}$, as a function of t , s ,

$$\Sigma_{\pm} = A_t t + B_t t^2 + A_s s + B_s s^2, \quad (8)$$

where the values of all coefficients A_k , B_k for the three nanoparticle shapes are reported in Tables S2 and S3 (SM Sec. 1.9 [24]).

As an application, we refined the prediction for the spherical nanoparticles, where the effects arising from changes in the local dielectric constant and plasma frequency were treated separately (SM 1.9 [24]). To capture the overall screening effect induced by $t > 0$, ϵ_h was diminished to a smaller mean-field value. The improved best fits (Fig. S29 [24]) predict $\epsilon_h = 1.709$ (versus 1.77) and $\omega_p = 13.18$ PHz (versus 13.11 PHz). It is instructive to see that the equivalence of the two effects is not accurately captured by the Drude model, which would predict $(\delta\omega_p/\delta\epsilon_h) = 2.89$ PHz, in marked contrast to the correct value, 1.17 PHz.

Finally, a slight plasma-frequency correction was also applied to the transitions in Fig. 4 to improve consistency with the measured wavelengths (SM 3.3 [24]).

IV. POLYNOMIAL SOLUTION OF DRUDE AND NONRADIATIVE POLARIZABILITY MODEL

Here we illustrate the effect of retaining the frequency-dependent prefactor in the extinction cross section. The derivative entering the peak condition returns two terms

$$\epsilon_0 \left(\frac{\partial \sigma_{\text{ext}}}{\partial \omega} \right) = \left(\frac{\partial k}{\partial \omega} \right) \text{Im}[\alpha] + k \left(\frac{\partial \text{Im}[\alpha]}{\partial \omega} \right). \quad (9)$$

When the dielectric model is of the Drude type, e.g.,

$$\epsilon(\omega) = 1 - \frac{\omega_p^2}{\omega^2 + iG_D \omega_p \omega}, \quad (10)$$

the calculation of the characteristic function is simplified and can be conveniently expressed in terms of all characteristic parameters. For illustrative purposes, we report the explicit result when only the dynamic depolarization term is included in Eq. (3), $\text{Im}[\beta] \equiv 0$. In this case, the solution of the extremum problem is in the end equivalent to an eighth-order polynomial constraint

$$P_8(\rho_1, \rho_2, G_D, L_{\text{eff}}; \Omega) = \mathcal{P}_0 + \left(\frac{\Omega}{\Omega_A} \right)^2 \mathcal{P}_2 + \left(\frac{\Omega}{\Omega_A} \right)^4 \mathcal{P}_4 = 0, \quad (11)$$

with $\rho_1 = \epsilon_h + L_{\text{eff}} - \epsilon_h L_{\text{eff}}$, $\rho_2 = \epsilon_h - 1$, $\Omega = \omega/\omega_p$, and $\mathcal{P}_k$ are fourth-degree polynomials. If the k prefactor is artificially kept fixed during differentiation, the condition approaches a Fröhlich-like analysis and identifies

$$\mathcal{P}_0 = 3\rho_1^2 \Omega^4 + \rho_1(\rho_1 G_D^2 - 2L_{\text{eff}})\Omega^2 - L_{\text{eff}}^2, \quad (12)$$

$$\mathcal{P}_2 = 10\rho_1 \rho_2 \Omega^4 + 6(\rho_1 + G_D^2 \rho_1 \rho_2 - \rho_2 L_{\text{eff}})\Omega^2 - 2L_{\text{eff}}, \quad (13)$$

$$\mathcal{P}_4 = 7\rho_2^2 \Omega^4 + 5\rho_2(G_D^2 \rho_2 + 2)\Omega^2 + 3. \quad (14)$$

In the full extinction-peak calculation, the prefactor is differentiated together with the polarizability. This gives the corresponding coefficients $\mathcal{P}'_k$:

$$\mathcal{P}'_0 = 2(L_{\text{eff}} - 1)^2(\rho_1^2 \Omega^4 - L_{\text{eff}}^2), \quad (15)$$

$$\mathcal{P}'_2 = (L_{\text{eff}} - 1)^2 \mathcal{P}_2, \quad (16)$$

$$\mathcal{P}'_4 = (L_{\text{eff}} - 1)^2 \mathcal{P}_4. \quad (17)$$

The gauge term $(L_{\text{eff}} - 1)^2$ must be noted as a factor common to each polynomial which vanishes only when the static depolarization is maximal. Equation (15) yields the quasistatic, damping-independent resonant frequency $\Omega = \sqrt{L_{\text{eff}}/\rho_1}$ to be compared with that produced by Eq. (12) for small G_D . It is worth noting that neither of these results for the frequency coincides with those derived from the study of a mechanical oscillator representative of the plasmonic vibration due to a mismatch of the type $\rho_1 \rightarrow \epsilon_h$ [13]. Correspondingly, it can be proven that the dominant contribution to the extinction-peak scales in both scenarios as $\sigma_{\text{ext}}^*/(k_p V_p) \sim 1/G_D$, emphasizing the infeasibility of the purely lossless case in this framework. The comparison between $\mathcal{P}'_k$ and $\mathcal{P}_k$ shows explicitly that the optical-theorem prefactor changes the peak condition, and the characteristic polynomial is not a Fröhlich equation corrected *a posteriori*, but the direct extremum condition of the extinction cross section.

When dynamic depolarization effects become relevant, the polynomials must be corrected in Eq. (11) based on the (dimensionless) characteristic frequency $\Omega_A^2 = 4\pi a_{\text{eff}} v^2 / (V_p \omega_p^2)$, with $v = c/\sqrt{\epsilon_h}$ being the wave velocity in the medium. Conceptually, Ω_A measures the highest frequency that the electron system can sustain before appreciable phase variations develop as a consequence of dynamic depolarization, and can be described as the following ratio:

$$\Omega_A = \frac{\lambda_p}{2\pi \ell_{\text{eff}}}, \quad (18)$$

where $k_p = 2\pi/\lambda_p = \omega_p/v$ means the plasma wave number. For example, if $\epsilon_h = 1$ and $G_D \approx 0$ then $\mathcal{P}_0 = 3\Omega^4 - 2L_{\text{eff}}\Omega^2 - L_{\text{eff}}^2$, $\mathcal{P}_2 = 6\Omega^2 - 2L_{\text{eff}}$, $\mathcal{P}_4 = 3$, and the extremal condition $\mathcal{P}(1, 0, 0, L_{\text{eff}}; \Omega) = 0$ consistently redshifts the quasistatic $\omega_{\text{res}}^{\text{qs}} = \sqrt{L_{\text{eff}}} \omega_p$:

$$\frac{\omega_{\text{res}}^{\text{qs}}}{\omega_p} = (1 + \Omega_A^{-2})^{-\frac{1}{2}} \approx 1 - \frac{V_p \omega_p^2}{8\pi a_{\text{eff}} v^2} + \mathcal{O}(\Omega_A^{-4}). \quad (19)$$

Although qualitatively significant, such Drude results are of limited quantitative value. It can also be proven that they can be readily extended to the case of radiative damping by an additional characteristic retardation frequency $\Omega_R = 4\pi v^3 / (V_p \omega_p^3)$, yielding an estimation of the threshold controlling when the k^3 contributions (scattering, radiative reaction, etc.) begin to matter.

V. DISCUSSION OF MODEL EXTENSIONS

Our description is based on an effective polarizability, with an ad hoc but self-consistent closure among optical descriptors; here the extinction-peak wavelength, geometric descriptors, such as particle volume, and depolarization

descriptors. This further motivates a geometro-optical space where analogous closures can be constructed for more complex scenarios. In addition to numerical cost, two additional limits appear: (i) identifiability, because different physical effects can produce similar spectral changes, and (ii) mode mixing, as compressed models may be contaminated by non-dominant modes.

A first situation of interest involves significantly nonuniform depolarization due to inhomogeneous media and/or nonuniform fields. In the quasistatic limit, the internal field can be written through a nonlocal surface operator of Neumann-Poincaré type acting on the boundary field

$$\mathbf{E}(\mathbf{r}) = \mathbf{E}_0(\mathbf{r}) - \left(\frac{\varepsilon/\varepsilon_h - 1}{4\pi} \right) \oint_S \frac{\mathbf{n}' \otimes \mathbf{e}_R}{\rho'^2} \mathbf{E}(\mathbf{r}') dS', \quad (20)$$

which turns the polarizability into a functional of the field on the surface S [50]. For axisymmetric particles, such as nanorods, nanobicones, and nanobipyramids, strong tip or edge inhomogeneities imply that assigning three constant static depolarization terms L_i is exact only in the homogeneous quasistatic limit. Otherwise, they should be regarded as effective, illumination- and environment-dependent quantities. A practical route can be the following: (i) solve the full electromagnetic problem for a chosen illumination along the direction j ; (ii) define a representative internal field, or polarization, by volume averaging; and (iii) invert the uniform-ellipsoid formula to obtain an effective $L_j^{\text{eff}}(\omega)$ reproducing the averaged internal field. This depolarization factor becomes frequency dependent, generally complex because of phase lag, and implicitly incorporates near-field and radiative effects.

When nonlocal interactions among subwavelength constituents become relevant, as in the discrete dipole approximation (DDA) and its lattice-dispersion-relation variants, LDR and surface-corrected LDR (SCLDR), the local field at site i includes the retarded discrete Green-tensor contributions from all other sites. Conceptually, this renormalizes the depolarization operator by lattice-mediated terms, with details depending on the chosen DDA normalization. A closely related picture holds for periodic arrays, where the coupled response under fixed incidence and polarization enters through the Bloch-projected retarded dipole lattice sum S_e , leading to

$$\alpha_{\text{eff}}^{-1} = \alpha_0^{-1} - \frac{2}{3} i k_h^3 - S_e, \quad (21)$$

with k_h the host wave number. Once S_e is expressed in terms of lattice geometry [51], the geometro-optical characterization remains applicable. A reciprocal-space formulation with the dyadic Green's function, $\mathbf{S}(\mathbf{k}, \mathbf{q})$, clarifies the emergence of

near-field quasistatic and far-field radiative chain plasmons with distinct resonance and decay regimes. Under dilute filling and away from lattice resonances, an effective-medium approximation can be used to dress each dipole into a homogeneous response at the obvious cost of losing lattice fine structure. The same logic extends to core-shell and multilayer particles, with additional dielectric functions and volume fractions [52,53], to effective-medium or dressed-polarizability descriptions [54,55], and to supported or environmentally dressed particles, where the effective polarizability depends on the distance to nearby interfaces [56].

VI. CONCLUSION

A high-dimensional plasmonic peak-finding problem is reduced to a differential state equation for the extinction maximum, with geometry entering via a small set of physically interpretable depolarization descriptors. We derived the characteristic polynomial that accurately governs this maximum under the MLWA closure, leading to compact geometro-optical manifolds for analyzing plasmonic shape transitions in arbitrary systems, and offering a practical route for experimentalists toward morphology inference aided by data-driven analysis. Importantly, knowledge of the extinction peak position via precise characteristic equations enables formerly inaccessible integrodifferential calculations. Beyond extinction and homogeneous systems, this idea can be generalized to scattering and absorption maxima, linewidth extrema, and more complex architectures (multilayers, multimode particles, interacting assemblies, environmental dressing, nonuniform illumination, etc.). Model extension needs separate state equations or additional descriptors which lie outside the scope of this work. For metal clusters or ultrasmall particles (below ~ 5 nm), where confinement and nonlocal surface effects are relevant (e.g., Feibelman d parameters) [39], the polarizability should be rebuilt from a quantum-corrected response.

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DATA AVAILABILITY

Calibration tables and symbolic coefficients are available at [57]. The polynomial implementation is available via the authors' calculator [58].

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