# Universal analytical modeling of plasmonic nanoparticles

- ELECTRONIC SUPPLEMENTAL INFORMATION -

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#### I. SELF-CONSISTENT RELATION FOR THE OPTICAL ELECTRIC FIELD IN THE PRESENCE OF A PARTICLE

We consider a homogeneous metal particle of local isotropic permittivity  $\epsilon_{\rm m}(\omega)$  placed in a uniform host medium of permittivity  $\epsilon_{\rm h}(\omega)$  and exposed to an external electric field  $\mathbf{E}^{\rm ext}(\mathbf{r},\omega)$ , where  $\omega$  is the frequency of light. For monochromatic light, the full time-dependent electric field is given by  $2\text{Re}\{\mathbf{E}(\mathbf{r},\omega)e^{-i\omega t}\}$ , and similarly for other quantities. A current  $\mathbf{j}^{\rm ind}(\mathbf{r},\omega)$  is induced in the particle, which permits writing the total electric field as<sup>1</sup>

$$\mathbf{E}(\mathbf{r},\omega) = \mathbf{E}^{\text{ext}}(\mathbf{r},\omega) + \frac{\mathrm{i}}{\omega\epsilon_{\mathrm{h}}} \left( k_{\mathrm{h}}^{2} \mathcal{I}_{3} + \nabla \otimes \nabla \right) \cdot \int d^{3}\mathbf{r}' \frac{\mathrm{e}^{\mathrm{i}k_{\mathrm{h}}|\mathbf{r}-\mathbf{r}'|}}{|\mathbf{r}-\mathbf{r}'|} \mathbf{j}^{\text{ind}}(\mathbf{r}',\omega), \tag{S1}$$

where  $k_{\rm h} = \sqrt{\epsilon_{\rm h}} \, \omega/c$  is the light wave vector in the host medium, c is the speed of light in vacuum, and  $\mathcal{I}_3$  is the 3 × 3 unit matrix. Equation (S1) allows us to obtain a self-consistent relation for the electric field by expressing the induced current  $\mathbf{j}^{\rm ind}(\mathbf{r},\omega) = f(\mathbf{r})\sigma(\omega)\mathbf{E}(\mathbf{r},\omega)$  in terms of the effective metal conductivity

$$\sigma(\omega) = -\mathrm{i}\omega \left[\epsilon_{\mathrm{m}}(\omega) - \epsilon_{\mathrm{h}}(\omega)\right] / 4\pi$$

and a filling function  $f(\mathbf{r})$  that is 1 for  $\mathbf{r}$  inside the metal and takes a vanishing positive value outside of it. Inserting these expressions into eqn (S1), we obtain

$$\mathbf{E}(\mathbf{r},\omega) = \mathbf{E}^{\text{ext}}(\mathbf{r},\omega) + \frac{1}{\mu(\omega)} \left( k_{\text{h}}^2 \mathcal{I}_3 + \nabla \otimes \nabla \right) \cdot \int d^3 \mathbf{r}' f(\mathbf{r}') \frac{\mathrm{e}^{\mathrm{i}k_{\text{h}}|\mathbf{r}-\mathbf{r}'|}}{|\mathbf{r}-\mathbf{r}'|} \mathbf{E}(\mathbf{r}',\omega), \tag{S2}$$

where

$$\mu(\omega) = \frac{4\pi}{\epsilon_{\rm m}/\epsilon_{\rm h} - 1}$$

Now, multiplying both sides of eqn (S2) by  $\sqrt{f(\mathbf{r})}$  and defining

$$\vec{\mathcal{E}}(\mathbf{r},\omega) = \sqrt{f(\mathbf{r})} \, \mathbf{E}(\mathbf{r},\omega),$$

we find

$$\vec{\mathcal{E}}(\mathbf{r},\omega) = \vec{\mathcal{E}}^{\text{ext}}(\mathbf{r},\omega) + \frac{1}{\mu(\omega)} \int d^3 \mathbf{r}' \mathcal{M}(\mathbf{r},\mathbf{r}') \cdot \vec{\mathcal{E}}(\mathbf{r}',\omega),$$
(S3)

where

$$\mathcal{M}(\mathbf{r},\mathbf{r}') = \sqrt{f(\mathbf{r})f(\mathbf{r}')} \left(k_{\rm h}^2 \mathcal{I}_3 + \nabla \otimes \nabla\right) \frac{\mathrm{e}^{\mathrm{i}k_{\rm h}|\mathbf{r}-\mathbf{r}'|}}{|\mathbf{r}-\mathbf{r}'|} \tag{S4}$$

is a linear symmetric operator.

#### II. ELECTROSTATIC LIMIT

In the  $c \to \infty$  limit, eqn (S4) becomes

$$\mathcal{M}^{(0)}(\mathbf{r},\mathbf{r}') = \sqrt{f(\mathbf{r})f(\mathbf{r}')} \nabla \otimes \nabla \frac{1}{|\mathbf{r}-\mathbf{r}'|},$$

where  $\mathcal{M}^{(0)}$  is a real symmetric operator that consequently admits an orthogonal set of real eigenmodes  $\vec{\mathcal{E}}_j = \sqrt{f} \mathbf{E}_j$  and eigenvalues  $\mu_j$  satisfying

$$\vec{\mathcal{E}}_{j}(\mathbf{r}) = \frac{1}{\mu_{j}} \int d^{3}\mathbf{r}' \mathcal{M}^{(0)}(\mathbf{r}, \mathbf{r}') \cdot \vec{\mathcal{E}}_{j}(\mathbf{r}'), \tag{S5}$$

$$\int d^3 \mathbf{r} \, \vec{\mathcal{E}}_j(\mathbf{r}) \cdot \vec{\mathcal{E}}_{j'}(\mathbf{r}) = L^3 \delta_{jj'},\tag{S6}$$

$$\sum_{j} \vec{\mathcal{E}}_{j}(\mathbf{r}) \otimes \vec{\mathcal{E}}_{j}(\mathbf{r}') = L^{3} \delta(\mathbf{r} - \mathbf{r}') \mathcal{I}_{3}.$$
(S7)

The last expression (completeness relation) must be understood in the subspace of electrostatic fields (i.e., irrotational and divergenceless vector distributions). Here, we introduce a characteristic length of the particle L (e.g., the length for a rod) that renders the mode fields and eigenvalues dimensionless. These relations allow us to expand the solution of eqn (S3) in terms of electrostatic eigenmodes as

$$\mathbf{E}(\mathbf{r},\omega) = \sum_{j} \frac{C_{j}^{\text{ext}}(\omega)}{1 - \mu_{j}/\mu(\omega)} \mathbf{E}_{j}(\mathbf{r})$$
$$= \sum_{j} \left[ 1 - \frac{\epsilon_{\text{m}}/\epsilon_{\text{h}} - 1}{\epsilon_{j} - 1} \right]^{-1} C_{j}^{\text{ext}}(\omega) \mathbf{E}_{j}(\mathbf{r})$$
(S8)

with expansion coefficients

$$C_j^{\text{ext}}(\omega) = \frac{1}{L^3} \int d^3 \mathbf{r} f(\mathbf{r}) \, \mathbf{E}_j(\mathbf{r}) \cdot \mathbf{E}^{\text{ext}}(\mathbf{r}, \omega).$$

In eqn (S8) we define the mode permittivity  $\epsilon_j$  through the relation  $\mu_j = 4\pi(\epsilon_j - 1)^{-1}$ .

#### **III. PERTURBATIVE SOLUTION INCLUDING RETARDATION**

A direct extension of eqns (S5)-(S8) permits us to express the general solution of Maxwell's equations in terms of  $k_{\rm h}$ -dependent complex eigenmodes  $\tilde{\vec{\mathcal{E}}}_j = \sqrt{f} \,\tilde{\mathbf{E}}_j$  and eigenvalues  $\tilde{\mu}_j$  of the symmetric operator  $\mathcal{M}$ , which satisfy

$$\tilde{\vec{\mathcal{E}}}_{j}(\mathbf{r}) = \frac{1}{\tilde{\mu}_{j}} \int d^{3}\mathbf{r}' \,\mathcal{M}(\mathbf{r},\mathbf{r}') \cdot \tilde{\vec{\mathcal{E}}}_{j}(\mathbf{r}'), \qquad (S9)$$

$$\int d^{3}\mathbf{r} \,\tilde{\vec{\mathcal{E}}}_{j}(\mathbf{r}) \cdot \tilde{\vec{\mathcal{E}}}_{j'}(\mathbf{r}) = L^{3}\delta_{jj'},$$

$$\sum_{j} \tilde{\vec{\mathcal{E}}}_{j}(\mathbf{r}) \otimes \tilde{\vec{\mathcal{E}}}_{j}(\mathbf{r}') = L^{3}\delta(\mathbf{r} - \mathbf{r}')\mathcal{I}_{3},$$
(S10)

where the last expression (completeness) is valid in the subspace of divergenceless vector fields (i.e., solutions satisfying the Coulomb law  $\nabla \cdot \mathbf{E}$  inside the particle). The solution for the field now becomes

$$\mathbf{E}(\mathbf{r},\omega) = \sum_{j} \frac{C_{j}^{\text{ext}}(\omega)}{1 - (\epsilon_{\text{m}}/\epsilon_{\text{h}} - 1)\tilde{\mu}_{j}/4\pi} \tilde{\mathbf{E}}_{j}(\mathbf{r}), \qquad (S11)$$

where

$$\tilde{C}_{j}^{\text{ext}}(\omega) = \frac{1}{L^{3}} \int d^{3}\mathbf{r} f(\mathbf{r}) \,\tilde{\mathbf{E}}_{j}(\mathbf{r}) \cdot \mathbf{E}^{\text{ext}}(\mathbf{r},\omega).$$
(S12)

We intend to express the retarded eigenmodes and eigenvalues in terms of the electrostatic modes. For this purpose we take  $s = k_{\rm h} L/2\pi = \sqrt{\epsilon_{\rm h}} L/\lambda$  as a size parameter and write the perturbation expansion

$$\mathcal{M}(\mathbf{r},\mathbf{r}') = \mathcal{M}^{(0)}(\mathbf{r},\mathbf{r}') + \sum_{n=2}^{\infty} \mathcal{M}^{(n)}(\mathbf{r},\mathbf{r}'),$$

where we find the n = 1 term to be zero, while the  $n \ge 2$  terms are given by

$$\mathcal{M}^{(n)}(\mathbf{r},\mathbf{r}') = \frac{i2\pi s^n}{L^n} \sqrt{f(\mathbf{r})f(\mathbf{r}')} \; \frac{|\mathbf{r}-\mathbf{r}'|^{n-5}}{n(n-2)!} \left[ (n-3)(\mathbf{r}-\mathbf{r}') \otimes (\mathbf{r}-\mathbf{r}') + (1-n)|\mathbf{r}-\mathbf{r}'|^2 \mathcal{I}_3 \right].$$

Using the expansion  $\tilde{\mu}_j = \tilde{\mu}_j^{(0)} + \tilde{\mu}_j^{(1)} + \tilde{\mu}_j^{(2)} + \tilde{\mu}_j^{(3)} + \cdots$  for the eigenvalues and a similar one for the eigenmodes, where each term  $\tilde{\mu}_j^{(n)}$  is proportional to  $s^n$ , eqn (S9) leads to

$$\begin{bmatrix} \tilde{\mu}_{j}^{(0)} + \tilde{\mu}_{j}^{(1)} + \tilde{\mu}_{j}^{(2)} + \tilde{\mu}_{j}^{(3)} + \cdots \end{bmatrix} \begin{bmatrix} \tilde{\vec{\mathcal{E}}}_{j}^{(0)}(\mathbf{r}) + \tilde{\vec{\mathcal{E}}}_{j}^{(1)}(\mathbf{r}) + \tilde{\vec{\mathcal{E}}}_{j}^{(2)}(\mathbf{r}) + \tilde{\vec{\mathcal{E}}}_{j}^{(3)}(\mathbf{r}) + \cdots \end{bmatrix}$$
(S13)

$$= \int d^3 \mathbf{r}' \left[ \mathcal{M}^{(0)}(\mathbf{r},\mathbf{r}') + \mathcal{M}^{(2)}(\mathbf{r},\mathbf{r}') + \mathcal{M}^{(3)}(\mathbf{r},\mathbf{r}') + \cdots \right] \cdot \left[ \tilde{\mathcal{E}}_{j}^{(0)}(\mathbf{r}') + \tilde{\mathcal{E}}_{j}^{(1)}(\mathbf{r}') + \tilde{\mathcal{E}}_{j}^{(2)}(\mathbf{r}') + \tilde{\mathcal{E}}_{j}^{(3)}(\mathbf{r}') + \cdots \right].$$

This expansion of retarded modes in terms of electrostatic ones involves a severe approximation: the electrostatic modes have zero rotational, so they lead to a vanishing magnetic field  $\mathbf{B} = (-ic/\omega)\nabla \times \mathbf{E}$ . In essence, we are neglecting magnetic modes, both in the their contribution to retardation corrections of the electrostatic modes and in the fact that they emerge with nonzero strength for finite size compared with the light wavelength. However, as we demonstrate through extensive numerical simulations, this is a good approximation for metallic nanoparticles in the size range under consideration. Nonetheless, a reasonable estimate for the magnetic field can be obtained from the electric one using the Maxwell equation  $\nabla \times \mathbf{H} = (-i\epsilon\omega/c)\mathbf{E}$ .<sup>2</sup> Keeping these considerations in mind, we proceed from eqn (S13) in a customary fashion by solving the equation

$$\sum_{l=0}^{l=n} \tilde{\mu}_j^{(n-l)} \tilde{\vec{\mathcal{E}}}_j^{(l)} = \sum_{l=0}^{l=n} \int d^3 \mathbf{r}' \, \mathcal{M}^{(n-l)}(\mathbf{r}, \mathbf{r}') \cdot \tilde{\vec{\mathcal{E}}}_j^{(l)}(\mathbf{r}') \tag{S14}$$

for each perturbation order n, using the solutions for lower orders < n. The electrostatic modes satisfy eqn (S14) for n = 0, so we assign  $\tilde{\mu}_j^{(0)} = \mu_j$  and  $\tilde{\vec{\mathcal{E}}}_j^{(0)} = \vec{\mathcal{E}}_j$ . Also, the vanishing of  $\mathcal{M}^{(1)}$  leads to  $\tilde{\mu}_j^{(1)} = 0$  and  $\tilde{\vec{\mathcal{E}}}_j^{(1)} = 0$ . After lengthy but straightforward algebra, we find the rest of the eigenvalues  $(n \ge 2)$  to be

$$\tilde{\mu}_j = \mu_j + 4\pi A_j(s) = 4\pi \left[ (\epsilon_j - 1)^{-1} + A_j(s) \right]$$
(S15)

with

$$A_j(s) = \sum_{n=2}^{\infty} a_{jn} s^n \tag{S16}$$

and

$$a_{jn} = \frac{(2\pi \mathbf{i})^n}{4\pi n(n-2)!L^{n+3}} \int d^3 \mathbf{r} f(\mathbf{r}) \int d^3 \mathbf{r}' f(\mathbf{r}')$$

$$\times \left\{ (n-3)|\mathbf{r} - \mathbf{r}'|^{n-5} \left[ (\mathbf{r} - \mathbf{r}') \cdot \mathbf{E}_j(\mathbf{r}) \right] \left[ (\mathbf{r} - \mathbf{r}') \cdot \mathbf{E}_j(\mathbf{r}') \right] + (1-n)|\mathbf{r} - \mathbf{r}'|^{n-3} \mathbf{E}_j(\mathbf{r}) \cdot \mathbf{E}_j(\mathbf{r}') \right\}.$$
(S17)

In this expression, the retardation corrections of the eigenvalue j are entirely expressed in terms of the electrostatic mode with the same index j. This result is rigorous up to order n = 3. For higher-order corrections, this result holds if we neglect the interactions between different electrostatic modes (crossed terms), which we find to be an excellent approximation for the particle sizes and morphologies considered in this paper, where we only retain terms up to n = 4 in practice.

### IV. LIGHT PLANE-WAVE SCATTERING

In the  $k_{\rm h}r \gg 1$  and  $r \gg r'$  limit, eqn (S2) reduces to

$$\mathbf{E}(\mathbf{r},\omega) = \mathbf{E}^{\text{ext}}(\mathbf{r},\omega) + \frac{1}{\epsilon_{\text{h}}} \left[ k_{\text{h}}^{2}\mathbf{p} + (\mathbf{p}\cdot\nabla)\nabla \right] \frac{\mathrm{e}^{\mathrm{i}k_{\text{h}}r}}{r},$$

where

$$\mathbf{p} = \frac{\epsilon_{\rm h}}{\mu(\omega)} \int d^3 \mathbf{r}' f(\mathbf{r}') \, \mathbf{E}(\mathbf{r}', \omega) \mathrm{e}^{-\mathrm{i}k_{\rm h}\mathbf{r}' \cdot \hat{\mathbf{r}}} \tag{S18}$$

is a generalized  $k_{\rm h}$ -dependent induced dipole moment.

We consider an incident plane wave propagating along z and polarized along x, which is taken to be a symmetry direction of the particle. Inserting the external field  $\mathbf{E}^{\text{ext}} = E_0 e^{\mathbf{i}k_h z} \hat{\mathbf{x}}$  into eqns (S11) and (S12), and this in turn into eqn (S18), we find  $\mathbf{p} = p_x \hat{\mathbf{x}}$  with

$$p_x = \frac{\epsilon_{\rm h} E_0}{4\pi L^3} \sum_j \frac{\left(\int d^3 \mathbf{r} \, f(\mathbf{r}) \, \tilde{E}_{jx}(\mathbf{r}) \mathrm{e}^{\mathrm{i}k_{\rm h}z}\right) \left(\int d^3 \mathbf{r} \, f(\mathbf{r}) \, \tilde{E}_{jx}(\mathbf{r}) \mathrm{e}^{-\mathrm{i}k_{\rm h}z}\right)}{1/(\epsilon_{\rm m}/\epsilon_{\rm h}-1) - 1/(\epsilon_j-1) - A_j(s)},\tag{S19}$$



FIG. S1: Size dependence of the mode volume. The dipole mode volume  $V_1^{k_h}$  (solid curves) is plotted as a function of  $s = k_h L/2\pi$ , calculated from eqn (S20) for rods (left panel) and triangles (right panel) of different aspect ratio R (see labels in the right plot). The results are normalized to the total volume of the particle V. Particle parameters L and Rare defined in Fig. 3 of the main paper. Dashed curves show the Taylor expansion of  $V_1^{k_h}$  up to terms of order  $R^2$ .

where we consider far-field emission along z as well. The numerator in this expression receives retardation corrections both from the mode fields  $\tilde{E}_{jx}$  and from the phase factors  $e^{\pm ik_h z}$ . As an indication that these corrections are small for the particle sizes usually targeted through colloid synthesis, we analyze the effect of the phase factors in Fig. S1 by computing

$$V_j^{k_{\rm h}} = \frac{1}{L^3} \left| \int d^3 \mathbf{r} f(\mathbf{r}) \,\mathrm{e}^{\mathrm{i}k_{\rm h}z} E_{jx}(\mathbf{r}) \right|^2 \tag{S20}$$

(*i.e.*, approximating  $\tilde{E}_{jx}$  by  $E_{jx}$ ). We observe that the results have a minor dependence on the retardation parameter  $s = k_{\rm h}L/2\pi$  for small s. Retardation corrections are in fact proportional to  $s^2$  in this numerator. In practice, we find that for the sizes and morphologies considered in this work, neglecting these corrections is an excellent approximation, so we write the noted numerator as an electrostatic mode volume

$$V_j \equiv V_j^0 = \frac{1}{L^3} \left| \int d^3 \mathbf{r} f(\mathbf{r}) E_{jx}(\mathbf{r}) \right|^2.$$
(S21)

This allows us to express the dipole  $p_x = \alpha E_0$  in terms of the polarizability

$$\alpha(\omega) = \frac{\epsilon_{\rm h}}{4\pi} \sum_{j} \frac{V_j}{1/(\epsilon_{\rm m}/\epsilon_{\rm h}-1) - 1/(\epsilon_j-1) - A_j(s)}.$$
(S22)

Importantly, in virtue of eqn (S7), the mode volumes satisfy the sum rule

$$\sum_{j} V_j = V,$$

where V is the total volume of the particle. Actually, the numerator of eqn (S19), which includes retardation, also satisfies this sum rule as a result of the closure relation (S10) for the retarded mode fields. Additionally, the  $a_{j3}$  coefficient [see eqn (S17)] can be expressed in terms of the corresponding mode volume, so the correction term in the denominator of eqn (S22) can be written from eqn (S16) as

$$A_j(s) = a_{j2}s^2 + \frac{4\pi^2 iV_j}{3L^3}s^3 + a_{j4}s^4 + \cdots$$
(S23)

We finally note that the extinction and the angle-integrated elastic scattering cross-sections can be written in terms of the polarizability as

$$\sigma^{\text{ext}} = \frac{4\pi\omega}{\sqrt{\epsilon_{\text{h}}}c} \text{Im}\left\{\alpha(\omega)\right\}$$

and

$$\sigma^{\rm sca} = \frac{8\pi\omega^4}{3c^4} \, |\alpha(\omega)|^2 \, .$$

$$\mathbf{E}(\mathbf{r},\omega) \approx \sum_{j} \frac{C_{j}^{\text{ext}}(\omega)}{1 - (\epsilon_{\text{m}}/\epsilon_{\text{h}} - 1) \left[1/(\epsilon_{j} - 1) + A_{j}\right]} \mathbf{E}_{j}(\mathbf{r}).$$
(S24)

The mode energies are then well captured by this expression, while the spatial profiles and strengths are reasonably well approximated by the nonretarded modes for the particle sizes and shapes considered in this work.

Finally, as we note that in the main paper and in the additional results presented below, the lowest-order j = 1 dipole mode of each particle is modeled with four real parameters:  $\epsilon_1$ ,  $V_1$ ,  $a_{12}$ , and  $a_{14}$ . We further approximate the retarded mode field by the nonretarded field  $\mathbf{E}_1$ .

#### V. LOCAL DENSITY OF OPTICAL STATES (LDOS)

We calculate this quantity as a function of position **r** and frequency  $\omega$  using the expression<sup>3</sup>

$$LDOS_{\hat{\mathbf{n}}} = Im\{\hat{\mathbf{n}} \cdot \mathbf{E}(\mathbf{r},\omega)\}/(2\pi^2\omega),$$

where  $\mathbf{E}(\mathbf{r}, \omega)$  is the electric field produced by a unit dipole  $\hat{\mathbf{n}}$  placed at  $\mathbf{r}$  and oscillating at frequency  $\omega$ . The real part of this field diverges, but the imaginary part takes a finite value, which in vacuum becomes

$$\mathrm{LDOS}^{0}_{\hat{\mathbf{n}}} = \omega^2 / 3\pi^2 c^3.$$

The direct field produced by the dipole in the homogeneous host medium at a position  $\mathbf{r}'$  is  $(1/\epsilon_h)(k_h^2 + \nabla \otimes \nabla) e^{ik_h |\mathbf{r}-\mathbf{r}'|} / |\mathbf{r}-\mathbf{r}'| \cdot \hat{\mathbf{n}}$ , which upon insertion into eqn (S12), using eqn (S9), allows us to write

$$\tilde{C}_j^{\text{ext}}(\omega) = \frac{\tilde{\mu}_j}{\epsilon_{\text{h}}L^3} \tilde{\mathbf{E}}_j(\mathbf{r}) \cdot \hat{\mathbf{n}}.$$

Inserting this expression into eqn (S11), we find

$$\frac{\text{LDOS}_{\hat{\mathbf{n}}}}{\text{LDOS}_{\hat{\mathbf{n}}}^{0}} = \frac{6\pi\sqrt{\epsilon_{\mathrm{h}}}}{k_{\mathrm{h}}^{3}L^{3}} \text{Im} \left\{ \sum_{j} \frac{\left(\hat{\mathbf{n}} \cdot \tilde{\mathbf{E}}_{j}(\mathbf{r})\right)^{2}}{4\pi/\tilde{\mu}_{j} - (\epsilon_{\mathrm{m}}/\epsilon_{\mathrm{h}} - 1)} \right\}$$

Assuming that one mode j = 1 dominates the sum, approximating  $\tilde{\mathbf{E}}_1 \approx \mathbf{E}_1$ , and using eqns (S15) and (S23), we finally obtain

$$\frac{\text{LDOS}_{\hat{\mathbf{n}}}}{\text{LDOS}_{\hat{\mathbf{n}}}^{0}} \approx \frac{6\pi\sqrt{\epsilon_{\mathrm{h}}}}{k_{\mathrm{h}}^{3}L^{3}} \left(\hat{\mathbf{n}} \cdot \mathbf{E}_{1}(\mathbf{r})\right)^{2} \text{Im} \left\{ \frac{1}{\left[1/(\epsilon_{1}-1)+A_{1}\right]^{-1}-(\epsilon_{\mathrm{m}}/\epsilon_{\mathrm{h}}-1)} \right\},\tag{S25}$$

which is the expression used in the main text to calculate the analytical LDOS.

#### VI. PLASMON QUANTUM YIELD EXPRESSED AS THE RATIO OF POWERS FOR DIFFERENT TRANSFER CHANNELS

In the main text we argue the plasmon quantum yield, defined as the ratio of radiative plasmon decay to total plasmon decay, can be calculated from the power associated with light-emission and metal-absorption channels,  $P^{\text{emi}}$  and  $P^{\text{abs}}$ , respectively, as  $Y = P^{\text{emi}}/(P^{\text{emi}} + P^{\text{abs}})$ , and that the resulting expression coincides with the ratio between elastic-scattering and extinction cross-sections of the particle for light polarization along the plasmon dipole. Here, we prove that this is indeed the case.

The power absorbed by the metal under the influence of a monochromatic source can be obtained from the general expression

$$P^{\rm abs} = \frac{\omega}{2\pi} {\rm Im}\{\epsilon_{\rm m}(\omega)\} \int d\mathbf{r} f(\mathbf{r}) |\mathbf{E}(\mathbf{r},\omega)|^2.$$
(S26)

We now use eqn (S24) for the electric field and consider that the sum is dominated by a mode j = 1, so that the rest of the terms can be neglected. The integral in eqn (S26) can be directly performed using the orthonormality of the modes (eqn (S6)), which readily leads to the expression

$$P^{\rm abs} = \frac{\epsilon_{\rm h}^2 L^3 \omega}{2\pi} {\rm Im} \left\{ \frac{1}{\epsilon_{\rm h} - \epsilon_{\rm m}} \right\} \left| \frac{C_1^{\rm ext}}{g_1} \right|^2, \tag{S27}$$

where  $g_1 = (\epsilon_m/\epsilon_h - 1)^{-1} - (\epsilon_1 - 1)^{-1} - A_1$ .

The emitted power can be obtained from the expression<sup>3</sup>

$$P^{\rm emi} = \frac{4\sqrt{\epsilon_{\rm h}}k^3\omega}{3}|\mathbf{p}|^2,\tag{S28}$$

where **p** is the dipole induced in the particle by the external source. Now, using eqn (S18) to obtain this dipole, neglecting the contribution to retardation originating in the exponential phase factor inside the spatial integral of that equation, and assuming again a dominant mode j = 1, we find

$$\mathbf{p} = \frac{\epsilon_{\rm h}}{4\pi} \frac{C_1^{\rm ext}}{g_1} \int d\mathbf{r} f(\mathbf{r}) \mathbf{E}_1(\mathbf{r}).$$

Inserting this expression into eqn (S28), and assimilating the square of the spatial integral to  $V_1L^3$  (see eqn (S21)), we obtain

$$P^{\text{emi}} = \frac{\epsilon_{\text{h}} L^3 V_1 k_{\text{h}}^3 \omega}{12\pi^2} \left| \frac{C_1^{\text{ext}}}{g_1} \right|^2.$$
(S29)

Finally, combining eqns (S27) and (S29), we find

$$Y = \frac{P^{\text{emi}}}{P^{\text{emi}} + P^{\text{abs}}} = \left[1 + \frac{3\lambda^3}{4\pi^2\sqrt{\epsilon_{\text{h}}}V_1} \operatorname{Im}\left\{\frac{1}{\epsilon_{\text{h}} - \epsilon_{\text{m}}}\right\}\right]^{-1},\tag{S30}$$

which coincides with eqn (13) of the main text.

## VII. RELATION BETWEEN QUANTUM YIELD, LDOS, AND FIELD ENHANCEMENT

We define the field enhancement (FE) for a given direction  $\hat{\mathbf{n}}$  at a position  $\mathbf{r}$  as the squared modulus of the electric field component along that direction when the structure is illuminated by an optical external field also oriented along  $\hat{\mathbf{n}}$ . Using eqns (S11) and (S12), assuming that the term j = 1 dominates the sum over modes, approximating  $\tilde{\mathbf{E}}_1 \approx \mathbf{E}_1$ , and identifying  $(C_1^{\text{ext}})^2 = V_1/L^3$  according to eqn (S21) for a unit incident field, we find

$$FE_{\hat{\mathbf{n}}} \approx \frac{V_1}{L^3} \frac{\left(\hat{\mathbf{n}} \cdot \mathbf{E}_1(\mathbf{r})\right)^2}{\left|1 - (\epsilon_{\mathrm{m}}/\epsilon_{\mathrm{h}} - 1)\tilde{\mu}_1/4\pi\right|^2}.$$
(S31)

Now, combining eqns (S25) and (S31) we find

$$\frac{\mathrm{FE}_{\hat{\mathbf{n}}}}{\left(\mathrm{LDOS}_{\hat{\mathbf{n}}}/\mathrm{LDOS}_{\hat{\mathbf{n}}}^{0}\right)} \approx \frac{1}{\sqrt{\epsilon_{\mathrm{h}}}} \left[ 1 + \left(6\pi/k_{\mathrm{h}}^{3}V_{1}\right) \left| (\epsilon_{1}-1)^{-1} + A_{1} \right|^{2} \mathrm{Im}\{\epsilon_{\mathrm{m}}/\epsilon_{\mathrm{h}}-1\} \right]^{-1}.$$
 (S32)

Noticing that for a frequency near the j = 1 resonance one has  $(\epsilon_m/\epsilon_h - 1)^{-1} \approx (\epsilon_1 - 1)^{-1} + A_1$  (*i.e.*, a pole in eqn (S24)), we can approximate the right-hand side of eqn (S32) so that the expression inside the square brackets becomes exactly the same as the one inside the square brackets of eqn (S30). We thus conclude the approximate relation

$$Y \approx \sqrt{\epsilon_{\mathbf{h}}} \frac{(\mathrm{FE}_{\hat{\mathbf{n}}})}{(\mathrm{LDOS}_{\hat{\mathbf{n}}}/\mathrm{LDOS}_{\hat{\mathbf{n}}}^{0})},$$

which is numerically validated in Fig. 14 of the main paper. Incidentally, we note that the factor  $\sqrt{\epsilon_{\rm h}}$  enters this expression explicitly because the LDOS in the homogeneous host is  $\sqrt{\epsilon_{\rm h}} \times (\text{LDOS}_{\hat{\mathbf{n}}}^0)$ .

#### VIII. MODEL PARAMETERS FOR ADDITIONAL PARTICLE MORPHOLOGIES

In the main paper, we concentrate on three common particle morphologies (rods, triangles, and cube cages), for which model parameters are provided in Fig. 3 and Table 1. We supplement those results with additional parameters for other common morphologies: ellipsoids, bicones, disks, rings, and bipyramids. Figure S2 and Table S1 show the four parameters that allow us to compute the polarizability for each of these new types of particles near their respective lowest-order dipole plasmons as a function of aspect ratio R, which is defined in the top insets of Fig. S2. These parameters are used in the analytical curves of Figs. 2, 8(C-F), 9(C-F), and 10(C-F) of the main paper. Additionally, we provide parameters for transversal modes (Table S2) used in the analytical calculations of Fig. S3.



FIG. S2: Model parameters for various additional particle morphologies. We show the resonant in-vacuum permittivity  $\epsilon_1$ , the mode volume  $V_1$ , and two of the expansion coefficients  $a_{jn}$  in eqn (S23), as a function of aspect ratio R, for the lowest-order dipole mode (j = 1) of five selected morphologies (see upper insets). Symbols:  $\epsilon_1$  values extracted by fitting the corresponding absorption spectra (computed in the electrostatic limit),  $V_1^0$  values calculated from eqn (S21), and  $a_{12}$  and  $a_{14}$  values obtained from eqn (S17). Solid curves: analytical fitting functions given in Table S1. Symbol and curve colors correspond to the different shapes of the upper insets. The electrostatic mode field  $\mathbf{E}_1$  is used in the evaluation of eqns (S17) and (S21), as obtained from the electrostatic solution, after normalization according to eqn (S6). Details of the geometries are as follows: ellipsoids are axially-symmetric and prolate; bicones have smooth tips with rounding radius L/40R and smooth circular base edge with rounding radius L/100R; disks have semicircular edge profiles; rings have circular sections; bipyramids have pentagonal cross-section and smooth tips with rounding radius (1 + 2.1R)L/80; squared rods have sharp edges and smooth corners with rounding radius 0.3L; and cylinders have smooth edges with rounding radius L/40R.

	$\epsilon_1$	$V_1/V$	$a_{12}$	$a_{14}$	$V/L^3$
ellipsoid	$-0.871 - 1.35 R^{1.54}$	0.994	$5.52/(1-\epsilon_1)$	$-9.75/R^{2.53}$	$\pi/6R^2$
bicone	$-0.687 - 2.54 R^{1.5}$	$0.648 - 0.441/R^{0.687}$	$1.34/(1-\epsilon_1)$	$-1.04/(1-\epsilon_1)$	$0.262/R^{2}$
disk	$-0.479 - 1.36 R^{0.872}$	0.944	$7.05/(1-\epsilon_1)$	$-10.9/R^{0.98}$	$f_{ m disk}$
ring	$1.39 - 1.31 R^{1.73}$	$0.514 + 2.07/R^{2.67}$	$7.24/(1-\epsilon_1)$	$-19.1/(1-\epsilon_1)$	$\pi^2 (R-1)/4R^3$
bipyramid	$1.43 - 4.52 R^{1.12}$	$1.96 - 1.73/R^{0.207}$	$2.89/(1-\epsilon_1)$	$-1.79/(1-\epsilon_1)$	$0.219/R^{2}$
squared rod	$-2.28 - 1.47 R^{1.49}$	$0.904 - 0.411/R^{2.26}$	$-0.573 + 3.31/R^{0.747}$	$0.213 - 13.1/R^{1.97}$	$1/R^{2}$
cylinder	$-1.59 - 1.96 R^{1.4}$	$0.883 - 0.149/R^{3.97}$	$-1.05 + 3.02/R^{0.494}$	$0.0796 - 9.08/R^{2.08}$	$\pi/4R^2$
tetrahedron	-6.35	0.352	0.459	-0.416	$1/6\sqrt{2}$
octahedron	-3.85	0.395	0.547	-0.918	1/6
decahedron	-4.19	0.576	0.654	-1.05	$\approx 0.123$

TABLE S1: Fitting functions for the parameters considered in Fig. S2. The rightmost column gives the particle volume in units of  $L^3$ , including tip and edge rounding. In the last three entries, L corresponds to the side length of the tetrahedron, the corner-to-corner distance of the octahedron, and twice the radius of the pentagon base of the decahedron, respectively (without inclusion of edge and corner rounding). The cube is included here as a square rod with R = 1. The  $V/L^3$  fraction for the rounded disk is  $f_{\text{disk}} = \pi (4 + 3(R - 1)(2R + \pi - 2))/24R^3$ .

	$\epsilon_1$	$V_1/V$	$a_{12}$	$a_{14}$
mode 1 -	$-1.75 + 3.19/R^{6.14}$	$0.0679 + 1.83/R^{2.1}$	$0.0148 + 3.69/R^{2.86}$	$0.0142 - 16.9/R^{3.58}$
$\operatorname{mode} 2$ –	$-0.978 - 0.661/R^{1.1}$	$0.891 - 2.28/R^{2.53}$	$-21.7 + 22.7/R^{0.0232}$	$1.48 - 3.67/R^{0.458}$
$\operatorname{mode} 3$ –	-1.57 + 0.0446R	-0.0346 + 0.0111R	$-0.0117 + 0.773/R^{1.46}$	$-0.256 + 0.0554 R^{0.758}$

TABLE S2: Fitted parameters for the first three transversal modes used in Fig. S3 for nanorods. Values for mode 3 are only applicable to  $R \ge 4$ .



FIG. S3: **Transversal modes in nanowires.** Same as Fig. 5 of the main paper, but for incident light polarized along the transversal rod direction (see inset to (A)). The parameters used for the analytical model are given in Table S2.

#### IX. DESCRIPTION OF TRANSVERSAL MODES

We show in Fig. S3 the ability of our analytical approach to describe transversal plasmons in nanorods. For this polarization, several modes are piled up in a narrow spectral range, so we have to include the three lowest-order modes in order to achieve the good agreement shown in the figure between analytical theory and BEM numerical simulations.

## X. EXTINCTION VS ABSORPTION

We compare in Fig. S4 extinction and absorption spectra for gold nanorods with different sizes and aspect ratios. The analytical model agrees well with BEM numerical simulations for both the wavelength positions of extinction and absorption maxima (Fig. S4(A)) and the spectral shape (Fig. S4(B)).

#### XI. OVERVIEW COMPARISON OF EXPERIMENTAL PLASMON WIDTHS

The spectral widths of experimentally observed plasmon bands are usually broadened by several undesired effects related to sample preparation and particle quality. For example, a finite distribution in particle size and shape in colloidal suspensions implies that the measured spectra are averaged over a large number of particles in the sample, which present variations in details such as aspect ratio, edge and corner rounding, metal volume, and other aspects of their morphology. Also, the quality of the metal (*e.g.*, the presence of defects and grain



FIG. S4: **Extinction vs absorption.** We plot the wavelengths for peak extinction (red curves) and absorption (blue curves) as a function of aspect ratio R for gold nanorods of two different side lengths, L = 30 and L = 190 nm (A). As a specific example, we show the extinction and absorption spectra of a gold nanorod with L = 210 nm and R = 2 (B). In all cases, analytical results (solid curves) agree well with numerical simulations (broken curves).



FIG. S5: Analytical model versus experiment: plasmon quality factor. We plot the quality factor of the lowestorder dipolar plasmons in different types of gold particles as a function of size length L (A) and aspect ratio R (B), taken from different experimental sources (symbols for rods,<sup>4–6</sup> bipyramids,<sup>7</sup> disks,<sup>8</sup> and triangles<sup>9</sup>) and compared with the predictions from the analytical model (solid curves). (Reference numbers correspond to the list in this ESI document.)

boundaries) is an important factor that affects the response in lithographically carved particles. These effects are not captured by the idealized model of the particles used in theoretical calculations. Therefore, the simulated plasmon widths are typically smaller than those observed experimentally. In this respect, electromagnetic simulations can be understood to provide an ideal lower bound for spectral broadening, which is only reached when identical, defect-free particles are considered.

We present in Fig. S5 the plasmon quality factor Q obtained from available experimental spectra for gold nanoparticles<sup>4–9</sup> (symbols), compared with our analytical model (solid curves). The figure is complementary to Fig. 11 of the main paper, where we show a comparison of plasmon wavelengths for the same particles. As anticipated, the measured Q's are lower than the corresponding calculated values, although the decreasing trends with increasing R are similar in both of them. In some cases, such as disks and bipyramids of large length and aspect ratio, the agreement between experiment and theory is rather good, indicating that the measured samples have a comparatively small dispersion in size and shape.

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