Localized surface plasmon resonances of simple tunable plasmonic nanostructures

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SI Mathematical Preliminary

In order to find the constant coefficient term described in Section 2 of the manuscript, we made frequent use of the orthogonality property of the Legendre function of the first kind. This is given in Refs.[4,6] as:

$$\frac{1}{\sigma_l}\int_{-1}^{1} P_l(u)P_n(u)du = \delta_{ln}. \tag{S.1}$$

Eq. (S.1), with $\sigma_l \equiv 1/(l+\frac{1}{2})$, enables us to integrate the set of linear equations which were obtained after applying the respective boundary conditions on the solution of the Laplace equation for the different nanostructures. This set of linear equations is then solved to obtain the constant coefficient term of interest in terms of the amplitude of the external potential.

Due to azimuthal symmetry, we have ignored the ϕ dependence of the electrostatic potentials inside and outside the nanostructures, in the respective coordinate systems involved.

SII Fundamental Nanostructures

SII.1 Solid Sphere

The solution of the Laplace equation $\triangle\Phi(r,\theta) = 0$ in spherical coordinates, for the potentials in the medium outside the sphere, and inside the sphere are respectively, governed by:[3–5]

$$\Phi_o(r,\theta) = \sum_{n=1}^{\infty}[B_n r^n + C_n r^{-(n+1)}]P_n(\cos\theta), \tag{S.2}$$

$$\Phi_i(r,\theta) = \sum_{n=1}^{\infty} A_n r^n P_n(\cos\theta), \tag{S.3}$$

where the subscripts o and i denote outside and inside respectively. At the sphere boundary, both the potential and the normal component of the displacement field must be continuous, leading to the following boundary conditions:

$$\Phi_o(a,\theta) = \Phi_i(a,\theta), \tag{S.4}$$

$$\varepsilon_m \frac{\partial\Phi_o(r,\theta)}{\partial r}\Big|_{r=a} = \varepsilon(\omega)\frac{\partial\Phi_i(r,\theta)}{\partial r}\Big|_{r=a}. \tag{S.5}$$

Setting $u \equiv \cos\theta$, combining Eqs. (S.2) and (S.3) and Eqs. (S.4) and (S.5), multiplying both sides of the set of equations obtained by $P_l(u)$. integrating the set of equations obtained via Eq. (S.1), and solving for C_l in terms of B_l, we obtain:

$$C_l = -\alpha_l(\omega)B_l, \tag{S.6}$$

where

$$\alpha_l(\omega) = \frac{l[\varepsilon(\omega) - \varepsilon_m]a^{2l+1}}{l\varepsilon(\omega) + (l+1)\varepsilon_m} \tag{S.7}$$

is the multipole polarizability of the solid sphere.
Applying the Fröhlich condition to Eq. (S.7), and solving for $\Re[\varepsilon(\omega_r)]$ leads to:

$$\Re[\varepsilon(\omega_r)] = -\Big(\frac{l+1}{l}\Big)\varepsilon_m. \tag{S.8}$$

Substituing Eq. (S.8) into Eq. (2) of the manuscript, we obtain the well-known multipole LSPR of a solid sphere as:

$$\omega_l^s(\varepsilon_m,\varepsilon_\infty) = \omega_p\sqrt{\frac{l}{l\varepsilon_\infty + (l+1)\varepsilon_m}}. \tag{S.9}$$

SII.2 Cavity Sphere

To obtain the LSPR of the cavity sphere, we will use Dielectric Reversal (**DR**). This technique is not entirely new. It had been mentioned in Ref.[1] To do this, we will start from Eq. (S.8). By reversing the position of the dielectric constants, and replacing ε_m with ε_c, we obtain:

$$\varepsilon_c = -\Big(\frac{l+1}{l}\Big)\Re[\varepsilon(\omega_r)]. \tag{S.10}$$

Substituing Eq. (S.10) into Eq. (2) of the manuscript, we obtain the well-known multipole LSPR of a cavity sphere as:

$$\omega_l^c(\varepsilon_c, \varepsilon_\infty) = \omega_p\sqrt{\frac{l+1}{l\varepsilon_c + (l+1)\varepsilon_\infty}}. \tag{S.11}$$

SII.3 Solid Spheroid

The solution of the Laplace equation $\triangle\Phi(v, w) = 0$ in prolate spheroidal coordinates, for the potentials in the medium outside the spheroid, and inside the spheroid are respectively, governed by:[6,8,9] [1]

$$\Phi_o(v, w) = \sum_{n=1}^{\infty}[B_n P_n(v)P_n(w) + C_n Q_n(v)P_n(w)], \tag{S.12}$$

$$\Phi_i(v, w) = \sum_{n=1}^{\infty} A_n P_n(v)P_n(w). \tag{S.13}$$

At the spheroid surface s, both the potential and the normal component of the displacement field must be continuous, leading to the following boundary conditions:

$$\Phi_o(v_s, w) = \Phi_i(v_s, w), \tag{S.14}$$

$$\varepsilon_m \frac{\partial\Phi_o(v, w)}{\partial v}\Big|_{v=v_s} = \varepsilon(\omega)\frac{\partial\Phi_i(v, w)}{\partial v}\Big|_{v=v_s}. \tag{S.15}$$

Combining Eqs. (S.12) and (S.13) and Eqs. (S.14) and (S.15), multiplying both sides of the set of equations obtained by $P_l(w)$, integrating the set of equations obtained via Eq. (S.1), and solving for C_l in terms of B_l, we obtain:

$$C_l = -\alpha_l^{\|}(\omega)B_l, \tag{S.16}$$

where

$$\alpha_l^{\|}(\omega) = \frac{\varepsilon(\omega) - \varepsilon_m}{\varepsilon(\omega)\frac{Q_l(v_s)}{P_l(v_s)} - \varepsilon_m\frac{Q_l'(v_s)}{P_l'(v_s)}} \tag{S.17}$$

is the longitudinal multipole polarizability of the prolate spheroid.
Applying the Fröhlich condition on Eq. (S.17) leads to:

$$\Re[\varepsilon(\omega_r)] = \varepsilon_m\frac{P_l(v_s)Q_l'(v_s)}{P_l'(v_s)Q_l(v_s)}. \tag{S.18}$$

Substituing Eq. (S.18) into Eq. (2) of the manuscript, we obtain the longitudinal multipole LSPR of a solid prolate spheroid as:

$$\omega_l^{s\|}(\varepsilon_\infty, \varepsilon_m, v_s) = \omega_p\sqrt{\frac{P_l'(v_s)Q_l(v_s)}{\varepsilon_\infty P_l'(v_s)Q_l(v_s) - \varepsilon_m P_l(v_s)Q_l'(v_s)}}, \tag{S.19}$$

[1] Caution: For convenience, we will like to keep using $A_n, B_n, C_n, ...$ to denote the constant coefficients in the series expansion of the potentials for the different nanostructures, but their actual values will continue to differ as we go from one nanostructure to another.

where $v_s = 1/e_s,\ e_s = \sqrt{1-q_s^{-2}},\ 0 < e_s < 1$, and $q_s = b_s/a_s,\ b_s > a_s,\ q_s > 1$. e_s is the eccentricity of a prolate spheroid, and q_s is its aspect ratio.
In the dipole limit: $l = 1$, let us evaluate these Legendre functions and their derivatives $\forall\ v$, since we shall continue to make use of the results. Thus:

$$P_1(v) = v \implies P_1'(v) = 1, \tag{S.20}$$

$$Q_1(v) = \frac{v}{2}\ln\left(\frac{v+1}{v-1}\right) - 1 = (v\coth^{-1}v) - 1 \implies Q_1'(v) = -\frac{1}{v(v^2-1)}[1 - Q_1(v)(v^2-1)]. \tag{S.21}$$

Then we can define the longitudinal geometric factor of a prolate spheroid as:

$$L^{\parallel} = Q_1(v)(v^2-1), \tag{S.22}$$

enabling us to re-write $Q_1(v)$ and $Q_1'(v)$ as:

$$Q_1(v) = \frac{L^{\parallel}}{(v^2-1)},\quad Q_1'(v) = -\frac{1}{v}\left(\frac{1-L^{\parallel}}{v^2-1}\right). \tag{S.23}$$

Substituting Eqs. (S.23) and (S.20) into Eq. (S.19) for $v = v_s$ leads to the longitudinal dipolar LSPR of a solid prolate spheroid:

$$\omega_1^{s\parallel}(\varepsilon_\infty, \varepsilon_m, L_s^{\parallel}) = \omega_p\sqrt{\frac{L_s^{\parallel}}{\varepsilon_\infty L_s^{\parallel} + \varepsilon_m(1-L_s^{\parallel})}}. \tag{S.24}$$

To obtain the transverse geometric factor of a prolate spheroid, we employ the sum rule[5] :

$$L^{\parallel} + 2L^{\perp} = 1 \ \Rightarrow\ L^{\perp} = \frac{1}{2}\Big(1 - L^{\parallel}\Big). \tag{S.25}$$

There are two short axes of equal length a in a prolate spheroid and one long axis of length b. The transverse geometric factor $L^{\perp}$ is degenerate in either of the two short axes. Eq. (S.25) allows us to obtain the transverse dipolar LSPR of a solid prolate spheroid by replacing $L^{\parallel}$ with $L^{\perp}$ in Eq. (S.24).

To obtain the longitudinal dipolar LSPR of a solid oblate spheroid, we need to obtain the longitudinal geometric factor of the spheroid. Following the approach in Refs.,[8,9] the radial coordinate v is complex in oblate spheroidal coordinates. Thus, to transform from prolate to oblate, we replace v with iv in Eqs. (S.19)-(S.21) and (S.23), we use $v_s = \sqrt{e_s^{-2}-1},\ 0 < e_s < 1$,[8] where e_s is the eccentricity of the oblate spheroid, and $q_s = b_s/a_s,\ b_s < a_s,\ 0 < q_s < 1$,[7] is the aspect ratio of the oblate spheroid. With these transformations, we obtain the longitudinal multipole LSPR of the solid oblate spheroid as:

$$\omega_l^{s\parallel}(\varepsilon_\infty, \varepsilon_m, iv_s) = \omega_p\sqrt{\frac{P_l'(iv_s)Q_l(iv_s)}{\varepsilon_\infty P_l'(iv_s)Q_l(iv_s) - \varepsilon_m P_l(iv_s)Q_l'(iv_s)}}, \tag{S.26}$$

and Eqs. (S.20), (S.21) and (S.23) become:

$$P_1(iv) = iv \implies P_1'(iv) = 1, \tag{S.27}$$

$$Q_1(iv) = \frac{iv}{2}\ln\left(\frac{iv+1}{iv-1}\right) - 1 = (v\cot^{-1}v) - 1 \implies Q_1'(iv) = \frac{1}{iv(v^2+1)}[1 + Q_1(iv)(v^2+1)], \tag{S.28}$$

and

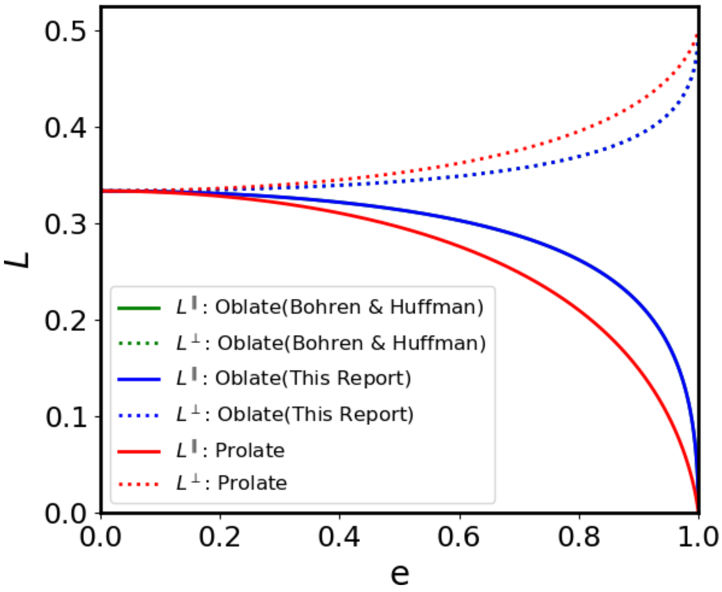
$$Q_1(iv) = -\left(\frac{L^{\parallel}}{v^2+1}\right),\quad Q_1'(iv) = \frac{1}{iv}\left(\frac{1-L^{\parallel}}{v^2+1}\right) \tag{S.29}$$

respectively. From Eq. (S.28), we define the longitudinal geometric factor of the oblate spheroid as [2]:

$$L^{\parallel} \equiv \frac{1}{2}\Big[1 + Q_1(iv)(v^2+1)\Big]. \tag{S.30}$$

[2] The expression we derived here looks quite different from the one given in Ref.[5] However, Fig. (SII.3) shows that Eq. (S.30) completely agree with Ref.,[5] where $v = 1/e$, while we have used $v = \sqrt{e^{-2}-1}$, following the approach in Ref.[8] A factor of $\frac{1}{2}$ introduced in Eq. (S.30) ensures that the equation agrees with the geometric factor in Ref.[5] Also note that directly transforming Eq. (S.22) leads to a result that does not agree with Ref.[5]

Substituting Eqs. (S.27) and (S.29) into Eq. (S.26) for $v = v_s$ we obtain the dipolar LSPR of



S 1: The geometric factors of the spheroids plotted against the eccentricity e. The geometric factors of a prolate spheroid vary from that of a sphere ($e = 0$) to a needle ($e = 1$), while those of an oblate spheroid vary from that of a sphere ($e = 0$) to a disk ($e = 1$). The blue curves are from Eqs. (S.30) and (S.25) of this report, with $v = \sqrt{e^{-2} - 1}$. The green curves are from the expression given in Bohren and Huffman,[5] with $v = 1/e$. The blue and green curves completely agree as shown. Note that the geometric factors for the prolate spheroid as derived here(the red curves) are the same as that of Ref.[5]

a solid oblate spheroid, which is similar to Eq. (S.24) but with Eq. (S.22) replaced with Eq. (S.30).

The transverse LSPR of the solid oblate spheroid is obtained by making use of Eq. (S.25), as was discussed for the prolate spheroid.

Geometric Reduction (**GR**). In the dipole limit, we can reduce the LSPR of a solid spheroid to that of a solid sphere by substituting the geometric factor of an isotropic sphere into Eq. (S.24). An isotropic sphere has three symmetry axes of equal lengths. The geometric factor of the sphere is degenerate in either of the three axes, and it is polarization-independent.[5] Hence, Eq. (S.25) reduces to:

$$3L = 1 \implies L = \frac{1}{3}. \tag{S.31}$$

Observe that substituting Eq. (S.31) into Eq. (S.24) leads to the dipole limit of Eq. (S.9).

SII.4 Cavity Spheroid

DR. By reversing the position of the dielectric constants in Eq. (S.18) and replacing ε_m with ε_c, and v_s with v_c, we obtain:

$$\varepsilon_c = \Re[\varepsilon(\omega_r)] \frac{P_l(v_c)Q_l'(v_c)}{P_l'(v_c)Q_l(v_c)} \tag{S.32}$$

Substituting Eq. (S.32) into Eq. (2) of the manuscript, we obtain the longitudinal multiple LSPR of a cavity prolate spheroid:

$$\omega_l^{c\parallel}(\varepsilon_\infty, \varepsilon_c, v_c) = \omega_p \sqrt{\frac{P_l(v_c)Q_l'(v_c)}{\varepsilon_\infty P_l(v_c)Q_l'(v_c) - \varepsilon_c P_l'(v_c)Q_l(v_c)}}. \tag{S.33}$$

In the dipole limit: $l = 1$, we substitute Eqs. (S.23) and (S.20) into Eq. (S.33) for $v = v_c$ to obtain the longitudinal dipole LSPR of a cavity prolate spheroid:

$$\omega_1^{c\|}(\varepsilon_c, \varepsilon_\infty, L_c^{\|}) = \omega_p \sqrt{\frac{1 - L_c^{\|}}{\varepsilon_\infty(1 - L_c^{\|}) + \varepsilon_c L_c^{\|}}}. \tag{S.34}$$

The longitudinal dipolar LSPR of a cavity oblate spheroid is obtained by replacing the geometric factor in Eq. (S.34) with Eq. (S.30).

The transverse dipolar LSPR of the cavity prolate and oblate spheroids can be obtained by making use of Eq. (S.25).

GR of the dipolar LSPR of a cavity spheroid to that of a cavity sphere is done by substituting Eq. (S.31) into Eq. (S.34) to obtain the dipole limit of Eq. (S.11).

SIII Core-Shell Nanostructures

SIII.1 Core-Shell Sphere

The solution of the Laplace equation $\triangle\Phi(r, \theta) = 0$ in spherical coordinates, for the potentials in the core region, the shell region, and in the medium outside the nanoshell can be represented respectively as:[2,12]

$$\Phi_c(r, \theta) = \sum_{n=1}^{\infty} A_n r^n P_n(u), \tag{S.35}$$

$$\Phi_s(r, \theta) = \sum_{n=1}^{\infty} [B_n r^n + C_n r^{-(n+1)}] P_n(u), \tag{S.36}$$

$$\Phi_m(r, \theta) = \sum_{n=1}^{\infty} [D_n r^n + E_n r^{-(n+1)}] P_n(u), \tag{S.37}$$

with $u \equiv \cos\theta$. At the boundaries, both the potential and the normal component of the displacement field must be continuous, leading to the following boundary conditions:

$$\Phi_c(a, \theta) = \Phi_s(a, \theta), \tag{S.38}$$

$$\Phi_s(b, \theta) = \Phi_m(b, \theta), \tag{S.39}$$

$$\varepsilon_c \frac{\partial \Phi_c(r, \theta)}{\partial r}\Big|_{r=a} = \varepsilon_s(\omega) \frac{\partial \Phi_s(r, \theta)}{\partial r}\Big|_{r=a}, \tag{S.40}$$

$$\varepsilon_s(\omega) \frac{\partial \Phi_s(r, \theta)}{\partial r}\Big|_{r=b} = \varepsilon_m \frac{\partial \Phi_m(r, \theta)}{\partial r}\Big|_{r=b}, \tag{S.41}$$

where the subscripts c, s and m denote core, shell, and medium respectively.

Combining Eqs. (S.35)-(S.37) and (S.38)-(S.41), multiplying both sides of the set of equations obtained by $P_l(u)$, integrating them via Eq. (S.1), and solving for E_l in terms of D_l to obtain:

$$E_l = -\alpha_l(\omega) D_l, \tag{S.42}$$

where

$$\alpha_l(\omega) = \frac{l[\varepsilon_s(\omega) x_l - \varepsilon_m y_l] b^{2l+1}}{\varepsilon_s(\omega) l x_l + \varepsilon_m (l+1) y_l} \tag{S.43}$$

is the multipole polarizability of the nanoshell, with

$$x_l = 1 - \frac{(l+1)[\varepsilon_s(\omega) - \varepsilon_c]}{l\varepsilon_c + (l+1)\varepsilon_s(\omega)} q^{2l+1} \tag{S.44}$$

and

$$y_l = 1 + \frac{l[\varepsilon_s(\omega) - \varepsilon_c]}{l\varepsilon_c + (l+1)\varepsilon_s(\omega)} q^{2l+1}, \tag{S.45}$$

where $q = a/b$ is the aspect ratio of the nanoshell.

Applying the Fröhlich condition on Eq. (S.43) leads to:

$$\Re[\varepsilon_s(\omega_r)]l\left[1-\frac{(l+1)\Big[\Re[\varepsilon_s(\omega_r)]-\varepsilon_c\Big]}{l\varepsilon_c+(l+1)\Re[\varepsilon_s(\omega_r)]}q^{2l+1}\right]=-\varepsilon_m(l+1)\left[1+\frac{l\Big[\Re[\varepsilon_s(\omega_r)]-\varepsilon_c\Big]}{l\varepsilon_c+(l+1)\Re[\varepsilon_s(\omega_r)]}q^{2l+1}\right]. \tag{S.46}$$

Solving for $\Re[\varepsilon_s(\omega_r)]$ leads to:

$$\Re[\varepsilon_s(\omega_r)]=\frac{-\left[\varepsilon_c l\left(l+(l+1)q^{2l+1}\right)+\varepsilon_m(l+1)\left((l+1)+lq^{2l+1}\right)\right]\pm\sqrt{\left[\varepsilon_c l\left(l+(l+1)q^{2l+1}\right)+\varepsilon_m(l+1)\left((l+1)+lq^{2l+1}\right)\right]^2-4\varepsilon_c\varepsilon_m\left[l(l+1)\left(1-q^{2l+1}\right)\right]^2}}{2l(l+1)\left(1-q^{2l+1}\right)}. \tag{S.47}$$

Substituting Eq. (S.47) for $\Re[\varepsilon(\omega_r)]$ in Eq.(2) of the manuscript, we obtain the multipolar LSPR of the nanoshell as:

$$\omega_{l\pm}=\frac{\omega_p}{\sqrt{2}}\sqrt{\frac{\begin{vmatrix} l(l+1) & -[l^2\varepsilon_c+(l+1)^2\varepsilon_m] \\ 1 & [2\varepsilon_\infty+q^{2l+1}(\varepsilon_m+\varepsilon_c-2\varepsilon_\infty)]\end{vmatrix}\pm\sqrt{\begin{vmatrix}(l+1)^2 & \varepsilon_c \\ l^2 & \varepsilon_m\end{vmatrix}^2+l(l+1)q^{2l+1}\begin{vmatrix}[l(l+1)q^{2l+1}(\varepsilon_c-\varepsilon_m)^2] & -2 \\ [l\varepsilon_c+(l+1)\varepsilon_m]^2+\varepsilon_c\varepsilon_m(2l+1)^2 & 1\end{vmatrix}}}{\begin{vmatrix}[(l+1)\varepsilon_m+l\varepsilon_\infty] & -l(l+1)q^{2l+1} \\ [\varepsilon_\infty(\varepsilon_m+\varepsilon_c-\varepsilon_\infty)-\varepsilon_m\varepsilon_c] & [l\varepsilon_c+(l+1)\varepsilon_\infty]\end{vmatrix}}}. \tag{S.48}$$

Symmetrization (**S**) of Eq. (S.48) is done by setting $q = 0$ in the symmetric part (ω_{l-}), to obtain the multipolar LSPR of a solid sphere i.e Eq. (S.9) as follows:

$$\omega_{l-}(q=0)=\frac{\omega_p}{\sqrt{2}}\sqrt{\frac{\begin{vmatrix} l(l+1) & -[l^2\varepsilon_c+(l+1)^2\varepsilon_m] \\ 1 & 2\varepsilon_\infty\end{vmatrix}-\begin{vmatrix}(l+1)^2 & \varepsilon_c \\ l^2 & \varepsilon_m\end{vmatrix}}{\begin{vmatrix}[(l+1)\varepsilon_m+l\varepsilon_\infty] & 0 \\ [\varepsilon_\infty(\varepsilon_m+\varepsilon_c-\varepsilon_\infty)-\varepsilon_m\varepsilon_c] & [l\varepsilon_c+(l+1)\varepsilon_\infty]\end{vmatrix}}}=\omega_p\sqrt{\frac{l}{l\varepsilon_\infty+(l+1)\varepsilon_m}}. \tag{S.49}$$

Anti-Symmetrization (**AS**) of Eq. (S.48) is done by setting $q = 0$ in the antisymmetric part (ω_{l+}), to obtain the multipolar LSPR of a cavity sphere i.e Eq. (S.11) as follows:

$$\omega_{l+}(q=0)=\frac{\omega_p}{\sqrt{2}}\sqrt{\frac{\begin{vmatrix} l(l+1) & -[l^2\varepsilon_c+(l+1)^2\varepsilon_m] \\ 1 & 2\varepsilon_\infty\end{vmatrix}+\begin{vmatrix}(l+1)^2 & \varepsilon_c \\ l^2 & \varepsilon_m\end{vmatrix}}{\begin{vmatrix}[(l+1)\varepsilon_m+l\varepsilon_\infty] & 0 \\ [\varepsilon_\infty(\varepsilon_m+\varepsilon_c-\varepsilon_\infty)-\varepsilon_m\varepsilon_c] & [l\varepsilon_c+(l+1)\varepsilon_\infty]\end{vmatrix}}}=\omega_p\sqrt{\frac{l+1}{l\varepsilon_c+(l+1)\varepsilon_\infty}}. \tag{S.50}$$

In the dipole limit ($l = 1$), Eq. (S.48) reduces to (after some re-arrangement):

$$\omega_{1\pm}=\frac{\omega_p}{\sqrt{2}}\sqrt{\frac{\begin{vmatrix} 3 & -(1+2f_c) \\ (\varepsilon_m+\varepsilon_c-2\varepsilon_\infty) & (\varepsilon_m+2\varepsilon_\infty)\end{vmatrix}\pm\sqrt{\begin{vmatrix}4 & \varepsilon_c \\ 1 & \varepsilon_m\end{vmatrix}^2+4f_c\begin{vmatrix}(1+f_c) & -3\varepsilon_m \\ (\varepsilon_m+5\varepsilon_c) & (\varepsilon_c-\varepsilon_m)^2\end{vmatrix}}}{\begin{vmatrix}(2\varepsilon_m+\varepsilon_\infty) & -2f_c \\ \varepsilon_\infty(\varepsilon_m+\varepsilon_c-\varepsilon_\infty)-\varepsilon_m\varepsilon_c & (\varepsilon_c+2\varepsilon_\infty)\end{vmatrix}}}, \tag{S.51}$$

where $f_c = (a/b)^3$ is the core-volume fraction of the nanoshell.

Note that **S** $[\omega_{1-}(f_c = 0)]$ and **AS** $[\omega_{1+}(f_c = 0)]$ of Eq. (S.51) leads to the dipole limit of Eq. (S.9) and Eq. (S.11) respectively.

SIII.2 Core-Shell Spheroid

The solution of the Laplace equation $\triangle\Phi(v, w) = 0$ in prolate spheroidal coordinates, for the potentials in the core region, the shell region, and in the medium outside a nanorice(a core-shell prolate spheroid) can be represented respectively as:[6,8,10]

$$\Phi_c(v,w) = \sum_{n=1}^{\infty} A_n P_n(v) P_n(w), \tag{S.52}$$

$$\Phi_s(v,w) = \sum_{n=1}^{\infty} [B_n P_n(v) P_n(w) + C_n Q_n(v) P_n(w)], \tag{S.53}$$

$$\Phi_m(v,w) = \sum_{n=1}^{\infty} [D_n P_n(v) P_n(w) + E_n Q_n(v) P_n(w)]. \tag{S.54}$$

At the boundaries, both the potential and the normal component of the displacement field must be continuous, leading to the following boundary conditions:

$$\Phi_c(v_c, w) = \Phi_s(v_c, w), \tag{S.55}$$

$$\Phi_s(v_s, w) = \Phi_m(v_s, w), \tag{S.56}$$

$$\varepsilon_c \frac{\partial \Phi_c(v,w)}{\partial v}\Big|_{v=v_c} = \varepsilon_s(\omega) \frac{\partial \Phi_s(v,w)}{\partial v}\Big|_{v=v_c}, \tag{S.57}$$

$$\varepsilon_s(\omega) \frac{\partial \Phi_s(v,w)}{\partial v}\Big|_{v=v_s} = \varepsilon_m \frac{\partial \Phi_m(v,w)}{\partial v}\Big|_{v=v_s}. \tag{S.58}$$

Combining Eqs. (S.52)-(S.54 and (S.55)-(S.58), multiplying both sides of the set of equations obtained by $P_l(w)$, integrating them via Eq. (S.1), and solving for E_l in terms of D_l to obtain:

$$E_l = -\alpha_l^{\parallel}(\omega) D_l, \tag{S.59}$$

where

$$\alpha_l^{\parallel}(\omega) = \frac{\varepsilon_s(\omega) y_l P_l(v_s) - \varepsilon_m x_l P_l'(v_s)}{\varepsilon_s(\omega) y_l Q_l(v_s) - \varepsilon_m x_l Q_l'(v_s)} \tag{S.60}$$

is the longitudinal multipole polarizability of the nanorice, with

$$x_l = P_l(v_s) + \left[\frac{Q_l(v_s)[\varepsilon_s(\omega) - \varepsilon_c]}{\varepsilon_c \frac{Q_l(v_c)}{P_l(v_c)} - \varepsilon_s(\omega) \frac{Q_l'(v_c)}{P_l'(v_c)}} \right] \tag{S.61}$$

and

$$y_l = P_l'(v_s) + \left[\frac{Q_l'(v_s)[\varepsilon_s(\omega) - \varepsilon_c]}{\varepsilon_c \frac{Q_l(v_c)}{P_l(v_c)} - \varepsilon_s(\omega) \frac{Q_l'(v_c)}{P_l'(v_c)}} \right]. \tag{S.62}$$

Applying the Fröhlich condition on Eq. (S.60) leads to:

$$(\Re[\varepsilon_s(\omega_r)])^2 (\Omega - \Delta) + \Re[\varepsilon_s(\omega_r)](\beta + \zeta - \Omega_1 - \Omega_3) + (\Omega_2 - \Lambda) = 0, \tag{S.63}$$

and solving for $\Re[\varepsilon_s(\omega_r)]$ leads to:

$$\Re[\varepsilon_s(\omega_r)] = \frac{-(\beta + \zeta - \Omega_1 - \Omega_3) \pm \sqrt{(\beta + \zeta - \Omega_1 - \Omega_3)^2 - 4(\Omega - \Delta)(\Omega_2 - \Lambda)}}{2(\Omega - \Delta)}. \tag{S.64}$$

Substituting Eq. (S.64) for $\Re[\varepsilon(\omega_r)]$ in Eq. (2) of the manuscript, we obtain the longitudinal multipolar LSPR of the nanorice:

$$\omega_{l\pm}^{\parallel} = \frac{\omega_p}{\sqrt{2}} \sqrt{\frac{\begin{vmatrix} 2\varepsilon_\infty & -1 \\ [\beta + \zeta - \Omega_1 - \Omega_3] & (\Omega - \Delta) \end{vmatrix} \pm \sqrt{\begin{vmatrix} \beta & 1 \\ \zeta & 1 \end{vmatrix}^2 + \begin{vmatrix} (\Omega_1 + \Omega_2) & -4 \\ [\Lambda\Omega - \Omega_2(\Omega - \Delta)] & [\Omega_1 + \Omega_2 - 2(\beta + \zeta)] \end{vmatrix}}}{\begin{vmatrix} [\varepsilon_\infty^2(\Omega - \Delta) + (\Omega_2 - \Lambda)] & -\varepsilon_\infty \\ [\beta + \zeta - \Omega_1 - \Omega_3] & 1 \end{vmatrix}}}, \tag{S.65}$$

where

$$\Lambda \equiv \varepsilon_m \varepsilon_c \frac{Q_l'(v_s) Q_l(v_c) P_l(v_s)}{P_l(v_c)}, \; \beta \equiv \varepsilon_m \frac{Q_l'(v_s) Q_l'(v_c) P_l(v_s)}{P_l'(v_c)}, \; \zeta \equiv \varepsilon_c \frac{Q_l(v_s) Q_l(v_c) P_l'(v_s)}{P_l(v_c)}, \quad \text{(S.66)}$$

$$\Delta \equiv \frac{Q_l(v_s) Q_l'(v_c) P_l'(v_s)}{P_l'(v_c)}, \; \Omega \equiv Q_l(v_s) Q_l'(v_s), \; \Omega_1 \equiv \varepsilon_m \Omega, \; \Omega_2 \equiv \varepsilon_c \Omega_1, \; \Omega_3 \equiv \varepsilon_c \Omega. \quad \text{(S.67)}$$

The longitudinal multipole LSPR of a core-shell oblate spheroid can be obtained by making the transformations: $v_s \to i v_s$ and $v_c \to i v_c$, in Eqs. (S.66) and (S.67) respectively, and taking note of the fact that the radial coordinate v is defined differently in an oblate spheroid.[8–10]

S of Eq. (S.65) is done by setting $\Omega = 0$ in the symmetric part ($\omega_{l-}^{\parallel}$), to obtain the longitudinal multipolar LSPR of a solid prolate spheroid as follows (with Eqs. (S.66) and (S.67):

$$\omega_l^{s\parallel} = \omega_{l-}^{\parallel}(\Omega = 0) = \frac{\omega_p}{\sqrt{2}} \sqrt{\frac{\begin{vmatrix} 2\varepsilon_\infty & -1 \\ (\beta+\zeta) & -\Delta \end{vmatrix} - \begin{vmatrix} \beta & 1 \\ \zeta & 1 \end{vmatrix}}{\begin{vmatrix} -\varepsilon_\infty^2 \Delta - \Lambda & -\varepsilon_\infty \\ \beta + \zeta & 1 \end{vmatrix}}} = \omega_p \sqrt{\frac{P_l'(v_s) Q_l(v_s)}{\varepsilon_\infty P_l'(v_s) Q_l(v_s) - \varepsilon_m P_l(v_s) Q_l'(v_s)}}. \quad \text{(S.68)}$$

AS of Eq. (S.65) is done setting $\Omega = 0$ in the antisymmetric part ($\omega_{l+}^{\parallel}$), to obtain the longitudinal multipolar LSPR of a cavity prolate spheroid as follows (with Eqs.(S.66) and (S.67):

$$\omega_l^{c\parallel} = \omega_{l+}^{\parallel}(\Omega = 0) = \frac{\omega_p}{\sqrt{2}} \sqrt{\frac{\begin{vmatrix} 2\varepsilon_\infty & -1 \\ (\beta+\zeta) & -\Delta \end{vmatrix} + \begin{vmatrix} \beta & 1 \\ \zeta & 1 \end{vmatrix}}{\begin{vmatrix} -\varepsilon_\infty^2 \Delta - \Lambda & -\varepsilon_\infty \\ \beta + \zeta & 1 \end{vmatrix}}} = \omega_p \sqrt{\frac{P_l(v_c) Q_l'(v_c)}{\varepsilon_\infty P_l(v_c) Q_l'(v_c) - \varepsilon_c P_l'(v_c) Q_l(v_c)}} \quad \text{(S.69)}$$

In the dipole limit ($l = 1$) with Eqs.(S.66) and (S.67), the terms in Eq. (S.65) simplify as follows:

$$\beta - \zeta = \frac{1}{v_c(v_c^2-1)(v_s^2-1)} [\varepsilon_m (1 - L_c^{\parallel})(1 - L_s^{\parallel}) - \varepsilon_c L_c^{\parallel} L_s^{\parallel}], \quad \text{(S.70)}$$

$$2\varepsilon_\infty(\Omega - \Delta) + (\beta + \zeta - \Omega_1 - \Omega_3) =$$

$$\frac{1}{v_c(v_c^2-1)(v_s^2-1)} \left[2L_s^{\parallel}\varepsilon_\infty + \varepsilon_m(1 - L_c^{\parallel} - L_s^{\parallel}) + L_s^{\parallel}[L_c^{\parallel} + f_c(1 - L_s^{\parallel})](\varepsilon_m + \varepsilon_c - 2\varepsilon_\infty) \right], \quad \text{(S.71)}$$

$$\varepsilon_\infty[\varepsilon_\infty(\Omega - \Delta) + (\beta + \zeta - \Omega_1 - \Omega_3)] + (\Omega_2 - \Lambda) =$$

$$\frac{1}{v_c(v_c^2-1)(v_s^2-1)} \left[[\varepsilon_m(1 - L_s^{\parallel}) + \varepsilon_\infty L_s^{\parallel}][\varepsilon_\infty(1 - L_c^{\parallel}) + \varepsilon_c L_c^{\parallel}] + f_c L_s^{\parallel}(1 - L_s^{\parallel})[\varepsilon_\infty(\varepsilon_m + \varepsilon_c - \varepsilon_\infty) - \varepsilon_m \varepsilon_c] \right], \quad \text{(S.72)}$$

$$(\Omega_1 + \Omega_3)[\Omega_1 + \Omega_3 - 2(\beta + \zeta)] + 4[\Lambda\Omega - \Omega_2(\Omega - \Delta)] =$$

$$\frac{1}{v_c v_s(v_c^2-1)(v_s^2-1)^3} L_s^{\parallel}(1 - L_s^{\parallel}) \left[L_s^{\parallel}[2L_c^{\parallel} + f_c(1 - L_s^{\parallel})](\varepsilon_c - \varepsilon_m)^2 + 2\varepsilon_m[\varepsilon_m + \varepsilon_c + (L_c^{\parallel} + L_s^{\parallel})(\varepsilon_c - \varepsilon_m)] \right]. \quad \text{(S.73)}$$

Substituting Eqs. (S.70) and (S.73) into Eq. (S.65), we obtain the longitudinal dipolar LSPR of the core-shell spheroid:

$$\omega_{1\pm}^{\parallel} = \frac{\omega_p}{\sqrt{2}} \sqrt{\frac{\begin{vmatrix} 2L_s^{\parallel}\varepsilon_\infty + \varepsilon_m(1 - L_c^{\parallel} - L_s^{\parallel}) & -L_s^{\parallel}[L_c^{\parallel} + f_c(1 - L_s^{\parallel})] \\ (\varepsilon_m + \varepsilon_c - 2\varepsilon_\infty) & 1 \end{vmatrix} \pm \sqrt{\begin{vmatrix} \varepsilon_m(1 - L_c^{\parallel}) & \varepsilon_c L_c^{\parallel} \\ L_s^{\parallel} & 1 - L_s^{\parallel} \end{vmatrix}^2 + f_c L_s^{\parallel}(1 - L_s^{\parallel}) \begin{vmatrix} L_s^{\parallel}[2L_c^{\parallel} + f_c(1 - L_s^{\parallel})] & -2\varepsilon_m \\ \varepsilon_m + \varepsilon_c + (L_c^{\parallel} + L_s^{\parallel})(\varepsilon_c - \varepsilon_m) & (\varepsilon_c - \varepsilon_m)^2 \end{vmatrix}}}{\begin{vmatrix} [\varepsilon_m(1 - L_s^{\parallel}) + \varepsilon_\infty L_s^{\parallel}] & -f_c L_s^{\parallel}(1 - L_s^{\parallel}) \\ \varepsilon_\infty(\varepsilon_m + \varepsilon_c - \varepsilon_\infty) - \varepsilon_m \varepsilon_c & [\varepsilon_\infty(1 - L_c^{\parallel}) + \varepsilon_c L_c^{\parallel}] \end{vmatrix}}}, \quad \text{(S.74)}$$

where $L_c^{\parallel}$ and $L_s^{\parallel}$ are the geometric factors evaluated on the core and shell respectively.

Eq. (S.74) can be used to obtain the longitudinal dipolar LSPR of a core-shell prolate spheroid or a core-shell oblate spheroid by making use of Eqs. (S.9) and (S.11) or Eqs. (S.10) and (S.12) of the manuscript respectively. The core-volume fractions of the spheroids, and their aspect ratios are given in the manuscript.

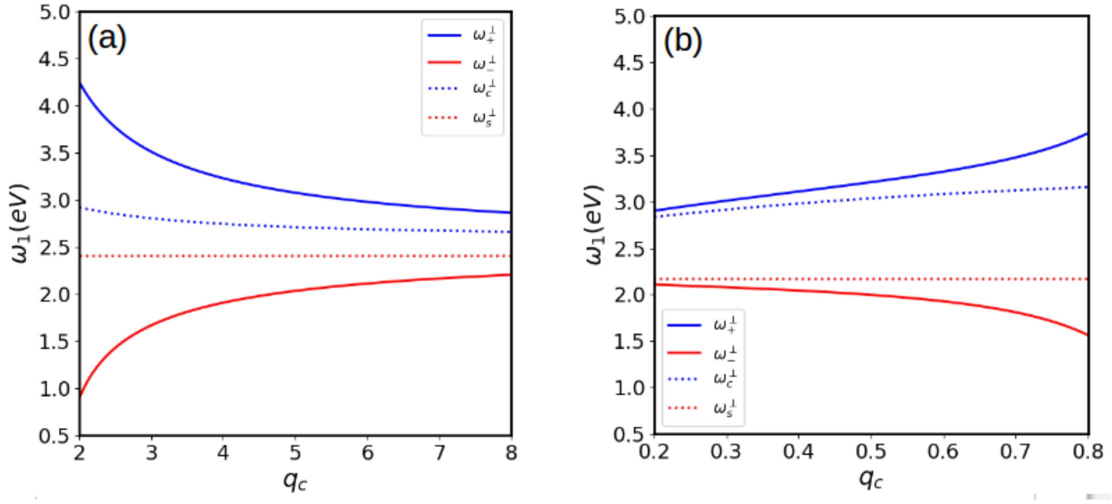
The transverse dipolar LSPR of the core-shell spheroid can be obtained by making use of Eqs. (S.74) and (S.25). **S** of Eq. (S.74) leads to the longitudinal dipolar LSPR of the solid spheroid i.e Eq. (S.24) as follows:

$$\omega^{\parallel}_{1-}(f_c=0) = \frac{\omega_p}{\sqrt{2}}\sqrt{\frac{\begin{vmatrix} 2L^{\parallel}_s\varepsilon_\infty+\varepsilon_m(1-L^{\parallel}_c-L^{\parallel}_s) & -L^{\parallel}_s L^{\parallel}_c \\ (\varepsilon_m+\varepsilon_c-2\varepsilon_\infty) & 1 \end{vmatrix} - \begin{vmatrix} \varepsilon_m(1-L^{\parallel}_c) & \varepsilon_c L^{\parallel}_c \\ L^{\parallel}_s & 1-L^{\parallel}_s \end{vmatrix}}{\begin{vmatrix} [\varepsilon_m(1-L^{\parallel}_s)+\varepsilon_\infty L^{\parallel}_s] & 0 \\ \varepsilon_\infty(\varepsilon_m+\varepsilon_c-\varepsilon_\infty)-\varepsilon_m\varepsilon_c & [\varepsilon_\infty(1-L^{\parallel}_c)+\varepsilon_c L^{\parallel}_c] \end{vmatrix}}} = \omega_p\sqrt{\frac{L^{\parallel}_s}{\varepsilon_\infty L^{\parallel}_s+\varepsilon_m(1-L^{\parallel}_s)}}. \tag{S.75}$$

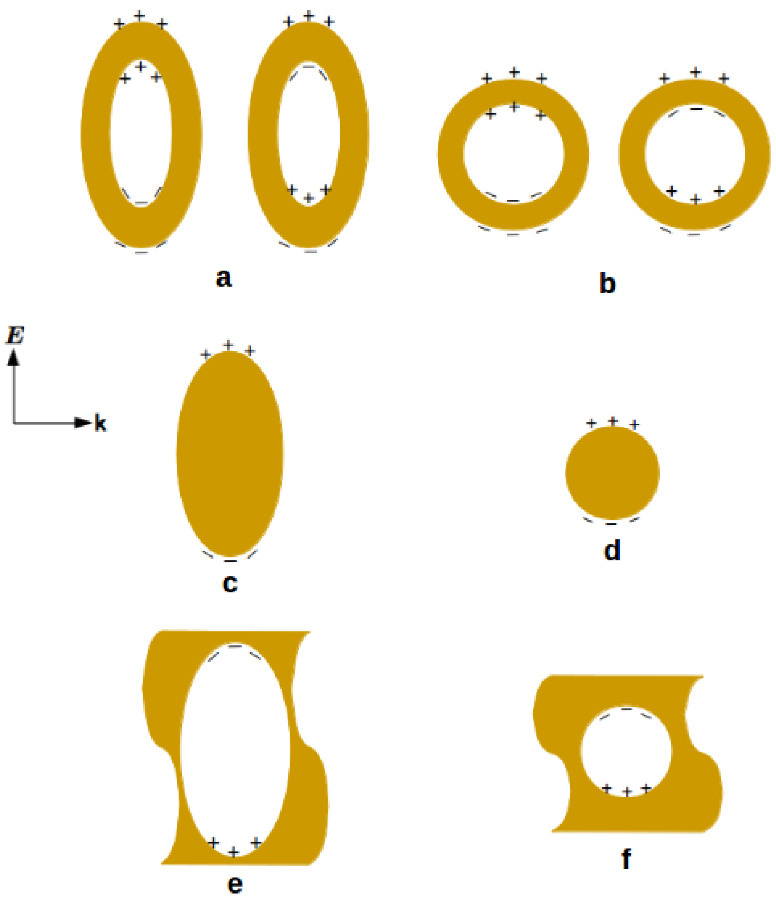
AS of Eq. (S.74) leads to the longitudinal dipolar LSPR of the cavity spheroid i.e Eq. (S.26) as follows:

$$\omega^{\parallel}_{1+}(f_c=0) = \frac{\omega_p}{\sqrt{2}}\sqrt{\frac{\begin{vmatrix} 2L^{\parallel}_s\varepsilon_\infty+\varepsilon_m(1-L^{\parallel}_c-L^{\parallel}_s) & -L^{\parallel}_s L^{\parallel}_c \\ (\varepsilon_m+\varepsilon_c-2\varepsilon_\infty) & 1 \end{vmatrix} + \begin{vmatrix} \varepsilon_m(1-L^{\parallel}_c) & \varepsilon_c L^{\parallel}_c \\ L^{\parallel}_s & 1-L^{\parallel}_s \end{vmatrix}}{\begin{vmatrix} [\varepsilon_m(1-L^{\parallel}_s)+\varepsilon_\infty L^{\parallel}_s] & 0 \\ \varepsilon_\infty(\varepsilon_m+\varepsilon_c-\varepsilon_\infty)-\varepsilon_m\varepsilon_c & [\varepsilon_\infty(1-L^{\parallel}_c)+\varepsilon_c L^{\parallel}_c] \end{vmatrix}}} = \omega_p\sqrt{\frac{1-L^{\parallel}_c}{\varepsilon_\infty(1-L^{\parallel}_c)+\varepsilon_m L^{\parallel}_c}}. \tag{S.76}$$

GR of Eq. (S.74) to obtain the dipolar LSPR of a core-shell sphere i.e Eq. (S.51), is done by making use of Eq. (S.31) to set $L_c = L_s = 1/3$ in Eq. (S.74) and re-defining f_c as $(a/b)^3$.



S 2: Plots of the transveres dipolar symmetric ($\omega_-^\perp$) and antisymmetric ($\omega_+^\perp$) modes in **(a)** a nanorice of aspect ratio: $q_s = 1.8$, and **(b)** a core-shell oblate spheroid of aspect ratio: $q_s = 0.9$, against their different core-aspect ratios: q_c, and the transverse dipolar LSPR of the solid and cavity spheroid plasmons; $\omega_s^\perp$ and $\omega_c^\perp$ respectively, on the same axis. The following dielectric constants were used: $\varepsilon_m = 1.78$, $\varepsilon_c = 2.1$ (silica).



S 3: Surface charge distributions in the symmetric and antisymmetric modes respectively, of: **a**. a nanorice and **b**. a nanoshell, and **c-f**: Surface charge distributions in the fundamental nanostructures, upon the application of a uniform electric field **E** polarized along the x-axis, as indicated by the wavevector **k**.

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