SUPPLEMENTAL APPENDIX

In the supplemental material, we derive Equations 1 and 3 from the second section of the main text (Theory) in greater detail.

DERIVATION OF EQUATION 1

Maxwell's Equations

To begin, we consider a single metal sphere irradiated by y-propagating and z-polarized laser light at wavelength λ. The sphere is embedded in an external medium (viz., vacuum, gas, or liquid) with dielectric constant, ε_o. The dielectric constant of the sphere is ε_1 and is assumed to be independent of the sphere size. The sphere, laser E field, and Cartesian coordinate system are shown in Figure 1*A* for the case $a/\lambda = 1.0$.

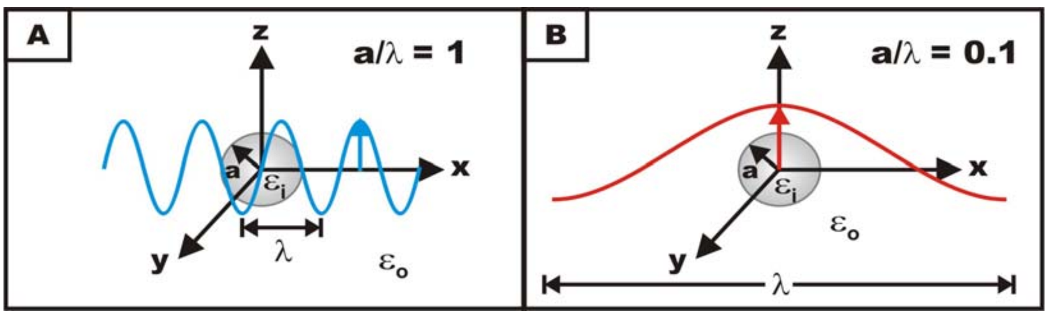

Figure 1. A sphere with radius *a* embedded in a dielectric medium (ε_0) and irradiated by x-propagating, z-polarized light of wavelength λ. (*a*) $a/\lambda = 1$. (*b*) $a/\lambda = 0.1$ (the quasi-static field case).

The laser E field has the general form

$$\vec{\mathbf{E}} = E_x\hat{\mathbf{x}} + E_y\hat{\mathbf{y}} + E_z\hat{\mathbf{z}}, \qquad \text{(S.1)}$$

where $\hat{\mathbf{x}}, \hat{\mathbf{y}}, \hat{\mathbf{z}}$ are unit vectors along the Cartesian axes x, y, z. The values of E_x, E_y, and E_z are controlled by polarization to be $E_x = E_y = 0$ and E_z = non-zero for an x-propagating, z-polarized wave:

$$E_z = E_z^0 \cos\left[2\pi\left(\frac{x}{\lambda} - \upsilon t\right)\right]. \qquad \text{(S.2)}$$

Substituting $\frac{2\pi}{\lambda} = k$ and $2\pi\nu = \omega$ gives

$$E_z = E_z^0 \cos(kx - \omega t). \qquad \text{(S.3)}$$

The general solution to this problem involves solving Maxwell's equations (Equations S.4) to find the time-dependent electric and magnetic fields in all regions of space:

$$\nabla \cdot \mathbf{E} = \frac{\rho}{\varepsilon_0} \quad \text{(S.4a)} \qquad \nabla \times \mathbf{E} = -\frac{\partial \mathbf{B}}{\partial t}, \quad \text{(S.4b)}$$

$$c^2 \nabla \times \mathbf{B} = \frac{\partial \mathbf{E}}{\partial t} + \frac{\mathbf{j}}{\varepsilon_0} \quad \text{(S.4c)} \qquad \nabla \cdot \mathbf{B} = 0. \quad \text{(S.4d)}$$

Substantial simplification in the mathematics of this situation, while retaining the essence of the physics, can be obtained by making the long wavelength approximation. If we require that $\lambda > 400$ nm, then $kx << \omega t$ so that

$$\mathrm{E_z} = E_z^0 \cos \omega t, \quad \text{(S.5)}$$

and if we further require that $a/\lambda < 0.1$, the electric field of the laser will be $\mathbf{E_o}$, a vector pointing along the z axis, that can be assumed to be spatially independent for distances on the order of the sphere size. These conditions are depicted in Figure 1*B*.

The external applied field $\mathbf{E_o}$ is approximately constant in time so that

$$\frac{\partial \mathbf{E}}{\partial t} = 0 \text{ and } \frac{\partial \mathbf{B}}{\partial t} = 0.$$

Thus Maxwell's equations reduce to the equations for electrostatics (Equation S.6) and magnetostatics (Equations S.7).

Electrostatics:

$$\nabla \cdot \mathbf{E} = \frac{\rho}{\varepsilon_0} \quad \text{(S.6a)} \qquad \nabla \times \mathbf{E} = 0 \quad \text{(S.6b)}$$

Magnetostatics:

$$\nabla \times \mathbf{B} = \frac{\mathbf{j}}{\varepsilon_0 c^2} \quad \text{(S.7a)} \qquad \nabla \cdot \mathbf{B} = 0 \quad \text{(S.7b)}$$

This means that for static charges and currents, electricity and magnetism are distinct phenomena.

The problem we wish to focus on is the solution of the electrostatic equations for the electric field inside and outside the metal sphere. Thus we ignore the magnetostatic equations. The metal sphere is a conductor and has no net charge density (i.e. $\rho = 0$) so that

$$\nabla \cdot \mathbf{E} = 0 \quad \text{(S.8a)} \qquad \nabla \times \mathbf{E} = 0. \quad \text{(S.8b)}$$

In order to calculate the **E**(x,y,z) field, we need to know the scalar potential, **Φ**(x,y,z), so that the field can be obtained from

$$\mathbf{E} = -\nabla \mathbf{\Phi}. \tag{S.9}$$

The scalar potential, **Φ**(x,y,z), can be obtained from

$$\nabla \cdot \nabla \mathbf{\Phi} = 0, \tag{S.10}$$

which gives Laplace's equation:

$$\nabla^2 \mathbf{\Phi} = 0. \tag{S.11}$$

Laplace's Equation

We start by converting Laplace's equation in Cartesian coordinates to spherical coordinates using the relationships

$x = r \sin\theta \cos\phi$ $\quad y = r \sin\theta \sin\phi$ $\quad z = r \cos\theta$

$r = (x^2 + y^2 + z^2)^{1/2}$ $\quad \theta = \cos^{-1}\left(\frac{z}{r}\right)$ $\quad \phi = \tan^{-1}\left(\frac{y}{x}\right)$

and the coordinate system defined in Figure 2:

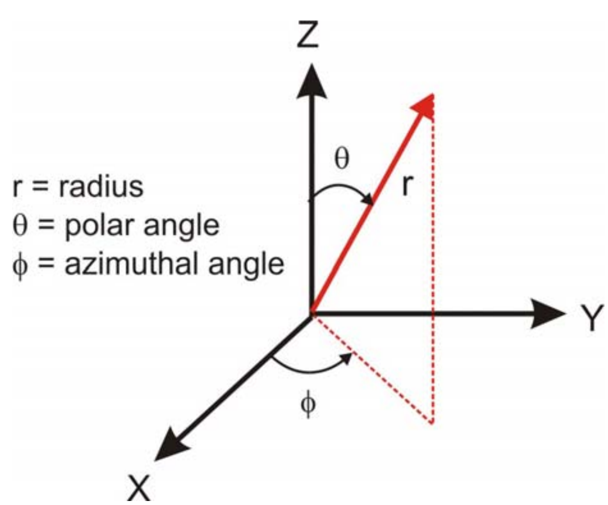

Figure 2. Coordinate axes system for Cartesian and polar coordinates.

Thus we can rewrite Equation S.11

$$\nabla^2(r,\theta,\phi)\mathbf{\Phi}(r,\theta,\phi) = 0. \qquad \text{(S.12)}$$

Recall that in spherical coordinates,

$$\nabla^2(r,\theta,\phi) = \frac{1}{r}\frac{\partial^2}{\partial r^2}r + \frac{1}{r^2}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right], \qquad \text{(S.13)}$$

or the equivalent form

$$\nabla^2(r,\theta,\phi) = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]. \qquad \text{(S.14)}$$

We now can separate the variables into radial and angular components.

Radial and Angular Separation of Variables

Assume the solution is of the form

$$\mathbf{\Phi}(r,\theta,\phi) = F(r)Y(\theta,\phi), \qquad \text{(S.15)}$$

and substitute Equation S.15 into S.12 to give

$$\nabla^2(r,\theta,\phi)\left[F(r)Y(\theta,\phi)\right] = I + II + III = 0, \qquad \text{(S.16)}$$

where (using Equation S.13)

$$I = \frac{1}{r}\frac{\partial^2}{\partial r^2}\left[rF(r)Y(\theta,\phi)\right] \qquad \text{(S.17a)}$$

$$II = \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial[F(r)Y(\theta,\phi)]}{\partial\theta}\right) \qquad \text{(S.17b)}$$

$$III = \frac{1}{r^2\sin^2\theta}\frac{\partial^2[F(r)Y(\theta,\phi)]}{\partial\phi^2}. \qquad \text{(S.17c)}$$

Because the r-dependent operators act only on $F(r)$ and the θ,ϕ operators act only on $Y(\theta,\phi)$, we can separate terms and rewrite Laplace's equation as

$$I + II + III = Y(\theta,\phi)\left[\frac{\partial^2 F(r)}{\partial r^2} + \frac{2}{r}\frac{\partial F(r)}{\partial r}\right] + \frac{F(r)}{r^2}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y(\theta,\phi)}{\partial\theta}\right)\right] + \frac{F(r)}{r^2}\left[\frac{1}{\sin^2\theta}\frac{\partial^2 Y(\theta,\phi)}{\partial\phi^2}\right] = 0. \quad \text{(S.18)}$$

Now do the following to Equation S.18: (*a*) rearrange to get all the *F(r)* terms on one side of the equation and all the $Y(\theta,\phi)$ terms on the other side and (*b*) divide both sides first by $Y(\theta,\phi)$ followed by $F(r)/r^2$ to get

$$\frac{r^2}{F(r)}\left[\frac{\partial^2 F(r)}{\partial r^2} + \frac{2}{r}\frac{\partial F(r)}{\partial r}\right] = -\frac{1}{Y(\theta,\phi)}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y(\theta,\phi)}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2 Y(\theta,\phi)}{\partial\phi^2}\right]. \quad \text{(S.19)}$$

The only way to maintain this equality is for each side of this expression to be equal to a constant. We arbitrarily call this constant *G*. As a result Laplace's equation is now separated into two equations, one dealing with the radial dependence (Equation S.20a) and one with the angular dependence (Equation S.20b):

$$\frac{r^2}{F(r)}\left[\frac{\partial^2 F(r)}{\partial r^2} + \frac{2}{r}\frac{\partial F(r)}{\partial r}\right] = G \quad \text{(S.20a)}$$

$$\left\{\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y(\theta,\phi)}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2 Y(\theta,\phi)}{\partial\phi^2}\right\} = -GY(\theta,\phi). \quad \text{(S.20b)}$$

Separating Polar and Azimuthal Angles

A second separation of variables is required to isolate the θ- and ϕ- dependent parts of Laplace's equation. For this, we assume

$$Y(\theta,\phi) = P(\theta)Q(\phi). \quad \text{(S.21)}$$

Substituting Equation S.21 into Equation S.20b yields

$$\left\{\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial[P(\theta)Q(\phi)]}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2[P(\theta)Q(\phi)]}{\partial\phi^2}\right\} = -G\left[P(\theta)Q(\phi)\right]. \quad \text{(S.22)}$$

Because $\frac{\partial}{\partial\theta}$ only operates on *P(θ)* and $\frac{\partial^2}{\partial\phi^2}$ operates only on $Q(\phi)$, we have

$$\left\{\frac{Q(\phi)}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\left[P(\theta)\right]}{\partial\theta}\right)+\frac{P(\theta)}{\sin^2\theta}\frac{\partial^2\left[Q(\phi)\right]}{\partial\phi^2}\right\}=-G\left[P(\theta)Q(\phi)\right]. \tag{S.23}$$

Divide through both sides by $Q(\phi)$, then by $P(\theta)$, and multiply by $\sin^2\theta$ to get

$$\left\{\frac{\sin^2\theta}{\mathrm{P}(\theta)\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\left[\mathrm{P}(\theta)\right]}{\partial\theta}\right)+\frac{\sin^2\theta}{\mathrm{Q}(\phi)\sin^2\theta}\frac{\partial^2\left[\mathrm{Q}(\phi)\right]}{\partial\phi^2}\right\}=-\mathrm{G}\sin^2\theta. \tag{S.24}$$

Now rearrange to get all θ on the left-hand side and all ϕ on the right-hand side to get

$$\left\{\frac{\sin\theta}{P(\theta)}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\left[P(\theta)\right]}{\partial\theta}\right)\right\}+G\sin^2\theta=-\frac{1}{Q(\phi)}\frac{\partial^2\left[Q(\phi)\right]}{\partial\phi^2}. \tag{S.25}$$

This is only true for all θ,ϕ if both sides equal a constant arbitrarily called D so that

$$\left\{\frac{\sin\theta}{P(\theta)}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\left[P(\theta)\right]}{\partial\theta}\right)\right\}+G\sin^2\theta=D \tag{S.26a}$$

$$-\frac{1}{Q(\phi)}\frac{\partial^2\left[Q(\phi)\right]}{\partial\phi^2}=D. \tag{S.26b}$$

SUMMARY OF SEPARATION OF VARIABLES

Radial Equation: $$\frac{r^2}{F(r)}\left[\frac{\partial^2F(r)}{\partial r^2}+\frac{2}{r}\frac{\partial F(r)}{\partial r}\right]=G$$

Polar Equation: $$\left\{\frac{\sin\theta}{P(\theta)}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\left[P(\theta)\right]}{\partial\theta}\right)\right\}+G\sin^2\theta=D$$

Azimuthal Equation: $$-\frac{1}{Q(\phi)}\frac{\partial^2\left[Q(\phi)\right]}{\partial\phi^2}=D$$

Solving the Azimuthal Equation

Because the azimuthal equation (Equation S.26b) is a function of ϕ only, replace partial derivatives by ordinary derivatives and rearrange to get

$$\frac{d^2Q(\phi)}{d\phi^2}+DQ(\phi)=0. \tag{S.27}$$

Solutions to this equation have the form

$$Q(\phi)=e^{im\phi} \tag{S.28}$$

only if

$$m^2 = D. \tag{S.29}$$

This can be checked by direct substitution:

$$\frac{dQ(\phi)}{d\phi}=ime^{im\phi} \quad and \quad \frac{\mathrm{d}^2Q(\phi)}{d\phi^2}=i^2m^2e^{im\phi}=-m^2e^{im\phi}. \tag{S.30}$$

Therefore,

$$-m^2e^{im\phi}+De^{im\phi}=0 \qquad \text{if and only if } m^2 = D. \tag{S.31}$$

The boundary condition on $Q(\phi)$ is $Q(\phi)$ must be single-valued and continuous over $0 \le \phi \le 2\pi$ so that $Q(\phi)=\mathrm{Q}(\phi+\pi)$.

Substituting $Q(\phi)=e^{im\phi}$ into the boundary condition, we get $e^{im\phi}=e^{im(\phi+2\pi)}$. This reduces to

$$1 = e^{im2\pi} = \cos 2\pi m + i \sin 2\pi m,$$

- for $m = 0$; cos0 = 1 and sin0 = 0 $\therefore$ $e^{i2\pi(0)} = 1$
- for $m = \pm 1$; $\cos \pm 2\pi = 1$ and $\sin \pm 2\pi = 0$ $\therefore$ $e^{i2\pi(\pm 1)} = 1$
- for $m = 2\pm$; $\cos \pm 4\pi = 1$ and $\sin \pm\pi = 0$ $\therefore$ $e^{i2\pi(\pm 2)} = 1$.

So the final result is

$$Q_m(\phi)=e^{im\phi} \tag{S.32}$$

where $m^2 = D$ and $m = 0, \pm 1; \pm 2; \pm 3; \ldots$.

Solving the Polar Equation

Because the polar equation (Equation S.26a) is a function of θ only, replace partial derivatives by ordinary derivatives and substitute $m^2 = D$ to get

$$\left\{\frac{\sin\theta}{P(\theta)}\frac{d}{d\theta}\left(\sin\theta\frac{d\left[P(\theta)\right]}{d\theta}\right)\right\}+G\sin^2\theta=m^2. \tag{S.33}$$

Divide both sides by $\sin^2\theta$, multiply through by $P(\theta)$ and rearrange to get

$$\frac{1}{\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\left[P(\theta)\right]}{d\theta}\right)+\left(G-\frac{m^2}{\sin^2\theta}\right)P(\theta)=0. \tag{S.34}$$

Carry out the indicated derivatives and then substitute $x = \cos\theta$ and use the appropriate trigonometric relationships to get

$$(1-x^2)\frac{d^2P(\theta)}{dx^2}-2x\frac{dP(\theta)}{dx}+\left(G-\frac{m^2}{(1-x^2)}\right)P(\theta)=0. \tag{S.35}$$

Equation S.35 is the associated Legendre equation.

The solution of this equation is summarized below:

$$G = l(l+1); \quad \text{where } l = 0, 1, 2, 3, \ldots$$

and

$$P(\theta)=\sqrt{\frac{2l+1}{2}\frac{(l-|m|)!}{(l+|m|)!}}P_l^{|m|}(\cos\theta). \tag{S.36}$$

Combining the Azimuthal and Axial Solutions

Now we are in a position to combine the results for the polar and azimuthal equations to give the total angular dependence. By our original assumption,

$$Y(\theta,\phi)=P(\theta)Q(\phi) \quad \text{(from S.21)}$$

where: $Q_m(\phi)=e^{im\phi}$ (from S.32)

with $m = 0, \pm1, \pm2, \pm3, \ldots.$

and $$\mathrm{P}_i^{|m|}(\theta) = \sqrt{\frac{2l+1}{2}\frac{(l-|m|)!}{(l+|\mathrm{m}|)!}}P_l^{|m|}(\cos\theta) \quad \text{(from S.36)}$$

with $l = 0,\ 1,\ 2,\ 3,\ \ldots.$

so that: $$Y_{1,m}(\theta,\phi) = \sqrt{\frac{2l+1}{4\pi}\frac{(l-|m|)!}{(l+|\mathrm{m}|)!}}P_l^{|m|}(\cos\theta)e^{im\phi} \quad \text{(S.37)}$$

with $l = 0, 1, 2, 3, \ldots.$ and $\mathrm{m} = -l, -l+1, \ldots\ 0, 1, 2, \ldots\ l-1, l.$

These are the NORMALIZED SPHERICAL HARMONICS. The table on the following page shows these relationships for varying values of l and m.

Table of $Y_{l,m}(\theta,\phi)$

The first few normalized spherical harmonics, $Y_{l,m}(\theta,\phi)$

$$Y_{00} = \frac{1}{2(\pi)^{1/2}}$$

$$Y_{10} = \frac{1}{2}\left(\frac{3}{\pi}\right)^{1/2}\cos\theta$$

$$Y_{1\pm1} = \mp\frac{1}{2}\left(\frac{3}{2\pi}\right)^{1/2}\sin\theta\exp(\pm i\phi)$$

$$Y_{20} = \frac{1}{4}\left(\frac{5}{\pi}\right)^{1/2}(3\cos^2\theta - 1)$$

$$Y_{2\pm1} = \mp\frac{1}{2}\left(\frac{15}{2\pi}\right)^{1/2}\sin\theta\cos\theta\exp(\pm i\phi)$$

$$Y_{2\pm2} = \frac{1}{4}\left(\frac{15}{2\pi}\right)^{1/2}\sin^2\theta\exp(\pm 2i\phi)$$

$$Y_{30} = \frac{1}{4}\left(\frac{7}{\pi}\right)^{1/2}(5\cos^3\theta - 3\cos\theta)$$

$$Y_{3\pm1} = \mp\frac{1}{8}\left(\frac{21}{\pi}\right)^{1/2}(5\cos^2\theta - 1)\sin\theta\exp(\pm 1\phi)$$

$$Y_{3\pm2} = \frac{1}{4}\left(\frac{105}{2\pi}\right)^{1/2}\sin^2\theta\cos\theta\exp(\pm 2i\phi)$$

$$Y_{3\pm3} = \mp\frac{1}{8}\left(\frac{35}{\pi}\right)^{1/2}\sin^3\theta\exp(\pm 3i\phi)$$

Solving the Radial Equation

Since the radial equation (Equation S.20a) is a function of *r* only, replace partial derivatives by ordinary derivatives and substitute $G = l(l + 1)$ to get

$$\frac{r^2}{F_l(r)}\left[\frac{d^2F_l(r)}{dr^2}+\frac{2}{r}\frac{dF_l(r)}{dr}\right]=l(l+1) \tag{S.38}$$

Rearrange to a more standard form:

$$\frac{d^2F_l(r)}{dr^2}+\frac{2}{r}\frac{dF_l(r)}{dr}-l(l+1)\frac{F_l(r)}{r^2}=0. \tag{S.39}$$

Assume a trial solution of the form $F_l(\mathrm{r}) = \mathrm{r}^n$ and calculate the derivatives to get

$$\frac{dF_l(r)}{dr}=\frac{d[r^n]}{dr}=nr^{n-1} \tag{S.40a}$$

$$\frac{d^2F_l(r)}{dr^2}=\frac{d}{dr}\left[\frac{d[r^n]}{dr}\right]=\frac{d}{dr}\left[nr^{n-1}\right]=n(n-1)r^{n-2}. \tag{S.40b}$$

Now substitute the derivatives (Equations S.40a and S.40b) and the trial function into the radial equation (Equation S.39) to get

$$n(n-1)r^{n-2}+\frac{2}{r}nr^{n-1}-\frac{l(l+1)\mathrm{r}^n}{r^2}=0. \tag{S.41}$$

Rearrange to get

$$n(n-1)r^{n-2}+2nr^{n-2}-l(l+1)\mathrm{r}^{n-2}=0. \tag{S.42}$$

Divide through by r^{n-2} and simplify to get the quadratic:

$$n^2+n-l(l+1)=0. \tag{S.43}$$

Solve the quadratic for *n*; this yields two solutions:

$$n=l \quad \text{and} \quad n=-(l+1). \tag{S.44}$$

Thus there are two solutions to the radial equation

$$F_l(r) = \begin{cases} r^l \\ r^{-(l+1)} \end{cases}, \tag{S.45}$$

which can be combined to a general solution with coefficients to be determined by the appropriate boundary conditions for the problem:

$$F_l(r) = Ar^l + Br^{-(l+1)}. \tag{S.46}$$

Combining the Radial and Angular Solutions

Combine the solutions for radial, polar, and azimuthal equations to give a general solution for Laplace's Equation in spherical coordinates.

So the general solution for

$$\nabla^2(r,\theta,\phi)\mathbf{\Phi}_{l,m}(r,\theta,\phi) \qquad \text{(from S.12)}$$

is

$$\mathbf{\Phi}_{l.m}(r,\theta,\phi) = F_l(r)Y_{l,\mathrm{m}}(\theta,\phi) \tag{S.47a}$$

$$\mathbf{\Phi}_{l,m}(r,\theta,\phi) = \left[A_l r^l + B_l r^{-(l+1)}\right] P_l^{|m|}(\cos\theta)e^{im\phi}, \tag{S.47b}$$

with $l = 0, 1, 2, \ldots$ and $m = -l, -l+1, \ldots -2, -1, 0, 1, 2, \ldots, l-1, l$.

Applying Boundary Conditions to the Solution

At this point it is useful to go back to the physical picture of the metal sphere in a constant electric field (viz., the long wavelength approximation, Figure 1*B*) to see the origin of the geometrically derived boundary conditions. It is clear that the geometry of this problem is axially symmetric (Figure 1*B*/2). Thus there is no dependence on the azimuthal angle, ϕ. This corresponds to the $\boldsymbol{m = 0}$ solutions of the azimuthal equation.

In general the E field inside the sphere will be different from that outside the sphere. We know that the incident E field will not be affected by the sphere as you move far from the sphere (i.e. $r \to \infty$). We also know that the field at the center of the sphere should have some finite value (i.e. the field will be nonzero). These three conditions can be expressed mathematically as follows:

1) $\mathbf{E_{in}} \neq \mathbf{E_{out}}$
2) as $r \to \infty$ $\quad \mathbf{E_{out}} \to E_0\hat{\mathbf{z}}$
3) as $r \to 0$ $\quad \mathbf{E_{in}} \to \textit{finite}$

Because we know that $m = 0$ by axial symmetry, let us examine some solutions of Equations S.46, S.37, and S.47 for specific values of l.

▪ **For m = 0, l = 0:**

$$F_0 = \left[A_0 + \frac{B_0}{r} \right] \qquad\qquad Y_{00} = \frac{1}{\sqrt{4\pi}},$$

so that

$$\mathbf{\Phi}_{00} = \frac{1}{\sqrt{4\pi}} \left[A_0 + \frac{B_0}{r} \right]. \tag{S.48}$$

Evaluating Equation S.48 for $r \to 0$ and $r \to \infty$ we get

$$\mathbf{\Phi}_{00}(r \to 0) = \infty \text{ and } \mathbf{\Phi}_{00}(r \to \infty) = \frac{A_0}{\sqrt{4\pi}}.$$

Because $\mathbf{E} = -\Lambda\mathbf{\Phi}$, these solutions correspond to

$$\mathbf{E_{in}}(r \to 0) = \infty \text{ and } \mathbf{E_{out}}(r \to \infty) = 0.$$

These solutions violate the three boundary conditions established above.

$$\therefore \quad A_0 = B_0 = 0$$

▪ **For *m* = 0, *l* = 1:**

$$F_1 = \left[A_1 r + \frac{B_1}{r^2} \right] \qquad\qquad Y_{10} = \sqrt{\frac{3}{4\pi}} \cos\theta.$$

If we subsume $\sqrt{\frac{3}{4\pi}}$ into the constants A_1 and B_1 to be determined by the boundary conditions, we get

$$\mathbf{\Phi}_{10}(r,\theta) = A_1 r \cos\theta + \frac{B_1 \cos\theta}{r^2}. \tag{S.49}$$

Convert to Cartesian coordinates using

$$z = r\cos\theta \quad \text{and} \quad r = \left(x^2 + y^2 + z^2\right)^{1/2}$$

to get

$$\mathbf{\Phi}_{10}(x,y,z) = A_1 z + \frac{B_1 z}{\left(x^2+y^2+z^2\right)^{3/2}}. \qquad \text{(S.50)}$$

Now calculate the E field from $\mathbf{E}(x,y,z) = -\Lambda\mathbf{\Phi}_{10}(x,y,z)$ recalling that $\nabla = \nabla_x\hat{\mathbf{x}} + \nabla_y\hat{\mathbf{y}} + \nabla_z\hat{\mathbf{z}}$ and

$$\nabla_x = \frac{\partial}{\partial x}, \quad \nabla_y = \frac{\partial}{\partial y}, \quad \nabla_z = \frac{\partial}{\partial z}.$$

Thus,

$$\mathbf{E}(x,y,z) = -\left(\frac{\partial}{\partial x}\hat{\mathbf{x}} + \frac{\partial}{\partial y}\hat{\mathbf{y}} + \frac{\partial}{\partial z}\hat{\mathbf{z}}\right)\mathbf{\Phi}_{10}(x,y,z)$$

$$\mathbf{E}(x,y,z) = -\left(\frac{\partial}{\partial x}\hat{\mathbf{x}} + \frac{\partial}{\partial y}\hat{\mathbf{y}} + \frac{\partial}{\partial z}\hat{\mathbf{z}}\right)\left[A_1 z + \frac{B_1 z}{\left(x^2+y^2+z^2\right)^{3/2}}\right]. \qquad \text{(S.51)}$$

Compute $\mathbf{E}(x,y,z)$ by taking the partial derivatives for each component of the field separately and applying the chain rule as needed to get

$$\mathbf{E}(x,y,z) = -A_1\hat{\mathbf{z}} - B_1\left[\frac{\hat{\mathbf{z}}}{\left(x^2+y^2+z^2\right)^{3/2}} - \frac{3z\left(x\hat{\mathbf{x}}+y\hat{\mathbf{y}}+z\hat{\mathbf{z}}\right)}{\left(x^2+y^2+z^2\right)^{5/2}}\right]. \qquad \text{(S.52)}$$

Now we must solve for A_1 and B_1 using the boundary conditions at the surface of the sphere (viz., r = a). Remember that

$$r = \left(x^2+y^2+z^2\right)^{1/2}.$$

Summary of boundary conditions	
Inside vs. outside of sphere	Sphere surface ($r = a$)
Condition 1A: $\mathbf{E}_{out}(x,y,z) \rightarrow E_0\hat{\mathbf{z}}$ as $r \rightarrow \infty$	Condition 2A: $\varepsilon_{in}\mathbf{E}_{r,in} = \varepsilon_{out}\mathbf{E}_{r,out}$ (radial BC)
Condition 1B: $\mathbf{E}_{in}(x,y,z) \rightarrow$ *finite* as $r \rightarrow 0$	Condition 2B: E_θ and E_ϕ are continuous (tangential BC)

▪ Applying condition 1A to Equation S.52: $\mathbf{E}_{out}(x,y,z) \to E_0\hat{\mathbf{z}}$ as $r \to \infty$

$$\mathbf{E}_{out}(x,y,z) = -A_{1,out}\hat{\mathbf{z}} - B_{1,out}\left[\frac{\hat{\mathbf{z}}}{r^3} - \frac{3z(x\hat{\mathbf{x}} + y\hat{\mathbf{y}} + z\hat{\mathbf{z}})}{r^5}\right]. \tag{S.53}$$

Term in [ ] goes to 0 as $r \to \infty$. Thus,

$$-A_{1,out} = E_0. \tag{S.54}$$

▪ Applying condition 1B: $\mathbf{E}_{in}(x,y,z) \to \textit{finite}$ as $r \to 0$

$$\mathbf{E}_{in}(x,y,z) = -A_{1,in}\hat{\mathbf{z}} - B_{1,in}\left[\frac{\hat{\mathbf{z}}}{r^3} - \frac{3z(x\hat{\mathbf{x}} + y\hat{\mathbf{y}} + z\hat{\mathbf{z}})}{r^5}\right] \tag{S.55}$$

Term in [ ] goes to ∞ as $r \to 0$. Thus to keep the field finite,

$$B_{1,in} = 0. \tag{S.56}$$

▪ Applying condition 2A: $\varepsilon_{in}\mathbf{E}_{r,in} = \varepsilon_{out}\mathbf{E}_{r,out}$ (radial BC)

First we must compute the radial components of **E**. The relationship between the spherical coordinate components of **E** and the Cartesian coordinate components of **E** is given by (see D. Fitts, *Vector Analysis in Chemistry*, McGraw-Hill, NewYork, 1974, pp. 124--25)

$$\mathbf{E}(x,y,z) = E_x\hat{\mathbf{x}} + E_y\hat{\mathbf{y}} + E_z\hat{\mathbf{z}} \tag{S.57a}$$

and

$$\mathbf{E}(r,\theta,\phi) = E_r\hat{\mathbf{r}} + E_\theta\hat{\boldsymbol{\theta}} + E_\phi\hat{\boldsymbol{\varphi}}. \tag{S.57b}$$

To get E_r, E_θ, and E_ϕ from E_x, E_y, and E_z, use the following:

$$E_r = \sin\theta\cos\phi E_x + \sin\theta\sin\phi E_y + \cos\theta E_z$$

$$E_\theta = \cos\theta\cos\phi E_x + \cos\theta\sin\phi E_y - \sin\theta E_z$$

$$E_\phi = -\sin\phi E_x + \cos\phi E_y,$$

as well as the following relationships between the unit vectors:

$$\hat{\mathbf{r}}\cdot\hat{\mathbf{x}} = \sin\theta\cos\phi \qquad \hat{\boldsymbol{\theta}}\cdot\hat{\mathbf{x}} = \cos\theta\cos\phi \qquad \hat{\boldsymbol{\varphi}}\cdot\hat{\mathbf{x}} = -\sin\phi$$

$$\hat{\mathbf{r}}\cdot\hat{\mathbf{y}} = \sin\theta\sin\phi \qquad \hat{\boldsymbol{\theta}}\cdot\hat{\mathbf{y}} = \cos\theta\sin\phi \qquad \hat{\boldsymbol{\varphi}}\cdot\hat{\mathbf{y}} = \cos\phi$$

$$\hat{\mathbf{r}}\cdot\hat{\mathbf{z}} = \cos\theta \qquad \hat{\boldsymbol{\theta}}\cdot\hat{\mathbf{z}} = -\sin\theta \qquad \hat{\boldsymbol{\varphi}}\cdot\hat{\mathbf{z}} = 0.$$

So we see that these can be combined to give

$$E_r = \hat{\mathbf{r}} \cdot \hat{\mathbf{x}} E_x + \hat{\mathbf{r}} \cdot \hat{\mathbf{y}} E_y + \hat{\mathbf{r}} \cdot \hat{\mathbf{z}} E_z$$
$$E_\theta = \hat{\boldsymbol{\theta}} \cdot \hat{\mathbf{x}} E_x + \hat{\boldsymbol{\theta}} \cdot \hat{\mathbf{y}} E_y + \hat{\boldsymbol{\theta}} \cdot \hat{\mathbf{z}} E_z$$
$$E_\phi = \hat{\boldsymbol{\varphi}} \cdot \hat{\mathbf{x}} E_x + \hat{\boldsymbol{\varphi}} \cdot \hat{\mathbf{y}} E_y + \hat{\boldsymbol{\varphi}} \cdot \hat{\mathbf{z}} E_z .$$

Now rearrange $\mathbf{E_{in}}$(x,y,z) into the form

$$\mathbf{E}_{in}\left(x,y,z\right) = E_{x,in}\hat{\mathbf{x}} + E_{y,in}\hat{\mathbf{y}} + E_{z,in}\hat{\mathbf{z}}. \qquad \text{(S.58)}$$

And rearrange Equation S.55 to match the form of Equation S.58:

$$\mathbf{E}_{in}\left(x,y,z\right) = \left[\frac{3B_{1,in}zx}{r^5}\right]\hat{\mathbf{x}} + \left[\frac{3B_{1,in}zy}{r^5}\right]\hat{\mathbf{y}} + \left[\frac{3B_{1,in}z^2}{r^5} - \frac{B_{1,in}}{r^3} - A_{1,in}\right]\hat{\mathbf{z}}. \qquad \text{(S.59)}$$

Thus, using the unit vector relationships, we get

$$\begin{aligned}\mathbf{E}_{r,in} &= (\sin\theta\cos\phi)\left[\frac{3B_{1,in}zx}{r^5}\right] + (\sin\theta\sin\phi)\left[\frac{3B_{1,in}zy}{r^5}\right] + \\ &(\cos\theta)\left[\frac{3B_{1,in}z^2}{r^5} - \frac{B_{1,in}}{r^3} - A_{1,in}\right],\end{aligned} \qquad \text{(S.60)}$$

and similarly from Equation S.53,

$$\begin{aligned}\mathbf{E}_{r,out} &= (\sin\theta\cos\phi)\left[\frac{3B_{1,out}zx}{r^5}\right] + (\sin\theta\sin\phi)\left[\frac{3B_{1,out}zy}{r^5}\right] + \\ &(\cos\theta)\left[\frac{3B_{1,out}z^2}{r^5} - \frac{B_{1,out}}{r^3} - A_{1,out}\right].\end{aligned} \qquad \text{(S.61)}$$

Evaluate Equation S.60 using $B_{1,in} = 0$ determined from the boundary condition 1B:

$$\mathbf{E}_{r,in} = -A_{1,in}\cos\theta. \qquad \text{(S.62)}$$

Now evaluate Equation S.61 using $A_{1,out} = -E_0$:

$$\begin{aligned}\mathbf{E}_{r,out} &= (\sin\theta\cos\phi)\left[\frac{3B_{1,out}zx}{r^5}\right] + (\sin\theta\sin\phi)\left[\frac{3B_{1,out}zy}{r^5}\right] + \\ &(\cos\theta)\left[\frac{3B_{1,out}z^2}{r^5} - \frac{B_{1,out}}{r^3} + E_0\right].\end{aligned} \qquad \text{(S.63)}$$

Rearrange Equation S.63 and substitute the following:

$$\sin\theta\cos\phi = \frac{x}{r}, \quad \sin\theta\sin\phi = \frac{y}{r}, \quad \text{and} \quad \cos\theta = \frac{z}{y}$$

to give

$$\mathbf{E}_{r,out} = E_0\cos\theta + B_{1,out}\left[\frac{-\cos\theta}{r^3} + \frac{3}{r^5}\left(z^2\cos\theta + \frac{zy^2}{r} + \frac{zx^2}{r}\right)\right]. \tag{S.64}$$

We are now ready to use boundary condition 2A: $\varepsilon_{in}\mathbf{E}_{r,in} = \varepsilon_{out}\mathbf{E}_{r,out}$; inserting Equations S.62 and S.64 into the boundary condition:

$$-\varepsilon_{in}A_{1,in}\cos\theta = \varepsilon_{out}E_0\cos\theta - \frac{\varepsilon_{out}B_{1,out}\cos\theta}{r^3} + \frac{3\varepsilon_{out}B_{1,out}}{r^5}\left(z^2\cos\theta + \frac{zy^2}{r} + \frac{zx^2}{r}\right). \tag{S.65}$$

Divide through by cosθ and substitute $z = r\cos\theta$ to give

$$-\varepsilon_{in}A_{1,in} = \varepsilon_{out}E_0 - \frac{\varepsilon_{out}B_{1,out}}{r^3} + \frac{3\varepsilon_{out}B_{1,out}}{r^5}\left(z^2 + \frac{zy^2}{z} + \frac{zx^2}{z}\right). \tag{S.66}$$

Recall that $r^2 = (x^2 + y^2 + z^2)$ so Equation S.66 can be simplified to

$$-\varepsilon_{in}A_{1,in} = \varepsilon_{out}E_0 - \frac{\varepsilon_{out}B_{1,out}}{r^3} + \frac{3\varepsilon_{out}B_{1,out}}{r^5}(r^2). \tag{S.67}$$

Canceling r^2, combining terms, and factoring out ε_{out} gives

$$-\varepsilon_{in}A_{1,in} = \varepsilon_{out}\left[E_0 + \frac{2B_{1,out}}{r^3}\right]. \tag{S.68}$$

Letting $r = a$ as we are interested in the surface of the sphere,

$$-\varepsilon_{in}A_{1,in} = \varepsilon_{out}\left[E_0 + \frac{2B_{1,out}}{a^3}\right]. \tag{S.69}$$

We cannot simplify this expression any further, so we now turn to our next boundary condition.

▪ Applying condition 2B: E_θ and E_ϕ are continuous (tangential BC)

Consider the axial case where $E_{\theta,in} = E_{\theta,out}$

Recall

$$E_\theta = \hat{\boldsymbol{\theta}} \cdot \hat{\mathbf{x}} E_x + \hat{\boldsymbol{\theta}} \cdot \hat{\mathbf{y}} E_y + \hat{\boldsymbol{\theta}} \cdot \hat{\mathbf{z}} E_z. \tag{S.70}$$

Using Equation S.59 and the unit vector relationships, we get

$$\begin{aligned} E_{\theta,in} &= (\cos\theta\cos\phi)\left[\frac{3B_{1,in}zx}{r^5}\right] + (\cos\theta\sin\phi)\left[\frac{3B_{1,in}zy}{r^5}\right] + \\ &(-\sin\theta)\left[\frac{3B_{1,in}z^2}{r^5} - \frac{B_{1,in}}{r^3} - A_{1,in}\right] \end{aligned} \tag{S.71}$$

and similarly from Equation S.53 in analogy to Equation S.71 above:

$$\begin{aligned} E_{\theta,out} &= (\cos\theta\cos\phi)\left[\frac{3B_{1,out}zx}{r^5}\right] + (\cos\theta\sin\phi)\left[\frac{3B_{1,out}zy}{r^5}\right] + \\ &(-\sin\theta)\left[\frac{3B_{1,out}z^2}{r^5} - \frac{B_{1,out}}{r^3} - A_{1,out}\right]. \end{aligned} \tag{S.72}$$

Evaluate Equation S.71 using $B_{1,in} = 0$ (Equation S.56) determined from boundary condition 1B:

$$E_{\theta,in} = A_{1,in}\sin\theta. \tag{S.73}$$

Now evaluate Equation S.72 using $A_{1,out} = -E_0$ (Equation S.54) determined from boundary condition 1A:

$$\begin{aligned} E_{\theta,out} &= (\cos\theta\cos\phi)\left[\frac{3B_{1,out}zx}{r^5}\right] + (\cos\theta\sin\phi)\left[\frac{3B_{1,out}zy}{r^5}\right] + \\ &(-\sin\theta)\left[\frac{3B_{1,out}z^2}{r^5} - \frac{B_{1,out}}{r^3} - E_0\right]. \end{aligned} \tag{S.74}$$

Rearrange Equation S.74 to get

$$\begin{aligned} E_{\theta,out} &= -E_0\sin\theta + \frac{B_{1,out}\sin\theta}{r^3} - \frac{3B_{1,out}z^2\sin\theta}{r^5} + \\ &\frac{3B_{1,out}zy\cos\theta\sin\phi}{r^5} + \frac{3B_{1,out}zx\cos\theta\cos\phi}{r^5}. \end{aligned} \tag{S.75}$$

Equate $E_{\theta,in}$ (Equation S.73) and $E_{\theta,out}$ (Equation S.75) according to boundary condition 2B and divide by $\sin\theta$ to get

$$A_{1,in} = -E_0 + \frac{B_{1,out}}{r^3} - \frac{3B_{1,out}z^2}{r^5} + \frac{3B_{1,out}zy\cos\theta\sin\phi}{r^5\sin\theta} + \frac{3B_{1,out}zx\cos\theta\cos\phi}{r^5\sin\theta}. \qquad \text{(S.76)}$$

Substitute $\frac{x}{r\sin\theta} = \cos\phi$ and $\frac{y}{r\sin\theta} = \sin\phi$ into Equation S.76 and simplify to get

$$A_{1,in} = -E_0 + \frac{B_{1,out}}{r^3} - \frac{3B_{1,out}z^2}{r^5} + \frac{3B_{1,out}zy^2\cos\theta}{r^6\sin^2\theta} + \frac{3B_{1,out}zx^2\cos\theta}{r^6\sin^2\theta}. \qquad \text{(S.77)}$$

Substitute $z = r\cos\theta$ into Equation S.77 and simplify to get

$$A_{1,in} = -E_0 + \frac{B_{1,out}}{r^3} - \frac{3B_{1,out}z^2}{r^5} + \frac{3B_{1,out}\cos^2\theta}{r^5\sin^2\theta}(x^2 + y^2). \qquad \text{(S.78)}$$

Substitute $(x^2 + y^2) = r^2\sin^2\theta$ and simplify to get

$$A_{1,in} = -E_0 + \frac{B_{1,out}}{r^3} - \frac{3B_{1,out}z^2}{r^5} + \frac{3B_{1,out}r^2\cos^2\theta}{r^5}. \qquad \text{(S.79)}$$

Substitute $z^2 = r^2\cos^2\theta$ to get

$$A_{1,in} = -E_0 + \frac{B_{1,out}}{r^3} - \frac{3B_{1,out}z^2}{r^5} + \frac{3B_{1,out}z^2}{r^5}. \qquad \text{(S.80)}$$

And this finally simplifies to

$$A_{1,in} = -E_0 + \frac{B_{1,out}}{r^3}. \qquad \text{(S.81)}$$

Let $r = a$ to yield the final result:

$$A_{1,in} = -E_0 + \frac{B_{1,out}}{a^3}. \qquad \text{(S.82)}$$

Solving for the Final E Field Expressions (Equation 1)

We now have two equations in two unknowns to solve for $A_{1,in}$ and $B_{1,out}$, i.e. Equations S.69 and S.82 reproduced below:

$$-\varepsilon_{in}A_{1,in} = \varepsilon_{out}\left[E_0 + \frac{2B_{1,out}}{a^3}\right] \tag{S.69}$$

$$A_{1,in} = -E_0 + \frac{B_{1,out}}{a^3}. \tag{S.82}$$

Solve for $A_{1,in}$ first by eliminating $B_{1,out}$. Multiply both sides of Equation S.82 by $-2\varepsilon_{out}$ and add to Equation S.69 to get

$$-A_{1,in} = \left[\frac{3\varepsilon_{out}}{(2\varepsilon_{out}+\varepsilon_{in})}\right]E_0. \tag{S.83}$$

Now solve for $B_{1,out}$ to get

$$B_{1,out} = a^3 E_0\left[\frac{\varepsilon_{in}-\varepsilon_{out}}{(\varepsilon_{in}+2\varepsilon_{out})}\right]. \tag{S.84}$$

Recall our previous expressions for E_{in}(x,y,z) (Equation S.55) and E_{out}(x,y,z) (Equation S.53). Substituting Equations S.56 and S.83 into Equation S.55, we obtain

$$\mathbf{E}_{in}\left(x,y,z\right) = \left(\frac{3\varepsilon_{out}}{2\varepsilon_{out}+\varepsilon_{in}}\right)E_0\hat{\mathbf{z}}. \tag{S.85}$$

Substituting Equations S.54 and S.84 into Equation S.53, we obtain

$$\mathbf{E}_{out}\left(x,y,z\right) = E_0\hat{\mathbf{z}} - \left[\frac{\varepsilon_{in}-\varepsilon_{out}}{\left(\varepsilon_{in}+2\varepsilon_{out}\right)}\right]a^3E_0\left[\frac{\hat{\mathbf{z}}}{r^3} - \frac{3z}{r^5}\left(x\hat{\mathbf{x}}+y\hat{\mathbf{y}}+z\hat{\mathbf{z}}\right)\right]. \tag{S.86}$$

This is Equation 1 from the main text.

DERIVATION OF EQUATION 3

This derivation originates from References 25 and 40 in the main text. We begin by considering the shift in the localized surface plasmon resonance (LSPR) originating from the adsorption of a layer of thickness d and refractive index n_A onto the nanoparticle surface. At all distances greater than d from the nanoparticle surface, we assume that there is an external environment with refractive index n_E. Thus the distance-dependent refractive index can be written as

$$n(z) = \begin{cases} n_A & 0 \le z \le d \\ n_E & d < z < \infty \end{cases}. \tag{S.87}$$

We are interested in measuring the wavelength-shift in the LSPR spectrum due to the introduction of the adsorption layer; this can be expressed as follows:

$$\Delta\lambda = m \cdot \left(n_{final} - n_{initial}\right), \tag{S.88}$$

where m is the bulk refractive index sensitivity of the nanoparticles (in units of energy RIU^{-1} where RIU is a refractive index unit) and $n_{initial}$ and n_{final} are the refractive indices of the initial state and the final state, respectively. We can define $n_{initial}$ as the external environment in the absence of the adsorption layer; i.e. $n_{initial} = n_E$. However, the refractive index of the final state is more complex because it involves some combination of the refractive index of both the adsorbed layer as well as the external environment, as shown in Equation S.87 above. Moreover, the refractive index should be weighted by the distant-dependent intensity of the electromagnetic (EM) field since the fields that probe the local refractive index are more intense closer to the nanoparticle surface (see, for example, Figure 5 in the text). We can approximate the EM field as decaying exponentially with some characteristic length given by l_d:

$$E(z) = E_0 \exp\left(-z/l_d\right). \tag{S.89}$$

Thus, to normalize the refractive index by the relative field intensity (e.g. I/I_0), we need to use the EM field squared and our normalization factor becomes

$$\left[\exp\left(-z/l_d\right)\right]^2 = \exp\left(-2z/l_d\right). \tag{S.90}$$

We can now define an effective refractive index, n_{eff}, which normalizes the z-dependent refractive index by the intensity factor in Equation S.90:

$$n_{eff} = \frac{2}{l_d}\int_0^{\infty} n(z)\exp\left(-2z/l_d\right)dz. \tag{S.91}$$

The factor of $2/l_d$ normalizes the integral such that $n_{eff} = n_E$ in the absence of an adsorption layer. Inserting Equation S.87 into Equation S.91 and expanding the integral, we get

$$n_{eff} = \frac{2}{l_d}\left[\int_0^{d} n_A \exp\left(-2z/l_d\right)dz + \int_d^{\infty} n_E \exp\left(-2z/l_d\right)dz\right]. \tag{S.92}$$

Evaluating this integral yields the following expression:

$$n_{eff} = n_A\left[1 - \exp\left(-2d/l_d\right)\right] + n_E \exp\left(-2d/l_d\right). \tag{S.93}$$

If we now substitute n_{eff} for n_{final} and n_E for $n_{initial}$ in Equation S.88 above, we get the following result:

$$\Delta\lambda = m\cdot\left(n_{eff} - n_E\right) = m\cdot\left\{n_A\left[1-\exp\left(\frac{-2d}{l_d}\right)\right] + n_E\exp\left(\frac{-2d}{l_d}\right) - n_E\right\}. \qquad \text{(S.94)}$$

Grouping the n_E terms and rearranging, we get

$$\Delta\lambda = m\cdot\left(n_A - n_E\right)\left[1-\exp\left(\frac{-2d}{l_d}\right)\right]. \qquad \text{(S.95)}$$

This is Equation 3 from the main text.

It is important to note that this equation reduces simply to $\Delta\lambda = m\cdot\left(n_A - n_E\right)$ in bulk solvents (where d goes to infinity) where n_A is the refractive index of the new solvent and n_E is the refractive index of the original bulk medium. Moreover, this approach also works for multilayer systems, as shown in References 25 and 40, following the same derivation.

Because this equation is valid for both SPR and LSPR wavelength-shift measurements, we can use it to directly compare the performance of the two types of sensors:

$$\frac{\Delta\lambda_{LSPR}}{\Delta\lambda_{SPR}} = \frac{m_{LSPR}}{m_{SPR}}\frac{\left[1-\exp\left(\frac{-2d}{l_{d,LSPR}}\right)\right]}{\left[1-\exp\left(\frac{-2d}{l_{d,SPR}}\right)\right]}. \qquad \text{(S.96)}$$

Here the $(n_A - n_E)$ terms cancel out because we are comparing sensor performance under identical experimental conditions. From the literature, we know the following relationships (References 25 and 40 from main text): m_{SPR} = 9000 nm RIU^{-1} and m_{LSPR} = 200 nm RIU^{-1}. This indicates that the SPR outperforms the LSPR sensor for sensing changes in bulk refractive index by a factor of 45. However, as previously stated, the response of the two techniques becomes comparable when measuring short range changes in refractive index due to a molecular adsorption layer. This is due to the difference in the EM-field decay length, i.e. $l_{d,SPR}$ = 200 nm and $l_{d,LSPR}$ = 5 nm. Inserting the values for l_d and m into Equation S.96, we can now directly compare the wavelength-shift performance of the two sensors as a function of layer thickness as shown in Figure 3.

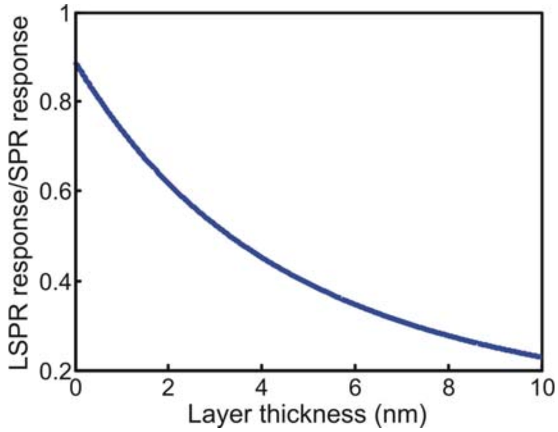

Figure 3. Comparison of the LSPR and SPR wavelength-shift responses using Equation S.96 and values m_{SPR} = 9000 nm RIU^{-1}, m_{LSPR} = 200 nm RIU^{-1}, $l_{d,SPR}$ = 200 nm, and $l_{d,LSPR}$ = 5 nm.

As the layer thickness approaches zero, the response of the two sensors becomes nearly identical (i.e, the ratio approaches one). Thus, despite the large difference in the bulk refractive index responses, the two sensors are comparable for thin adsorption layers, which is important for most sensing applications (such as sensing antigen-antibody binding).

At this point, we have only considered the bulk refractive index response (*m*) and the EM-field decay length (l_d) for comparing the LSPR and surface plasmon resonance (SPR) sensor response. However, one should also account for the different surface areas of the two substrates by normalizing against the number of adsorbed molecules to get the wavelength-shift response per molecule. We can approximate this by comparing the area occupied by the metal for an SPR thin film with the area occupied by a nanoparticle array.

Consider a 10 × 10-μm region of an NSL-fabricated sample. In the case when 500-nm diameter nanospheres are used as a deposition mask, approximately 460 spheres can occupy that space (owing to the fact that it is a hexagonally close-packed array rather than a square array). Thus, one can subtract the area occupied by the spheres ($460*\pi*0.25^2 = 90.3$ μm^2) from the area of the region of interest (100 μm^2) to get an approximate value of the area occupied by the nanoparticles (9.7 μm^2). Compared to a continuous thin film which will occupy all 100 μm^2 of the region of interest, the nanoparticles occupy only 9.7 μm^2, or 90.3% less area.

If we now consider a full-coverage adsorbed monolayer, the LSPR sensor response originates from 90.3% fewer molecules than the SPR sensor. Thus, in terms of sensor response per adsorbed molecule, the LSPR sensor actually outperforms the SPR sensor. As future experiments push toward sensing smaller concentrations (even single molecules), this feature of LSPR sensors will become increasingly important.