Lecture 9 (ECE545)

Our aim in this lecture and the next one is to study another type of plasmon excitation, known as localized surface plasmon resonan-ce (LSPR). This is an excitation at the surface of a metal nanoparticle and differs from SPR in two respects: (a) Unlike SPR, LSPR is excited on a non-planar interface (such as, spherical or elliptical nanoparticles)

(b) LSPR is highly localized around the metal nanoparticle.

As we'll see shortly, we can analyze it using Laplace's equation (the same equation used for electrostatics) instead of wave equation.

Recall, Laplace's equation is: $\nabla^2 \Phi = 0$, where Φ is the potential. For spherical nanoparticles, we must solve Laplace's equation in spherical coordinates. So, before we embark on a study of LSPR, it would be very useful to brush up solutions of Laplace's equation in spherical coordinates.

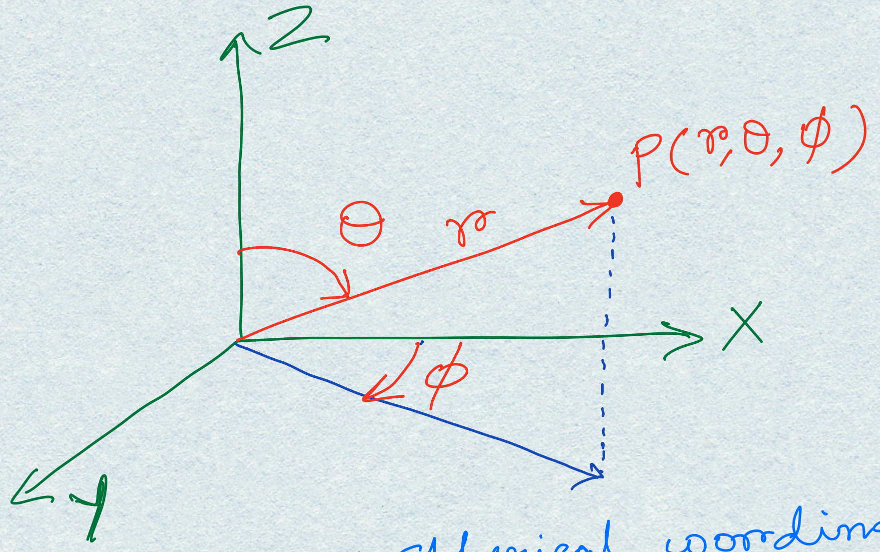


Fig 1: Spherical coordinate system.

Laplace's equation $\nabla^2 \Phi = 0$, in spherical coordinate is written as:

$$\frac{1}{r}\left(\frac{\partial^2}{\partial r^2}(r\Phi)\right) + \frac{1}{r^2 \sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta \frac{\partial\Phi}{\partial\theta}\right)$$

$$+ \frac{1}{r^2 \sin^2\theta}\frac{\partial^2 \Phi}{\partial \phi^2} = 0$$

$$\text{———} \quad (1)$$

The above equation can be solved using method of separation of variables. We assume that the solution has a form

$$\Phi = \frac{U(r)}{r} P(\theta) Q(\phi) \text{ ——— } (2)$$

Substituting eqn (2) in eqn (1), we have:

$$\frac{1}{r}\frac{\partial^2}{\partial r^2}(UPQ) + \frac{1}{r^2 \sin\theta}\frac{\partial}{\partial\theta}\left\{\sin\theta \frac{\partial}{\partial\theta}\left(\frac{UPQ}{r}\right)\right\}$$

$$+ \frac{1}{r^2 \sin^2\theta}\frac{\partial^2}{\partial\phi^2}\left(\frac{UPQ}{r}\right) = 0$$

$$\Rightarrow P\Theta \frac{d^2U}{dr^2} + \frac{U\Theta}{r^2 \sin\theta} \frac{d}{d\theta}\left(\sin\theta \frac{d\Theta}{d\theta}\right)$$

$$+ \frac{UP}{r^2 \sin^2\theta} \frac{d^2\Theta}{d\phi^2} = 0$$

Mutliplying both sides by $\frac{r^2 \sin^2\theta}{UP\Theta}$,

$$r^2 \sin^2\theta \left[\frac{1}{U} \frac{d^2U}{dr^2} + \frac{1}{P r^2 \sin\theta} \frac{d}{d\theta}\left(\sin\theta \frac{d\Theta}{d\theta}\right)\right]$$

$$+ \frac{1}{\Theta} \frac{d^2\Theta}{d\phi^2} = 0 \quad \text{———} \quad (3)$$

Now, the term within the parentheses depends on r, θ and the last term depends on ϕ. Since they add up to zero for all values of r, θ and ϕ, each of them must be constant.

Let $\frac{1}{\Theta} \frac{d^2\Theta}{d\phi^2} = -m^2$

$$\Rightarrow \frac{d^2\Theta}{d\phi^2} + m^2\Theta = 0$$

$$\Rightarrow \Theta = e^{\pm im\phi} \quad \text{———} \quad (4)$$

For Θ to be single valued, m must be integer.

From eqn (3):

$$r^2 \sin^2\theta \left[\frac{1}{U} \frac{d^2U}{dr^2} + \frac{1}{P r^2 \sin\theta} \frac{d}{d\theta}\left(\sin\theta \frac{dP}{d\theta} \right) \right] - m^2 = 0$$

$$\Rightarrow r^2 \left[\frac{1}{U} \frac{d^2U}{dr^2} + \frac{1}{P r^2 \sin\theta} \frac{d}{d\theta}\left(\sin\theta \frac{dP}{d\theta} \right) \right] - \frac{m^2}{\sin^2\theta} = 0$$

[Dividing both sides by $\sin^2\theta$]

$$\Rightarrow \frac{r^2}{U} \frac{d^2U}{dr^2} + \left[\frac{1}{P \sin\theta} \frac{d}{d\theta}\left(\sin\theta \cdot \frac{dP}{d\theta} \right) - \frac{m^2}{\sin^2\theta} \right] = 0 \qquad \text{——— (5)}$$

Again, the first term depends only on r and the term in the parentheses depends only on θ. So, each of them must be constant.

Let, $\frac{r^2}{U}\frac{d^2U}{dr^2} = l(l+1)$

$$\Rightarrow \frac{d^2U}{dr^2} - \frac{l(l+1)}{r^2}U = 0 \quad \text{------ (6)}$$

The solution to the above equation is:

$$U(r) = Ar^{l+1} + Br^{-l} \quad \text{------ (7)}$$

[Note that l is yet to be determined]

From eqn.(6) we have:

$$\frac{1}{\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{dP}{d\theta}\right) + \left[l(l+1) - \frac{m^2}{\sin^2\theta}\right]P = 0$$

$$\text{------ (8)}$$

The above equation can be put in a simpler form by making a change of variable:

$$x = \cos\theta$$

$$\therefore \frac{d}{dx} \equiv \frac{d}{d(\cos\theta)} \equiv \frac{d}{d\theta}\cdot\frac{d\theta}{d(\cos\theta)}$$

$$\equiv -\frac{1}{\sin\theta}\frac{d}{d\theta}$$

$\therefore$ Eqn (8) becomes:

$$\frac{d}{dx}(1-x^2)\frac{dP}{dx} + \left[l(l+1) - \frac{m^2}{1-x^2}\right]P = 0$$

$$\text{------ (9)}$$

Equation (9) is known as generalized Legendre's equation.

For problems with azimuthal symmetry, we have $m=0$ and eqn. (9) further simplifies to:

$$\frac{d}{dx}(1-x^2)\frac{dP}{dx} + l(l+1)P = 0 \qquad (10)$$

This is known as ordinary Legendre's equation. The solutions are given by a linear superposition of the following Legendre's polynomials of order $l = 0, 1, 2, \ldots$:

$$P_0(x) = 1$$

$$P_1(x) = x$$

$$P_2(x) = \frac{1}{2}(3x^2-1)$$

$$P_3(x) = \frac{1}{2}(5x^3-3x)$$

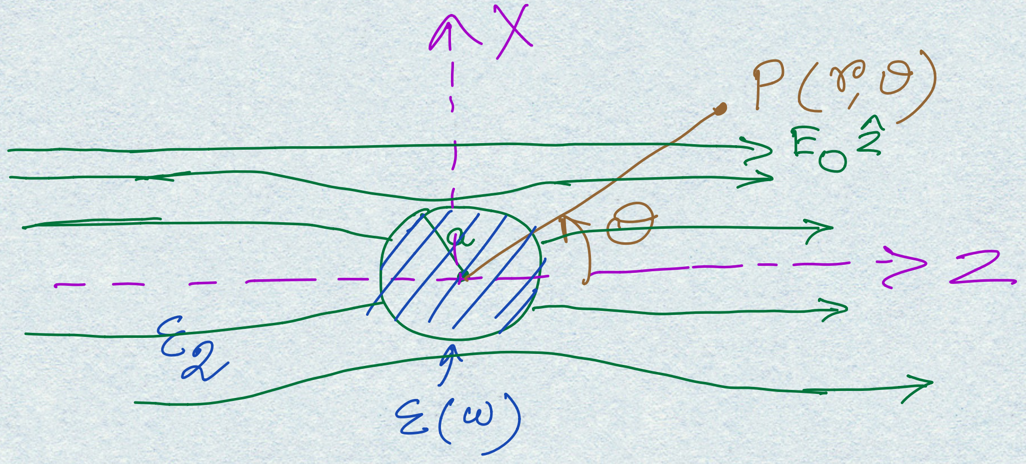
$\vdots$

and so on.

In general, one can find out $P_l(x)$ from Rodrigues' formula:

$$P_l(x) = \frac{1}{2^l\, l!}\frac{d^l}{dx^l}(x^2-1)^l \qquad (11)$$

Sub-wavelength metal particles:



Consider a metal nanoparticle of dielectric constant $\varepsilon(\omega)$ is embedded in a dielectric medium with a dielectric constant ε_2.

We assume that $a << \lambda$, λ being the wavelength of the incident field $\vec{E} = E_0\hat{z}$.

The incident electromagnetic field will not have any significant phase variation over the particle. The interaction of such particle can be analyzed by Laplace's equation since phase variation is essentially an electromagnetic phenomenon and insignificant in this case. Such approximation is known as the quasi-static approximation.

Assume, Φ_{in} is the potential inside the particle and Φ_{out} is the potential in the background medium.

Our approach is pretty straightforward here: ① Solve $\nabla^2 \Phi = 0$ for Φ_{in} and Φ_{out}.

② Find out $\vec{E}$ from Φ within and outside the metal particle and match the boundary condition at $r = a$ and some other points.

(will be clarified in a bit)

Inside:

$$\Phi_{in} = \sum_{l=0}^{\infty} A_l r^l P_l(\cos\theta) \quad \text{—— (12)}$$

Note that, the r-dependence is given by $\left(A_l r^l + D_l r^{-(l+1)}\right)$ in the most general form. But as the center of the nanoparticle is located at the origin, presence of $\frac{1}{r^{(l+1)}}$ terms will blow up the solution. So, only r^l terms are present.

Outside:

$$\Phi_{out} = \sum_{l=0}^{\infty} \left[B_l r^l + C_l r^{-(l+1)}\right] P_l(\cos\theta) \quad \text{—— (13)}$$

In addition to the boundary conditions at $r = a$, we have an additional boundary condition available as $r \to \infty$. In this limit, the field must be E_0 (in other words, the presence of the particle at origin should not affect the field at a very large distance).

So, the potential $\Phi_{out} \rightarrow -E_0 z$ as $r \rightarrow \infty$.

$$\therefore \Phi_{out}\Big|_{r\rightarrow\infty} = -E_0 r \cos\theta \qquad \text{——— (14)}$$

Comparing eqns. (13) and (14), the only non-zero B_l is $\boxed{B_1 = -E_0}$.

$$\therefore \Phi_{out} = -E_0 r P_1(\cos\theta) + \sum_{l=0}^{\infty} C_l r^{-(l+1)} P_l(\cos\theta) \qquad \text{——— (15)}$$

At $r = a$, we have two boundary conditio-ns available:

① Tangential $\vec{E}$ (E_θ):

$$-\frac{1}{r}\frac{\partial \Phi_{in}}{\partial \theta}\Big|_{r=a} = -\frac{1}{r}\frac{\partial}{\partial \theta}\Phi_{out}\Big|_{r=a}$$

$$\Rightarrow \frac{\partial \Phi_{in}}{\partial \theta}\Big|_{r=a} = \frac{\partial \Phi_{out}}{\partial \theta}\Big|_{r=a} \qquad \text{——— (16)}$$

(2) Normal $\vec{D}$ (D_r):

$$-\varepsilon \frac{\partial \Phi_{in}}{\partial r}\Big|_{r=a} = -\varepsilon_2 \frac{\partial \Phi_{out}}{\partial r}\Big|_{r=a} \qquad \text{———— (17)}$$

Eqn (16) yields:

$$\sum_{l=0}^{\infty} A_l a^l P_l'(\cos\theta)$$

$$= -E_0 a P_1'(\cos\theta) + \sum_{l=0}^{\infty} C_l a^{-(l+1)} P_l'(\cos\theta)$$

Equating coefficients of $P_l'(\cos\theta)$,

$$a A_1 = -E_0 a + C_1 \frac{1}{a^2}$$

$$\Rightarrow A_1 = -E_0 + \frac{C_1}{a^3} \qquad \text{———— (18)}$$

and $$A_l = \frac{C_l}{a^{(2l+1)}} \text{ for } l \neq 1 \qquad \text{———— (19)}$$

Eqn. (17) yields:

$$\sum_{l=0}^{\infty} \varepsilon/\varepsilon_2 \, A_l l a^{(l-1)} P_l(\cos\theta)$$

$$= -E_0 P_1(\cos\theta) - \sum_{l=0}^{\infty} C_l (l+1) a^{-(l+2)} P_l(\cos\theta)$$

$$\therefore \ \frac{\varepsilon}{\varepsilon_2} A_1 = -E_0 - \frac{2C_1}{a^3} \quad \text{——— (20)}$$

and, $A_l \, l \left(\frac{\varepsilon}{\varepsilon_2}\right) = -\frac{(l+1) C_l}{a^{(2l+1)}}$ ——— (21)

Eqn. (19) and (21) can only be satisfied only if $A_l = C_l = 0$ for $l \neq 1$.

Multiplying eqn (18) by 2 and adding to eqn. (20),

$$A_1 \left(2 + \frac{\varepsilon}{\varepsilon_2}\right) = -3E_0$$

$$\Rightarrow \boxed{A_1 = -\frac{3E_0}{\left(2 + \frac{\varepsilon}{\varepsilon_2}\right)}} \quad \text{——— (22)}$$

Substituting this in eqn. (18),

$$-\frac{3E_0}{\left(2 + \frac{\varepsilon}{\varepsilon_2}\right)} = -E_0 + \frac{C_1}{a^3}$$

$$\Rightarrow E_0 \left[1 - \frac{3}{2 + \frac{\varepsilon}{\varepsilon_2}}\right] = \frac{C_1}{a^3}$$

$$\Rightarrow \boxed{C_1 = a^3 E_0 \frac{\left(\varepsilon/\varepsilon_2 - 1\right)}{\left(\varepsilon/\varepsilon_2 + 2\right)}} \qquad \text{———} \; (23)$$

$$\therefore \quad \Phi_{in} = -\frac{3}{\left(\varepsilon/\varepsilon_2 + 2\right)} E_0 r \cos\theta \qquad \text{———} \; (24)$$

$$\Phi_{out} = -E_0 r \cos\theta + \left[\frac{\left(\varepsilon/\varepsilon_2 - 1\right)}{\left(\varepsilon/\varepsilon_2 + 2\right)}\right] E_0 a^3 \frac{\cos\theta}{r^2}$$

$$\text{———} \; (25)$$