Light interacting with small particles

1. The spectra of the extinction and scattering cross-sections of a silver nano-sphere ($R = 25$nm) in a homogeneous background medium are plotted in Figure 1 .

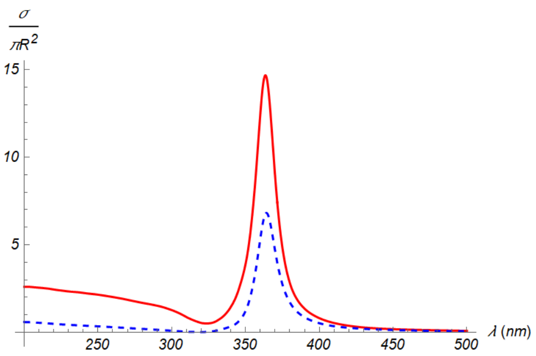

Figure 1: Cross section (normalized by the geometric cross section) of a silver sphere of radius $R = 25$nm in air.

A. Associate the dotted and full lines to the extinction, σ_{ext} and scattering σ_{scat} cross-sections respectively (dotted line: .... cross-section; full line: .... cross-section).

Solution : (dotted line: **scattering** cross-section; full line: **extinction** cross-section).

B. Give the expression for the absorption cross section, σ_{abs}, in terms of σ_{ext} and σ_{scat}.

Solution : For particles of any size and shape, cross sections by definition obey the general relation:

$$\sigma_{\text{abs}} = \sigma_{\text{ext}} - \sigma_{\text{scat}} \ .$$

C. What is remarkable about the size of the cross sections with respect to the geometric size of the sphere ? Do you expect similar behavior to be possible for individual atoms ? (Hint : If you are unsure, come back to the question after answering the next question.)

Solution : The cross sections in fig. 1 can be much larger than the geometric cross section of the particle. This occurs because a resonance phenomenon modifies the Poynting vectors of the fields far beyond the physical boundaries of the particle itself. Given that it is resonance that is the key, and not particle size, a single atom can have a cross section as large as our silver 'meta' atom. Indeed as seen in the next exercise, where the limit size of the cross sections depends on the wavelength, not the particle size.

2. One remarks that the silver sphere modeled in fig. 1 is quite small with respect to the in-medium wavelengths, λ, of all the 'incident' electric fields, $\boldsymbol{E}_{\text{inc}}(\omega)$, considered in the graph. Consequently, one expects the silver particle to be principally described by its

induced electric dipole moment, $\boldsymbol{p}(\omega)$. For a particle with isotropic linear response, $\boldsymbol{p}(\omega)$ is related to the incident field strength, $\boldsymbol{E}_{\rm inc}(\omega)$, via the polarizability, $\alpha(\omega)$, defined by the relation:

$$\boldsymbol{p}(\omega) = \epsilon_0 \varepsilon_b \alpha(\omega) \boldsymbol{E}_{\rm inc}(\omega) \ .$$

From considerations involving the Poynting vector and radiation flux, the extinction and scattering cross sections of an electric dipole scatterer can be expressed in terms of polarizability, $\alpha(\omega)$, as :

$$\sigma_{\rm ext} = k \, {\rm Im}\, m \left\{ \alpha(\omega) \right\} \qquad \sigma_{\rm scat} = \frac{k^4}{6\pi} \left| \alpha(\omega) \right|^2 \ . \tag{1}$$

Energy conservation during a scattering process imposes that the polarizability satisfies the inequality:

$$\frac{k^3}{6\pi} \left| \alpha(\omega) \right|^2 \leq {\rm Im}\, m \left\{ \alpha(\omega) \right\} \ , \tag{2}$$

A. What are the physical dimension of σ and α ? Explain why these are physically reasonable dimensions.

   Solution : σ has the dimensions of surface *i.e.* m^2, while polarizability has the dimensions of volume, m^3.

B. Express the inequality of eq.(2) in terms of cross-sections given in eq.(1). The inequality becomes an equality in the case of scattering in the absence of loss into material degrees of freedom. What does this say about the extinction and scattering cross sections in this case ?

   Solution : Substitution of eq. (1)) in eq. (2)), tells us that:

$$\sigma_{\rm scat} \leq \sigma_{\rm ext}$$

C. Write the complex valued $\alpha(\omega) = \alpha'(\omega) + i\alpha''(\omega)$, (with $\alpha'(\omega)$ and $\alpha''(\omega)$ real valued). Express eq.(2) in terms of α' and α'', and deduce the constraint imposed on the possible values of α''. What constraint does this place on $\sigma_{\rm ext}$?

   Solution : Eq.(2) can be written:

$$\alpha'^2 + \alpha''^2 \leq \frac{6\pi}{k^3} \alpha''(\omega) \ , \tag{3}$$

   and we see that the maximum value of $|\alpha(\omega)|$ is obtained for $\alpha' = 0$, i.e. $\alpha(\omega) = i\alpha''(\omega)$, purely imaginary, the constraint of eq.(3),

$$\alpha'' \leq \frac{6\pi}{k^3} \ .$$

   In this case, $\sigma_{\rm ext} = k \, {\rm Im}\, m \left\{ \alpha(\omega) \right\}$, and the limit of cross section of a dipole scatterer is,

$$\sigma_{\rm ext} \leq \frac{6\pi}{k^2} \ .$$

D. Recalling that the wavenumber is related to the wavelength in the external medium by, $k = 2\pi/\lambda$, use the results of the previous question, and the approximation $\pi \simeq 3$ to find the often stated (but seldom derived) *unitary limit* for a dipole interaction cross section: $\sigma \lesssim \frac{\lambda^2}{2}$.

Solution : With the definition $k = \frac{2\pi}{\lambda}$,

$$\sigma_{\text{ext}} \leq \frac{6\pi\lambda^2}{4\pi^2} \approx \frac{\lambda^2}{2}\,.$$

The value $\sigma_{\text{ext}} \simeq \lambda^2/2$ is is often called the *unitary limit* of cross section that a dipole scatterer cannot surpass. This limitation on mono-mode cross sections plays an important rule in photonics. It is often considered a "quantum" result since the unitary limit first achieved notoriety in quantum scattering theory. Nevertheless, it is a fundamental property of wave scattering theories in general and doesn't require field quantization in its proof (but it does remain true in quantum theories).

3. The *quasi-static* expression for the electric dipolar polarizability of a sphere of volume, V, and dielectric permittivity ε_s, immersed in a background medium of dielectric permittivity, ε_b, can be cast:

$$\alpha_{\text{qs}} \equiv \lim_{\omega\to 0} \alpha(\omega) = 3V\frac{\varepsilon_s - \varepsilon_b}{\varepsilon_s + 2\varepsilon_b}\,. \tag{4}$$

A. Since we expect α_{qs} to be a reasonable approximation for a sphere much smaller than the wavelength, what does fig. 1 tell us about the permittivity of silver around 365nm ?

Solution : Since we are clearly near a resonance, we expect $\text{Re}\{\varepsilon_{\text{Au}}\} \sim -2\varepsilon_b$. so the real part of the permittivity of silver must be negative, which is indeed the case. The denominator of eq. (4) is not zero however since $\text{Im}\{\varepsilon_{\text{Au}}\} \neq 0$

B. A commonly employed model for including 'radiative corrections' to the quasi-static polarizability is given by:

$$\alpha(\omega) \simeq \frac{\alpha_{\text{qs}}}{1 - i\frac{k^3}{6\pi}\alpha_{\text{qs}}}\,. \tag{5}$$

What is the value of $\alpha(\omega)$ when $\alpha_{\text{qs}} \to \infty$. Comment this result based on your results from question 2. Why is this model superior to simply using the quasi-static value for polarizability ?

Solution : When $\alpha_{\text{qs}} \to \infty$ this implies that $\alpha(\omega) \to i\frac{6\pi}{k^2}$ which is the unitary limit that we studied in the previous question.

C. **Free-space electromagnetic Green's function and the electric dipole :** The electromagnetic free-space dyadic Green function can be written :

$$\overleftrightarrow{\boldsymbol{g}}(\boldsymbol{r}) = \frac{e^{i\kappa r}}{4\pi\kappa^2 r^3}\text{P.V.}\left\{(1 - i\kappa r)\left(3\boldsymbol{u}_r\boldsymbol{u}_r - \overleftrightarrow{\mathbb{I}}\right) + \kappa^2 r^2\left(\overleftrightarrow{\mathbb{I}} - \boldsymbol{u}_r\boldsymbol{u}_r\right)\right\} - \frac{\overleftrightarrow{\mathbb{I}}}{3\kappa^2}\delta^3(\boldsymbol{r})\,, \tag{6}$$

where $\boldsymbol{u}_r \equiv \frac{\boldsymbol{r}}{r}$ is the unit vector in the radial direction, $\kappa \equiv \frac{\omega\sqrt{\varepsilon_b\mu_b}}{c} \equiv \frac{2\pi}{\lambda_b}$, is the wavenumber in the external(background) medium, and finally P.V. stands for principal value (associated with a 3D exclusion volume at the origin on account of the field being undefined when $r \to 0$. With $\overleftrightarrow{\boldsymbol{g}}$, one can directly obtain the time harmonic electric field of an oscillating dipole, $\boldsymbol{p}$, oriented along the unit vector $\boldsymbol{n_p}$ (*i.e.* $\boldsymbol{p} = |\boldsymbol{p}|\boldsymbol{n_p}$) and positioned at the coordinate system origin is :

$$\begin{aligned}
\boldsymbol{E}_{\mathrm{p}}(\boldsymbol{r}) &= \frac{\omega^2}{\epsilon_0 c^2} \overleftrightarrow{\boldsymbol{g}}(\boldsymbol{r}) \cdot \boldsymbol{p} \\
&= \mathrm{P.V.} \left\{ \frac{e^{i\kappa r}}{4\pi\varepsilon_b\epsilon_0 r^3} \left[\kappa^2 r^2 \left[\boldsymbol{p}_e - \boldsymbol{u}_r \left(\boldsymbol{u}_r \cdot \boldsymbol{p}_e \right) \right] + (1 - i\kappa r)(3(\boldsymbol{u}_r \cdot \boldsymbol{p})\boldsymbol{u}_r - \boldsymbol{p}) \right] \right\} \\
&\quad - \frac{\boldsymbol{p}}{3\varepsilon_b\epsilon_0} \delta^3(\boldsymbol{r}) \ .
\end{aligned} \tag{7}$$

a) Explain the physical relevance of the $-\frac{\boldsymbol{p}}{3\varepsilon_b\epsilon_0}\delta^3(\boldsymbol{r})$ term in eq.(7) and explain why it is directed in the direction opposite to the dipole, $\boldsymbol{p}$.

Solution :

$$\boldsymbol{E}_{\mathrm{n.f.}}(\boldsymbol{r}) = \frac{e^{i\kappa r}}{4\pi\varepsilon_b\epsilon_0 r^3} \left[3(\boldsymbol{u}_r \cdot \boldsymbol{p})\boldsymbol{u}_r - \boldsymbol{p} \right] - \frac{\boldsymbol{p}}{3\varepsilon_b\epsilon_0} \delta^3(\boldsymbol{r}) \ .$$

The ‘traditional’ near field term is the first of these two terms, and it is called the near field because it the other field contributions when r is small on account of its r^3 dependence; Nevertheless, the delta function term at the position of the dipole can also be thought of as a ‘near’ field since it dominates all others at the position of the dipole, $\boldsymbol{r} = \boldsymbol{0}$.

b) In order to better visualize the dipole field, let us define the z axis to lie along the dipole axis, $\boldsymbol{p} = |\boldsymbol{p}|\boldsymbol{n_p} \longrightarrow |\boldsymbol{p}|\boldsymbol{u}_z$, and adopt spherical coordinates for the dipole field using the fact that $\boldsymbol{u}_z = \cos\theta \boldsymbol{u}_r - \sin\theta \boldsymbol{u}_\theta$. In spherical coordinates, the dipole electric field in eq.(7) is written $\boldsymbol{E}_{\mathrm{p}}(\boldsymbol{r}) = E_r(r,\theta)\boldsymbol{u}_r + E_\theta(r,\theta)\boldsymbol{u}_\theta$, which for $r > 0$ is :

$$E_r(r,\theta) = \frac{|\boldsymbol{p}|\cos\theta}{4\pi\varepsilon_b\epsilon_0} \frac{\exp(i\kappa r)}{r} \kappa^2 \left[\frac{2}{\kappa^2 r^2} - \frac{2i}{\kappa r} \right] \tag{8a}$$

$$E_\theta(r,\theta) = \frac{|\boldsymbol{p}|\sin\theta}{4\pi\varepsilon_b\epsilon_0} \frac{\exp(i\kappa r)}{r} \kappa^2 \left[\frac{1}{\kappa^2 r^2} - \frac{i}{\kappa r} - 1 \right] \ , \tag{8b}$$

where we omit the delta function contribution which plays no role for $r > 0$. **Identify** the near, intermediate, and far fields parts of each of these field components. What do you remark about the far-field component of E_r ?

Solution : The third (last) term of eq. (8b) are the far-field radiative dipole terms that propagate off to infinity

$$\boldsymbol{E}_{\mathrm{i.f.}}(r\boldsymbol{u}_r) = \frac{-i\kappa e^{i\kappa r}}{4\pi\varepsilon_b\epsilon_0 r^2} \left[3(\boldsymbol{u}_r \cdot \boldsymbol{p})\boldsymbol{u}_r - \boldsymbol{p} \right] \ .$$

The second terms of eq. (8a) and eq. (8b) are the intermediate field, and their first terms are the near-field.

Bonus : What does this last point imply for light scattering of unpolarized light by small particles at angles perpendicular to the incident field wave vector $\boldsymbol{k}$? ($\boldsymbol{k}$ must be perpendicular to $\boldsymbol{p} = |\boldsymbol{p}|\boldsymbol{u}_z$ meaning that $\boldsymbol{k}$ lies in the xy-plane.)

Solution : When setting $\theta = \pi/2$ in eq. (8), we see that the far-field is polarized in the $\boldsymbol{u}_\theta$ direction. This means that light scattering from a small particle is linearly polarized. You can easily verify this by using a linear polarizer to verify that light coming from straight overhead at sunset is indeed linearly polarized.

c) The electric field has no ϕ component, but another field in the harmonic electric dipole problem *only* has a ϕ component in spherical coordinates with the expression :

$$F_\phi = \frac{|\boldsymbol{p}|\sin\theta}{4\pi\varepsilon_b\epsilon_0}\frac{\exp(i\kappa r)}{r}\kappa^2\left[-\frac{i}{\kappa r}-1\right]\sqrt{\frac{\epsilon_0\varepsilon_b}{\mu_0\mu_b}}\,, \tag{9}$$

Using your knowledge of this problem to **identify the field**, F_ϕ, and **explain** what role it plays in the oscillating electric dipole.

Solution : The F_ϕ function is the magnetic field associated with the electric dipole. Without having carried out the calculation, there are several indications of this: F_ϕ is orthogonal to the electric field given in eq. (8). Also, F_ϕ has the dimensions of magnetic field due to the presence of the factor $\sqrt{\epsilon_0/\mu_0}$. Yet another indication is that F_ϕ doesn't have a near-field component.

c) The component of the dipole's electric field parallel to $\boldsymbol{p}$ ($E_{||}(r,\theta) \equiv \boldsymbol{n_p}\cdot\boldsymbol{E}_{\mathrm{p}}$) plays an important role in the quantum theory of spontaneous emission and in antenna theory. **Demonstrate that** (hint : easiest to demonstrate using eq.(7) and $\boldsymbol{n_p} = \boldsymbol{u}_z = \cos\theta\boldsymbol{u}_r - \sin\theta\boldsymbol{u}_\theta$) :

$$E_{||}(r,\theta) = \frac{|\boldsymbol{p}|}{4\pi\varepsilon_b\epsilon_0}\frac{\exp(i\kappa r)}{r}\mathrm{P.V.}\left[\kappa^2\sin^2\theta + \frac{1}{r^2}\left(3\cos^2-1\right) - \frac{i\kappa}{r}\left(3\cos^2\theta-1\right)\right]\,, \tag{10}$$

and again identify the *far-field*, *near-field*, and *intermediate-field* contributions.

d) Green function theory tells us that the local density of states (or local density of modes) is related to the *imaginary part* of $E_z(r,\theta)$ in eq.(11). This is indeed possible since even though the real part of E_z diverges as $r\to 0$, $\mathrm{Im}(E_z)$ remains finite. **Use the development of the exponential** for small arguments ($\exp(ix) = 1 + ix - \frac{x^2}{2} + \ldots$) to **verify** that for small values of r :

$$\mathrm{Im}\left[E_z(r,\theta)\right] = \frac{|\boldsymbol{p}|\kappa^3}{4\pi\varepsilon_b\epsilon_0}\mathrm{P.V.}\left[\sin^2\theta + O(r^2)\right]\,. \tag{11}$$

e) The 3D P.V. can be viewed as averaging field over the surface of the exclusion volume, which in this context means that we must average over all possible angles :

$$\mathrm{P.V.}\left[\sin^2\theta\right] \longrightarrow \frac{1}{2}\int_{-1}^{1}\sin^2\theta d(\cos\theta) \longrightarrow \frac{1}{2}\int_{-1}^{1}\left(1-\cos^2\theta\right)d(\cos\theta) = \frac{2}{3}\,, \tag{12}$$

so that one finally obtains :

$$\lim_{r\to 0}\mathrm{Im}\left[E_z(r,\theta)\right] = \frac{|\boldsymbol{p}|\kappa^3}{6\pi\varepsilon_b\epsilon_0}\,. \tag{13}$$

With this result, show by referring back to eq.(7), the important result for local density of states calculations that :

$$\mathrm{Im}\left\{\boldsymbol{n_p}\cdot\overleftrightarrow{\boldsymbol{g}}(\boldsymbol{0})\cdot\boldsymbol{n_p}\right\} = \frac{\kappa}{6\pi}\,. \tag{14}$$

Importance of this result : A spectral expansion of the Green's function and mode counting arguments like those studied in class for black-body radiation, yield the formula for the free space density of states :

$$\rho_{\mathrm{f.s}}(\boldsymbol{r},\omega) = \frac{6\omega}{\pi c^2}\,\mathrm{Im}\left\{\boldsymbol{n_p}\cdot\overleftrightarrow{\boldsymbol{g}}(\boldsymbol{r},\boldsymbol{r})\cdot\boldsymbol{n_p}\right\} = \frac{\omega^2}{\pi^2 c^3}\ , \tag{15}$$

where we used to the result of eq. (14) for the free-space Green's function. The advantage of this formula is that it remains valid for an inhomogeneous environment, provided that one replaces the free space Green's function, $\overleftrightarrow{\boldsymbol{g}}(\boldsymbol{r},\boldsymbol{r})$ by a Green's function, $\overleftrightarrow{\boldsymbol{G}}(\boldsymbol{r},\boldsymbol{r})$, describing the inhomogeneous material environment. In practice this amounts to placing a point-like electric dipole at a given position and determining the field scattered back onto this same position (and in same direction) as dipole emitter. The "local density of states", so determined can be significantly different from the free density of states, $\omega^2/(\pi^2 c^3)$, as has been repeatedly shown by both theory and experiment using nano-structuring of matter near the emitter, or highly reflecting surfaces. Note: The terminology "local" density of states is in reference to the fact that the local density of states is a function of the dipole's position with respect to the material structure modifying the density of states from its free-field value.
