Introduction to Physics of Nanoparticles and Nano structures

Part I: Physics of Nanoparticles **Questions on Module 6**

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1. The time harmonic em fields ($\vec{E}(\vec{x})$, $\vec{H}(\vec{x})$) with time dependence $e^{-i\omega t}$ in a linear isotropic homogeneous medium must satisfy the equations

$$\nabla^2\vec{E} + q^2\vec{E} = 0, \qquad \vec{\nabla}\cdot\vec{E} = 0,$$

$$\nabla^2\vec{H} + q^2\vec{H} = 0, \qquad \vec{\nabla}\cdot\vec{H} = 0,$$

where $q^2 = \omega^2\varepsilon\mu$. In addition the fields must satisfy the relations

$$\vec{\nabla}\times\vec{E} = i\omega\mu\vec{H}, \qquad \vec{\nabla}\times\vec{E} = -i\omega\varepsilon\vec{H}.$$

Show that if $\psi(\vec{x})$ is a scalar field satisfying the scalar wave equation, $\nabla^2\psi + q^2\psi = 0$, then the vector fields $\vec{M}(\vec{x})$ and $\vec{N}(\vec{x})$ satisfy all the equations for the em fields if

$$\vec{M} = \vec{\nabla}\times(\vec{c}\psi(\vec{x})), \qquad \text{and} \quad \vec{N} = \frac{1}{q}\vec{\nabla}\times\vec{N},$$

where $\vec{c}$ is a constant vector (can also be the radial position vector $\vec{r}$).

2. The vector spherical harmonics are defined as

$$\vec{M}_{eml} = \vec{\nabla}\times(\vec{r}\,\psi_{eml}), \qquad \vec{M}_{oml} = \vec{\nabla}\times(\vec{r}\,\psi_{oml}),$$

$$\vec{N}_{eml} = \frac{1}{q}\vec{\nabla}\times(\vec{M}_{eml}), \qquad \vec{N}_{oml} = \frac{1}{q}\vec{\nabla}\times(\vec{M}_{oml}),$$

where

$$\psi_{eml} = z_l(\rho)P_l^m(\cos\theta)\cos m\phi, \qquad \psi_{oml} = z_l(\rho)P_l^m(\cos\theta)\sin m\phi,$$

with $\rho = qr$, $m = 0, 1, \cdots,$ z_l denoting any of the four spherical Bessel functions j_l, y_l, $h_l^{(1)} = j_l + iy_l$, and $h_l^{(2)} = j_l - iy_l$, and P_l^m denoting the *Associated Legendre functions.*

(a) Express the vector spherical harmonics defined above in terms of the components along the unit vectors ($\hat{e}_r$, $\hat{e}_\theta$, $\hat{e}_\phi$) in the spherical polar coordinates.

(b) Using the properties of P_l^m, show that,

$$\int_0^{2\pi} d\phi \int_0^{\pi} d\theta \sin\theta\, \vec{M}_{em'l'}\cdot\vec{M}_{oml} = 0, \qquad \text{for all } m, m', l, l',$$

$$\int_0^{2\pi} d\phi \int_0^{\pi} d\theta \sin\theta\, \vec{N}_{em'l'}\cdot\vec{N}_{oml} = 0, \qquad \text{for all } m, m', l, l',$$

$$\int_0^{2\pi} d\phi \int_0^{\pi} d\theta \sin\theta\, \vec{M}_{om'l'}\cdot\vec{N}_{oml} = 0, \qquad \text{for all } m, m', l, l',$$

$$\int_0^{2\pi} d\phi \int_0^{\pi} d\theta \sin\theta \, \vec{M}_{em'l'} \cdot \vec{N}_{eml} = 0, \qquad \text{for all } m, m', l, l',$$

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$$\int_0^{2\pi} d\phi \int_0^{\pi} d\theta \sin\theta \, \vec{M}_{em'l'} \cdot \vec{M}_{eml} = 0, \qquad \text{for all } m, m', l \neq l',$$

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$$\int_0^{2\pi} d\phi \int_0^{\pi} d\theta \sin\theta \, \vec{N}_{om'l'} \cdot \vec{N}_{oml} = 0, \qquad \text{for all } m, m', l \neq l',$$

(c) Consider a plane x-polarized wave $\vec{E}_i = E_o \hat{e}_x e^{i\vec{q}.\vec{r}}$.
Show that

$$\vec{E}_i = \sum_{l=1}^{\infty} E_l \left[\vec{M}_{o1l}^{(1)} - i\vec{N}_{e1l}^{(1)} \right], \qquad \vec{H}_i = -\frac{q}{\omega\mu} \sum_{l=1}^{\infty} E_l \left[\vec{M}_{e1l}^{(1)} + i\vec{N}_{o1l}^{(1)} \right], \quad \rho = qr,$$

where $E_l = E_o \frac{(2l+1)}{l(l+1)} \, i^l$, and superscript (1) indicates choosing j_l for z_l.

(d) Let $(\vec{E}_s, \vec{H}_s)$ be the em fields scattered by a sphere of radius R with refractive index $N_1 = n_1 + ik_1$ (relative to the medium outside the sphere), when a plane x-polarized wave $\vec{E}_i = E_o \hat{e}_x e^{iqz}$ scatters against the sphere, and $(\vec{E}_1, \vec{H}_1)$ be the em fields inside the sphere.

(i) Show that

$$\vec{E}_s = \sum_{l=1}^{\infty} E_l \left[ia_l \, \vec{N}_{e1l}^{(3)} - b_l \, \vec{M}_{o1l}^{(3)} \right], \qquad \vec{H}_s = \frac{q}{\omega\mu} \sum_{l=1}^{\infty} E_l \left[ib_l \, \vec{N}_{e1l}^{(3)} + a_l \, \vec{M}_{o1l}^{(3)} \right], \quad \rho = qr,$$

$$\vec{E}_1 = \sum_{l=1}^{\infty} E_l \left[c_l \, \vec{M}_{o1l}^{(1)} - id_l \, \vec{N}_{e1l}^{(1)} \right], \qquad \vec{H}_i = -\frac{q_1}{\omega\mu_1} \sum_{l=1}^{\infty} E_l \left[d_l \, \vec{M}_{e1l}^{(1)} + ic_l \, \vec{N}_{o1l}^{(1)} \right], \quad \rho = q_1 r,$$

where $q_1 = qN_1$, and the superscript (3) indicates choosing $h_l^{(1)}$ for z_l. Determine the unknown coefficients a_l, b_l, c_l and d_l using appropriate boundary conditions.

(ii) Find the conditions for exciting the normal modes of the sperical particle.

(iii) Show that the scattering cross-section C_{sca} and the extinction cross sction C_{ext} for the sperical particle are given by

$$C_{sca} = \frac{2\pi}{q^2} \sum_{l=1}^{\infty} (2l+1) \left[|a_l|^2 + |b_l|^2 \right],$$

$$C_{ext} = \frac{2\pi}{q^2} \sum_{l=1}^{\infty} (2l+1)\, Re[a_l + b_l].$$

(iv) For the x-polarized incident plane wave find the amplitude scattering matrix elements S_1, S_2, S_3, and S_4, and then find the relation between Stoke's parameters for the incident and scattered waves.

(v) Using the small ρ expansions for spherical Bessel functions, show that for small size parameter x for a sphere,

$$a_1 = -i\frac{2x^3}{3}\frac{(m^2-1)}{(m^2+2)} - i\frac{2x^5}{5}\frac{(m^2-2)(m^2-1)}{(m^2+2)^2} + \frac{4x^6}{9}\frac{(m^2-1)^2}{(m^2+2)^2} + O(x^7),$$

$$b_1 = -i\frac{x^5}{45}(m^2-1) + O(x^7), \qquad a_2 = -i\frac{x^5}{15}\frac{(m^2-1)}{(2m^2+3)} + O(x^7), \qquad b_2 = O(x^7),$$

where m is the refractive index of the particle relative to that of its surrounding medium.

(vi) Show that accurate to order x^6, the 4×4 scattering matrix (Mueller matrix) is given by

$$\frac{9|a_1|^2}{4q^2r^2}\begin{bmatrix} \frac{1}{2}(\cos^2\theta+1) & \frac{1}{2}(\cos^2\theta-1) & 0 & 0 \\ \frac{1}{2}(\cos^2\theta-1) & \frac{1}{2}(\cos^2\theta+1) & 0 & 0 \\ 0 & 0 & \cos\theta & 0 \\ 0 & 0 & 0 & \cos\theta \end{bmatrix}.$$

(vii) Show that for unpolarized incident light of irradiance I_i, the irradiance of light scattered from a spherical partcile of radius R is

$$I_s = \frac{8\pi^4 N^4 R^6}{\lambda^4 r^2}\frac{|m^2-1|^2}{|m^2+2|^2}(1+\cos^2\theta)\, I_i,$$

where λ is the wavelength in free space and N is the refractive index of the medium surrounding the particle.

(viii) Show that, when the incident light is unpolarized, the degree of polarization for light scattered by a sphere is

$$P = \frac{1-\cos^2\theta}{1+\cos^2\theta}.$$

(ix) Show that accurate to order x^4, the extinction efficiency Q_{ext} and the scattering efficiency Q_{sca} are given by

$$Q_{ext} = 4x\, Im\left[\frac{(m^2-1)}{(m^2+2)}\left(1 + \frac{x^2}{15}\frac{(m^2-1)}{(m^2+1)}\frac{(m^4+27m^2+38)}{2m^2+3)}\right)\right] + \frac{8x^4}{3}\, Re\left[\frac{(m^2-1)^2}{(m^2+2)^2}\right],$$

$$Q_{sca} = \frac{8x^4}{3} \frac{|m^2-1|^2}{|m^2+2|^2}.$$

3. Using electrostatic approximation, show that the effective polarizability α for a spherical particle of radius R and dielectric permittivity ε_1 surrounded by a nonabsorbing medium of dielectric permittivity ε_m is given by

$$\alpha = 4\pi R^3 \frac{(\varepsilon_1 - \varepsilon_m)}{(\varepsilon_1 + 2\varepsilon_m)}.$$

   Thereby show that the scattering and extinction cross sections arte given by

$$C_{sca} = \pi R^2 \frac{8x^4}{3} \frac{|\varepsilon_1 - \varepsilon_m|^2}{|\varepsilon_1 + 2\varepsilon_m|^2},$$

$$C_{ext} = \pi R^2 \, 4x \, Im \left[\frac{\varepsilon_1 - \varepsilon_m}{\varepsilon_1 + 2\varepsilon_m} \right]$$

   where x is the size parameter defined as $x = 2\pi R\sqrt{\varepsilon_m}/\lambda$, with λ denoting the wavelength in vacuum.

4. For N identical spheres of volume v_{sph} each, embedded in a medium of dielectric function ϵ_m, the Clausius-Mossotti formula gives the effective dielectric function ϵ_M for the system as

$$\frac{(\epsilon_M - \epsilon_m)}{(\epsilon_M + 2\epsilon_m)} = f\alpha, \qquad \text{(Maxwell} - \text{Garnet theory)},$$

   where $f \equiv nv_{sph}$, $n \equiv N/V$ being the density of spheres.

5. Consider an ellipsoidal particle of semiaxes $a > b > c$. Choose a along x-axis, b along y-axis and c along z-axis.

   (a) Using electrostatic approximation, and ellipsoidal coordinates, show that (consult Bohren and Huffmann), if the dielectric permittivity of the particle is ε_1 and that of the surrounding nonabsorbing medium is ε_m (assume $\mu = 1$ for all the media), then the effective polarizability α_j ($j = x, y, z$) for the particle along the j^{th} principal axis is given by

$$\alpha_j = 4\pi abc \frac{(\varepsilon_1 - \varepsilon_m)}{3\varepsilon_m + 3L_j(\varepsilon_1 - \varepsilon_m)},$$

   where the so called *geometrical factor* L_js are defined by ($x \equiv 1$, $y \equiv 2$, $z \equiv 3$)

$$L_1 = \frac{abc}{2} \int_0^\infty \frac{dq}{(a^2+q)f(q)}, \qquad L_2 = \frac{abc}{2} \int_0^\infty \frac{dq}{(b^2+q)f(q)}, \qquad L_3 = \frac{abc}{2} \int_0^\infty \frac{dq}{(c^2+q)f(q)},$$

   with $f(q) = \sqrt{(a^2+q)(b^2+q)(c^2+q)}$.

   (b) Show that $L_1 + L_2 + L_3 = 1$.

(c) Show that for a prolate (cigar shaped) sphereoid, for which $b = c$,

$$L_1 = g^2(e)\left[-1 + \frac{1}{2e}\ln\frac{1+e}{1-e}\right],$$

where $e^2 = 1 - b^2/a^2$ and $g(e) = \sqrt{1-e^2}/e$.

(d) Show that for a oblate (pancake shaped) sphereoid, for which $b = a$,

$$L_1 = \frac{g(e)}{2e^2}\left[\frac{\pi}{2} - \tan^{-1} g(e)\right] - \frac{g^2(e)}{2},$$

where $e^2 = 1 - c^2/a^2$ and $g(e) = \sqrt{1-e^2}/e$.

(e) Show that for a randomly oriented ellipsoid,

$$\langle C_{abs}\rangle = \frac{q}{3}\, Im\,[\alpha_1 + \alpha_2 + \alpha_3]\,, \qquad \langle C_{sca}\rangle = \frac{q^4}{18\pi}\left[|\alpha_1|^2 + |\alpha_2|^2 + |\alpha_3|^2\right].$$

6. Consider a coated ellipsoidal particle of semiaxes $a_1 > b_1 > c_1$ for the inner (core) ellipsoid with dielectric permittivity ε_1, and $a_2 > b_2 > c_2$ for the outer (coat) ellipsoid with dielectric permittivity ε_2, placed in a nonabsorbing medium of dielectric permittivity ε_m (assume $\mu = 1$ for all the media).

(a) Using the electrostatic approximation, and ellipsoidal coordinates (same as in the previous problem, only the boundary conditions are to be implemented at the additional interface between the core and the coat), show that the effective polarizability α_3 (along z-axis) for the particle is

$$\alpha_3 = \frac{4\pi abc}{3}\,\frac{(\varepsilon_2 - \varepsilon_m)[\varepsilon_2 + (\varepsilon_1 - \varepsilon_2)(L_3^{(1)} - fL_3^{(2)})] + f(\varepsilon_1 - \varepsilon_2)}{[\varepsilon_2 + (\varepsilon_1 - \varepsilon_2)(L_3^{(1)} - fL_3^{(2)})][\varepsilon_m + (\varepsilon_2 - \varepsilon_m)L_3^{(2)}] + fL_3^{(2)}\varepsilon_2(\varepsilon_1 - \varepsilon_2)},$$

where $f = (a_1b_1c_1)/(a_2b_2c_2)$, the volume fraction of the core, and

$$L_3^{(k)} = \frac{a_kb_kc_k}{2}\int_0^\infty \frac{dq}{(c_k^2 + q)f_k(q)},$$

with $f_k(q) = \sqrt{(a_k^2 + q)(b_k^2 + q)(c_k^2 + q)}$, $(k = 1, 2)$.

(b) Reduce the result above to the case of a coated sphere for which $\alpha_1 = \alpha_2 = \alpha_3 = \alpha$, and then show that the particle becomes invisible (i.e., $\alpha = 0$) if the coating material is such that

$$f\,\frac{(\varepsilon_1 - \varepsilon_2)}{(\varepsilon_1 + 2\varepsilon_2)} = \frac{(\varepsilon_m - \varepsilon_2)}{(\varepsilon_m + 2\varepsilon_2)}.$$

(c) Reduce the result above further to the case of a coated sphere with ultra thin coating, by taking $a_2 = a_1 + d$ where the coating thickness d is very small compared with a_2.

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