PHYS2202 Nonlinear Optics
Problem Set 2 solutions

1. (20 points) **Local field factors**

   We noted in lecture that for the general case of non-spherical symmetry, the local electric field, $\vec{E}^{(\mathrm{loc})}$, can be written in terms of the macroscopic electric field, $\vec{E}$ and the polarization, $\vec{P}$ as

   $$\vec{E}^{(\mathrm{loc})} = \vec{E} + \frac{1}{\epsilon_0}\overleftrightarrow{L}\cdot\vec{P}.$$

   (*Note that the ppt handout has an error; $1/\epsilon_0$ is replaced in the notes by 4π, a relic from writing the equation in my notes in gaussian units rather than SI units.) We determined the value of $\overleftrightarrow{L}$ by a *mean field* approximation in which we represent the medium, which in reality consists of discrete atomic or molecular units, by a continuous medium. If we assumed that the system has spherical symmetry (or more generally is isotropic), we were able to calculate that the tensor $\overleftrightarrow{L}$ reduces to $\overleftrightarrow{L} = L\mathbf{1} = \frac{1}{3}\mathbf{1}$ ($\mathbf{1}$ is the identity matrix). The local field factor is then the same in all directions and given by

   $$f(\omega) = 1 + (\epsilon_r - 1)L,$$

   where ϵ_r is the relative permittivity.

   Given the dramatic implications of the local field factor in nonlinear optics, it is important to consider systems that are not isotropic. Indeed, in the case of anisotropic systems, the $\overleftrightarrow{L}$ takes different forms. (Fortunately, in the case of a linear relationship between the polarization and the local electric field, $\overleftrightarrow{L}$ can always be written in a diagonal form.) In general, for molecules with elongated or oblate shape, one can use ellipsoidal cavities with semiaxes a_1, a_2, and a_3, and one finds that

   $$L_i = \frac{a_1 a_2 a_3}{2}\int_0^\infty \frac{1}{(s+a_i^2)\sqrt{(s+a_1^2)(s+a_2^2)(s+a_3^2)}}ds,$$

   which can be evaluated numerically.

   Here we will just investigate molecular crystals of closely packed molecules of simple symmetry.

   (a) Suppose that the we are dealing with molecules that are rod-like (having a cylindrical form with radius r much smaller than the length l).

      i. Calculate the elements of the matrix $\overleftrightarrow{L}$.

         For the rod-like molecule, we carve out a cylindrical cavity. For an electric field along the long axis, there is a surface charge at the ends given by $\sigma = -\vec{P}\cdot\hat{n}$, where $\hat{n}$ is the surface normal vector pointing out of the cavity. For a long, rod-like molecule, this then just looks like point charges at each end of the cavity (the finite extent of the charge doesn't matter if it is far away) with charge $q = \sigma A = \pm P\pi r^2$. Since there are two point charges, the electric field produced at the center of the cavity is just of magnitude

         $$E^{(\mathrm{cav})} = 2\frac{1}{4\pi\epsilon_0}\frac{q}{(l/2)^2} = \frac{2}{\pi\epsilon_0}\frac{(\pi r^2 P)}{l^2} = \frac{2r^2}{\epsilon_0 l^2}P. \tag{1}$$

In the limit that $r/l \to 0$, we get

$$\lim_{r/l \to 0} E^{(\text{cav})} = 0, \tag{2}$$

so that

$$\lim_{r/l \to 0} L_{\parallel} = \epsilon_0 \left[\lim_{r/l \to 0} E_{\parallel}^{(\text{cav})} \right] / P_{\parallel} = 0 \tag{3}$$

Suppose instead that we apply an electric field perpendicular to the long axis of the cylindrical cavity. The surface charge on the curved surfaces of the cavity is

$$\sigma\left(\phi\right) = -\vec{P} \cdot \hat{n} = -P\cos\phi, \tag{4}$$

where ϕ is the azimuthal angle. To determine the field that this produces at the center of the cavity, we can treat the surface charge as a continuous distribution of infinite line charges (infinity is a good approximation to a finite line charge when we are near the line charge as is the case here for small r). The field a distance r from an infinite line charge is, per application of Gauss's law, of magnitude

$$E_{\text{line}} = \frac{\lambda}{2\pi\epsilon_0} \frac{1}{s}. \tag{5}$$

Here, the line charge is azimuthally varying: $\lambda\left(\phi\right) = \sigma\left(\phi\right) r d\phi = Pr\cos\phi d\phi$. The total electric field at the center of the cavity only has a component along $\vec{P}$ due to symmetry (there is an equal amount of charge at $\phi + \pi$ as at ϕ). Its magnitude is given by just integrating

$$\vec{E}^{(\text{cav})} \cdot \hat{P} = \int_{\phi=0}^{2\pi} \frac{Pr\cos\phi d\phi}{2\pi\epsilon_0} \frac{1}{r} \cos\phi = \frac{P}{2\pi\epsilon_0} \int_{\phi=0}^{2\pi} \cos^2\phi \, d\phi = \frac{1}{2\epsilon_0} P. \tag{6}$$

We now see that $L_{\perp} = \frac{1}{2}$. If we call the long axis the z axis, the tensor $\overleftrightarrow{L}$ for the rod-like molecule is

$$\overleftrightarrow{L}_{\text{rod}} = \begin{pmatrix} 1/2 & 0 & 0 \\ 0 & 1/2 & 0 \\ 0 & 0 & 0 \end{pmatrix}. \tag{7}$$

  ii. To realize the largest local field factor, in what direction should the polarization of the electric field be?
  In this case, we should choose $\vec{E}$ perpendicular to the long axis.
  iii. What are the values of the largest and smallest local field factor if $\epsilon_r = 4$.

The local field factor is just $f\left(\omega\right) = 1 + \left(\epsilon_r\left(\omega\right) - 1\right) L$, so the smallest local field factor will be for $\vec{E}$ along z, for which $f(\omega) = 1$. The largest value will be

$$f_{\text{max}} = 1 + (4 - 1)(1/2) = 2.5. \tag{8}$$

(b) Answer the preceding questions for molecules that have a disk-like form (having a cylindrical form but with $r \gg l$).

  i. The idea is exactly the same. Now, for $\vec{E}$ along the axis normal to the planes of the disk (again, we call this the z axis), the surface charge density for the cavity is $\sigma = -\vec{P} \cdot \hat{n} = \mp P$. At the center of the disk, the two planar charge distributions look like infinite planes of charge density $\pm\sigma$. This just looks like

a capacitor; the field magnitude is just $E^{(\text{cav})} = \sigma/\epsilon_0 = P/\epsilon_0$. Note that this is constant regardless of how thin the disk may be. We see that in this case $L_{||} = 1$. For an electric field perpendicular to the z axis, the situation is exactly the same as for the cylinder, except that we now have only a circumferencial line charge, and this line charge has vanishing density in the limit that the disk thickness goes to zero. Therefore, $\lim_{l \to 0} E^{(\text{cav})} = 0$ and so $L_\perp = 0$. A little more quantitatively, our differential charge element is $dq\,(\cos\phi) = \sigma\,(\theta)\,lr\,d\phi = -\vec{P}\cdot\hat{n}\,(\cos\phi)\,lr\,d\phi = -Plr\cos\phi\,d\phi$, for which

$$E = \vec{E}\cdot\hat{P} = \frac{Plr}{4\pi\epsilon_0 r^2}\int_0^{2\pi}\cos^2\phi\,d\phi = \frac{Pl}{4\epsilon_0 r}. \tag{9}$$

As expected, this goes to zero as $l/r \to 0$.

Our $\overset{\leftrightarrow}{L}$ matrix is then

$$\overset{\leftrightarrow}{L}_{\text{disk}} = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix}. \tag{10}$$

ii. To realize the largest local field factor, in what direction should the polarization of the electric field be?

In this case, we should choose $\vec{E}$ along the z axis.

iii. What are the values of the largest and smallest local field factor if $\epsilon_r = 4$.

The largest value will be

$$f_{\text{max}} = 1 + (4-1)(1) = 4. \tag{11}$$

(c) Everything else being equal (for example, molecules that pack with the same number density), for what shape molecule (spherical, rod-like, or disk-like) do we expect to yield a molecular crystal with the largest local field factor?

We see that the largest local field factor is obtained along the short axis of the disk. Note that our calculations of the polarizabilities α_{ii} of molecules with the shapes discussed here are basically the inverse of the tensor elements L_{ii}. For example, while the rod is highly polarizable along z and not so along x and y, the $L_{zz}^{(\text{rod})} = 0$. Likewise, $L_{xx}^{(\text{rod})} = L_{yy}^{(\text{rod})}$ is 3/2 times that of a crystal of spherical molecules, whereas the polarizability of the rod in the radial direction is 2/3 that of the spherical molecule.