Physics 712
Chapter 3 Problems

2. [10] A hydrogen atom in the 2P\textsubscript{z} state has charge density given by

\[ \rho(x) = q \delta^3(x) - \frac{qr^2}{32 \pi a^6} e^{-r/a} \cos^2 \theta \]

Show that this has no \(l = 0\) or \(l = 1\) multipole moment, but it does have an \(l = 2\) moment. Find the leading order contribution to the potential at large \(r\).

The multipole moments are given by

\[ q_{lm} = \int r' \rho(x) Y_{lm}^*(\theta, \phi) d^3x \]

Because of the factor of \(r'\), the delta function only contributes to \(l = m = 0\), to which it contributes

\[ q \int \delta^3(x) Y_{00}^* d^3x = q Y_{00}^* = q/\sqrt{4\pi} \].

A quick way to do the other term is to note (from quantum problem 7.5 again) that \(\cos^2 \theta = \frac{2}{3} \sqrt{\pi} Y_{00}(\theta, \phi) + \frac{4}{3} \sqrt{\frac{2}{\pi}} Y_{20}(\theta, \phi)\). We therefore have

\[ q_{lm} = \int r' \rho(x) Y_{lm}^*(\theta, \phi) d^3x \]

\[ = \frac{q}{\sqrt{4\pi}} \delta_{l0} \delta_{m0} - \frac{q}{32 \pi a^6} \int Y_{lm}^*(\theta, \phi) \left[ \frac{2}{3} \sqrt{\pi} Y_{00}(\theta, \phi) + \frac{4}{3} \sqrt{\frac{2}{\pi}} Y_{20}(\theta, \phi) \right] d\Omega \int_0^\infty r' r^2 e^{-r/a} r^2 dr . \]

We can then use the orthonormality of the spherical harmonics to simplify this to

\[ q_{lm} = \frac{q}{\sqrt{4\pi}} \delta_{l0} \delta_{m0} - \frac{q}{32 \pi a^6} \left( \frac{2}{3} \sqrt{\pi} \delta_{l0} \delta_{m0} + \frac{4}{3} \sqrt{\frac{2}{\pi}} \delta_{l2} \delta_{m0} \right) a^{l+5}(l+4)! \]

\[ = \frac{q}{\sqrt{4\pi}} \delta_{l0} \delta_{m0} - \frac{q a^2}{32 \pi a^6} 2 \cdot 24 \sqrt{\pi} \delta_{l0} \delta_{m0} - \frac{q a^7}{32 \pi a^6} 720 \sqrt{\pi} \delta_{l2} \delta_{m0} \]

\[ = \left( \frac{q}{\sqrt{4\pi}} - \frac{q}{2\sqrt{\pi}} \right) \delta_{l0} \delta_{m0} - \frac{6 \sqrt{5} qa^2}{\sqrt{\pi}} \delta_{l2} \delta_{m0} = -\frac{\sqrt{5} qa^2}{\sqrt{\pi}} \delta_{l2} \delta_{m0} . \]

Not only did we find that the \(l = 2\) is the first non-vanishing contribution, it is the only contribution. Hence outside the charge distribution, the potential is

\[ \Phi(x) = \frac{1}{\varepsilon_0} \sum_{l=0}^{\infty} \frac{1}{2l+1} r^{-l-1} \sum_{m=-l}^{l} q_{lm} Y_{lm}(\theta, \phi) = \frac{q_{20}}{5 \varepsilon_0 r^3} Y_{20}(\theta, \phi) = -\frac{6qa^2}{\varepsilon_0 \sqrt{5\pi r^3}} Y_{20}(\theta, \phi) . \]

You can, if you wish, then substitute in the explicit form \(Y_{20}(\theta, \phi) = \sqrt{\frac{5}{4\pi}} \left( \frac{1}{2} \cos^2 \theta - \frac{1}{2} \right)\) to write this as

\[ \Phi(x) = \frac{3qa^2}{2\pi \varepsilon_0 r^3} (1 - 3 \cos^2 \theta) . \]
3. [15] Consider the three molecules at right. In each case, find only the leading multipole moment (smallest \( l \)), and then find the potential far from the molecule, keeping only the leading term. Assume the \( z \)-direction is to the right and the \( x \)-direction is up. Assume that any gray atom has charge \(-2q\), any white atom has charge \(+q\), and any black atom has charge \(+4q\), and all bonds have length \( a \). The bond angle is \( \alpha \) for the middle molecule; for the last one it is 180.

For a discrete set of charges, the charge density is \( \rho(x) = \sum_i q_i \delta(x - x_i) \), and therefore, the multipole moments will be

\[
q_{lm} = \int r' Y^*_{lm}(\theta, \phi) \rho(x) d^3x = \sum_i q_i r'_i Y^*_{lm}(\theta_i, \phi_i)
\]

Let’s start with the first one, which I’ll call OH\(^{-}\). If we put the gray atom at the origin (\( r = 0 \)), then the white one will be at \( r = a \) and \( \theta = 0 \). The first multipole will be

\[
q_{00} = \sum_i q_i Y^*_{00}(\theta_i, \phi_i) = \frac{1}{\sqrt{4\pi}} \sum_i q_i = \frac{1}{\sqrt{4\pi}} (-2q + q) = -\frac{q}{\sqrt{4\pi}}
\]

Since this is non-vanishing, it’s the leading order term, and hence the potential is given by

\[
\Phi_{\text{OH}^{-}}(x) = \frac{q_{00}}{\varepsilon_0 (2 \cdot 0 + 1) r} Y_{00}(\theta, \phi) = -\frac{q}{\varepsilon_0 r \sqrt{4\pi}} = \frac{q}{4\pi \varepsilon_0 r}
\]

The second one, which I’ll call H\(_2\)O, has no net charge, so clearly it will have no \( l = 0 \) component. Let’s put the central atom at the origin, then it will not contribute to any of the higher multipole moments because of the factor of \( r^l \). The two white atoms are both at polar angle \( \theta = \frac{1}{2} \alpha \), and the azimuthal angle is \( \phi = 0 \) for one and \( \phi = \pi \) for the other. We therefore would have, for \( l > 0 \),

\[
q_{lm} = qa' \left[ Y^*_{lm}(\frac{1}{2} \theta, 0) + Y^*_{lm}(\frac{1}{2} \theta, \pi) \right].
\]

For \( l = 1 \), this works out to

\[
q_{10} = qa \left[ Y^*_{10}(\frac{1}{2} \alpha, 0) + Y^*_{10}(\frac{1}{2} \alpha, \pi) \right] = qa \sqrt{\frac{3}{4\pi}} \left[ \cos \left( \frac{1}{2} \alpha \right) + \cos \left( \frac{1}{2} \alpha \right) \right] = \frac{3}{4\pi} qa \cos \left( \frac{1}{2} \alpha \right),
\]

\[
q_{1,\pm1} = qa \left[ Y^*_{1,\pm1}(\frac{1}{2} \alpha, 0) + Y^*_{1,\pm1}(\frac{1}{2} \alpha, \pi) \right] = \mp qa \sqrt{\frac{3}{8\pi}} \left[ \sin \left( \frac{1}{2} \alpha \right) + \sin \left( \frac{1}{2} \alpha \right) e^{\pm i\pi} \right] = 0.
\]

So there is only one term to this order, and the potential is, to leading order:

\[
\Phi_{\text{H}_2\text{O}}(x) = \frac{q_{10}}{\varepsilon_0 (2 \cdot 1 + 1) r^2} Y_{10}(\theta, \phi) = \frac{qa}{3\varepsilon_0 r^2} \sqrt{\frac{3}{4\pi}} \cos \left( \frac{1}{2} \alpha \right) \frac{3}{\sqrt{4\pi}} \cos \theta = \frac{qa \cos \left( \frac{1}{2} \alpha \right) \cos \theta}{2\pi \varepsilon_0 r^2}.
\]

For our final molecule, which I’ll call CO\(_2\), the total charge is again zero, so \( q_{00} = 0 \). For the higher multipoles, the gray atoms are at \( r = a \) and \( \theta = 0 \) or \( \theta = \pi \), so the multipoles are given by
\[ q_{lm} = -2qa' \left[ Y^*_{lm}(0,\theta) + Y^*_{lm}(\pi,\theta) \right]. \]

One disturbing thing about this expression is that the azimuthal angle is ambiguous. Fortunately, the spherical harmonics vanish at \( \theta = 0 \) and \( \theta = \pi \) unless \( l = 0 \), and for \( l = 0 \), the terms have no azimuthal dependence, so it doesn’t matter. Indeed, we have an explicit formula for the spherical harmonics at \( \theta = 0 \), and we can use parity to get it at \( \theta = \pi \), so it turns out

\[
q_{lm} = -2qa' \sqrt{\frac{2l+1}{4\pi}} \left[ 1 + (-1)^l \right] \delta_{m0} = \begin{cases} -2qa' \sqrt{(2l+1)/\pi} & m = 0, l \text{ even} \\ 0 & \text{otherwise} \end{cases}
\]

This applies only for \( l > 0 \). The first non-zero term is \( l = 2 \), so we have

\[
q_{20} = -2qa^2 \sqrt{\frac{5}{\pi}}
\]

The potential far away is then

\[
\Phi_{\text{CO}_2}(x) = \frac{q_{20}}{\epsilon_0 (2 \cdot 2 + 1)r^3} Y_{20}(\theta,\phi) = \frac{-2qa^2}{5\epsilon_0 r^3} \sqrt{\frac{5}{\pi}} \sqrt{\frac{5}{4\pi}} (3\cos^2 \theta - 1) = \frac{qa^2}{2\pi \epsilon_0 r^3} (1 - 3\cos^2 \theta).
\]