Physics 712
Chapter 3 Problems

2. [10] A hydrogen atom in the 2P$_z$ state has charge density given by

$$\rho(\mathbf{x}) = q\delta^3(\mathbf{x}) - \frac{qr^2}{32\pi a^5} e^{-r/a} \cos^2\theta$$

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

$$q_{lm} = \int r^l \rho(\mathbf{x}) Y_{lm}^*(\theta,\phi)\, d^3\mathbf{x}$$

Because of the factor of r^l, the delta function only contributes to $l = m = 0$, to which it contributes $q\int \delta^3(\mathbf{x}) Y_{00}^* d^3\mathbf{x} = qY_{00}^* = q\big/\sqrt{4\pi}$. A quick way to do the other term is to note (from quantum problem 7.5 again) that $\cos^2\theta = \frac{2}{3}\sqrt{\pi}Y_{00}(\theta,\phi) + \frac{4}{3}\sqrt{\frac{\pi}{5}}Y_{20}(\theta,\phi)$. We therefore have

$$q_{lm} = \int r^l \rho(\mathbf{x}) Y_{lm}^*(\theta,\phi)\, d^3\mathbf{x}$$
$$= \frac{q}{\sqrt{4\pi}}\delta_{l0}\delta_{m0} - \frac{q}{32\pi a^5}\int Y_{lm}^*(\theta,\phi)\left[\tfrac{2}{3}\sqrt{\pi}Y_{00}(\theta,\phi) + \tfrac{4}{3}\sqrt{\tfrac{\pi}{5}}Y_{20}(\theta,\phi)\right] d\Omega \int_0^\infty r^l r^2 e^{-r/a} r^2 dr\,.$$

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

$$q_{lm} = \frac{q}{\sqrt{4\pi}}\delta_{l0}\delta_{m0} - \frac{q}{32\pi a^5}\left(\tfrac{2}{3}\sqrt{\pi}\delta_{l0}\delta_{m0} + \tfrac{4}{3}\sqrt{\tfrac{\pi}{5}}\delta_{l2}\delta_{m0}\right) a^{l+5}(l+4)!$$
$$= \frac{q}{\sqrt{4\pi}}\delta_{l0}\delta_{m0} - \frac{qa^5 2\cdot 24\sqrt{\pi}}{32\pi a^5 3}\delta_{l0}\delta_{m0} - \frac{qa^7 4\cdot 720\sqrt{\pi}}{32\pi a^5 3\sqrt{5}}\delta_{l2}\delta_{m0}$$
$$= \left(\frac{q}{\sqrt{4\pi}} - \frac{q}{2\sqrt{\pi}}\right)\delta_{l0}\delta_{m0} - \frac{6\sqrt{5}qa^2}{\sqrt{\pi}}\delta_{l2}\delta_{m0} = -6\sqrt{\frac{5}{\pi}}qa^2\delta_{l2}\delta_{m0}\,.$$

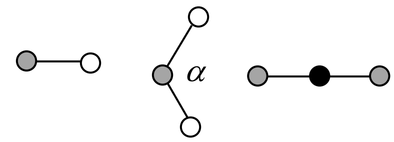
Not only did we find that the $l = 2$ is the first non-vanishing contribution, it is the *only* contribution. Hence outside the charge distribution, the potential is

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

You can, if you wish, then substitute in the explicit form $Y_{20}(\theta,\phi) = \sqrt{\frac{5}{4\pi}}\left(\frac{3}{2}\cos^2\theta - \frac{1}{2}\right)$ to write this as

$$\Phi(\mathbf{x}) = \frac{3qa^2}{2\pi\varepsilon_0 r^3}\left(1 - 3\cos^2\theta\right).$$

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 -2*q*, any white atom has charge +*q*, and any black atom has charge +4*q*, and all bonds have length *a*. The bond angle is α for the middle molecule; for the last one it is 180.



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

$$q_{lm} = \int r^l Y_{lm}^*(\theta,\phi)\rho(\mathbf{x})\,d^3\mathbf{x} = \sum_i q_i r_i^l Y_{lm}^*(\theta_i,\phi_i)$$

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

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

The second one, which I'll call H_2O, 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 $l > 0$,

$$q_{lm} = qa^l\left[Y_{lm}^*\left(\tfrac{1}{2}\theta,0\right) + Y_{lm}^*\left(\tfrac{1}{2}\theta,\pi\right)\right].$$

For $l = 1$, this works out to

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

$$q_{1,\pm1} = qa\left[Y_{1,\pm1}^*\left(\tfrac{1}{2}\alpha,0\right) + Y_{10}^*\left(\tfrac{1}{2}\alpha,\pi\right)\right] = \mp qa\sqrt{\frac{3}{8\pi}}\left[\sin\left(\tfrac{1}{2}\alpha\right) + \sin\left(\tfrac{1}{2}\alpha\right)e^{\mp i\pi}\right] = 0.$$

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

$$\Phi_{\mathrm{H_2O}}(\mathbf{x}) = \frac{q_{10}}{\varepsilon_0(2\cdot 1+1)r^2}Y_{10}(\theta,\phi) = \frac{qa}{3\varepsilon_0 r^2}\sqrt{\frac{3}{\pi}}\cos\left(\tfrac{1}{2}\alpha\right)\sqrt{\frac{3}{4\pi}}\cos\theta = \frac{qa\cos\left(\tfrac{1}{2}\alpha\right)\cos\theta}{2\pi\varepsilon_0 r^2}.$$

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

$$q_{lm} = -2qa^l \left[Y_{lm}^*(0,?) + Y_{lm}^*(\pi,?) \right].$$

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

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

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

$$\Phi_{CO_2}(\mathbf{x}) = \frac{q_{20}}{\varepsilon_0 (2 \cdot 2 + 1) r^3} Y_{20}(\theta, \phi) = \frac{-2qa^2}{5\varepsilon_0 r^3} \sqrt{\frac{5}{\pi}} \frac{1}{4} \sqrt{\frac{5}{\pi}} \left(3\cos^2\theta - 1 \right) = \frac{qa^2}{2\pi\varepsilon_0 r^3} \left(1 - 3\cos^2\theta \right).$$