Dipole Matrix Elements

We really need to get good at the so called "dipole matrix elements." In a few weeks we'll learn how to do these in general. For now we'll settle for understanding some of their symmetries. The dipole matrix elements are defined to be,

$$\langle n,\ell,m|\vec{r}\,|n',\ell',m'\rangle = \langle n,\ell,m|x|n',\ell',m'\rangle\hat{i} + \langle n,\ell,m|y|n',\ell',m'\rangle\hat{j} + \langle n,\ell,m|z|n',\ell',m'\rangle\hat{k}.$$

Let's look at the x term, $\langle x\rangle \equiv \langle n,\ell,m|x|n',\ell',m'\rangle = \langle n,\ell,m|r\sin\theta\cos\phi|n',\ell',m'\rangle$.

In terms of the spherical harmonics, $\langle x\rangle = \int R_{n\ell}^{*}R_{n'\ell'}r^{3}\,dr\int Y_{\ell}^{m*}Y_{\ell'}^{m'}\sin\theta\cos\phi\,d\Omega$.

This radial integral will be the same for x, y, and z so let's just write it as,

$$\langle x\rangle = \Re(n,n',\ell,\ell')\int Y_{\ell}^{m*}Y_{\ell'}^{m'}\sin\theta\cos\phi\,d\Omega.$$

The spherical harmonics can be written in terms of the associated Legendre functions and exponentials in ϕ as in eq. 4.32

$$\langle x\rangle = \Re C(\ell,\ell',m,m')\int P_{\ell}^{m*}(\cos\theta)P_{\ell'}^{m'}(\cos\theta)\sin\theta d(\cos\theta)\int_{0}^{2\pi} e^{-im\phi}(\cos\phi)e^{im'\phi}\,d\phi,$$

$$\langle x\rangle = \Re\Theta(\ell,\ell',m,m')\int_{0}^{2\pi} e^{-im\phi}(\cos\phi)e^{im'\phi}\,d\phi \text{ where}$$

$$\Theta(\ell,\ell',m,m') \equiv C(\ell,\ell',m,m')\int P_{\ell}^{m*}(\cos\theta)P_{\ell'}^{m'}(\cos\theta)\sin\theta d(\cos\theta)$$

Writing cosϕ in terms of complex exponentials,

$$\langle x\rangle = \Re\Theta\int_{0}^{2\pi} e^{-im\phi}\left(\frac{e^{i\phi}+e^{-i\phi}}{2}\right)e^{im'\phi}\,d\phi = \Re\Theta\tfrac{1}{2}\left(\int_{0}^{2\pi} e^{i(m'-m+1)\phi}\,d\phi + \int_{0}^{2\pi} e^{i(m'-m-1)\phi}\,d\phi\right)$$

The ϕ integrals are delta functions, $\langle x\rangle = \Re\Theta\pi\left(\delta_{m',m-1}+\delta_{m',m+1}\right)$.

So, $\langle x\rangle$ only has a value when m' = m ± 1. Similarly, for $\langle y\rangle$. For $\langle z\rangle$,

$$\langle z\rangle = \Re\Theta\int_{0}^{2\pi} e^{-im\phi}e^{im'\phi}\,d\phi = \Re\Theta\int_{0}^{2\pi} e^{i(m'-m)\phi}\,d\phi = \Re\Theta 2\pi\delta_{m',m}.$$

In summary, you will only get values for $\langle x\rangle$ and $\langle y\rangle$ only when m' = m ± 1 and you will only get values for $\langle z\rangle$ when m' = m.