Chem 2430 Answers HW # 4

1) Orthonality of $e^{im\phi}$ and $e^{in\phi}$

$$\langle m|n\rangle = \int_0^{2\pi} e^{i(n-m)\phi}\, d\phi = \left.\frac{e^{i(n-m)\phi}}{n-m}\right|_0^{2\pi} = 0,\ n \neq m.$$

2) $$\rho = r^2(2-r)^2 e^{-r} = r^2(4-4r+r^2)e^{-r} = (4r^2-4r^3+r^4)e^{-r}$$

$$\partial\rho/\partial r = [8r-12r^2+4r^3-4r^2+4r^3-r^4]e^{-r} = 0$$

$$8-16r+8r^2-r^3 = 0 \quad | \quad \text{Extrema } r = 3-\sqrt{5},\ 2,\ 3+\sqrt{5}$$

$3-\sqrt{5}$ and $3+\sqrt{5}$ are maxima, $r=2$ is a minimum.

3) $$A\langle 1s|z|2p_z\rangle = \cancel{\frac{A}{\sqrt{\pi}\,4\sqrt{2\pi}}\int e^{-r}(r\cos\theta)(r\cos\theta)r^2\sin\theta}\ ?$$

$$\psi_{1s} = \frac{1}{\sqrt{\pi}}e^{-r},\quad \psi_{2p_z} = \frac{1}{4\sqrt{2\pi}}\, z\, e^{-r/2}$$

$$\langle 1s|z|2p_z\rangle = \frac{A}{\sqrt{\pi}\,4\sqrt{2\pi}}\int e^{-r}(r\cos\theta)^2 r^2 \sin\theta\, dr\, d\theta\, d\phi$$

$$= \frac{A\,2\pi}{4\sqrt{2}\,\pi}\int e^{-r} r^4 e^{-r/2} dr \int_0^{\pi}(\cos\theta)^2\sin\theta\, d\theta$$

$$= -\frac{A}{2\sqrt{2}}\left.\frac{\cos^3\theta}{3}\right|_0^{\pi}\int_0^{\infty} r^4 e^{-3/2\, r}\, dr = \frac{A}{\sqrt{2}\,3}\int_0^{\infty} r^4 e^{-\frac{3}{2}r}\, dr$$

$$= \frac{256}{243}\frac{A}{\sqrt{2}}$$

4) $$\frac{\mu(DF)}{\mu(HF)} = \frac{(2\cdot 19/21)}{(1\cdot 19/20)} = 1.905$$

$$Be(DF) = \frac{20.96}{1.905} = 11.00\ \text{cm}^{-1}$$

The maximum in the J distribution will be reduced by a factor of $\sqrt{1.905}$ or by 1.38.