Chem 2430 HW #4 Answers

1. $x = \sqrt{\dfrac{\hbar}{2m\omega}}\,(a + a^{+})$

$$\langle 0|x^4|0\rangle = \left(\frac{\hbar}{2m\omega}\right)^2 \langle 0|(a+a^{+})^4|0\rangle$$

$$= \frac{\hbar^2}{4m^2\omega^2}\langle 0|aaa^{+}a^{+} + aa^{+}aa^{+}|0\rangle$$

$$= \frac{\hbar^2}{4m^2\omega^2}(2+1) = \frac{3}{4}\frac{\hbar^2\omega^2}{k^2}$$

$$\langle 0|x^3|1\rangle = \left(\frac{\hbar}{2m\omega}\right)^{3/2}\langle 0|(a+a^{+})^3|1\rangle = \left(\frac{\hbar}{2m\omega}\right)^{3/2}\langle 0|aaa^{+} + aa^{+}a|1\rangle$$

$$= \left(\frac{\hbar}{2m\omega}\right)^{3/2}(2+1)$$

$$\frac{|\langle 0|x^3|1\rangle|^2}{\hbar\omega} = \left(\frac{\hbar}{2m\omega}\right)^{3}\frac{1}{\hbar\omega}\,9 = \frac{9\hbar^2}{8m^3\omega^4} = \frac{9}{8}\frac{\hbar^2\omega^2}{k^3}$$

$$\langle 0|x^3|3\rangle = \left(\frac{\hbar}{2m\omega}\right)^{3}\langle 0(a+a^{+})^3|3\rangle = \left(\frac{\hbar}{2m\omega}\right)^{3/2}\langle 0|aaa|3\rangle$$

$$= \left(\frac{\hbar}{2m\omega}\right)^{3/2}\sqrt{3}\sqrt{2}$$

$$\frac{|\langle 0|x^3|3\rangle|^2}{3\hbar\omega} = \frac{6}{3\hbar\omega}\left(\frac{\hbar}{2m\omega}\right)^3 = \frac{1}{4}\frac{\hbar^2\omega^2}{k^3}$$

The two x^3 terms combine to give $\frac{11}{8}\frac{\hbar^2\omega^2}{k^3}$

The potential is described by $\frac{1}{2}kx^2 + \gamma x^3 + \delta x^4$

So the energy is given by

$$\tfrac{1}{2}\hbar\omega + \frac{3}{4}\frac{\hbar^2\omega^2}{k^2}\gamma + \frac{11}{8}\frac{\hbar^2\omega^2}{k^3}\delta^2$$

Note: if you wanted to calculate the energy of the $|0\rangle \to |1\rangle$ transition, you would need to also evaluate

$\langle 1|x^4|1\rangle$, $\langle 1|x^3|0\rangle$, $\langle 1|x^3|2\rangle$, $\langle 1|x^3|4\rangle$

2. $\hat{L}^2 \psi = 6\psi$ (we are assuming $\hbar = 1$)

Since $\hat{L}^2 \psi = l(l+1)\psi$, this implies $l = 2$

There are five orientations: $m_L = -2, -1, 0, 1, 2$.

3. $^{1}H^{35}Cl$ $J = 0 \rightarrow 1$ transition at $21.2\ cm^{-1}$.

$E = J(J+1)B$

$E_0 \rightarrow E_1 = 2B$

So $B_e = 10.6\ cm^{-1}$

$$\frac{1}{2\mu r^2} = B_e$$

In atomic units μ is 1.786×10^3, $B_e = 4.829 \times 10^{-5}$

So $r = 2.4077$ au $\rightarrow 1.274\ \mathring{A}$