Physics 4424
Quantum Mechanics
Due April 5, 2017
Assignment 8
Courage is fear that has said its prayers.
–William Shakespeare in *RichardIII*

1. Griffiths 4.13 (a) Normalize R_{20} and construct the function ψ_{200}.

The normalization for the radial wave function require $\int_0^\infty |R|^2 \, r^2 dr = 1$

Using $R_{20} = \left(\frac{c_0}{2a}\right)\left(1 - \frac{r}{2a}\right)e^{-r/2a}$ we let $z = \frac{r}{a}$ so that we have

$1 = \left(\frac{c_0}{2a}\right)^2 a^3 \int_0^\infty \left(1 - \frac{z}{2}\right)^2 e^{-z}z^2 = \frac{1}{2}c_0^2 a$

Therefore,

$$c_0 = \sqrt{\frac{2}{a}}.$$

Using $Y_0^0 - \frac{1}{\sqrt{4\pi}}$ we find that

$\psi_{200} = \frac{1}{\sqrt{4\pi}}\sqrt{\frac{2}{a}}\frac{1}{2a}\left(1 - \frac{r}{2a}\right)e^{-r/2a}$

$$\psi_{200} = \frac{1}{\sqrt{2\pi a}}\frac{1}{2a}\left(1 - \frac{r}{2a}\right)e^{-r/2a}$$

(b) Normalize R_{21} and construct $\psi_{211}, .\psi_{210}$, and ψ_{21-1}.

Using $R_{21} = \frac{c_0}{4a^2}re^{-r/2a}$ and the normalization condition we require

$1 = \left(\frac{c_0}{4a^2}\right)^2 a^5 \int_0^\infty z^4 e^{-z} dz = \frac{3}{2}c_0^2 a$

so that

$$c_0 = \sqrt{\frac{2}{3a}}$$

Using the table of spherical harmonics we construct

$$\psi_{21\pm 1} = \mp\frac{1}{\sqrt{\pi a}}\frac{1}{8a^2}re^{-r/2a}\sin\theta e^{\pm i\phi}$$

$$\psi_{210} = \frac{1}{\sqrt{2\pi a}} \frac{1}{4a^2} r e^{-r/2a} \cos\theta$$

2. Griffiths 4.15 (a) Find $< r >$ and $< r^2 >$ for an electron in the ground state of hydrogen. Express your answers in terms of the Bohr radius.

Using the ground state wave function, $\psi_{100} = \frac{1}{\sqrt{\pi a^3}} e^{-r/a}$ we find the expectation value

$< r^n >= \frac{1}{\pi a^3} \int \int \int r^n e^{-2r/a} \left(r^2 \sin\theta dr d\theta d\phi\right) = \frac{4\pi}{\pi a^3} \int_0^\infty r^{n+2} e^{-2r/a} dr$

Therefore,

$< r >= \frac{4}{a^3} \int_0^\infty r^3 e^{-2r/a} dr = \frac{4}{a^3} 3! \left(\frac{a}{2}\right)^4 = \frac{3}{2}a$

$< r^2 >= \frac{4}{a^3} \int_0^\infty r^4 e^{-2r/a} dr = \frac{4}{a^3} 4! \left(\frac{a}{2}\right)^5 = 3a^2$

(b) Find $< x >$ and $< x^2 >$ for an electron in the ground state of hydrogen.

$< x >= 0$

$< x^2 >= \frac{1}{3} \langle r^2 \rangle = a^2$

(c) Find $< x^2 >$ in the state $n = 2, \ell = 1, m = 1$.

Here we have no symmetry, so we calculate the expectation value by brute force:

We use $\psi_{211} = -\frac{1}{\sqrt{\pi a}} \frac{1}{8a^2} r e^{-r/2a} \sin\theta e^{i\phi}$

$x = r \sin\theta \cos\phi$

$\langle x^2 \rangle = \frac{1}{\pi a} \frac{1}{(8a^2)^2} \int_0^{2\pi} \int_0^\pi \int_0^\infty \left(r^2 e^{-r/a} \sin^2\theta\right) \left(r^2 \sin^2\theta \cos^2\phi\right) r^2 \sin\theta dr d\theta d\phi$

$\langle x^2 \rangle = \frac{1}{64\pi a^5} \int_0^\infty r^6 e^{-r/a} dr \int_0^\pi \sin^5\theta d\theta \int_0^{2\pi} \cos^2\phi d\phi$

$\langle x^2 \rangle = \frac{1}{64\pi a^5} \left(6! a^7\right) \left(2\frac{2 \cdot 4}{1 \cdot 3 \cdot 5}\right) \left(\frac{1}{2} 2\pi\right) = 12a^2$

3. A rigid rotator is known to be in the (normalized!) state

$$\psi(\theta, \phi) = \frac{2Y_{11} - 3Y_{6-1} - iY_{61}}{\sqrt{14}}$$

(a) What is the probability of obtaining $\hbar$ in a measurement of L_z?

The probability of measuring $\hbar$ for L_z comes from both Y_{11} and Y_{61}. Therefore,

$P(m = 1) = |a_{11}|^2 + |a_{61}|^2 = \frac{4}{14} + \frac{1}{14} = \frac{5}{14}$.

(b) What is the probability of measuring $42\hbar^2$ for L^2?

$$P\left(l=6\right) = |a_{6-1}|^2 + |a_{61}|^2 = \frac{9}{14} + \frac{1}{14} = \frac{5}{7}.$$

(c) What is the probability of finding the rotator with energy $E = 0$?

We know that since $E_l = \dfrac{l(l+1)\hbar^2}{2I}$, E_0 implies that $l = 0$. Since no component of the wavefunction has this value, we obtain

$$P\left(E=0\right) = 0$$

4. At a given instant, a rigid rotator is in the state

$$\psi\left(\theta, \varphi\right) = \sqrt{\frac{3}{4\pi}} \sin\theta \sin\varphi$$

(a) What possible value of L_z will a measurement find and with what probability will these values occur?

First, we express ψ as a superposition of spherical harmonics:

$$\psi\left(\theta, \varphi\right) = \sum_{l=0}^{\infty} \sum_{m=-l}^{l} a_{lm} Y_{lm}\left(\theta, \phi\right).$$

However, we can "eyeball" the wavefunction and, using our knowledge of the forms of the spherical harmonics, realize that it must be a superposition of Y_{11} and Y_{1-1} :

$$\psi\left(\theta, \varphi\right) = \frac{i}{\sqrt{2}}\left(Y_{11} + Y_{1-1}\right)$$

Therefore, the values of L_z that can be measured are $+\hbar$ and $-\hbar$ with the probabilities of $\dfrac{1}{2}$ each.

(b) What is $< L_z >$ for this state?

$$< L_z >= \frac{1}{2}\hbar + \frac{1}{2}\left(-\hbar\right) = 0$$

(c) Determine $< L^2 >$ for this state.

$$< L^2 >= l\left(l+1\right)\hbar^2 = 1\left(1+1\right)\hbar^2$$

$$< L^2 >= 2\hbar^2$$

5. Consider the eigenstate $|lm_l>$ of L^2 and L_z. (a) Show that the expectation values of L_x^2 and L_y^2 are

$$< lm_l|L_x^2|lm_l >=< lm_l|L_y^2|lm_l >= \frac{1}{2}\left(l\left(l+1\right)-m_l^2\right)\hbar^2$$

We know that $\widehat{L}_z^2\,|lm\rangle = m^2\hbar^2\,|lm\rangle = m^2\hbar^2\,|lm\rangle$ and $\widehat{L}^2\,|lm\rangle = l\left(l+1\right)\hbar^2\,|lm\rangle$.
Since $L^2 = L_x^2 + L_y^2 + L_z^2$ we have $L_x^2 + L_y^2 = L^2 - L_z^2$ so that
$\langle L_x^2\rangle + \langle L_y^2\rangle = \langle L^2\rangle - \langle L_z^2\rangle$.
Assuming that $\langle L_x^2\rangle = \langle L_y^2\rangle$ we have
$\langle L_x^2\rangle = \langle L_y^2\rangle = \frac{1}{2}\{\langle L^2\rangle - \langle L_z^2\rangle\}$

$$\langle L_x^2\rangle = \langle L_y^2\rangle = \frac{1}{2}\left\{l\left(l+1\right)-m^2\right\}\hbar^2$$

Q.E.D.

(b) Determine the rms uncertainties for L_x and L_y.

Using $(\Delta L_x)^2 = \langle L_x^2\rangle - \langle L_x\rangle^2$ and $\widehat{L}_x = \frac{1}{2}\left(\widehat{L}_+ + \widehat{L}_-\right)$ we see that, due to the orthonormality of the states $|lm>, \langle L_x\rangle = 0$. Therefore,

$\Delta L_x = \sqrt{\langle L_x^2\rangle} = \sqrt{\frac{1}{2}\left[l\left(l+1\right)-m^2\right]}\hbar$

Of course, a similar result holds for ΔL_y.

(c) Using your result from (b) discuss the physical interpretation for the case $l=0$, $m_l=0$.

If $l=0, m=0$ then $\Delta L_x = 0, \Delta L_y = 0$ since there is zero angular momentum for the state.

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6. The carbon monoxide molecule, CO, absorbs a photon with a frequency of 1.15×10^{13} Hz, making a purely rotational transition from an $l = 0$ to an $l = 1$ energy level. Determine the internuclear distance for this molecule.

We can treat the CO molecule as a rigid rotator with moment of inertia $I = \mu r^2$, where $\mu = \dfrac{m_C m_O}{m_C + m_O}$ and r is the internuclear separation. Using $E_l = \dfrac{l\,(l+1)\,\hbar^2}{2I}$, the photon has energy

$$E = h\nu = \frac{1\,(1+1)\,\hbar^2}{2I} - 0 = \frac{\hbar^2}{I}$$

Substituting for I we find

$$h\nu = \frac{\hbar h}{2\pi \mu r^2}\text{so that}$$

$$r = \sqrt{\frac{\hbar}{2\pi\nu\mu}} = \sqrt{\frac{1.0546 \times 10^{-34}}{2\pi\,(1.15 \times 10^{11})\,\dfrac{(12)\,(16)\,(1.67 \times 10^{-27})}{12 + 16}}} = 1.129\,0 \times 10^{-10}\,\text{m}$$

$$r = 0.112\,\text{nm}$$

7. The ratio of the number of molecules in the rotational level l, with energy E_l, to the number in the $l = 0$ ground state, with energy E_0, in a sample of molecules in equilibrium at temperature T is given by

$$(2l + 1)\,e^{\dfrac{-(E_l - E_0)}{kT}}$$

where $2l+1$ is the degeneracy of level with energy E_l. (a) Show that the population of rotational energy levels first increases and then decreases with increasing l.

Since $E_l = \dfrac{l\,(l+1)\,\hbar^2}{2I}$, $E_0 = 0$, we substitute to get

$$R = (2l + 1)\,e^{\dfrac{-l\,(l+1)\,\hbar^2}{2IkT}}$$

Taking the derivative w.r.t. l we get:

$$\frac{dR}{dl} = \frac{d}{dl}\left((2l+1)\,e^{\dfrac{-l\,(l+1)\,\hbar^2}{2IkT}}\right) = \left(2 - (2l+1)^2\,\frac{\hbar^2}{2IkT}\right)e^{\dfrac{-l\,(l+1)\,\hbar^2}{2IkT}}$$

This shows that there is a maximum values, and, so, the ratio must increase with increasing l and then decrease.

(b) Which energy level will be occupied by the largest number of molecules of HCl at room temperature? Compare your result with the intensities of the absorption spectrum shown below. What do you deduce about the temperature of the gas?
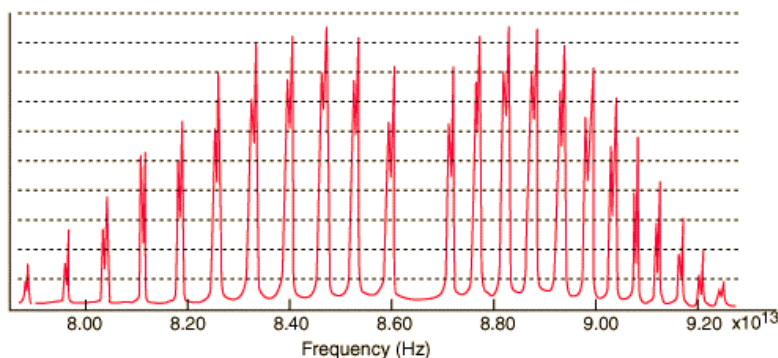
A vibrational rotational absorption spectrum for HCl. Each peak is double because of the presence of two isotopes of chlorine gas—^{35}Cl and the less abundant ^{37}Cl.

First, we realize that the photon energy for a transition from the l to the $l-1$ state is
$$\Delta E = \frac{k\,(k+1)\,\hbar^2}{2I} - \frac{(k-1)\,(k-1+1)\,\hbar^2}{2I} = k\frac{\hbar^2}{I} \quad \text{where } k = 1, 2, 3, ...$$
Since k can take on all values up to some large number where the molecule flies apart, there will occur a great variety of evenly spaced photon energies. This is the origin of the bands of closely spaced lines which are characteristic of molecular spectra.

We must also consider the vibrational energy levels of the diatomic molecule. We know from our analysis of the simple harmonic oscillator that $E_{nvib} = \left(n + \dfrac{1}{2}\right)\hbar\omega$. In absorbing light energy, a molecule will increase its vibrational quantum number by one $(\Delta n_{vib} = \pm 1)$ and either increase or decrease its angular momentum quantum number by one $(\Delta l = \pm 1)$. Thus, the energy of the absorbed photon is
$$\Delta E_{aborbed} = \Delta E_{vib} + \frac{\hbar^2}{I}\begin{cases} k\,(k+1) - (k+1)\,(k+2) & k \longrightarrow k+1 \\ k\,(k+1) - (k-1)\,k & k \longrightarrow k-1 \end{cases}$$

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$$\Delta E_{aborbed} = \Delta E_{vib} + \frac{\hbar^2}{I} \begin{cases} -2k\,(k+1) & k = 0, 1, 2, ... \\ +2k & k = 1, 2, 3, ... \end{cases}$$

The value of $k = 0$ is excluded in the second case because k cannot decrease if it is already zero.

For the spectrum of HCl, we give the values of k for the various lines below. The gap near the center represents the missing value of $k = 0$ above. The primes represent the $k \longrightarrow k - 1$ transitions.
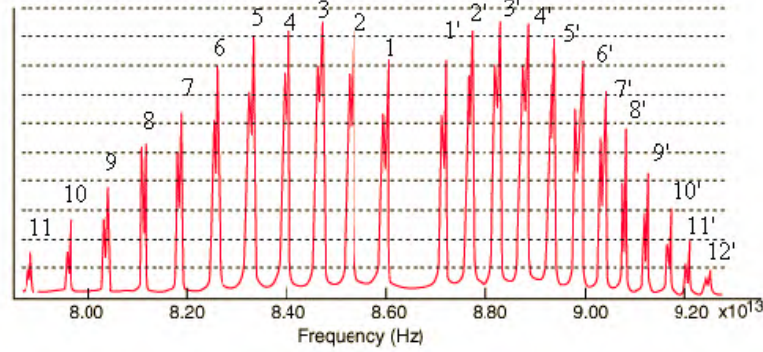
From the graph we see that $k = 3$ for the maximum.

Setting the ratio equal to 0 we have

$$\left(2 - (2l + 1)^2\, \frac{\hbar^2}{2IkT} \right) e^{\frac{-l\,(l+1)\,\hbar^2}{2IkT}} = 0, \text{ Solution is: } l = \frac{1}{2} \frac{-\hbar - 2\sqrt{IkT}}{\hbar}$$

So

$l_{\max} = \dfrac{1}{2} \dfrac{-\hbar - 2\sqrt{IkT}}{\hbar}$.   Using $l_{\max} = 3$ we have

$3 = \dfrac{1}{2} \dfrac{-\hbar - 2\sqrt{IkT}}{\hbar}$, Solution is: $\left\{ T = \dfrac{49}{4} \dfrac{\hbar^2}{Ik} \right\}$

Careful measurements have found that $\dfrac{\hbar^2}{2I} = 1.28 \times 10^{-3}\,\text{eV}$.

Hence

$T = \dfrac{49}{2}\,(1.28 \times 10^{-3}\,\text{eV}) / (8.617 \times 10^{-5}\,\text{eV}/\text{K}) = 363.\,93\,\text{K}$