LULEÅ UNIVERSITY OF TECHNOLOGY
Division of Physics

Solution to written exam in QUANTUM PHYSICS F0047T
Examination date: 2016-01-12
The solutions are just suggestions. They may contain several alternative routes.

1. Rewrite the wave function in terms of spherical harmonics: (polar coordinates:
$x = r\sin\theta\sin\phi$, $y = r\sin\theta\cos\phi$, $z = r\cos\theta$ and hence
$xy = r^2\sin^2\theta\sin\phi\cos\phi = r^2\sin^2\theta(e^{i2\phi} - e^{-i2\phi})/4i$ using the Euler relations) the appropriate
spherical harmonics can now be identified $Y_{2,-2} = \frac{1}{4}\sqrt{\frac{15}{2\pi}}\sin^2\theta e^{-i2\phi}$ and $Y_{2,2} = \frac{1}{4}\sqrt{\frac{15}{2\pi}}\sin^2\theta e^{i2\phi}$
and we arrive at

$$\psi(\mathbf{r}) = \psi(x,y,z) = N \cdot xy \cdot e^{-r/3a_0} = N\frac{r^2}{4i}\sqrt{\frac{32\pi}{15}}(Y_{2,2} - Y_{2,-2})e^{-r/3a_0} . \qquad (1)$$

As all the involved $Y_{l,m}$ have $l = 2$ the probability to get $\mathbf{L}^2 = 2(2+1)\hbar^2 = 6\hbar^2$ is one. For the
operator L_z we note the two spherical harmonics have the same pre factor (one has -1 and the
other has +1 but the absolute value square is the same) ie they will have the same probability.
The probability to find $m = 2\hbar$ is $\frac{1}{2}0$, for $m = 1\hbar$ is 0, for $m = 0\hbar$ is 0 for $m = -1\hbar$ is 0, and for
$m = -2\hbar$ is $\frac{1}{2}$. As all the involved $Y_{l,m}$ have $l = 2$ the probability to get $\mathbf{L}^2 = 2(2+1)\hbar^2 = 6\hbar^2$ is
one.

b. To calculate the expectation value $<r>$ we need to normalise the given wave function if we
wish to do the integral. In order to achieve this in a simple way is to identify the radial wave
function. As l is equal to 2 we know that n cannot be equal to 1 or 2 it has to be **larger** or
equal to 3. By inspection of eq (1) and 2 we find $n = 3$ this function has the correct exponential
and the correct power of r (r^2) and hence $R_{3,2}(r) = \frac{2\sqrt{2}}{27\sqrt{5}}\left(\frac{Z}{3a_0}\right)^{3/2}\left(\frac{Zr}{a_0}\right)^2 e^{-Zr/3a_0}$. We also note
that $Y_{2,2}$ and $Y_{2,-2}$ are normalised but the sum $(Y_{2,2} - Y_{2,-2})$ is not normalised. As the
normalisation integral will produce 1+1=2, the sum has to be changed to $(\frac{1}{\sqrt{2}}Y_{2,2} - \frac{1}{\sqrt{2}}Y_{2,-2})$ in
order to be normalised. Note that $R_{3,2}(r)$ contains an r^2 term as also a $e^{-r/3a_0}$ term. The wave
function can now be completed to the following normalized wave function (note that we do not
need to calculate the constant N as all separate parts of $\psi(r)$ are normalised by them selves)

$$\psi(\mathbf{r}) = \psi(x,y,z) = N \cdot xy \cdot e^{-r/3a_0} = R_{3,2}(r)\left(\frac{1}{\sqrt{2}}Y_{2,2} - \frac{1}{\sqrt{2}}Y_{2,-2}\right)$$

From physics handbook page 292 you find

$$\langle r \rangle = \frac{1}{2}\left[3n^2 - l(l+1)\right]\left(\frac{a_0}{Z}\right) = \frac{1}{2}\left[3\ 3^2 - 2(2+1)\right]\left(\frac{a_0}{1}\right) = \frac{21}{2}a_0 =$$

$$10.5 \cdot 0.5292 \text{ Å} = 5.56 \text{ Å}.$$

You may also do the integral directly like this (only the part depending on r are of interest as
the angular parts just will be the normalising integral):

$$\langle r \rangle = \int_0^\infty \int_0^\pi \int_0^{2\pi} d\phi\ d\theta\ dr\ r^2\sin(\theta)\ r\ |\ R_{3,2}(r)\ |^2\ \left|\frac{1}{\sqrt{2}}Y_{2,2} - \frac{1}{\sqrt{2}}Y_{2,-2}\right|^2 =$$

$$\int_0^\infty dr\ r^3\ |\ R_{3,2}(r)\ |^2 = \frac{21}{2}a_0 = 10.5 \cdot 0.5292 \text{ Å} = 5.56 \text{ Å}.$$

2. a) There are 4 states the system can have with the energys and (degeneracys) $\hbar\omega$ (1), $2\hbar\omega$ (2) and $3\hbar\omega$ (1). The partition sum is given by:

$$Z = \sum_{n_1=0,n_2=0}^{n_1=1,n_2=1} e^{-(n_1+n_2+1.0)\hbar\omega/k_BT} = e^{-1.0\hbar\omega/k_BT} + 2e^{-2.0\hbar\omega/k_BT} + e^{-3.0\hbar\omega/k_BT}$$

b) There is one state of the lower energy and there are **two** states with the next higher energy. The probability to find the system in a state of energy is proportional to the Boltzmann factor, we arrive at the following equation for the probabilities.

$$\frac{1e^{-1,0\hbar\omega/k_BT}}{Z} = \frac{2e^{-2,0\hbar\omega/k_BT}}{Z} \tag{2}$$

and this reduces to $e^{1\hbar\omega/k_BT} = 2$ which evaluates to $T = \frac{1\hbar\omega}{k_B\ln 2}$.

c) The partition sum at this specific temperature is given by: $(k_BT = \frac{1\hbar\omega}{\ln 2})$ $(\frac{1}{k_BT} = \frac{\ln 2}{1\hbar\omega})$ we arrive at the following

$$Z = e^{-1.0\hbar\omega/k_BT} + 2e^{-2.0\hbar\omega/k_BT} + e^{-3.0\hbar\omega/k_BT} = e^{-1.0\ln 2} + 2e^{-2.0\ln 2} + e^{-3.0\ln 2} =$$

$$\frac{1}{2} + 2\frac{1}{4} + \frac{1}{8} = \frac{1}{2} + \frac{1}{2} + \frac{1}{8} = 1 + \frac{1}{8} = \frac{9}{8}$$

The probability P will be (put Z into one of the terms in eq (2).

$$P = \frac{e^{-1,0\ln 2}}{\frac{9}{8}} = \frac{1}{2} \cdot \frac{8}{9} = \frac{4}{9} \approx 0.444...$$

As a check we can calculate for the state with the highest energy

$$P_3 = \frac{e^{-3,0\ln 2}}{\frac{9}{8}} = \frac{1}{8} \cdot \frac{8}{9} = \frac{1}{9} \approx 0.111...$$

and we can easily conclude the probabilities add up to one.

3. (a) There are two ways to reach a solution for this. The usual rule for the vibrational transition is $\Delta n = \pm 1$ and this would correspond to a photon of energy $h\nu_1 = \hbar\omega$, note only approximately as we also need a change in the rotational quantum number l. Here we also allow for anharmonic transitions $\Delta n = \pm 2$ corresponding to photons of energy $h\nu_2 = 2\hbar\omega$. Considering the relation between wavelength and frequency for an electromagnetic wave the photon of frequency ν_2 will have only half the wavelength compared to the ν_1 photon. Hence the upper is the anharmonic transition and the lower is the harmonic transition.

The second route is to note that the anharmonic transitions are much rarer. Comparing the scales for the intensity we note that the lower has an intensity of more than a factor of 1000 larger than the upper spectra. Hence events contributing to the upper spectra are much rarer compared to events contributing to the lower spectra. We can draw the same conclusion the upper is the anharmonic transition and the lower is the harmonic transition. After this we do not need to consider the upper anharmonic spectra any more.

(b) Take data from the lower spectra as this is for the harmonic transitions $\Delta n = \pm 1$.

The energy levels of a molecule, due to vibrations and rotation, are given by $E_{n,l} = (n + \frac{1}{2})\hbar\omega + \frac{\hbar^2}{2I}l(l+1)$. The selection rule for a dipole transition is to change l by one unit $\Delta l = \pm 1$. In figure 1 a principal layout of the levels is shown. We first need to
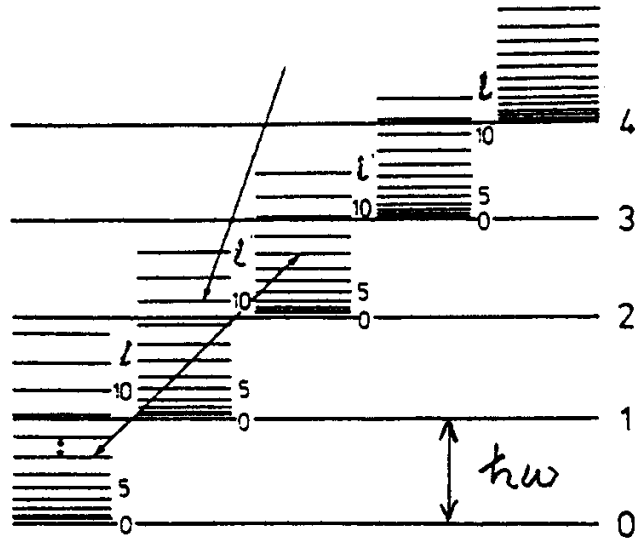
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Figure 1: Energy levels for a diatomic molecule. The long horisontal lines mark the $l = 0$ levels, with the vibrational quantum number n to the right. The spacing in energy between these lines is $\hbar\omega$. The states with higher l-values (the rotational bands) give a dense sequence of states for each n-value. The arrows show two possible transitions, one harmonic ($n = 2 \to n = 1$) and one anharmonic ($n = 2 \to n = 0$).

establish the relation between the spectra and the energy levels. For the lower spectra (of the problem) we have $\Delta n = -1$ (minus sign = emission spectra) and two possible $\Delta l = \pm 1$.

We start with an analysis of the transitions between energy levels.

One series has $\Delta n = -1, \Delta l = -1$: Ie a change from a level with $l + 1$ to a level with l.

The energy difference will be
$\Delta E = \hbar\omega + \frac{\hbar^2}{2I}(l + 1)(l + 2) - \frac{\hbar^2}{2I}l(l + 1) = \frac{\hbar^2}{I}(l + 1), l = 0, 1, 2, 3$, which gives the following energies (for photons):

$\hbar\omega + \frac{\hbar^2}{I}$, $\hbar\omega + 2\frac{\hbar^2}{I}$, $\hbar\omega + 3\frac{\hbar^2}{I}$, $\hbar\omega + 4\frac{\hbar^2}{I}$, ...

A similar analysis gives the other series $\Delta n = -1, \Delta l = +1$ ($l \to l + 1$):

$\hbar\omega - \frac{\hbar^2}{I}$, $\hbar\omega - 2\frac{\hbar^2}{I}$, $\hbar\omega - 3\frac{\hbar^2}{I}$, $\hbar\omega - 4\frac{\hbar^2}{I}$, ...

All these energy differences (photon energies) will appear in the spectra. It is also clear that there is always a change in the rotational quantum number l, $\Delta l = \pm 1$. It therefore seems as if there is a line missing for the unalowed transition $\Delta l = 0$ in the spectrum corresponding to the energy $\hbar\omega$

The strength of the coupling constant is embedded in the in the frequency ω of the oscillator, given by the missing line. The distance between the two atoms is given by the energy difference between the lines from the rotational transitions.

Extrapolate the 'wave length' of the missing line: $\lambda = 4.6 + \frac{4.7-4.6}{34.8}23.0 = 4.67\mu$m. The energy of the missing line corresponds to $\hbar\omega$ of the oscillator.

The strength k of the bond is from $\omega = \sqrt{k/\mu}$ where μ is the reduced mass. For carbon monoxide we have the reduced mass $\mu = \frac{m_C m_O}{m_C + m_O} = \frac{12.011 \cdot 15.999}{12.011 + 15.999} = 6.86055$u
$= 6.86055 \cdot 1.660538 \cdot 10^{-27} = 1.13922 \cdot 10^{-26}$ kg.

To calculate the distance between the atoms we have to use the moment of inertia $I = \mu R^2$. This is related to the energy difference between the rotational spectral lines $\Delta E = \frac{\hbar^2}{I}$. The energy of a photon is given by $E = \frac{hc}{\lambda}$. As the given spektra are given as intensity as a

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function of wave length λ we have two options to calculate for ΔE. We can estimate the λ of two adjecent lines invert these two and calculate the difference. Or we do like this differentiate $E = \frac{hc}{\lambda}$ $dE = -\frac{hc}{\lambda^2}d\lambda$ we can now relate a difference in λ to a difference in energy E.

From the graph we find the separation between 11 lines (10 spaces) is 32.8mm. This can be transformed to a line separation $\Delta\lambda = \frac{0.10}{34.8}\frac{32.8}{10} = 0.00943\mu$m. From this we can calculate $\Delta E = \frac{hc}{\lambda^2}\Delta\lambda$. Omit the minus sign as we calculate photon energies.

NOTE In the literature one often finds spectra in units of λ^{-1} inverse wave length which in principle is an energy scale. For that case the energy difference is written $\Delta E = \frac{\hbar^2}{I} = hc\Delta\lambda^{-1}$. Here $\Delta\lambda^{-1} = \frac{1}{\lambda_2} - \frac{1}{\lambda_1}$ where λ_1, λ_2 are two consecutive lines of the rotational spectra. This $\Delta\lambda^{-1}$ can be related to $\Delta\lambda$ by $\Delta\lambda^{-1} = -\frac{\lambda}{\lambda^2}$. The minus signs we can omit as long as we keep in mind that a photon has a positiv energy. Hence this equates to $\Delta\lambda^{-1} = \frac{0.00943}{4.67^2} = 4.324 \cdot 10^{-4}(\mu\text{m})^{-1} = 4.324 \cdot 10^2(\text{m})^{-1}$.

Now back to the solution.
Now we can calculate $I = \mu R^2 = \frac{m_C m_O}{m_C + m_O}R^2$ to arrive at

$$R = \sqrt{\frac{h\lambda^2}{4\pi^2\ c\ \Delta\lambda\ \mu}} = \sqrt{\frac{6.626\ 10^{-34}\ (4.67 \cdot 10^{-6})^2}{4\pi^2 \cdot 2.997\ 10^8 \cdot 0.00943 \cdot 10^{-6} \cdot 1.13922\ 10^{-26}}} = 1.066\ 10^{-10}\text{m} \quad (3)$$

$$\approx 1.07\ 10^{-10}\text{m}\ \ \text{or}\ \ 1.1\ 10^{-10}\text{m}. \quad (4)$$

In wikepedia you find $R = 1.12\ 10^{-10}$m for Carbon monoxide.

(c) The missing line would represent a transition with no change of the rotational quantum number l, ie $\Delta l = 0$. This is not allowed according to the selection rule that states that $\Delta l = \pm 1$.

4. Use the spin matrixes to evaluate the expectation values.

$$< S_x >= \frac{1}{9}(2+i, 2)\frac{\hbar}{2}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}\begin{pmatrix} 2 - i \\ 2 \end{pmatrix} = \frac{4}{9}\hbar$$

$$< S_y >= \frac{1}{9}(2+i, 2)\frac{\hbar}{2}\begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}\begin{pmatrix} 2 - i \\ 2 \end{pmatrix} = \frac{2}{9}\hbar$$

$$< S_z >= \frac{1}{9}(2+i, 2)\frac{\hbar}{2}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}\begin{pmatrix} 2 - i \\ 2 \end{pmatrix} = \frac{1}{18}\hbar$$

If one squares a spin matrix σ_i^2 you will find a result proportional to the unit matrix for all three indecies x, y or z.

$$S_x^2 = \frac{\hbar^2}{4}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} = \frac{\hbar^2}{4}\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$$

We arrive at:

$$< S_x^2 >=< S_y^2 >=< S_z^2 >= \hbar^2\frac{1}{36}(2+i, 2)\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}\begin{pmatrix} 2 - i \\ 2 \end{pmatrix} = \frac{1}{4}\hbar^2$$

5. (a) $i\hbar \frac{\partial^2}{\partial t^2} \cos \omega t = -i\hbar\omega \frac{\partial}{\partial t} \sin \omega t = -i\hbar\omega^2 \cos \omega t$ **YES**

   (b) $\frac{\partial}{\partial x} e^{ikx} = ik e^{ikx}$ **YES**

   (c) $\frac{\partial}{\partial x} e^{-ax^2} = -2ax e^{-ax^2}$ **NO**

   (d) $\frac{\partial}{\partial x} \cos kx = -k \sin kx$ **NO**

   (e) $\frac{\partial}{\partial x} kx = k$ **NO**

   (f) $\hat{P} \sin(kx) = \sin(-kx) = -\sin(kx)$ **YES**

   (g) $-i\hbar \frac{\partial}{\partial z} C(1 + z^2) = -i\hbar C(0 + 2z)$ **NO**

   (h) $-\frac{\hbar}{2}\frac{\partial}{\partial z} C e^{-3z} = -\frac{\hbar}{2} C(-3) e^{-3z} \propto \psi(z)$ **YES**

   (i) $\frac{C}{2}(z^2 - \frac{\partial^2}{\partial z^2}) z e^{-\frac{1}{2}z^2} =$? This has to be done in some steps. Start by doing this derivative first: $-\frac{\partial^2}{\partial z^2} z e^{-\frac{1}{2}z^2} = -\frac{\partial}{\partial z}\left(e^{-\frac{1}{2}z^2} - z^2 e^{-\frac{1}{2}z^2}\right) = -\left(-z e^{-\frac{1}{2}z^2} - 2z e^{-\frac{1}{2}z^2} + z^3 e^{-\frac{1}{2}z^2}\right) = 3z e^{-\frac{1}{2}z^2} - z^3 e^{-\frac{1}{2}z^2}$.

   Now you go back to the start: $\frac{C}{2}(z^2 - \frac{\partial^2}{\partial z^2}) z e^{-\frac{1}{2}z^2} = \frac{C}{2}\left(z^3 e^{-\frac{1}{2}z^2} + 3z e^{-\frac{1}{2}z^2} - z^3 e^{-\frac{1}{2}z^2}\right) = \frac{C}{2}\left(+3z e^{-\frac{1}{2}z^2}\right) = \propto \psi(z)$ **YES**