

Solution to written exam in QUANTUM PHYSICS F0047T

Examination date: 2019-03-21

The solutions are just suggestions. They may contain several alternative routes.

1. (a) The time independent wave function is (we notice that 36% and 64% add up to 100%)

$$\Psi(x) = \frac{3}{5}\psi_1(x) + \frac{4}{5}\psi_2(x)$$

From this we have to construct the time-dependent solution. We also have to take into consideration that $\langle x \rangle$ is at a minimum at $t = 0$. We have to allow for a phase factor on each one of the eigenfunctions.

$$\Psi(x, t) = \frac{3}{5}e^{-i\theta_1}\psi_1(x)e^{-i\frac{3}{2}\hbar\omega t/\hbar} + \frac{4}{5}e^{-i\theta_2}\psi_2(x)e^{-i\frac{5}{2}\hbar\omega t/\hbar} = \frac{3}{5}e^{-i\theta_1}\psi_1(x)e^{-i3\omega t/2} + \frac{4}{5}e^{-i\theta_2}\psi_2(x)e^{-i5\omega t/2} \quad (1)$$

Now we turn to the condition $\langle x \rangle$ at a minimum at $t = 0$. We will make use of the recursion relation for the eigenfunctions.

$$xu_n(x) = \frac{b}{\sqrt{2}} \left(\sqrt{n+1} u_{n+1}(x) + \sqrt{n} u_{n-1}(x) \right), \text{ where } b = \frac{1}{\alpha} = \sqrt{\frac{\hbar}{m\omega}}.$$

In the calculation for $\langle x \rangle$ we will need:

$$\begin{aligned} x\psi_1(x) &= \frac{1}{\alpha\sqrt{2}} \left(\sqrt{2}\psi_2(x) + \sqrt{1}\psi_0(x) \right) = \frac{1}{\alpha} \left(\psi_2 + \frac{1}{\sqrt{2}}\psi_0 \right) \\ x\psi_2(x) &= \frac{1}{\alpha\sqrt{2}} \left(\sqrt{3}\psi_3(x) + \sqrt{2}\psi_1(x) \right) = \frac{1}{\alpha} \left(\frac{\sqrt{3}}{\sqrt{2}}\psi_3 + \psi_1 \right) \end{aligned}$$

Now

$$\langle x \rangle = \int \left(\frac{3}{5}e^{i\theta_1}\psi_1^*(x)e^{i3\omega t/2} + \frac{4}{5}e^{i\theta_2}\psi_2^*(x)e^{i5\omega t/2} \right) x \left(\frac{3}{5}e^{-i\theta_1}\psi_1(x)e^{-i3\omega t/2} + \frac{4}{5}e^{-i\theta_2}\psi_2(x)e^{-i5\omega t/2} \right)$$

Making use of the recursion relation we get

$$\langle x \rangle = \int \left(\frac{3}{5}e^{i\theta_1}\psi_1^*(x)e^{i3\omega t/2} + \frac{4}{5}e^{i\theta_2}\psi_2^*(x)e^{i5\omega t/2} \right) \cdot$$

$$\frac{1}{\alpha} \left[\frac{3}{5}e^{-i\theta_1}e^{-i3\omega t/2} \left(\psi_2(x) + \frac{1}{\sqrt{2}}\psi_0(x) \right) + \frac{4}{5}e^{-i\theta_2}e^{-i5\omega t/2} \left(\frac{\sqrt{3}}{\sqrt{2}}\psi_3(x) + \psi_1(x) \right) \right]$$

Retaining the the non-orthogonal parts we arrive at

$$\langle x \rangle = \frac{12}{25\alpha} \left(e^{i(\omega t + \theta_2 - \theta_1)} + e^{-i(\omega t + \theta_2 - \theta_1)} \right) = \frac{24}{25\alpha} \cos(\omega t + \theta_2 - \theta_1) \quad (2)$$

The minimum of eq.2 at $t = 0$ occurs when $\theta_2 - \theta_1 = \pi$. The minimum value is

$$\langle x \rangle = -\frac{24}{25\alpha} \quad (3)$$

$$\begin{aligned}\Psi(x, t) &= \frac{3}{5}e^{-i\theta_1}\psi_1(x)e^{-i3\omega t/2} + \frac{4}{5}e^{-i\theta_2}\psi_2(x)e^{-i5\omega t/2} = \\ &= e^{-i\theta_1} \left(\frac{3}{5}\psi_1(x)e^{-i3\omega t/2} + \frac{4}{5}e^{-i(\theta_2-\theta_1)}\psi_2(x)e^{-i5\omega t/2} \right)\end{aligned}\quad (4)$$

$$\Psi(x, t) = e^{-i\theta_1} \left(\frac{3}{5}\psi_1(x)e^{-i3\omega t/2} + \frac{4}{5}e^{-i\pi}\psi_2(x)e^{-i5\omega t/2} \right)\quad (5)$$

Concluding that the time-dependent wave function is given by eq. 5.

- (b) The momentum operator is $-i\hbar\frac{\partial}{\partial x}$ we can use this on the two eigenfunction $\psi_1(x)$ and $\psi_2(x)$. But we can also try to use the previous calculation for $\langle x \rangle$ and the relation $\langle p \rangle = m\frac{d\langle x \rangle}{dt}$. Starting from $\langle x \rangle$ eq. 2

$$\langle x \rangle = \frac{24}{25\alpha} \cos(\omega t + \pi) = -\frac{24}{25\alpha} \cos(\omega t)$$

Now $\langle p \rangle$ will be

$$\langle p \rangle = m\frac{d}{dt} \frac{24}{25\alpha} \cos(\omega t + \pi) = -m\omega \frac{24}{25\alpha} \sin(\omega t + \pi) = \sqrt{\hbar m \omega} \frac{24}{25} \sin(\omega t)$$

- (c) The eigenfunctions $\psi_1(x)$ and $\psi_2(x)$ are eigenfunctions of the Hamiltonian and will not change with time (energy is conserved). $\langle E \rangle = (0.36 \cdot \frac{3}{2} + 0.64 \cdot \frac{5}{2})\hbar\omega = 2.14\hbar\omega$.

2. First normalise the wave function. $\int_0^a A^2 x^2 (a-x)^2 dx = 1$. This gives $A = \sqrt{\frac{30}{a^5}}$. The eigenfunctions are $\psi_n(x) = \sqrt{\frac{2}{a}} \sin(\frac{n\pi}{a}x)$ and the corresponding eigenvalues are $E_n = \frac{n^2\pi^2\hbar^2}{2ma^2}$.

- a) To find the time evolution of the wave function $\Psi(x, t)$ we need to expand the wave function in the eigenfunctions $\psi_n(x)$. The coefficients c_n of the expansion are given by

$$c_n = \int_0^a \sqrt{\frac{30}{a^5}} x(a-x) \sqrt{\frac{2}{a}} \sin(\frac{n\pi}{a}x) = \sqrt{\frac{30}{a^5}} \int_0^a ax \sin(\frac{n\pi}{a}x) - x^2 \sin(\frac{n\pi}{a}x)$$

Calculate the two following integrals:

$$\int_0^a x \sin(\frac{n\pi}{a}x) = -\frac{a^2}{n\pi} (-1)^n \quad \text{and}$$

$$\int_0^a x^2 \sin(\frac{n\pi}{a}x) = -\frac{a^3}{n\pi} (-1)^n + \frac{2a^3}{n^3\pi^3} ((-1)^n - 1)$$

Evaluating for c_n gives:

$$c_n = \sqrt{\frac{30}{a^5}} \int_0^a ax \sin(\frac{n\pi}{a}x) - x^2 \sin(\frac{n\pi}{a}x) = \frac{4\sqrt{15}}{(n\pi)^3} (1 - (-1)^n)\quad (6)$$

We calculate some of the coefficients (just for inspection):

$$\begin{aligned}c_1 &= \frac{4\sqrt{15}}{(n\pi)^3} 2 = 0.999277 & c_2 &= 0 \\ c_3 &= \frac{4\sqrt{15}}{27(n\pi)^3} 2 = 0.03701 & c_4 &= 0 \\ c_5 &= \frac{4\sqrt{15}}{125(n\pi)^3} 2 = 0.0079942 & c_6 &= 0\end{aligned}$$

We note that only c_n where n is an odd integer are non-zero. This is used later. We can now construct the time dependent wave function

$$\Psi(x, t) = \sum_n c_n \psi_n(x) e^{-iE_n t/\hbar}$$

where c_n are given by eq. 6, $\psi_n(x)$ are the eigenfunctions and $E_n = \frac{n^2 \pi^2 \hbar^2}{2ma^2}$ are the eigenenergies.

b) We are now starting the calculation of $\langle x \rangle$ as a function of time. We write:

$$\langle x \rangle = \int_0^a \sum_m c_m^* \psi_m^*(x) e^{+iE_m t/\hbar} x \sum_n c_n \psi_n(x) e^{-iE_n t/\hbar} \quad (7)$$

Inspection of eq. 7 reveals that we have to calculate the following integral:

$$\int_0^a \sin\left(\frac{m\pi}{a}x\right) x \sin\left(\frac{n\pi}{a}x\right)$$

Using the relation

$$2 \sin\left(\frac{\alpha + \beta}{2}\right) \sin\left(\frac{\alpha - \beta}{2}\right) = \cos(\beta) - \cos(\alpha)$$

$$\int_0^a \sin\left(\frac{m\pi}{a}x\right) x \sin\left(\frac{n\pi}{a}x\right) = \frac{1}{2} \int_0^a x \left(\cos\left(\frac{\pi x}{a}(m - n)\right) - \cos\left(\frac{\pi x}{a}(m + n)\right) \right) \quad (8)$$

There are two integrals to calculate and start with the one with $m - n$ and assume $m \neq n$. Start with

$$\begin{aligned} \int_0^a x \cos\left(\frac{\pi x}{a}(m - n)\right) &= \left[x \frac{a}{(m - n)\pi} \sin\left(\frac{\pi x}{a}(m - n)\right) \right]_0^a - \int_0^a \frac{a}{(m - n)\pi} \sin\left(\frac{\pi x}{a}(m - n)\right) = \\ &= 0 + \left[x \frac{a^2}{(m - n)^2 \pi^2} \cos\left(\frac{\pi x}{a}(m - n)\right) \right]_0^a = \frac{a^2}{(m - n)^2 \pi^2} (-1)^{m-n} - \frac{a^2}{(m - n)^2 \pi^2} = 0 \end{aligned}$$

The reason for the last to equal zero is the both m and n are odd numbers (see previous part a) so the difference is an even integer. From this calculation we can also conclude that the integral

$$\int_0^a x \cos\left(\frac{\pi x}{a}(m + n)\right) = 0$$

The case $m = n$ will become:

$$\int_0^a x \cos(0) = \left[\frac{x^2}{2} \right]_0^a = \frac{a^2}{2}$$

Now we have calculated all the integrals in eq.8 and we can proceed to calculate $\langle x \rangle$ in eq. 7. Note that the double sum in eq. 7 collapses into a single sum.

$$\langle x \rangle = \sum_m c_m^* \frac{2}{a} e^0 \frac{1}{2} \frac{a^2}{2} c_m = \frac{a}{2} \sum_m c_m^* c_m = \frac{a}{2}$$

The sum $\sum_m c_m^* c_m = 1$ as the wave function is normalised. So the expectation value of x is equal to $\frac{a}{2}$ and is independent of time.

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

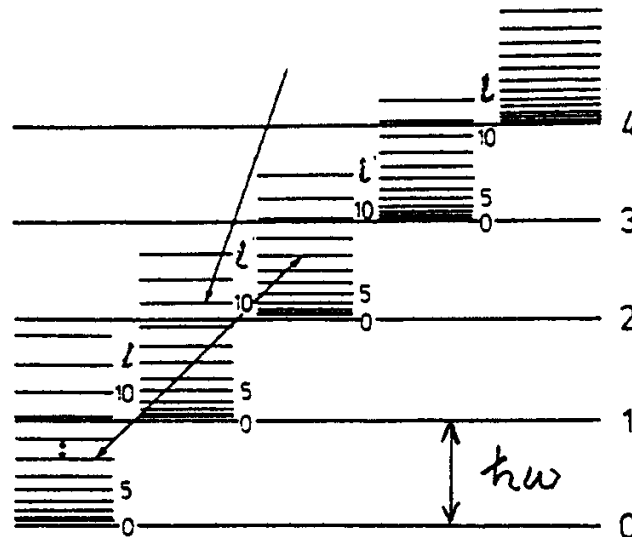


Figure 1: Energy levels for a diatomic molecule. The long horizontal lines mark the $l = 0$ levels, with the vibrational quantum number n to the right. The spacing in energy between these lines is $\hbar\omega$. The states with higher l -values (the rotational bands) give a dense sequence of states for each n -value. The arrows show two possible transitions, one harmonic ($n = 2 \rightarrow n = 1$) and one anharmonic ($n = 2 \rightarrow n = 0$).

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 $\Delta n = -1, \Delta l = -1$: i.e. 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):

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

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

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

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 unallowed 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: $\lambda = 4.6 + \frac{4.7-4.6}{34.8}23.0 = 4.67\mu\text{m}$. 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 $\mu = \frac{m_C m_O}{m_C + m_O} = \frac{12.011 \cdot 15.999}{12.011 + 15.999} = 6.86055\text{u}$
 $= 6.86055 \cdot 1.660538 \cdot 10^{-27} = 1.13922 \cdot 10^{-26} \text{ kg}$.

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 spectra are given as intensity as a function of wave length λ we have two options to calculate for ΔE . We can estimate the λ of two adjacent lines invert these two and calculate the difference. Or we do like this differentiate $E = \frac{hc}{\lambda}$ and get $dE = -\frac{hc}{\lambda^2}d\lambda$ 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. The data is for the missing centre line with 5 space to left and 5 to the right. This gives an estimate of $\Delta\lambda$ at the centre. This can be transformed to a line separation $\Delta\lambda = \frac{0.10}{34.8} \frac{32.8}{10} = 0.00943\mu\text{m}$. 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 $\Delta\lambda^{-1} = -\frac{\Delta\lambda}{\lambda^2}$. The minus signs we can omit as long as we keep in mind that a photon has a positive energy. Hence this equates to $\Delta\lambda^{-1} = \frac{0.00943}{4.67^2} = 4.324 \cdot 10^{-4}(\mu\text{m})^{-1} = 4.324 \cdot 10^2(\text{m})^{-1}$, at the centre (see above).

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

$$R = \sqrt{\frac{h\lambda^2}{4\pi^2 c \Delta\lambda \mu}} = \sqrt{\frac{6.626 \cdot 10^{-34} (4.67 \cdot 10^{-6})^2}{4\pi^2 \cdot 2.997 \cdot 10^8 \cdot 0.00943 \cdot 10^{-6} \cdot 1.13922 \cdot 10^{-26}}} = 1.066 \cdot 10^{-10}\text{m} \quad (9)$$

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

In wikipedia you find $R = 1.12 \cdot 10^{-10}\text{m}$ 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. Rewrite $L_z^2 + L_y^2 = L^2 - L_x^2$, which gives the Hamiltonian

$$H = \frac{L^2 - L_x^2}{2\hbar^2} + \frac{L_x^4}{4\hbar^2} = \frac{L^2 - L_x^2}{4\hbar^2}.$$

Here we use the freedom to orient the coordinate system such that the appropriate operators are L_x and L^2 instead of the usual conventional L_z and L^2 . The eigenfunctions are not the ordinary spherical harmonics but we know the eigenvalue spectrum that is the same. Lets denote the eigenfunctions by \tilde{Y}_{l,m_x}

$$H\tilde{Y}_{l,m_x} = \left(\frac{L^2 - L_x^2}{2\hbar^2} + \frac{L_x^4}{4\hbar^2} \right) \tilde{Y}_{l,m_x} = \left(\frac{l(l+1)\hbar^2 - m_x^2\hbar^2}{2\hbar^2} + \frac{m_x^2\hbar^2}{4\hbar^2} \right) \tilde{Y}_{l,m_x}.$$

Hence the energies are:

$$E_{l,m_x} = \left(\frac{l(l+1)}{2} - \frac{m_x^2}{4} \right).$$

An important issue is the relation between l and m_x , ie $l = 0, 1, 2, 3, \dots$ and $m_x = -l, -l+1, \dots, 0, l-1, l$. Or it may also be expressed through some kind of treatment where it from the treatment is clear how l and m_x are related. The lowest (ground state) energy is $E_{0,0} = 0$ ($l = 0$ no rotation).

$$l = 1 \rightarrow m_x = 0, \pm 1, \text{ gives } E_{1,0} = \frac{2}{2} = 1\text{eV } E_{1,\pm 1} = \frac{3}{4}\text{eV}$$

$$l = 2 \rightarrow m_x = 0, \pm 1, \pm 2, \text{ gives } E_{2,0} = 3\text{eV } E_{2,\pm 1} = \frac{11}{4}\text{eV } E_{2,\pm 2} = 2\text{eV}$$

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

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

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.

$$\frac{1e^{-1.0\hbar\omega/k_B T}}{Z} = \frac{2e^{-2.0\hbar\omega/k_B T}}{Z} \quad (11)$$

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

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

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

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

The probability P will be (put Z into one of the terms in eq (11)).

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

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

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

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