

## Solution to written exam in QUANTUM PHYSICS F0047T

Examination date: 2014-08-30

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

1. (a) There are several ways to determine  $A$ . One is to integrate and use the normalization condition to solve for  $A$ . A different path (done here) is to write the given wave function in terms of eigenfunctions. The eigenfunctions are (PH)  $\psi(x) = \sqrt{\frac{2}{a}} \sin(\frac{n\pi x}{a})$ . We can directly conclude that the given wave function consists of eigenfunctions with  $n = 1$  and  $n = 5$ , we can write:

$$\psi(x, 0) = \frac{A\sqrt{2}}{\sqrt{2a}} \sin\left(\frac{\pi x}{a}\right) + \frac{\sqrt{2}}{\sqrt{2 \cdot 5a}} \sin\left(\frac{5\pi x}{a}\right) = \frac{A}{\sqrt{2}} \psi_1(x, 0) + \frac{1}{\sqrt{10}} \psi_5(x, 0)$$

As both eigenfunctions are orthonormal the normalisation integral reduces to  $\frac{A^2}{2} + \frac{1}{10} = 1$  and hence  $A = \sqrt{\frac{18}{10}} = \sqrt{\frac{9}{5}} = \frac{3}{\sqrt{5}}$

- (b) The wave function contains only  $n = 1$  and  $n = 5$  eigenfunctions and therefore the only possible outcomes of an energy measurement are  $E_1 = \frac{\hbar^2 \pi^2}{2ma^2}$  with probability  $\frac{A^2}{2} = 0.9$  and  $E_5 = \frac{\hbar^2 \pi^2}{2ma^2} 25$  with probability  $1 - 0.9 = 0.1$ . The average energy is given by  $\langle E \rangle = 0.9E_1 + 0.1E_5 = \frac{\hbar^2 \pi^2}{2ma^2} (0.9 + 0.1 \cdot 25) = 3.4 \cdot \frac{\hbar^2 \pi^2}{2ma^2} = 1.7 \cdot \frac{\hbar^2 \pi^2}{ma^2}$
- (c) The time dependent solution is given by  $\Psi(x, t) = \sum_{n=1}^{\infty} c_n \psi_n(x) e^{-iE_n t/\hbar}$  and hence

$$\Psi(x, t) = \sqrt{\frac{9}{10}} \psi_1(x, 0) e^{-i\frac{\hbar \pi^2 t}{2ma^2}} + \frac{1}{\sqrt{10}} \psi_5(x, 0) e^{-i\frac{25\hbar \pi^2 t}{2ma^2}}$$

2. Rewrite the wave function in terms of spherical harmonics: (polar coordinates:  $x = r \sin \theta \sin \phi$ ,  $z = r \cos \theta$  and hence  $zx = r^2 \cos \theta \sin \theta (e^{i\phi} + e^{-i\phi})/2$  using the Euler relations) the appropriate spherical harmonics can now be identified and we arrive at

$$\psi(\mathbf{r}) = \psi(x, y, z) = N(zx) e^{-r/3a_0} = N \frac{r^2}{2} \sqrt{\frac{8\pi}{15}} (-Y_{2,1} + Y_{2,-1}) e^{-r/3a_0} . \quad (1)$$

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 0, for  $m = 1\hbar$  is  $\frac{1}{2}$ , for  $m = 0\hbar$  is 0 for  $m = -1\hbar$  is  $\frac{1}{2}$ , and for  $m = -2\hbar$  is 0. 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  $\langle r \rangle$  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  $Y_{2,1}$  and  $Y_{2,-1}$  are normalised but the sum  $(-Y_{2,1} + Y_{2,-1})$  is not normalised. The sum has to be changed to  $(-\frac{1}{\sqrt{2}}Y_{2,1} + \frac{1}{\sqrt{2}}Y_{2,-1})$  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)

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

From physics handbook page 292 you find

$$\langle r \rangle = \frac{1}{2} [3n^2 - l(l+1)] \left( \frac{a_0}{Z} \right) = \frac{1}{2} [3 \cdot 3^2 - 2(2+1)] \left( \frac{a_0}{1} \right) = \frac{21}{2} a_0 = 10.5 \cdot 0.5292 \text{ \AA} = 5.56 \text{ \AA}.$$

You may also do the integral directly like this:

$$\langle r \rangle = \int_0^\infty \int_0^\pi \int_0^{2\pi} d\phi d\theta dr r^2 \sin(\theta) r |R_{3,2}(r)|^2 \left| \left( -\frac{1}{\sqrt{2}}Y_{2,1} + \frac{1}{\sqrt{2}}Y_{2,-1} \right) \right|^2 = \int_0^\infty dr r^3 |R_{3,2}(r)|^2 = \frac{21}{2} a_0 = 10.5 \cdot 0.5292 \text{ \AA} = 5.56 \text{ \AA}.$$

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  $\nu_2$  will have only half the wavelength compared to the  $\nu_1$  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.

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 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

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

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

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

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

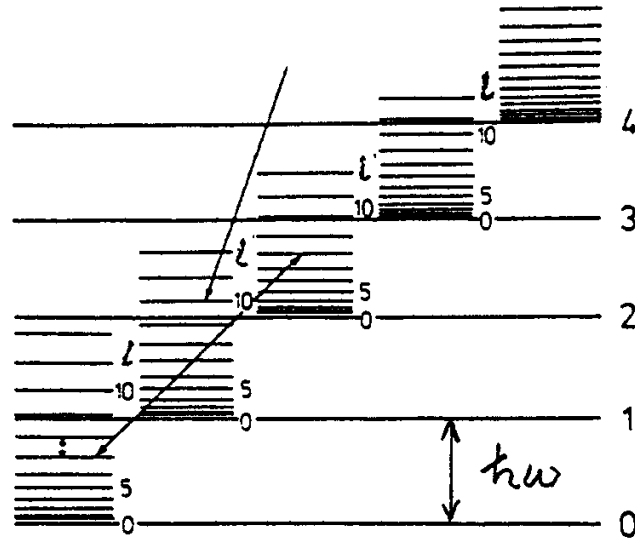


Figure 1: Energy levels for a diatomic molecule. The long horizontal lines mark the  $l = 0$  levels, with the vibrational quantum number  $n$  to the right. The spacing in energy between these lines is  $\hbar\omega$ . The states with higher  $l$ -values (the rotational bands) give a dense sequence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

All these energy differences will appear in the spectra. It is also clear that there is always a change in the rotational quantum number  $l$ . It therefore seems as if there is a line missing for the unaltered 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  $\omega$  of the oscillator, given by the missing line.

Extrapolate the 'wave length' of the missing line:  $\lambda = 3.9 + \frac{4.0-3.9}{20.5}2.05 = 3.91\mu\text{m}$ . 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  $\mu$  is the reduced mass. For hydrogen bromide we have  $\mu = \frac{1.00798 \cdot 79.904}{1.00798 + 79.904} = 0.99542\text{u} = 0.99542 \cdot 1.660538 \cdot 10^{-27} = 1.6529 \cdot 10^{-27} \text{ kg}$ .

For the strength of the bond we evaluate  $k = \omega^2\mu = 4\pi^2 \frac{c^2}{\lambda^2}\mu = 4\pi^2 \left(\frac{2.998 \cdot 10^8}{3.91 \cdot 10^{-6}}\right)^2 1.6529 \cdot 10^{-27} = 0.38363 \text{ kN/m} \approx 0.384 \text{ kN/m}$ .

- (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. a

The spinor is not normalised and we need to do this first:

$$1 = \chi^* \chi = |A|^2 (2 - 5i, 3 + i) \begin{pmatrix} 2 + 5i \\ 3 - i \end{pmatrix} = |A|^2 |2 + 5i|^2 |3 - i|^2 \rightarrow A = \frac{1}{\sqrt{39}}$$

Note an expectation value is always a real number, never a complex one! Even if you had taken  $A$  to be a complex number like  $A = \frac{i}{\sqrt{39}}$  it would not change the expectation value as the expectation value below only involves  $|A|^2$ .

$$\langle S_x \rangle = \frac{1}{39} (2 - 5i, 3 + i) \frac{\hbar}{2} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \begin{pmatrix} 2 + 5i \\ 3 - i \end{pmatrix} = \frac{1}{39} \hbar$$

$$\langle S_y \rangle = \frac{1}{39} (2 - 5i, 3 + i) \frac{\hbar}{2} \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \begin{pmatrix} 2 + 5i \\ 3 - i \end{pmatrix} = -\frac{17}{39} \hbar$$

$$\langle S_z \rangle = \frac{1}{39} (2 - 5i, 3 + i) \frac{\hbar}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \begin{pmatrix} 2 + 5i \\ 3 - i \end{pmatrix} = \frac{19}{78} \hbar$$

**b**

Measurement along the  $x$  direction means:  $S = (1, 0, 0) \cdot (S_x, S_y, S_z) = S_x$ . The idea is to expand the initial spinor  $\chi$  into the eigenspinors of  $S_x$ . So we start to calculate the eigenvalues and eigenspinors to  $S_x$ . The spin operator  $S_x$  is

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

we find the eigenvalues from the following equation

$$S_x \chi = \lambda \chi \Leftrightarrow \frac{\hbar}{2} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \begin{pmatrix} a \\ b \end{pmatrix} = \lambda \begin{pmatrix} a \\ b \end{pmatrix} \quad (2)$$

We find the eigenvalues from the equation

$$\begin{vmatrix} -\lambda & \frac{\hbar}{2} \\ \frac{\hbar}{2} & -\lambda \end{vmatrix} = 0 \Rightarrow \lambda = \pm \frac{\hbar}{2}$$

The eigenspinors to  $S_x$  corresponding to the  $+\frac{\hbar}{2}$  we get from

$$\frac{\hbar}{2} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \begin{pmatrix} a \\ b \end{pmatrix} = +\frac{\hbar}{2} \begin{pmatrix} a \\ b \end{pmatrix}$$

The two equations above are linearly dependent and one of them is

$$a = b \Leftrightarrow \text{let } b = 1 \text{ and hence } a = 1$$

This gives the unnormalised spinor

$$\begin{pmatrix} 1 \\ 1 \end{pmatrix} \text{ and after normalisation we have } \chi_{x+} = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 1 \end{pmatrix}$$

The other eigenspinor  $\chi_{x-}$  has to be orthogonal to  $\chi_{x+}$ . An appropriate choice is:

$$\chi_{x-} = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ -1 \end{pmatrix}$$

This eigenspinor  $\chi_{x-}$  is orthogonal to the eigenspinor  $\chi_{x+}$ .

Now we can expand the initial spinor  $\chi$  in these eigenspinors of  $S_x$ .

$$\chi = \frac{1}{\sqrt{39}} \begin{pmatrix} 2 + 5i \\ 3 - i \end{pmatrix} = b_+ \chi_{x+} + b_- \chi_{x-}$$

The coefficient  $b_+$  is given by

$$b_+ = \chi_{x+}^* \chi = \frac{1}{\sqrt{78}} (1 \quad 1) * \begin{pmatrix} 2 + 5i \\ 3 - i \end{pmatrix} = \frac{1}{\sqrt{78}} (2 + 5i + 3 - i) = \frac{1}{\sqrt{78}} (5 + 4i)$$

A similar calculation gives  $b_-$  :

$$b_- = \chi_{x-}^* \chi = \frac{1}{\sqrt{78}} (1 \quad -1) * \begin{pmatrix} 2 + 5i \\ 3 - i \end{pmatrix} = \frac{1}{\sqrt{78}} (2 + 5i - 3 + i) = \frac{1}{\sqrt{78}} (-1 + 6i)$$

We may now check that  $|b_+|^2 + |b_-|^2 = 1$

$$|b_+|^2 + |b_-|^2 = \frac{1}{78} (25 + 16 + 1 + 36) = 1 \quad \text{ok}$$

The probability (to get  $+\frac{\hbar}{2}$ ) is given by  $|b_+|^2$ .

$$|b_+|^2 = \frac{1}{78} (25 + 16) = \frac{41}{78} \approx \mathbf{0.526}$$

and (to get  $-\frac{\hbar}{2}$ ) is given by  $|b_-|^2$ .

$$|b_-|^2 = \frac{1}{78} (1 + 36) = \frac{37}{78} \approx \mathbf{0.474}$$

You may make the following check for consistency:

$$\langle S_x \rangle = \left( \frac{41}{78} \left( \frac{\hbar}{2} \right) + \frac{37}{78} \left( -\frac{\hbar}{2} \right) \right) = \frac{1}{39} \hbar$$

The same result as in part **a**.

5. The system is initially in its ground state. The initial state when the particle is under the influence of a potential characterized by the frequency  $\omega_1$  is the ground state  $\psi_0^{(\omega_1)}$ . Immediately after the change to  $\omega_2$  we need to analyse the 'new' system with the new eigenfunctions  $\psi_j^{(\omega_2)}$ . The relation between the 'old' and the 'new' system is given by the completeness relation

$$\psi_0^{(\omega_1)} = \sum_{j=0}^{\infty} c_j \psi_j^{(\omega_2)} \quad (3)$$

where the coefficients  $c_j$  describe the spectral distribution for the new eigenstates in relation to the initial. The probability to find the system in the state  $j$  is given by  $|c_j|^2$ . Here we will use the ground state prior to the sudden change  $\psi_0^{(\omega_1)} = \sqrt{\frac{m\omega_1}{\hbar\pi}} e^{-\frac{m\omega_1 x^2}{\hbar^2}}$  and also the ground and first excited state after the change.

In **a** we have to calculate  $c_0$ , which is given by the integral:

$$c_0 = \int (\psi_0^{(\omega_2)})^* \psi_0^{(\omega_1)} dx \quad (4)$$

The ground state wave function (after) is  $\psi_0^{(\omega_2)} = \sqrt[4]{\frac{m\omega_2}{\hbar\pi}} e^{-\frac{m\omega_2 x^2}{\hbar^2}}$ . Now calculate  $c_0$  according to

$$c_0 = \int \sqrt[4]{\frac{m\omega_2}{\hbar\pi}} e^{-\frac{m\omega_2 x^2}{\hbar^2}} \sqrt[4]{\frac{m\omega_1}{\hbar\pi}} e^{-\frac{m\omega_1 x^2}{\hbar^2}} dx = \int \sqrt{\frac{m}{\hbar\pi}} \sqrt[4]{\omega_1\omega_2} e^{-\frac{m(\omega_1+\omega_2)x^2}{\hbar^2}} dx \quad (5)$$

Make a change of variables  $\sqrt{\frac{m(\omega_1+\omega_2)}{2\hbar}} x = y$  and  $dx = \sqrt{\frac{2\hbar}{m(\omega_1+\omega_2)}} dy$ .

$$c_0 = \int \sqrt{\frac{m}{\hbar\pi}} \sqrt{\frac{2\hbar}{m(\omega_1+\omega_2)}} \sqrt[4]{\omega_1\omega_2} e^{-y^2} dy = \sqrt[4]{\frac{4\omega_1\omega_2}{(\omega_1+\omega_2)^2}} \quad (6)$$

The probability for the system to be in the new ground state is  $|c_0|^2 = \sqrt{\frac{4\omega_1\omega_2}{(\omega_1+\omega_2)^2}} = \frac{2\sqrt{\omega_1\omega_2}}{(\omega_1+\omega_2)}$ .

In **b)** we have to make a similar calculation as in **a)**. We can however note that the wave function for the first excited state is  $\psi_1^{(\omega_2)} = \sqrt[4]{\frac{m\omega_2}{\hbar\pi}} \sqrt{2} \frac{m\omega_2}{\hbar\pi} x e^{-\frac{m\omega_2 x^2}{\hbar^2}}$ . This is however an **odd** function and hence the integrand for  $c_1$  is odd and we arrive at  $c_1 = 0.00$