LULEÅ UNIVERSITY OF TECHNOLOGY
Division of Physics

Solution to written exam in QUANTUM PHYSICS F0047T
Examination date: 2013-03-19

1. This is a 2 dimensional problem with a Schrödinger equation (where $V(x, y) = 0$) like

$$-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\Psi(x, y) - \frac{\hbar^2}{2m}\frac{d^2}{dy^2}\Psi(x, y) = E\Psi(x, y)$$

This equation is separable and the ansatz $\Psi(x, y) = \psi(x) * \psi(y)$ gives the following result

$$-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\psi_x(x) - \frac{\hbar^2}{2m}\frac{d^2}{dy^2}\psi_y(y) = E_x\psi_x(x) + E_y\psi_y(y)$$

ie two independent one dimensional Schrödinger equations one for the variable x and on for y. We therefor solve the one dimensional problem first and after that we construct the two dimensional solution. To find the eigenfunctions we need to solve the Schrödinger equation which is (in the region where $V(x)$ is zero)

$$-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\Psi = E\Psi \ \rightarrow \ \frac{d^2}{dx^2}\Psi + k^2\Psi = 0 \text{ where } k^2 = \frac{2mE}{\hbar^2}$$

Solutions are of the kind:
$$\Psi(x) = A\cos kx + B\sin kx$$

Now we need to take the boundary conditions for the wave function Ψ $\left(\Psi(-\frac{a}{2}) = \Psi(\frac{a}{2}) = 0\right)$ into account.

$$A\cos(-\frac{ka}{2}) + B\sin(-\frac{ka}{2}) = 0 \text{ and } A\cos(\frac{ka}{2}) + B\sin(\frac{ka}{2}) = 0$$

Adding the two conditions gives: $\cos(\frac{ka}{2}) = 0$ and subtracting them gives $\sin(\frac{ka}{2}) = 0$. These two conditions cannot be fulfilled at the same time, so either A or B has to be zero. We start with $A = 0$ and we get the following solution: The normalising constant $B = \sqrt{\frac{2}{a}}$ you get from the condition $\int_{-a/2}^{a/2} |\Psi|^2 \, dx = 1$. The condition $\sin(\frac{ka}{2}) = 0$ gives $\frac{ka}{2} = \frac{\pi}{2} * (even - integer)$. The solution is:

$$\psi_n(x) = \sqrt{\frac{2}{a}}\sin(\frac{n\pi x}{a}) \ \text{ with eigenenergys } E_n = \frac{n^2\pi^2\hbar^2}{2Ma^2} \ \text{ where } \ n = 2, 4, 6, ... \quad (1)$$

In a similar way the other function is analysed ($A = 0$) which gives: The condition $\cos(\frac{ka}{2}) = 0$ gives $\frac{ka}{2} = \frac{\pi}{2} * (odd - integer)$. The solution is:

$$\psi_n(x) = \sqrt{\frac{2}{a}}\cos(\frac{n\pi x}{a}) \ \text{ with eigenenergys } E_n = \frac{n^2\pi^2\hbar^2}{2Ma^2} \ \text{ where } \ n = 1, 3, 5, ... \quad (2)$$

The eigenfunctions in the y direction are the same as for the x direction as the potential is similar for this direction. Now we have the eigenfunctions of the one dimensional problem and the solution to the 2 dimensional problem is readily produced. The eigenfunctions are:

$$\Psi_{n,m}(x, y) = \psi_n(x) \cdot \psi_m(y) \text{ eigenenergys } E_{n,m} = E_n + E_m \text{where } n = 1, 2, ,. \text{ and } m = 1, 2, ,. \quad (3)$$

In the area where the potential is infinite the wave function is equal to zero.

An **alternative route** taken by many students has been to present a calculation with the following boundary conditions: Ψ ($\Psi(0) = \Psi(a) = 0$) into account. In this case the solution is for these boundary conditions:

$$\psi_n(x) = \sqrt{\frac{2}{a}}\sin(\frac{n\pi x}{a}) \quad \text{with eigenenergys } E_n = \frac{n^2\pi^2\hbar^2}{2Ma^2} \quad \text{where} \quad n = 1, 2, 3, ... \quad (4)$$

This solution has to be adapted to the boundary conditions related to this exam problem:

$$\psi_n(x) = \sqrt{\frac{2}{a}}\sin(\frac{n\pi}{a}(x + \frac{a}{2})) \quad \text{with eigenenergys } E_n = \frac{n^2\pi^2\hbar^2}{2Ma^2} \quad \text{where} \quad n = 1, 2, 3, ... \quad (5)$$

$\psi_n(x) = \sqrt{\frac{2}{a}}\sin(\frac{n\pi x}{a} + \frac{n\pi}{2}) = \sqrt{\frac{2}{a}}\left(\sin(\frac{n\pi x}{a}) \cdot \cos(\frac{n\pi}{2}) + \cos(\frac{n\pi x}{a}) \cdot \sin(\frac{n\pi}{2})\right)$. We see that we recover the solution in eq (1), (2) and (3) as we let n run from 1 to ∞.

b) The ground state eigenfunction is given by (using eq. (2))

$$\Psi_{n=1,m=1}(x, y) = \psi_1(x) \cdot \psi_1(y) = \sqrt{\frac{2}{a}}\cos(\frac{\pi x}{a}) \cdot \sqrt{\frac{2}{a}}\cos(\frac{\pi y}{a}) \quad (6)$$

The next lowest state eigenfunction is given by (using eq. (2) and (1)). Note there are two eigenfunctions with the same energy ($\Psi_{n=1,m=2}(x, y)$) you may use either one of them.

$$\Psi_{n=2,m=1}(x, y) = \psi_2(x) \cdot \psi_1(y) = \sqrt{\frac{2}{a}}\sin(2\frac{\pi x}{a}) \cdot \sqrt{\frac{2}{a}}\cos(\frac{\pi y}{a}) \quad (7)$$

Orthogonality is defined as

$$\int_x \int_y \Psi_{n_1,m_1}(x, y)\Psi_{n_2,m_2}(x, y) = \delta_{n_1,n_2} \, \delta_{m_1,m_2} \quad (8)$$

by explicit calculation

$$\int_{x=-a/2}^{a/2} \int_{y=-a/2}^{a/2} \left(\frac{2}{a}\cos(\frac{\pi x}{a}) \cdot \cos(\frac{\pi y}{a})\right) \cdot \left(\frac{2}{a}\sin(2\frac{\pi x}{a}) \cdot \cos(\frac{\pi y}{a})\right) = \text{calculations} = 0 \quad (9)$$

this is a separable integral (in x and y), suggestion do the integral in x first as this will be zero as they belong to different eigenvalues. Thus the calculation ends with a zero as it should.

2. A measurement of the spin in the direction $\hat{n} = \sin(\frac{\pi}{4})\hat{e}_y + \cos(\frac{\pi}{4})\hat{e}_z = \frac{1}{\sqrt{2}}\hat{e}_y + \frac{1}{\sqrt{2}}\hat{e}_z$. The spin operator $S_{\hat{n}}$ is

$$S_{\hat{n}} = \frac{1}{\sqrt{2}}S_y + \frac{1}{\sqrt{2}}S_z = \frac{\hbar}{2\sqrt{2}}\begin{pmatrix} 1 & -i \\ i & -1 \end{pmatrix}$$

The eigenvalue equation is

$$S_{\hat{n}}\chi = \lambda\chi \Leftrightarrow \frac{\hbar}{2\sqrt{2}}\begin{pmatrix} 1 & -i \\ i & -1 \end{pmatrix}\begin{pmatrix} a \\ b \end{pmatrix} = \lambda\begin{pmatrix} a \\ b \end{pmatrix} \quad (10)$$

We find the eigenvalues from

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

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

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

$$\frac{a}{\sqrt{2}} - \frac{ib}{\sqrt{2}} = a \Leftrightarrow a(\sqrt{2} - 1) = -ib \quad \text{let} \quad b = 1 \quad \text{and hence} \quad a = \frac{-i}{\sqrt{2} - 1}$$

This gives the unnormalised spinor

$$\begin{pmatrix} -\frac{i}{\sqrt{2}-1} \\ 1 \end{pmatrix} \quad \text{and after normalisation we have} \quad \chi_{\hat{n}+} = \frac{1}{\sqrt{2(2+\sqrt{2})}}\begin{pmatrix} -\frac{i}{\sqrt{2}-1} \\ 1 \end{pmatrix}$$

Now we can expand the initial eigenspinor χ_+ in these eigenspinors to S_n, the second eigenspinor you can get from orthogonality to the first one.

$$\begin{pmatrix} 1 \\ 0 \end{pmatrix} = A\frac{1}{\sqrt{2(2+\sqrt{2})}}\begin{pmatrix} -\frac{i}{\sqrt{2}-1} \\ 1 \end{pmatrix} + B\frac{1}{\sqrt{2(2+\sqrt{2})}}\begin{pmatrix} 1 \\ \frac{-i}{\sqrt{2}-1} \end{pmatrix}$$

The coefficients are subjected to the normalisation condition $|A|^2 + |B|^2 = 1$. The coefficient A can be obtained by multiplying the previous equation from the left with $\chi_{\hat{n}+}^*$.

$$A = \frac{1}{\sqrt{2(2+\sqrt{2})}}\begin{pmatrix} -\frac{i}{\sqrt{2}-1} & 1 \end{pmatrix} * \begin{pmatrix} 1 \\ 0 \end{pmatrix} = -\frac{i}{\sqrt{2}-1} \cdot \frac{1}{\sqrt{2(2+\sqrt{2})}}$$

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

$$|A|^2 = \frac{3+2\sqrt{2}}{4+2\sqrt{2}} = 0.8535533906$$

and (to get $-\frac{\hbar}{2}$) for $|B|^2$.

$$|B|^2 = \frac{1}{4+2\sqrt{2}} = 0.1464466094$$

To find the probability for $+\frac{\hbar}{2}$ in the z-direction for the up state of S_n express the state in the eigenspinors to S_z.

$$\chi_{\hat{n}+} = \frac{1}{\sqrt{2(2+\sqrt{2})}}\begin{pmatrix} -\frac{i}{\sqrt{2}-1} \\ 1 \end{pmatrix} = -\frac{i}{\sqrt{2}-1} \cdot \frac{1}{\sqrt{2(2+\sqrt{2})}}\begin{pmatrix} 1 \\ 0 \end{pmatrix} + \frac{1}{\sqrt{2(2+\sqrt{2})}}\begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

3

The probability is given by the square of the coefficient:

$$\left| -\frac{i}{\sqrt{2}-1} \cdot \frac{1}{\sqrt{2(2+\sqrt{2})}} \right|^2 = 0.8535533906$$

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.

   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
   $\Delta E = \hbar\omega + \frac{\hbar^2}{2I}(l+1)(l+2) - \frac{\hbar^2}{2I}l(l+1) = \frac{\hbar^2}{I}(l+1), l = 0, 1, 2, 3$, 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 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 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.
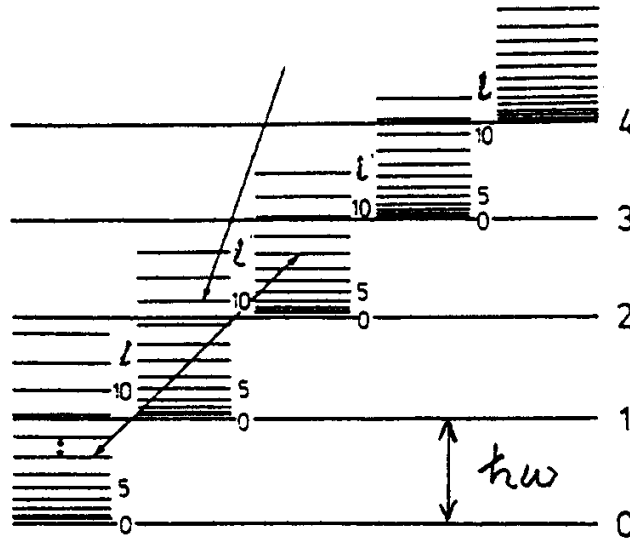
Figure 1: Energy levels for a diatomic molecule. The long horisontal lines mark the $l = 0$ levels, with the vibrational quantum number n to the right. The spacing in energy between these lines is $\hbar\omega$. The states with higher l-values (the rotational bands) give a dense sequence of states for each n-value. The arrows show two possible transitions, one harmonic ($n = 2 \to n = 1$) and one anharmonic ($n = 2 \to n = 0$).

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

For the strength of the bond we evaluate $k = \omega^2\mu = 4\pi^2\frac{c^2}{\lambda^2}\mu = 4\pi^2(\frac{2.998 \cdot 10^8}{3.91 \cdot 10^{-6}})^2 1.6529 \cdot 10^{-27} = 0.38363$ kN/m ≈ 0.384 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. Use a test function $f(r, \theta, \phi)$ to calculate the commutator.

$$
\begin{aligned}
[L_z, \sin\phi]\, f(r, \theta, \phi) &= \left[-i\hbar\frac{\partial}{\partial\phi}, \sin\phi\right] f(r, \theta, \phi) \\
&= -i\hbar\frac{\partial}{\partial\phi}\sin\phi f(r, \theta, \phi) - \sin\phi\left(-i\hbar\frac{\partial}{\partial\phi}\right) f(r, \theta, \phi) \\
&= -i\hbar\cos\phi f - i\hbar\sin\phi\frac{\partial f}{\partial\phi} + i\hbar\sin\phi\frac{\partial f}{\partial\phi} \\
&= -i\hbar\cos\phi f(r, \theta, \phi).
\end{aligned}
$$

Thus, $[L_z, \sin\phi] = -i\hbar\cos\phi$.

5. 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 $\tilde{Y}_{l,m_x}$

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

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 $l = 0, 1, 2, 3, ...$ and $m_x = -l, -l+1, ..., 0, l-1, l$. 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).

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

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

.

.

.