PHYS457 - Honours Quantum Mechanics

Homework 3 - Solutions

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

$$(2\ell + 1)e^{-(E_\ell - E_0)/k_B T}$$

where the factor $2\ell+1$ reflects the number of rotational states with energy E_ℓ, that is, the degeneracy of this energy level.

(a) Show that the population of rotational energy levels first increases and then decreases with increasing ℓ.

Solution. For any of the $2\ell + 1$ states with energy E_ℓ, the population is $e^{-E_\ell/k_B T}$. Thus, the total population of molecules with rotational energy level E_ℓ is

$$n_\ell = (2\ell + 1)e^{-E_\ell/k_B T}.$$

We know that $E_\ell = \frac{\hbar^2 \ell(\ell+1)}{2\mu r_0^2}$, where $\mu = \frac{m_1 m_2}{m_1 + m_2}$ is the reduced mass of the two-body problem and r_0 is the equilibrium distance of the two masses. As we want to find how n_ℓ changes with ℓ, we compute its derivative and look at where it is positive/negative:

$$\frac{\mathrm{d}n_\ell}{\mathrm{d}\ell} = 2e^{-\frac{\hbar^2 \ell(\ell+1)}{2\mu r_0^2 k_B T}} - \frac{\hbar^2}{\mu r_0^2 k_B T}(2\ell + 1)^2 e^{-\frac{\hbar^2 \ell(\ell+1)}{2\mu r_0^2 k_B T}} = e^{-\frac{\hbar^2 \ell(\ell+1)}{2\mu r_0^2 k_B T}} \left(2 - \frac{\hbar^2}{\mu r_0^2 k_B T}(2\ell + 1)^2\right),$$

which is positive when

$$\ell < \sqrt{\frac{\mu r_0^2 k_B T}{2\hbar^2}} - \frac{1}{2}$$

and negative otherwise. Thus, the population does indeed increase and then decrease with increasing ℓ. The point at which it starts decreasing will be determined by the specific values of μ, r_0 and the temperature.

(b) Which energy level will be occupied by the largest number of molecules for HCl at room temperature? Compare you result with the intensities of the absorption spectrum in Fig. 9.9. What do you deduce about the temperature of the gas?

Solution. Based on the previous question, we know that the population is maximal when

$$\ell = \sqrt{\frac{\mu r_0^2 k_B T}{2\hbar^2}} - \frac{1}{2}. \tag{1}$$

Of course, this value might not be an integer, in which case the most populated energy level would be one whose associated quantum number ℓ is closest. For HCl, the reduced mass is $\mu = 1.628 \times 10^{-27}$ kg and the internuclear distance is $r_0 = 1.27 \times 10^{-10}$ m (p.325 Townsend). At room temperature ($T = 293$ K), we find $\ell = 2.7$. Thus, we expect the third rotational energy level to be most occupied. This agrees with Fig. 9.9 in Townsend, hence we deduce that the temperature of the gas that was used for the figure was around room temperature as well. Indeed, if it showed that the second energy level was most prevalent (i.e., a higher second peak), we would deduce that the temperature would be around $T = 200$ K.

9.12 The wavefunction for a particle is of the form $\psi(\boldsymbol{r}) = (x + y + z)f(r)$. What are the values that a measurement of $\boldsymbol{L}^2$ can yield? What values can be obtained by measuring L_z? What are the probabilities of obtaining these results? *Suggestion*: Express the wavefunction in spherical coordinates and then in terms of the $Y_{l,m}$'s.

Solution. We will follow the suggestion and write x, y and z in spherical coordinates:

$$\begin{aligned} x &= r\sin\theta\cos\phi, \\ y &= r\sin\theta\sin\phi, \\ z &= r\cos\theta. \end{aligned}$$

The wavefunction in spherical coordinates is

$$\psi(\boldsymbol{r}) = \psi(r,\theta,\phi) = (\sin\theta\cos\phi + \sin\theta\sin\phi + \cos\theta)rf(r).$$

Looking at a table of spherical harmonics, we notice that only those who have $\ell = 1$ are relevant ($Y_{1,0}$ has $\cos\theta$ and both $Y_{1,\pm1}$ have $\sin\theta$; to get $\cos\phi$ and $\sin\phi$ we can combine $e^{i\phi}$ and $e^{-i\phi}$). Indeed, we can write

$$\begin{aligned} &\sin\theta\cos\phi + \sin\theta\sin\phi + \cos\theta \\ &\quad = \sqrt{\frac{2\pi}{3}}\left(Y_{1,-1}(\theta,\phi) - Y_{1,1}(\theta,\phi)\right) + i\sqrt{\frac{2\pi}{3}}\left(Y_{1,-1}(\theta,\phi) + Y_{1,1}(\theta,\phi)\right) + 2\sqrt{\frac{\pi}{3}}Y_{1,0}(\theta,\phi). \end{aligned}$$

The only possible value a measurement of $\boldsymbol{L}^2$ would yield is one associated to $\ell = 1$, that is, $1(1+1)\hbar^2 = 2\hbar^2$. Further, the values that can be obtained by measuring L_z are those associated to $m = -1, 0, 1$. To find their probabilities, we first have to normalize the (angular part of the) wavefunction $\psi(\boldsymbol{r})$. Since

$$\begin{aligned} &\sin\theta\cos\phi + \sin\theta\sin\phi + \cos\theta \\ &\quad = \left(\sqrt{\frac{2\pi}{3}} + i\sqrt{\frac{2\pi}{3}}\right)Y_{1,-1}(\theta,\phi) + 2\sqrt{\frac{\pi}{3}}Y_{1,0}(\theta,\phi) + \left(-\sqrt{\frac{2\pi}{3}} + i\sqrt{\frac{2\pi}{3}}\right)Y_{1,1}(\theta,\phi), \end{aligned}$$

the normalizing constant N has

$$N^2 = \frac{2\pi}{3}\left|1+i\right|^2 + \frac{4\pi}{3} + \frac{2\pi}{3}\left|-1+i\right|^2 = 4\pi.$$

The probabilities are then

$$\Pr[m=-1] = \frac{1}{4\pi}\left|\sqrt{\frac{2\pi}{3}} + i\sqrt{\frac{2\pi}{3}}\right|^2 = \frac{1}{3},$$
$$\Pr[m=0] = \frac{1}{4\pi}\left|2\sqrt{\frac{\pi}{3}}\right|^2 = \frac{1}{3},$$
$$\Pr[m=1] = \frac{1}{4\pi}\left|-\sqrt{\frac{2\pi}{3}} + i\sqrt{\frac{2\pi}{3}}\right|^2 = \frac{1}{3}.$$

9.13 A particle is in the orbital angular momentum state $|\ell, m\rangle$. Evaluate ΔL_x and ΔL_y for this state. Which states satisfy the equality in the uncertainty relation

$$\Delta L_x \Delta L_y \geq \frac{\hbar}{2}|\langle L_z\rangle|. \tag{2}$$

Suggestion: One approach is to use $L_x = (L_+ + L_-)/2$ and so on. Another is to take advantage of the expectation values of L_x^2 and L_y^2 in an eigenstate of L_z.

Solution. As $L_z|\ell, m\rangle = m\hbar|\ell, m\rangle$, we have $\langle L_z\rangle = \langle \ell, m| m\hbar |\ell, m\rangle = m\hbar$. To compute ΔL_x, we consider the first approach suggested and we write

$$L_x = \frac{1}{2}(L_+ + L_-), \qquad L_y = \frac{1}{2i}(L_+ - L_-).$$

Recall that $\Delta L_x = \sqrt{\langle L_x^2\rangle - \langle L_x\rangle^2}$, where

$$\langle L_x\rangle = \left\langle \frac{1}{2}(L_+ + L_-)\right\rangle = \frac{1}{2}\Big(\langle \ell, m| L_+ |\ell, m\rangle + \langle \ell, m| L_- |\ell, m\rangle \Big) = 0$$

and

$$\begin{aligned}
\langle L_x^2\rangle &= \left\langle \frac{1}{4}(L_+ + L_-)^2\right\rangle \\
&= \frac{1}{4}\langle \ell, m| (L_+^2 + L_+L_- + L_-L_+ + L_-^2) |\ell, m\rangle \\
&= \frac{1}{4}\Big(\langle \ell, m| L_+L_- |\ell, m\rangle + \langle \ell, m| L_-L_+ |\ell, m\rangle \Big) \\
&= \frac{\hbar^2}{4}\Big(\sqrt{\ell(\ell+1) - m(m-1)}\sqrt{\ell(\ell+1) - (m-1)m} \\
&\qquad + \sqrt{\ell(\ell+1) - m(m+1)}\sqrt{\ell(\ell+1) - (m+1)m}\Big) \\
&= \frac{\hbar^2}{2}\Big(\ell(\ell+1) - m^2\Big).
\end{aligned}$$

Similarly, we have that

$$\langle L_y \rangle = \frac{1}{2i}\Big(\langle \ell, m| \, L_+ \, |\ell, m\rangle - \langle \ell, m| \, L_- \, |\ell, m\rangle \Big) = 0$$

as well as

$$\begin{aligned}
\left\langle L_y^2 \right\rangle &= -\frac{1}{4}\Big(\langle \ell, m| \, L_+^2 - L_+L_- - L_-L_+ + L_-^2 \, |\ell, m\rangle \Big) \\
&= \frac{1}{4}\Big(\langle \ell, m| \, L_+L_- \, |\ell, m\rangle + \langle \ell, m| \, L_-L_+ \, |\ell, m\rangle \Big) \\
&= \left\langle L_x^2 \right\rangle .
\end{aligned}$$

Putting everything together we have $\Delta L_x = \Delta L_y$, and the uncertainty relation eq. (2) becomes

$$\frac{\hbar^2}{2}\Big(\ell(\ell+1) - m^2 \Big) \geq \frac{\hbar^2}{2} m.$$

The equality is satisfied when $m^2 + m - \ell(\ell+1) = 0$, that is

$$m(m+1) = \ell(\ell+1).$$

We infer that the states which saturate the inequality are those that have $m = \ell$, meaning $|\ell, \ell\rangle$.

9.20 The wavefunction of a rigid rotator with a Hamiltonian $H = \boldsymbol{L}^2/2I$ is given by

$$\langle \theta, \phi | \psi(0) \rangle = \sqrt{\frac{3}{4\pi}} \sin\theta \sin\phi.$$

(a) What is $\langle \theta, \phi | \psi(t) \rangle$? *Suggestion*: Express the wavefunction in terms of the $Y_{\ell,m}$'s.

Solution. Looking at a table of spherical harmonics, we find that the wavefunction can be obtained by a judicious linear combination of $Y_{1,\pm 1}$. Precisely,

$$\langle \theta, \phi | \psi(0) \rangle = \frac{i}{\sqrt{2}} \left(Y_{1,-1}(\theta, \phi) + Y_{1,1}(\theta, \phi) \right).$$

As both $Y_{1,\pm 1}$ are eigenstates of $\boldsymbol{L}^2$ with eigenvalue $1(1+1)\hbar^2 = 2\hbar^2$, we find

$$\begin{aligned}
\langle \theta, \phi | \psi(t) \rangle &= \langle \theta, \phi | \, e^{-\frac{iHt}{\hbar}} \, |\psi(0)\rangle \\
&= \langle \theta, \phi | \, e^{-\frac{iHt}{\hbar}} \left(\frac{i}{\sqrt{2}} \left(|1, -1\rangle + |1, 1\rangle \right) \right) \\
&= e^{-\frac{2i\hbar t}{2I}} \, \langle \theta, \phi | \left(\frac{i}{\sqrt{2}} \left(|1, -1\rangle + |1, 1\rangle \right) \right) \\
&= \frac{i e^{-\frac{i\hbar t}{I}}}{\sqrt{2}} \left(Y_{1,-1}(\theta, \phi) + Y_{1,1}(\theta, \phi) \right).
\end{aligned}$$

(b) What values of L_z will be obtained if a measurement is carried out and with what probability will these values occur?

Solution. Recall that $L_z |\ell, m\rangle = m\hbar$. As time passes, the wavefunction $\psi(t)$ only acquires a *global* phase. The probabilities associated to the measurements of L_z will thus not change in time (interference between states only happens when they evolve with different phases $e^{-iEt/\hbar}$, i.e., when their energies are different). Since $|\psi(t)\rangle$ is

$$|\psi(t)\rangle = \frac{ie^{-\frac{i\hbar t}{I}}}{\sqrt{2}} \left(|1,-1\rangle + |1,1\rangle\right),$$

then only the values with $m = \pm 1$ are possible with associated probabilities

$$\Pr[m=-1] = |\langle 1,-1|\psi(t)\rangle|^2 = \frac{1}{2}, \qquad \Pr[m=1] = |\langle 1,1|\psi(t)\rangle|^2 = \frac{1}{2}.$$

As expected, the probabilities do not depend on time.

(c) What is $\langle L_x \rangle$ for this state? *Suggestion*: Use bra-ket notation and express the operator L_x in terms of raising and lowering operators.

Solution. In terms of raising and lowering operators, $L_x = (L_+ + L_-)/2$. We find that

$$\begin{aligned}
\langle L_x \rangle &= \frac{1}{2} \langle \psi(t)| (L_+ + L_-) |\psi(t)\rangle \\
&= \left(\frac{-i}{\sqrt{2}}(\langle 1,-1| + \langle 1,1|)\right) \frac{(L_+ + L_-)}{2} \left(\frac{i}{\sqrt{2}}(|1,-1\rangle + |1,1\rangle)\right) \\
&= \frac{1}{4}\Big(\big(\langle 1,-1| + \langle 1,1|\big)\big(\hbar\sqrt{2}\,|1,0\rangle + \hbar\sqrt{2}\,|1,0\rangle\big)\Big) \\
&= 0.
\end{aligned}$$

(d) If a measurement of L_x is carried out, what result(s) will be obtained? With what probability?

Solution. Denote the L_z eigenstates $|\ell, m\rangle_z \equiv |\ell, m\rangle$. To proceed, we first write $|\psi(t)\rangle$ in terms of eigenstates of L_x. To this end, for $\ell = 1$, we have

$$L_x = \frac{\hbar}{\sqrt{2}} \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix},$$

in the ordered basis $\{\, |1,1\rangle_z, |1,0\rangle_z, |1,-1\rangle_z \,\}$. Diagonalizing, we find the three eigenstates

$$|1,-1\rangle_x = \frac{1}{2}\begin{pmatrix} 1 \\ -\sqrt{2} \\ 1 \end{pmatrix}, \qquad |1,0\rangle_x = \frac{1}{\sqrt{2}}\begin{pmatrix} -1 \\ 0 \\ 1 \end{pmatrix}, \qquad |1,1\rangle_x = \frac{1}{2}\begin{pmatrix} 1 \\ \sqrt{2} \\ 1 \end{pmatrix}$$

which have $L_x |1,m\rangle_x = \hbar m |1,m\rangle_x$. We can see that

$$|\psi(t)\rangle = \frac{ie^{-\frac{i\hbar t}{I}}}{\sqrt{2}} \left(|1,-1\rangle_z + |1,1\rangle_z\right) = \frac{ie^{-\frac{i\hbar t}{I}}}{\sqrt{2}} \left(|1,-1\rangle_x + |1,1\rangle_x\right).$$

Measuring L_x hence yields the two possible results $\pm\hbar$, each with a $1/2$ probability.