

Solution to written exam in QUANTUM PHYSICS AND STATISTICAL PHYSICS
F0018T / MTF131

Examination date: 2008-08-30

Note solutions are more detailed compared to previous solutions, earlier than October 2007.

1. A 2p state has quantum numbers $n = 2$ and $l = 1$ (see textbook for explanation for notation of l quantum numbers as "s, p, d and f"). The relevant radial part of the wave function is:

$R_{21}(r) = \frac{1}{\sqrt{3}} \left(\frac{Z}{2a_0}\right)^{3/2} \frac{Zr}{a_0} e^{-Zr/2a_0}$. The probability to find the particle in the range r och $r + dr$ is given by: $P(r)dr = R_{21}(r)^2 r^2 dr$ and hence $P(r) = R_{21}(r)^2 r^2 = \text{konstant } r^4 e^{-Zr/a_0}$.

The extreme is where the derivative is zero.

$\frac{dP(r)}{dr} = 4r^3 e^{-Zr/a_0} - r^4 \frac{Z}{a_0} e^{-Zr/a_0} = r^3 (4 - r \frac{Z}{a_0}) e^{-Zr/a_0} = 0$. The maximum appears at $r = 4a_0$. It is a maximum as $P(0) = P(\infty) = 0$ and $P(r) \geq 0$ and hence a maximum. You can also study the sign change of the derivative to the left and right of the extremum or you can investigate the sign of the second derivative at the extreme.

If there are no external electric or magnetic fields the energy of the hydrogenic levels depends only on the principal quantum number n and not on the angular momentum quantum numbers l and m_l .

For this case the following states have the same energy:

I) 3s with $m_l = 0$, 3p with $m_l = 1$, 3p with $m_l = -1$, 3p with $m_l = 0$.

II) 4d with $m_l = 1$, 4p with $m_l = 0$, 4p with $m_l = -1$.

III) 5d with $m_l = 1$, 5p with $m_l = -1$, 5s with $m_l = 0$.

2. The eigenfunctions of the infinite square well in one dimension are (Here a solution of the S.E. in one dimension is adequate). The width of the well is a .

$$\psi_n(x) = \sqrt{\frac{2}{a}} \sin \frac{n\pi x}{a} \quad \text{and the eigenenergys are } E_n = \frac{n^2 \pi^2 \hbar^2}{2ma^2} \quad \text{where } n = 1, 2, 3, \dots$$

In three dimensions the eigenfunctions and eigenenergys are (Here an argument about separation of variables is needed to justify the structure of the solution)

$\Psi_{n,m,l}(x, y, z) = \psi_n(x) \cdot \psi_m(y) \cdot \psi_l(z)$ and eigenenergys $E_{n,m} = E_n + E_m + E_l$ where the indecies are $n = 1, 2, 3, \dots$, $m = 1, 2, 3, \dots$ and $l = 1, 2, 3, \dots$

a) The eigenfunctions inside the box are (note the sidelength is $a/2$ for one of the sides)

$$\Psi_{n,m,l}(x, y, z) = \sqrt{\frac{2}{a}} \sin \frac{n\pi x}{a} \cdot \sqrt{\frac{2}{a}} \sin \frac{m\pi y}{a} \cdot \sqrt{\frac{4}{a}} \sin \frac{l\pi 2y}{a} \quad \text{where } n = 1, 2, 3, \dots, m = 1, 2, 3, \dots \text{ and } l = 1, 2, 3, \dots$$

The eigenfunctions outside the box are $\Psi_{n,m,l}(x, y, z) = 0$

b) The six lowest eigenenergys are (note the 4 associated to the quantum number l this is due to that the length of the box along the z direction is only half of the other two that are of equal length):

$$E_{n,m,l} = \frac{\pi^2 \hbar^2}{2ma^2} (n^2 + m^2 + 4l^2), \quad \text{where the 6 lowest are } (n^2 + m^2 + 4l^2) = 6, 9, 12, 14, 18, \text{ and } 21.$$

c) The six lowest eigenenergys have degeneracy (different ways to choose n, m, l to form the same energy) (either one, two or four) as follows:

$$\begin{aligned}
E_{1,1,1} &= \text{one state} \quad (n^2 + m^2 + 4l^2 = 6) \\
E_{1,2,1} &= E_{2,1,1} = \text{two states} \quad (n^2 + m^2 + 4l^2 = 9) \\
E_{2,2,1} &= \text{one state} \quad (n^2 + m^2 + 4l^2 = 12) \\
E_{1,3,1} &= E_{3,1,1} = \text{two states} \quad (n^2 + m^2 + 4l^2 = 14) \\
E_{2,3,1} &= E_{3,2,1} = \text{two states} \quad (n^2 + m^2 + 4l^2 = 17) \\
E_{1,1,2} &= \text{one state} \quad (n^2 + m^2 + 4l^2 = 18)
\end{aligned}$$

Energy number 7 is special as the degeneracy is 4 but all four are not connected through a symmetry operation, ie some of these states are accidentally degenerated. These four can be grouped in the following way.

$$\begin{aligned}
E_{1,2,2} &= E_{2,1,2} = \text{two states} \quad (n^2 + m^2 + 4l^2 = 21) \\
E_{1,4,1} &= E_{4,1,1} = \text{two states} \quad (n^2 + m^2 + 4l^2 = 21)
\end{aligned}$$

3. The overall strategy is as follows. The specific heat we get from the entropy which we get from the free energy and to reach the free energy we need to calculate the partition function.

The partition function of the rotor is (approximation for the low temperature limit, in this limit the rotor will spend most of its time in the ground state and little time in the lowest excited state and negligible time in higher excited states)

$$Z_{\text{rot}} = \sum_{j=0}^{\infty} (2j+1) e^{-j(j+1) \frac{\hbar^2}{2I\tau}} \approx 1 + 3e^{-\frac{\hbar^2}{I\tau}} = 1 + 3e^{-x} \quad \text{where } x = \frac{\hbar^2}{I\tau} \gg 1 \text{ in the low temperature limit.}$$

For N identical molecules $Z_{\text{rot}}^{(N)} = \frac{1}{N!} Z_{\text{rot}}^N$, and hence the free energy is

$$F_{\text{rot}} = -N\tau \ln Z_{\text{rot}} + \tau \ln N! = -N\tau \ln(1 + 3e^{-x}) + \tau \ln N! \approx -3N\tau e^{-x} + \tau \ln N! = -3N\tau e^{-\frac{\hbar^2}{I\tau}} + \tau \ln N!.$$

The entropy is: $\sigma_{\text{rot}} = -\left(\frac{\partial F}{\partial \tau}\right)_V \approx$

$$3N(1+x)e^{-x} + \ln N! = 3N\left(1 + \frac{\hbar^2}{I\tau}\right)e^{-\frac{\hbar^2}{I\tau}} + \ln N! \quad \text{and the specific heat in the low temperature limit is: } (C_v)_{\text{rot}} = \tau \left(\frac{\partial \sigma}{\partial \tau}\right)_V \approx 3Nx^2 e^{-x} = 3N \left(\frac{\hbar^2}{I\tau}\right)^2 e^{-\frac{\hbar^2}{I\tau}}.$$

An alternative route is as follows. You can also calculate the inner energy

$$U = -\tau^2 \left(\frac{\partial F}{\partial \tau}\right)_{V,N} = 3N \left(\frac{\hbar^2}{I\tau}\right) e^{-\frac{\hbar^2}{I\tau}}. \quad \text{From this you reach the specific heat as well.}$$

4. $Z = 1 + e^{\frac{mB}{\tau}} + e^{-\frac{mB}{\tau}} \approx 1 + 1 + \frac{mB}{\tau} + \frac{1}{2} \left(\frac{mB}{\tau}\right)^2 + 1 - \frac{mB}{\tau} + \frac{1}{2} \left(\frac{mB}{\tau}\right)^2 = 3\left(1 + \frac{1}{3} \left(\frac{mB}{\tau}\right)^2\right)$

$$F = -\tau \ln Z = -\tau \left[\ln 3 + \ln\left(1 + \frac{1}{3} \left(\frac{mB}{\tau}\right)^2\right) \right] \approx -\tau \left[\ln 3 + \frac{1}{3} \left(\frac{mB}{\tau}\right)^2 \right]$$

$$\sigma = -\frac{\partial F}{\partial \tau}_V = \ln 3 - \frac{1}{3} \left(\frac{mB}{\tau}\right)^2. \quad \text{The decrease in entropy is } \frac{1}{3} \left(\frac{mB}{\tau}\right)^2 \text{ and } A = \frac{1}{3} (mB)^2$$

5. (a) $\langle H \rangle = \frac{1}{2}0.27 + \frac{1}{4}1.08 + \frac{3}{16}3.65 + \frac{1}{16}4.06 = 1.343125 \approx 1.34\text{eV}.$

Uncertainty is defined by: $\langle \Delta H \rangle = \sqrt{\langle H^2 \rangle - \langle H \rangle^2}$

$$\langle H^2 \rangle = \frac{1}{2}(0.27)^2 + \frac{1}{4}(1.08)^2 + \frac{3}{16}(3.65)^2 + \frac{1}{16}(4.06)^2 = 3.85624375 \text{ (eV)}^2.$$

$$\langle \Delta H \rangle = \sqrt{3.85624375 - 1.343125^2} = 1.432571 \approx 1.43\text{eV}$$

- (b) The expression is not unique as we only know the probabilities which are the squares of the coefficients. In the evaluation of $\langle H \rangle$ and $\langle H^2 \rangle$ only the probabilities are important that's why a different sign \pm is of no importance in this calculation.

One is: $\Psi(z) = \frac{1}{\sqrt{2}}\psi_1(z) + \frac{1}{2}\psi_2(z) + \frac{\sqrt{3}}{4}\psi_3(z) + \frac{1}{4}\psi_4(z).$

Another is: $\Psi(z) = \frac{1}{\sqrt{2}}\psi_1(z) - \frac{1}{2}\psi_2(z) + \frac{\sqrt{3}}{4}\psi_3(z) - \frac{1}{4}\psi_4(z).$