

Ch 21b Winter 2008
Solutions for Problem Set #2
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Problem 1.

(a) (5 points)

$$Q(T) = \sum_{J=0}^{\infty} (2J+1) e^{-\frac{E_J}{kT}} \quad (1)$$

where

$$E_J = BJ(J+1)cm^{-1} \quad (2)$$

Incorporating the (2) into (1) we get

$$Q(T) = \sum_{J=0}^{\infty} (2J+1) e^{-\frac{BJ(J+1)}{kT}} \quad (3)$$

By replacing the summation with integral we get

$$\begin{aligned} Q(T) &= \sum_{J=0}^{\infty} (2J+1) e^{-\frac{BJ(J+1)}{kT}} \Delta J \\ &= \int_0^{\infty} (2J+1) e^{-\frac{BJ(J+1)}{kT}} dJ \\ &= \frac{kT}{B} \int_0^{\infty} e^{-\frac{BJ(J+1)}{kT}} d\left(\frac{BJ(J+1)}{kT}\right) \\ &= -\frac{kT}{B} e^{-\frac{BJ(J+1)}{kT}} \Bigg|_0^{\infty} \\ &= \frac{kT}{B} \end{aligned} \quad (4)$$

(Since this integral form works for large J only, making the following approximation would also be OK.

$$Q(T) = \sum_{J=0}^{\infty} (2J+1) e^{-\frac{BJ(J+1)}{kT}} \Delta J = \sum_{J=0}^{\infty} (2J) e^{-\frac{BJ^2}{kT}} \Delta J \quad (5)$$

That will make the integral much easier and the result is the same.

(b) (10 points)

By converting the energy unit of **B** back into Joule,

$$B = h \cdot 4549.06 \text{ MHz} = 3.014 \times 10^{-24} \text{ J} \quad (6)$$

and using integrated formula (4) we get

$$Q(T) = \frac{kT}{B}$$
$$Q(20K) = 91.57$$
$$Q(200K) = 915.7$$

Using direct summation, we can also estimate the $Q(T)$ by truncating the summation at some value.

The table in the right shows the summation truncated at different J value. We can see that the summation converges at $J=31$ for **20K** and $J=100$ for **200K**. (This number may vary if you use different criteria of converging.) So we have

$$Q(20K) = 92.08$$
$$Q(200K) = 917.8$$

J	20K	J	200K
0	1.00	0	1.0
1	3.94	1	4.0
2	8.62	2	9.0
3	14.76	3	15.9
4	22.00	4	24.7
5	29.93	5	35.3
6	38.15
7	46.30	76	916.3
8	54.06	77	916.6
9	61.18	78	916.7
10	67.51	79	916.9
11	72.97	80	917.0
12	77.53	81	917.2
13	81.25	82	917.3
14	84.19	83	917.3
15	86.45	84	917.4
16	88.15	85	917.5
17	89.40	86	917.5
18	90.29	87	917.6
19	90.91	88	917.6
20	91.33	89	917.6
21	91.61	90	917.7
22	91.79	91	917.7
23	91.91	92	917.7
24	91.98	93	917.7
25	92.02	94	917.7
26	92.05	95	917.7
27	92.06	96	917.7
28	92.07	97	917.7
29	92.07	98	917.7
30	92.07	99	917.7
31	92.08	100	917.8
32	92.08	101	917.8
33	92.08	102	917.8
34	92.08	103	917.8
35	92.08	104	917.8

(c) (10 points)

Since $Q(T)$ is the same for each J state, we just need to find out the maximum value of

$$(2J+1)e^{-\frac{BJ(J+1)}{kT}}$$

Taking first order derivative

$$\begin{aligned}\frac{d}{dJ}(2J+1)e^{-\frac{BJ(J+1)}{kT}} &= 0 \\ 2e^{-\frac{BJ(J+1)}{kT}} + (2J+1)\left(-\frac{B}{kT}\right)(2J+1)e^{-\frac{BJ(J+1)}{kT}} &= 0 \\ J_{\max} &= \frac{1}{2}\left(\sqrt{\frac{2kT}{B}} - 1\right)\end{aligned}$$

When temperature T is high enough, the -1 can be omitted:

$$J_{\max, \text{large } J} = \sqrt{\frac{kT}{2B}}$$

(d) (5 points)

For **20K** and **200K**, using the above formula

$$\begin{aligned}J_{\max, 20K} &= \frac{1}{2}\left(\sqrt{\frac{2kT}{B}} - 1\right) = 6 \\ J_{\max, 200K} &= \frac{1}{2}\left(\sqrt{\frac{2kT}{B}} - 1\right) = 21\end{aligned}$$

Doing it numerically will give the same result.

Problem 2

(a) (10 points)

First, let us recall the definition of a complete and orthonormal basis set.

For a give basis set $\{|f\rangle\}$, it is considered to be complete when any arbitrary wave function can be expanded by the basis set:

$$|\psi\rangle = \sum_f c_f |f\rangle \quad (1)$$

It is considered to be orthonormal when

$$\langle i | j \rangle = \delta_{ij} \quad (2)$$

Multiple (1) by each basis in the basis set we get

$$\langle f | \psi \rangle = c_f \quad (3)$$

Substitute c_f in (1) using (3) we get

$$\begin{aligned} |\psi\rangle &= \sum_f c_f |f\rangle \\ &= \sum_f |f\rangle c_f \\ &= \sum_f |f\rangle \langle f | \psi \rangle \\ &= \left(\sum_f |f\rangle \langle f | \right) |\psi\rangle \end{aligned} \quad (4)$$

So,

$$\sum_f |f\rangle \langle f | = 1 \quad (5)$$

This is called closure relation.

(b) (15 points)

Recall the Schrodinger equation

$$H|f\rangle = E_f|f\rangle$$

for state $|k\rangle$ an $\langle m|$, we have

$$\begin{aligned} H|k\rangle &= E_k|k\rangle \\ \langle m|H &= E_m\langle m| \end{aligned}$$

Use these relations, the right part of the equation become

$$\begin{aligned} &-\frac{\mu}{\hbar^2}(E_m - E_k)\langle m|x|k\rangle \\ &= -\frac{\mu}{\hbar^2}\left\{\langle m|E_mx|k\rangle - \langle m|xE_k|k\rangle\right\} \\ &= -\frac{\mu}{\hbar^2}\left\{\langle m|Hx|k\rangle - \langle m|xH|k\rangle\right\} \\ &= -\frac{\mu}{\hbar^2}\langle m|Hx - xH|k\rangle \\ &= -\frac{\mu}{\hbar^2}\langle m|[H, x]|k\rangle \end{aligned}$$

Expand the Hamiltonian, the commuter becomes

$$\begin{aligned} [H, x] &= Hx - xH \\ &= \left[-\frac{\hbar^2}{2\mu}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right) + V \right]x - x\left[-\frac{\hbar^2}{2\mu}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right) + V \right] \\ &= \left[-\frac{\hbar^2}{2\mu}\left(x\frac{\partial^2}{\partial x^2} + 2\frac{\partial}{\partial x} + x\frac{\partial^2}{\partial y^2} + x\frac{\partial^2}{\partial z^2}\right) + Vx \right] - \left[-\frac{\hbar^2}{2\mu}\left(x\frac{\partial^2}{\partial x^2} + x\frac{\partial^2}{\partial y^2} + x\frac{\partial^2}{\partial z^2}\right) + xV \right] \\ &= -\frac{\hbar^2}{\mu}\frac{\partial}{\partial x} \end{aligned}$$

So we have

$$\begin{aligned} -\frac{\mu}{\hbar^2}(E_m - E_k)\langle m|x|k\rangle &= -\frac{\mu}{\hbar^2}\langle m|[H, x]|k\rangle \\ &= -\frac{\mu}{\hbar^2}\left\langle m\left|-\frac{\hbar^2}{\mu}\frac{\partial}{\partial x}\right|k\right\rangle \\ &= \langle m|x|k\rangle \end{aligned}$$

Problem 3 (10 points)

The solution for the rotational part of Schrodinger equation gives us the following formula of energy level for diatomic molecules

$$E_J = BJ(J+1)$$

Sp generally, the ground state($J=0$) have zero energy. In other words, the system doesn't have zero-point rotational energy. That's the case for HD.

However, for homonuclear diatomic molecule which have a rotational symmetry, we need to consider the nuclear wave function to see the allowed states.

For H atom which have spin of $\frac{1}{2}$, the total wave function

$$\Psi = \Psi_{elec} \Psi_{vib} \Psi_{rot} \Psi_{ns}$$

need to be antisymmetric for H as a Fermion. That means when we exchange the two H atom, the total wave function need to change sign.

$$\psi(1,2) = -\psi(2,1)$$

For ground state H_2 , Ψ_{elec} and Ψ_{vib} are symmetric. And the exchange of the two H atom will cause the rotational wave function to change sign by $(-1)^J$

$$Y_{J,M_J}(\theta + \pi, \phi) = (-1)^J Y_{J,M_J}(\theta, \phi)$$

Clearly we can see that a even J gives a symmetric state while an odd J gives an antisymmetric state. As for the nuclear spin states, two Fermions combined together will give four different states, three of them are symmetric and the other one antisymmetric.

$$\begin{aligned} \text{Symmetric: } \sigma_+(1,2) &= \begin{cases} \alpha(1)\alpha(2) \\ \frac{1}{\sqrt{2}}\{\alpha(1)\beta(2) + \beta(1)\alpha(2)\} \\ \beta(1)\beta(2) \end{cases} \\ \text{Antisymmetric: } \sigma_-(1,2) &= \frac{1}{\sqrt{2}}\{\alpha(1)\beta(2) - \beta(1)\alpha(2)\} \end{aligned}$$

To make the total wave function antisymmetric, even J symmetric rotation states must come with antisymmetric nuclear spin states. And the odd J antisymmetric rotation states must be combined with symmetric nuclear spin states. In natural H_2 sample, both exists. The H_2 of symmetric nuclear spin states is called ortho- H_2 , while the other one is called para- H_2 . And the ratio is 3:1 because there are three symmetric states and one antisymmetric state. At low temperatures, given the low speed of conversion from ortho states to para state, most ortho H_2 would stay in ortho states. And for these

ortho-H₂, only odd J are allowed. So the lowest energy state would have $J=1$, which give the non-zero zero point energy of

$$E_1 = BJ(J+1) = 2B$$

As for D₂, D have spin 1. It is a Boson and must have symmetric total wave function. Similar to H₂, the electronic wave function and the vibrational wave function are symmetric. Rotational wave functions are symmetric for even J and antisymmetric for odd J . But, for the nuclear spin states, two spin 1 D atom gives $3*3=9$ states compared with the $2*2=4$ for H₂. The nine states can be divided into three groups, each have five, three and one states respectively, compared with the $3+1$ for H₂. Again, six(5+1) of them are symmetric and three of them are antisymmetric. So the six symmetric states must have even J to get symmetric total wave function. And the three antisymmetric states must have odd J states. At low temperature, the nuclear spin states are preserved, so the three states would have odd J and non-zero zero point energy of

$$E_1 = BJ(J+1) = 2B$$