

## E0160: The calculation of $Z(T)$ for AB and AA molecules

Submitted by: Shira Wurzburg

### The problem:

A diatomic molecule  $AB$  can be regarded as two atoms that are connected by a spring of length  $r_0$ , and vibration frequency  $\omega_0$ . The total angular momentum is  $\ell = 0, 1, 2, \dots$ . The masses of the atoms are  $m_A$  and  $m_B$ , and they have spins  $S_A$  and  $S_B$ .

(a) Explain what are the conditions that allow to ignore all the excited vibrational levels, so you can treat the molecule as a rigid body ("rotor").

(b) Calculate the partition function of the diatomic molecule, assuming that it is like a classical rigid rotor. Define the condition on the temperature for this approximation to hold.

(c) Calculate the partition function of the diatomic molecule, if the temperature is very low, taking only the  $\ell = 0, 1$  states into account.

(d) How the previous answers are modified for an  $AA$  molecule that is composed of two identical spin 0 atoms?

(e) How the previous answers are modified for an  $AA$  molecule that is composed of two identical spin 1/2 atoms? What is the probability to find the spin configuration in a triplet state? Relate to the two limits in (b) and (c).

### The solution:

(a) The energy of the molecule is composed of three contributions: the kinetic energy of the center of mass  $E_p = p^2/2M$ , where  $M = m_A + m_B$ , the rotational modes of the relative coordinate  $E_l = l(l+1)/2\mu r^2$ , where  $\mu = m_A m_B / (m_A + m_B)$  (and  $\hbar = 1$ ), and the vibrational modes of the relative coordinate  $E_n = \omega_0(n+1/2)$ . If the temperature is low enough  $T \ll \omega_0$ , then we can approximate the system as being in the ground state  $n = 0$ . If  $\omega_0$  is also much slower than the other energy scales, we can take the inter-masses distance to be fixed  $r = r_0$  (the Born-Oppenheimer approximation).

(b) According to the above approximations, we can ignore the vibrational modes, since they only shift the energy. In the absence of spin-orbit coupling or magnetic field the spins give only degeneracy. Therefore the partition function is

$$Z(\beta) = \int \frac{d^3x d^3p}{(2\pi)^3} e^{-\beta p^2/2M} \cdot (2S_A + 1)(2S_B + 1) \sum_{l=0}^{\infty} (2l+1) e^{-\beta l(l+1)/2\mu r_0^2} = V \left( \frac{m}{\pi\beta} \right)^{3/2} \cdot Z_{ang}, \quad (1)$$

where  $Z_{ang}$  denotes the angular part. For  $T \gg 2\mu r_0^2$  we can approximate the sum over  $l$  by an integral,  $l(l+1) \approx l^2$  and  $2l+1 \approx 2l$ . Thus

$$\begin{aligned} Z_{ang} &\approx (2S_A + 1)(2S_B + 1) \int_0^{\infty} dl 2l e^{-\beta l^2/2\mu r_0^2} \\ &= (2S_A + 1)(2S_B + 1) \left[ \frac{\mu r_0^2}{-\beta} \int_0^{\infty} dl \frac{d}{dl} e^{-\beta l^2/2\mu r_0^2} \right] = (2S_A + 1)(2S_B + 1) \frac{\mu r_0^2}{\beta}. \end{aligned} \quad (2)$$

This is the classical rigid rotor limit.

(c) On the opposite limit of  $T \ll 2\mu r_0^2$  we can take only the two first term  $l = 0, 1$

$$Z_{ang} \approx (2S_A + 1)(2S_B + 1) \left( 1 + 3e^{-\beta/\mu r_0^2} \right). \quad (3)$$

(d) For two identical spin-0 atoms  $M = 2m$ ,  $\mu = m/2$ ,  $S_A = S_B = 0$ . Furthermore, since they are bosons the total wavefunction must be even under exchanging the two atoms. And since their total spin is 0, the orbital angular momentum must be even  $l = 0, 2, \dots$ . In the low temperature limit we should now take only  $l = 0, 2$

$$Z_{ang} \approx 1 + 5e^{-3\beta/\mu r_0^2} = 1 + 5e^{-6\beta/mr_0^2}. \quad (4)$$

In the high temperature limit the integral remains the same. This is expected, since in high temperature each particle can be in a variety of states, and the quantum restriction over the parity of the wavefunction is negligible.

(e) For two identical spin- $\frac{1}{2}$  atoms the total fermionic wavefunction must be odd under exchange. If the total spin is 0, which is odd under exchange, then  $l$  must be even. While if the total spin is 1, which is even,  $l$  must be odd. Therefore

$$Z_{ang} = \sum_{l=0,2}^{\infty} (2l+1)e^{-\beta l(l+1)/mr_0^2} + 3 \sum_{l=1,3}^{\infty} (2l+1)e^{-\beta l(l+1)/mr_0^2}. \quad (5)$$

The probability to find the spin configuration in a triplet state  $P_{tri}(\beta)$  is

$$P_{tri}(\beta) = \frac{3 \sum_{l=1,3}^{\infty} (2l+1)e^{-\beta l(l+1)/mr_0^2}}{Z_{ang}} = \frac{1}{1 + \frac{\sum_{l=0,2}^{\infty} (2l+1)e^{-\beta l(l+1)/mr_0^2}}{3 \sum_{l=1,3}^{\infty} (2l+1)e^{-\beta l(l+1)/mr_0^2}}}. \quad (6)$$

For  $T \rightarrow 0$

$$P_{tri}(\beta \rightarrow \infty) \approx \frac{1}{1 + \frac{1}{9e^{-\beta^2/mr_0^2}}} \approx 9e^{-2\beta/mr_0^2}. \quad (7)$$

One can see that in this limit the molecule is probably in the singlet state, due to the preferred orbital angular momentum  $l = 0$ . For  $T \rightarrow \infty$  the sums are approximately the same integral, and

$$P_{tri}(\beta \rightarrow 0) \approx \frac{1}{1 + \frac{1}{3}} = \frac{3}{4}. \quad (8)$$

As expected from the fact that the molecule has equal probability to be in any of the four spin state.