Problem 1 (15 points: 3 points per question). Consider one mole of non-interacting hypothetical particles at a given temperature T. Assume each particle can occupy one of the three energy levels with the following energies: $\varepsilon_0 = 0$; $\varepsilon_1 = 3\varepsilon$; $\varepsilon_2 = 5\varepsilon$. The degeneracy numbers for these energy levels are 3, 1, 5, respectively. Answer the following questions:

A. Write the expression for the molecular partition function q.

$$q = 3 + e^{-3\varepsilon\beta} + 5e^{-5\varepsilon\beta}$$

B. What are the values of q at T → 0 and at T → ∞?

q=3 at T → 0

q=9 at T → ∞

C. You found that at 0 °C the two upper levels are equally populated. Determine the value of ε.

$$e^{-3\varepsilon\beta} = 5e^{-5\varepsilon\beta} \Rightarrow e^{2\varepsilon\beta} = 5 \Rightarrow 2\varepsilon\beta = \ln 5 \Rightarrow \varepsilon = \frac{k_B T}{2}\ln 5 = 3.03\ 10^{-21}\text{ J}$$

From this equation we can also get $e^{-\varepsilon\beta} = 5^{-\frac{1}{2}}$, which can be substituted into the equation for q in problem A to give $q = 3 + e^{-3\varepsilon\beta} + 5e^{-5\varepsilon\beta} = 3 + 2\times e^{-3\varepsilon\beta} = 3 + 2\times 5^{-3/2} = 3.1789$ at this temperature. These results are not directly related to answering Q.C but can be useful to answer the remaining questions.

D. Calculate the total energy of the system at this temperature.

There are several ways to calculate the total energy. Here is just one of them. Using equation

$E = -N\frac{d}{d\beta}\ln q$ and the expression for q from Q.A, we get

$$E = N_A\frac{3\varepsilon\times e^{-3\varepsilon\beta} + 5\times 5\varepsilon\times e^{-5\varepsilon\beta}}{q} = N_A\varepsilon\frac{3e^{-3\varepsilon\beta} + 25e^{-5\varepsilon\beta}}{3 + e^{-3\varepsilon\beta} + 5e^{-5\varepsilon\beta}} = N_A\varepsilon\frac{3\times 5^{-3/2} + 5\times 5^{-3/2}}{3 + 2\times 5^{-3/2}} = 0.2251 N_A\varepsilon,$$

where N_A is the Avogadro number (recall that $R=N_A*k_B$). Using the expression for ε from Q.C,

we get $E = 0.2251 N_A\varepsilon = 0.2251\times\frac{\ln 5}{2}\times RT = 0.1811\times RT = 411.05$ J

Another way to calculate the total energy is to use purely statistical considerations:

$E = a_0\varepsilon_0 + a_1\varepsilon_1 + a_2\varepsilon_2 = \frac{N_A}{q}\left(0 + 3\varepsilon\times e^{-3\varepsilon\beta} + 5\times 5\varepsilon\times e^{-5\varepsilon\beta}\right)$, which gives us the same expression as above.

E. Calculate the entropy of the system at this temperature.

$$S = \frac{E}{T} + R\ln q = 0.1811R + R\ln(3 + 2\times 5^{-3/2}) = 0.1811R + 1.1565R = 1.3377R = 11.11\text{ J/K}$$

Problem 2 (10 points). You use microwave spectroscopy to analyze a gas sample containing a mixture of Ne, H_2, N_2, NO, O_2, CH_4, and CO_2. The absorption spectrum corresponding to pure rotational transitions consists of a series of equally-spaced peaks separated by 3.4077 cm^{-1}. Based on this information answer the following questions:

A. (5 points) Identify the molecule responsible for the observed absorption spectrum. *Explain your reasoning.*

In order to be MW active, the compound must possess a non-zero permanent dipole moment. Ne is an atom, hence no permanent dipole moment, and H_2, N_2, O_2, CH_4, and CO_2 don't possess a permanent dipole moment by symmetry.
The only compound from this mixture that possesses a non-zero permanent dipole moment is NO. It must be responsible for the observed MW absorption.

B. (5 points) Determine the bond length in that molecule. *Show your calculations*. (Make sure you convert cm^{-1} to m^{-1} properly)

Reflecting the selection rules for rotational spectroscopy, an absorption spectrum corresponding to rotational transitions consists of peaks/lines corresponding to transitions J → J+1, i.e. J=0 → J=1; J=1 → J=2; J=2 → J=3 and so on. The frequency of such a transition is $\nu_{J\to J+1} = 2cB(J+1)$ or, in terms of wavenumbers: $\tilde{\nu}_{J\to J+1} = 2B(J+1)$. As we discussed several times in class, regardless of the *J* value, the spacing between two peaks/lines in the spectrum is $\Delta\tilde{\nu} = \tilde{\nu}_{J+1\to J+2} - \tilde{\nu}_{J\to J+1} = 2B = \frac{h}{4\pi^2 c\mu r^2}$, because $B = \frac{h}{8\pi^2 c\mu r^2}$. Solving this equation for the bond length gives: $r = \frac{1}{2\pi}\sqrt{\frac{h}{c\mu\,\Delta\tilde{\nu}}}$. Substituting here the value of $\Delta\tilde{\nu}$ = 3.4077 cm^{-1} = 340.77 m^{-1} (note that 1 cm^{-1} =100 m^{-1}), the reduced mass of NO μ = 14×16/30 amu = 7.4667 amu = 1.2395×10^{-26} kg, and the relevant physical constants, we get: $r = 1.1509 \times 10^{-10}$ m = 1.1509 Å for the bond length in NO.