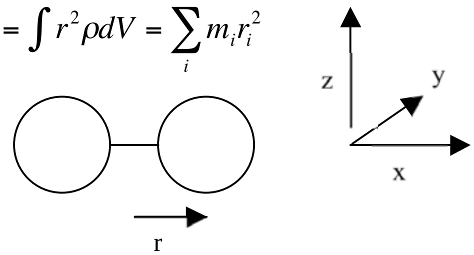
# Homework 3 Solutions

*2. Rotational energy levels of a diatomic molecule*

In the simple 2 atom dumbbell molecule, the rotational energy levels are

$$E = \frac{h^2}{8\pi^2 I} j(j+1)$$

where $I$ is the Moment of inertia: $I = \int r^2 \rho dV = \sum_i m_i r_i^2$




*a. Calculate the first 4 energy levels of each of the 3 rotational modes of $N_2$.*

The first step is to determine the rotational moment of inertia for each of the three modes. Note that modes 1 and 2 where the $N_2$ barbell rotated around the y and z axes are identical. Mode 3, where the barbell rotates around the x-axis which is the axis that runs between the center of the two nitrogen atoms is quite different as we discussed in class.

**MASS**:

The mass of an atom of nitrogen is approximately 0.014 kg/mole / $N_A$ = 2.3e-26 kg.

**Radius**:

We need to determine the distances of the masses from rotational axis for each mode. As discussed in class, in two of the modes the distance of the two nitrogen atoms from the rotational axis are identical. In the third mode, the distance is much smaller and the energy levels are therefore much higher. In fact, in the 3$^{rd}$ mode the nuclear distance from the spin axis is so small, we need to consider the electrons separate from the protons and neutrons.

**1$^{st}$ & 2$^{nd}$ modes**

Molecular nitrogen has a covalent bond of length 1.09 Å which runs from the center of one nitrogen atom to the center of the other. Therefore, for the first 2 modes, the radial distance from the spin axis to the center of mass of one nitrogen atom is half the bond length which is r = 0.545 Å = $5.45\text{x}10^{-11}$ m.

The moment of inertia is 2 $m_N$ $r^2$ = 1.38e-46 kg $m^2$.

**3$^{rd}$ mode**

For the third rotational mode, the spin axis runs through the center of the two nitrogen atoms. The moment of inertia actually has two contributions, the contribution from the nucleus of each nitrogen atom plus each electron cloud.

*Nucleus contribution*: The radius of the nucleus is extremely small, approximately 3e-15 m. The contribution from the nucleus of each atom is therefore approximately 2.3e-26 kg $(3\text{e-}15\ \text{m})^2$ = 4.2e-55 kg $m^2$.

*Electron contribution*:The mass of an electron is approximately 1/1836 that of a proton. There are 7 electrons in a nitrogen atom. The mass of electrons in a nitrogen atom is 6.3e-30 kg. The radius of the electrons around the spin axis is approximately the radius of the atom, 6.5e-11 m.

The moment of inertia due to the electrons is 6.3e-30 kg (6.5e-11 m)$^2$ = 5.35e-50 kg m$^2$. This is much larger than the moment of inertia of the nucleus.

So the moment of inertia of the third mode is actually associated with the electrons rather than the nucleus such that the energy constant $\frac{h^2}{8\pi^2 I}$ for the third mode is approximately 2 x 1836 = 3600 times larger than the first two modes.

In the table below is shown both the nucleus and the electron contributions in order to give credit for the nuclear estimates. However, the true answer for mode 3 is the electron column.

| j | E(J) modes 1&2 | Mode 3: E(J) nucleus | Mode 3: E(J) electron |
|---|---|---|---|
| 0 | 0.00E+00 | 0.00E+00 | 0.00E+00 |
| 1 | 8.05E-23 | 2.64E-14 | 2.08E-19 |
| 2 | 2.42E-22 | 7.91E-14 | 6.24E-19 |
| 3 | 4.83E-22 | 1.58E-13 | 1.25E-18 |

| j | E(eV) modes 1&2 | Mode 3: E(eV) nucleus | Mode 3: E(eV) electron |
|---|---|---|---|
| 0 | 0.00E+00 | 0.00E+00 | 0.00E+00 |
| 1 | 5.03E-04 | 1.64E+05 | 1.30E+00 |
| 2 | 1.51E-03 | 4.93E+05 | 3.89E+00 |
| 3 | 3.02E-03 | 9.87E+05 | 7.79E+00 |

*b. Use the Boltzmann distribution to show that one of the 3 modes will not be populated at typical Earth temperatures.*

The Boltzmann distribution represents the probability of an energy level being populated. The probability of an energy level, $E_j$, being populated relative to the probability of the ground state, $E_0$, being populated is $\exp(-E_j/k_BT)/\exp(-E_0/k_BT) = \exp(-E_j/k_BT)$ because $E_0 = 0$.

We'll assume the atmospheric temperature is 250K.

The table shows the probability of the energy levels being populated relative to the probability that the ground state energy level will be populated.

| j | Modes 1&2 probability of Population | Mode 3 Probability of population |
|---|---|---|
| 0 | 1.00 | 1.00E+00 |
| 1 | 0.98 | 6.78E-27 |
| 2 | 0.93 | 3.11E-79 |
| 3 | 0.87 | 9.69E-158 |

We see the probability of mode 3 states being populated is extremely low.

*3. Assume air is made of 79% $N_2$, 20% $O_2$ and 1% Ar.*

*a. Calculate $C_v$ and $C_p$ of dry air (no water in the air) in J/kg/K using the simple molar specific heats, $C_v$', for diatomic molecules (5/2 R*) and monatomic molecules (3/2 R*).*

| | N2 | O2 | Ar | Total | |
|---|---|---|---|---|---|
| makeup | 0.79 | 0.2 | 0.01 | 1 | |
| mass | 28 | 32 | 39.948 | | g/mole |
| Cv mole | 20.79 | 20.79 | 12.4716 | | J/mole/K |
| Cv | 742.36 | 649.56 | 312.2 | | J/kg/K |
| Cv total | 586.46 | 129.91 | 3.12 | **719.5** | J/kg/K |
| | | | | | |
| Cp mole | 29.1004 | 29.1004 | 20.7860 | | J/mole/K |
| Cp | 1039.3 | 909.39 | 520.33 | | J/kg/K |
| Cp total | 821.05 | 181.88 | 5.2033 | **1008.1** | J/kg/K |

*b. Find the actual heat capacity of air and compare your result to it.*

Wallace & Hobbs indicate on page 467 that $C_v$ and $C_p$ for dry air are 717 and 1004 J/kg/K respectively. Our estimates are 0.35% and 0.4% higher than those of WH. So we have made a very good estimate. With slightly better estimates of the $N_2$, $O_2$ and Ar fractions of air we could presumably get even closer.

*4. Assume water is present in the atmosphere at a mixing ratio of 1%. Assume all of the water condenses out and that resulting the latent heat energy is transferred to the heat capacity energy storage of the air.*

*a. How much will the temperature of the air increase?*
*(For simplicity, ignore the heating of the condensed water droplets.)*

The basic equation of the energy transfer is

$$m_{H2O}\, L_v = m_{air}\, C_p\, \Delta T \quad \text{or} \quad \rho_{H2O}\, L_v = \rho_{air}\, C_p\, \Delta T$$

The 1% mixing ratio is ambiguous because it could be either the volume or the mass mixing ratio. The following table shows the two solutions

| | Mass mixing ratio | Volume mixing ratio |
|---|---|---|
| Mass of $H_2O$ relative to air | $m_{H2O} = 0.01\, m_{air}$ | $m_{H2O} = 0.01\, m_{air}\, 18/28.97$ |
| Energy balance | $0.01\, m_{air}\, L_v = m_{air}\, C_p\, \Delta T$ | $18/28.97\;\; 0.01\, m_{air}\, L_v = m_{air}\, C_p\, \Delta T$ |
| Air temperature change eqn | $\Delta T = mix\,\frac{L_v}{C_p}$ | $\Delta T = mix\,\frac{18}{28.97}\frac{L_v}{C_p}$ |
| Air temperature change | 24.9 $^{o}$C | 15.5$^{o}$C |

where $L_v$ = 2.5e6 J/kg, $C_p$ = 1004 J/kg/K and mix ratio = 1%.

*b. What is the fractional change in the air density? State any assumptions you make in determining the fractional density change.*

$$P = n\,R^*\,T = \rho\,R\,T \quad \text{so} \quad \rho = P/RT$$

Pressure is held constant during the energy exchange so

$$d\rho = \frac{P}{R}\left(-\frac{dT}{T^2}\right) = -\frac{P}{RT}\left(\frac{dT}{T}\right) = -\rho\frac{dT}{T}$$

$$\frac{d\rho}{\rho} = -\frac{dT}{T}$$

If the original temperature were 288 K, the fractional change in density would be
-24.9/288 = -8.7% or -15.5/288 = -5.4%

*5. Calculate the dry adiabatic temperature lapse rate of the atmosphere of Titan in K/km. Assume the atmosphere is made of 97% $N_2$ and 3% methane.*

$C_p$ = 0.97 1039 + 0.03 2000 = 1068 J/kg/K

dT/dz = -g/$C_p$ = 1.352 m/s2 / 1068 J/kg/K = -1.27 K/km

*6. Consider air at 250 mb with a temperature of 225K.*

*a. What is its potential temperature?*

The equation for potential temperature is

$$\theta = T\left(\frac{P_{surf}}{P}\right)^{R/C_p}$$

Using $P$ = 250 mb, $P_{surf}$ = 1013 mb , $T$ = 250K, $C_P$ = 1004 J/kg/K, $R$ = 287.1 J/kg/K yields $\theta$ = 335.7 K = 62.5$^o$C = 145$^o$F.

*b. Suppose an airliner flies at this altitude and needs to pressurize the cabin while simultaneously circulating air in from the outside, will the airliner need an air conditioner? Why?*

The potential temperature is very hot, much too hot for humans. SO an air conditioner will have to be used if the airliner is fully pressurized to sea level.

*c. Based on the previous two answers, provide an explanation as to why do airliners don't fully pressurize the cabins to sea level pressure.*

If the airliner were only pressurized to 850 mb, there would be less compressional heating.

$$\theta = T\left(\frac{P_{surf}}{P}\right)^{R/C_p}$$

Using $P$ = 250 mb, $P_{surf}$ = 800 mb , $T$ = 250K, $C_P$ = 1004 J/kg/K, $R$ = 287.1 J/kg/K yields $\theta$ = 314 K = 41$^o$C = 105$^o$F about 40$^o$F cooler than the temperature when compressing the air to 1013 mb. An air conditioner would still be needed but the cooling required is reduced substantially.