

# Molecular energy levels

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## 1 Introduction

Statistical mechanics provides the bridge between properties on a molecular scale and those on a macroscopic scale. We therefore need to know a little about the quantum mechanics of molecules. It turns out that, at least for the issues we will tackle in this course, we mostly need to know about the energy levels a molecule is allowed to occupy. It's also useful to know a little about the associated spectroscopies.

You should already know that molecules occupy specific energy levels, the most familiar example being the energy levels associated with the placement of electrons in molecular orbitals. In many cases, there are simple expressions which are at least approximately valid for the energy stored by a molecule in different types of motion. This is the topic we will study in this lecture.

Our starting point is the separation of molecular energy ( $\epsilon$ ) into different contributions:

$$\epsilon = \epsilon_{\text{trans}} + \epsilon_{\text{vib}} + \epsilon_{\text{rot}} + \epsilon_{\text{elec}}.$$

In this equation,  $\epsilon_{\text{trans}}$  is the translational kinetic energy, i.e.  $\frac{1}{2}mv^2$  for the whole molecule;  $\epsilon_{\text{vib}}$  is the vibrational energy;  $\epsilon_{\text{rot}}$  is the rotational energy associated with rotations of the whole molecule as a unit; and  $\epsilon_{\text{elec}}$  is the electronic energy, i.e. the energy of the electrons in orbitals. There can be other terms (e.g. terms associated with intermolecular forces, or even with non-bonding intramolecular forces in larger molecules), and some terms are not appropriate in every situation (e.g. the lack of free rotation in solution), but certainly for molecules in the gas phase, these are the main contributions

to the energy. These four contributions to the energy are not completely independent. For example, rotation of a molecule introduces an effective centrifugal force which stretches the bonds and therefore affects the vibrational energy. However, treating these energy terms as separate is a good starting point.

## 2 Spectroscopy

There are many different kinds of spectroscopy, but the underlying principles are always the same:

- A molecule makes a transition between two energy levels.
- Energy must be conserved.
- One or more photons absorbed or emitted or, sometimes, a change in the energy of a photon, must account for the change in energy of the molecule.

In absorption spectroscopy, the only type we will consider here, a photon is absorbed by a molecule, causing a transition from a lower to a higher energy level. It follows that the energy of the photon must match a difference between two energy levels in the molecule, i.e. that  $E_{\text{photon}} = \Delta\epsilon = \epsilon_i - \epsilon_j$ . While  $i$  and  $j$  can represent states which differ in several quantum numbers (associated with the types of energy discussed above), it is often the case that just one type of energy has changed. For example, many molecules have a rotational spectrum which is due, as the name implies, to changes in the rotational energy.

## 3 Translational kinetic energy in the gas phase

In the simplest treatment (no intermolecular forces or externally applied fields, i.e. an ideal gas in a simple container), a molecule in the gas phase is just a particle in a box. The energy of a particle in a rectangular box can be decomposed into  $x$ ,  $y$  and  $z$  components. The energy levels associated with the  $x$  component are given by

$$\epsilon_{n_x} = \frac{n_x^2 h^2}{8mL_x^2},$$

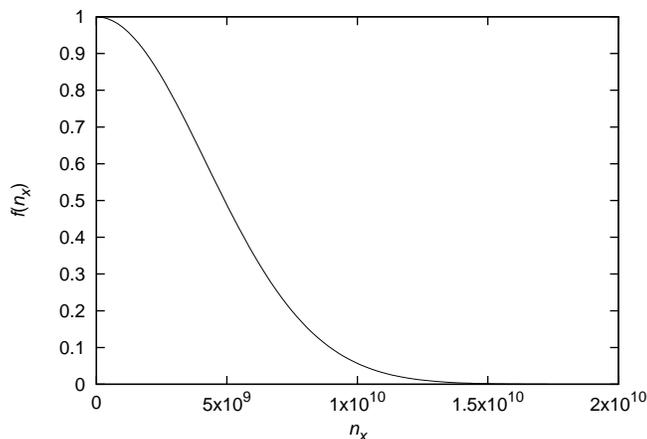


Figure 1: Translational Boltzmann factor for  $N_2$  in a 0.1 m long container at 298 K.

where  $n_x$  is a quantum number (1,2,3,...),  $h$  is Planck's constant,  $m$  is the mass of the molecule, and  $L_x$  is the length of the box in this dimension. Obviously, similar equations hold in the  $y$  and  $z$  directions.

Let's look at the Boltzmann factor (i.e. the term  $e^{-\epsilon/(kT)}$ ) for the  $x$  component of the translational energy for, say, a molecule of  $N_2$  in a 1 L container at 298 K. If the container is a cube, it would have a side of length  $L_x = 0.1$  m. The mass of an  $N_2$  molecule is  $4.65 \times 10^{-26}$  kg. Thus,

$$\epsilon_{n_x} = 1.18 \times 10^{-40} n_x^2,$$

which gives

$$f(n_x) = e^{-2.87 \times 10^{-20} n_x^2}.$$

Figure 1 shows the Boltzmann factor plotted as a function of  $n_x$ . Note that this factor only becomes small for extremely large values of the quantum number ( $> 10^{10}$ ). In other words, a very large number of states are accessible at this temperature.

Suppose that we consider a typical state within the range of likely energies, say one with  $n_x = 5 \times 10^9$ . This would have an energy of  $2.95 \times 10^{-21}$  J. Now consider  $\Delta\epsilon$ , the difference in energy between two adjacent energy levels:

$$\Delta\epsilon = 1.18 \times 10^{-40} [(n_x + 1)^2 - n_x^2] = 1.18 \times 10^{-40} (2n_x + 1) \approx 2.36 \times 10^{-40} n_x.$$

For  $n_x = 5 \times 10^9$ ,  $\Delta\epsilon = 1.18 \times 10^{-30}$  J. This is *enormously* smaller than  $\epsilon$  itself, so the energy of a gas molecule in a normal container behaves like a continuous variable. Another way to see this is to convert the energy level spacing into a photon wavelength:

$$\lambda = \frac{hc}{\Delta\epsilon} = 168 \text{ km.}$$

This is an enormous wavelength, well beyond the radio wavelength (in the metre range), again indicating that this difference in energy is negligible. Accordingly, we would not be able to do the simplest kinds of spectroscopic experiments (absorption or emission) to study the translational motion of molecules in a gas.

## 4 Vibrational energy

Let's start with the simplest case, that of a diatomic molecule. It has a single vibrational mode, namely stretching of the bond between the two atoms. In the harmonic oscillator approximation (treating the molecule as two marbles connected by a spring), the energy is given by

$$\epsilon_v = hc\tilde{\nu} \left( v + \frac{1}{2} \right). \quad (1)$$

Here, the quantum number  $v$  takes the values  $0, 1, 2, \dots$ ;  $h$  and  $c$  are the usual universal constants; and  $\tilde{\nu}$  is a constant that depends on the stiffness of the bond and on the masses of the two atoms.

The energy levels in this case are equally spaced. In fact, they are separated by  $hc\tilde{\nu}$ . If we wanted to do a simple absorption spectroscopy experiment with a diatomic molecule, we would expect it to absorb photons which have a multiple of this quantum of energy, representing a change in the vibrational quantum number  $v$  of 1, 2, 3 or more units. This is indeed what we observe, although for reasons which you will study in your quantum mechanics course, only heteronuclear diatomics undergo straightforward absorption, and the intensities for  $\Delta v > 1$  are always extremely small.

As you probably know, we find vibrational transitions in the infrared range, at wavenumbers of a few hundred reciprocal centimetres. This corresponds to photon energies of about  $10^{-20}$  J. Because the transition energy

for  $\Delta v = 1$  is just  $hc\tilde{\nu}$ , vibrational spectroscopy gives us the molecular parameter  $\tilde{\nu}$ , and thus the full set of vibrational energy levels, at least insofar as they are well approximated by a harmonic oscillator.

If you work out the relevant Boltzmann factors using the rough value for  $\Delta\epsilon$  given above, you will find that only the ground vibrational state ( $v = 0$ ) has a significant population at room temperature.

What happens when we have more than two atoms? In some ways, the picture isn't that different. We can still typically treat the vibrational energy levels as if they obey equation 1, except that we have to have one such equation for each vibrational mode (each different way for the molecule to vibrate), each with its own value of  $\tilde{\nu}$  (unless some of the modes are degenerate). How many vibrational modes are there? The answer to that question depends on the shape of the molecule. If we have  $N$  atoms, then there are  $3N$  ways those atoms can move ( $3N$  degrees of freedom, corresponding to the  $x$ ,  $y$  and  $z$  degrees of freedom of each atom). Three of those degrees of freedom can be associated with the translational motion of the whole molecule. If the molecule is **not** linear, then there are three independent rotation axes, and the molecule also has three rotational degrees of freedom. The rest of the degrees of freedom are vibrational degrees of freedom, so we have

$$\# \text{ of vibrational modes} = 3N - \{3 \text{ transl. modes}\} - \{3 \text{ rot. modes}\} = 3N - 6.$$

For linear molecules on the other hand, there are only two independent rotation axes (both perpendicular to the molecular axis) since rotation around the molecular axis doesn't actually move anything. Then we have

$$\# \text{ of vibrational modes} = 3N - \{3 \text{ transl. modes}\} - \{2 \text{ rot. modes}\} = 3N - 5.$$

**Example 4.1** Water has  $3(3) - 6 = 3$  vibrational modes.

**Example 4.2** Carbon dioxide is a linear molecule, so it has  $3(3) - 5 = 4$  vibrational modes. Two of the bending modes are degenerate: They correspond to bending the molecule with the carbon atom acting the "hinge". There are two such modes because you can bend the molecule back-and-forth or up-and-down. They have exactly the same value of  $\tilde{\nu}$  because they involve the same motion, just in two different planes.

## 5 Rotational energy

From the last section, we already know how to count the number of rotational modes of a molecule. Unfortunately, the energetics of rotation is not entirely straightforward, except in a few very simple cases. The only case we will consider here is that of a linear molecule. Assuming that the molecule is rigid, which is of course only an approximation given that molecules also vibrate, the rotational energy levels are given by

$$\epsilon_J = BJ(J + 1),$$

where  $J$  is a quantum number which can take the values  $0, 1, 2, \dots$ ; and  $B$  is a constant which depends on the distribution of mass along the molecular axis.

Rotation is a kind of angular momentum, and angular momentum in quantum mechanics is always associated with two quantum numbers, one for the size of the angular momentum vector, in this case  $J$ , and one for the projection of this vector onto a fixed axis in space, usually called the  $z$  axis, although this is completely arbitrary. This second quantum number is  $m_J$ , and can take any of the values between  $-J$  and  $J$ . This may sound familiar. In the hydrogen atom, we have orbital angular momentum quantum numbers  $\ell$  and  $m_\ell$  which follow the same relationship. The quantum number  $m_J$  doesn't affect the energy of a rotating molecule, so this represents a degeneracy of the energy level  $J$ . You should be able to see that the number of different states corresponding to the energy level  $J$  is  $g_J = 2J + 1$ .

In rotational absorption and emission, again for reasons you will see in your quantum mechanics course, only transitions with  $\Delta J = \pm 1$  are allowed. In an absorption experiment, we would expect to observe transitions with  $\Delta J = 1$ , for which

$$\Delta\epsilon = \epsilon_{J+1} - \epsilon_J = B(J + 1)(J + 2) - BJ(J + 1) = 2B(J + 1).$$

In rotational spectroscopy, we therefore get a series of lines, each corresponding to a different initial value of  $J$ . Again we can use the spectrum to determine a molecular parameter, this time the rotational constant  $B$ , which turns out to usually have values of a few reciprocal centimetres.

We can work out the Boltzmann factors for different values of  $J$  for a typical set of rotational levels of a linear molecule. This time, we need to

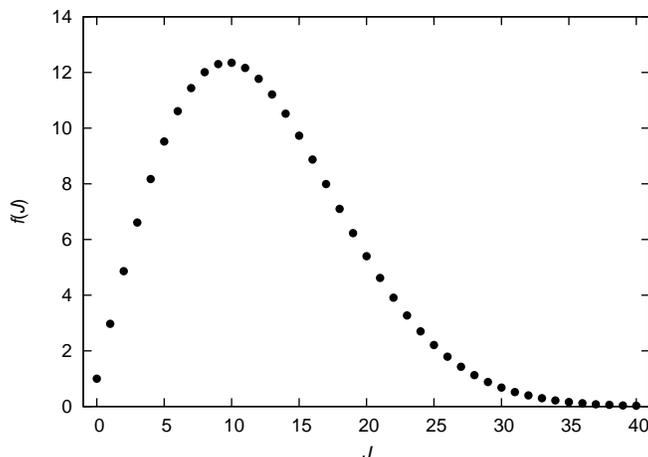


Figure 2: Rotational Boltzmann factors as a function of  $J$  for a rigid rotor with  $B = 1 \text{ cm}^{-1}$  at 298 K.

take the degeneracy of the levels into account. We get

$$f(J) = (2J + 1) \exp\left(\frac{-hcBJ(J + 1)}{kT}\right).$$

If we plot the unnormalized distribution  $f(J)$  vs  $J$ , we get the points shown in figure 2. This time, we see that many states are populated at room temperature, although clearly not as many as for the translational motion.

Returning to our spectroscopy experiment, for the same value of  $B$  as we used in figure 2, we would predict that the rotational spectrum would have lines at  $2 \text{ cm}^{-1}$ ,  $4 \text{ cm}^{-1}$ ,  $6 \text{ cm}^{-1}$ , and so on or, in energy units, about  $4 \times 10^{-23} \text{ J}$ ,  $8 \times 10^{-23} \text{ J}$ ,  $1.2 \times 10^{-22} \text{ J}$ , ... These lines are in the microwave region of the electromagnetic spectrum.

## 6 Electronic energy levels

In your other chemistry classes, you will have learned the basics of the molecular orbital theory. You may have noticed that your other professors never wrote down any equations for the energies of molecular orbitals. That's because there aren't any simple equations for these energies. We will therefore have to content ourselves with a few simple observations.

The electronic energy levels are almost always much more widely spaced than any of the other types of energy levels we have discussed. Electronic energy transitions are typically observed in the ultraviolet or visible range, which corresponds to photon wavelengths of a few hundred nm, or energies in the range of  $10^{-18}$  J. Consequently, the excited states are almost never populated at room temperature.

## 7 Nuclear energy levels

At some point, you will also have discussed NMR, which is based on the behavior of nuclear spins in a magnetic field. Nuclear spin is also a type of angular momentum, with a quantum number  $I$ . Unlike  $J$ , the value of  $I$  is fixed for a given nucleus, so there is no spectroscopy associated directly with this quantum number. However, in a magnetic field, the energies of states with different values of  $m_I$ , the quantum number which specifies the projection of the spin angular momentum vector onto, in this case, the magnetic field axis, are different. Specifically,

$$\epsilon_{m_I} = -\gamma\hbar B_0 m_I,$$

where  $\gamma$  is a constant for a given nucleus called the magnetogyric ratio,  $B_0$  is the strength of the external magnetic field, and  $\hbar = h/(2\pi)$ . Typical values of  $\gamma$  are around  $10^8 \text{ T}^{-1}\text{s}^{-1}$ . (T is the abbreviation for the Tesla, the SI unit of magnetic field strength.)

Being a type of angular momentum,  $I$  behaves like all other types of angular momentum. In particular,  $m_I$  can take any value between  $-I$  and  $I$ , in increments of 1. For a spin- $\frac{1}{2}$  nucleus like  $^1\text{H}$  or  $^{13}\text{C}$ ,  $I$  can be either  $-\frac{1}{2}$  or  $\frac{1}{2}$ , which leads to the “spin-flip” picture of NMR you have probably seen. Many nuclei have a spin other than  $\frac{1}{2}$ , notably  $^2\text{H}$  and  $^{14}\text{N}$ , both of which have  $I = 1$ . These nuclei have three nuclear spin states,  $m_I = -1, 0$  and  $1$ . For reasonable magnetic field strengths, you can verify the following:

- The splitting between adjacent energy levels corresponds to radiofrequency photons.
- There would be very little difference in population between these energy levels at room temperature.

<b>Type of energy</b>	<b>Spectral range</b>
Electronic	UV/visible
Vibrational	infrared
Rotational	microwave
Nuclear spin	radiofrequency
Translational	none

Table 1: Some types of molecular energy, in order of energy level spacing from largest to smallest, along with the corresponding spectral range in which transitions can be observed. Note that NMR requires a magnetic field, unlike the other spectroscopies mentioned here.

## 8 Summary

Table 1 shows the types of energy we have considered here placed in order of energy level spacing. It is useful to remember this order since a number of properties of interest to us are related to it. For example, the larger the energy gap between two states, the smaller the population of the upper state will be, so this order informs us about the number of excited states which are likely to be populated, with more at the bottom of this table and fewer at the top.