
Molecules

1 The Rotor

The rotor: The energy (Hamiltonian) for a rotor is

$$H = E = \frac{\vec{L}^2}{2I}. \quad (1)$$

We know what the eigenvalues of \vec{L}^2 are, so the energy levels are:

$$E_\ell = \frac{\hbar^2 \ell(\ell + 1)}{2I}. \quad (2)$$

The degeneracy of each level is $2\ell + 1$.

2 The Harmonic Oscillator

The Hamiltonian for the harmonic oscillator is probably the most important in physics. This is because any system, near the equilibrium point of its potential, experiences a linear force – not just springs.

The Hamiltonian for a harmonic oscillator is

$$H = E = \frac{p^2}{2m} + \frac{1}{2}Kx^2 \quad (3)$$

The corresponding Schrodinger equation

$$-\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} + \frac{1}{2}Kx^2\psi = E\psi. \quad (4)$$

The classical frequency of the oscillator is $\omega_o = \sqrt{\frac{K}{m}}$. As explained in your book the solutions have energy of a very simple form:

$$E_n = \hbar\omega_o\left(\frac{1}{2} + n\right). \quad (5)$$

The wave functions themselves are interesting. They are of the form:

$$\psi_n = H_n(x)e^{-\frac{\omega_o m x^2}{2\hbar}}. \quad (6)$$

The H_n 's are polynomials (of n 'th degree) in x , known as the Hermite polynomials.

Exercise: Check the solution for $n = 0$. Then for $n = 1$, using the energy eigenvalue $E = \frac{3}{2}\hbar\omega_o$, find H_1 (don't worry about the normalization of the wave function).

3 Molecules

What does this have to do with molecules?

We said that we can think of the following types of excitations in a molecule:

- Rotations – a diatomic molecule like H_2 rotates like a dumbbell (rotor).
- Vibrations: If R is the distance between the two nuclei,

$$V(R) = V(R_o) + \frac{K}{2}(R - R_o)^2 \quad K = \left. \frac{d^2V}{dR^2} \right|_{R_o}. \quad (7)$$

Note that this is exactly a harmonic oscillator Hamiltonian. $V(R_o)$ is just a constant in the energy, and doesn't matter; then call $x = (R - R_o)$.

- Electronic motions – so far we have been imagining that the nucleons are moving relatively slowly, so that the electrons are always in their ground state. It is possible to excite the electrons; these excitations will have energies of order a few electron volts, like atoms.

So the energy levels are given by

$$E_{n,\ell} = \hbar\omega_o\left(n + \frac{1}{2}\right) + \frac{\hbar^2\ell(\ell+1)}{2I}. \quad (8)$$

The vibrational energies are typically an order of magnitude larger than the rotational energies, so one has two “bands.” Transitions between the vibrational bands are typically in the infrared; those in the rotational bands in the microwave.

4 Thinking about the full Schrodinger Equation

We can derive these results by thinking about the Schrodinger equation directly. We focus on the motion of the nuclei. For a diatomic molecule, there are two nuclei. These are described by two vector positions (six coordinates overall). But three of these coordinates are just describe the overall motion of the center of mass. The three relative coordinates we call \vec{R} , the (vector) distance between the two nuclei ($\vec{R} = \vec{x}_1 - \vec{x}_2$). The potential for a diatomic molecule is just a function of the distance between the nuclei, $|\vec{R}|$. So we can separate variables. We use spherical coordinates, $\vec{R} = (R, \theta, \phi)$. We get the same equations we had for hydrogen, except that $r \rightarrow R$, and the potential is different. The angular part is solved by the $Y_{\ell,m}$'s, and the radial part satisfies (remember that the radial part, if we divide by R , looks like the equation for a single particle in a potential with a centrifugal term):

$$\left(-\frac{\hbar^2}{2\mu} \frac{d^2}{dR^2} + \frac{\hbar^2\ell(\ell+1)}{2\mu R^2} + V(R)\right)\chi = E\chi. \quad (9)$$

Now we Taylor series expand V and $1/R^2$ about R_o . In the angular momentum term, the leading piece is just

$$\frac{\hbar^2\ell(\ell+1)}{2\mu R_o^2} = \frac{\hbar^2\ell(\ell+1)}{2I} \quad (10)$$

In the potential piece, we get just the harmonic oscillator potential, with K as before.

So again we can read off the spectrum right away. The energy is

$$E_{\ell,n} = \hbar\omega_o\left(n + \frac{1}{2}\right) + \frac{\hbar^2\ell(\ell+1)}{2\mu R_o^2} \quad (11)$$

These are the same rotational and vibrational bands we wrote down above.

Exercise: Show that equation 11 follows from the Taylor expansion of Equation 9.

5 Statistical Mechanics of Molecules

Let's see how, for high temperature, the equipartition theorem holds for the rotational states.

First, for sufficiently high temperatures (when $e^\alpha \gg 1$), the velocities of the molecules obey the Maxwell-Boltzmann distribution. For each molecule, the ℓ 's will be distributed according to the Bose-Einstein distribution (why?). So if we want to determine the average *rotational* energy, we need to evaluate ($E_{rot} = \frac{\hbar^2}{2\mu I}$):

$$\sum_{\ell} \ell(\ell+1)E_{rot} \times \frac{2\ell+1}{e^{\beta\ell(\ell+1)E_{rot}} - 1}. \quad (12)$$

Note that we have included $2\ell+1$ to account for the degeneracy of the states.

For temperatures $T \ll E_{rot}$, only the term $\ell=1$ contributes, and the average energy is approximately zero. Once $T \gg E_{rot}$, however, we can approximate $\sum_{\ell} \approx \int d\ell$. So we need to evaluate the integral:

$$\langle E \rangle = \frac{\int_0^\infty d\ell 2\ell^3 E_{rot} e^{-\beta\ell^2 E_{rot}}}{\int_0^\infty d\ell 2\ell e^{-\beta\ell^2 E_{rot}}} \quad (13)$$

Exercise: Explain the factors in this expression. Note that we have simplified things by assuming that the temperature is large enough that we can use the Boltzmann distribution, and that ℓ is large so that $\ell^2 \gg \ell$, for example. The denominator is there because we need to average over the distribution.

This integral can be evaluated by the following trick. Note that

$$\langle E \rangle = -\frac{d}{d\beta} \ln \left(\int_0^\infty d\ell 2\ell E_{rot} e^{-\beta\ell^2 E_{rot}} \right) \quad (14)$$

Now because this is a derivative with respect to β , things simplify. The change of variables, $\beta\ell^2 = x^2$ gives that the right hand side is of the form

$$\langle E \rangle = -\frac{d}{d\beta} \ln(\beta^{-1} \times C) = \frac{1}{\beta} = kT \quad (15)$$

where C is a constant independent of T .

This is the equipartition theorem for two degrees of freedom, as promised.