

So you might be thinking... I thought I could avoid Quantum Mechanics?!?

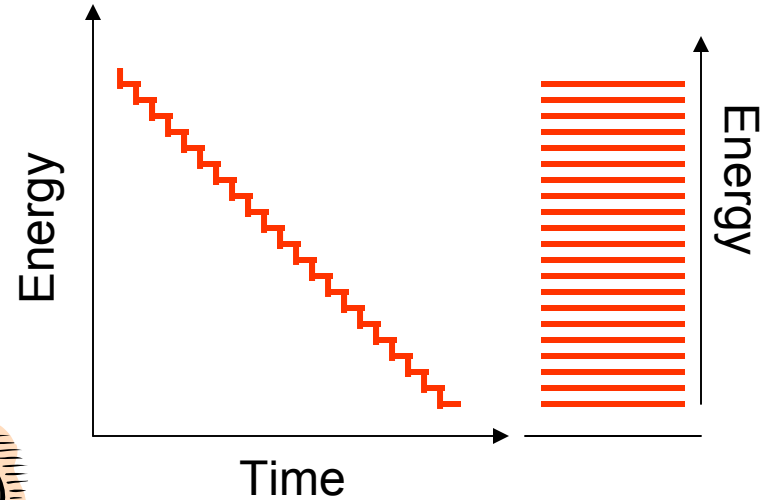
Well... we will focus on thermodynamics and kinetics, but we will consider this topic with reference to the *molecular basis* that underlies the laws of thermodynamics. Since molecules behave *quantum mechanically*, we will need to know a few of the *results* that are provided from quantum mechanics.

Those interested in more details should take CHE-372 this spring!



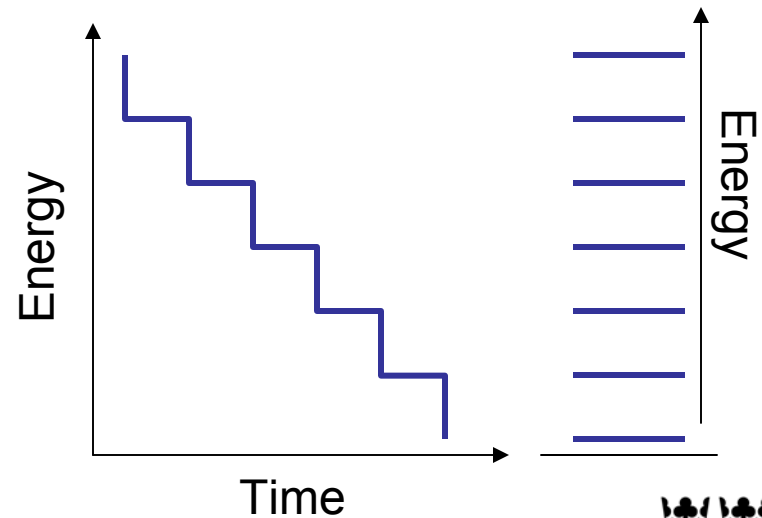
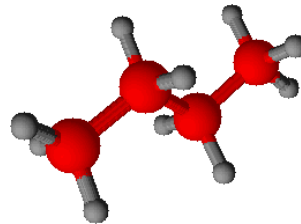
## Macroscopic

Big things, small relative energy spacings, energy looks *classical* (i.e., continuous)



## Microscopic

Small things, large relative energy spacings, must consider the energy levels to be quantized





Planck, 1900

Planck suggests that radiation (light, energy) can only come in quantized packets that are of size  $h\nu$ .

Energy (J) →  $E = h\nu$

Planck's constant  
 $h = 6.626 \times 10^{-34} \text{ J}\cdot\text{s}$

Frequency ( $\text{s}^{-1}$ )

Note that we can specify the energy by specifying *any one* of the following:

1. The frequency,  $\nu$  (units: Hz or  $\text{s}^{-1}$ ):
2. The wavelength,  $\lambda$ , (units: m or cm or mm):  
Recall:  $\nu\lambda = c$
3. The wavenumber,  $\tilde{\nu}$  (units:  $\text{cm}^{-1}$  or  $\text{m}^{-1}$ )

Recall:  $\tilde{\nu} = \frac{1}{\lambda}$



# Where can I put energy?

QM-4

Connecting macroscopic thermodynamics to a molecular understanding requires that we understand how energy is distributed on a molecular level.

**ATOMS:**

**MOLECULES:**

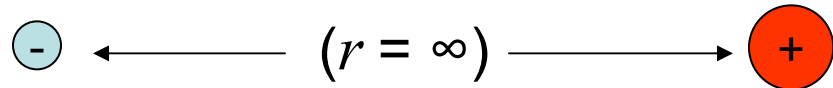
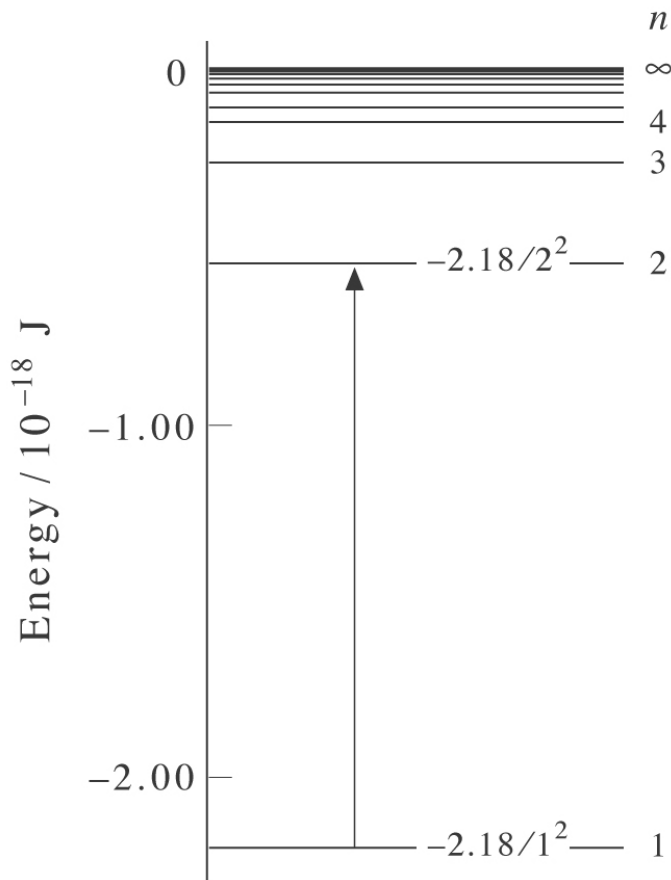




Convert J to  $\text{cm}^{-1}$ ; Can you?

$$\text{Electronic Energy Levels: } \mathcal{E}_{el} = \frac{-2.17869 \times 10^{-18}}{n^2} \text{ J} = \frac{-109680}{n^2} \text{ cm}^{-1}$$

$n$  must be an integer.



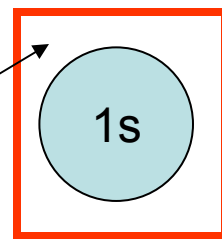
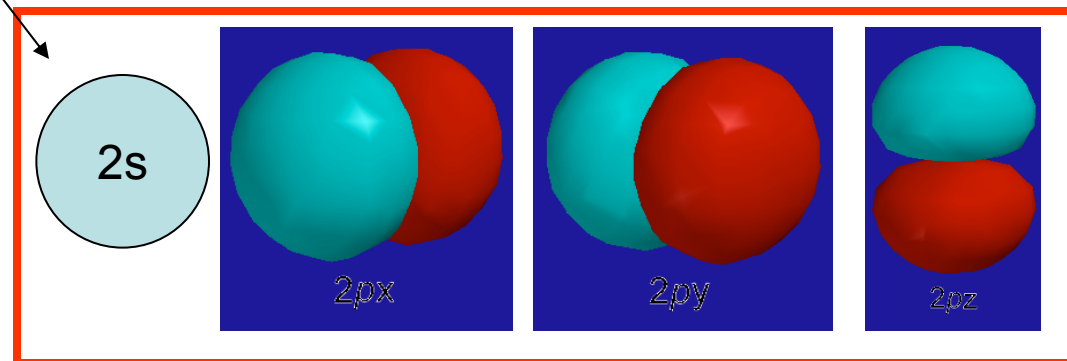
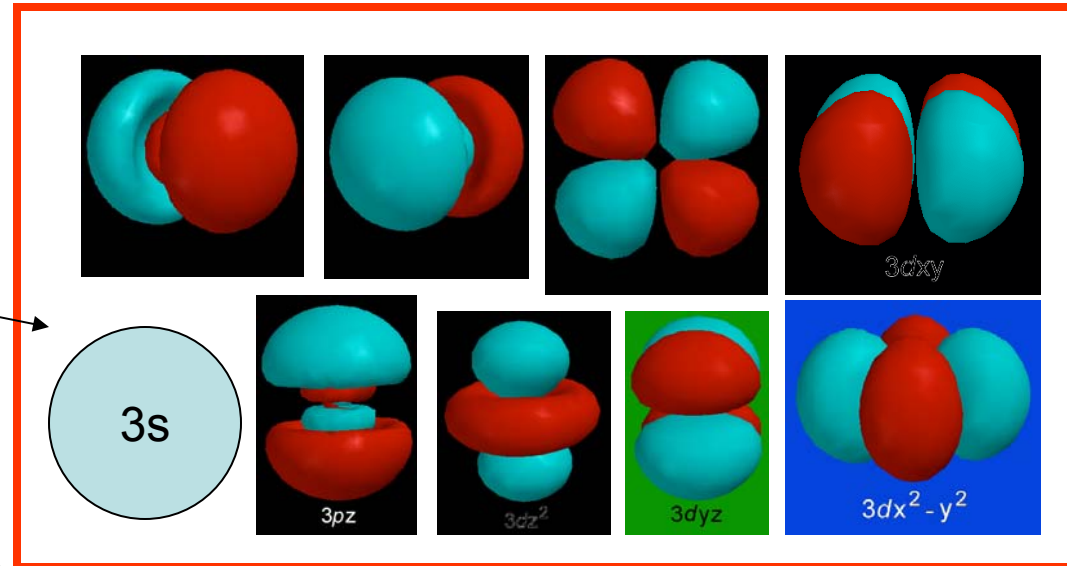
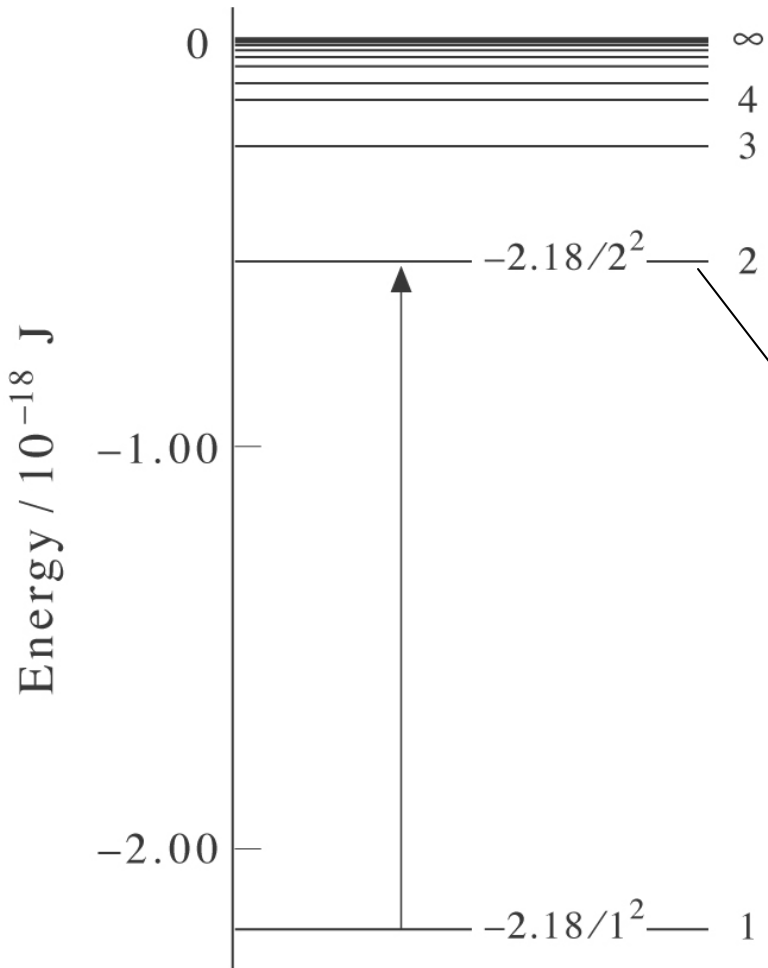
Series limit,  $n = \infty$ , the electron and proton are infinitely separated, there is no interaction.



# Wavefunctions and Degeneracy

QM-7

The wavefunctions are the atomic orbitals.



The number of wavefunctions, or states, with the same energy is called the *degeneracy*,  $g_{n^l}$ .



As we have seen, the electronic energy levels of the hydrogen atom are quantized. However, there is no simple formula for the electronic energy levels of any atom beyond hydrogen. In this case, we will rely on tabulated data.

TABLE 1.2

Data from “Moore’s tables”, listing the degeneracies and energies (in  $\text{cm}^{-1}$ ) of the first few states of atomic sodium.

Electron configuration	Degeneracy	Energy/ $\text{cm}^{-1}$
$3s$	2	0.00
$3p$	2	16 956.183
$3p$	4	16 978.379
$4s$	2	25 739.86
$3d$	6	29 172.855
$3d$	4	29 172.904
$4p$	3	30 266.88
$4p$	4	30 272.51
$5s$	2	33 200.696
$4d$	6	34 548.754
$4d$	4	34 548.789

<sup>a</sup>From C.E. Moore, *Atomic Energy Levels*, Natl. Bur. Std. Circ. No. 467 (US Government Printing Office, Washington, DC, 1949).

For the electronic energy levels, there is a large gap from the ground state to the first excited state. As a result, we seldom need to consider any states above the ground state at the typical energies that we will be working with.



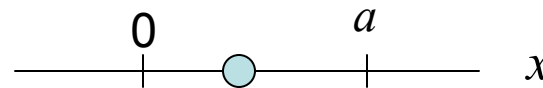
# ATOMS II: Translational Energy

# QM-9

In addition to electronic energy, atoms have translational energy.

To find the allowed translational energies we solve the Schrödinger equation for a particle of mass,  $m$ .

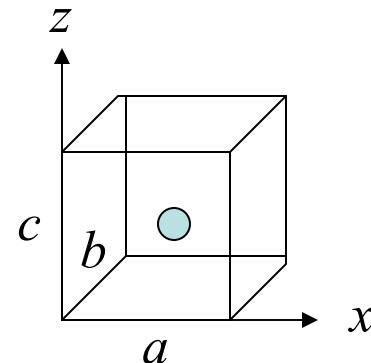
In 1D, motion is along the  $x$  dimension and the particle is constrained to the interval  $0 \leq x \leq a$ .



$$\mathcal{E}_n = \frac{n^2 h^2}{8ma^2} \quad n = 1, 2, 3, \dots$$

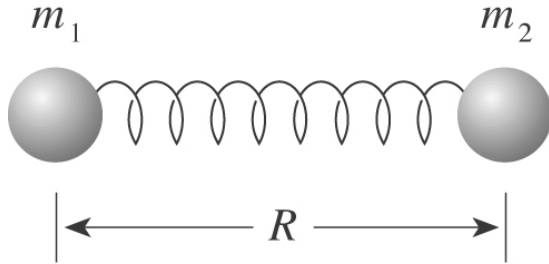
In 3D...

$$\mathcal{E}_{n_x, n_y, n_z} = \frac{h^2}{8m} \left( \frac{n_x^2}{a^2} + \frac{n_y^2}{b^2} + \frac{n_z^2}{c^2} \right) \quad \begin{array}{l} n_x = 1, 2, 3, \dots \\ n_y = 1, 2, 3, \dots \\ n_z = 1, 2, 3, \dots \end{array}$$



These states can be *degenerate*. For example, if  $a=b=c$ , then the two *different states* ( $n_x=1, n_y=1, n_z=2$ ) and ( $n_x=2, n_y=1, n_z=1$ ) have the *same energy*.





We model the vibrational motion as a harmonic oscillator, two masses attached by a spring.

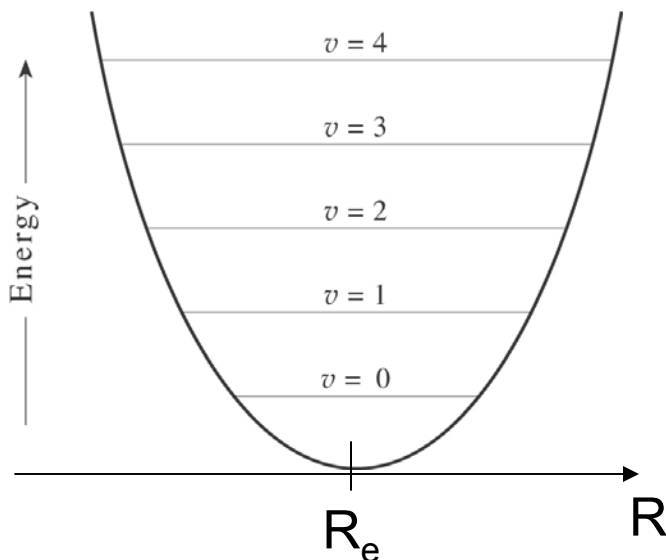
Solving the Schrodinger equation for the harmonic oscillator you find the following quantized energy levels:

nu and vee!

$$\epsilon_v = h\nu\left(v + \frac{1}{2}\right)$$

$$v = 0, 1, 2, \dots$$

## The energy levels



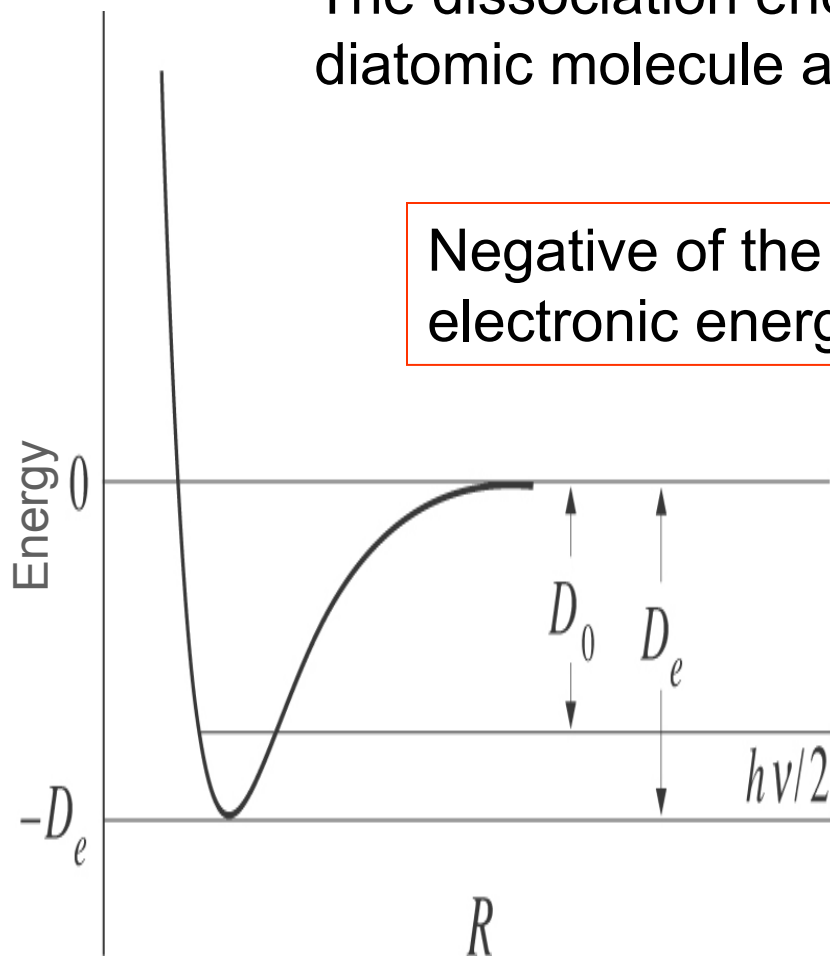
The level are non-degenerate, that is  $g_v=1$  for all values of  $v$ .

The energy levels are equally spaced by  $h\nu$ .

The energy of the lowest state is NOT zero. This is called the zero-point energy.



The dissociation energy and the electronic energy of a diatomic molecule are related by the zero point energy.



Negative of the electronic energy

$$\longrightarrow D_e = D_0 + \frac{h\nu}{2}$$

Dissociation energy

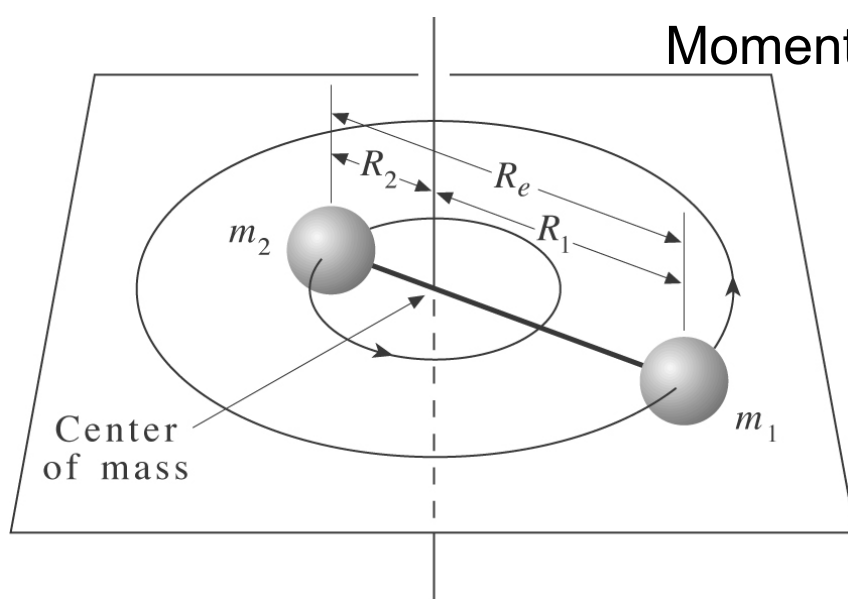
For  $H_2$ ...

$$D_e = 458 \text{ kJ}\cdot\text{mol}^{-1}$$

$$D_0 = 432 \text{ kJ}\cdot\text{mol}^{-1}$$

$$\tilde{\nu} = 4401 \text{ cm}^{-1} (=52 \text{ kJ}\cdot\text{mol}^{-1})$$

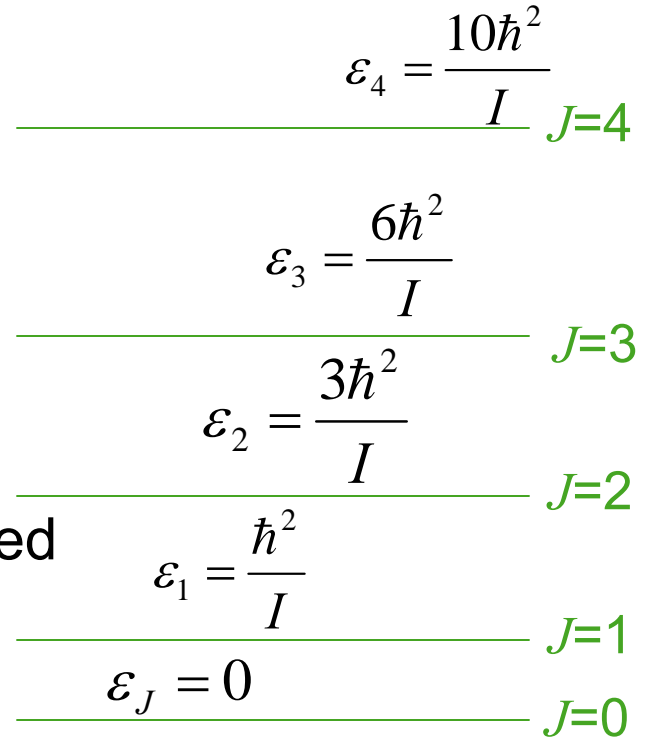




Moment of inertia:  $I = m_1 R_1^2 + m_2 R_2^2$

Treating a diatomic molecule as a rigid rotor, and solving the Schrödinger equation, you find the following quantized energy levels...

$$\varepsilon_J = \frac{\hbar^2}{2I} J(J+1) \quad J = 0, 1, 2, \dots$$



The degeneracy of these energy levels is:

$$g_J = 2J + 1$$

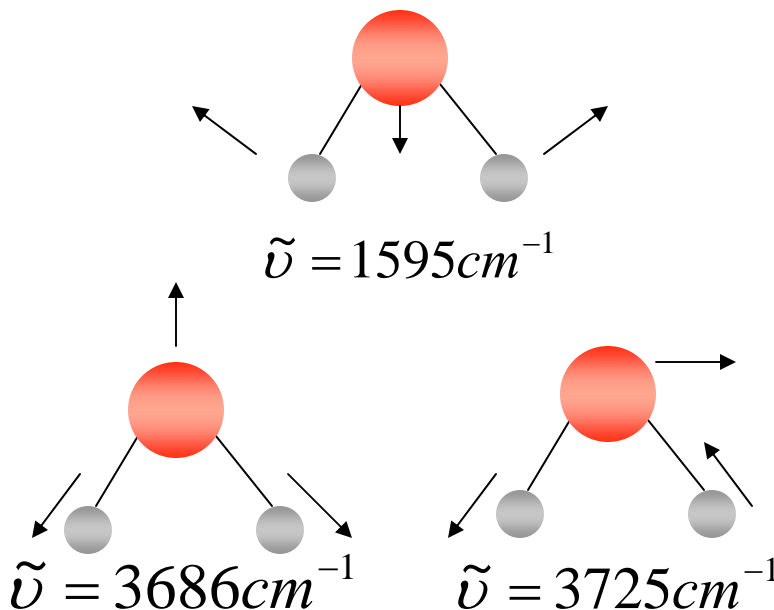


For polyatomic molecules we can consider each of the  $n_{vib}$  vibrational degrees of freedom as independent harmonic oscillators. We refer to the characteristic independent vibrational modes as *normal modes*.

Since the normal modes are independent, the total energy is just the sum:

$$\mathcal{E}_{vib} = \sum_{j=1}^{n_{vib}} h\nu_j \left( \nu_j + \frac{1}{2} \right)$$

For example, water has 3 normal modes:



EX-QM4

Ans: 4503  $\text{cm}^{-1}$



Linear molecules: The same as diatomics with the moment of inertia defined for more than 2 nuclei:

$$\varepsilon_J = \frac{\hbar^2}{2I} J(J+1) \quad J = 0, 1, 2, \dots \quad g_J = 2J + 1 \quad I = \sum_{j=1}^n m_j (x_j - x_{cm})^2$$

Nonlinear molecules: There is one moment of inertia for each of the 3 rotational axes. This leads to three ways to define polyatomic rotors:

Spherical top (baseball,  $\text{CH}_4$ ):  $I_A = I_B = I_C$

Symmetric top (American football,  $\text{NH}_3$ ):  $I_A = I_B \neq I_C$

Asymmetric top (Boomerang,  $\text{H}_2\text{O}$ ):  $I_A \neq I_B \neq I_C$



To specify the position of a molecule with  $n$  nuclei in space we require  $3n$  coordinates, this is 3 Cartesian coordinates for each nucleus. We say there are  **$3n$  degrees of freedom**.

We can divide these into translational, rotational, and vibrational degrees of freedom:

	Degrees of Freedom ( $3n$ in total)
<b>Translation:</b>	
Motion of the center of mass	3
<b>Rotation (Orientation about COM):</b>	
Linear Molecule	2
Non-Linear Molecule	3
<b>Vibration (position of <math>n</math> nuclei):</b>	
Linear Molecule	$3n-5$
Non-Linear Molecule	$3n-6$



# Total Energy

QM-16

The total energy is the energy of each degree of freedom:

$$\mathcal{E} = \mathcal{E}_{trans} + \mathcal{E}_{rot} + \mathcal{E}_{vib} + \mathcal{E}_{elec}$$

$$\mathcal{E}_{n_x, n_y, n_z} = \frac{h^2}{8m} \left( \frac{n_x^2}{a^2} + \frac{n_y^2}{b^2} + \frac{n_z^2}{c^2} \right)$$

$$n_x = 1, 2, 3, \dots$$

$$n_y = 1, 2, 3, \dots$$

$$n_z = 1, 2, 3, \dots$$

$$\mathcal{E}_v = h\nu \left( v + \frac{1}{2} \right)$$

For each vib. DOF

Look up values in  
a table (i.e.,  $D_e$ ).

$$\mathcal{E}_J = \frac{\hbar^2}{2I} J(J+1)$$

$$J = 0, 1, 2, \dots$$

For linear molecules.

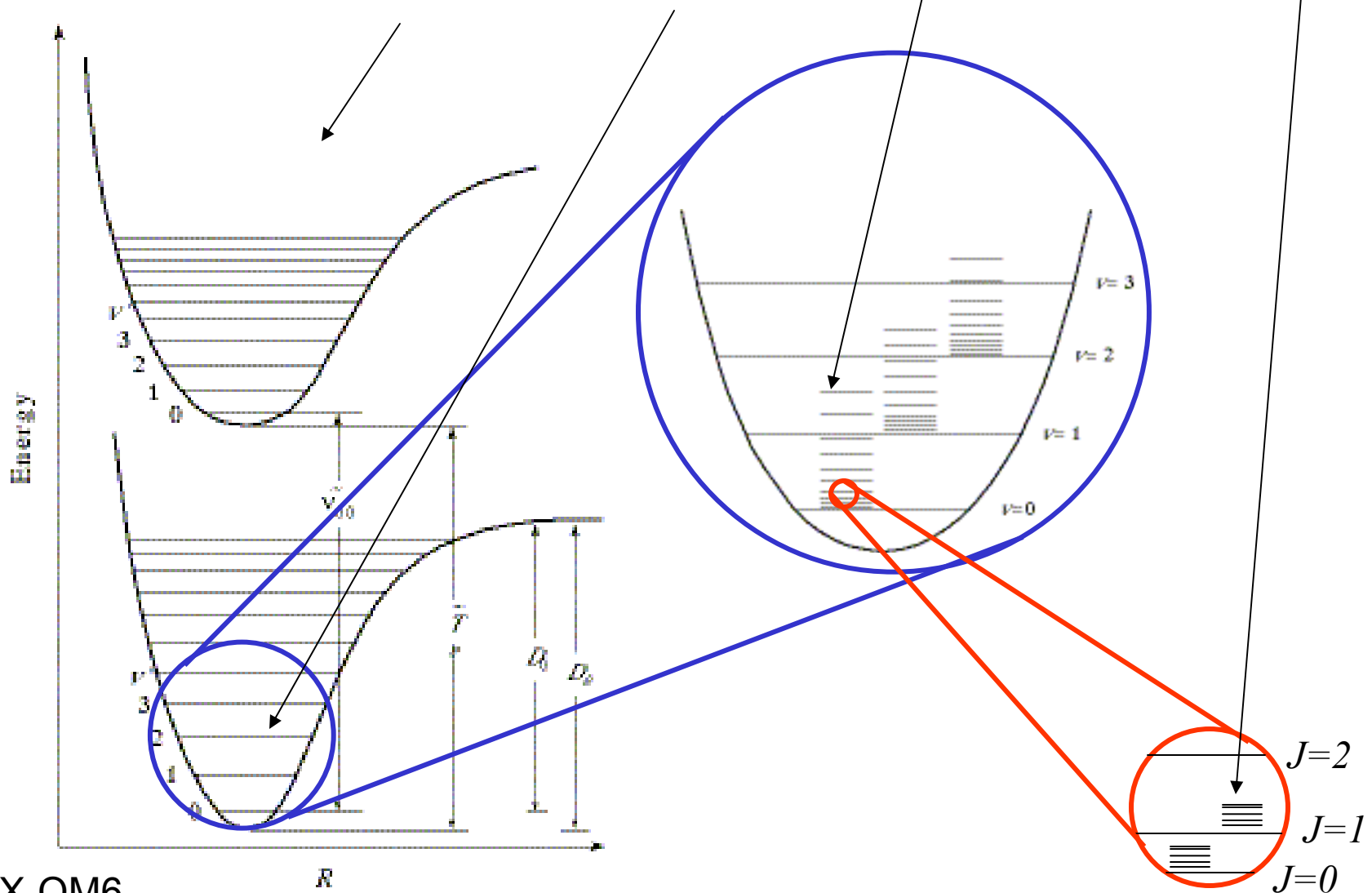


# Relative Energy Spacings

QM-17

The general trend in energy spacing:

Electronic > Vibrations > Rotations > > Translations



EX-QM6





Ludwig Boltzmann

The Boltzmann distribution determines the relative population of quantum energy states.

$$p_j = \frac{e^{-E_j/k_B T}}{\sum_i e^{-E_i/k_B T}}$$

Probability that a randomly chosen system will be in state  $j$  with  $E_j$

Partition function

This equation is the key equation in ***statistical mechanics***, the topic of the next few sections of this class. Statistical mechanics is used to comprehend ‘macroscopic’ thermodynamics in terms of a ‘microscopic’ molecular basis.

