Intro/Review of Quantum

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

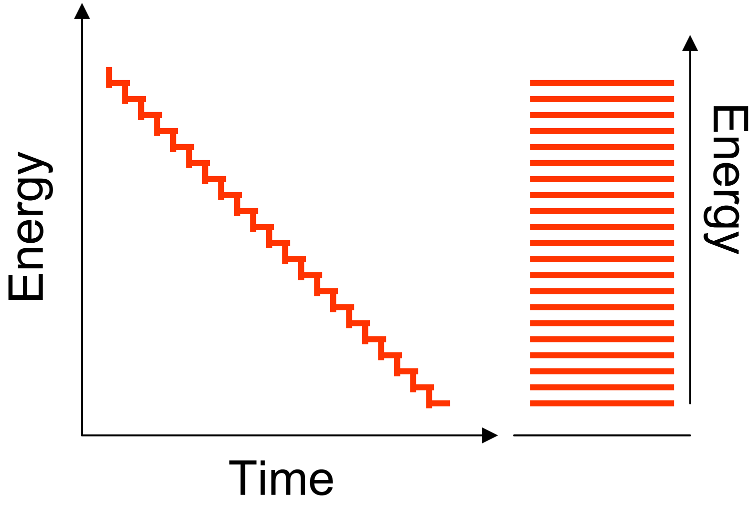
Well… we will focus on thermodynamics and kinetics, but we will consider this topic with reference to the *molecular basis* that underlies the laws of thermodynamics. Since molecules behave *quantum mechanically*, we will need to know a few of the *results* that are provided from quantum mechanics.

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

Energy is Quantized

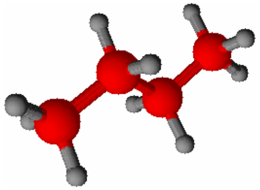
Macroscopic

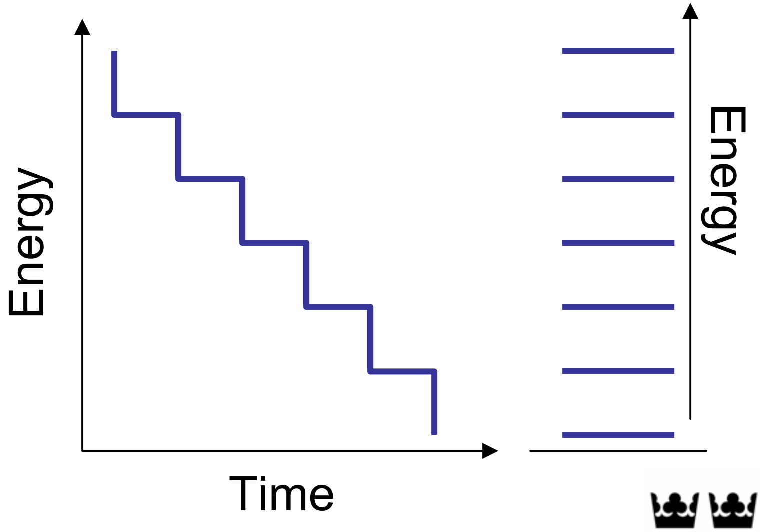
Big things, small relative energy spacings, energy looks *classical* (i.e., continuous)



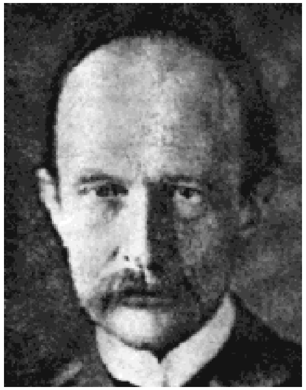
Microscopic

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





Energy is Quantized by h



Planck, 1900

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

Energy (J)

$$\boxed{E = h\upsilon}$$

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

Frequency (s^{-1})

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

1. The frequency, ν (units: Hz or s^{-1}):

2. The wavelength, λ, (units: m or cm or mm):

   Recall: $\upsilon\lambda = c$

3. The wavenumber, $\tilde{\upsilon}$ (units: cm^{-1} or m^{-1})

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

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:

Schrödinger Equation

Schrödinger

Erwin Schrödinger formulated an equation used in quantum mechanics to solve for the energy of different systems:

$$\hbar = \frac{h}{2\pi}$$

$$-\frac{\hbar^2}{2m}\underset{\substack{\uparrow\\ \text{Kinetic energy}}}{\frac{\partial^2}{\partial x^2}}\psi(x)+\underset{\substack{\uparrow\\ \text{Potential energy}}}{V(x)}\psi(x)=\underset{\substack{\uparrow\\ \text{Total energy}}}{\varepsilon}\psi(x)$$

$\psi(x)$ is the ***wavefunction***. The wavefunction is the most complete possible description of the system.

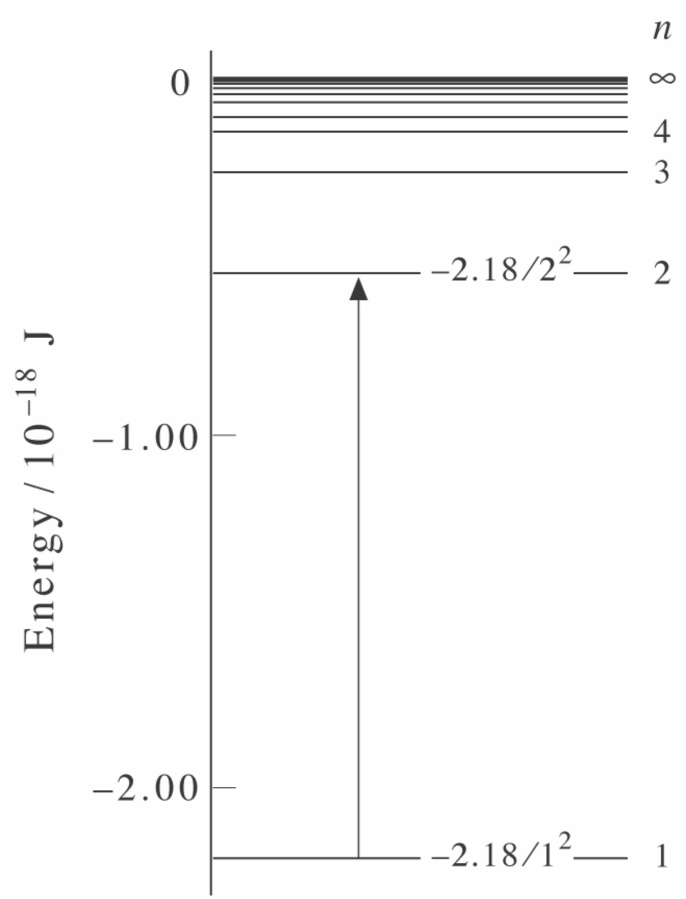
Solving the differential equation (S.E.) gives one set of ***wavefunctions***, $\psi(x)$ and a set of associated ***eigenvalues*** (i.e., energies) E.

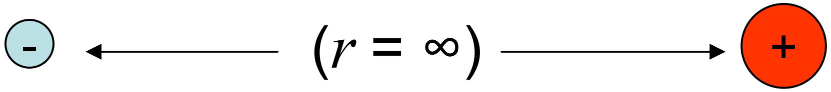
Interested in solving this problem for specific systems?!?! Take CHE 372 in the spring! Meanwhile, you are required such to be familiar with the ***solutions*** for the systems we will encounter.

ATOMS I: H atom electronic levels

Electronic Energy Levels: $$\varepsilon_{el} = \frac{-2.17869\times10^{-18}}{n^2}\overbrace{J = \frac{-109680}{n^2}cm^{-1}}^{\text{Convert J to cm}^{-1}\text{; Can you?}}$$

n must be an integer.

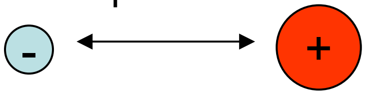




Series limit, n = ∞, the electron and proton are infinitely separated, there is no interaction.

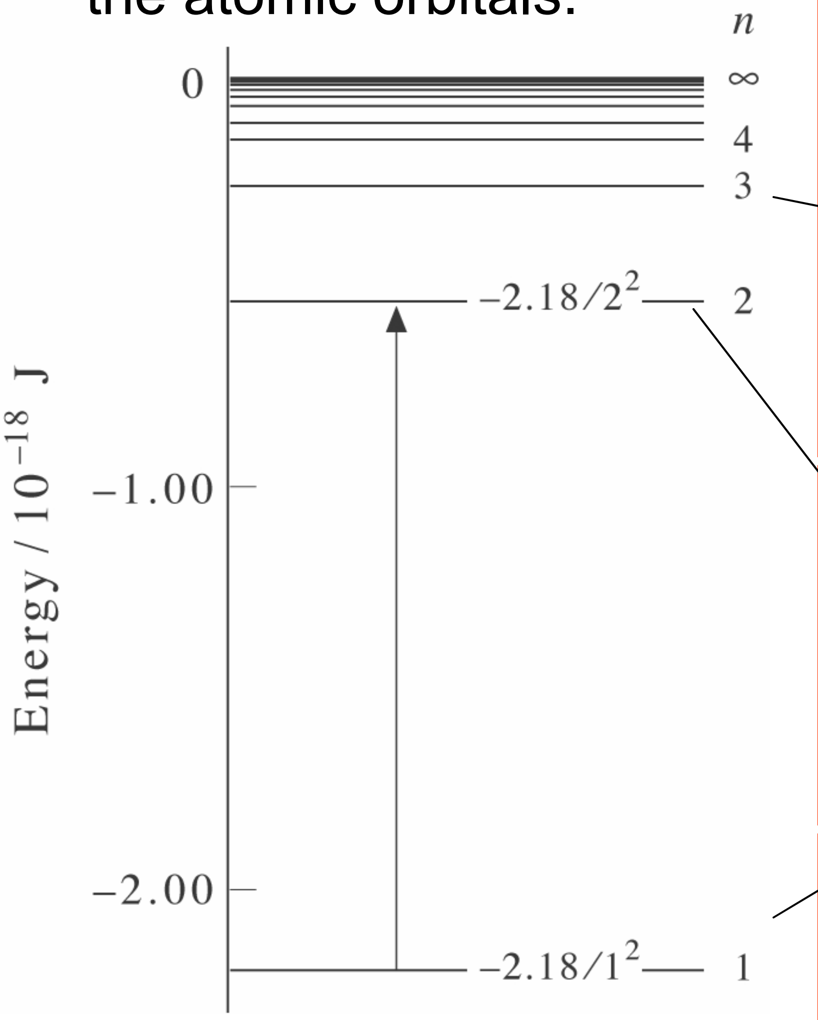
⋮

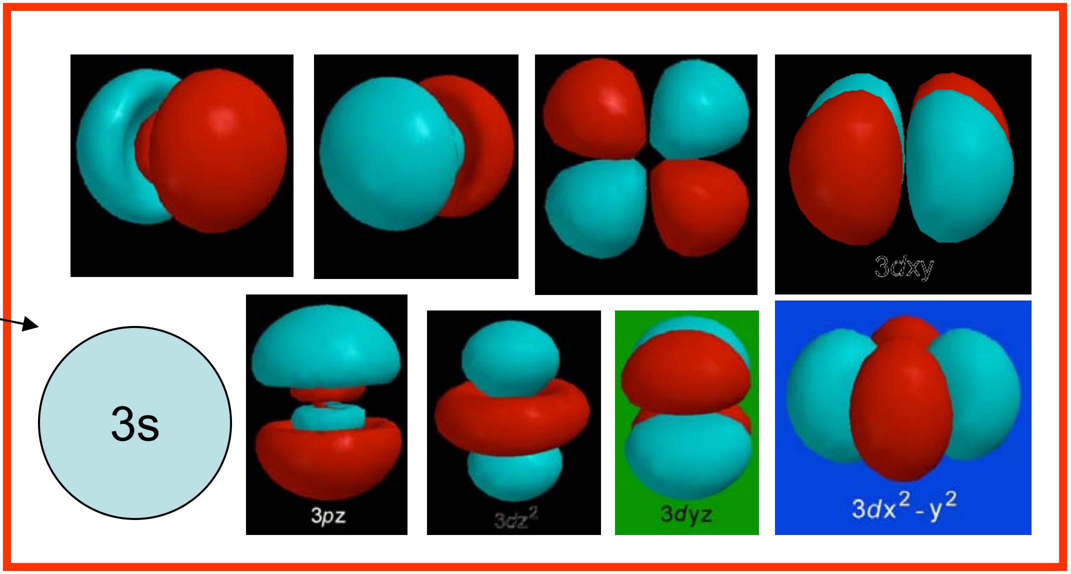
Ground state, n = 1, the most probable distance between the electron and proton is $r_{mp} = 5.3 \times 10^{-11}$ m.

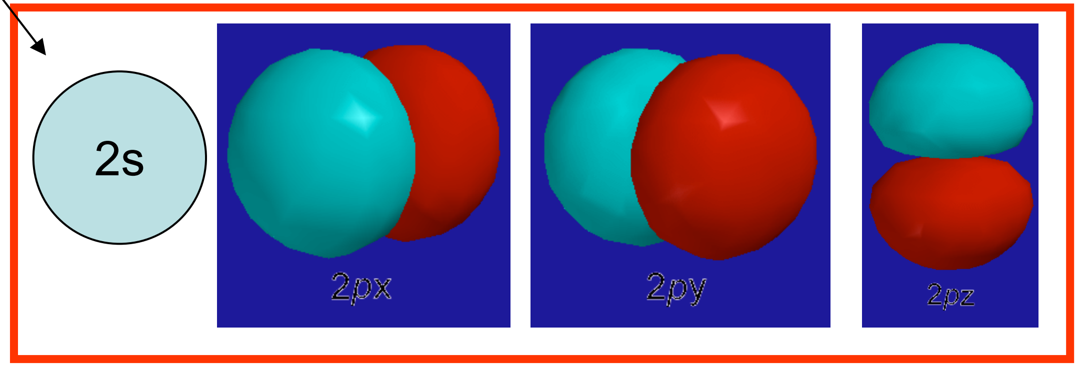


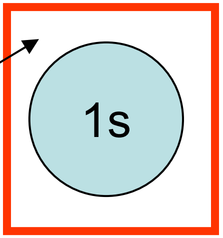
Wavefunctions and Degeneracy

The wavefunctions are the atomic orbitals.







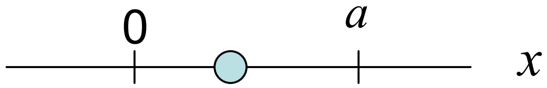


The number of wavefunctions, or states, with the same energy is called the *degeneracy, g_n.*

ATOMS II: Translational Energy

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*.

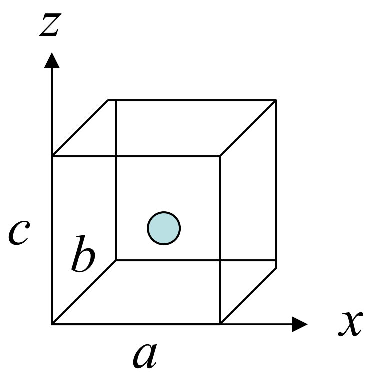


In 1D, motion is along the x dimension and the particle is constrained to the interval $0 \leq x \leq a$.

$$\boxed{\varepsilon_n = \frac{n^2 h^2}{8ma^2} \qquad n = 1,2,3,\ldots}$$

In 3D…

$$\boxed{\varepsilon_{n_x,n_y,n_z} = \frac{h^2}{8m}\left(\frac{n_x^2}{a^2} + \frac{n_y^2}{b^2} + \frac{n_z^2}{c^2}\right) \qquad \begin{aligned} n_x &= 1,2,3,\ldots \\ n_y &= 1,2,3,\ldots \\ n_z &= 1,2,3,\ldots \end{aligned}}$$



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*.

Electronic Energy Levels, Generally

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.

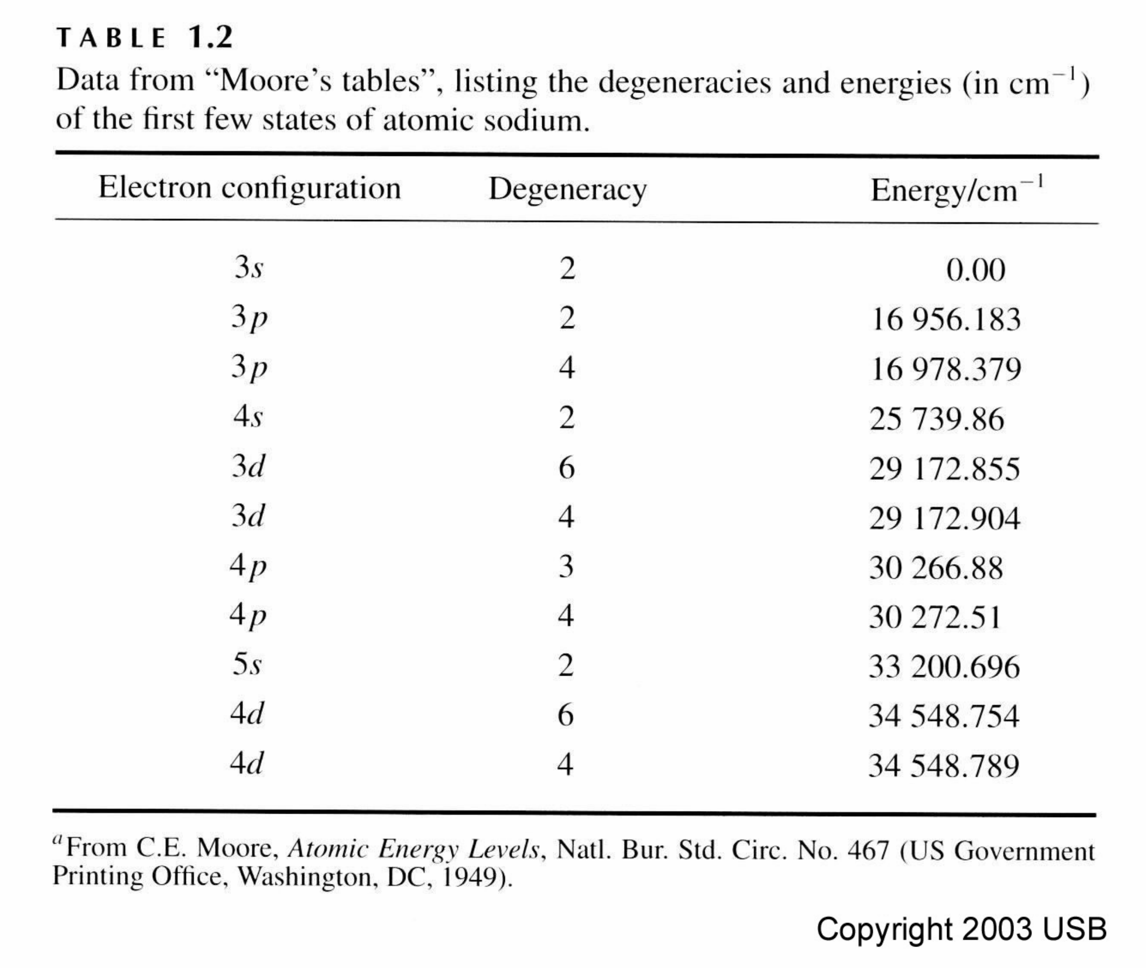


TABLE 1.2

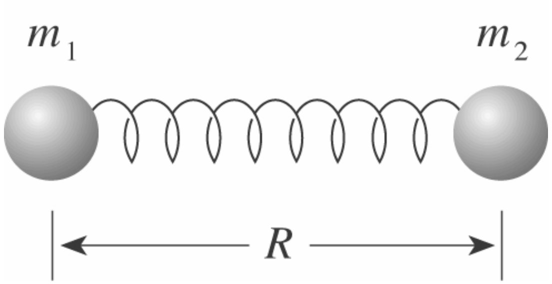
Data from "Moore's tables", listing the degeneracies and energies (in cm^{-1}) of the first few states of atomic sodium.

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

[a] 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.

MOLECULES I: Vibrational



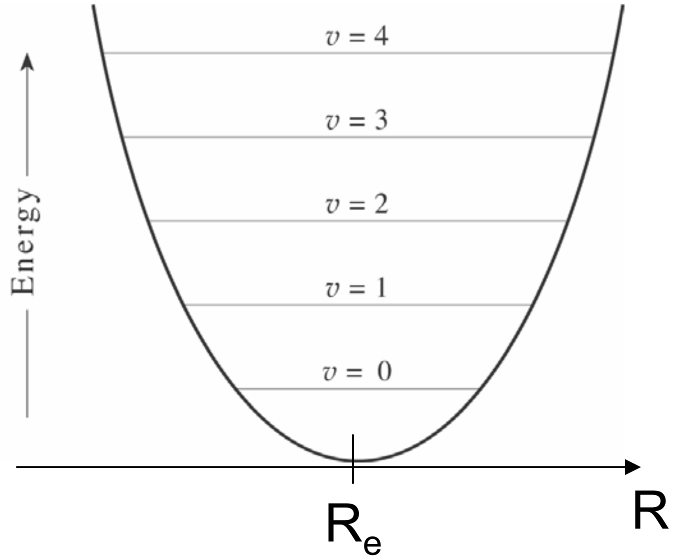
We model the vibrational motion as a harmonic oscillator, two masses attached by a spring.

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

nu and vee!

$$\boxed{\begin{gathered}\varepsilon_v = h\upsilon(v+\tfrac{1}{2}) \\ v = 0,1,2,\ldots\end{gathered}}$$

<u>The energy levels</u>



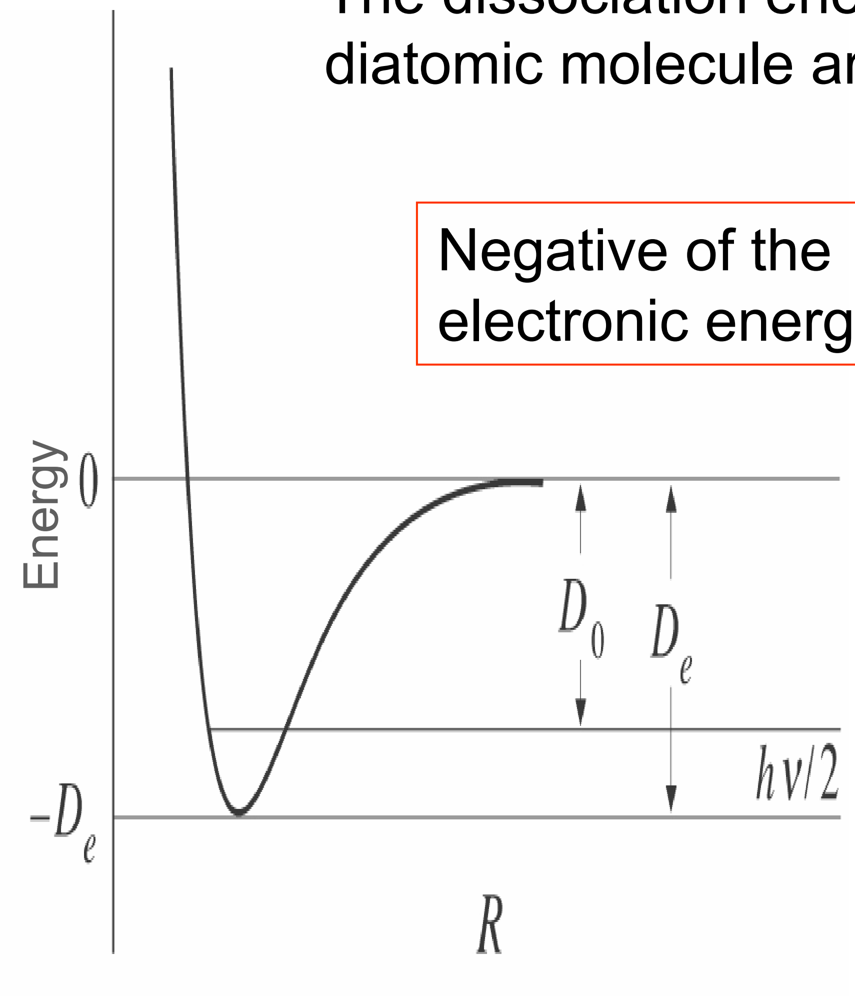
The level are <u>non-degenerate</u>, that is g_v=1 for all values of v.

The energy levels are <u>equally spaced</u> by $h\nu$.

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

Dissociation Energy

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



Negative of the electronic energy

$$D_e = D_0 + \frac{h\upsilon}{2}$$

Dissociation energy

For H_2…

D_e = 458 kJ·mol^{-1}

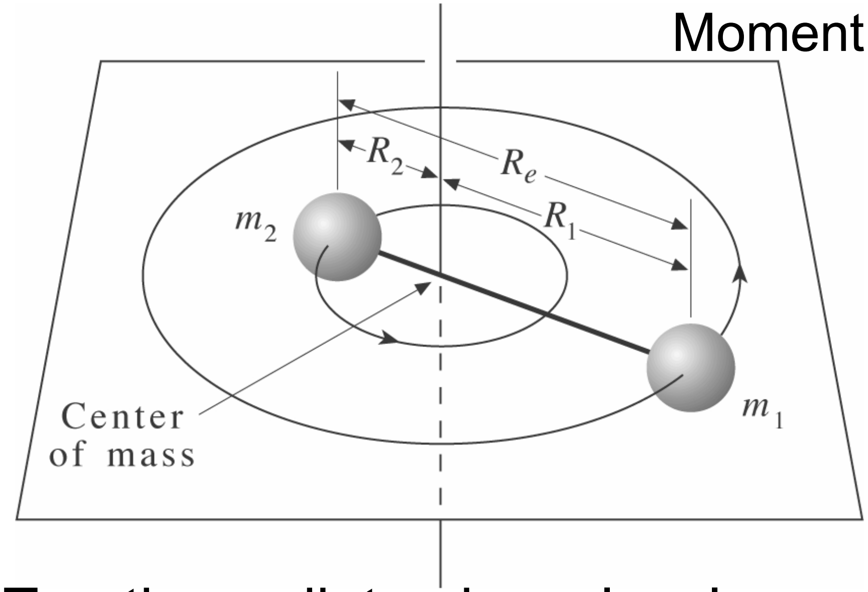
D_0 = 432 kJ·mol^{-1}

$\tilde{\upsilon}$= 4401 cm^{-1} (=52 kJ·mol^{-1})

MOLECULES II: Rotational

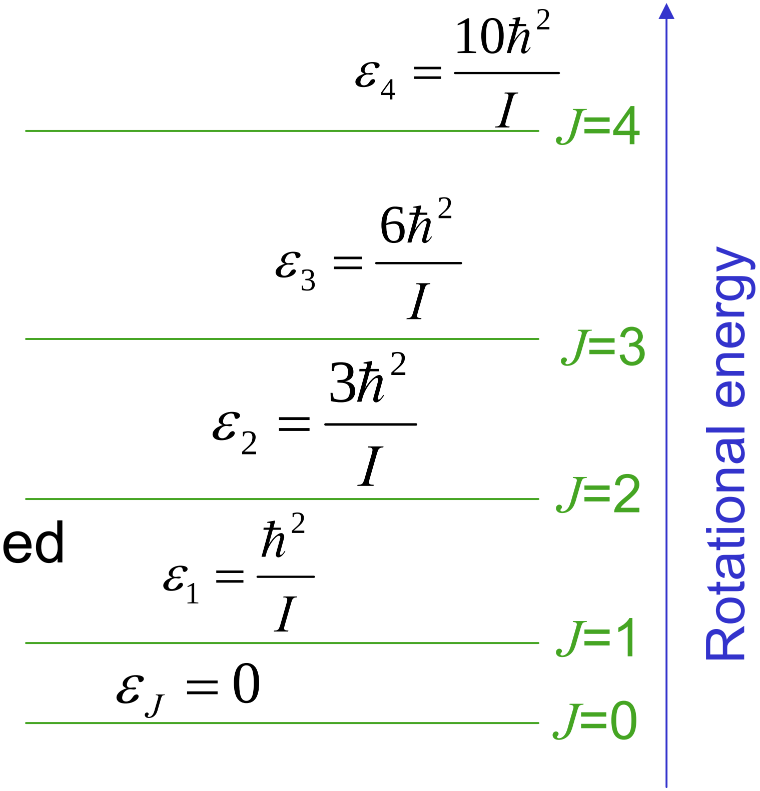
QM-12

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…

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



$\varepsilon_4 = \frac{10\hbar^2}{I}$ J=4

$\varepsilon_3 = \frac{6\hbar^2}{I}$ J=3

$\varepsilon_2 = \frac{3\hbar^2}{I}$ J=2

$\varepsilon_1 = \frac{\hbar^2}{I}$ J=1

$\varepsilon_J = 0$ J=0

Rotational energy

The degeneracy of these energy levels is:

$$g_J = 2J + 1$$

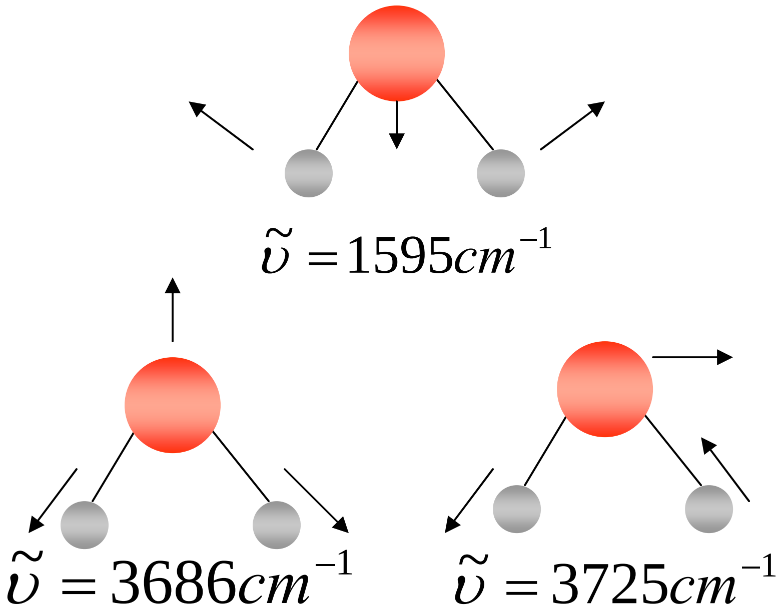
Polyatomic Molecules I: Vibrations

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:

$$\varepsilon_{vib} = \sum_{j=1}^{n_{vib}} h\upsilon_j \left(v_j + \tfrac{1}{2}\right)$$

For example, water has 3 normal modes: (3*n*-6=3)



$\tilde{\upsilon} = 1595cm^{-1}$

$\tilde{\upsilon} = 3686cm^{-1}$

$\tilde{\upsilon} = 3725cm^{-1}$

Polyatomic Molecules II: Rotations

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

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

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, CH_4): $I_A = I_B = I_C$

Symmetric top (American football, NH_3): $I_A = I_B \neq I_C$

Asymmetric top (Boomerang, $H_2$0): $I_A \neq I_B \neq I_C$

Degrees of Freedom

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)
Translation:	
Motion of the center of mass	3
Rotation (Orientation about COM):	
Linear Molecule	2
Non-Linear Molecule	3
Vibration (position of n nuclei):	
Linear Molecule	$3n$-5
Non-Linear Molecule	$3n$-6

Total Energy

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

$$\varepsilon = \varepsilon_{trans} + \varepsilon_{rot} + \varepsilon_{vib} + \varepsilon_{elec}$$

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

$$n_x = 1,2,3,\ldots$$
$$n_y = 1,2,3,\ldots$$
$$n_z = 1,2,3,\ldots$$

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

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

For linear molecules.

$$\varepsilon_v = h\upsilon(v + \tfrac{1}{2})$$

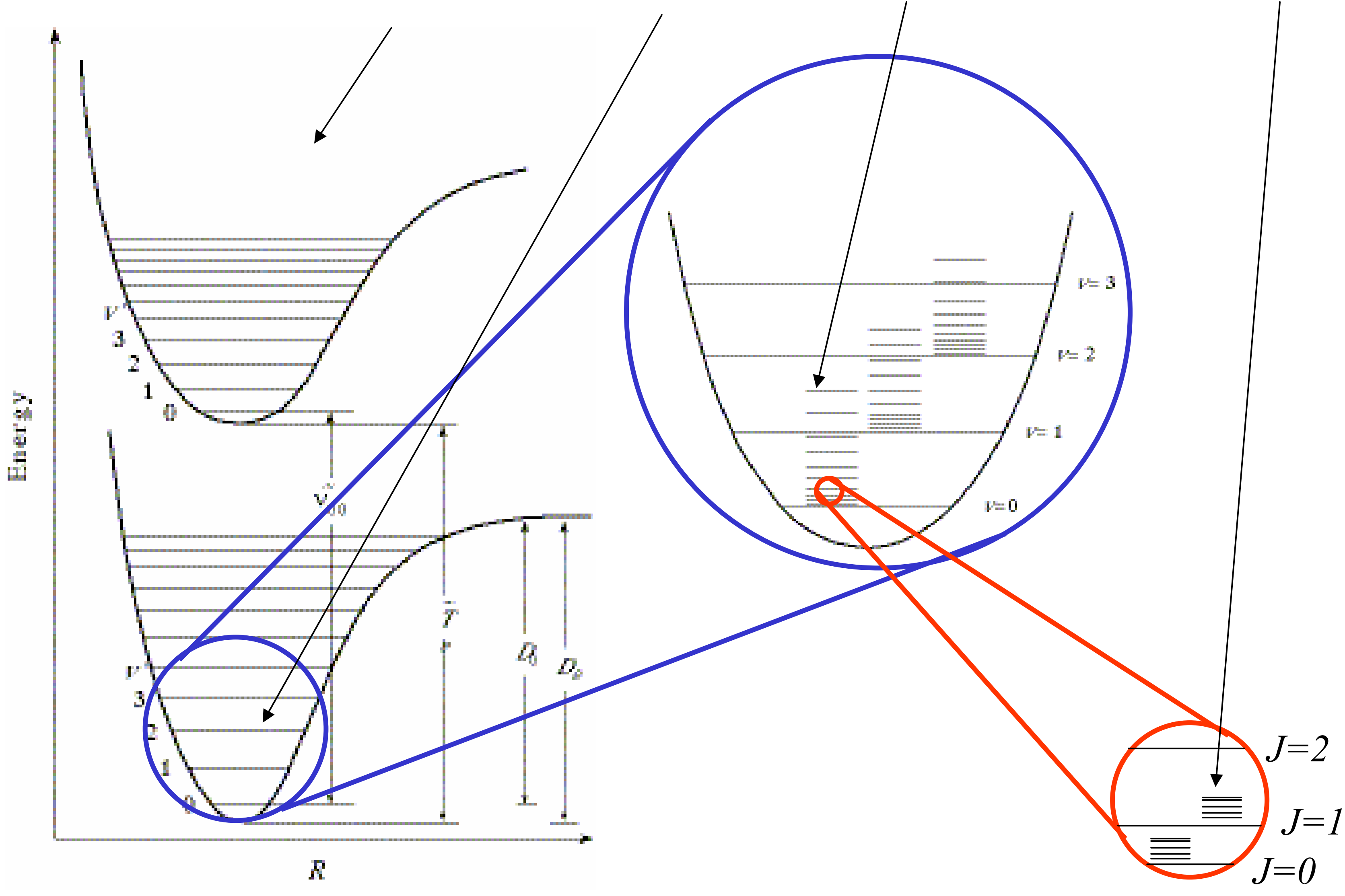
For each vib. DOF

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

Relative Energy Spacings

The general trend in energy spacing:

Electronic > Vibrations > Rotations > > Translations



Population: Boltzmann Distribution

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.