Chapter 2: Electronic, Vibrational and Spin Configurations of Electronically Excited States

Principles of Molecular Photochemistry
An Introduction

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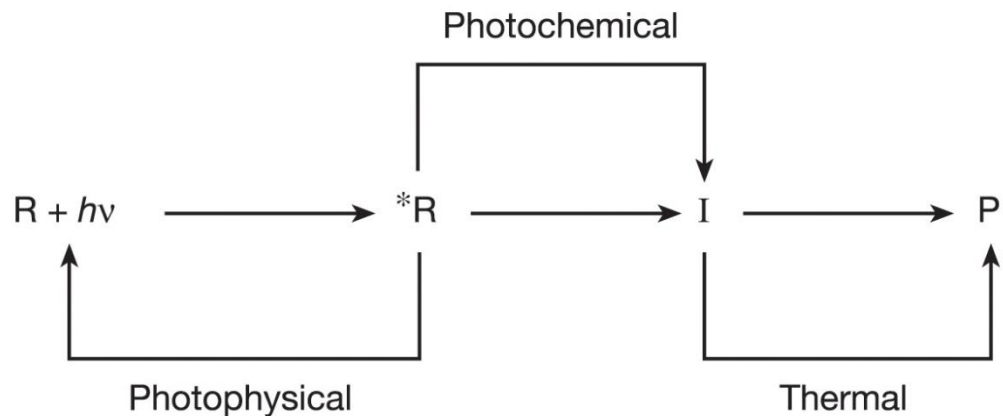J.C. Scaiano

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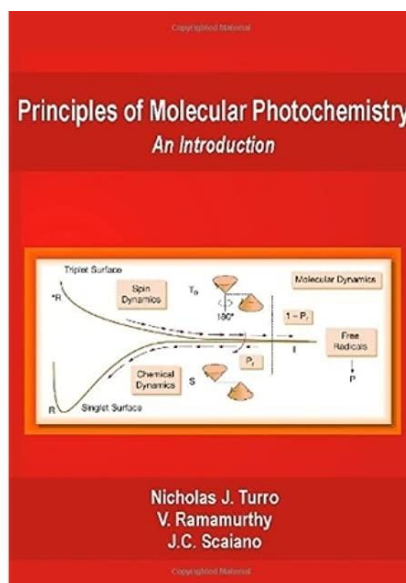
Visualization of the Electronically Excited Structures
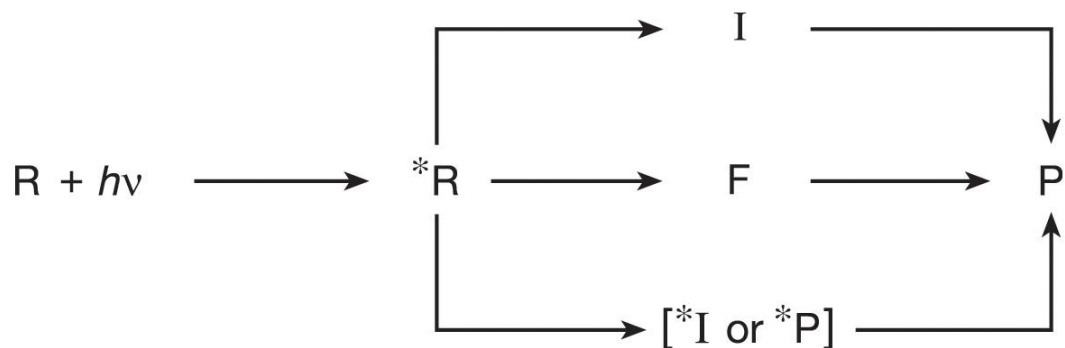
Scheme 1.2 copyright 2009 University Science Books

- Let us start by reviewing our working paradigm that we introduced in Chapter 1

- Electronically excited states, *R, are the critical initial transient structure in the photochemical reaction of *all* organic molecules

- Any *chemical* process that is produced directly from *R is called a primary photochemical process

- Any *physical* process that proceeds directly from *R is called a primary photophysical process

Visualization of the Electronically Excited Structures

Photochemical

R + $h\nu$ ⟶ *R ⟶ I ⟶ P

Photophysical   Thermal

Scheme 2.1 copyright 2009 University Science Books

- We have now expanded our working paradigm to include primary photophysical processes of *R for the most common pathway, *R → I → P

- These photophysical pathways (*R → R) generally compete with the photochemical pathways (*R → I)

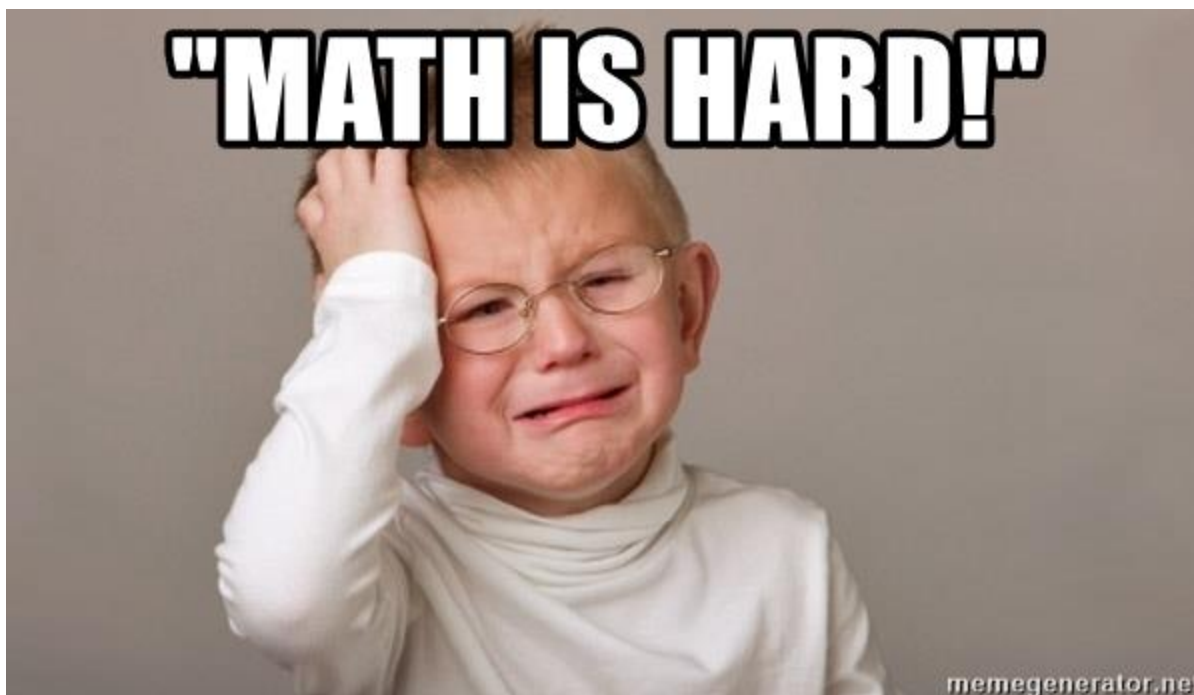# Visualization of the Electronically Excited Structures
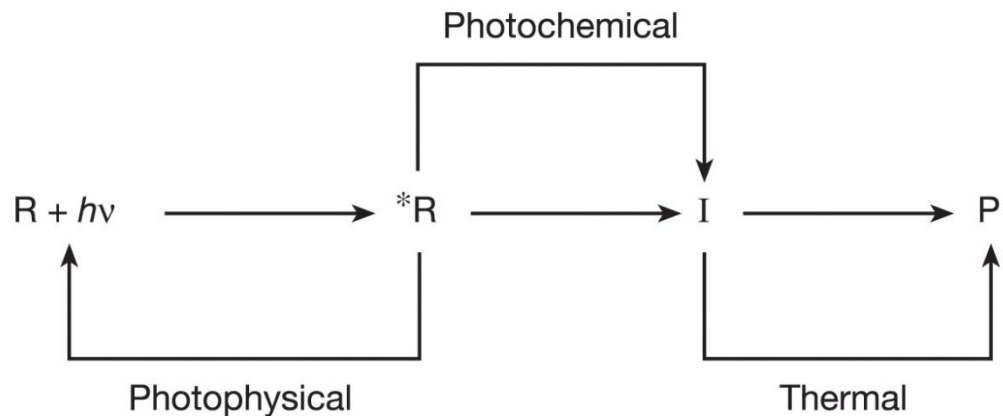
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- The reactive intermediate (I) undergoes conventional *thermal* processes leading to the observed product (P)

- Reminder: I represents common reactive intermediates, like radical pairs, biradicals, zwitterions, carbenes, etc. that are produced in the primary photochemical step *R → I

- The chemical pathways from I → P are called secondary thermal processes

Visualization of the Electronically Excited Structures

- Quantum mechanics provides the most general and effective paradigm of physics and chemistry for the description of molecular structure and dynamics of organic molecules

- However, quantum mechanics requires a mathematical sophistication that is well beyond the scope of this course

Visualization of the Electronically Excited Structures

- Quantum mechanics provides the most general and effective paradigm of physics and chemistry for the description of molecular structure and dynamics of organic molecules

- However, quantum mechanics requires a mathematical sophistication that is well beyond the scope of this course

- Nevertheless, we can *qualitatively* interpret the mathematical ideas of quantum mechanics through visualizable pictorial representations

- *We can translate the mathematics of quantum mechanics into pictures that can be translated into molecular structures (this Chapter) and molecular dynamics (Chapter 3)*

Molecular Wavefunctions and Molecular Structure

- Organic chemistry employs pictorial objects called *molecular structures* (Lewis structures and MOs) to make correlations with molecular function, properties, and reactivity

- Quantum mechanics uses mathematical objects called wave functions

- The wave function of any atomic or molecular system is a mathematical function that contains all the information necessary to determine any measurable property

- A complete wave function of any molecular system is composed of a rather complicated mathematical function represented by the symbol Ψ

Molecular Wavefunctions and Molecular Structure

- According to the laws of quantum mechanics, a wave function Ψ is produced by solving the Schrödinger "wave equation":

$$H\Psi = E\Psi$$

- The laws of quantum mechanics tell us that only certain "allowed" stable states can exist, and that these allowed states possess specific (quantized) energies

Erwin Schrödinger
Austrian-Irish Physicist
from Wikipedia

- Each of these stable states corresponds to a specific wave function (Ψ) that is a solution to the wave equation

$$H\Psi = E\Psi$$

- Each Ψ has an associated energy (E) that is produced by solutions of the wave equation

- H is called the "Hamiltonian" and corresponds to a mathematical "operator" for the *possible* energies (E) of the system

- These energies may be electronic energies of a molecule, vibrational energies of the atoms in a molecule, or the spin energies of electrons

Reward.

LOST CAT

"Schrödinger"

Last seen in a box in 1935, may be dead or alive.

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Molecular Wavefunctions and Molecular Structure

- The special properties of the wave equation are that the "allowed" (stable) wave functions have the remarkable property that when H is multiplied by Ψ the result, for certain values of E, is $H\Psi = E\Psi$

- The wave functions (Ψ) are called eigenfunctions, and the solutions (E) are called eigenvalues of the operator H
  - Eigen- derives from German for "proper"

- Only the eigenvalues that correspond to the solutions of the wave equation are the energies that are allowed for any stable state, that is, the energies of all molecular states (electronic, vibrational, spin) are quantized as a result of the wave features of the wave equation

Molecular Wavefunctions and Molecular Structure
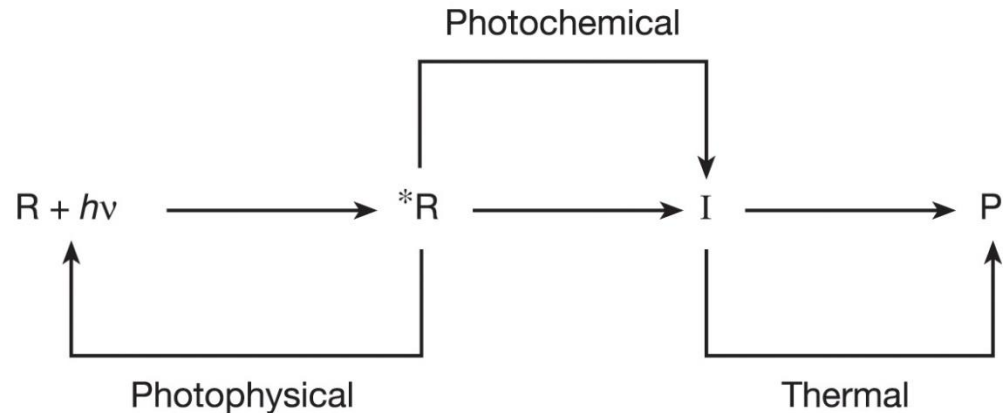
Scheme 2.1 copyright 2009 University Science Books

- We can think of a complete molecular wave function (Ψ) as a mathematical representation of the entire molecular structure (i.e., electronic, vibrational, spin)

- For the molecular structural representations of R, *R, I and P, there exist a corresponding wavefunction Ψ(R), Ψ(*R), Ψ(I), and Ψ(P), respectively

- A system whose wave function is an eigenfunction of some operator that represents a measurable property of a system is said to be in an eigenstate for the measured property

The Born–Oppenheimer Approximation

- For organic molecules, the most important method for determining molecular wave functions and associated energies is the Born–Oppenheimer approximation

- According to this approximation, *the motions of electrons in orbitals are much more rapid than nuclear vibrational motions*

- This approximation assumes that the low-mass, rapidly moving, negatively charged electrons can immediately adjust their distribution to the positive potential of slowly moving, heavy, massive nuclei

- The important consequence of this approximation is that electronic and nuclear motions can be treated mathematically, but independently
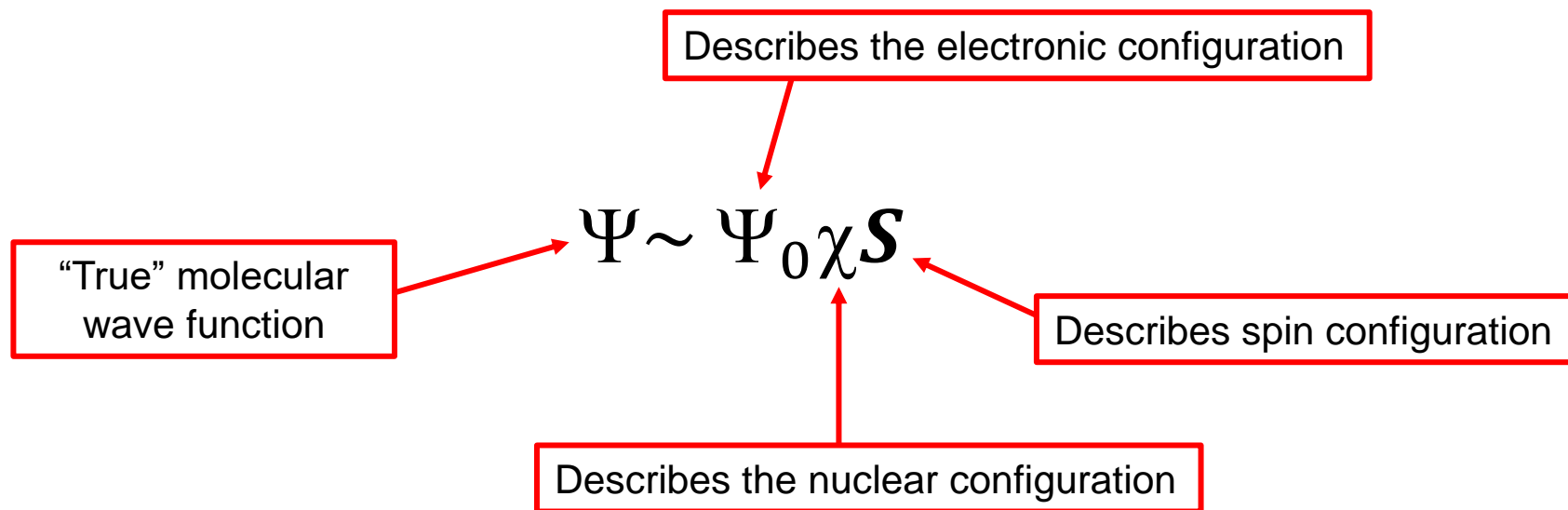

Max Born
German Physicist

J. Robert Oppenheimer
American Physicist

The Born–Oppenheimer Approximation

- The Born–Oppenheimer approximation makes it possible to compute a good first guess for Ψ, the "true" molecular wave functions of a molecule

- The Born–Oppenheimer approximation allows an approximate Ψ to be computed in terms of *three independent wave functions*

Describes the electronic configuration

$$\Psi \sim \Psi_0 \chi \boldsymbol{S}$$

"True" molecular wave function

Describes spin configuration

Describes the nuclear configuration

- *This approximation breaks down whenever there is a significant interaction between electrons and vibrations (called vibronic coupling) or between the spins and the orbiting electrons (called spin–orbit coupling)*

The Born–Oppenheimer Approximation

- Let us consider the approximate electronic wave function , Ψ_0, which we visualize in terms of electrons distributed in orbitals about a fixed field of positively charged nuclear structure

- A common approach to approximate Ψ_0 is not to solve the wave equation for all the electrons in the molecule (impossible because of complications from electron-electron repulsion) but to solve a fictitious molecule that contains only "one electron"

- The wave functions generated by solving the wave equation for the one-electron molecule are called "one-electron orbitals", ϕ_i, each which possess an eigenvalue of energy, E_i

$$\Psi_0 \sim \phi_1 \phi_2 \phi_3 \ldots \phi_n$$

Overlapping one-electron orbitals

Ground and Excited Electronic Configurations
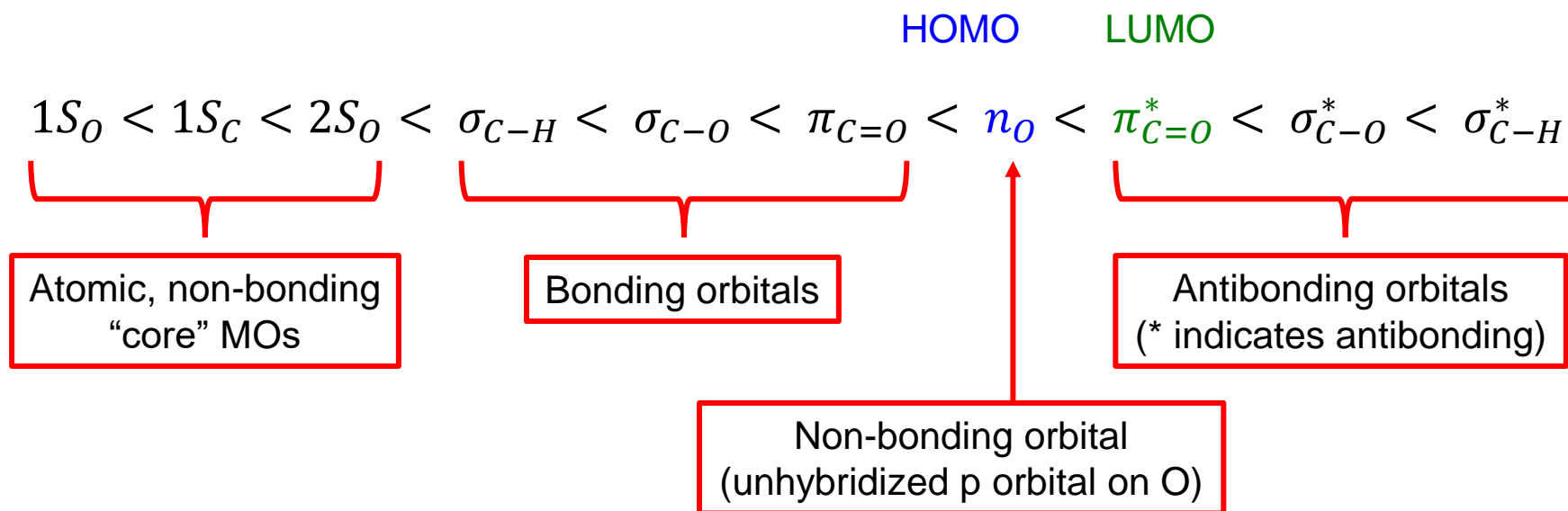
- An electronic configuration tells us how the electrons are distributed among the available orbitals and also provides a description of the electronic distribution of a molecule

- The ground configuration is defined as the configuration for which the orbitals are occupied produce the state of lowest energy (R)

- All other electronic configurations correspond to electronically excited states (*R)

- According to the state energy diagram, in addition to the ground state (S_0), we are interested mainly in the lowest energy electronically excited states (S_1 and T_1)

Ground and Excited Electronic Configurations

- Let's examine formaldehyde as an example

Formaldehyde
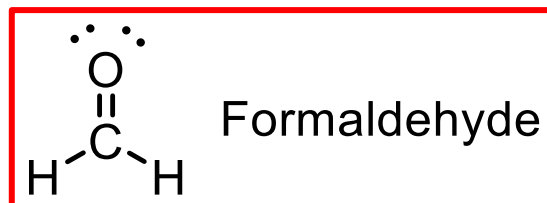
- This example captures the important features of ground- and excited-state configurations for many molecules of photochemical interest that possess a carbonyl

- The energies for the one-electron MOs (ϕ_i) are shown below:

HOMO   LUMO

$$1S_O < 1S_C < 2S_O < \sigma_{C-H} < \sigma_{C-O} < \pi_{C=O} < n_O < \pi_{C=O}^* < \sigma_{C-O}^* < \sigma_{C-H}^*$$

Atomic, non-bonding "core" MOs

Bonding orbitals

Antibonding orbitals (* indicates antibonding)

Non-bonding orbital (unhybridized p orbital on O)

Ground and Excited Electronic Configurations

- What is the electronic configuration of S_0 for formaldehyde?

- Formaldehyde has a total of 16 electrons, which must be distributed to fill the available MOs
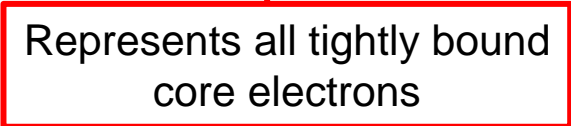 - *Remember the Pauli exclusion principle when distributing electrons!*

$$\Psi_0(H_2C{=}O) = (1S_O)^2(1S_C)^2(2S_O)^2(\sigma_{CH})^2(\sigma'_{CH})^2(\sigma_{CO})^2(\pi_{CO})^2(n_O)^2(\pi^*_{CO})^0$$

Ground and Excited Electronic Configurations

- A useful simplification is to _only consider valence electrons_, as the "core" electrons are so close to the nuclei that they are too stable to be perturbed

- Further, it suffices to only consider the highest energy valence electrons

- In the case of formaldehyde, we consider valence electrons in both the $\pi_{C=O}$ and n_O as they are of comparable energy

Ground state (S_0) of formaldehyde:

$$\Psi_0(H_2C=O) = K(\pi_{C=O})^2(n_O)^2(\pi^*_{C=O})^0$$

Represents all tightly bound core electrons

Construction of Electronic States from Electronic Configurations

- Following an analogous protocol to that followed for formaldehyde, we ignore the lower energy MOs and describe the ground-state electronic configuration of a second example, ethylene ($H_2C=CH_2$)

Ground state (S_0) of ethylene:

$$\Psi_0(H_2C=CH_2) = K(\pi_{C=C})^2(\pi^*_{C=C})^0$$

- With these two examples, _we know have a way of describing the orbital configuration of R and *R of any organic molecule for which the MOs are known or can be approximated_

Construction of Electronic States from Electronic Configurations

- We are now able to describe *R of formaldehyde and ethylene in terms of orbital configuration

- The lowest-energy electronic excited states (the most important for organic photochemistry) possess an electronic configuration where one electron has been removed from the HOMO and placed into the LUMO
  - $(HO)^1(LU)^1$

Formaldehyde

$${}^*\Psi(H_2C{=}O) = K(\pi_{C=O})^2(n_O)^1(\pi^*_{C=O})^1 \qquad\qquad n,\pi^* \text{ excited state (*R)}$$

$${}^*\Psi(H_2C{=}O) = K(\pi_{C=O})^1(n_O)^2(\pi^*_{C=O})^1 \qquad\qquad \pi,\pi^* \text{ excited state (**R)}$$

Ethylene

$${}^*\Psi(H_2C{=}CH_2) = K(\pi_{C=C})^1(\pi^*_{C=C})^1 \qquad\qquad \pi,\pi^* \text{ excited state (*R)}$$

Construction of Electronic States from Electronic Configurations
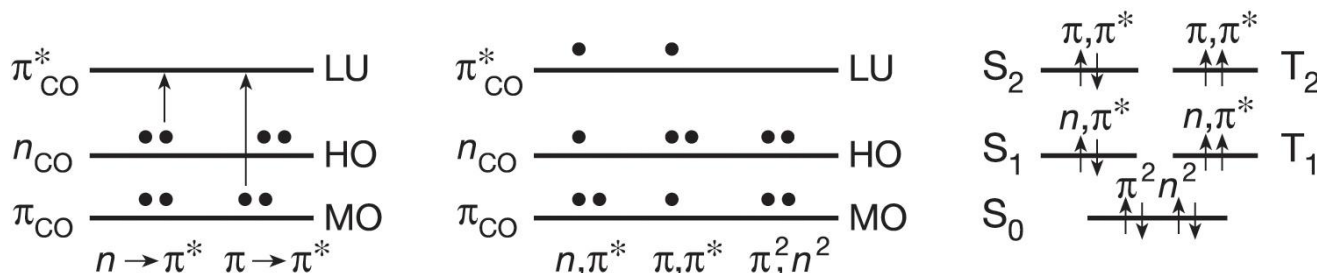
- The energies of the n and π orbitals of formaldehyde are similar in energy therefore formaldehyde will possess two electronically different transitions
  - $n \to \pi^*$ and $\pi \to \pi^*$, respectively

- These two transitions will in turn produce two corresponding excited-state configurations from excitation of the ground state
  - *R(n,π^*) and *R(π,π^*), respectively

- For carbonyl compounds, which of these two states is the lowest in energy depends on both structural and environmental factors

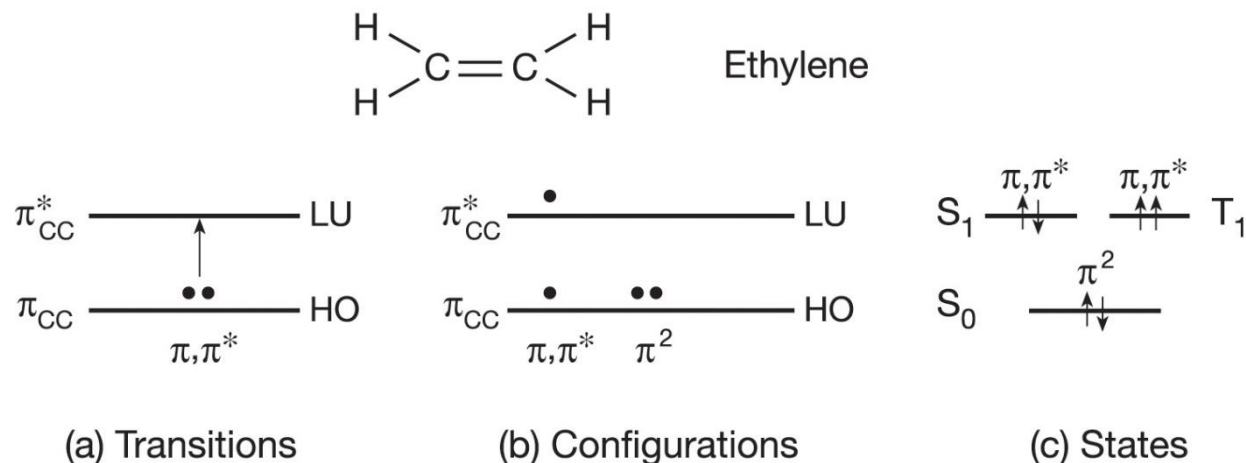# Construction of Electronic States from Electronic Configurations

Figure 2.1 copyright 2009 University Science Books

- Ethylene will only have one low-energy electronic transition ($\pi \rightarrow \pi^*$) and one corresponding lowest-lying electronic excited-state configuration, *R(π,π^*)

- This is because the σ orbitals are very low in energy and the σ^* orbitals are very high in energy

Characteristic Configurations of Singlet and Triplet States

- **The Pauli exclusion principle** states that no more than two electrons may occupy an orbital and if two electrons do occupy an orbital, they must be spin paired

- The Pauli principle demands that any ground-state molecule, in which all of the orbitals are filled with two electrons, must also have the two electrons spin paired in each orbital

- Therefore, _organic molecules are ground-state singlets_

- For *R, two electrons are orbitally unpaired (one in HOMO, one in LUMO)

- The Pauli principle allows, _but does not require_, the spins of two electrons to be paired if they _do not_ occupy the same orbital

Characteristic Configurations of Singlet and Triplet States

- For formaldehyde, four low-energy excited-states, two singlets and two triplets, result from the two lowest energy electronic configurations

State	Characteristic Orbitals	Characteristic Spin Electronic Configuration	Shorthand Description of State
S_2	π,π^*	$(\pi \uparrow)^1(n)^2(\pi^* \downarrow)^1$	$^1(\pi,\pi^*)$
T_2	π,π^*	$(\pi \uparrow)^1(n)^2(\pi^* \uparrow)^1$	$^3(\pi,\pi^*)$
S_1	n,π^*	$(\pi)^2(n \uparrow)^1(\pi^* \downarrow)^1$	$^1(n,\pi^*)$
T_1	n,π^*	$(\pi)^2(n \uparrow)^1(\pi^* \uparrow)^1$	$^3(n,\pi^*)$
S_0	π,n	$(\pi)^2(n)^2(\pi^*)^0$	$^1[(\pi)^2(n)^2]$

Characteristic Configurations of Singlet and Triplet States

- For ethylene, only two electronically excited-states are expected to be low-lying in energy

State	Characteristic Orbitals	Characteristic Spin Electronic Configuration	Shorthand Description of State
S_1	π,π^*	$(\pi \uparrow)^1(\pi^* \downarrow)^1$	$^1(\pi,\pi^*)$
T_1	π,π^*	$(\pi \uparrow)^1(\pi^* \uparrow)^1$	$^3(\pi,\pi^*)$
S_0	π^2	$(\pi)^2(\pi^*)^0$	$(\pi)^2$

Electronic Energy Difference between Molecular Singlet and Triplet States

- **Hund's rule**: when electrons are added to atomic orbitals of equal energy (those that are degenerate in energy), they must half-fill every orbital of equal energy, with the spins unpaired, before spin pairing in an orbital

- In other words, _when filling two orbitals of equal energy, the triplet state is lower in energy than the singlet state for the same orbital occupancy_

Friedrich Hund
German Physicist
from Wikipedia

- For organic photochemistry, Hund's rule can be rephrased for MOs as follows:

  For molecules possessing two half-filled orbitals, one a HOMO and the other a LUMO, the triplet state (↑↑) is always lower in energy than the energy of the corresponding singlet state (↑↓) derived from the same electronic (HO)^1(LU)^1 configuration

- For example, $E_S(n,\pi^*) > E_T(n,\pi^*)$ and $E_S(\pi,\pi^*) > E_T(\pi,\pi^*)$

Evaluation of Relative Singlet and Triplet Energies

- The basis for Hund's rule for the relative energies of singlet and triplet states for $(HO)^1(LU)^1$ systems is available by considering the implications of the Pauli exclusion principle

- Electrons in the singlet state are not compelled to obey the Pauli exclusion principle and both electrons may on occasion approach the same region of space

- <u>However</u>, the Pauli principle <u>*forbids*</u> the two spin unpaired electrons of a triplet from occupying the same region of space

- Therefore, electrons in the triplet state are able to minimize electron-electron repulsion relative to the singlet state

- Consequently, *the energy of the triplet state (E_T) will generally be lower than the energy of the singlet state (E_S)*

- In some cases, yes it can!
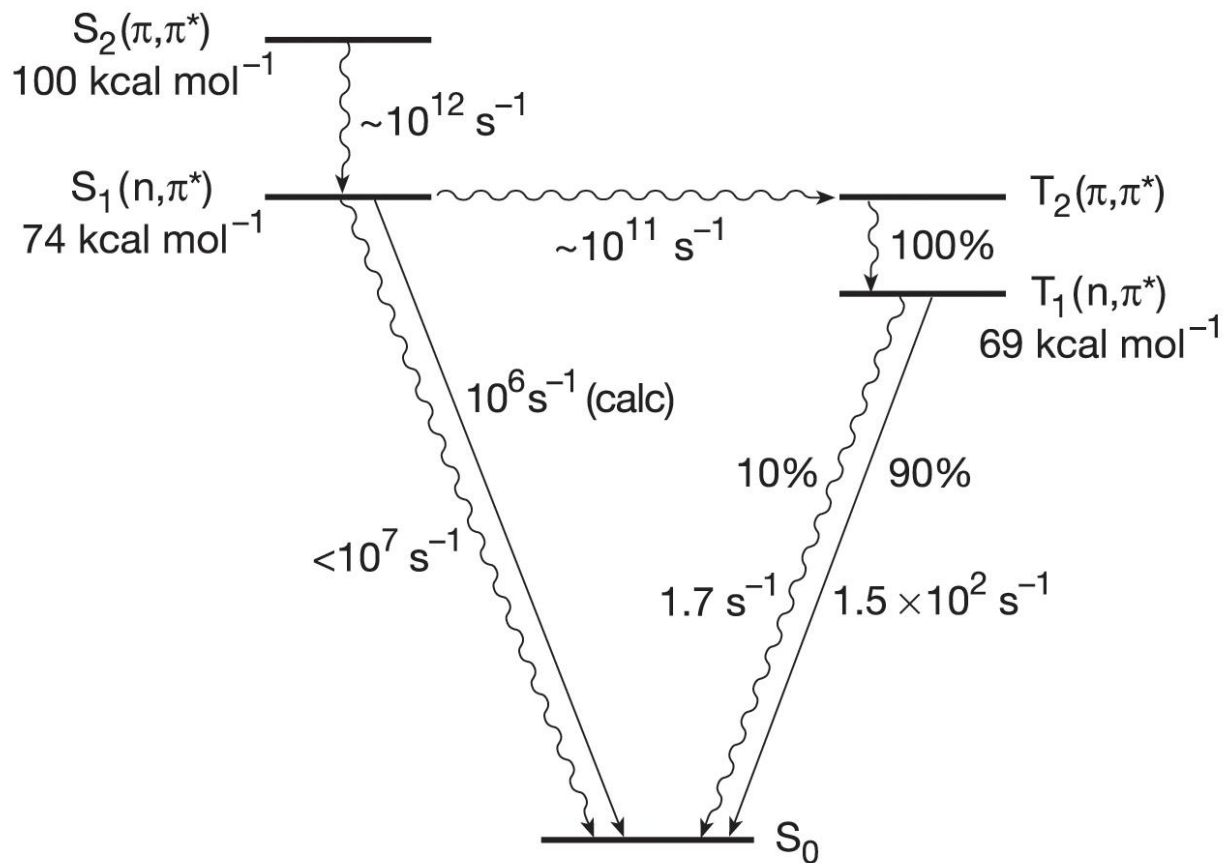- An example is the popular triplet photosensitizer, benzophenone

Figure 5.16 copyright 2009 University Science Books

Evaluation of Relative Singlet and Triplet Energies

- Reminder: Born–Oppenheimer approximation - the motions of electrons in orbitals are much more rapid than nuclear vibrational motions

- *The differences in energy between states in this approximation is entirely due to electron-electron repulsions*
  - The state with the smaller electron-electron repulsion will be lower in energy

- The magnitude of the electronic repulsion may be computed by integrating the repulsive interactions over the entire volume of the molecule

- Broken down into two types of integrals:
  1) The repulsions between electrons due to classical mechanical electrostatic interactions between negative charge distributions of electrons
     - Coulomb integral, symbol: K
  2) The first order quantum mechanical correction, J, to the value of electron-electron repulsion due to the Pauli exclusion principle
     - This correction, J, is known as the electron exchange energy and is equal to ΔE_{ST}

Evaluation of Relative Singlet and Triplet Energies

- As an example, let's consider the energies of S_0, S_1 and T_1 for formaldehyde

- The energies for S_0, S_1, and T_1 of formaldehyde are defined by equations **(1)**–**(3)** below, respectively

$$E_0 = 0 \text{ (by definition, as we are only concerned with } \Delta E) \qquad \textbf{(1)}$$

$$E_S = E_0(n,\pi^*) + K(n,\pi^*) + J(n,\pi^*) \qquad \textbf{(2)}$$

$$E_T = E_0(n,\pi^*) + K(n,\pi^*) - J(n,\pi^*) \qquad \textbf{(3)}$$

- <u>Triplet state:</u> When two electrons have parallel spins ($\uparrow\uparrow$), the average repulsion energy will be *less* than the repulsion energy computed by the classical models [i.e., $E_0(n,\pi^*) + K(n,\pi^*)$] because of the <u>*tendency of electrons with parallel spins to avoid each other, and thus reduce electron-electron repulsion*</u>

Evaluation of Relative Singlet and Triplet Energies

- Now let's calculate the singlet-triplet gap, ΔE_{ST}

$$\Delta E_{ST} = E_S - E_T$$

$$\Delta E_{ST} = [E_0(n,\pi^*) + K(n,\pi^*) + J(n,\pi^*)] - [E_0(n,\pi^*) + K(n,\pi^*) - J(n,\pi^*)]$$
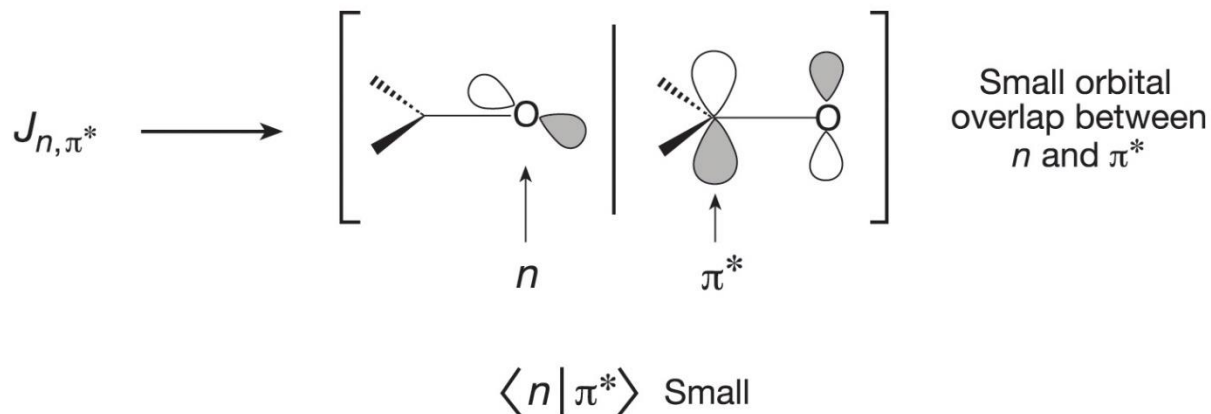
$$\boxed{\Delta E_{ST} = 2[J(n,\pi^*)] > 0}$$

- This qualitative result can be generalized: *The energy gap between a singlet and triplet state of the same electronic configuration of half-filled orbitals is purely the result of electronic exchange and is responsible for the observation that the energy of a triplet state is generally lower than that of a singlet state of the same electronic configuration for organic molecules*

- Therefore, if we can estimate the value of J, we can estimate the value of ΔE_{ST}

Question: In general, what is larger, $\Delta E_{ST}(n,\pi^*)$ or $\Delta E_{ST}(\pi,\pi^*)$?

- Let's answer this by looking at a pictorial representation of orbital overlap of both states for formaldehyde
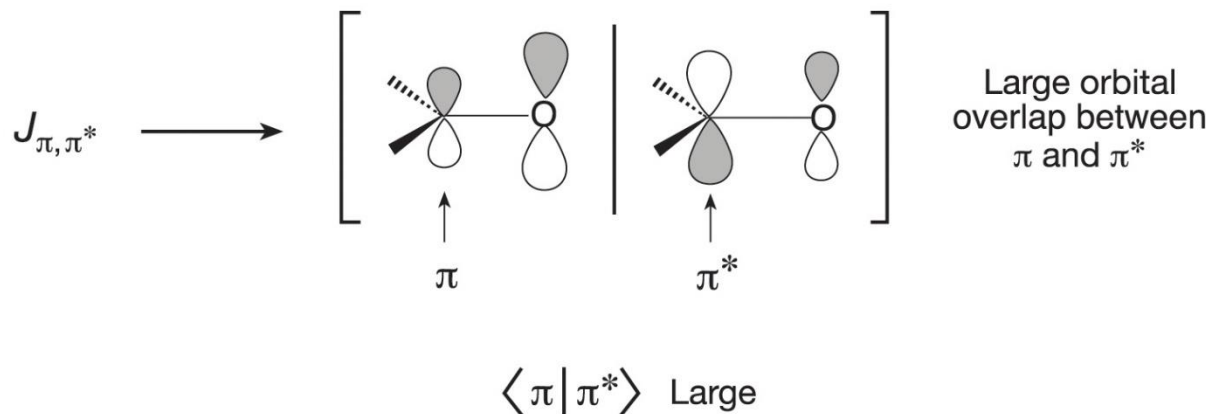

Equation 2.21a copyright 2009 University Science Books

Question: In general, what is larger, $\Delta E_{ST}(n,\pi^*)$ or $\Delta E_{ST}(\pi,\pi^*)$?

- Let's answer this by looking at a pictorial representation of orbital overlap of both states for formaldehyde

$J_{\pi,\pi^*} \longrightarrow$

Large orbital overlap between π and π^*

$\pi \qquad \pi^*$

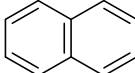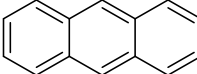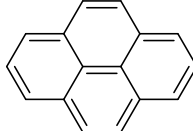$\langle \pi | \pi^* \rangle$ Large

Equation 2.21b copyright 2009 University Science Books

- We can conclude that $\Delta E_{ST}(n,\pi^*) < \Delta E_{ST}(\pi,\pi^*)$, in general, because the overlap a π with a π^* orbital will usually be greater than the overlap of an n with a π^* orbital

Examplars for ΔE_{ST} in Molecular Systems

- The table below list some experimental values for ΔE_{ST} and shows that states derived from n,π* configurations consistently have smaller ΔE_{ST} than states derived from π,π* configurations

Molecule	Configuration of S_1 & T_1	ΔE_{ST} (kcal/mol)
$H_2C{=}CH_2$	π,π*	~ 70
$H_2C{=}CH{-}CH{=}CH_2$	π,π*	~ 60
$H_2C{=}CH{-}CH{=}CH_2{-}CH{=}CH_2$	π,π*	~ 48
	π,π*	25[a] (52)[b]
	π,π*	31[a] (38)[b]
	π,π*	~34
	π,π*	30
$H_2C{=}O$	n,π*	10
$(CH_3)_2C{=}O$	n,π*	7
$(C_6H_5)_2C{=}O$	n,π*	5

[a]ΔE_{ST} between states of different orbital geometry. [b]ΔE_{ST} between states of the same orbital geometry.

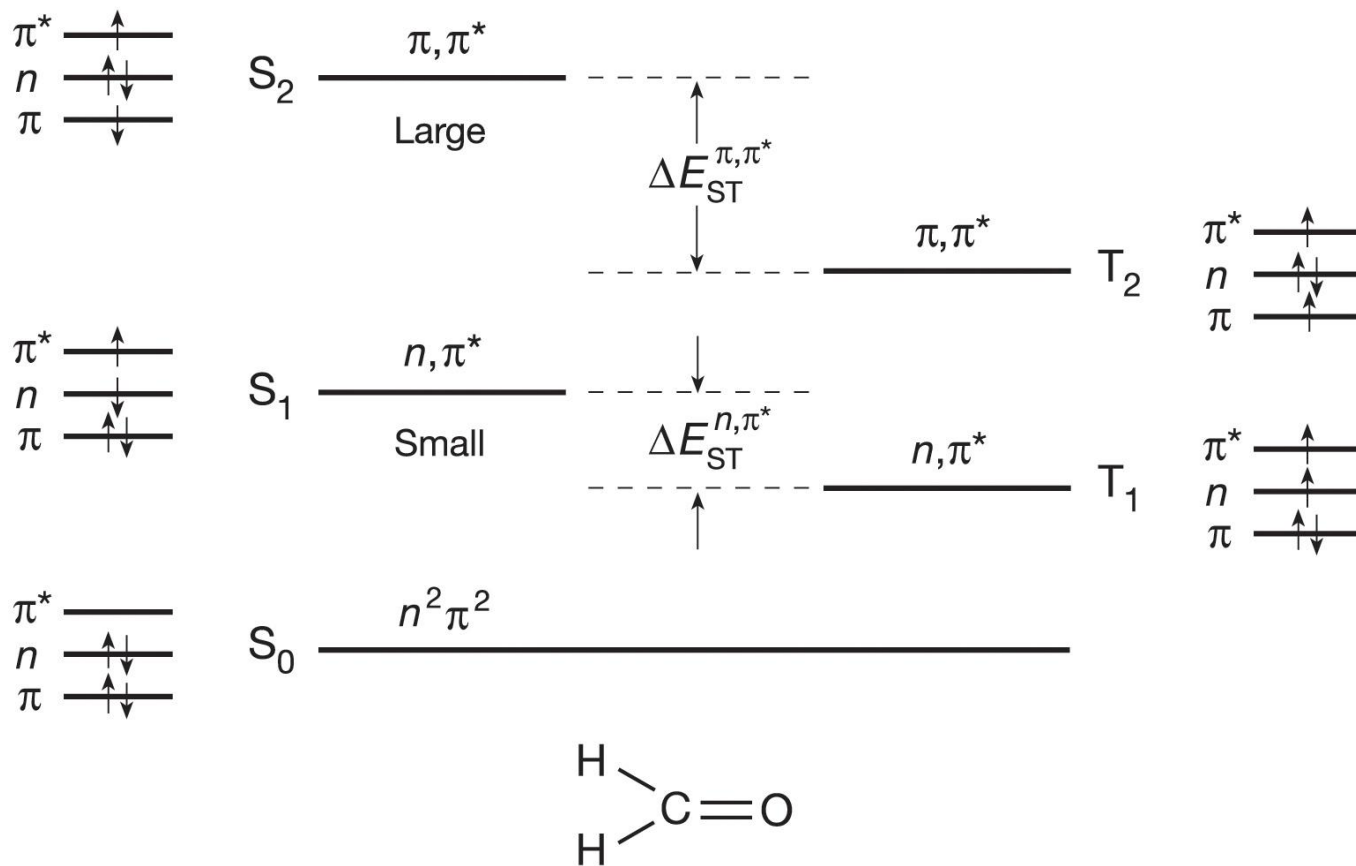- Finally, we can modify our state energy diagram for formaldehyde to include singlet-triplet splittings

Figure 2.2 copyright 2009 University Science Books

Spin Multiplicities

- The multiplicity (M) of a given state is the number of quantum mechanically allowed orientations of spin magnitude *S* in a magnetic field
  - Reminder: *S* = electron's spin wave function

- Spin multiplicity = M = 2*S* +1 = number of allowed orientations in space

- The multiplicities for a single electron and two coupled electrons are of the greatest interest in organic photochemistry

- For a single electron, the spin quantum number is 1/2, so

$$M = [2(1/2) + 1] = 2$$

- Since M = 2, there are *two and only two* allowed orientations of the electron spin vector in a magnetic field, corresponding to $M_S = +1/2$ and $M_S = -1/2$

- Since the are only two possible orientations of a single electron in a magnetic field, it is called a doublet and given the symbol D

Spin Multiplicities

- What about for situations involving the coupling of two electron spins, each of which occupies a separate orbital?

Orbital Occupancy	S	Multiplicity = $M = 2S + 1$	Name	Symbol
↑↓	(+½) + (−½)	1	Singlet	S
↑↑	(+½) + (+½)	3	Triplet	T

- Therefore, for S = 0 (↑↓), there only exist only one spin state (quantum number M_S = 0), a singlet state, and remains a singlet state in a magnetic field as it lacks a magnetic moment

- For S = 1 (↑↑), there are three allowed orientations (triplet state) in a magnetic field, corresponding to the quantum numbers M_S = +1, M_S = 0, and M_S = −1

The Classical Harmonic Oscillator

$$\Psi \sim \Psi_0 \chi \boldsymbol{S}$$

- We will now focus on how to visualize χ, the *vibrational* portion of the total molecular wave function (Ψ)

- Chemists often employ a simple classical model of molecular vibrations in which the positive nuclei of a molecule are viewed as oscillating back and forth in a potential field of electrons

- These back-and-forth oscillations of the nuclei are approximated by the motions of a *classical harmonic oscillator*

The Classical Harmonic Oscillator

- A harmonic oscillator is defined as any physical system that, when perturbed from its equilibrium state, experiences a restoring force (F) that is proportional to its displacement from its equilibrium position

- For a pair of masses connected by a flexible elastic string, with r_e as the equilibrium separation and r as an arbitrary separation that is different from r_e, the restoring force (F) to reposition the system is given by Hooke's law:

$$F = -k\Delta r = -k|r - r_e|$$

   where $\Delta r = |r - r_e|$ is the absolute displacement from the equilibrium separation, and k is the force constant for oscillation (proportionality constant that relates the amount of force required to achieve a certain displacement

- A classic harmonic oscillator that is originally at rest in its equilibrium position may be set into oscillation by some perturbation. After a certain period (relaxation time), the system returns to its equilibrium position by giving off the excess energy provided by the perturbation to its surroundings

The Classical Harmonic Oscillator

- From classical physics, force (F) is defined as the negative slope of the potential energy of the system (eq **4**)

- From calculus, this relationship implies the existence of a potential-energy function relating potential energy to the force constant (k) and the displacement from equilibrium (Δr) (eq **5**)

$$F = -d\,PE/d\Delta r \qquad (4)$$

$$PE = \frac{1}{2}k\Delta r^2 \qquad (5)$$

- Eq 5 provides the very important result that for a harmonic oscillator, the potential energy (PE) varies directly with the magnitude of k and directly with the magnitude of $(\Delta r)^2$

- Thus, harmonic oscillation can be characterized as a parabolic PE curve

The Classical Harmonic Oscillator

- Let's consider a vibrating (oscillating) diatomic molecule, X–Y

- For a classic harmonic oscillator, the relative vibrational motion of X with respect to Y is periodic, oscillating function of time *t*

- The frequency of oscillation, ν, follows eq **6**, where *k* is the force constant of the chemical bond between X and Y, and μ is the reduced mass of the two atoms forming the bond (eq **7**)

$$\nu\,(frequency) = \,(k/\mu)^{1/2} \qquad\qquad\qquad (\mathbf{6})$$
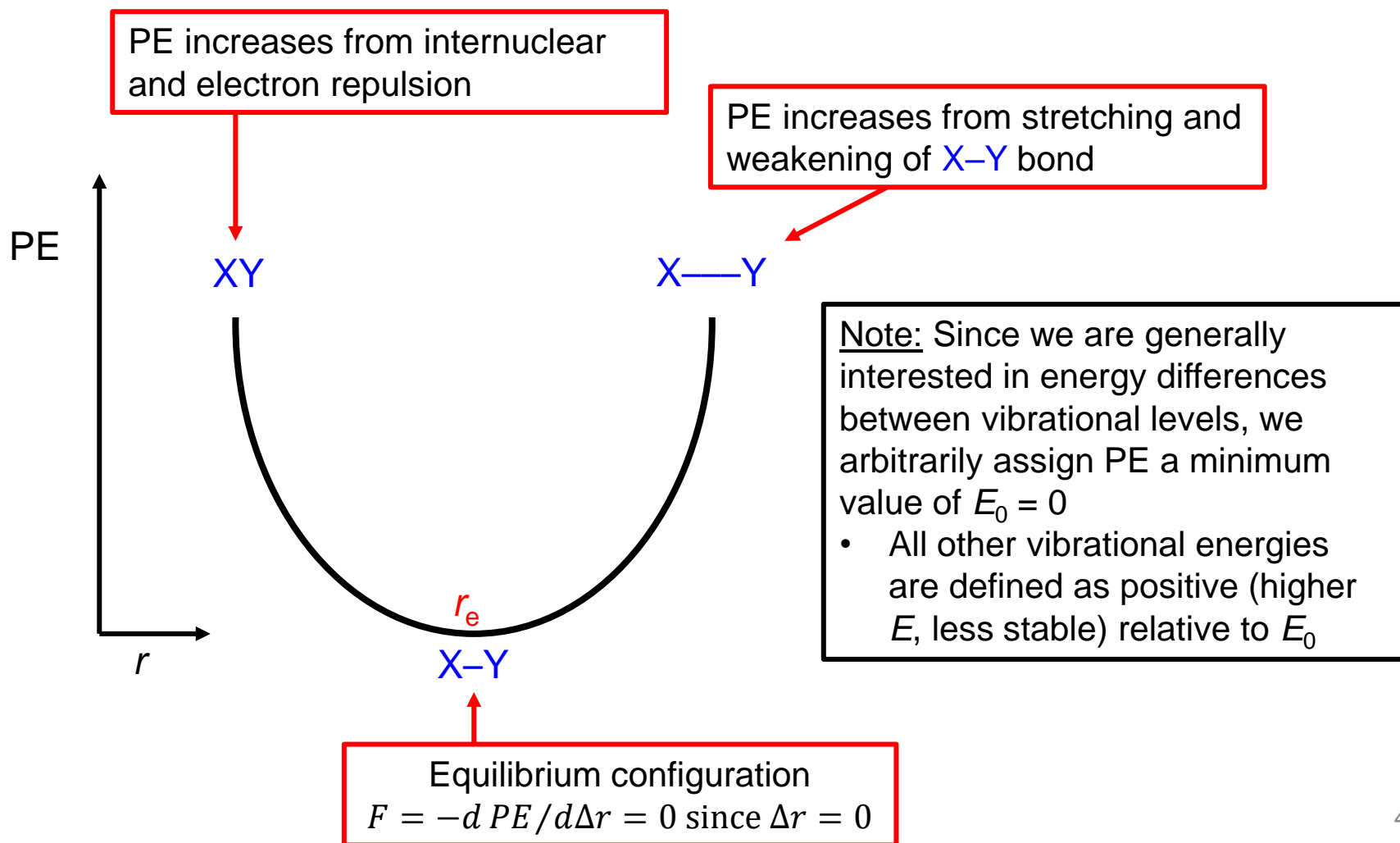
$$\mu = \,[(m_1 + m_2)/m_1 m_2]^{1/2} \qquad\qquad (\mathbf{7})$$

The Classical Harmonic Oscillator

- Based on eq **6** and **7**, we deduce the following of any classic harmonic oscillator:

1) The frequency of vibration (ν) of two masses, m_1 and m_2, is determined only by the reduced mass (μ) and the force constant (k), and not by the amplitude of motion

2) The larger the force constant (k) for a given pair of masses of reduced mass μ, the higher the frequency (ν)

3) The smaller the reduced mass (μ), the higher the frequency (ν)

- In quantum mechanics, the frequency of motion of a quantum particle is related to its energy by $\nu = E/h$
  - Higher ν of vibrations = higher E; lower ν of vibrations = lower E

- According to eq **5**, the plot of the PE of a vibrating diatomic molecule (X–Y) as a function of internuclear separation (r) should give a classic parabolic PE curve

PE increases from internuclear and electron repulsion

PE increases from stretching and weakening of X–Y bond

PE

XY

X——Y

r_e

r

X–Y

Note: Since we are generally interested in energy differences between vibrational levels, we arbitrarily assign PE a minimum value of $E_0 = 0$
- All other vibrational energies are defined as positive (higher E, less stable) relative to E_0

Equilibrium configuration
$F = -d\,PE/d\Delta r = 0$ since $\Delta r = 0$

The Classical Harmonic Oscillator

- Applying eq **6** and **7** to organic molecules leads to two important conclusions:

1) C–H bonds tend to be of the highest ν for organic molecule because they possess both large k (strong bonds, ~90-100 kcal mol^{-1}, which are analogous to stiff springs holding the atoms together), and small μ (H is the lightest atom)

2) Weak bonds (~60-80 kcal mol^{-1}) between two heavy atoms, such as C–Cl bond, will be very low ν because they possess both small k (weak bonds, analogous to soft spring holding the atoms together) and a large μ (the heavy Cl atoms dominates the value of μ)
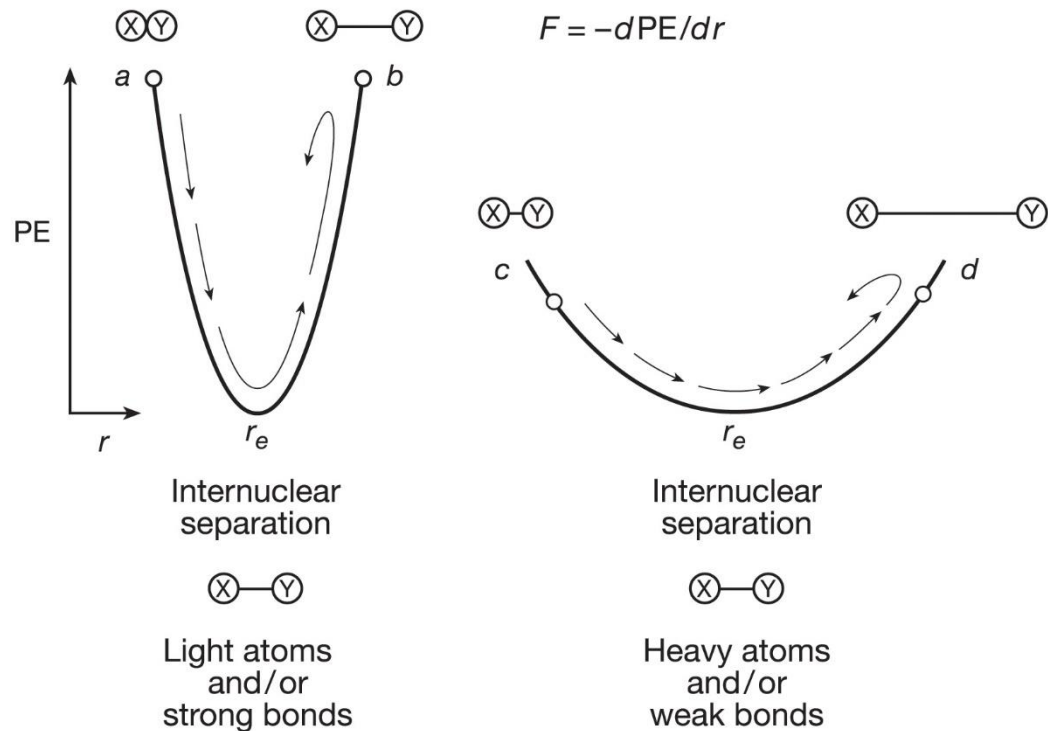

$$F = -d\,PE/dr$$

Internuclear separation — Light atoms and/or strong bonds

Internuclear separation — Heavy atoms and/or weak bonds

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The Classical Harmonic Oscillator

$$PE = \frac{1}{2}k\Delta r^2 \qquad\qquad (\mathbf{5})$$

- From equation **5**, we see that a strong bond (i.e. one with a large k) a large change in PE will occur with only a small displacement because PE is a quadratic function of the displacement , Δr

- A strong bond, therefore, corresponds to a PE curve with steep walls, such that small displacements cause a large increase in PE

- Such oscillators are relatively difficult to deform from their equilibrium geometry

- Since the frequency of ν is directly proportional to bond strength, a *steep* PE curve implies *higher* ν of vibration
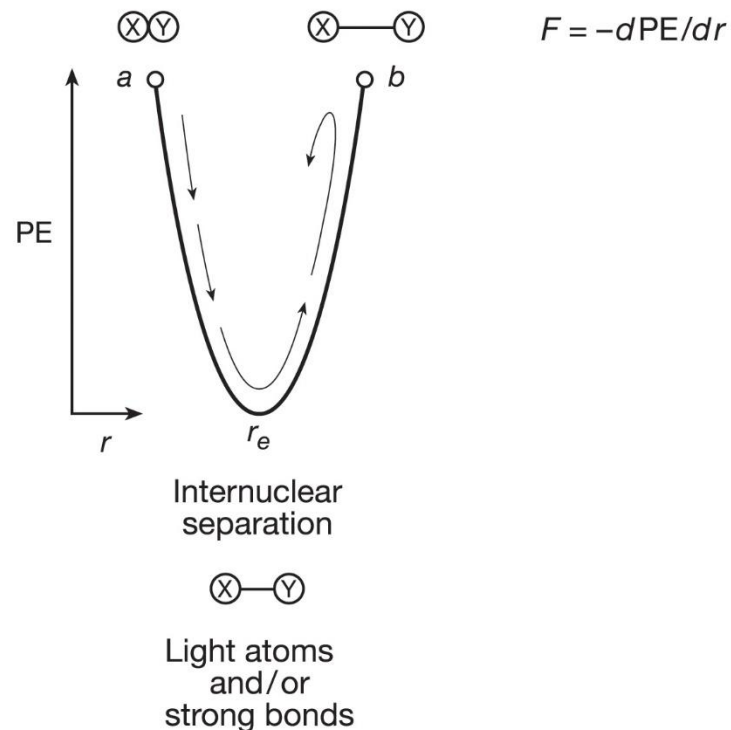
$F = -d\text{PE}/dr$

PE

Internuclear separation

Light atoms and/or strong bonds

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The Classical Harmonic Oscillator

$$PE = \frac{1}{2}k\Delta r^2 \qquad \textbf{(5)}$$

$$F = -d\text{PE}/dr$$

- On the other hand, a weak bond corresponds to a PE curve with shallow walls, such that large displacements do not cause a large increase in PE

- Since the frequency of ν is directly proportional to bond strength, a *shallow* PE curve implies *lower* ν of vibration

Internuclear
separation

Heavy atoms
and/or
weak bonds
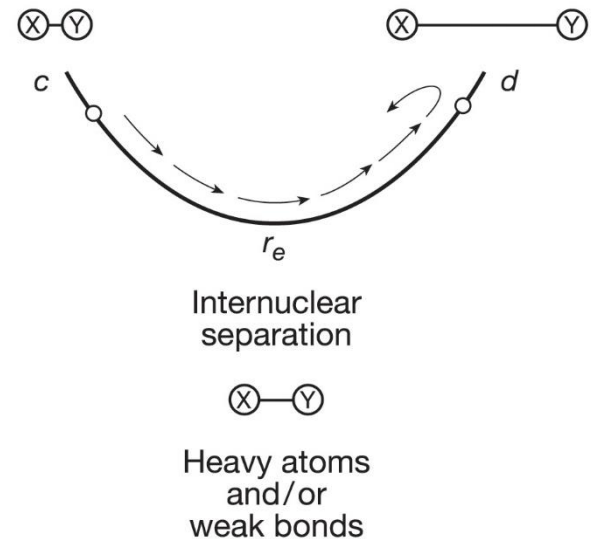
Vibrational Levels

- In quantum mechanics, the starting model for a vibrating molecule is a harmonic oscillator that obeys Hooke's law

- Solving the wave equation ($H\Psi = E\Psi$) for a harmonic oscillator obeying Hooke's law reveals that energy levels, E_υ, are quantized and characterized by a quantum number, υ

- The PE of each vibrational level, PE_υ, is given by eq **8**, where υ is the vibrational quantum number (υ = 0, 1, 2,…), ν is the vibrational frequency of the classical oscillator and h is Plank's constant

$$PE_v = h\nu(v + 0.5)$$ (**8**)

Vibrational Levels

- The figures below represent the quantum mechanical modification of the classical harmonic oscillator

- Displays the allowed energy levels whose energies are E_υ
  - Indicated by the horizontal lines (for $\upsilon = 0-6$) in the PE curves
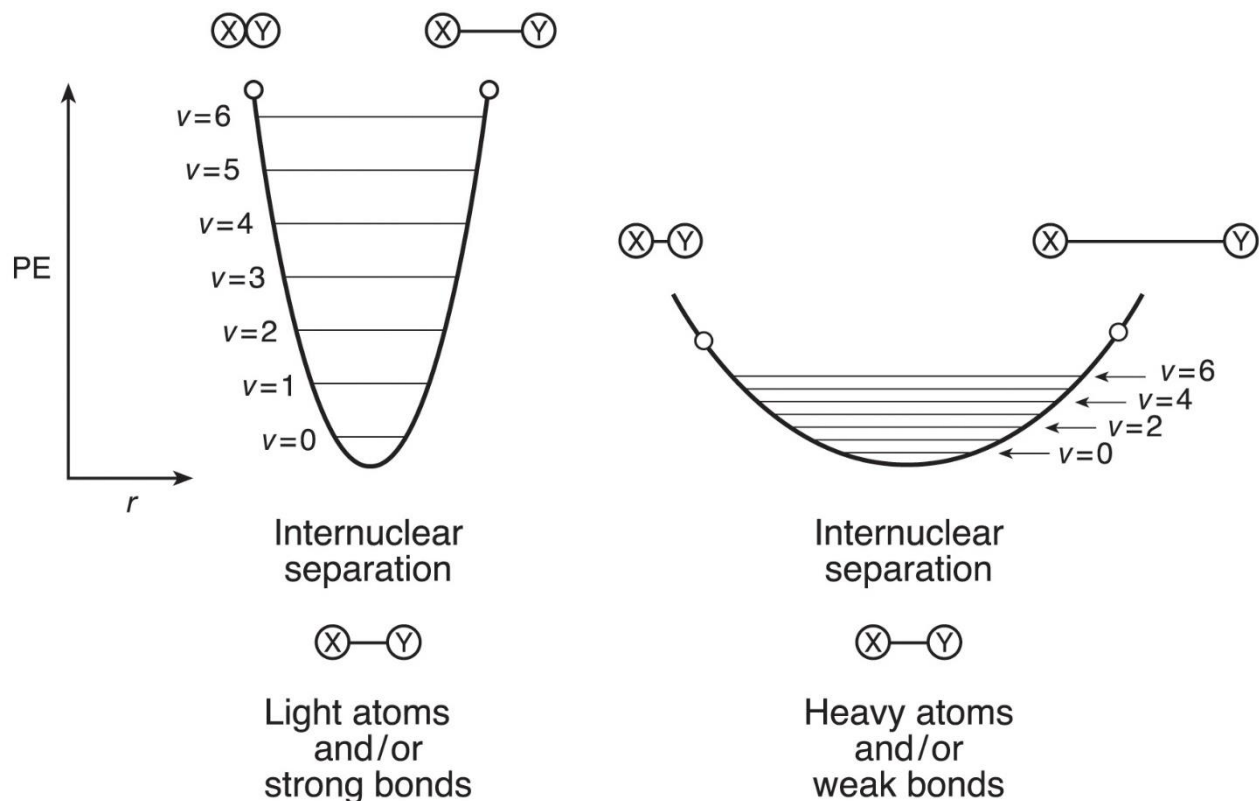

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Vibrational Levels

- A few important notes:

1) Only quantized PE values given by eq **8** are possible (stable) for the allowed values of the quantum number υ. In addition, vibrational energy levels for a quantum mechanical harmonic oscillator are *equally spaced* in units of hν above the $\upsilon = 0$ level

2) The zero-point vibrational energy of a quantum mechanical harmonic oscillator is not 0, but hν/2 (from eq **8**)

3) For the same value of υ, the PE is larger for a steeper potential well because the spacings between vibrational levels is larger for vibrations of higher frequencies (from eq **8**)

   - Notice that the steeper potential well (left on previous slide) has a higher zero-point energy ($\upsilon = 0$), which occurs because the frequency of the PE is greater

- Now, let's qualitatively add the mathematical form of the vibrational wave functions χ_υ for $\upsilon = 0$, 1−4, and 10

- These are plotted on the quantized energy levels (horizontal straight lines)

- Like any wave, such as a sine wave, it has an amplitude that continuously oscillates from mathematically positive (above horizontal line) and negative (below horizontal line) values

- The number of times χ_υ passes through zero (when wave crosses horizontal line) equals υ

- The wave function for $\upsilon = 0$ does not possess a node, so this vibrational wave function is analogous to the wave function of the 1s orbital
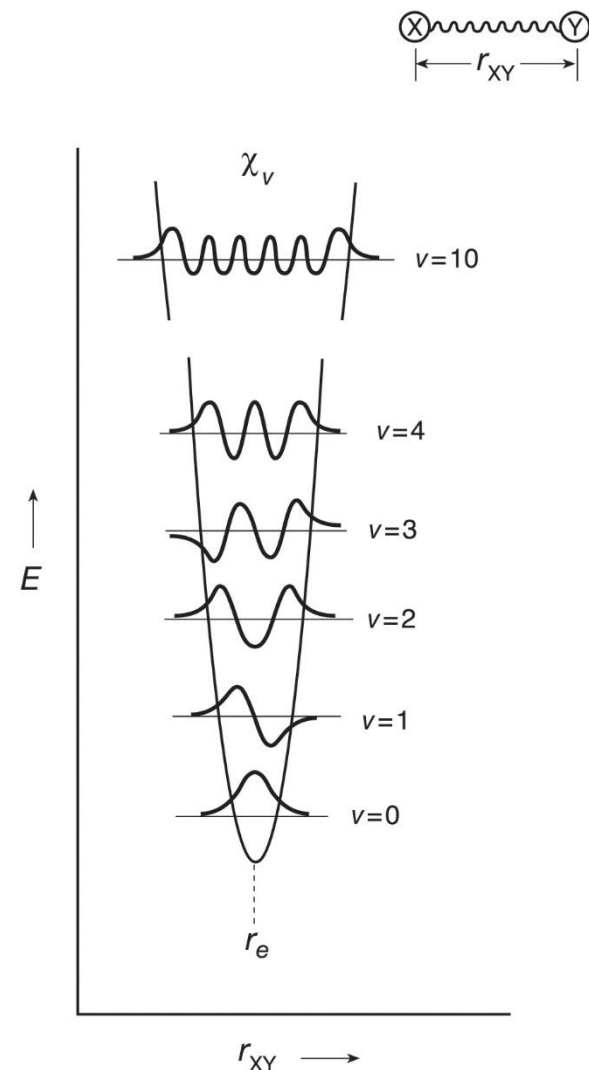

Figure 2.6 copyright 2009 University Science Books

- In quantum mechanics, it is the square of the wave function that is directly related to laboratory observations

- Since the square of the wave function represents the probability of finding particles (e.g. electrons, nuclei) in space, the function χ_υ^2 represents the probability of finding the nuclei at a given value of r during a vibration in a given energy level
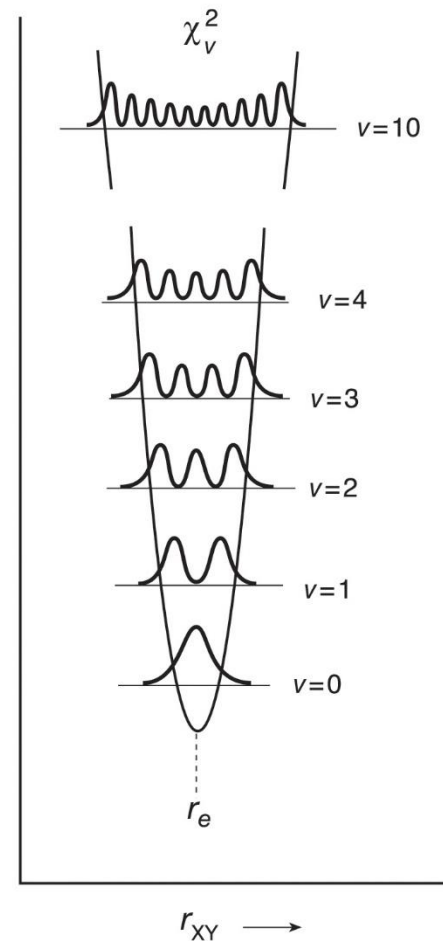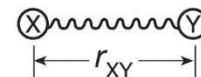
The Anharmonic Oscillator

- The harmonic oscillator is a good zero-order approximation for a vibrating atomic molecule X–Y for vibrations near the potential energy curve

- However, the model becomes less reliable and eventually fails for nuclear geometries to severe compressions and elongations of the X–Y bond

- For example, when a bond has been extended to two or three times its normal length (i.e., from 1−2 Å to 5−6 Å), the atoms X and Y experience very little restoring force (*bond is essentially broken*)

- Therefore, for a real molecule, the PE will rise more gradually than predicted by PE = $0.5k\Delta r^2$ when the bond is stretched because of the weakening of the X–Y bond at large r

The Anharmonic Oscillator

- Let's consider the diatomic molecule HCl

- The anharmonic oscillator considers first-order corrections to the zero-order harmonic oscillator model

- As the H–Cl bond stretches, the PE reaches a limiting value (the PE of the bond or the bond energy), the restoring force disappears, and the H–Cl bond breaks

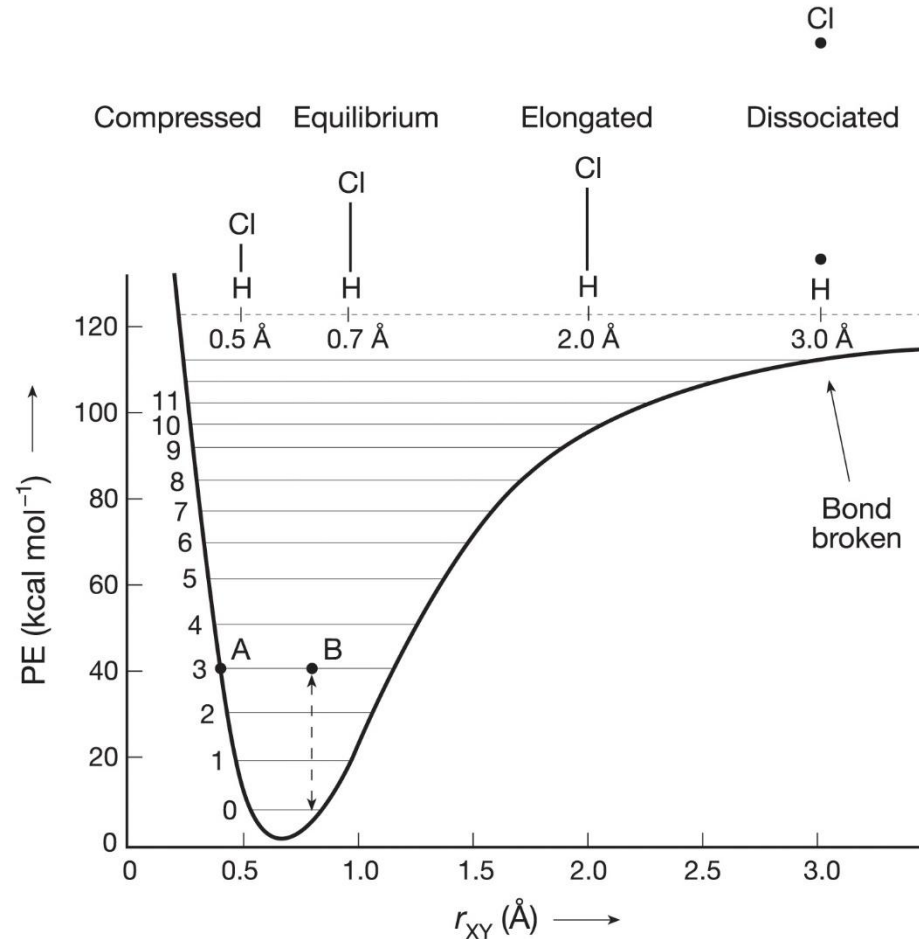- The energy of the asymptote corresponds to the dissociation energy of the HCl molecule

Figure 2.7 copyright 2009 University Science Books

The Anharmonic Oscillator

- Another important feature of an anharmonic oscillator is that _its vibrational levels, although quantized, are not equally separated in energy_

- The energy separations decrease slowly with increasing υ

- For example, the energy separation between $\upsilon = 0$ and $\upsilon = 1$ is ~12 kcal mol^{-1}, while the energy separation between $\upsilon = 10$ and $\upsilon = 11$ is only ~5 kcal mol^{-1}
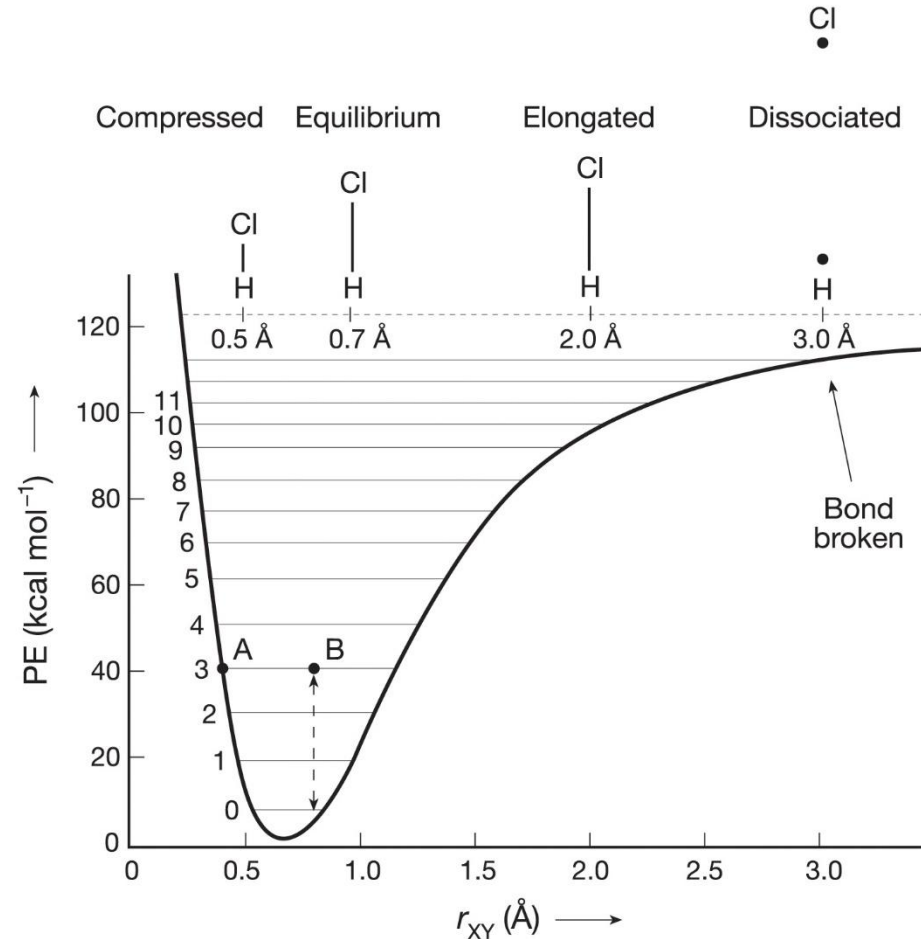

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Up Next…

Chapter 3: Transitions between States: Photophysical Processes