CHM 535/635
Molecular and Supramolecular Photochemistry

Chapters 1 & 2

Principles of Molecular Photochemistry: An Introduction

NJT, VR and JCS

Photochemistry

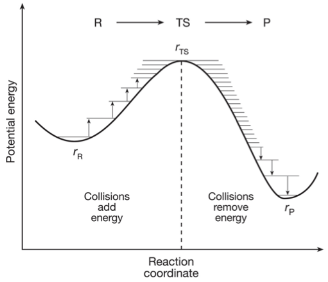
Interaction of Light with Matter (Molecules)

- *Organic Photochemistry*
- *Inorganic Photochemistry*
- *Photobiology*

What is the difference between thermochemistry and photochemistry?

- **Mode of activation**
  - Activated by collisions (heat; thermo)
  - Activated by light (photo)
- **Selectivity in activation**
  - Entire molecule gets activated
  - Only the chromophore that absorbs the light gets activated
- **Energy distribution**
  - Energy used for vibrational/rotational transition
  - Energy used for electronic transition only

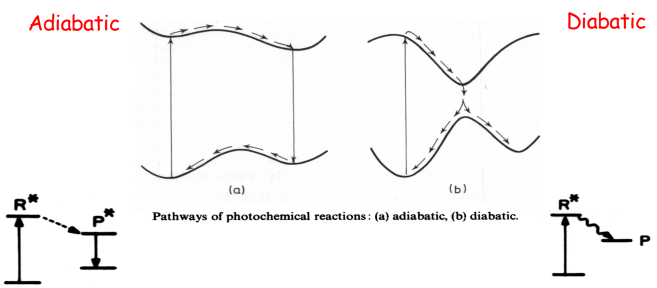
Visualization of Thermal Reactions



- Transition state connects a single reactant to a single product (intermediate) and it is a saddle point along the reaction course.
- Collisions are a reservoir of continuous energy (~ 0.6 kcal/mol per impact).
- Collisions can add or remove energy from a system.
- Concerned with a single surface.

Visualization of Photochemical Reactions

We need to deal with two surfaces (ground and excited state.



Pathways of photochemical reactions: (a) adiabatic, (b) diabatic.

The Basic Laws of Photochemistry

Grotthuss-Draper law

The First Law of Photochemistry: <u>light must be absorbed for photochemistry to occur.</u>

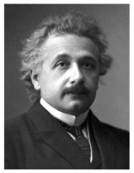
Grotthus

Drapper

Stark-Einstein law

The Second Law of Photochemistry: for <u>each photon</u> of light absorbed by a chemical system, <u>only one molecule</u> is activated for a photochemical reaction.

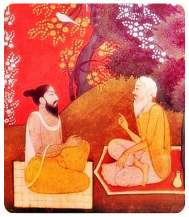
Stark



Einstein

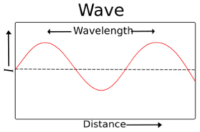
Interaction of Photon and Matter (Molecule)

- What is photon?
- What is matter?
- What is a molecule?
- How do they interact?
- What are the consequences of interaction?



What is photon?

Photon (Light) is a particle and a wave



Wavelength	λ	c/ν
Wavenumber:	υ	$1/\lambda$
Frequency:	ν	c/λ
Energy	$h\nu$	hc/λ
Einstein:	$Nh\nu$	Mole of photon (one Avagadro number of photon)
Velocity:	186,281 miles/sec; 2.9979×10^{10} cm/sec	
Charge:	0 (no charge)	
Spin	$1\,\hbar$	
Momentum:	E/c	
Mass:	Momentum/c (no real mass)	

Do photons have mass?

Since photons have particle-like properties, they should have mass.

The (relativistic) mass of photons can be calculated from Einstein's equation for special relativity.

$$E = h\nu = \frac{hc}{\lambda} \qquad E = mc^2$$

$$m = \frac{E}{c^2} = \frac{hc/\lambda}{c^2} = \frac{h/\lambda}{c} = p/c$$

= Momentum/C

Do photons have momentum?

We know momentum, p =mv

For photons, v = c, so….

$$p = mv$$

$$p = mc$$

$$p = \frac{h}{\lambda c}c$$

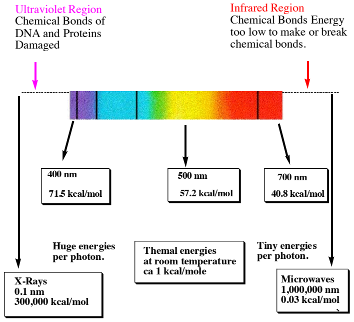
$$\boxed{p = \frac{h}{\lambda}}$$

Light and Energy Scales

E (kcal mol^{-1}) = [2.86 x 10^4 kcal mol^{-1}]/λ nm

E (kcal mol^{-1} nm) = 2.86 x10^4/700 nm = 40.8 kcal mol^{-1}

E (kcal mol^{-1} nm) = 2.86 x 10^4/200 nm = 143 kcal mol^{-1}



Ultraviolet Region
Chemical Bonds of
DNA and Proteins
Damaged

Infrared Region
Chemical Bonds Energy
too low to make or break
chemical bonds.

400 nm
71.5 kcal/mol

500 nm
57.2 kcal/mol

700 nm
40.8 kcal/mol

Huge energies
per photon.

Themal energies
at room temperature
ca 1 kcal/mole

Tiny energies
per photon.

X-Rays
0.1 nm
300,000 kcal/mol

Microwaves
1,000,000 nm
0.03 kcal/mol

The first paradigms: What is matter?

Lucretius: ca 99-55 BC

All *matter* consists of tiny fundamental building blocks now called ***atoms***

"All nature consists of twain of things: of *atoms* and of the void in which they're set."

"DE RERUM NATURA"
(Everything you wanted to know about the universe but were afraid to ask!)

John Dalton 1766-1844

All matter is composed of small indivisible particles termed *atoms*.
Atoms of a given element possess unique characteristics and weight.

"A New System of Chemical Philosophy"

Paradigm: Matter consists of tiny particles called atoms.

What is matter?

- Matter is collection of molecules
- Molecules are collection of atoms
- Atoms are collection of nuclei and electrons
- The fundamental components of matter and molecules are nuclei and electrons
- To understand matter and molecules one needs to know the location and energies of nuclei and electrons.

Electron

- It has dual wave and particle properties, just like a photon
- Negatively charged, does not vary with energy
- Electric charge oscillates with time
- It has spin of 1/2 $\hbar$
- It is a small magnet
- Coupled with protons and neutrons it holds atoms, molecules and everything in the world
- It is small, radius of 0.00028 nm and mass of $9.10938356 \times 10^{-31}$ kilograms

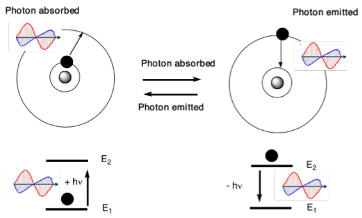
The Beginning: Atomic orbitals
Electronic transitions (oscillators) are quantized

Niels Bohr
Nobel Prize 1922

Light is emitted when an electron jumps from a higher orbit to a lower orbit and is absorbed when it jumps from a lower to higher orbit.

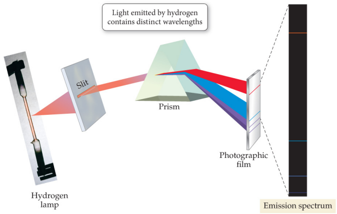
The energy and frequency of light emitted or absorbed is given by the difference between the two orbit energies,
E(photon) = E_2 - E_1 (energy difference)

Absorption and Emission in an Atom

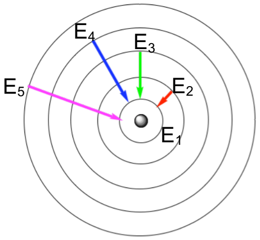


The basis of all photochemistry and spectroscopy!

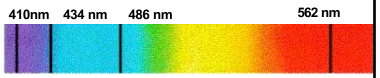
Theory and experiment



Schematic of the Experiment

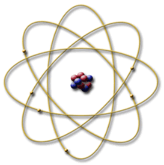


If all this is true then you should be able to "see" the spectrum of the electrons jumping from E_5, E_4, E_3, E_2, to E_1 and here is what we see.

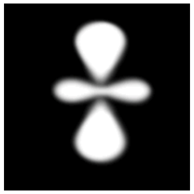


The "line" spectrum of hydrogen

Particle and Wave

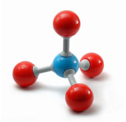


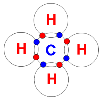
Bohr model (1913)
Electron is a particle

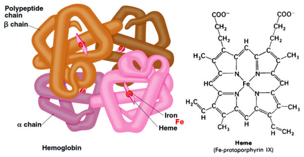


Wave-mechanical model
Schrödinger model (1926)
Electron is a wave

A molecule, a collection of atoms is defined by Ψ







Nobel Prize in Physics (1933)

$$H\Psi = E\Psi$$

Operator

Eigenvalue

Schrödinger equation

What is Ψ ?

Ψ defines a molecule in terms of nuclei and electrons

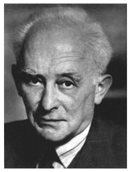
Ψ is made of three parts

$$\Psi = \Psi_o \quad \chi \quad S$$

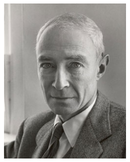
Electronic Nuclear Spin

The three parts are interconnected. So it is hard to define a molecule precisely in terms of Ψ

Born – Oppenheimer Approximation



Born Nobel Prize 1954



Oppenheimer

- Electronic motion faster than nuclear motion (vibration).
- Weak magnetic-electronic interactions separate spin motion from electronic and nuclear motion.

$$\Psi = \Psi_o \quad \chi \quad S$$

Electronic **Nuclear** **Spin**

Time scale matter

$$\Psi \quad = \quad \Psi_o \quad \chi \quad S$$

Born – Oppenheimer Approximation

Electronic motion and nuclear motion can be separated

- To understand molecules, first focus on the location and energies of electrons
- Understand: Ψ_o(electronic) independent of χ and S; then proceed to χ (nuclear) and S (spin)

Atomic to Molecular Orbitals

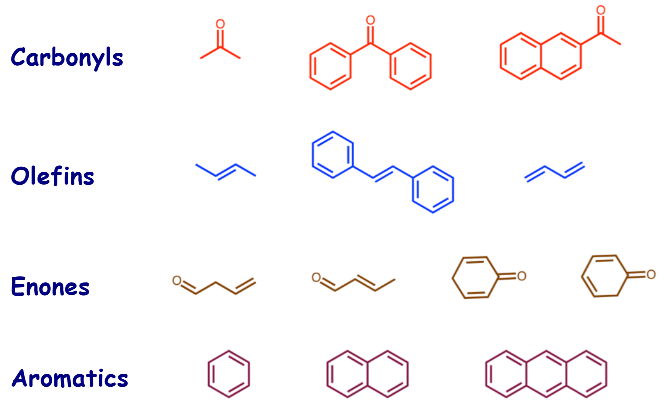
Books

- Valence, C. A. Coulson, 1952
- Molecular Orbital Theory for Organic Chemists, Andrew Streitwieser, 1961
- Notes on molecular orbital calculations, John D Roberts, 1962
- The Molecular Orbital Theory of Conjugated Systems, Lionel Salem, 1966
- The importance of antibonding orbitals, Milton Orchin, 1967
- Hückel Molecular Orbital Theory, Keith Yates, 1978

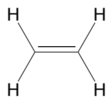
A classic book on chemical bonds

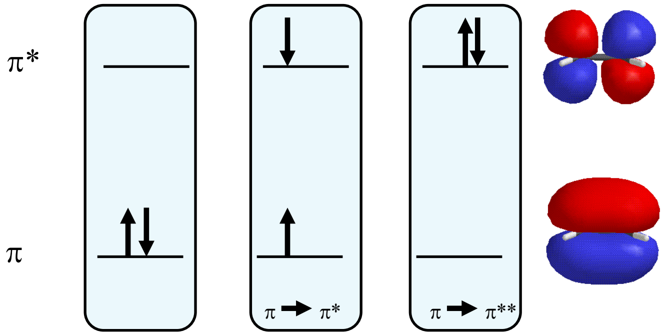
- The Nature of the Chemical Bond, L. Pauling, 1939

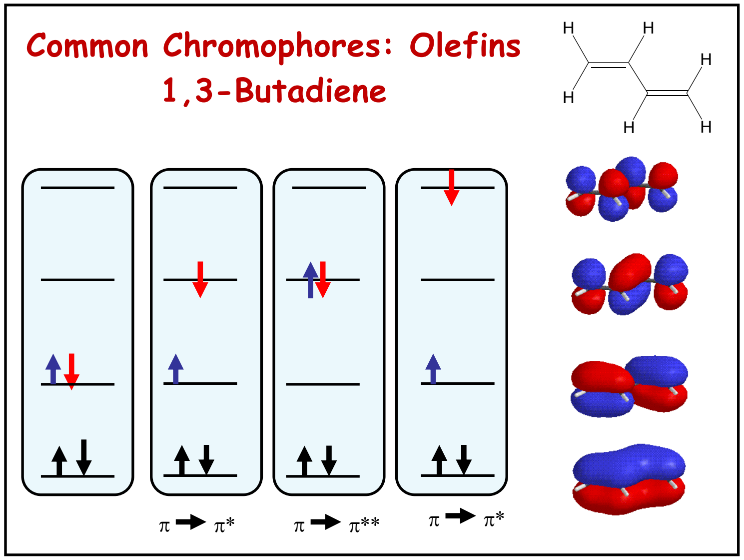
Examples of Common Organic Chromophores



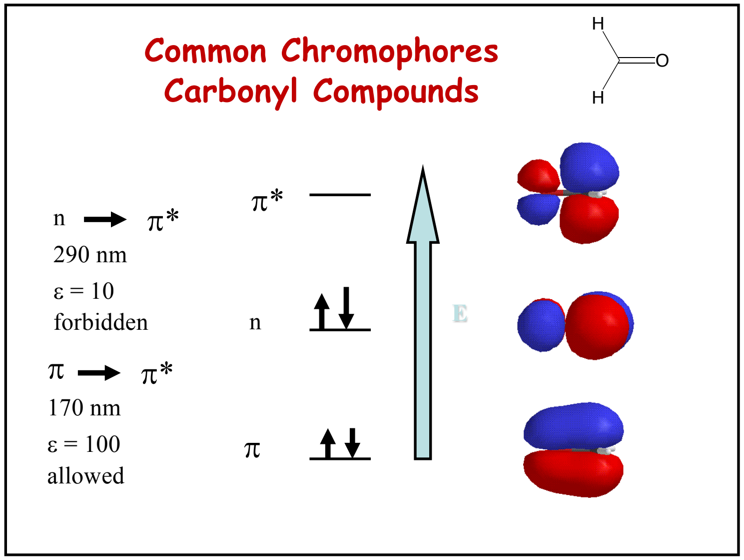
Common Chromophores: Olefins
Ethylene







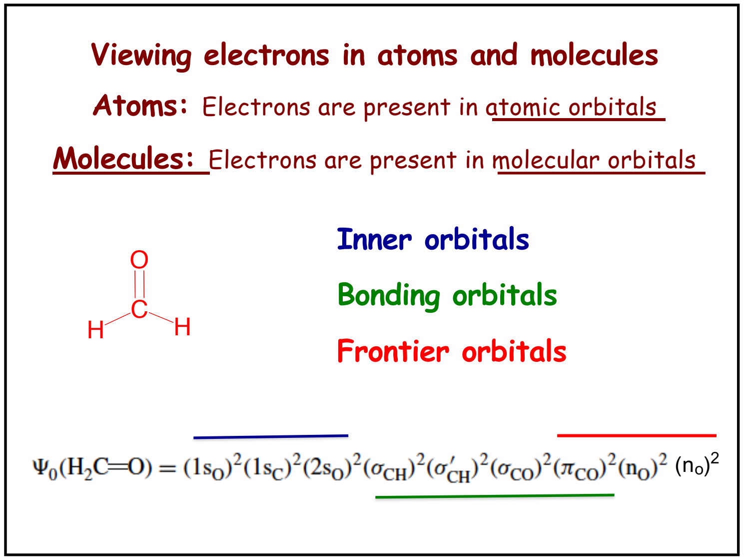
Common Chromophores: Olefins
1,3-Butadiene



Common Chromophores
Carbonyl Compounds

n → π*
290 nm
ε = 10
forbidden

π → π*
170 nm
ε = 100
allowed



Viewing electrons in atoms and molecules

Atoms: Electrons are present in atomic orbitals

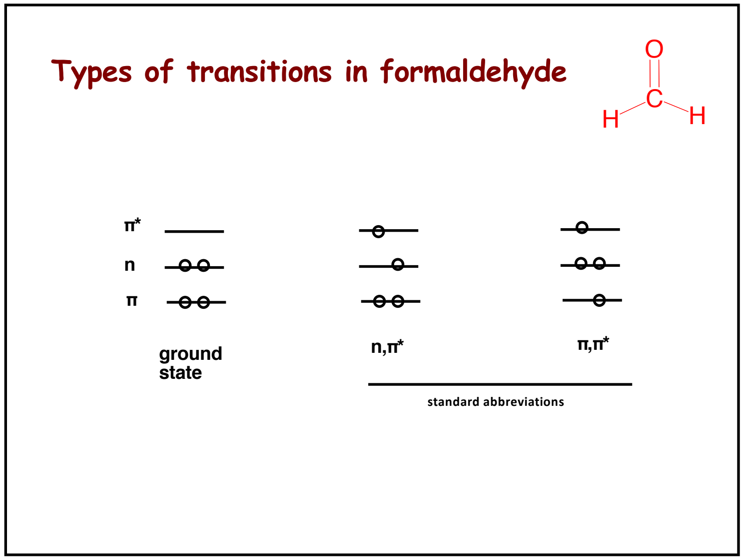
Molecules: Electrons are present in molecular orbitals

Inner orbitals

Bonding orbitals

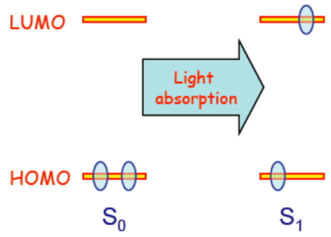
Frontier orbitals

$$\Psi_0(H_2C{=}O) = \overline{(1s_O)^2(1s_C)^2(2s_O)^2}\underline{(\sigma_{CH})^2(\sigma'_{CH})^2(\sigma_{CO})^2\overline{(\pi_{CO})^2}}\overline{(n_O)^2\ (n_o)^2}$$



Types of transitions in formaldehyde

Light absorption and electron movement



Excited state energies

The energy required to produce an electronically excited state

(R + hν → R*)

is obtained by inspecting the absorption spectrum of the molecule in question, as well as applying Einstein's resonance condition for the absorption of light.

$$\Delta E = |E_2 - E_1| = |E_2(^*\mathrm{R}) - E_1(\mathrm{R})| = h\nu = hc/\lambda$$

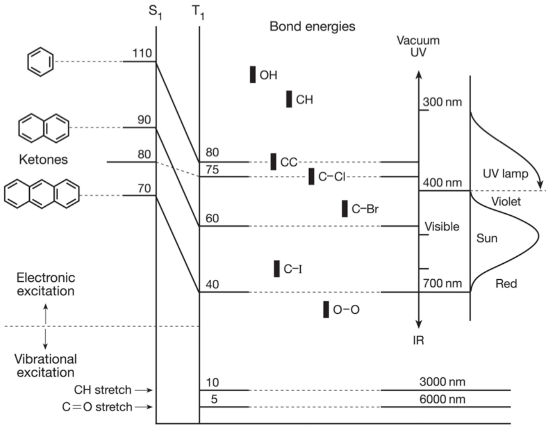
h is Planck's constant (1.58×10^{-34} cal s)

ν is the frequency (commonly given in units of s^{-1} = Hz)

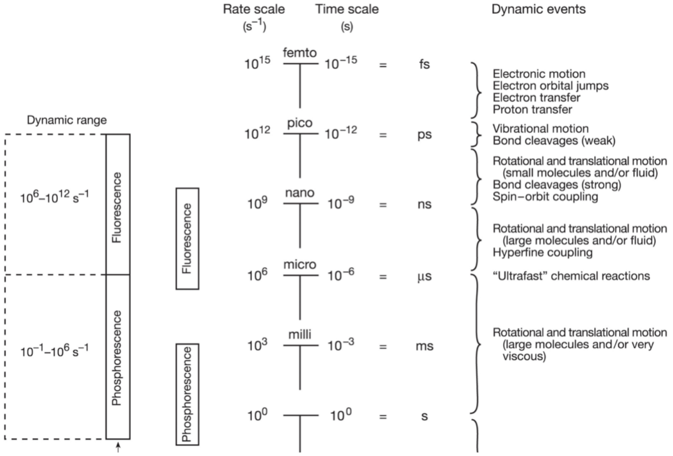
λ is the wavelength at which absorption occurs (commonly given in units of nanometers, nm),

c is the speed of light (3×10^{8} cm s^{-1})

Excitation energy, bond energy and radiation wavelength

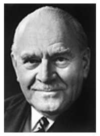


Time scales



Nobels in Photochemistry

Development of Flash Photolysis and Femtosecond Chemistry

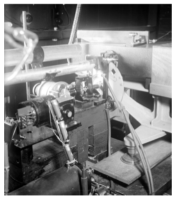

Norrish

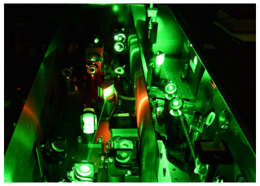

Porter


Zewail

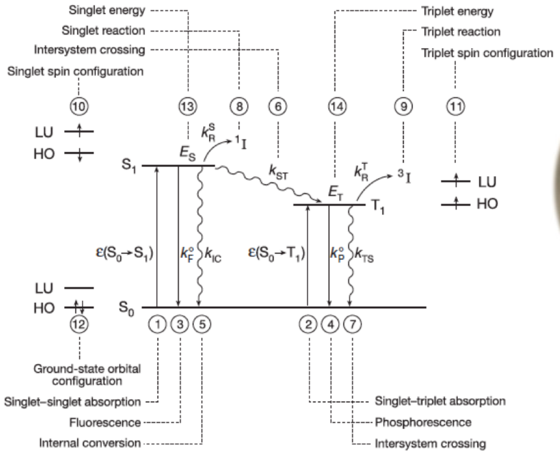
The Nobel Prize in Chemistry 1967

The Nobel Prize in Chemistry 1999





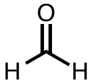
Jablonski Diagram




Alexander Jablonski
(1898-1980)

Formaldehyde

CH_2O



$$H\Psi = E\Psi$$

$$\Psi \quad = \quad \Psi_o \quad \chi \quad S$$

$$\Psi_0(H_2C{=}O) = \overline{(1s_O)^2(1s_C)^2(2s_O)^2}\underline{(\sigma_{CH})^2(\sigma'_{CH})^2(\sigma_{CO})^2}\overline{(\pi_{CO})^2(n_O)^2\ (n_o)^2}$$

Born-Oppenheimer Approximation

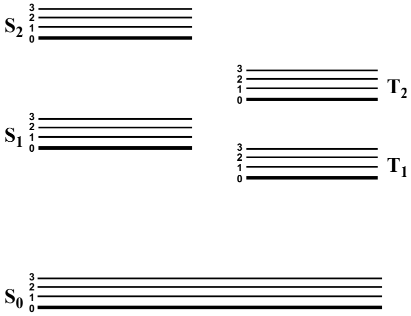
Motions of electrons in orbitals are much more rapid than nuclear vibrational motions

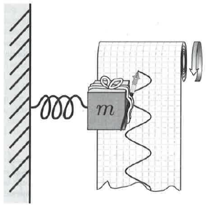
$$\Psi \quad \sim \quad \Psi_0\,\chi\,S$$

"true"
molecular wavefunction

(electronic)(nuclei)(spin)

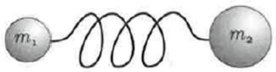
Energy level diagram of molecules





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

k is the force constant, Δr is the distance of displacement from equilibrium, F is the restoring force

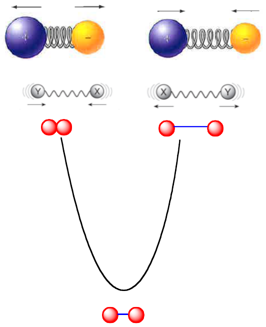


Born-Oppenheimer Approximation

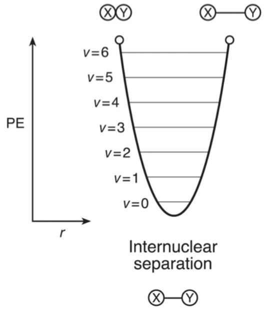
Motions of electrons in orbitals are much more rapid than nuclear vibrational motions

$$\underset{\text{"true" molecular wavefunction}}{\Psi} \sim \underset{\text{(electronic)}}{\Psi_0}\;\underset{\text{(nuclei)}}{\chi}\;\underset{\text{(spin)}}{S}$$

A Model for Vibrational Wavefunctions
The Classical Harmonic Oscillator



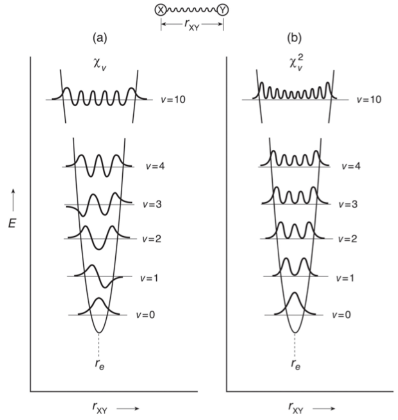
E_v = PE + KE



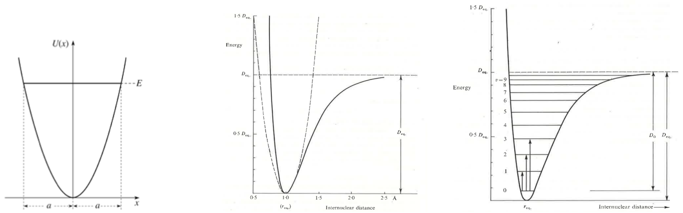
Quantized Harmonic Oscillator

$PE_v = h\nu(v + 1/2)$

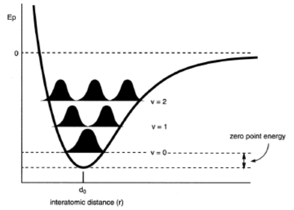
The Quantum Mechanical Version of the Classical Harmonic Oscillator



Harmonic and Anharmonic Oscillator

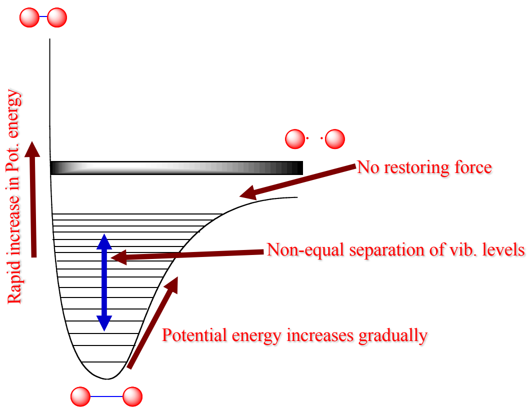


Harmonic **Anharmonic** **Anharmonic Quantized**



- Anharmonic
- Quantized energy level
- Probablity of location of the nuclei

The Anharmonic Quantum Mechanical Oscillator



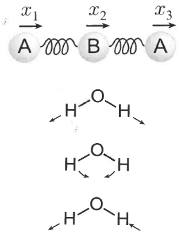
Rapid increase in Pot. energy

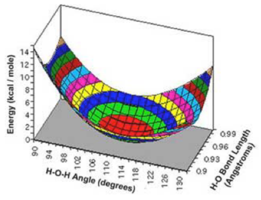
No restoring force

Non-equal separation of vib. levels

Potential energy increases gradually

Representation of Polyatomic Molecules





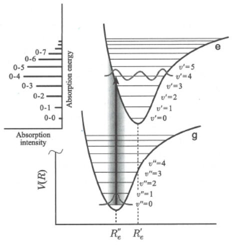
Water

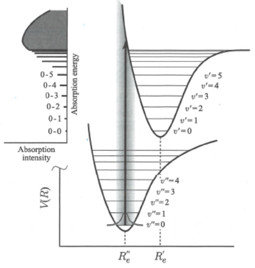
To represent molecules with more than three atoms one needs 3N–6 space

Polyatomic molecules are represented in two or three dimensional space.

What may appear to be a minimum, barrier or saddle point in one subspace may turn out to be nothing of the kind when viewed in another cross section

Vibrational parts for various electronic configurations





CHM 535/635
Molecular and Supramolecular Photochemistry

Spin

Turro book

p.56 - 69 (sec. 2.9 - 2.15)

p.82 - 108 (sec. 2.21 - 2.39)

Spin part

$$H\Psi = E\Psi$$

$$\Psi \quad = \quad \Psi_o \quad \chi \quad S$$

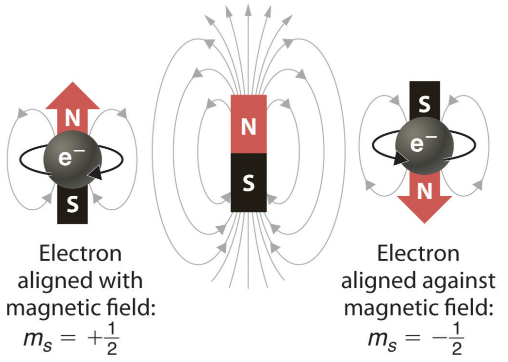
Born-Oppenheimer Approximation

Motions of electrons and nuclei are much more rapid than spin motion (change)

$$\Psi \sim \Psi_0 \; \chi \; S$$

"true" molecular wavefunction **(electronic)** **(nuclei)** **(spin)**

Electron Spin



Electron aligned with magnetic field: $m_s = +\frac{1}{2}$

Electron aligned against magnetic field: $m_s = -\frac{1}{2}$

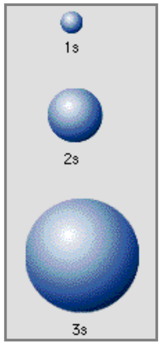
The Four Quantum Numbers

- Principal quantum number (*n*) - describes the SIZE of the orbital or ENERGY LEVEL of the atom.
- Angular quantum number (*l*) or sublevels - describes the SHAPE of the orbital.
- Magnetic quantum number (*m*) - describes an orbital's ORIENTATION in space.
- Spin quantum number (*s*) - describes the SPIN or direction (clockwise or counter-clockwise) in which an electron spins.

1. Principal Quantum Number (n)

Energy level

Size of the orbital



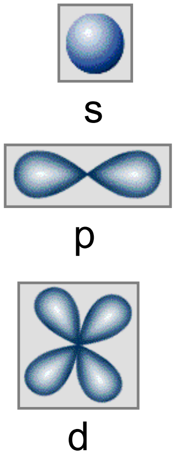
The energy levels corresponding to $n = 1, 2, 3, \ldots$ are called shells and each can hold $2n^2$ electrons.

The shells are labeled K, L, M, … for $n = 1, 2, 3, \ldots$.

2. Angular Momentum Quantum # (l)

Energy sublevel

Shape of the orbital



- determines the ***shape of the orbital***
- they are numbered but are also given letters referring to the orbital type
  - l=0 refers to the **s-orbitals**
  - l=1 refers to the **p-orbitals**
  - l=2 refers to the **d-orbitals**
  - l=3 refers to the **f-orbitals**

3. Magnetic Quantum Number (m_l)

Orientation of orbital

Specifies the number and shape of orbitals within each sublevel

- the third of a set of quantum numbers
- tells us ***how many*** orbitals there are of a particular type and ***their orientation in space of a particular orbital***
- only ***two electrons*** can fit in an orbital

4. Spin Quantum Number (m_s)

Electron spin ⇒ +½ or -½

An orbital can hold 2 electrons that spin in opposite directions.

A bit of History

http://www.lorentz.leidenuniv.nl/history/spin/goudsmit.html

Stern and Gerlach: How a Bad Cigar Helped Reorient Atomic Physics, B. Friedrich and D. Herschbach, *Physics Today*, December, 53-59, **2003**

George Uhlenbeck and Discovery of Electron Spin, A. Pias, *Physics Today*, December, 34-40, **1989**

Fifty years of spin: It might as well be spin
Samuel A. Goudsmit, *Physics Today* **29**, 6, 40, **1976**

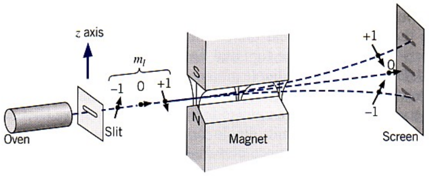
What is "intrinsic spin"?

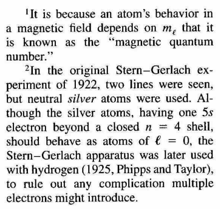
- Also called "spin", or spin angular momentum, or S
- It's a "degree of freedom", or quantum number: a "state" the particle has
- Does interact with magnetic fields like L
- NOT a physical rotation
- INTRINSIC property – like charge and mass! We have no model for what "makes it up/causes it" for fundamental particles
- Shows up most simply in Pauli exclusion principle

Otto Stern
Nobel Prize, 1943

Expectation and Observation
Stern & Gerlach ~1922


Scan ©American Institute of Physics



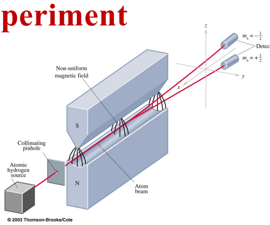


[1] It is because an atom's behavior in a magnetic field depends on m_ℓ that it is known as the "magnetic quantum number."

[2] In the original Stern–Gerlach experiment of 1922, two lines were seen, but neutral *silver* atoms were used. Although the silver atoms, having one 5s electron beyond a closed $n = 4$ shell, should behave as atoms of $\ell = 0$, the Stern–Gerlach apparatus was later used with hydrogen (1925, Phipps and Taylor), to rule out any complication multiple electrons might introduce.

The Stern-Gerlach experiment

- Experiment was confirmed using:



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Element	*Electronic Configuration*
H	$1s^1$
Na	$\{1s^2 2s^2 2p^6\} 3s^1$
K	$\{1s^2 2s^2 2p^6 3s^2 3p^6\} 4s^1$
Cu	$\{1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10}\} 4s^1$
Ag	$\{1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10}\} 5s^1$
Cs	$\{[Ag] 5s^2 5p^6\} 6s^1$
Au	$\{[Cs] 5d^{10} 4f^{14}\} 6s^1$

- In all cases, $l = 0$ and $s = 1/2$.

Stern-Gerlach and spin

O. Stern and W. Gerlach saw a beam of silver atoms split into two beams!

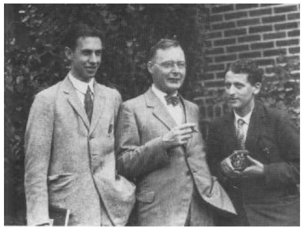
G. Uhlenbeck and S. Goudsmit suggested that each electron has its own intrinsic angular momentum – “spin” – with only two eigenvalues.

But electron spin has odd features. For example, its magnitude never changes, just its direction – and it has only two directions.

Thus far every eigenstate of an atom was associated with three quantum numbers *n*, *l* and *m*. But now we have to introduce a fourth quantum number, the spin: $m_s = \pm ½$.

Note: The nucleus, too, has spin angular momentum. But its magnetic moment is relatively tiny because the mass of a proton is about 2000 times the electron mass.

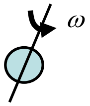
Some history titbits
Uhlenbeck & Goudsmit ~ 1925



The discovery note in *Naturwissenschaften* is dated 17 October 1925. One day earlier **Ehrenfest** had written to Lorentz to make an appointment and discuss a "very witty idea" of two of his graduate students. When Lorentz pointed out that the idea of a spinning electron would be incompatible with classical electrodynamics, Uhlenbeck asked Ehrenfest not to submit the paper. Ehrenfest replied that he had already sent off their note, and he added: "**You are both young enough to be able to afford a stupidity**!"

http://www.lorentz.leidenuniv.nl/history/spin/spin.html

Across the continent: Ralph Kronig & Spinning Electron

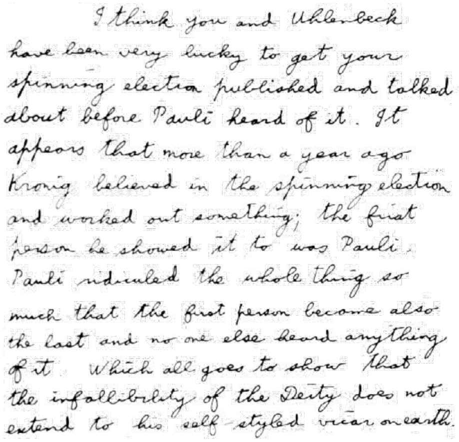


Ehrenfest's encouraging response to his students ideas contrasted sharply with that of Wolfgang Pauli.

At the same time, Ralph Kronig, a young Columbia University PhD who had spent two years studying in Europe, had come up with the idea of electron spin several months before Uhlenbeck and Goudsmit. He had put it before Pauli for his reactions, who had ridiculed it, saying that "it is indeed very clever but of course has nothing to do with reality. No, it's quite impossible." Pauli completely crushed Kronig. He did not publish his ideas on spin.

http://www.lorentz.leidenuniv.nl/history/spin/spin.html

Letter from Thomas to Goudsmit



I think you and Uhlenbeck
have been very lucky to get your
spinning electron published and talked
about before Pauli heard of it. It
appears that more than a year ago
Kronig believed in the spinning electron
and worked out something; the first
person he showed it to was Pauli.
Pauli ridiculed the whole thing so
much that the first person became also
the last and no one else heard anything
of it. Which all goes to show that
the infallibility of the Deity does not
extend to his self-styled vicar on earth.

Part of a letter by L.H. Thomas to Goudsmit (25 March 1926). Reproduced from a transparency shown by Goudsmit during his 1971 lecture. The original is presumably in the Goudsmit archive kept by the AIP Center for History of Physics.

http://www.lorentz.leidenuniv.nl/history/spin/goudsmit.html

Wolfgang Pauli
Nobel Prize, 1945
"for the discovery of the Exclusion Principle, also called the Pauli Principle."

Spin was first discovered in the context of the emission spectrum of alkali metals - "two-valued quantum degree of freedom" associated with the electron in the outermost shell.

In trying to understand splitting patterns and separations of line spectra, the concept of spin was proposed.

"*it is indeed very clever but of course has nothing to do with reality*". *W. Pauli*

A year later Goudsmit and Uhlenbeck, published a paper on this same idea.

Pauli finally formalized the theory of **Spin** in 1927 for which he received the Nobel Prize in 1945.

The Pauli Exclusion Principle

No two electrons can have identical quantum numbers. With three quantum numbers *n, l, m* two electrons in an orbital will have identical quantum numbers. This led eventually to the discovery of the spin of the electron.

Wolfgang Pauli
Nobel Prize, 1945

An empty orbital is fully described by the three quantum numbers: n, *l* and m_l

An electron in an orbital is fully described by the four quantum numbers: n, *l*, m_l and m_s

Visualization of Spin Chemistry

- Quantum mechanics requires mathematics for a quantitative treatment.
- Much of the mathematics of quantum mechanics can be visualized in terms of pictures that capture the qualitative aspects of the phenomena under consideration.
- Visualizations are incomplete, but it is important to note "correct" mathematical representations fail for complex systems as molecules.

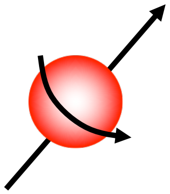
Spin

Visualize spin by resorting to a classical analogy of a spherical object executing a spinning motion about an axis, *i.e.*, a top or a gyroscope.

Develop a model which associates specific magnetic properties, *i.e.*, a magnetic moment, with the electron's spin angular momentum

Angular momentum is a property of a macroscopic object which is in a state of rotation about an axis.

Spin

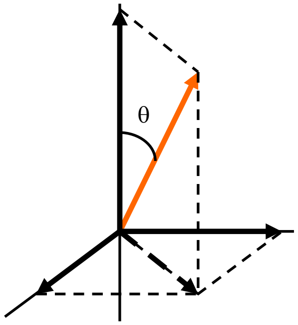


- Quantum particles possess an intrinsic angular momentum called spin which is not associated to a rotation about an axis, although we can visualize it as if it was generated by a rotation of the particle about its own axis
- Classically angular momentum is a property of a macroscopic object which is in rotation about an axis

Scalars and Vectors

- Some physical quantities are completely described by a magnitude (a single number): they are termed **scalar**
- Some other quantities have a directional quality and their description requires both a magnitude and a direction: they are termed **vectors**

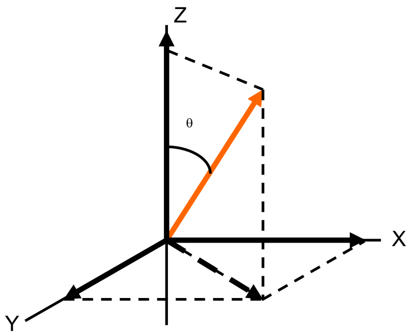
Angular momenta and vectors



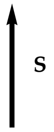
- Angular momenta are **vector quantities** since they are determined by their **magnitude** and **direction**.
- A vector quantity is graphically represented by an arrow.
- For angular momenta:
  - the **magnitude** of the momentum is represented by the length of the arrow
  - the **direction** of the momentum is represented by the direction of the arrow (tip)

Vector components

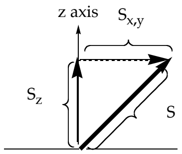
A vector can always be thought as the sum of three vectors oriented along each of the three cartesian axes x, y and z.



Electron spin angular momenta and vectors

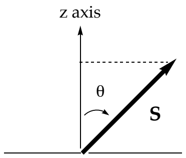


(a) An arbitrary Spin Vector is represented by the symbol , **S,** and by an arrow.



(b) Vector Length:
S is the total **length** of the spin angular momentum vector **S**; S_z is the length of the component on the spin angular momentum on the z axis; $S_{x,y}$ is the length of the component on the x or y axis.

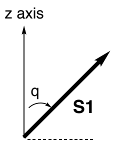
The length of a spin vector is termed the **magnitude** of its spin angular momentum. It is expressed in terms of $h/2\pi$ (Planck constant h unit: J s).

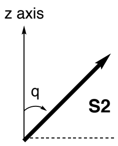


(c) Vector Direction: The **direction** of the spin angular momentum vector is given by the angle θ made by the vector with the z axis.

The **orientation** of a spin vector in spin space may be unambiguously defined by an angle, q, that the vector makes with respect to the z axis

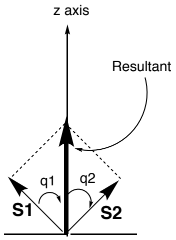
Multiple independent spins and coupled spins





S1 = **S_2**

(d) Two Equivalent Vectors **S_1** and **S_2**. The two spin vectors shown are identical (congruent) in spin space because they differ only by a parallel translation. They possess the same length, S, and direction, q.



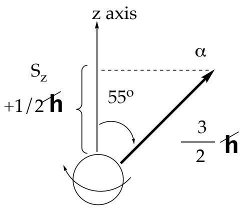
S1 + **S_2**

(c) Resultant Method of vector addition

Spin

- Electron possesses a fixed and characteristic spin angular momentum of ½ $\hbar$

$\hbar$: Planck's constant/ 2π



This is fixed independent of whether it is free or associated with a nucleus, regardless the orbital that it occupies, e.g., **s, p, d, nπ*, ππ*;** always the same.

If the electron spin were a classical quantity, the magnitude and direction of the vector representing the spin could assume any length and any orientation.

Only certain directions of the spin are allowed. This is termed spin multiplicity.

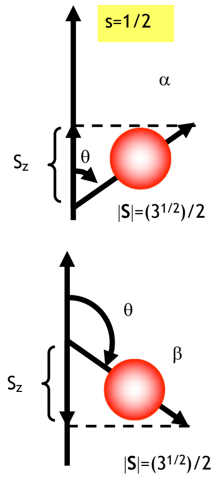
Quantum rules of electron spin angular momentum

- S, the **spin quantum number**, related to the length of the spin vector for an electron can assume only value ½
- **M_s** (**spin multiplicity**) related to the orientation of the spin vector

examples

S=0	1	singlet
S=1/2	2	doublet
S=1	3	triplet

Spin multiplicity= 2S+1



Spin multiplicity= 2S+1 = 2

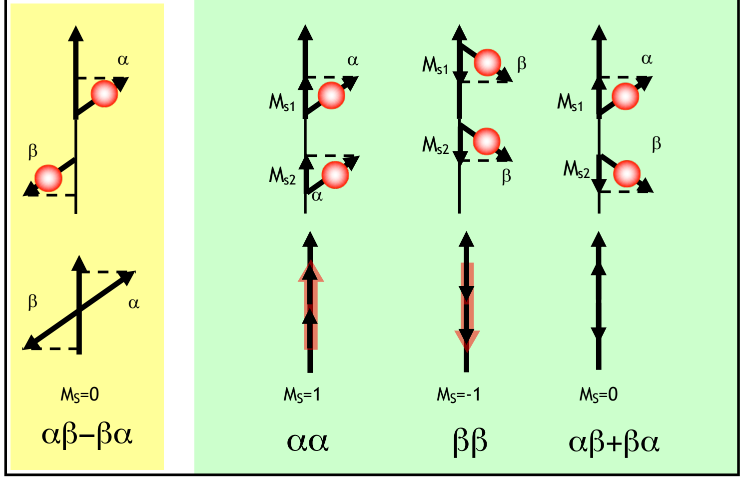
In particular for
S=1/2 →$|S|=(3^{1/2})/2$

θ=55° for M_s= 1/2

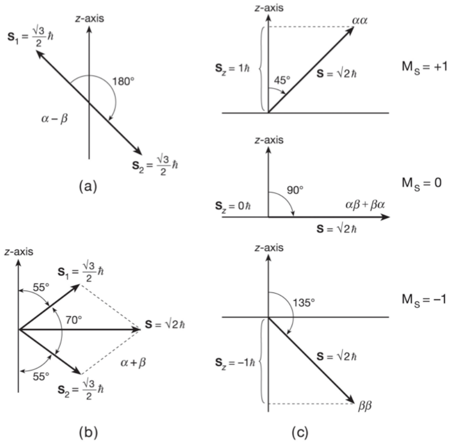
θ=125° for M_s=-1/2

Two spins of ½: S = 0
Spin multiplicity = 2S+1 = 1

Two spins of ½: S = 1
Spin multiplicity= 2S+1 = 3



2D Vector representations for two interacting electrons



Cones of possible orientations

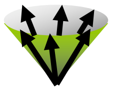
The uncertainty principle (Heisenberg) states that the length and the direction of the spin angular momentum are conjugate quantities: if one is measured precisely the other cannot be measured with any precision

↓

The length of the spin |**S**| and S_z are known because of the quantistic principles

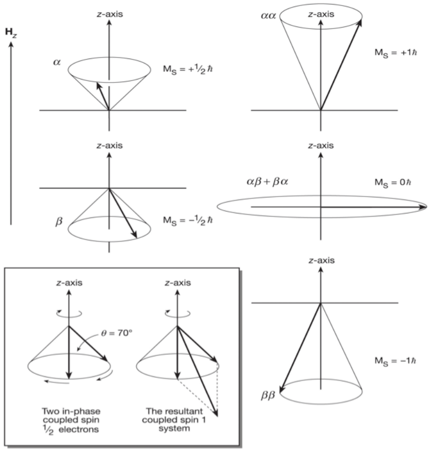
↓

The angle the spin forms with z is known but not its x and y components: it lies on a definite cone

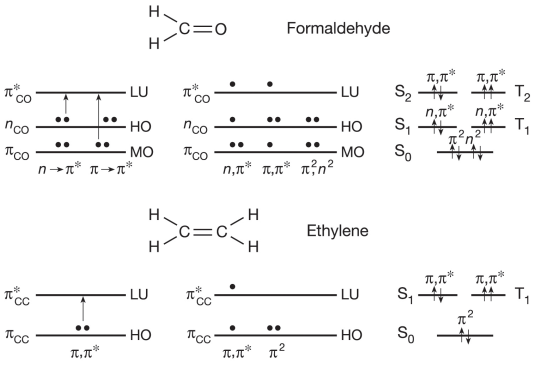


There is an infinite set of positions that the spin vector can assume in space making an angle of 55° with the z-axis, any one of which could correspond to the actual position of the spin vector. This is represented as a cone in a 3-D.

3D Vector representations for two interacting electrons

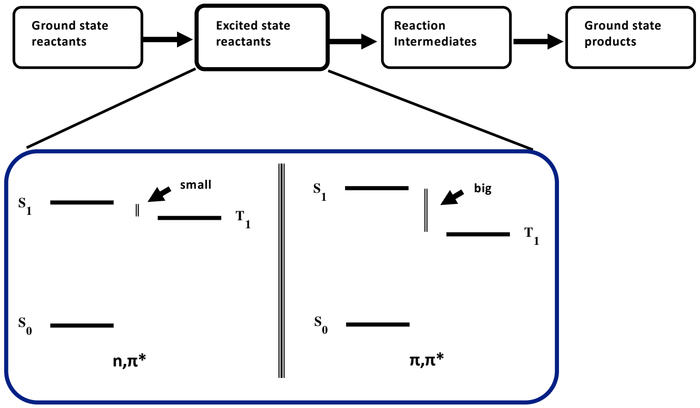


Electronic and Spin Configuration of States



(a) Transitions (b) Configurations (c) States

S_1-T_1 energy gap



Ground state reactants → Excited state reactants → Reaction Intermediates → Ground state products

Singlet-Triplet separation in molecules and diradical intermediates and Intersystem crossing

Role of exchange integral (J)

Why triplets are lower in energy than singlets?

What controls the singlet-triplet energy gap?

$$E_S = E_0(n,\pi^*) + K(n,\pi^*) + J(n,\pi^*)$$

$$E_T = E_0(n,\pi^*) + K(n,\pi^*) - J(n,\pi^*)$$

$$\Delta E_{ST} = E_S - E_T = E_0(n,\pi^*) + K(n,\pi^*) + J(n,\pi^*) - [E_0(n,\pi^*) + K(n,\pi^*) - J(n,\pi^*)]$$

$$\Delta E_{ST} = E_S - E_T = 2J(n,\pi^*)$$

$$J(n,\pi^*) = \langle n\phi(1)\pi^*(2)|e^2/r_{12}|\, n\phi(2)\pi^*(1)\rangle$$

$$J(n,\pi^*) \sim e^2/r_{12} \langle n\phi(1)\pi^*(2)|n\phi(2)\pi^*(1) \sim \langle \phi(1)|\phi(2)\rangle$$

overlap integral controls the gap

The Electron-Exchange Interaction in Molecules

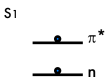
The Singlet and the Triplet states are split apart in energy by the *electron-exchange interaction*.

If the two electron did not interact each other, the 4 energy levels would be degenerate.

Considering only the isotropic contribution, electron-exchange interaction has the form of repulsive columbic interaction between the two charged particles (electrons).

$$\hat{H}_{exch} = J\hat{S}_1\hat{S}_2$$

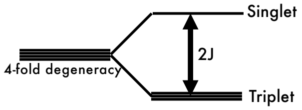
$$J_{n,\pi^*} = \left\langle n(1)\pi^*(2)\left|\frac{e^2}{r}\right|n(1)\pi^*(2)\right\rangle$$



Factorizing out from the integral the columbic term, the intensity of interaction is proportional to the overlap integral between the two states.

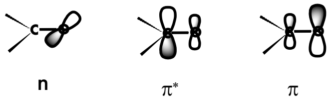
$$J_{n,\pi^*} \propto \left\langle n(1)\pi^*(2)\middle|n(1)\pi^*(2)\right\rangle = \left\langle n\middle|\pi^*\right\rangle$$

The repulsive interaction lowers the energy of the Triplet state, since the electrons are farther apart.



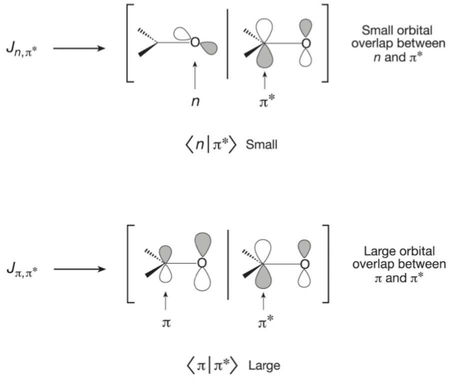
Large exchange splitting (J) reflects the fact that the unpaired electrons can approach quite closely.

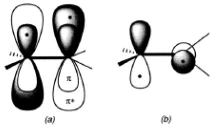
The Singlet-Triplet energy spacing depends on the overlap between the molecular orbital wavefunctions involved: $J(n,\pi^*) < J(\pi,\pi^*)$



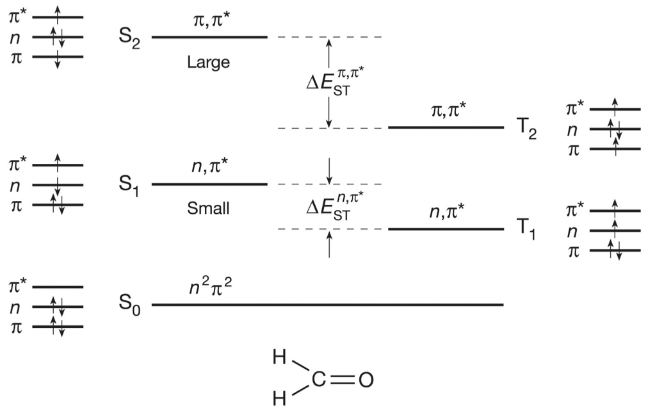
$$J(n,\pi^*) = \langle n(1)\pi^*(2)|e^2/r_{12}|n(2)\pi^*(1)\rangle$$

$$J(n,\pi^*) \sim e^2/r_{12}\langle n(1)\pi^*(2)|n(2)\pi^*(1) \sim \langle n|\pi^*\rangle$$

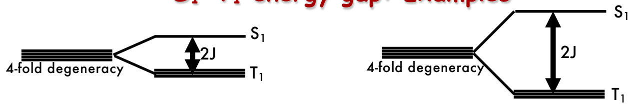




Energies of singlet and triplet states



S₁-T₁ energy gap: Examples



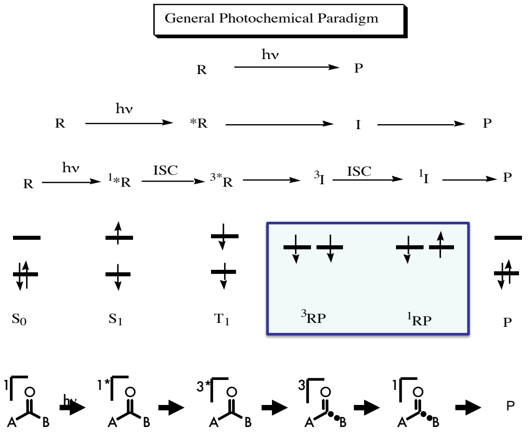
Splitting for n,π* states

Splitting for π,π* states

Molecule	Configuration of S_1 and T_1	ΔE_{ST} (kcal mol^{-1})
$CH_2{=}CH_2$	π,π*	~ 70
$CH_2{=}CH{-}CH{=}CH_2$	π,π*	~ 60
$CH_2{=}CH{-}CH{=}CH{-}CH{=}CH_2$	π,π*	~ 48
	π,π*	25[a] (52)[b]
	π,π*	31[a] (38)[b]
	π,π*	~ 34
	π,π*	30
$CH_2{=}O$	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 symmetry.
b. ΔE_{ST} between states of the same orbital symmetry.

Importance of intersystem crossing



General Photochemical Paradigm

$$R \xrightarrow{h\nu} P$$

$$R \xrightarrow{h\nu} {}^{*}R \longrightarrow I \longrightarrow P$$

$$R \xrightarrow{h\nu} {}^{1*}R \xrightarrow{ISC} {}^{3*}R \longrightarrow {}^{3}I \xrightarrow{ISC} {}^{1}I \longrightarrow P$$

One more factor to take into account

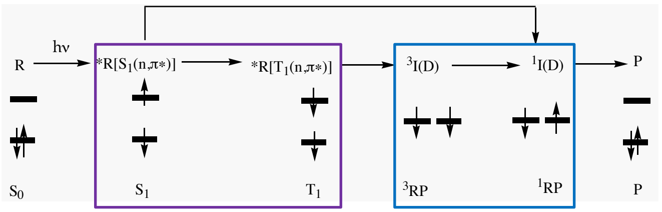
$\Delta E_{ST} = 2J$ in molecules here HOMO-LUMO gap is large

$\Delta E_{ST} = J - B$ in intermediates where HOMO-LUMO gap is very small

J:

B:

Electronic Energy Difference between Singlet and Triplet States in Diradical Reactive Intermediates, I(D)



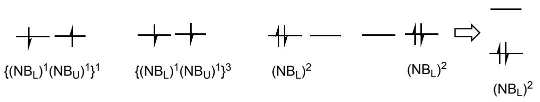
$S_1 > T_1$

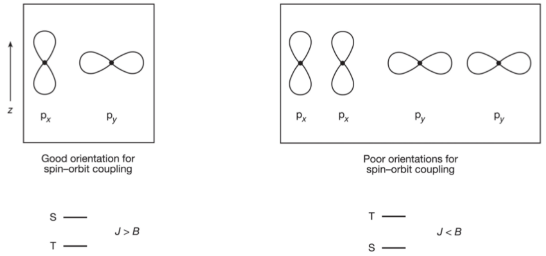
$S_1 > T_1$

$S_1 < T_1$

ΔE_{ST} = J - B

J will be proportional to the electron exchange integral for the $(NB_L)^1(NB_U)^1$ configuration and B will be proportional to the contribution of the $(NB_L)^2$ configuration. The latter corresponds to the bonding contribution.





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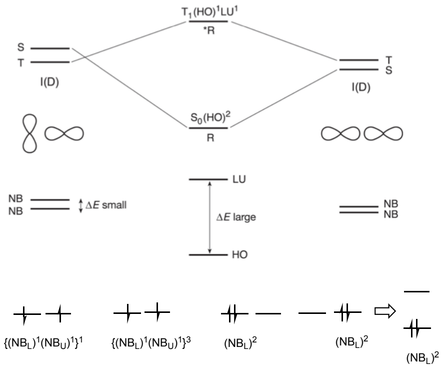
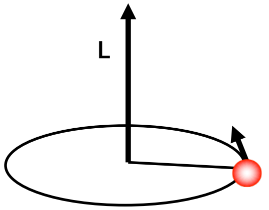


Electron orbital angular momentum

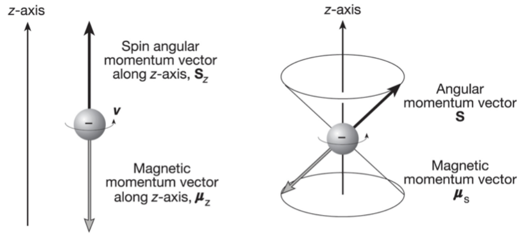
Orbital angular momentum can be visualized in terms of an electron of mass m_e travelling in a circular Bohr orbit of radius **r** with velocity **v**



An electron in a Bohr atom is modeled as a point charge rotating about a fixed axis centered in the nucleus. Then it possesses a orbital magnetic moment:

$$\mu_L = -(e/2m)\ L = -\gamma_e\ L$$

Spin angular momentum and Magnetic momentum are related



$\mu_s = \cancel{-(e/2m)\,S}$

$\mu_s = -(e/2m)\, g_e\, S = -\gamma_e\, g_e\, S$

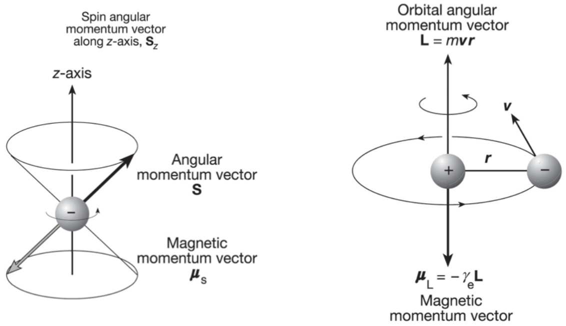
$\mu_L = -\gamma_e \mathbf{L}$

$\mu_S = -\gamma_e \mathbf{S}$ Expected but does not work

$\mu_S = -g_e \gamma_e \mathbf{S}$ Fudge factor called ‘g’ factor introduced.

g factor of the electron for free electrons and most organic molecules ≈2

Spin and orbital angular momenta and Magnetic momenta are related

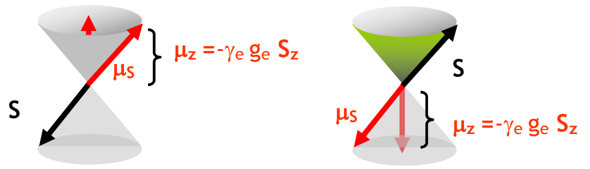


The vector model for the orbital angular momentum and the magnetic moment due to an electron in a Bohr orbit. The direction of the magnetic moment vector is **opposite** that of the direction of the angular momentum vector for an electron. The units of L are h/2π and the units of μL are J-G-1.

Magnetic moment of an electron

The magnetic moment μ_s associated with the spin is quantized in magnitude and orientation as the angular momentum from which it arises

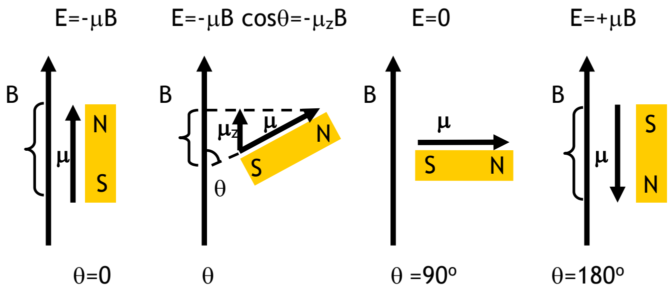
μ_s and **S**: lie antiparallel in two cones whose orientation is determined by S and M_s



Classical magnetic dipole in a magnetic fiel

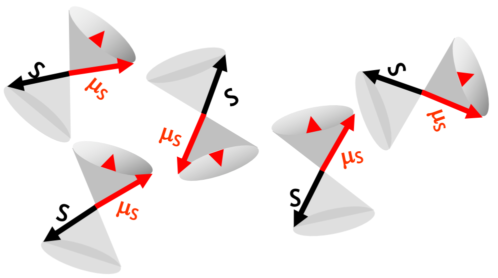
Magnetic moments interact with magnetic fields

$$E = -\mu \cdot B$$



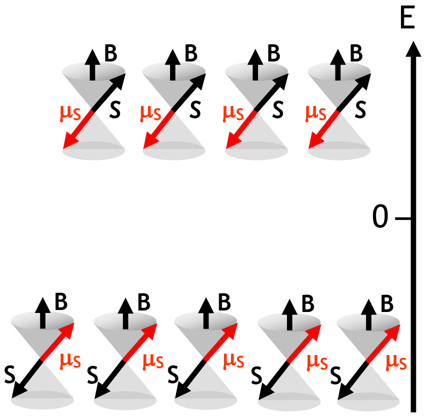
Quantum magnets in the absence of magnetic fields

- Spins are randomly oriented



Quantum magnetic energy levels in a strong applied magnetic field

- Spins are no more randomly oriented: they assume definite orientations with respect to the magnetic field
- Some orientations are favored with respect to some others because they correspond to lower energies of interaction: more spins tend to assume those orientations



Quantistic magnetic dipole in a strong magnetic field

Since the magnetic energy is proportional to the magnetic moment, the quantization of the spin angular momentum in a specified direction leads to the quantization of the energy levels of a magnetic dipole in a magnetic field. If B // z:

Zeeman energy

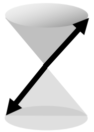
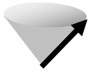
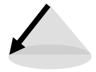
$$\boxed{E = -\mu B\cos\theta = -\mu_z B = g_e\beta_e B\, M_s}$$

For spin magnetic moments associated with S=1/2 two energy levels arise according to the possible orientation of the spin with respect to the magnetic field:

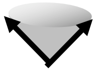
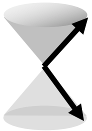
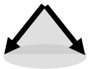
$$\begin{array}{ccc} M_S=-1/2 & & M_S=1/2 \\ \Downarrow & & \Downarrow \\ -1/2\ g_e\beta_e B & \text{and} & 1/2\ g_e\beta_e B \end{array}$$

Quantum magnetic energy levels in an applied magnetic field

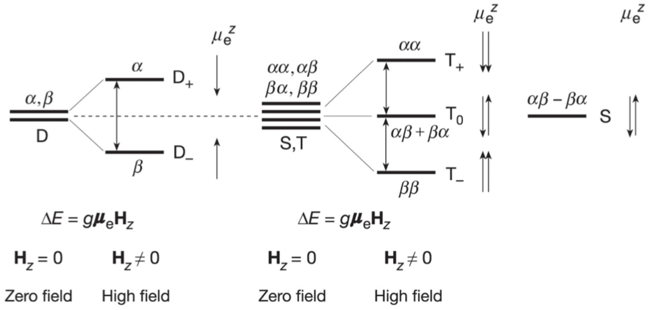
$$\boxed{E = -\mu B\cos\theta = -\mu_z B = -g_e\beta_e B\, M_s}$$

State	State symbol	M_s	Magnetic energy	Spin Function	Vector Representation
Singlet	S	0	0	αβ−βα	
Doublet	D	½	½ $g\mu_eB_z$	α	
Doublet	D	- ½	- ½ $g\mu_eB_z$	β	

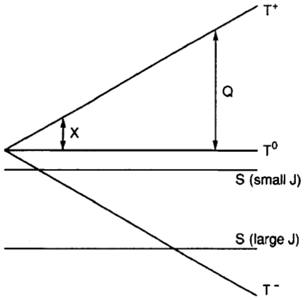
Quantum magnetic energy levels in an applied magnetic field

State	State symbol	M_s	Magnetic energy	Spin Function	Vector Representation
Triplet	T_+	+1	$g\mu_eB_z$	αα	
Triplet	T_0	0	0	αβ+βα	
Triplet	T_-	-1	$-g\mu_eB_z$	ββ	

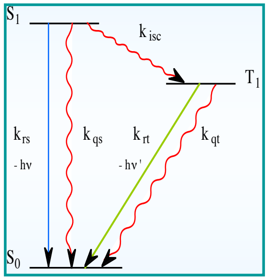
Magnetic energy diagram



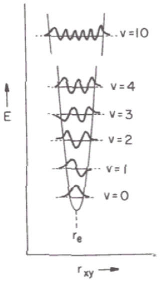
Dependence of singlet and triplet, and triplet sublevel separation on J and external magnetic field



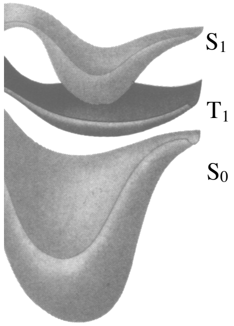
Visualizing molecules in ground and excited states



Molecule represented in one dimension



Molecule represented in two dimensions



Molecule represented in three dimensions