

Inorganic Chemistry

Bonding and Coordination Chemistry

Books to Refer:

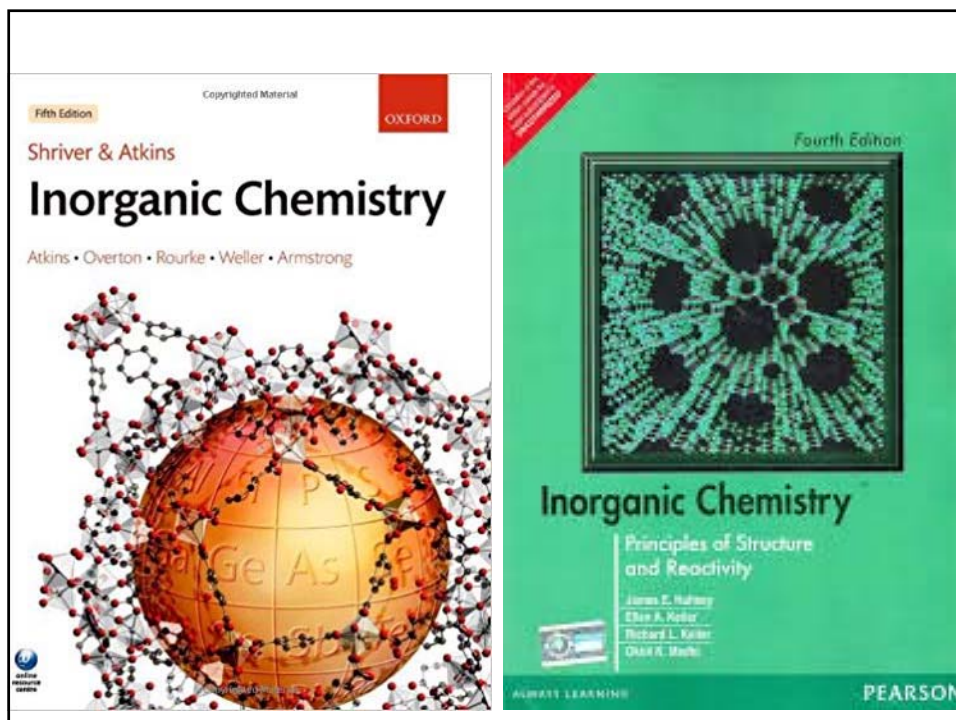
Inorganic Chemistry by Shriver & Atkins

Inorganic Chemistry by James E. Huheey

Physical Chemistry: Atkins

Rajakumar, A.

OC-110, Org. Chem. Building,
Department of Chemistry



Making Science Popular

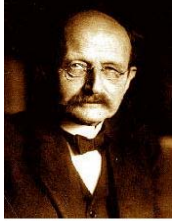


-Atomic Orbitals & Bonding in s,p,d systems:

MO theory

- Molecular orbitals of First row homonuclear diatomics
- Heteronuclear diatomic (CO only)
- Orbital mixing
- Metallic bonding

Black Body Radiation



1900 German physicist

$$\text{Max Planck } E = h\nu$$

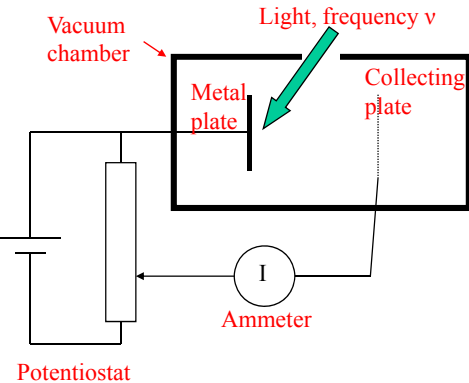
“Each electromagnetic oscillator is limited to discrete values and cannot be varied arbitrarily”

Uncertainty Principle: W. Heisenberg

It is impossible to specify the exact position and momentum of a particle simultaneously.

- $\Delta x \cdot \Delta p \geq h/4\pi$
- where h is Planck's Constant, a fundamental constant with the value 6.626×10^{-34} J s.

PHOTOELECTRIC EFFECT



Classical expectations

As intensity of light increases, force increases, so KE of ejected electrons should increase.

Electrons should be emitted whatever the frequency ν of the light.

Actual results:

Maximum KE of ejected electrons is independent of intensity, but dependent on ν

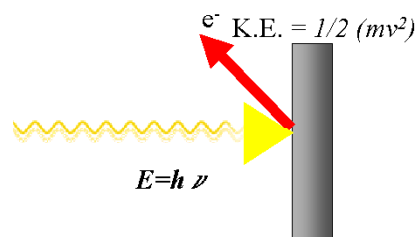
For $\nu < \nu_0$ (i.e. for frequencies below a cut-off frequency) no electrons are emitted.

Einstein

$$h \nu = \frac{1}{2} m v^2 + \phi$$

- $KE = \frac{1}{2} m v^2 = h\nu - \phi$
- ϕ is the work function
- $h\nu$ is the energy of the incident light.
- Light can be thought of as a bunch of particles which have energy $E = h\nu$.
- The light particles are called photons.

Photoelectric Effect



Louis de Broglie

- Particles can behave as wave.
- Relation between wavelength λ and the mass and velocity of the particles.
- $E = h\nu$ and also $E = mc^2$,
- E is the energy
- m is the mass of the particle
- c is the velocity.



Louis de Broglie

Wave & Particle Duality

- $E = mc^2 = h\nu$
- $mc^2 = h\nu$
- $p = h / \lambda$ { since $v = c / \lambda$ }
- $\lambda = h / p = h / mv$

Summary

Flaws of classical mechanics

Photoelectric effect

Heisenberg uncertainty principle limits simultaneous knowledge of conjugate variables

Light and matter exhibit **wave-particle duality**

Relation between wave and particle properties given by the **de Broglie relations**

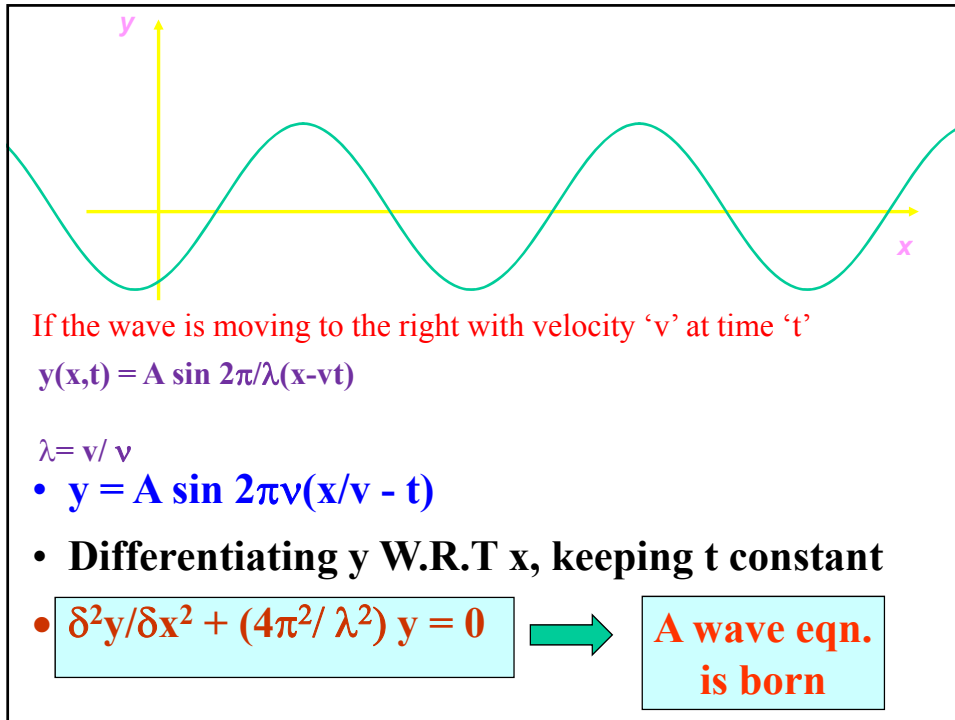
The state of a system in classical mechanics is defined by specifying all the forces acting and all the position and velocity of the particles.

Wave equation? **Schrödinger Equation.**



- **Most significant feature of the Quantum Mechanics: Limits the energies to discrete values – i.e. quantization of energy**

For every dynamical system, there exists a wave function Ψ that is a continuous, square-integrable, single-valued function of the coordinates of all the particles and of time, and from which all possible predictions about the physical properties of the system can be obtained.



- In three dimension the wave equation becomes:
- $\delta^2 \psi / \delta x^2 + \delta^2 \psi / \delta y^2 + \delta^2 \psi / \delta z^2 + (4\pi^2 / \lambda^2) \psi = 0$
- It can be written as $\nabla^2 \psi + (4\pi^2 / \lambda^2) \psi = 0$
- We have $\lambda = h/mv$
- $\nabla^2 \psi + (4\pi^2 m^2 v^2 / h^2) \psi = 0$
- $E = T + V$ or $T = (E - V)$ (E = total energy)
- V = Potential energy, T = Kinetic energy
- $T = 1/2 mv^2 = m^2 v^2 / 2m$
- $m^2 v^2 = 2m(E - V)$

- Wave equation, three dimensional w.r.t. x, y and z axis:

$$\delta^2\psi/\delta x^2 + \delta^2\psi/\delta y^2 + \delta^2\psi/\delta z^2 + (4\pi^2/\lambda^2)\psi = 0$$

- It can be written as $\nabla^2\psi + (4\pi^2/\lambda^2)\psi = 0$
- We have $\lambda = h/mv$
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 - $m^2v^2 = 2m(E-V)$

Hamiltonian operator

$$\nabla^2\psi + (8\pi^2m/h^2)(E - V)\psi = 0$$

- This can be rearranged as
- $\{(-h^2/8\pi^2m)\nabla^2 + V\}\psi = E\psi$

$$H\psi = E\psi$$

- $H = [(-h^2/8\pi^2m)\nabla^2 + V]$ **Hamiltonian operator**

$$\{(-h^2/8\pi^2m)(\partial^2/\partial x^2 + \partial^2/\partial y^2 + \partial^2/\partial z^2) + V\}\Psi = E\Psi \dots (X, Y \text{ and } Z - \text{axis})$$

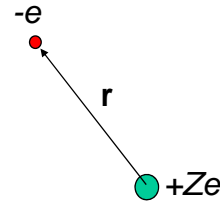
$$\delta^2y/\delta x^2 + (4\pi^2/\lambda^2)y = 0$$

How to write Hamiltonian for different systems?

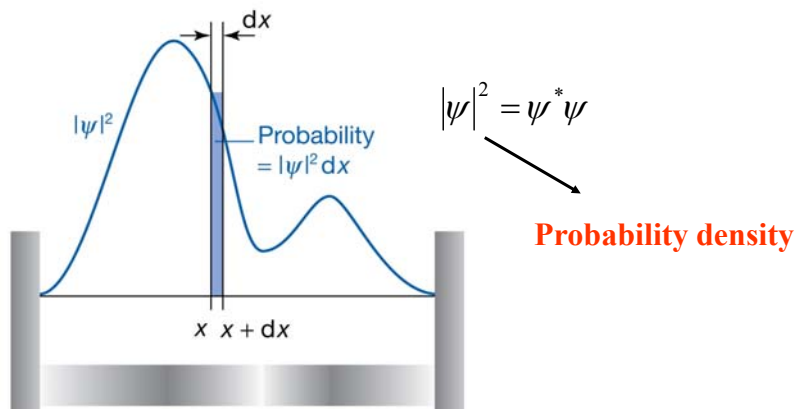
$$\{(-\hbar^2/8\pi^2m)\nabla^2 + V\} \Psi = E \Psi$$

• Hydrogen atom:

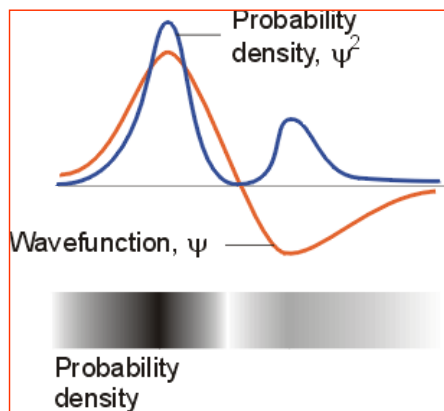
- $KE = \frac{1}{2} m (v_x^2 + v_y^2 + v_z^2)$
- $PE = -e^2/r$, (r = distance between the electron and the nucleus.)
- $H = \{(-\hbar^2/8\pi^2m) \nabla^2 - e^2/r\}$
- $\nabla^2 \Psi + (8\pi^2 m/\hbar^2)(E + e^2/r) \Psi = 0$
- If the effective nuclear charge is Ze
 - $H = \{(-\hbar^2/8\pi^2m) \nabla^2 - Ze^2/r\}$



The wave function Ψ is the probability amplitude



If the wavefunction of a particle has the value ψ at some point x , then the probability of finding the particle between x and $x + dx$ is proportional to $|\psi|^2 dx$.



The sign of the wave function has not direct physical significance: the positive and negative regions of this wave function both corresponds to the same probability distribution. Positive and negative regions of the wave function may corresponds to a high probability of finding a particle in a region.

Variation Method: Quick way to get E

- $H\Psi = E\Psi$
- $\Psi H\Psi = \Psi E\Psi = E\Psi \Psi$
- If Ψ is complex,
- $E = \int \Psi^* H \Psi d\tau / \int \Psi^* \Psi d\tau$
- $E = \langle \Psi | H | \Psi \rangle / \langle \Psi | \Psi \rangle$ (4)
- *Bra-Ket notation*

What does $E = \langle \Psi | H | \Psi \rangle / \langle \Psi | \Psi \rangle$ tell us ?

- **Given any Ψ , E can be calculated.**
- **If the wave function is not known, we can begin by educated guess and use *Variation Theorem*.**

$$\Psi_1 \Rightarrow E_1$$

$$\Psi_2 \Rightarrow E_2$$

“If a trial wave function is used to calculate the energy, the value calculated is never less than the true energy”
– **Variation Theorem.**

- $\Psi_1 \Rightarrow E_1$

- $\Psi_2 \Rightarrow E_2$

The Variation Theorem tells that

- $E_1, E_2 > E_g$, E_g true energy of the ground state
 - **IF, $E_1 > E_2$,**
- **Then E_2 and Ψ_2 is better approximation to the energy and corresponding wave function Ψ_2 to the true wave function**

Chemical Bonding

Molecular Orbital Theory

- MOT starts with the idea that the **quantum mechanical principles applied to atoms may be applied equally well to the molecules.**

When building the molecule- Aufbau Principle
(Building Principle) - Pauli Exclusion Principle.

**Simplest possible molecule:
 H_2^+ : 2 nuclei and 1 electron.**

- Let the two nuclei be labeled as A and B & wave functions as Ψ_A & Ψ_B .
- **Since the complete MO has characteristics separately possessed by Ψ_A and Ψ_B ,**
 - $\Psi = C_A \Psi_A + C_B \Psi_B$
 - **or $\Psi = N(\Psi_A + \lambda \Psi_B)$**
- $\lambda = C_B/C_A$, and N - normalization constant

This method is known as Linear Combination of Atomic Orbitals or **LCAO**

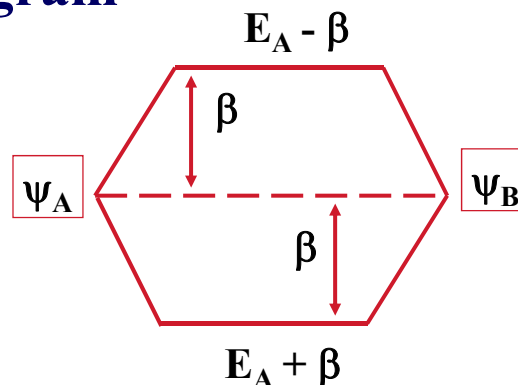
- Ψ_A and Ψ_B are same atomic orbitals except for their different origin.
- By symmetry Ψ_A and Ψ_B must appear with equal weight and we can therefore write
- $\lambda^2 = 1$, or $\lambda = \pm 1$
 - Therefore, the two allowed MO's are

- $\Psi = \Psi_A \pm \Psi_B$

For $\Psi_A + \Psi_B$
Calculated energy is $E \pm = E_A + \beta$

For $\Psi_A - \Psi_B$; $E = E_A - \beta$

Energy level diagram



Linear combination of atomic orbitals

Rules for linear combination

- 1. Atomic orbitals must be roughly of the same energy.**
- 2. The orbital must overlap one another as much as possible- atoms must be close enough for effective overlap.**
- 3. In order to produce bonding and antibonding MOs, either the symmetry of two atomic orbital must remain unchanged when rotated about the internuclear line or both atomic orbitals must change symmetry in identical manner.**

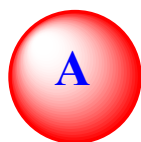
Rules for the use of MOs

- * When two AOs mix, two MOs will be produced**
- * Each orbital can have a total of two electrons (Pauli principle)**
- * Lowest energy orbitals are filled first (Aufbau principle)**
- * Unpaired electrons have parallel spin (Hund's rule)**

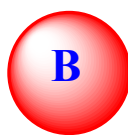
Bond order = $\frac{1}{2}$ (bonding electrons – antibonding electrons)

Linear Combination of Atomic Orbitals (LCAO)

The wave function for the molecular orbitals can be approximated by taking linear combinations of atomic orbitals.



ψ_A



ψ_B

$$\psi_{AB} = N(c_A \psi_A + c_B \psi_B)$$

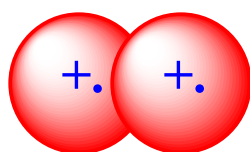
c – extent to which each AO contributes to the MO

$$\psi_{AB}^2 = (c_A^2 \psi_A^2 + 2c_A c_B \psi_A \psi_B + c_B^2 \psi_B^2)$$

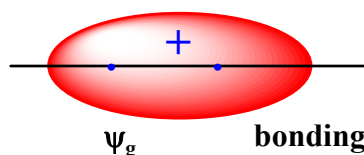
Probability density

Overlap integral

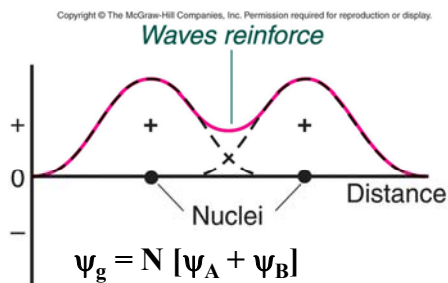
Constructive interference



$$c_A = c_B = 1$$



ψ_g bonding



Amplitudes of wave functions added

What holds the molecule together?

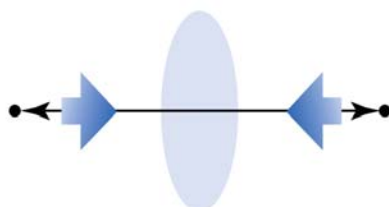
- ◆ There is nothing magic about the molecule being bonded

Electrons preferentially spend time between the two nuclei. They act as electrostatic “glue”

$$\psi_{AB}^2 = (c_A^2 \psi_A^2 + 2c_A c_B \psi_A \psi_B + c_B^2 \psi_B^2)$$

density between atoms

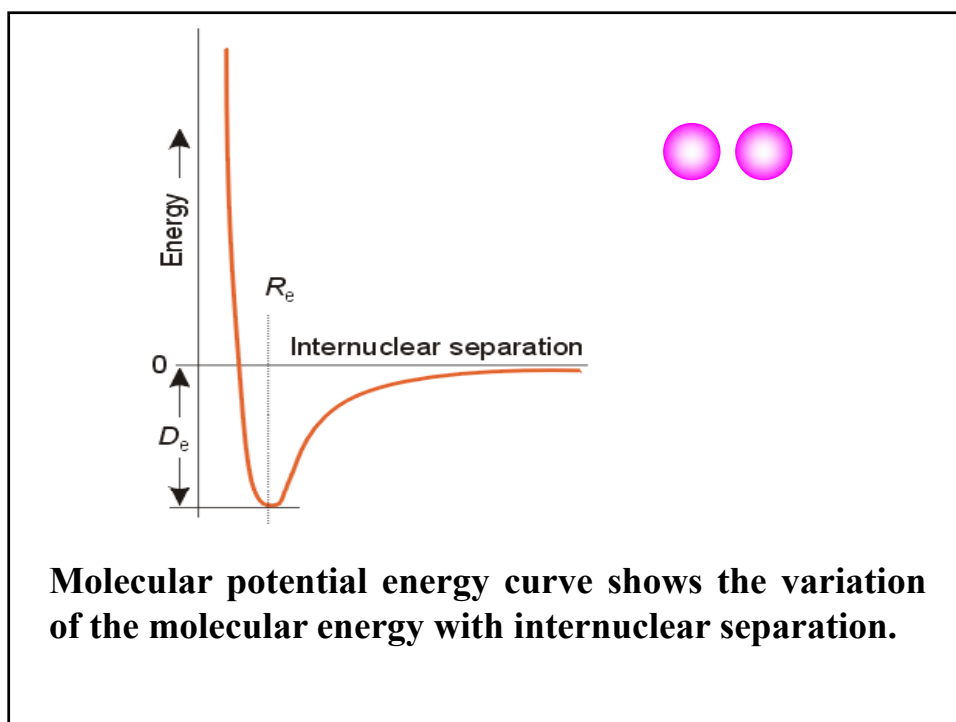
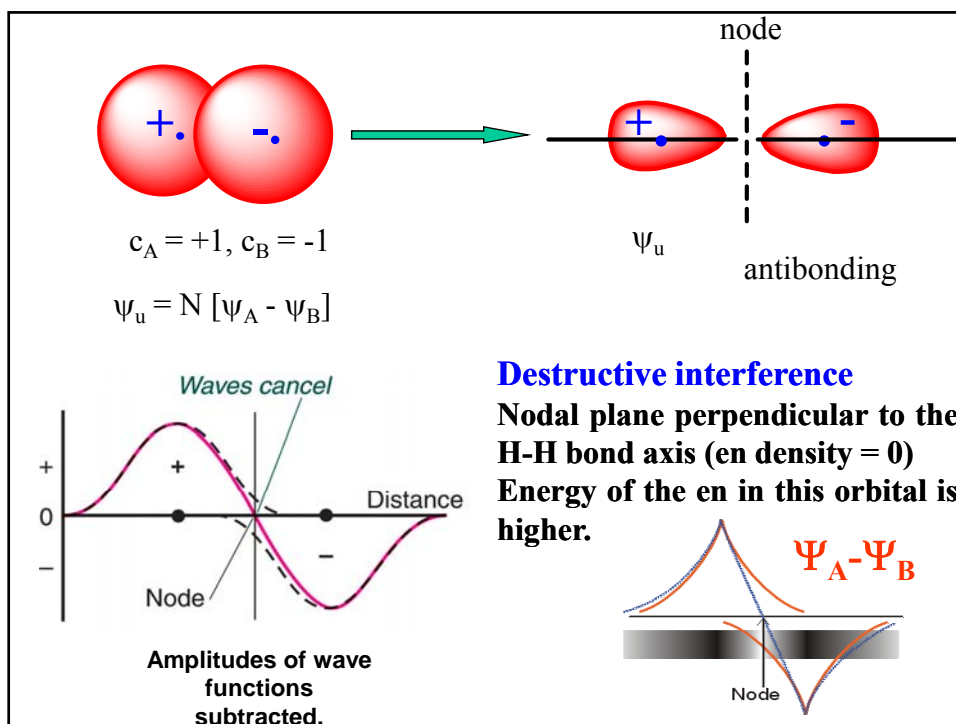
electron density on original atoms,

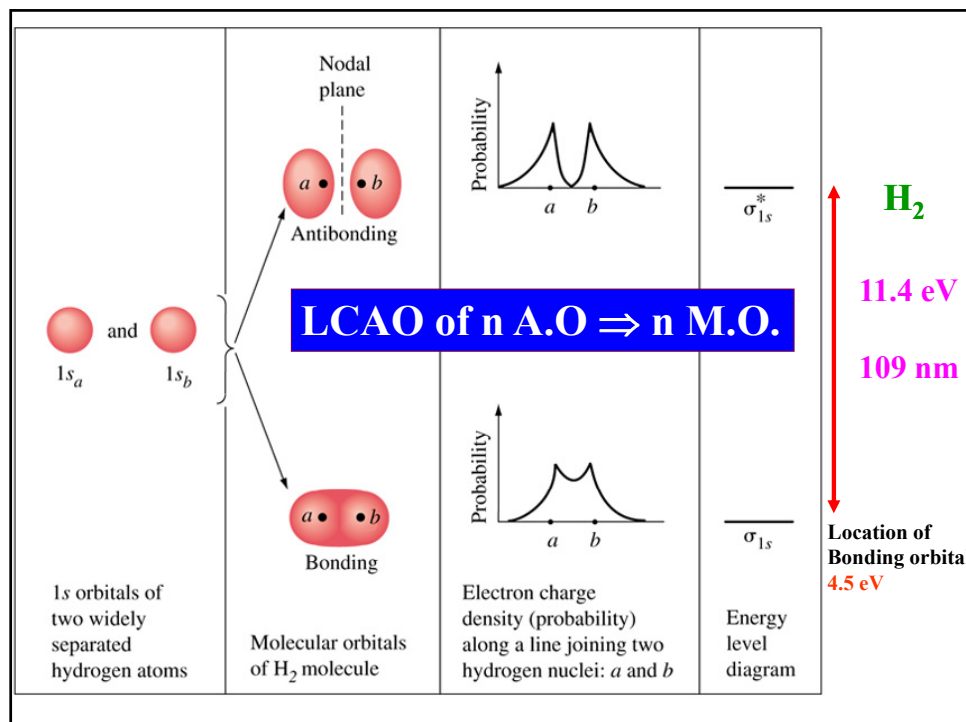


The accumulation of electron density between the nuclei put the electron in a position where it interacts strongly with both nuclei.

Nuclei are shielded from each other

The energy of the molecule is lower



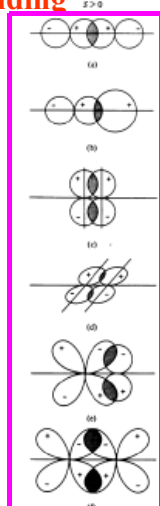


◆ The extent to which orbitals overlap can be evaluated using an overlap integral S .

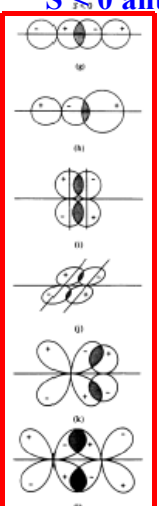
- $S = 0$ indicates that the orbitals do not overlap/interact with one another
- S depends on the symmetry of the orbital

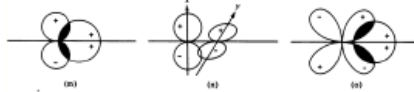
Bond strength depends on the degree of overlap

$S > 0$ **Bonding**



$S < 0$ **anti**





S = 0 nonbonding

Fig. 5.8 Arrangement of atomic orbitals resulting in positive (a-f), negative (g-l), and zero (m-o) overlap.