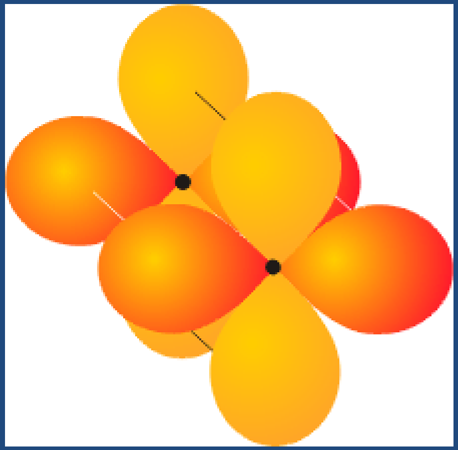
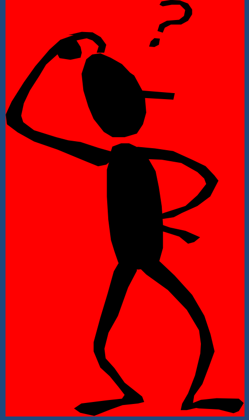
INTRODUCTION TO CHEMICAL BONDING



Failure of Classical Mechanics

- **Total energy, $E = \frac{1}{2} mv^2 + V(x)$**
- **$p = mv$ (p = momentum)**
- **$E = p^2/2m + V(x)$ ………..Eq.1**

- **Newton’s second law, which is a relation between the acceleration d^2x/dt^2 of a particle and the force F(x) it experiences.**
- **Therefore, $v = p/m$**
- **Or, p• = F(x),**
- **Continuos variation of energy is possible.**

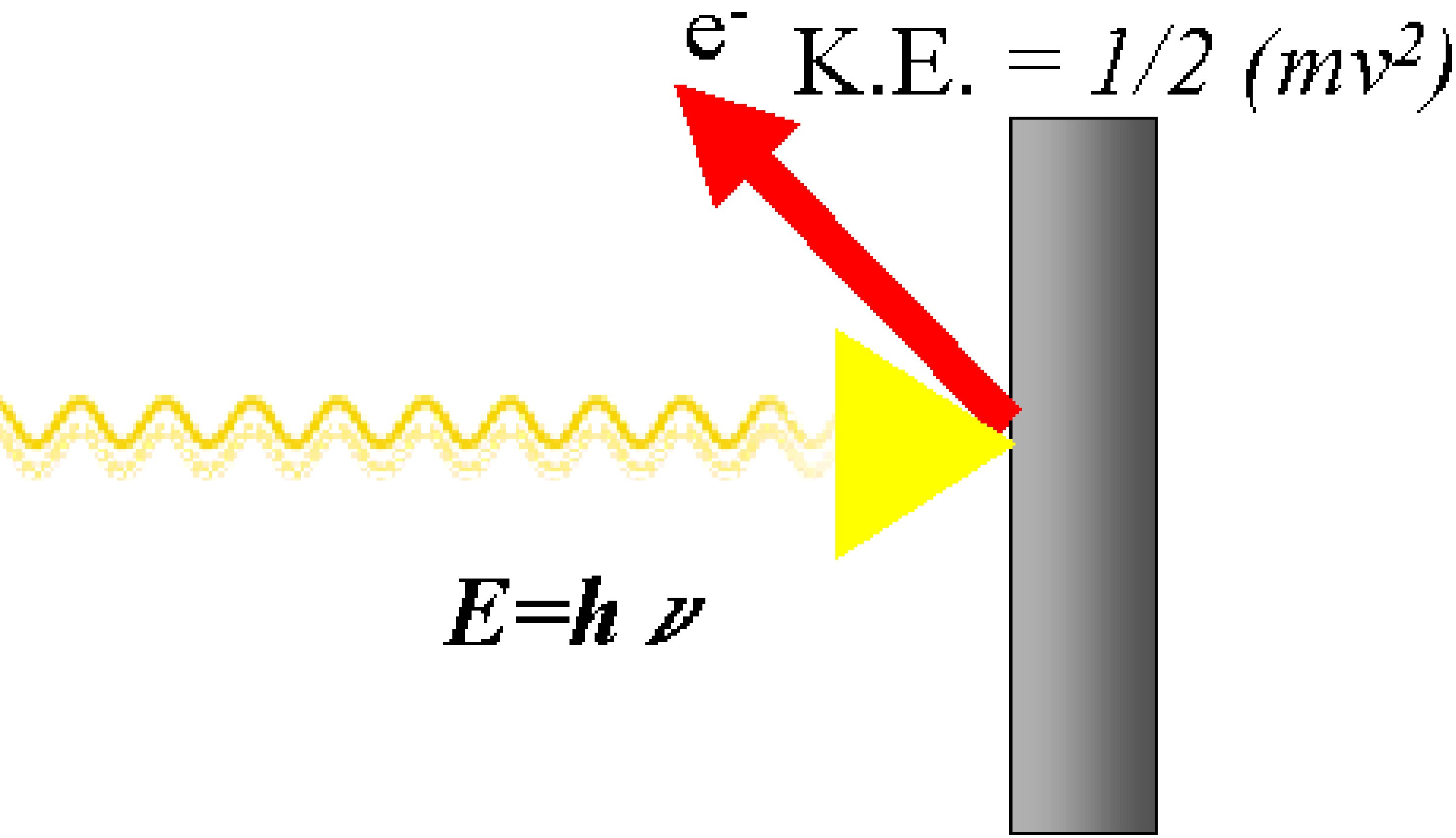


- Certain experiments done in late 19th century and early in this century gave results, totally at variance with the predictions of classical physics. All however, could be explained on the basis that, classical physics is wrong in allowing systems to possess arbitrary amounts of energy. For example, **photoelectric effect**.

A young Max Planck was to give a lecture on radiant heat. When he arrived he inquired as to the room number for the Planck lecture. He was told, "You are much too young to be attending the lecture of the esteemed professor Planck."

- Max Planck $E = h\nu$

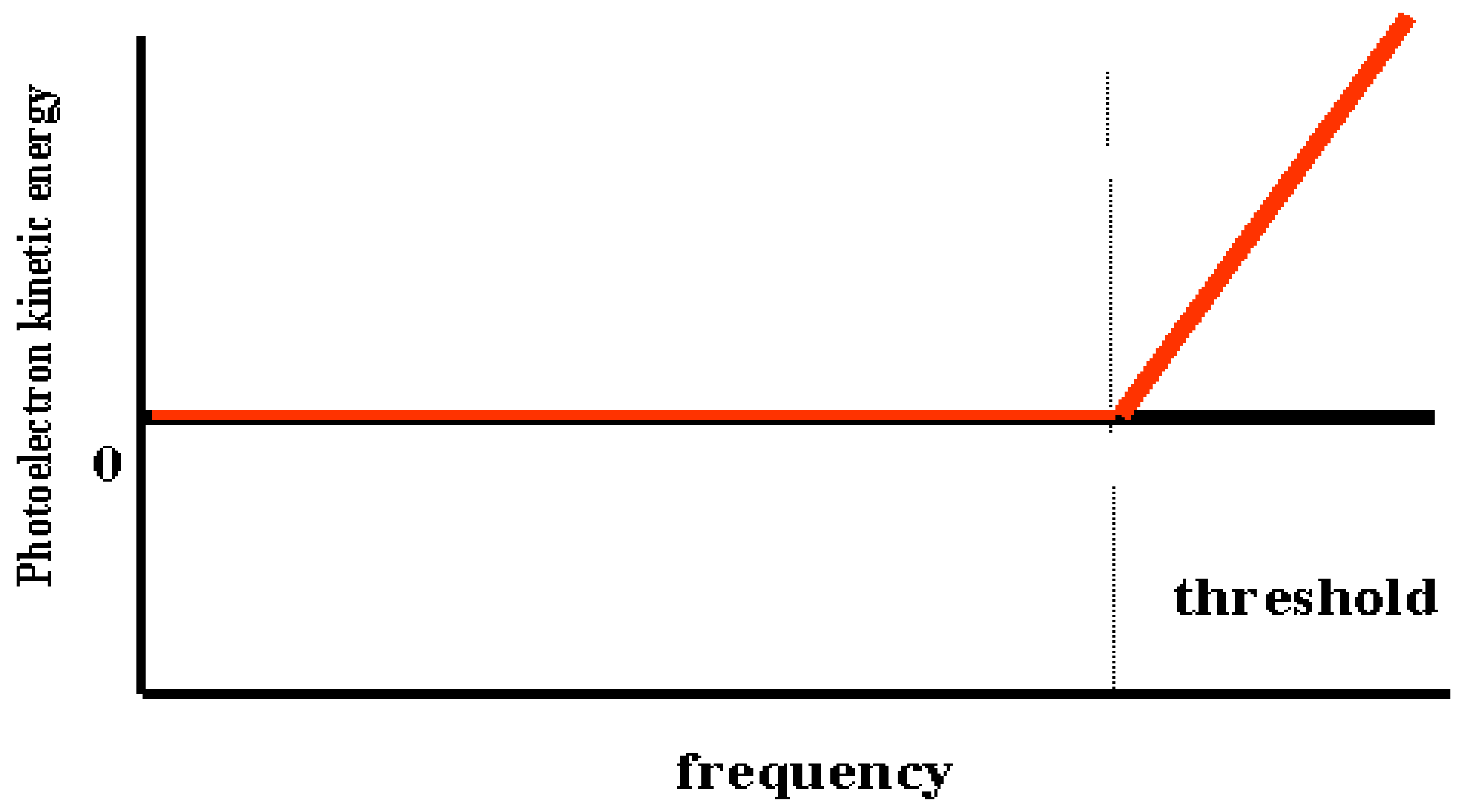
Photoelectric Effect



e^- K.E. = $1/2\ (mv^2)$

$E = h\,\nu$

Photoelectric Effect.

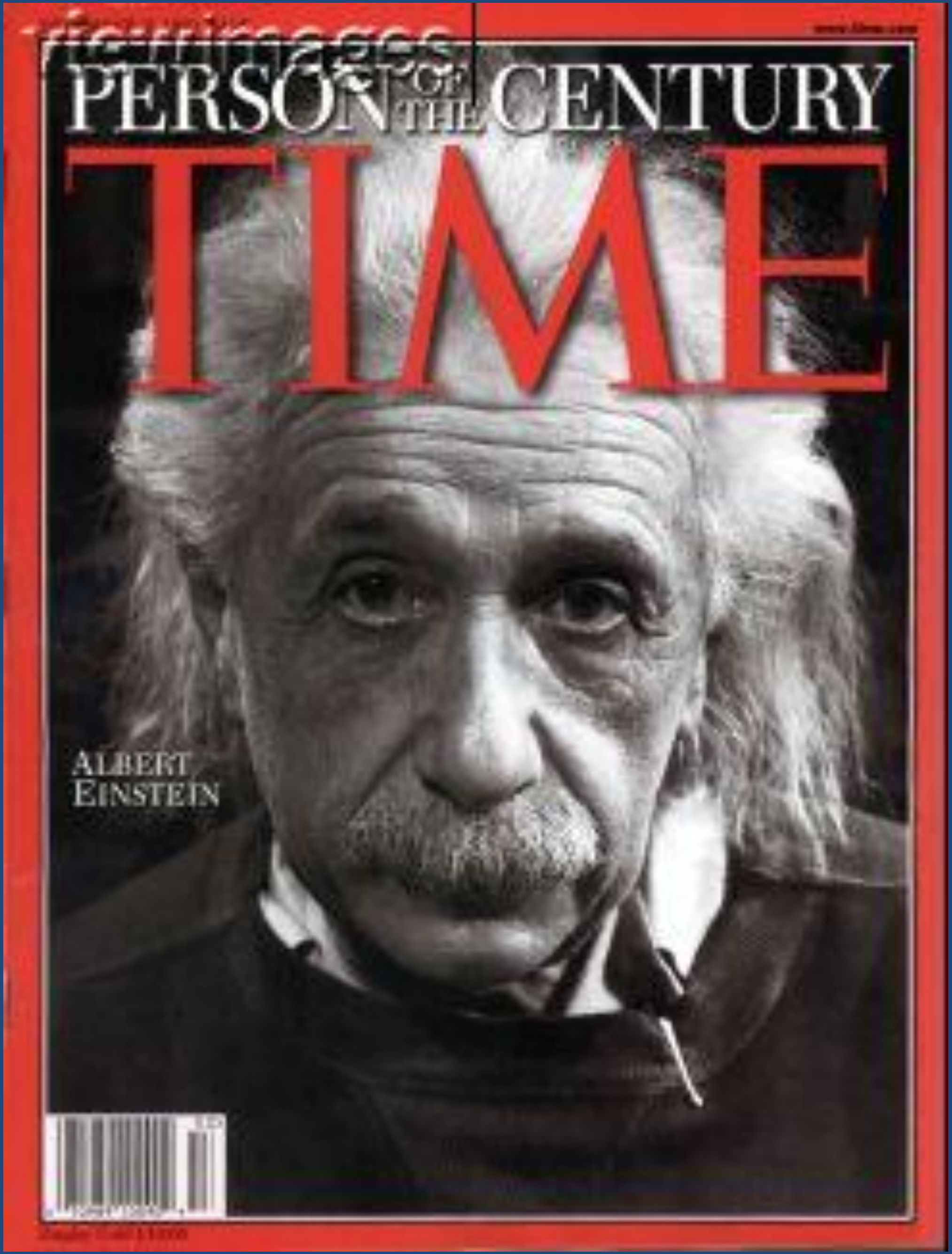


Major objections to the Rutherford-Bohr model

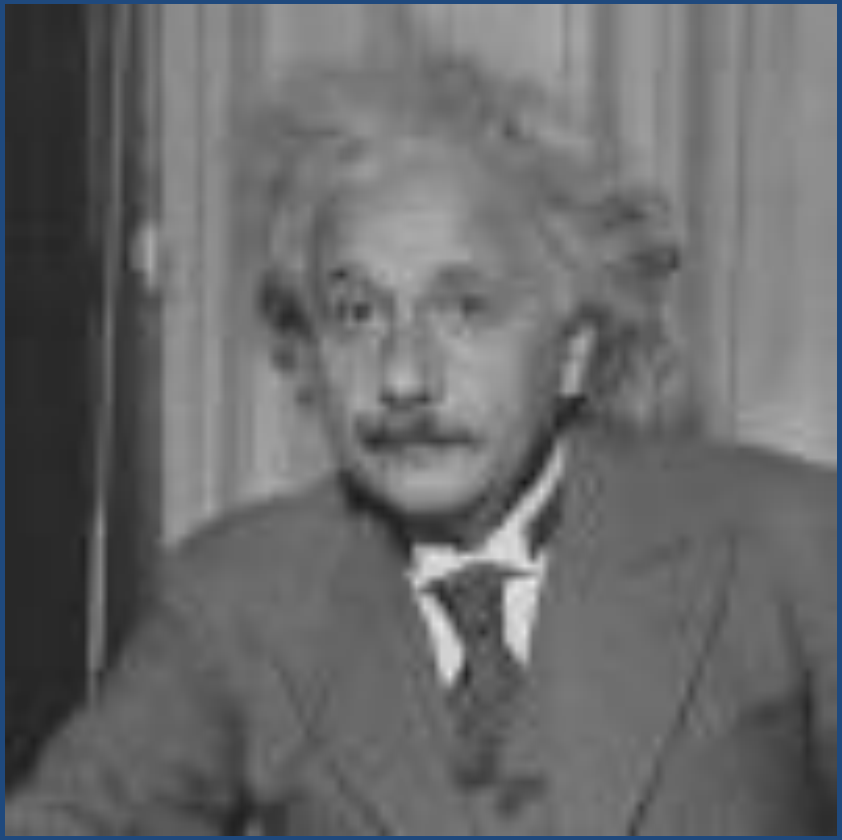
- **We are able to define the position and velocity of each electron precisely.**
- **In principle we can follow the motion of each individual electron precisely like planet.**

- **Neither is valid.**

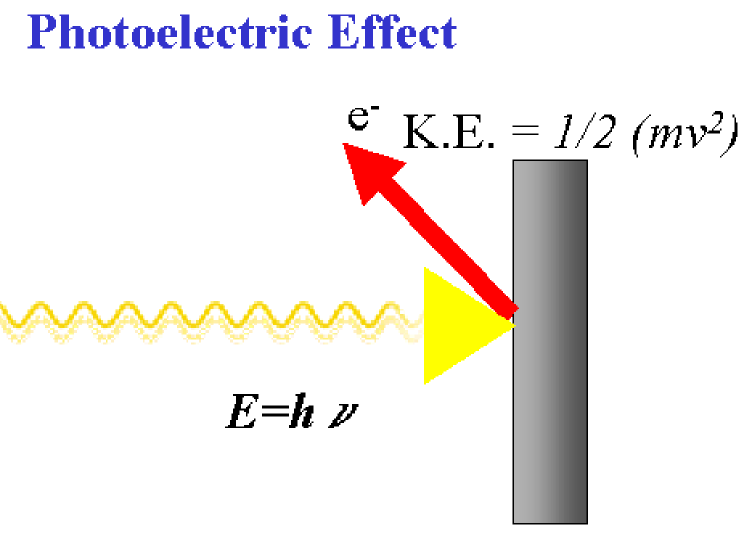
- **It is impossible to specify the exact position and momentum of a particle simultaneously.**
- **Uncertainty Principle.**
- **$\Delta x\ \Delta p \geq h/4\pi$ where *h* is Plank’s Constant, a fundamental constant with the value 6.626×10^{-34} J s.**


PERSON OF THE CENTURY
TIME
ALBERT EINSTEIN

Einstein could never accept some of the revolutionary ideas of quantum mechanics**("God does not play dice").** When reminded in 1927 that he revolutionized science 20 years earlier, Einstein replied, "A good joke should not be repeated too often."



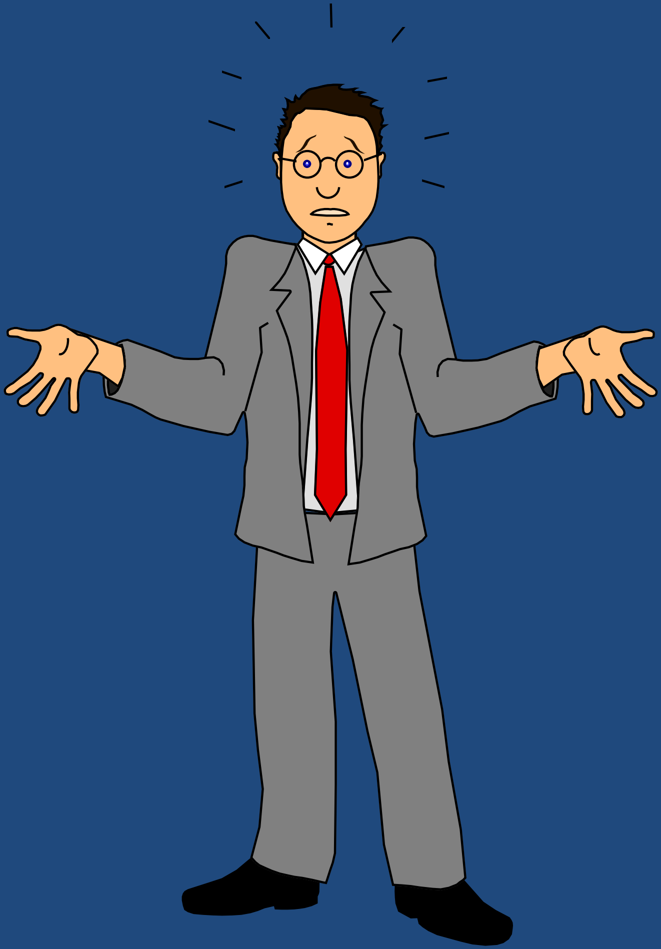
Einstein


Photoelectric Effect
e^-
K.E. = $1/2\ (mv^2)$
$E=h\ \nu$

KE $1/2mv^2 = h\nu - \phi$

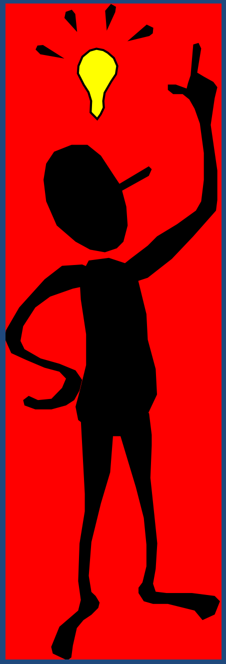
- ϕ is the work function
- $h\nu$ is the energy of the incident light.
- Light can be thought of as a bunch of particles which have energy $E = h\nu$. The light particles are called photons.

If light can behave as particles,why not particles behave as wave?



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.

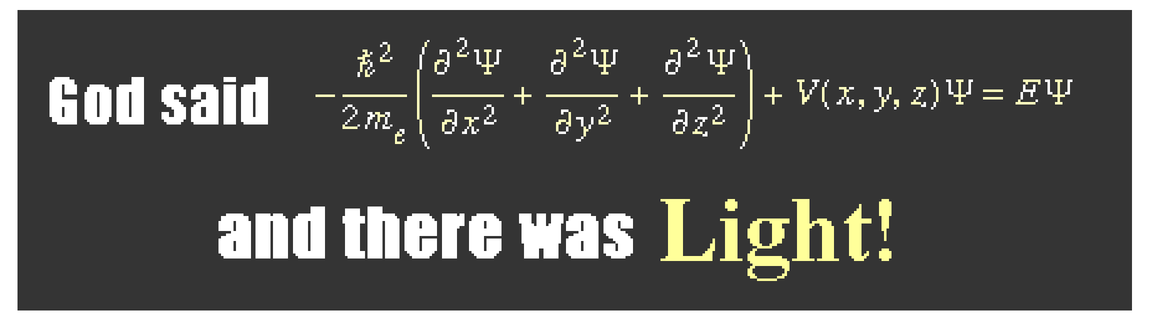


- $E = mc^2 = h\nu$
- $mc^2 = h\nu$
- $p = h/\lambda$ { since $\nu = c/\lambda$ }
- $\lambda = h/p = h/mv$
- **This is known as wave particle duality**

Wave equation?

SchrÖdinger Equation.

- **Energy Levels**
- Most significant feature of the Quantum Mechanics: Limits the energies to **discrete values**.
- **Quantization.**



God said $-\frac{\hbar^2}{2m_e}\left(\frac{\partial^2\Psi}{\partial x^2}+\frac{\partial^2\Psi}{\partial y^2}+\frac{\partial^2\Psi}{\partial z^2}\right)+V(x,y,z)\Psi=E\Psi$

and there was Light!

Classical Equation: Electromagnetic Radiation:

$$\frac{\partial^2 u}{\partial x^2} = \frac{1}{v^2}\frac{\partial^2 u}{\partial t^2}$$

u = Amplitude

Separate Variables

$$u(x,t) = \psi(x) f(t)$$

$$f(t)\frac{d^2\psi(x)}{dx^2} = \frac{1}{v^2}\psi(x)\frac{d^2 f(t)}{dt^2}$$

Introduce standard wave equation solution for *f(t)* $e^{i\omega t}$

We can write

$$\frac{d^2\psi(x)}{dx^2} = \frac{-\omega^2}{v^2}\psi(x)$$

Total Energy

$$E = \frac{p^2}{2m} + V(x)$$

Solution

$$p = \{2m[E - V(x)]\}^{1/2}$$

From de Broglie Equation

$$\lambda = \frac{h}{p} = \frac{h}{\{2m[E - V(x)]\}^{1/2}}$$

ω^2/v^2 in terms of λ

$\omega = 2\pi\upsilon$ and $\nu\lambda = v$

$$\frac{\omega^2}{v^2} = \frac{4\pi^2\nu^2}{v^2} = \frac{4\pi^2}{\lambda^2} = \frac{2m[E - V(x)]}{\hbar^2}$$

Therefore form

$$\frac{d^2\psi(x)}{dx^2} = \frac{-\omega^2}{v^2}\psi(x)$$

$$\frac{d^2\psi(x)}{dx^2} + \frac{2m}{\hbar^2}[E - V(x)]\psi(x) = 0$$

$$-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} + V(x)\psi(x) = E\psi(x)$$

Schroedinger Equation in One Dimension

$$-\frac{\hbar^2}{2m}\nabla^2\psi(\mathbf{r}) + V(\mathbf{r})\psi(\mathbf{r}) = E\psi(\mathbf{r})$$

Schroedinger Equation in Three dimension

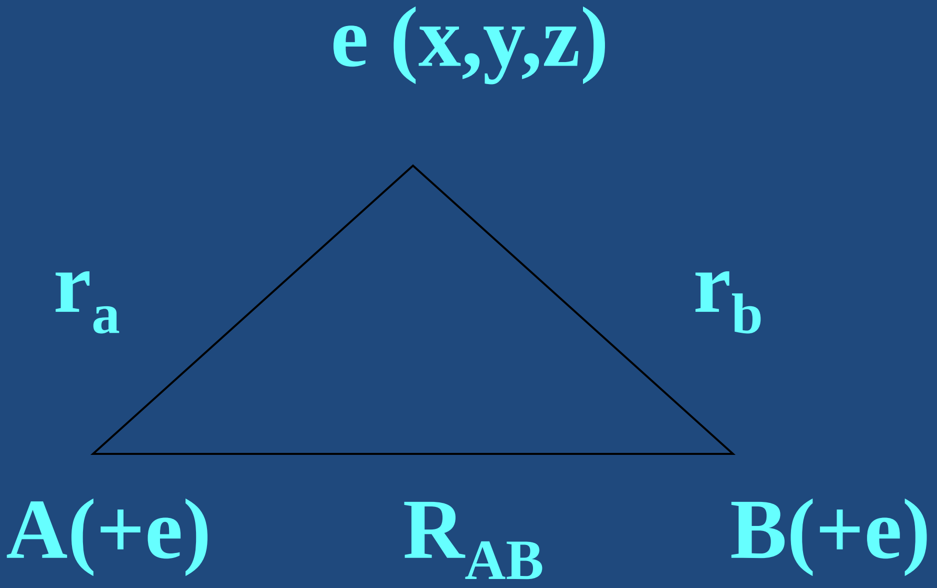
$H\psi = E\psi$

- **$H = -\hbar^2/2m\,\nabla^2 + V$; Hamiltonian operator**

How to write Hamiltonian for different systems?

- **Hydrogen atom:**
- **KE = ½ m $(v_x^2 + v_y^2 + v_z^2)$**
- **PE = $-e^2/r$, (r = distance between the electron and the nucleus.)**
- **$H = \{(-h^2/8\pi^2 m)\nabla^2 - e^2/r\}$**
- **$\nabla^2\Psi + 8\pi^2 m/h^2 (E+e^2/r)\Psi = 0$**
- **If the effective nuclear charge is Ze**
    - **$H = \{(-h^2/8\pi^2 m)\nabla^2 - Ze^2/r\}$**

H_2^+ molecule



e (x,y,z)

r_a

r_b

A(+e)

R_{AB}

B(+e)

- PE = V = $-e^2/r_a - e^2/r_b + e^2/R_{ab}$
- H = $-h^2/8\pi^2 m \nabla^2(- e^2/r_a - e^2/r_b + e^2/R_{ab})$

- The Wave equation is

- $\nabla^2 \Psi + 8\pi^2 m/h^2 (E + e^2/r_a + e^2/r_b - e^2/R_{ab}) \Psi = 0$

- **Characteristics of Wave Function** Born has been described as a moody and impulsive person. He would tell his student, "You must not mind my being rude. I have a resistance against accepting something new. I get angry and swear but always accept after a time if it is right."

Characteristics of Wave Function

- Heisenberg's Uncertainty principle: We can never know exactly where the particle is.
- Let ρ (x, y, z) be the probability function,
    - $\int \rho \, d\tau = 1$
- Our knowledge of the position of a particle can never be absolute.

Connection with Wave Function

- **Let Ψ (x, y, z) be the solution of the wave equation for the wave function. Then we may anticipate that**
- **ρ (x, y, z) $\propto \Psi^2$ (x, y, z)**
- **Choosing a constant in such a way that the $\propto$ is converted to =**
  - **ρ (x, y, z) = Ψ^2 (x, y, z)**
  - **$\therefore \int \Psi^2 \, d\tau = 1$**

- **Normalized wave function.**
- **If the function is not:**
- **$1/N^2 = \int \Psi^2(x, y, z)\, d\tau$**

- **If Ψ is complex then Ψ^2 is replaced by $\Psi\Psi^*$.**

Unacceptable and Acceptable wave functions:

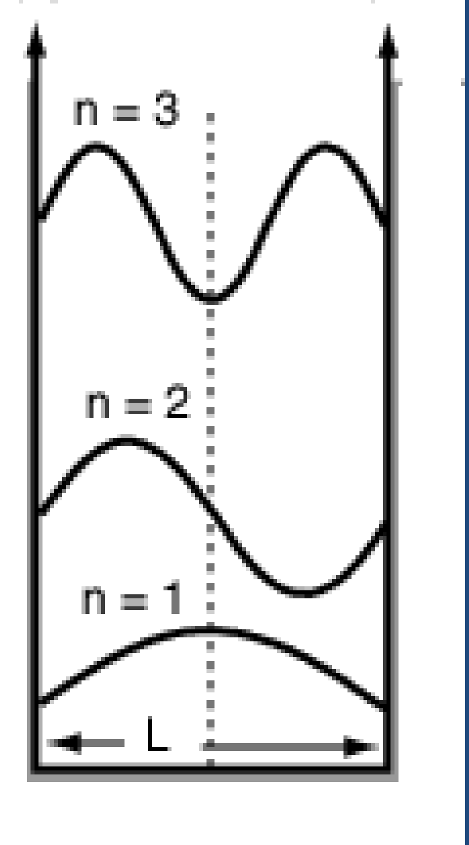
- Acceptable:
  - .For electron bound to an atom/molecule, the wave function must be every where *finite*.
  - *.Single valued.*
  - *.Continuous.*
  - *.Gradient* (dΨ/dt) *must be finite*
  - .$\int \Psi^2$ dτ *is finite*, so that Ψ can be normalized.
- Stationary States
- E = Eigen Value ;Ψ is Eigen Function

One Dimensional Box

- V = ∝

a

V = ∝



- V

V

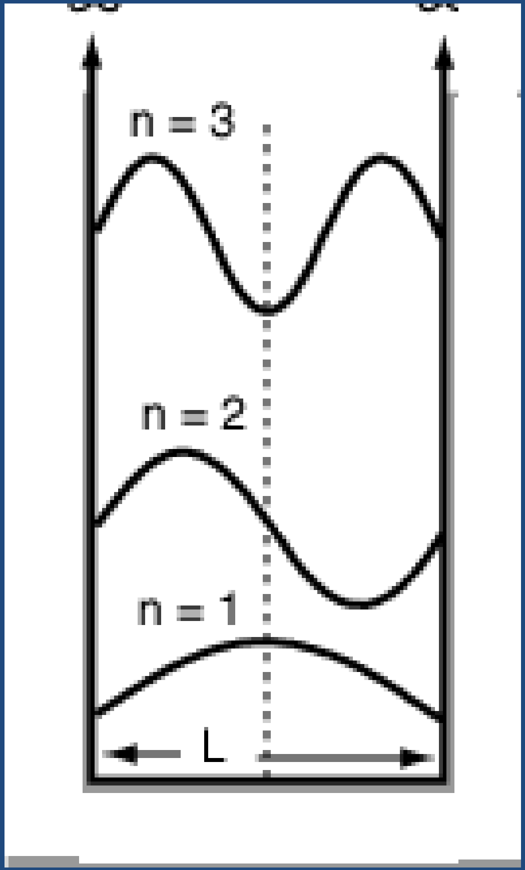
-

- x = 0

x = a

The Wave Eqn. is

- $d^2\Psi/dx^2 + 8\pi^2 m/h^2[E\Psi] = 0$
- $d^2\Psi/dx^2 + k^2\Psi = 0$
- $k^2 = 8\pi^2 m/h^2[E]$
- Solution is
- $\Psi = C \cos kx + D \sin kx$
- Applying Boundary conditions:
- $\Psi = 0$ at $x = 0 \Rightarrow C = 0$
- $\Psi = 0$ at $x = a$



- $\Psi = 0$ at $x = a$
- $D \sin ka = 0$
- $\sin ka = 0$ or $ka = n\pi$
- $n = 0, 1, 2, 3, 4$…….
- $\Psi_n = D \sin (n\pi/a)x$
- $k^2 = 8\pi^2 m/h^2[E]$ or $E = k^2h^2/ 8\pi^2 m$
- $E = n^2 h^2/ 8ma^2$
- $n = 0$ not acceptable: $\Psi_n = 0$
- Lowest kinetic Energy = $E_0 = h^2/8ma^2$

Need for Effective Approximate Method of Solving the Wave Equation.

- Born Oppenheimer Principle.
- How can we get the most suitable approximate wave function?
- How can we use this approximate wave function to calculate energy E?

Variation Method

- $H\Psi = E\Psi$
- $\Psi\ H\Psi = \Psi\ E\Psi = E\Psi\ \Psi$
- $E = \int \Psi H\ \Psi\ d\tau / \int \Psi^2\ d\tau$
- If Ψ is complex, $E = \int \Psi^* H\ \Psi\ d\tau / \int \Psi^*\ \Psi d\tau$
- $<\Psi/H/\ \Psi>\ /<\Psi/\ \Psi>$ ……4
- *Bra-Ket notation*

- E can be calculated. If the wave function is not known, we can either make an educated guess or use *Variation Theorem*.
- The nature of the equation 4 suggest that even if Ψ is not correct, we should consider a quantity *E* with dimension of energy, which is related to Ψ by

- $E = <\Psi/H/\Psi> / <\Psi/\Psi>$

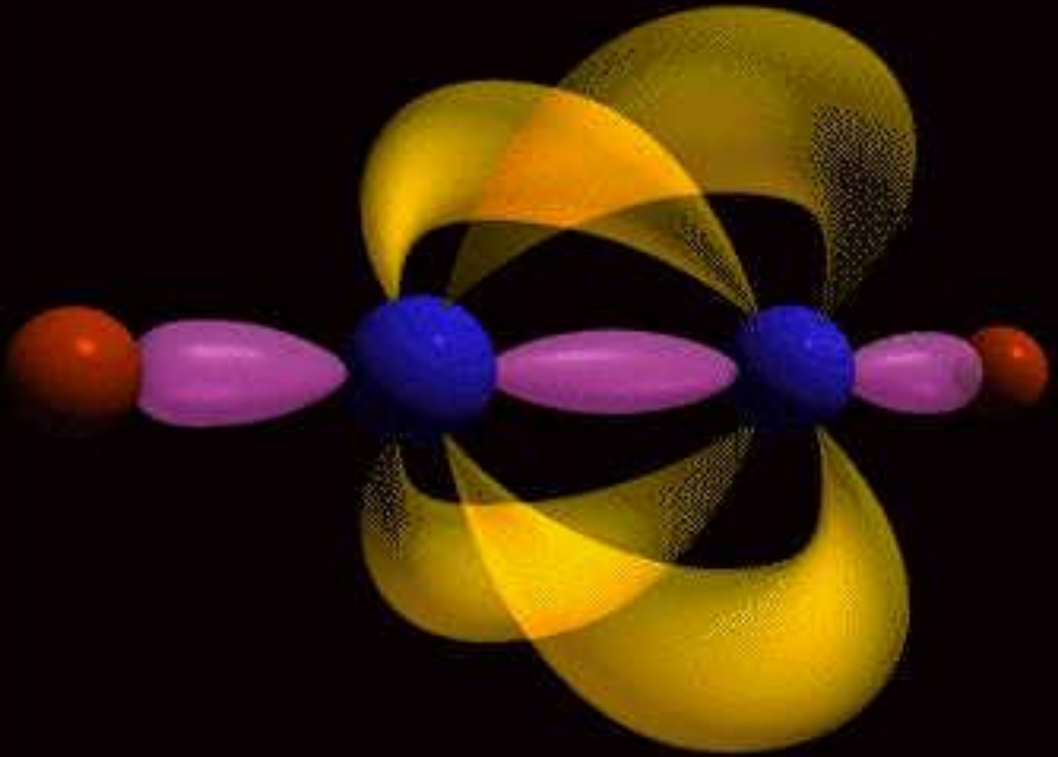
- $\Psi_1 \Rightarrow E_1$
- $\Psi_2 \Rightarrow E_2$
- The Variation Theorem tells that
- $E_1, E_2 > \mathrm{E}_g$, E_g ground state energy
- $E_1 > E_2$,
- E_2 and Ψ_2 is the better approximation.

- **We can chose a whole family of wave function at the same time, like trial function with one or more variable parameters C_1, C_2, C_3,….**
- **Then *E* is function of C_1, C_2, C_3 …….etc. C_1, C_2, C_3 …. Etc. are such that *E* is minimized with respect to them.**
- **We will utilize this method in explaining chemical bonding.**

Chemical Bonding

- **Two existing theories,**
- **Molecular Orbital Theory (MOT)**
- **Valence Bond Theory (VBT).**
- ***Molecular Orbital Theory***
- **MOT starts with the idea that the quantum mechanical principles applied to atoms may be applied equally well to the molecule**

Bonding in ethyne



We can write the following principles

- Each electron in a molecule is described by a certain wave function Ψ - Molecular Orbital (MO).
- Each Ψ is defined by certain quantum numbers, which govern its energy and its shape.
- Each Ψ is associated with a definite energy value.
- Each electron has a spin, ± ½ and labeled by its spin quantum number m_s.

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

Simplest possible molecule - H_2^+ two nuclei and a single electron.

- **Let the two nuclei be labeled as A and B. 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 $\Psi = N(\Psi_A + \lambda\, \Psi_B)$**
- **$\lambda = C_A/C_B$, 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 $\Psi_A + \Psi_B$ we can now calculate the energy

- **From Variation Theorem we can write the energy function as**

- **$E = <\Psi_A+\Psi_B/H/\Psi_A+\Psi_B>/<\Psi_A+\Psi_B/\ \Psi_A+\Psi_B>$**

Let us take the nominator of the right hand side of the above equation:

- $<\Psi_A+\Psi_B/H/\Psi_A+\Psi_B> = <\Psi_A/H/\Psi_A> +$
- $<\Psi_B/H/\Psi_B> +$
- $<\Psi_A/H/\Psi_B> +$
- $<\Psi_B/H/\Psi_A>$
- $= <\Psi_A/H/\Psi_A> + <\Psi_B/H/\Psi_B> + 2<\Psi_A/H/\Psi_B>$
- **Now $<\Psi_A/H/\Psi_A>$ or $<\Psi_B/H/\Psi_B>$ is the ground state energy of a hydrogen atom**

Now $<\Psi_A/H/\ \Psi_A>$ or $<\Psi_B/H/\ \Psi_B>$ is the ground state energy of a hydrogen atom

- let us call this as E_A
- $<\Psi_A/H/\ \Psi_B> \ = <\Psi_B/H/\ \Psi_A> = \beta\ =$ resonance integral.

The denominator:

- $<\Psi_A+\Psi_B/\ \Psi_A+\Psi_B> \ = <\Psi_A/\Psi_A> +$
- $<\Psi_B/\Psi_B> +$
- $<\Psi_A/\Psi_B> +$
- $<\Psi_B/\Psi_A>$
- $= \ <\Psi_A/\Psi_A> + <\Psi_B/\Psi_B> + 2<\Psi_A/\Psi_B>$
- $<\Psi_A/\Psi_B> = <\Psi_B/\Psi_A> = S$, **Overlap integral. Also we know that Ψ_A and Ψ_B are separately normalized, so $<\Psi_A/\Psi_A> = <\Psi_B/\Psi_B> = 1$**

- $E = [2E_A + 2\beta] / 2(1 + S)$
- Or $E_+ = [E_A + \beta] / (1 + S)$
- Similarly, $E_- = [E_A - \beta] / (1 - S)$
- Numerically S is very small, so if we neglect S, we can write
- $E_\pm = E_A \pm \beta$

Energy level diagram

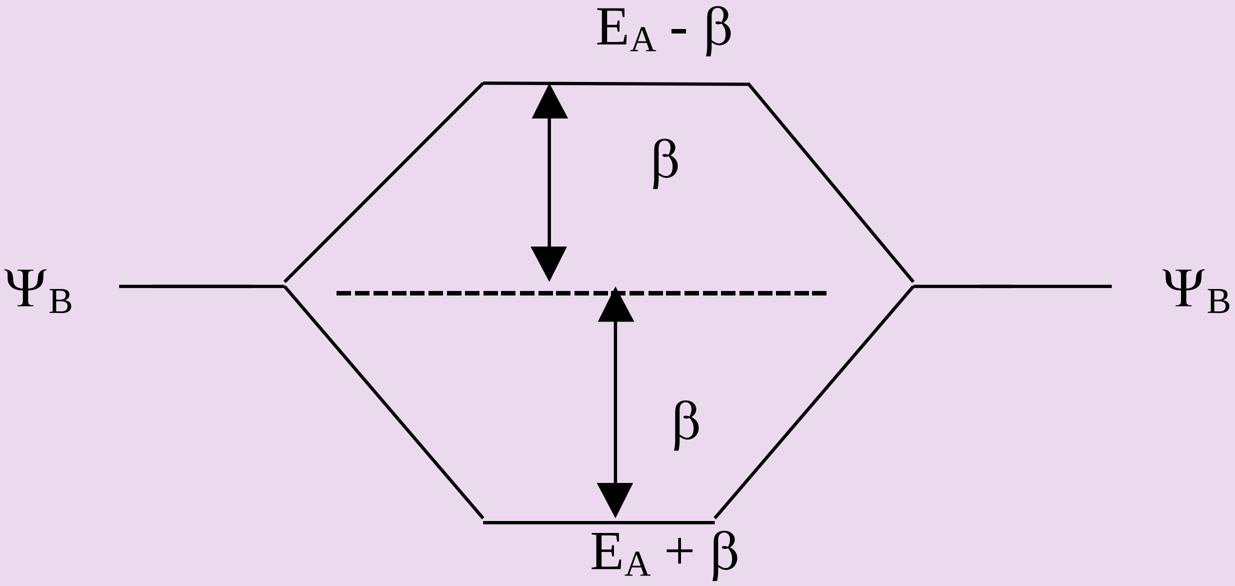
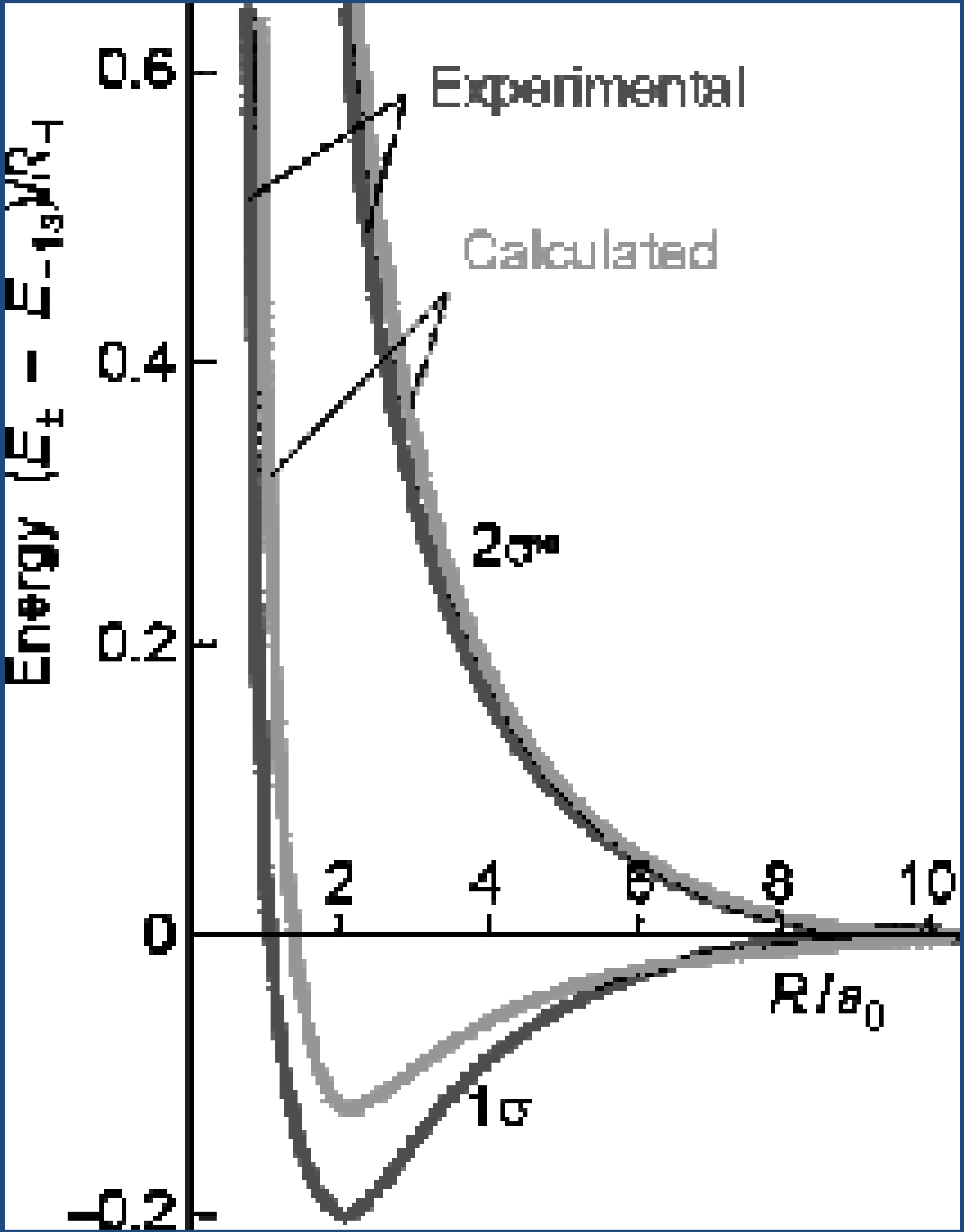
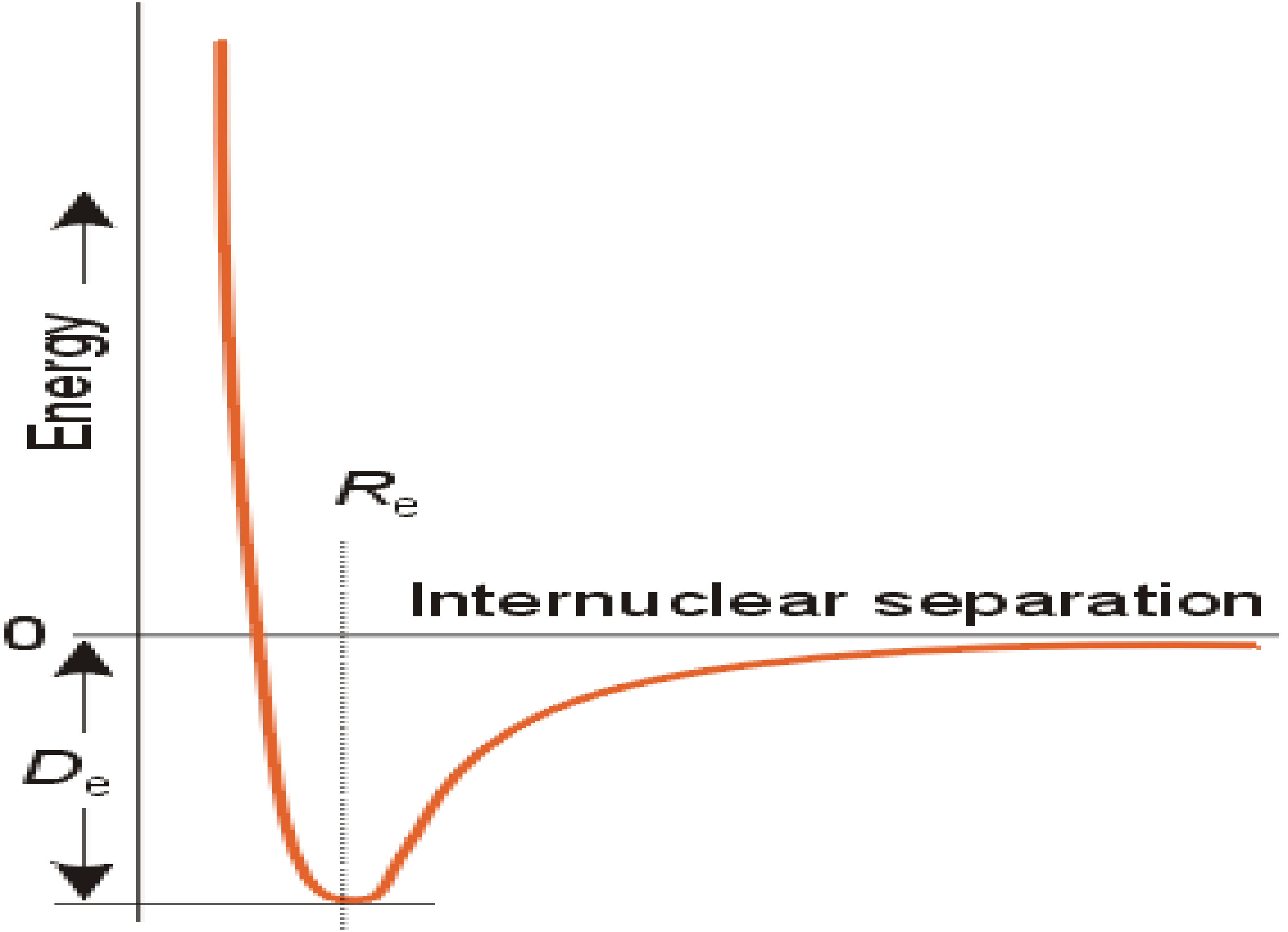
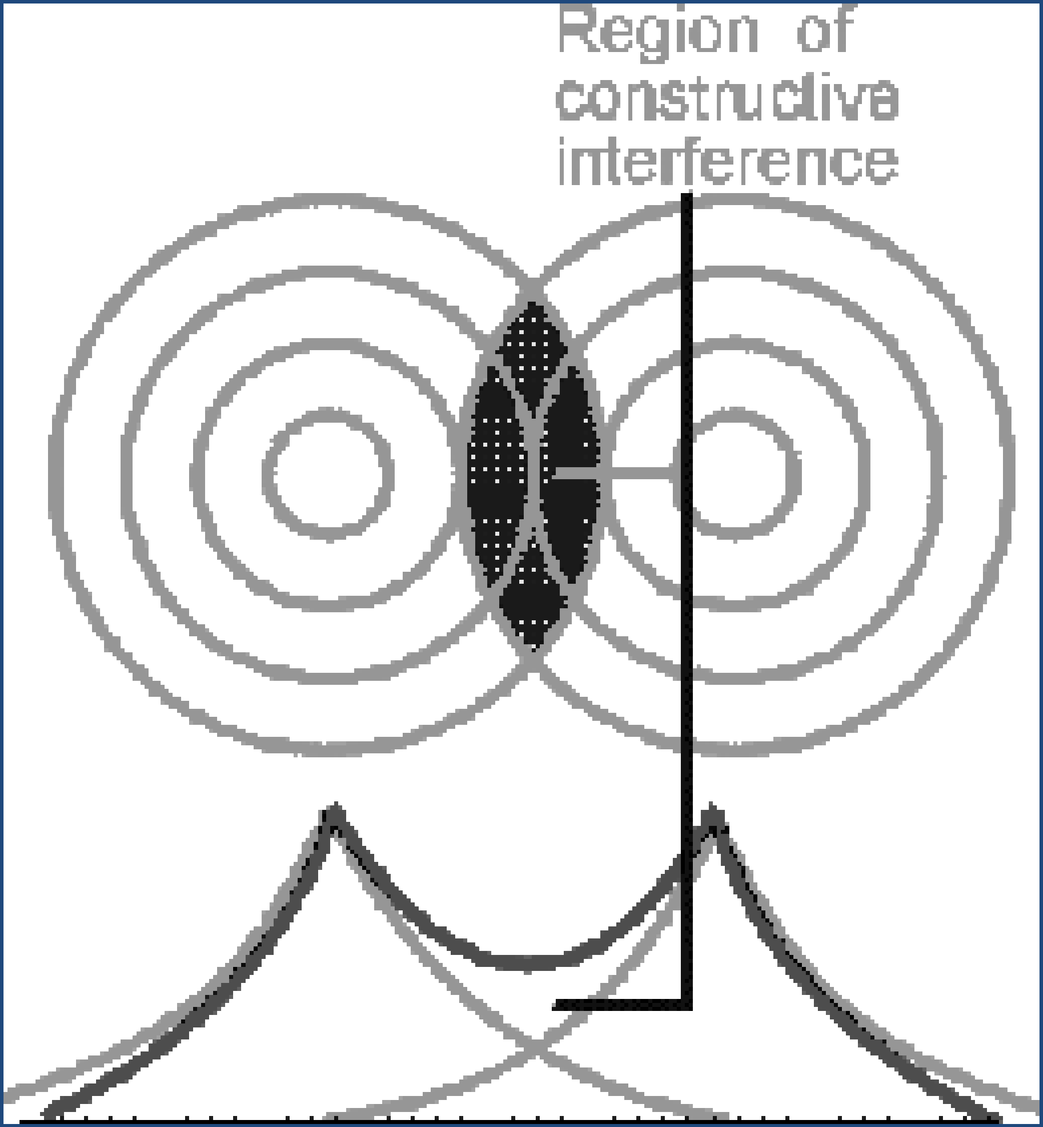
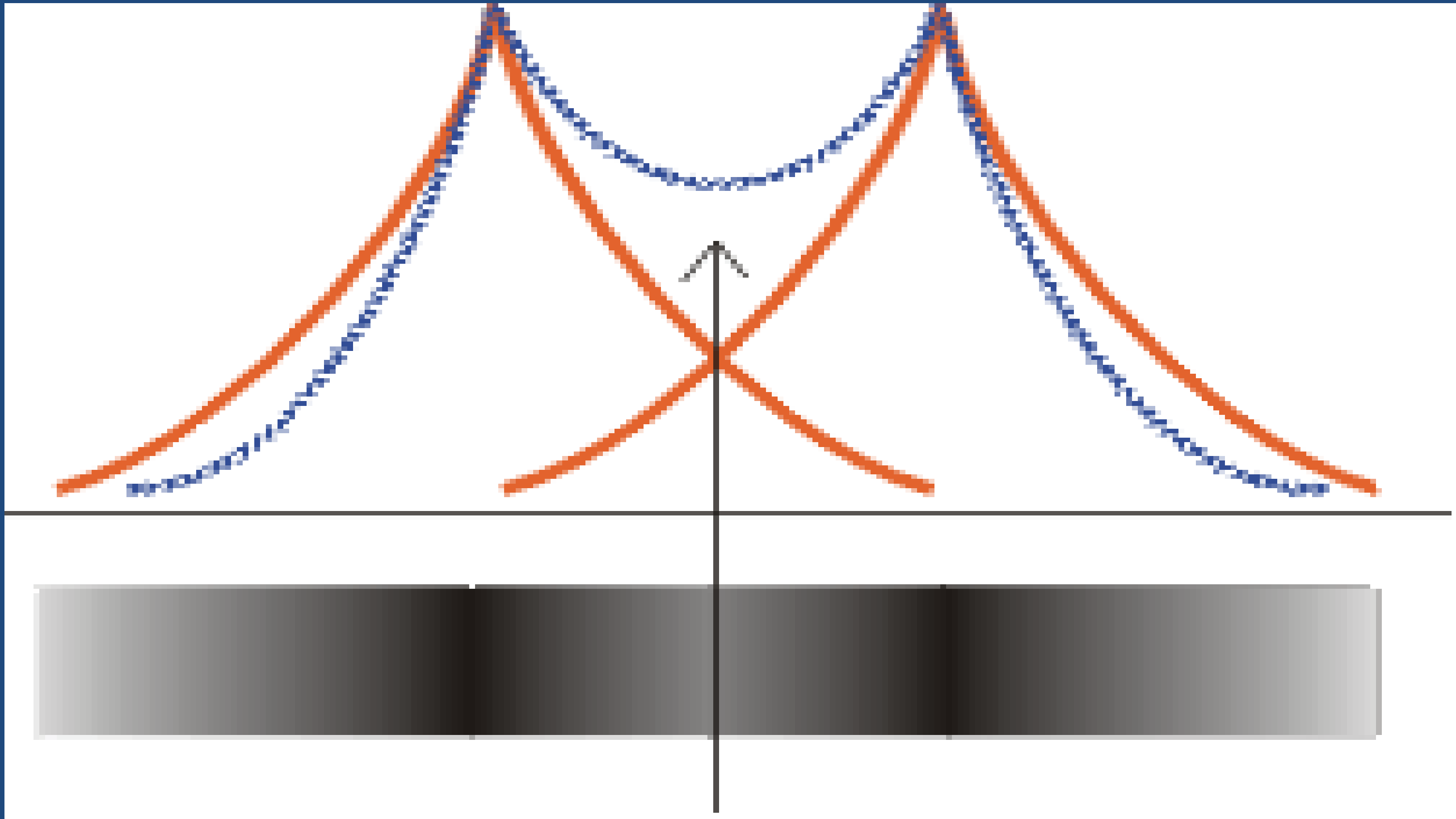

$E_A - \beta$
β
Ψ_B
Ψ_B
β
$E_A + \beta$

Figure 5

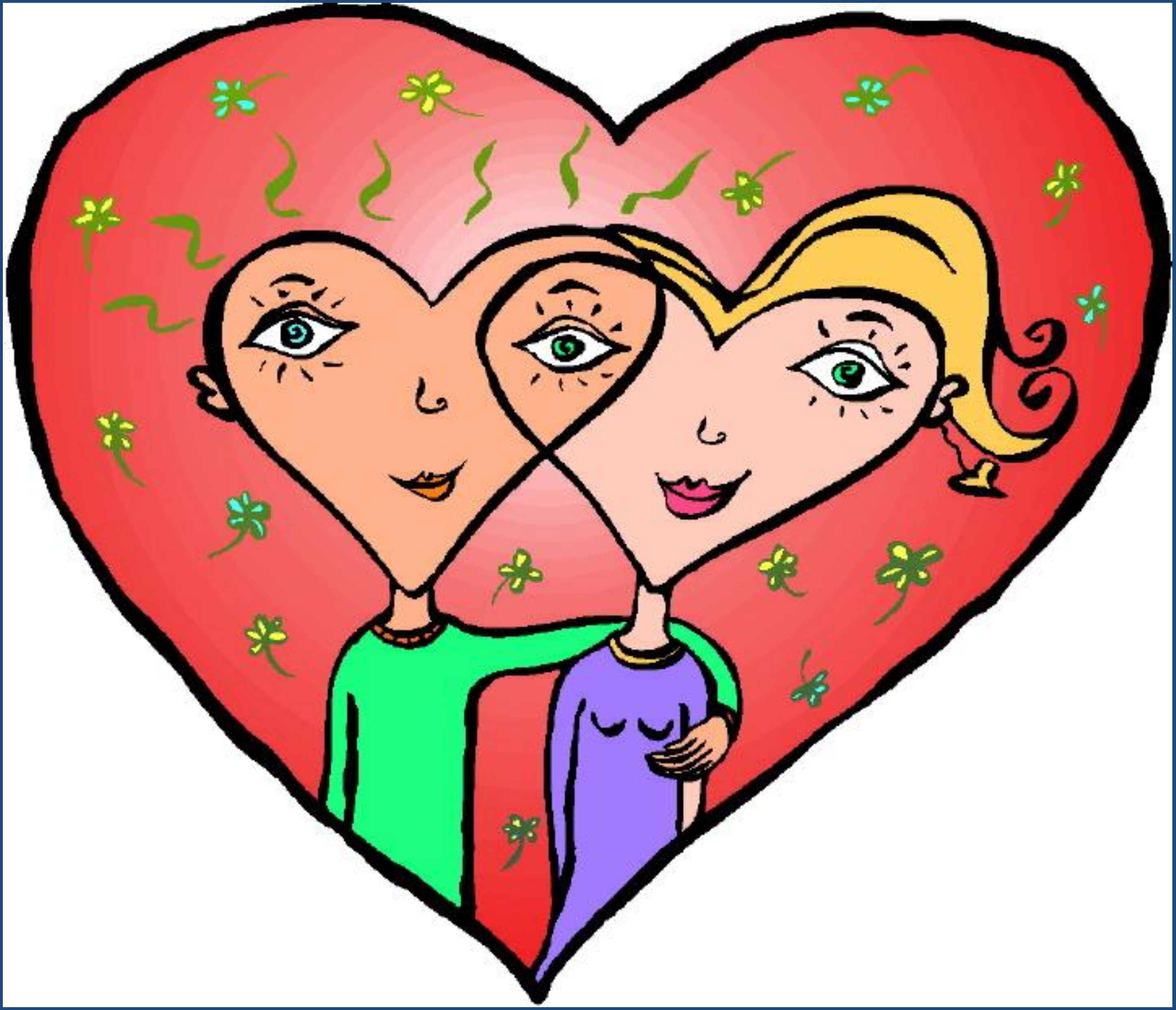

Experimental
Calculated
2σ*
1σ
Energy $(E_{\pm} - E_{1s})/E_h$
0.6
0.4
0.2
0
−0.2
2
4
6
8
10
R/a_0

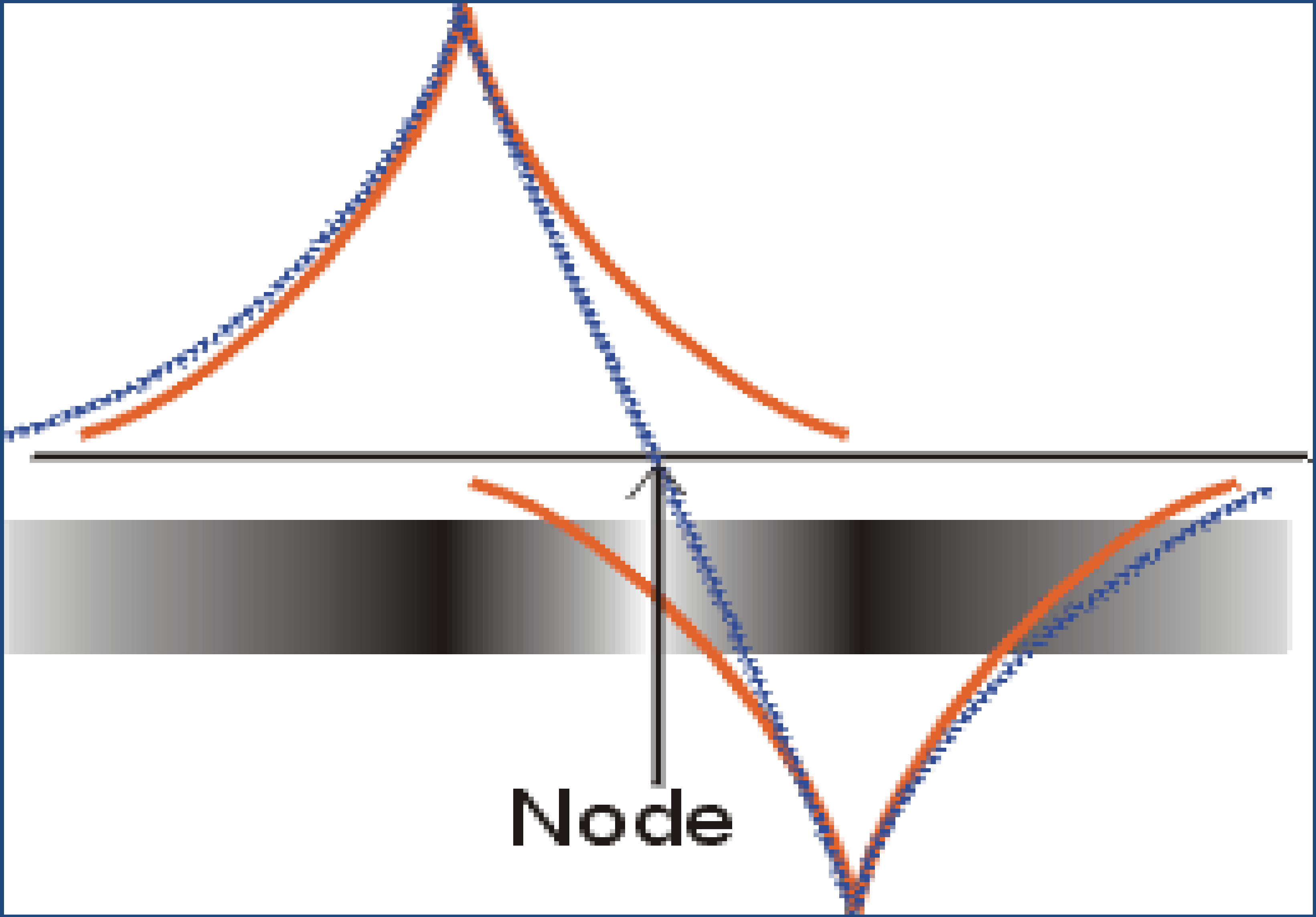

Energy
R_e
Internuclear separation
0
D_e


Region of constructive interference



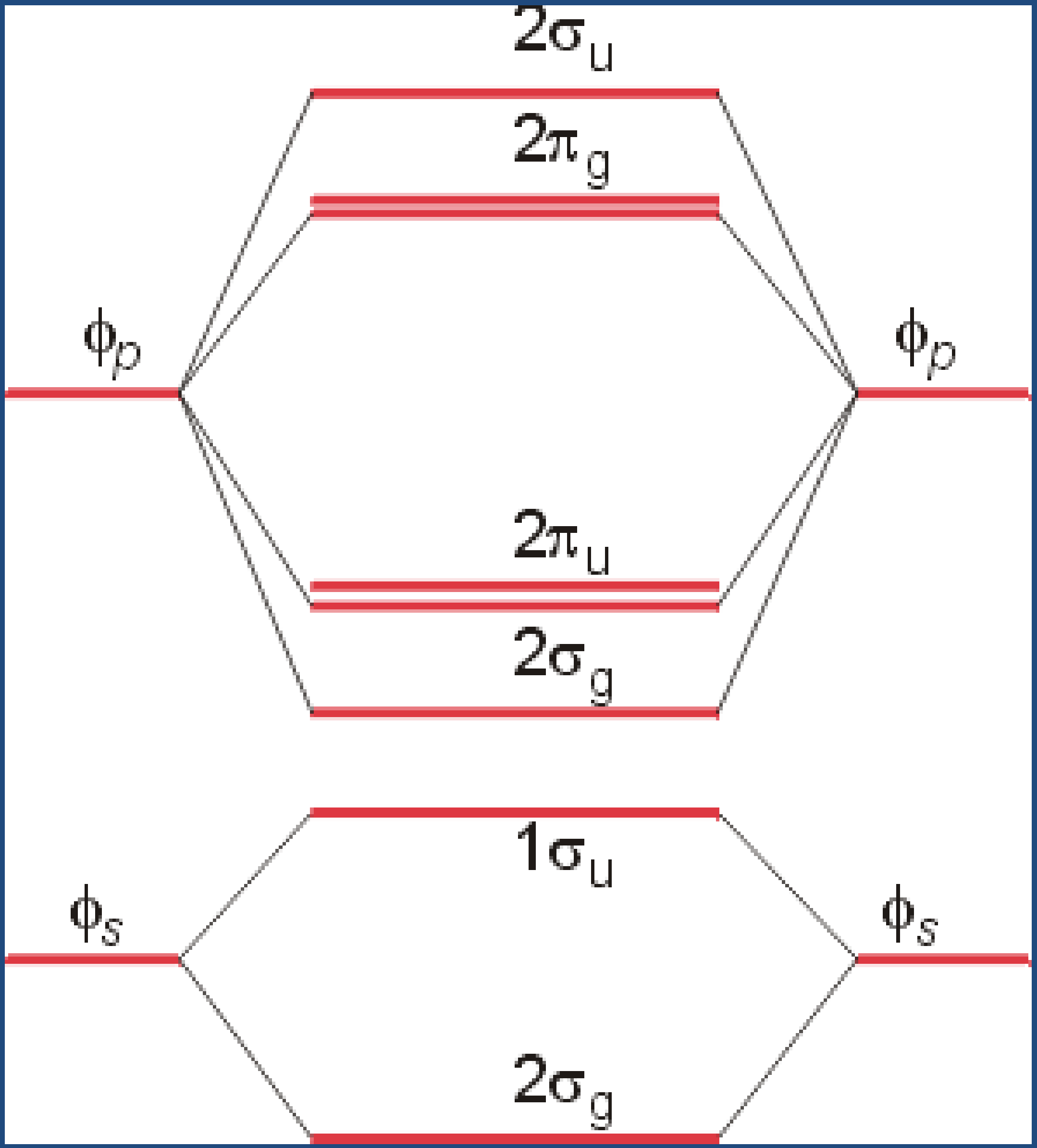
Enhanced density




Node

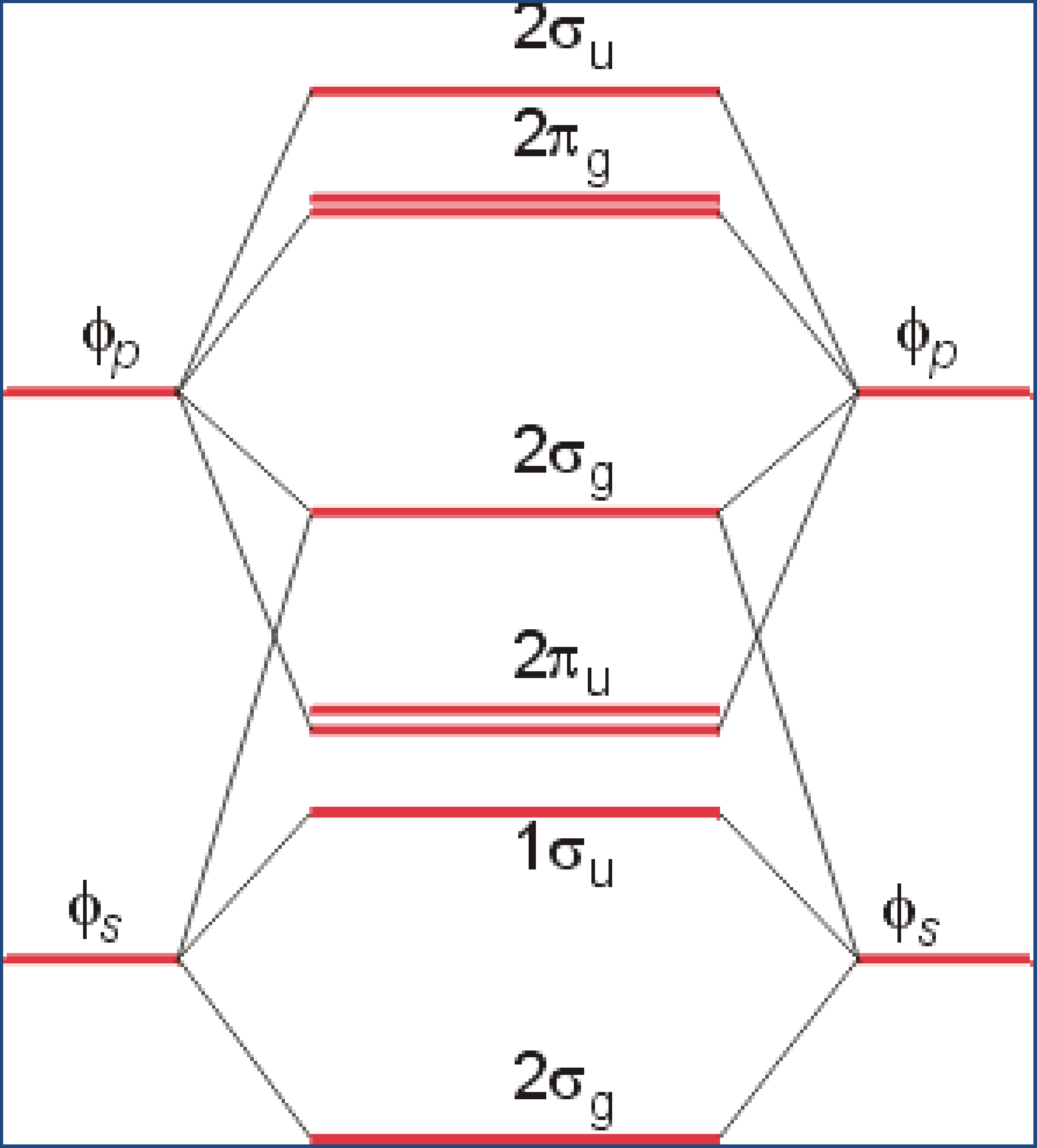
Homonuclear Diatomics

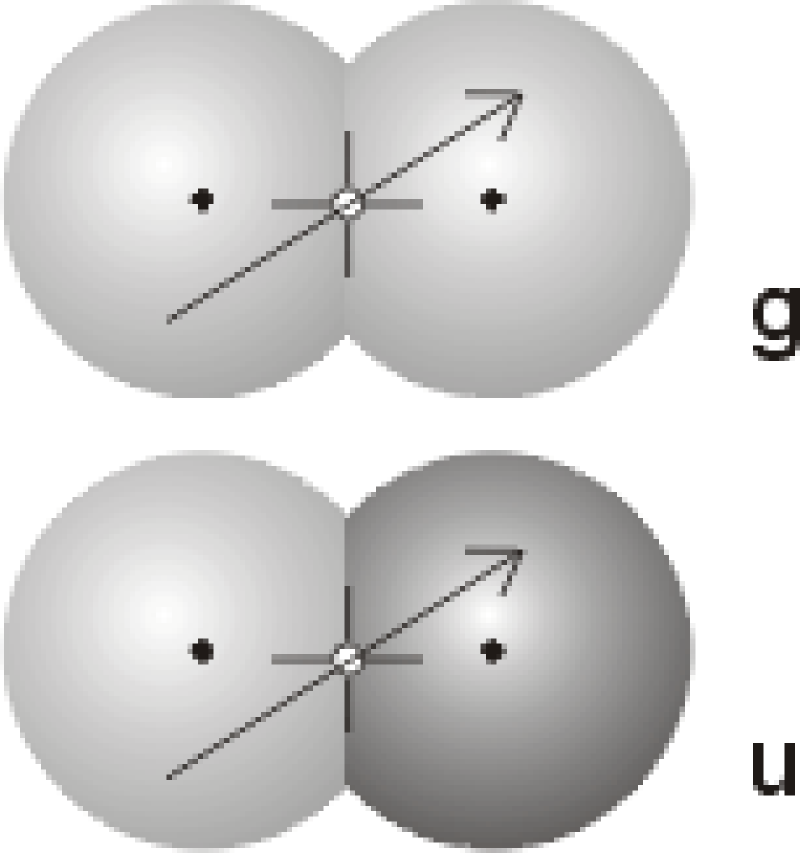
- **MOs may be classified according to- (i)Their symmetry around the molecular axis**
- **(ii)Their bonding and antibonding character.**
- **(iii) The atomic orbitals into which they separate at large internuclear distances.**
- $\sigma_{1s} < \sigma_{1s}^* < \sigma_{2s} < \sigma_{2s}^* < \sigma_{2p} < \pi_y(2p) = \pi_z(2p) < \pi_y^*(2p) = \pi_z^*(2p) < \sigma_{2p}^*$.


$2\sigma_u$
$2\pi_g$
ϕ_p
ϕ_p
$2\pi_u$
$2\sigma_g$
$1\sigma_u$
ϕ_s
ϕ_s
$2\sigma_g$

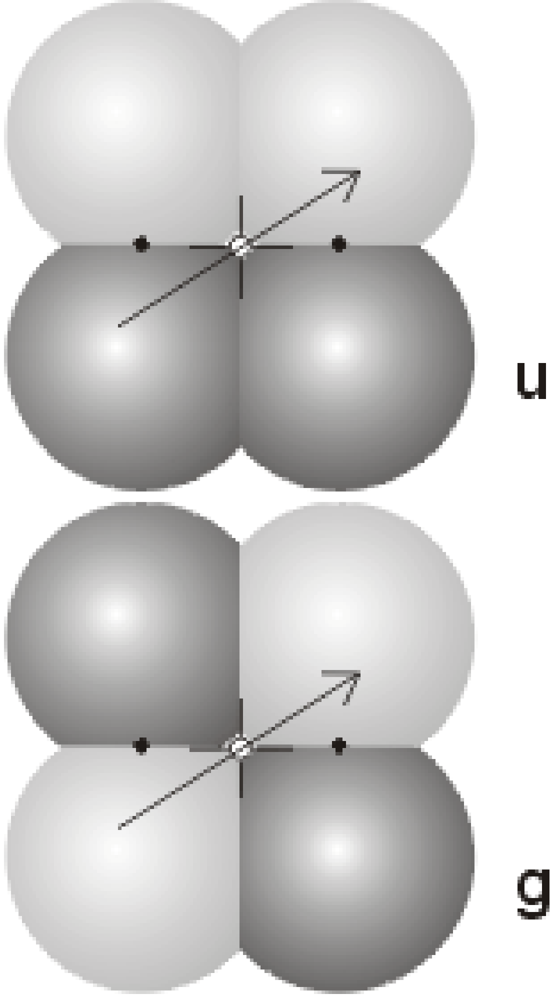
In drawing this diagram we have ignored one fact.

- We have assumed that there is no interaction between 2s and 2p orbitals.
- This is not true.
- Thus from Li to at least N there is strong interaction between the 2s and 2p orbitals.

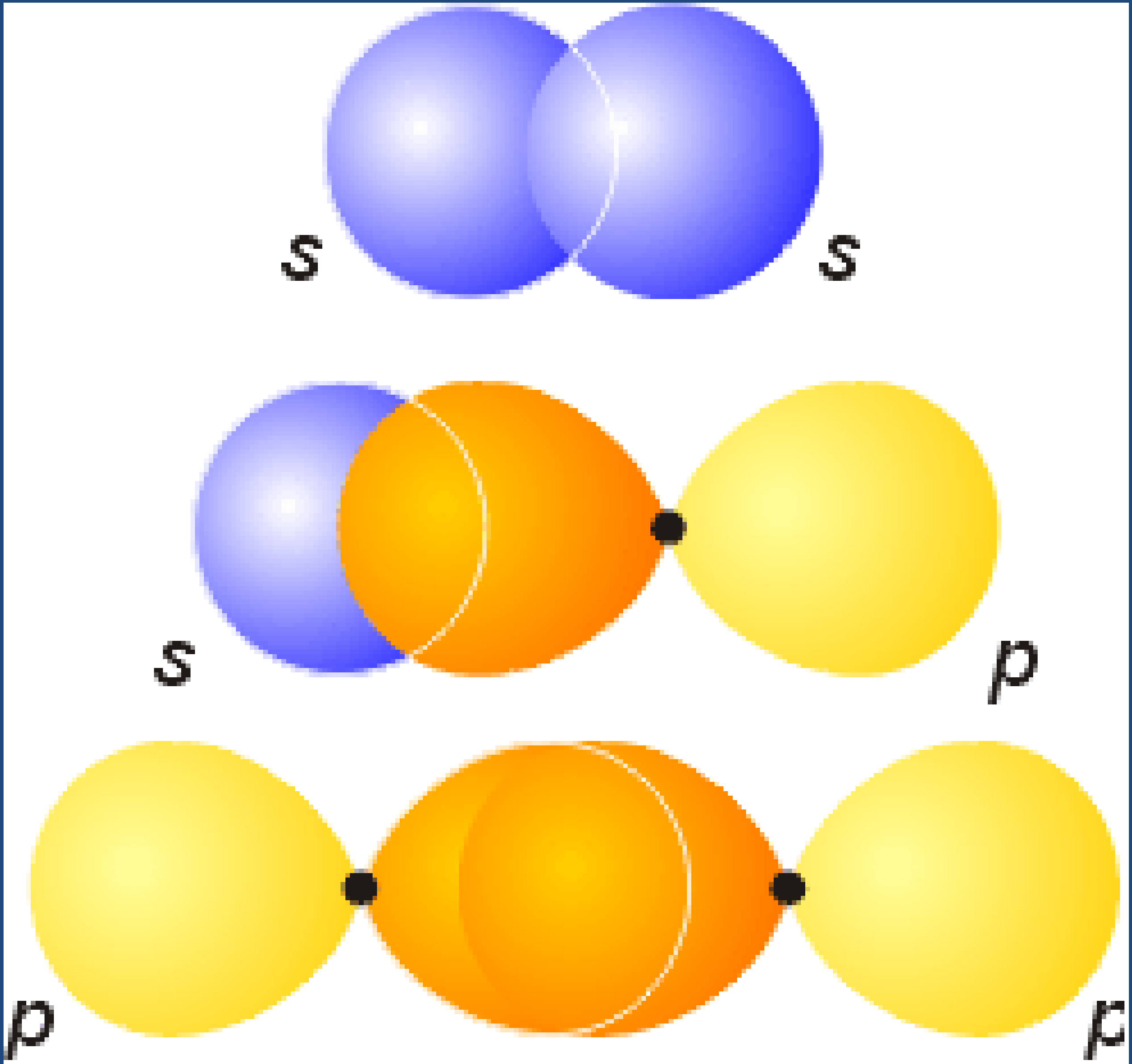

2σu
2πg
φp
φp
2σg
2πu
1σu
φs
φs
2σg

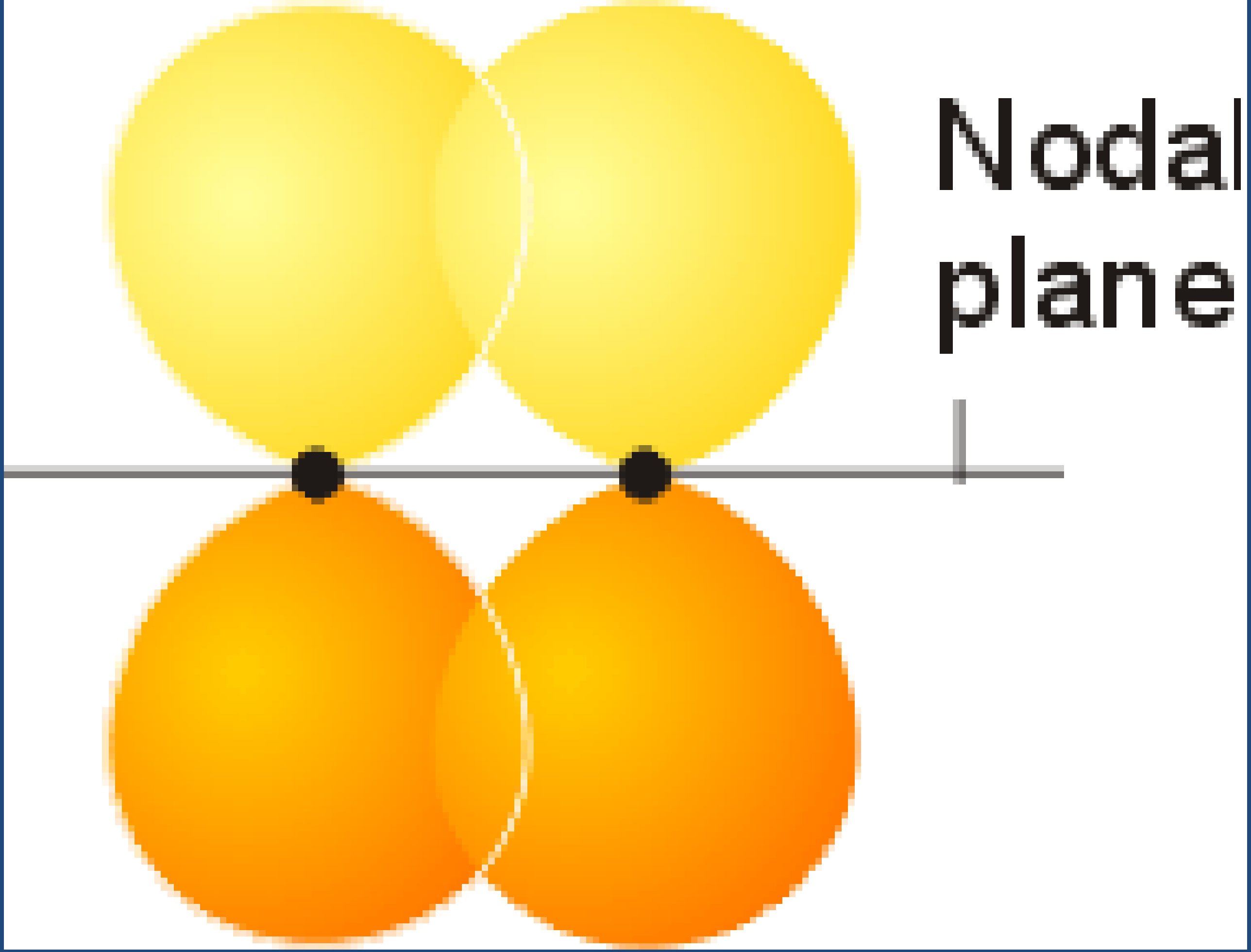


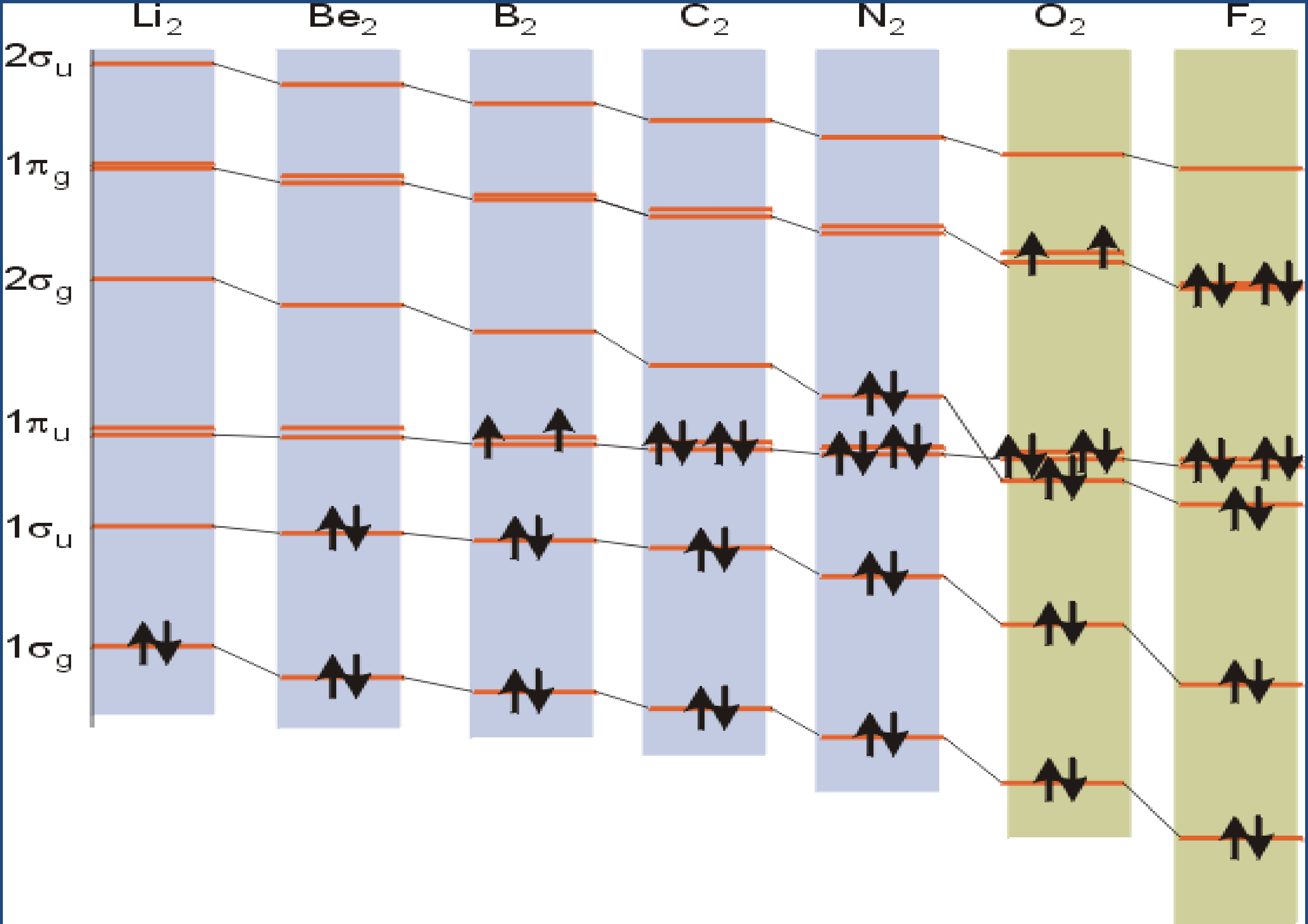
20 σ_g and σ_u orbitals



21 π_g and π_u orbitals

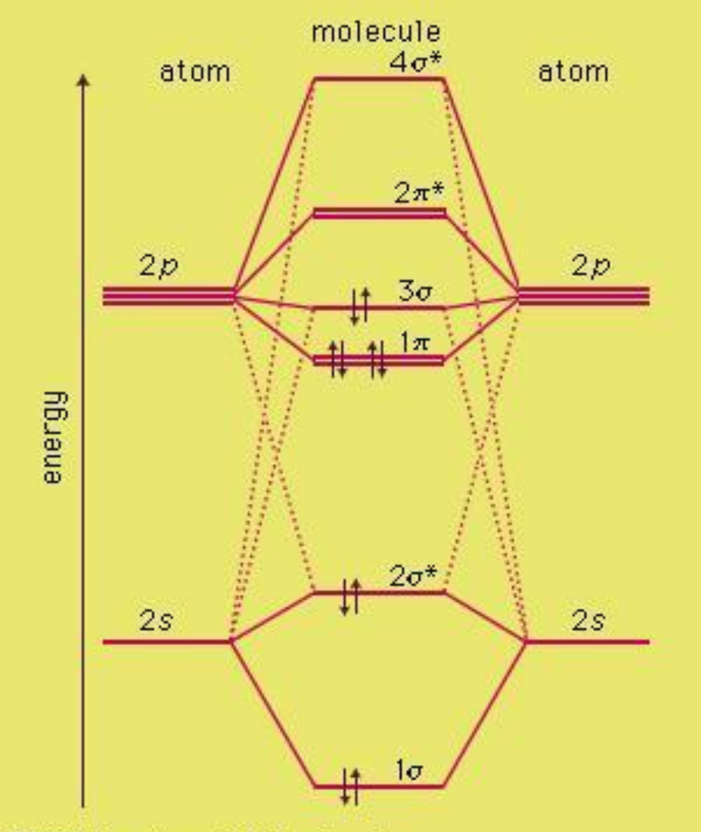

s
s
s
p
p
p


Nodal plane


Li_2
Be_2
B_2
C_2
N_2
O_2
F_2
$2\sigma_u$
$1\pi_g$
$2\sigma_g$
$1\pi_u$
$1\sigma_u$
$1\sigma_g$

Heteronuclear Diatomics

- **In the case of heteronuclear diatomic molecules whatever arguments are presented above are valid.**
- **The only difference is that the energy level diagram is not symmetrical.**
- **The bonding MOs are closer to the atomic orbitals which are lower in energy**
- **The antibonding MOs are closer to those higher in energy**


molecule
atom
atom
energy
$4\sigma^*$
$2\pi^*$
$2p$
$2p$
3σ
1π
$2\sigma^*$
$2s$
$2s$
1σ

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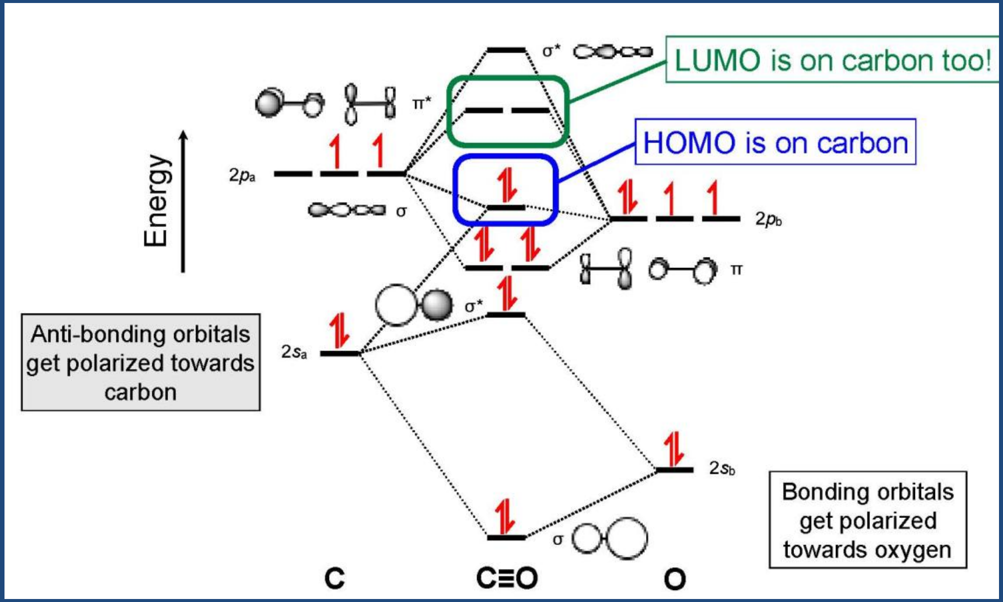

Energy
σ^*
π^*
$2p_a$
σ
$2p_b$
π
σ^*
$2s_a$
$2s_b$
σ
C
C≡O
O

LUMO is on carbon too!

HOMO is on carbon

Anti-bonding orbitals get polarized towards carbon

Bonding orbitals get polarized towards oxygen

Molecular Orbital Theory of Solids

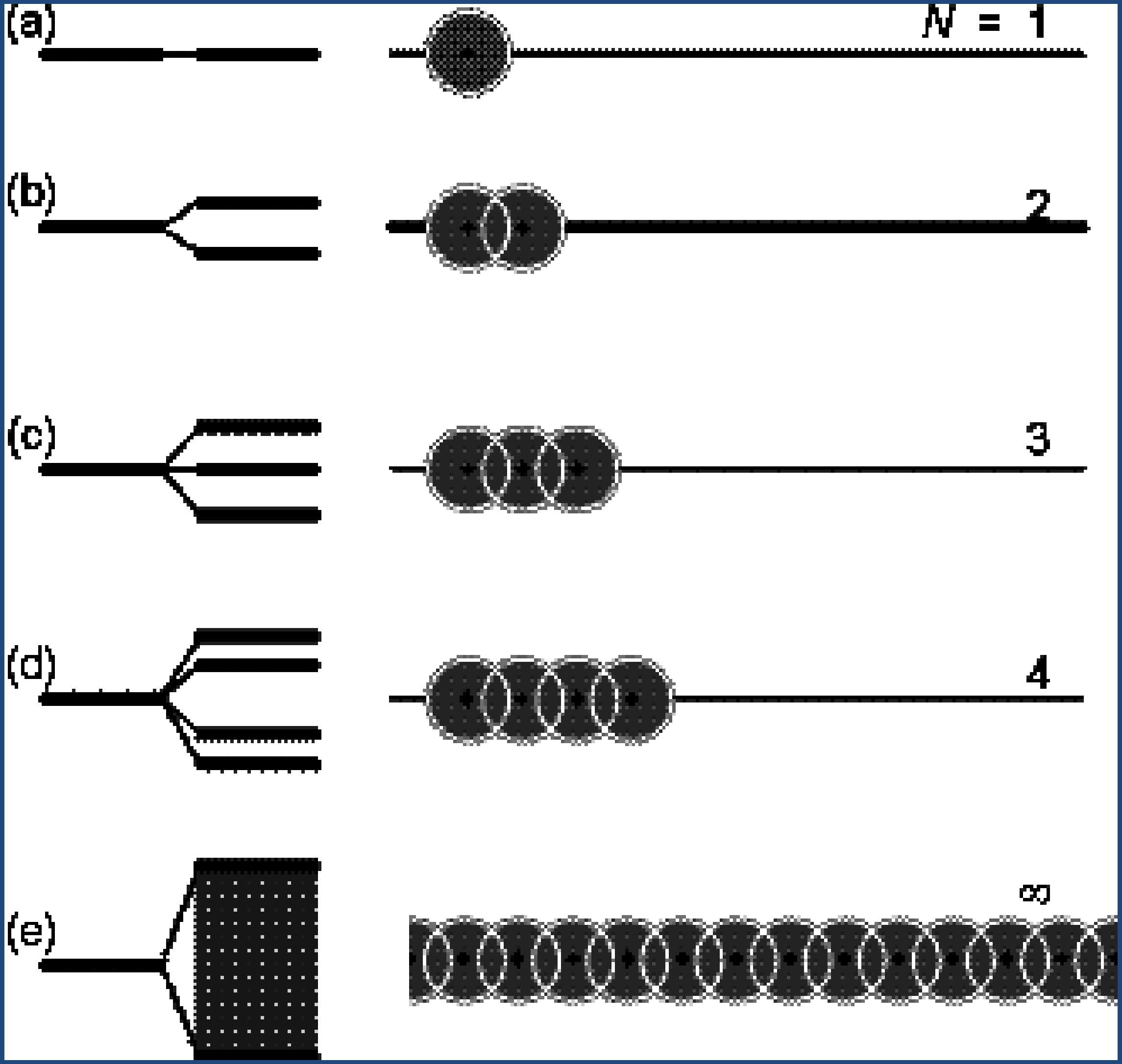
- The MOT extended to account for the properties of solids.
- Aggregations of virtually infinite number of atoms.
- Metals: (i)High Electrical Conductivity
- (ii) Thermal conductivity
- (iii) Luster
- (iv) Malleability.

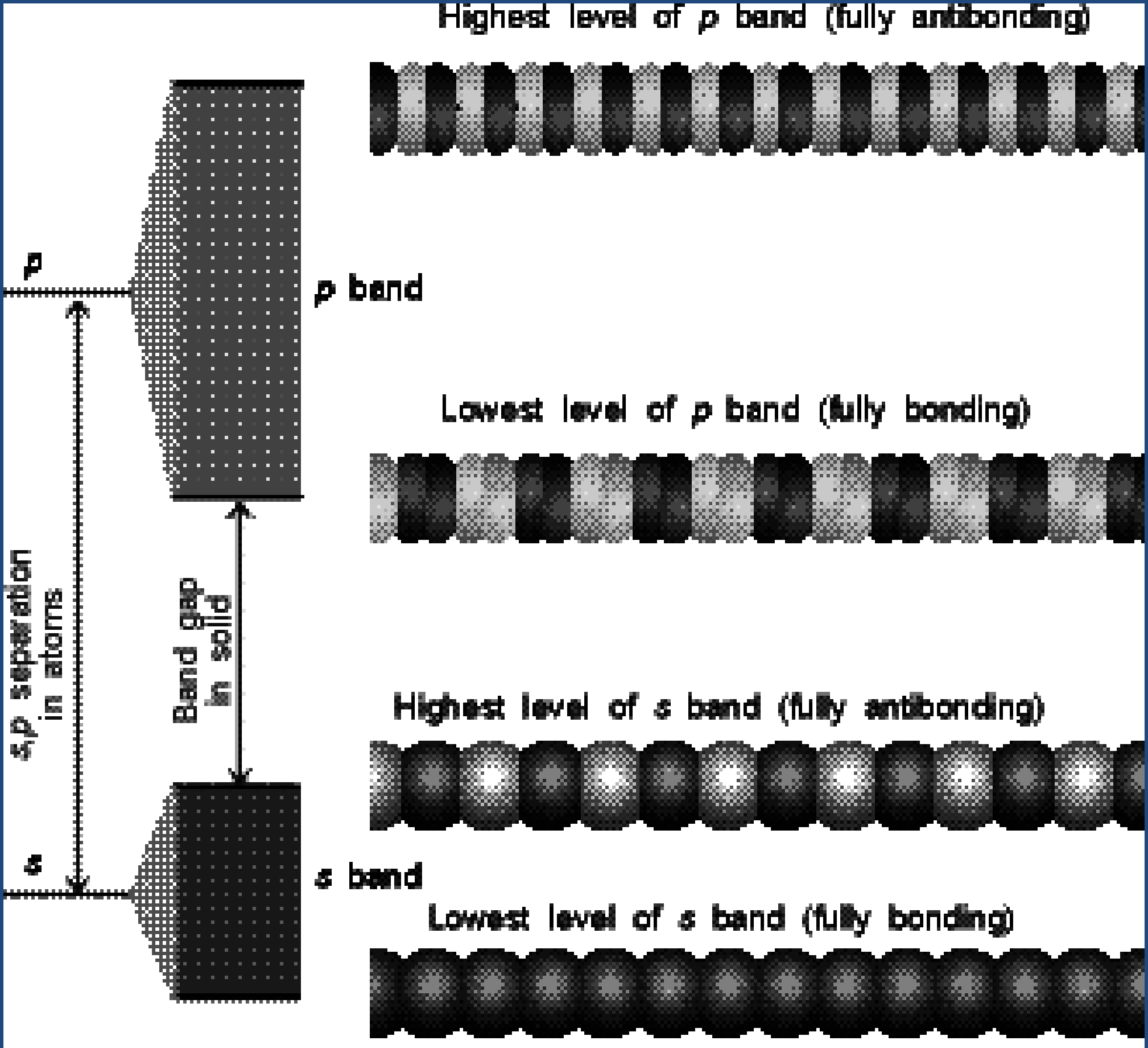
All these properties can be explained by the ability of the individual atom to contribute electrons to a common sea.

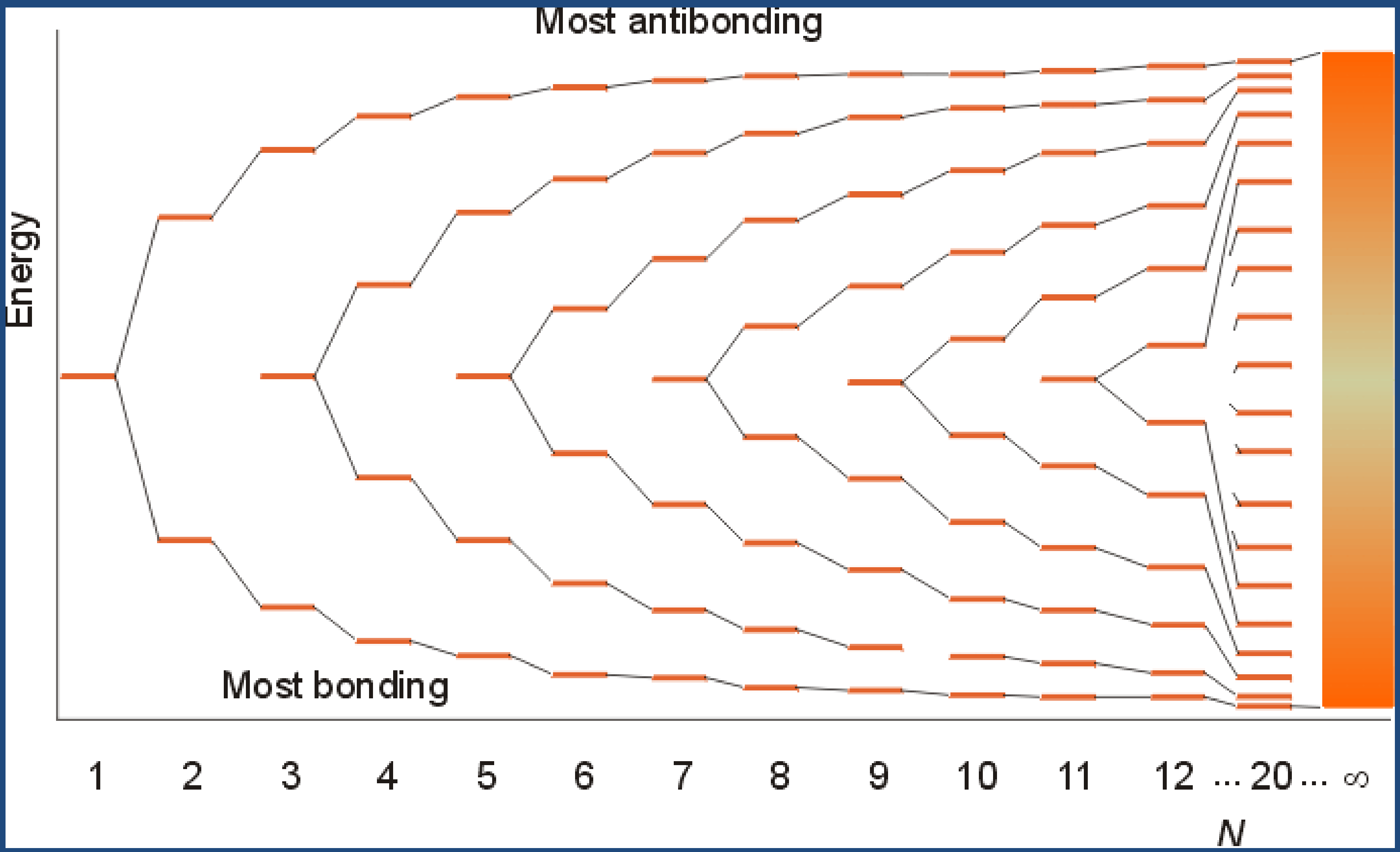
All these properties are due to high mobility of electrons.

Electronic conduction -

- ***semiconductors*.**
- **Temperature dependence of the electrical conductivity.**
- **Metals - the conductivity decreases with temperature**
- **Semiconductors - increases.**


(a)
N = 1
(b)
2
(c)
3
(d)
4
(e)
∞


Highest level of p band (fully antibonding)
p
p band
Lowest level of p band (fully bonding)
s,p separation in atoms
Band gap in solid
Highest level of s band (fully antibonding)
s
s band
Lowest level of s band (fully bonding)


Most antibonding
Energy
Most bonding
12 … 20 … ∞
N

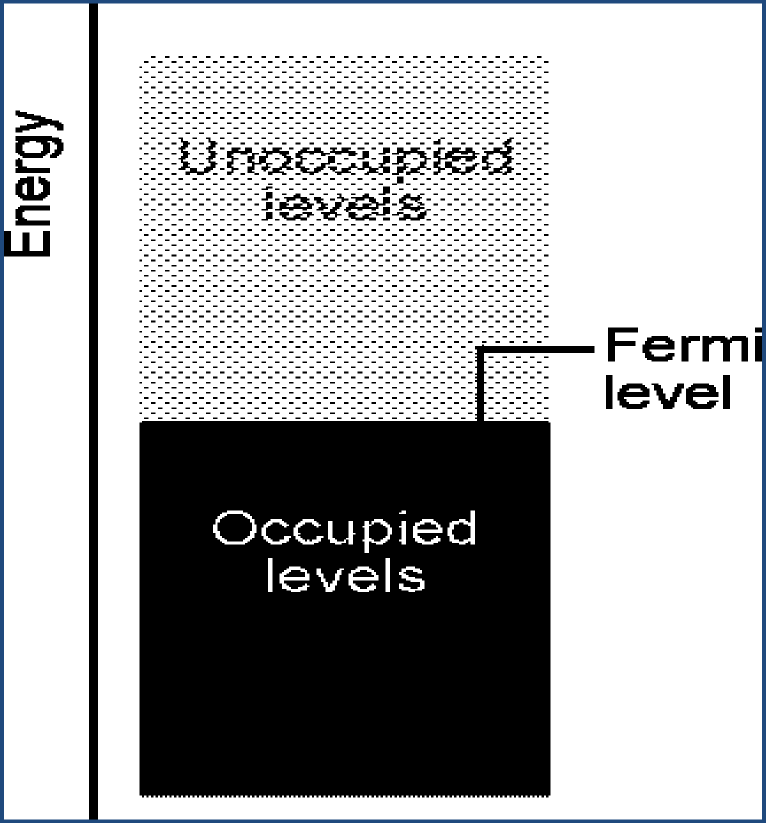
Electrons occupy the orbitals in the band in accord with the building-up principle.

- **If each atom supplies one s electron, then at T = 0 the lowest 1/2N are occupied.**
- **The highest occupied orbital at T = 0 is called the Fermi level**
- **At temperature above absolute zero, the population P of the orbitals is given by Fermi-Dirac distribution**

$P = 1/e^{(E-E_F)/kT} + 1$

E_F is the **Fermi energy,** the energy of the level for which $P = ½$.

The Fermi energy depends on the temperature and at $T = 0$ is equal to the energy of the Fermi level.


Energy
Unoccupied levels
Fermi level
Occupied levels