

# INTRODUCTION TO QUANTUM MECHANICS

## AND

## CHEMICAL BONDING

### Failure of Classical Mechanics

The classical mechanical approach to the description of the behavior of a system can be illustrated by two equations.

(i) Total energy of the particle in terms of its kinetic energy  $\frac{1}{2}mv^2$  and potential energy  $V(x)$  can be expressed as:

$$E = \frac{1}{2}mv^2 + V(x), \text{ where } x \text{ and } V \text{ are function of time } t.$$

$$p = mv \text{ (p = momentum)}$$

$$\text{Therefore, } E = \frac{p^2}{2m} + V(x) \dots\dots\dots \text{Eq.1}$$

Equation one can be interpreted as follows:

- (a) If we know both momentum and position of the particle, we can calculate it's total energy.
- (b)  $p = mv = m(dx/dt)$ . So, equation 1 is a differential equation for  $x$  as a function of time  $t$ . If the particle is of fixed energy, it might be possible to solve the equation and one can get the position & momentum as a function of time  $t$ . i. e. one can predict it's trajectory precisely.
- (ii) The second basic equation is 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.

We have from Newton's second Law

$$F = ma, \quad F = m \frac{dv}{dt} = m \frac{d^2x}{dt^2}$$

That is, if we know the force acting on the particle in every region of space we might be able to solve this equation and find it's momentum at all the times, and from that it's position. Also, continuous variation of energy is possible.

However, certain experiments done in late 19<sup>th</sup> 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**.

In photoelectric effect, when a metal surface is irradiated with light, electrons are emitted. It was shown that, (i) no electrons are ejected, if the frequency of the incident light does not exceeds a threshold value, that is characteristic of each metal, regardless of the intensity of the light. (ii) Kinetic energy of ejected electron is linearly proportional to the frequency (figure 1).

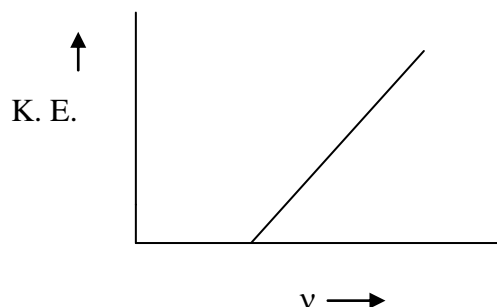


Figure 1

(iii) Even at low intensities of light, electrons are ejected immediately if the frequency is above the threshold frequency.

Similarly, Black body radiation is another experimental result, which could not be explained by classical physics. Apart from these, Major objections to the Rutherford-Bohr model of atom are:

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

Neither of these propositions is valid. In 1927, Werner Heisenberg showed that, it is impossible to specify the exact position and momentum of a particle simultaneously. This conclusion is expressed quantitatively by the **uncertainty principle**. The principle states that if the uncertainty in the position of a particle is  $\Delta x$  and the uncertainty in its momentum is  $\Delta p$ , then the product of these uncertainties must satisfy the relation  $\Delta x \Delta p \geq h/2\pi$  where  $h$  is **Plank's Constant**, a fundamental constant with the value  $6.626 \times 10^{-34}$  J s.

Einstein explained the photoelectric effect in the following manner.

The kinetic energy of the ejected electron,  $1/2mv^2 = hv - \phi$ , where  $\phi$  is the work function, i.e. the energy required to remove the electron from the metal, and  $h\nu$  is the energy of the incident light of frequency  $\nu$ . That is light can be thought of as a bunch of particles which have energy  $E = h\nu$ . The light particles are called **photons**.

*One can ask a question, if light can behave as particles, why not particles behave as wave?*

In fact, Louis de Broglie proposed that, particles could behave as wave. He derived the relation between wavelength  $\lambda$  and the mass and velocity of the particles.

We have  $E = h\nu$  and also  $E = mc^2$ , where,  $E$  is the energy,  $m$  is the mass of the particle and  $c$  is the velocity.

We can therefore write,  $mc^2 = h\nu$

$$\text{Momentum } p = h/\lambda \quad \{ \text{since } \nu = c/\lambda \}$$

$$\text{Therefore, } \lambda = h/p.$$

This is known as **wave particle duality**. Since particles can behave as wave, there must be a *wave equation*. Erwin Schrödinger formulated the wave equation that is known as **Schrödinger Equation**. The equation can be solved and the allowed energy values called **Energy Levels** can be found out from the solution of the equation. One of the most significant features of the Quantum Mechanics is that it limits the energies of particles- such as electrons in atoms or molecules to discrete values. This is in striking contrast to classical mechanics, where energies can take any value whatever the object. The restriction of any property to discrete values is called **quantization**.

Given below is a simple method for derivation of wave equation for any systems.

Let us consider, a particle moving along x-axis in a potential field  $V(x)$ . We can write the total energy of the system as sum of its kinetic energy and potential energy (Equation 1).

$$E = p^2/2m + V(x)$$

The rule for conversion of such an equation to the corresponding wave equation is that, replace  $p$  by  $h/2\pi i \cdot d/dx$ .

$$\text{Therefore, } p^2 = h/2\pi i \cdot d/dx (h/2\pi i \cdot d/dx) = -h^2/4\pi^2 \cdot d^2/dx^2$$

Replacing  $p^2$  in equation 1 we get

$$-h^2/8\pi^2m \cdot d^2/dx^2 + V(x) = E$$

This equation is meaningless because, the left-hand side of the equation is a differential operator, so there must be an operand. Let us call it as wave function  $\Psi(x)$ . Therefore, the wave equation for the equation 1 is

$$(-\hbar^2/8\pi^2m \cdot d^2/dx^2 + V) \Psi(x) = E \Psi(x) \dots\dots 2$$

Equation 2 can be rearranged to

$$d^2\Psi/dx^2 + 8\pi^2m/\hbar^2 (E - V)\Psi = 0$$

Similarly, in three dimensions, we can write,

$$\text{Kinetic energy} = \frac{1}{2} m (p_x^2 + p_y^2 + p_z^2)$$

Now putting  $p_x = \hbar/2\pi i \partial/\partial x$ ,  $p_y = \hbar/2\pi i \partial/\partial y$ ,  $p_z = \hbar/2\pi i \partial/\partial z$ , Equation 2 in three dimension can be written as

$$\{-\hbar^2/8\pi^2m (\partial^2/\partial x^2 + \partial^2/\partial y^2 + \partial^2/\partial z^2) + V\} \Psi = E \Psi \dots\dots 3$$

The differential operator  $(\partial^2/\partial x^2 + \partial^2/\partial y^2 + \partial^2/\partial z^2)$  is Laplacian operator and is designated by  $\nabla^2$ . So Equation 3 can be written as:

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

Since,  $\{-\hbar^2/8\pi^2m \nabla^2 + V\}$  or  $\{-\hbar^2/8\pi^2m (\partial^2/\partial x^2 + \partial^2/\partial y^2 + \partial^2/\partial z^2) + V\}$  is the operator for total energy, this known as **Hamiltonian Operator, H**. So, in terms of Hamiltonian Operator, Equation 3 can be written as:

$$H\Psi = E\Psi$$

How to write Hamiltonian for different systems?

#### Hydrogen atom:

The lone electron of charge  $e$  in the hydrogen atom moves in three dimensions in the field of a single proton. Therefore it's kinetic energy  $= \frac{1}{2} m (v_x^2 + v_y^2 + v_z^2)$  and it's potential energy  $= -e^2/r$ , where  $r$  is the distance between the electron and the nucleus. Therefore the Hamiltonian for the hydrogen atom can be written as:

$$H = \{-\hbar^2/8\pi^2m \nabla^2 - e^2/r\}$$

The wave equation for the hydrogen atom is

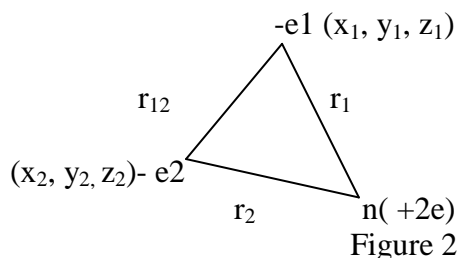
$$\nabla^2 \Psi + 8\pi^2 m/\hbar^2 (E + e^2/r) \Psi = 0$$

If the effective nuclear charge is  $Ze$ , then the Hamiltonian can be written as

$$H = \{-\hbar^2/8\pi^2m \nabla^2 - Ze^2/r\}$$

#### Helium Atom

He has two protons in its nucleus and two electrons. Therefore, if you consider the figure 2, the potential energy can be written as:



$$V = -2e^2/r_1 - 2e^2/r_2 + e^2/r_{12}$$

Therefore, the Hamiltonian  $H = -\hbar^2/8\pi^2m (\nabla_1^2 + \nabla_2^2) - 2e^2/r_1 - 2e^2/r_2 + e^2/r_{12}$

And the wave equation is

$$(\nabla_1^2 + \nabla_2^2) \Psi + 8\pi^2 m/\hbar^2 (E + 2e^2/r_1 + 2e^2/r_2 - e^2/r_{12}) \Psi = 0$$

#### H<sub>2</sub><sup>+</sup> molecule

It has two nuclei containing one proton each, and a single electron (figure 3)

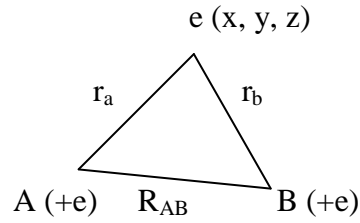


Figure 3

The potential energy is given by

$$V = -e^2/r_a - e^2/r_b + e^2/R_{ab}$$

Therefore Hamiltonian  $H = -\hbar^2/8\pi^2m \nabla^2 - e^2/r_a - e^2/r_b + e^2/R_{ab}$

The Wave equation is

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

H<sub>2</sub> molecule

It has two nuclei and two electrons (Figure 4)

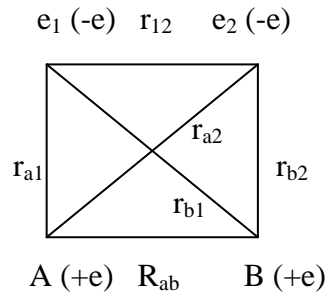


Figure 4

The Hamiltonian is

$$H = -\hbar^2/8\pi^2m (\nabla_1^2 + \nabla_2^2) - e^2/r_{a1} - e^2/r_{a2} - e^2/r_{b1} - e^2/r_{b2} + e^2/r_{12} + e^2/R_{AB}$$

And the wave equation is

$$(\nabla_1^2 + \nabla_2^2) \Psi + 8\pi^2 m/\hbar^2 (E + e^2/r_{a1} + e^2/r_{a2} + e^2/r_{b1} + e^2/r_{b2} - e^2/r_{12} - e^2/R_{AB}) \Psi = 0$$

### Characteristics of Wave Function

According to Heisenberg's Uncertainty principle we can never know exactly where the particle is. In such a case the best we can do is to give the probability that it is in the given region. This means that its position is defined by a probability function. Such a function will vary from place to place according to the probability. If we call it  $\rho(x, y, z)$ , then the particle is most likely to be found in those region where  $\rho$  is greatest. In fact  $\rho(dx, dy, dz) (\equiv \rho d\tau)$  is the probability that the particle is in the small volume  $dx dy dz$  ( $d\tau$ ) surrounding the point  $x, y, z$ . For this reason it is called Probability density. Since the total probability is unity, we can write:

$$\int \rho d\tau = 1$$

Our knowledge of the position of a particle can never be absolute.

### Connection with Wave Function

It is usually the square of the amplitude of a wave that has significance, rather than the amplitude itself. In the progressive wave along a stretched string, the total energy is

proportional to the square of amplitude. Thus, let  $\Psi(x, y, z)$  be the solution of the wave equation for the wave function. Then we may anticipate that

$$\rho(x, y, z) \propto \Psi^2(x, y, z)$$

Choosing a constant in such a way that the  $\propto$  is converted to =

$$\rho(x, y, z) = \Psi^2(x, y, z)$$

$$\therefore \int \Psi^2 d\tau = 1$$

Such wave function is called **Normalized** wave function. If the function is not normalized, it can be done by multiplication of the wave function by a constant  $N$  such that

$$1/N^2 = \int \Psi^2(x, y, z) d\tau$$

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

The Wave equation has infinite number of solutions all of which do not correspond to any physical or chemical reality. These functions are **unacceptable**. **Acceptable** wave functions must satisfy certain conditions. These are:

- i. For electron bound to an atom/molecule, the wave function must be every where *finite*.
- ii. *Single valued*.
- iii. *Continuous*.
- iv. *Gradient (dΨ/dt) must be finite*
- v.  $\int \Psi^2 d\tau$  is *finite*, so that  $\Psi$  can be normalized.

Wave equation contains a term  $E$ , total energy, therefore, solution of the function depends upon  $E$ . Also we have only certain of the solutions which are acceptable. That means that only for certain values of  $E$  there exist physically and chemically significant wave functions. We will call these solutions **Stationary States**, since they arise from a constant energy and in such cases it may be shown that, it is independent of time.  **$E$  is called Eigen Value and  $\Psi$  is Eigen Function.**

#### **Need for Effective Approximate Method of Solving the Wave Equation.**

Only for certain special forms of the potential function  $V$  is the wave equation completely soluble in closed terms. For example it is insoluble for all the atoms except those of hydrogenic in character. That is, those atoms where electron is supposed to move in a field of single effective nuclear charge.

For example, in methane,  $\text{CH}_4$ , there are 10 electrons and five nuclei, so the complete wave equation involves a total of  $3 \times 15 = 45$  independent variables, so it is insoluble. To make our task easier, we can assume that the nuclei are fixed in the space- **Born Oppenheimer Principle**, but still it is insoluble.

**How can we get the most suitable approximate wave function?**

**How can we use this approximate wave function to calculate energy  $E$ ?**

There are various methods available, however we will consider a simple but effective method **Variation Method**.

We have

$$H\Psi = E\Psi$$

$$\text{Or } E = \int \Psi H \Psi d\tau / \int \Psi^2 d\tau$$

$$\text{Or if } \Psi \text{ is complex, we can write } E = \int \Psi^* H \Psi d\tau / \int \Psi^* \Psi d\tau$$

The same equation can be written as

$$\langle \Psi / H / \Psi \rangle / \langle \Psi / \Psi \rangle \dots\dots 4$$

This notation is known as Bra-Ket notation

From this equation  $E$  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  $\Psi$  is not correct, we should consider a quantity  $E$  with dimension of energy, which is related to  $\Psi$  by

$$E = \langle \Psi / H / \Psi \rangle / \langle \Psi / \Psi \rangle$$

Let us call this as energy function. Now if we chose  $\Psi_1$  as the wave function and the corresponding energy as  $E_1$  and  $\Psi_2$  as the wave function and  $E_2$  as the corresponding energy-The Variation Theorem tells that

$E_1, E_2 > E_g$ , Where  $E_g$  is the true energy of the ground state unless  $\Psi_1$  &  $\Psi_2$  are true wave function of the system. Also, if

$E_1 > E_2$ ,  $E_2$  is the better approximation to the energy and the corresponding wave function  $\Psi_2$  to the true wave function. We can chose a whole family of wave function at the same time, like trial function with one or more variable parameters  $C_1, C_2, C_3, \dots$ . Then  $E$  is function of  $C_1, C_2, C_3, \dots$  etc.  $C_1, C_2, C_3, \dots$  Etc. are such that  $E$  is minimized with respect to them. We will utilize this method in explaining chemical bonding.

### **Chemical Bonding**

There are two existing theories, Molecular Orbital Theory (MOT) and Valence Bond Theory (VBT). VBT was developed by Linus Pouling and it was developed earlier. Later on MOT was developed by Mulickan. Both the theories are approximations and neither of these is complete and satisfactory.

### ***Molecular Orbital Theory***

MOT starts with the idea that the quantum mechanical principles applied to atoms may be applied equally well to the molecules and we can write the following principles

- i. Each electron in a molecule is described by a certain wave function  $\Psi$ , which because it represents the orbit of the electron in the molecule, is properly called Molecular Orbital (MO). MO's are polycentric and interpretation of  $\Psi$  is the same as that we have described earlier.
- ii. Each  $\Psi$  is defined by certain quantum numbers, which govern its energy and its shape.
- iii. Each  $\Psi$  is associated with a definite energy value, which represents very closely the energy required to remove it from the molecule by ionization. The total energy of the molecule is the sum of the energies of occupied MO's corrected for the mutual interaction between the electrons.
- iv. Each electron has a spin, which just as in the case of an atom has to have a value of  $\pm \frac{1}{2}$  and labeled by its spin quantum number  $m_s$ .
- v. When building the molecule, we determine the allowed orbitals and then adopt the Aufbau Principle (Building Principle) to feed the electrons into the allowed MO's taking due accounts of Pauli Exclusion Principle.

Now let us see how we can determine the allowed MO's of the simplest possible molecule  $H_2^+$ , that has two nuclei and a single electron.

Let the two nuclei be labeled as A and B. When the electron is in the neighborhood of A, the most significant parts of the Hamiltonian  $H$  are precisely those terms which would comprise the Hamiltonian of an electron in an isolated atom A. The other terms associated with B is not zero, but are small. The wave equation here resembles the wave equation of the isolated atom A and the corresponding wave function resembles

that of the isolated atom A,  $\Psi_A$ . Similarly in the neighborhood of B it is  $\Psi_B$ . Since the complete MO has characteristics separately possessed by  $\Psi_A$  and  $\Psi_B$ , naturally that we can guess that the wave function of the electron in the molecule is a linear combination of  $\Psi_A$  and  $\Psi_B$ . That is we can write

$$\Psi = C_A \Psi_A + C_B \Psi_B$$

$$\text{or } \Psi = N(\Psi_A + \lambda \Psi_B)$$

where,  $\lambda = C_A/C_B$ , and N is the normalization constant.

This method is known as Linear Combination of Atomic Orbitals or LCAO. In this particular case and also in the case of other homonuclear diatomic molecules,  $\Psi_A$  and  $\Psi_B$  are same atomic orbitals except for their different origin. By symmetry  $\Psi_A$  and  $\Psi_B$  must appear with equal weight and we can therefore write

$$\lambda^2 = 1, \text{ or } \lambda = \pm 1$$

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

$$E = \langle \Psi_A + \Psi_B | H | \Psi_A + \Psi_B \rangle / \langle \Psi_A + \Psi_B | \Psi_A + \Psi_B \rangle$$

$$E = \langle \Psi_A | H | \Psi_A \rangle + \langle \Psi_B | H | \Psi_B \rangle + \langle \Psi_A | H | \Psi_B \rangle + \langle \Psi_B | H | \Psi_A \rangle / \langle \Psi_A | \Psi_A \rangle + \langle \Psi_B | \Psi_B \rangle + \langle \Psi_A | \Psi_B \rangle + \langle \Psi_B | \Psi_A \rangle$$

$$\text{Or } E = \langle \Psi_A | H | \Psi_A \rangle + \langle \Psi_B | H | \Psi_B \rangle + 2\langle \Psi_A | H | \Psi_B \rangle / \langle \Psi_A | \Psi_A \rangle + \langle \Psi_B | \Psi_B \rangle + 2\langle \Psi_A | \Psi_B \rangle \dots\dots\dots 5$$

Now  $\langle \Psi_A | H | \Psi_A \rangle$  or  $\langle \Psi_B | H | \Psi_B \rangle$  is the ground state energy of a hydrogen atom, let us call this as  $E_A$  and  $\langle \Psi_A | H | \Psi_B \rangle = \langle \Psi_B | H | \Psi_A \rangle = \beta$ , resonance integral and  $\langle \Psi_A | \Psi_B \rangle = \langle \Psi_B | \Psi_A \rangle = S$ , Overlap integral. Also we know that  $\Psi_A$  and  $\Psi_B$  are separately normalized, so  $\langle \Psi_A | \Psi_A \rangle = \langle \Psi_B | \Psi_B \rangle = 1$  and we can write the equation

$$5 \text{ as } E = 2E_A + 2\beta / 2 + 2S$$

$$\text{Or } E_+ = E_A + \beta / 1 + S$$

$$\text{Similarly, } E_- = E_A - \beta / 1 - S$$

Numerically S is very small, so if we neglect S, we can write

$$E_{\pm} = E_A \pm \beta$$

Thus, it is clear from the above that the original pair of degenerate energy levels  $E_A$  and  $E_B$  splits into two after combination, one greater and the other less than the original energy. It also shows that the extent of splitting depends intimately on the magnitude of the resonance integral  $\beta$ . We could represent it on an energy level diagram as given below (figure 5).

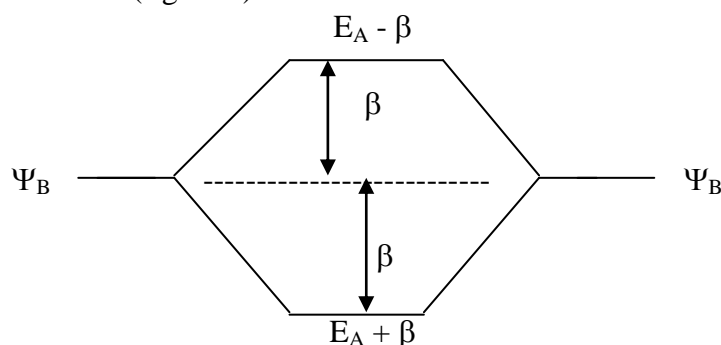


Figure 5

Since  $\beta$  is negative, the lowest energy is associated with + sign.

Next we ask ourselves 'What is the choice of  $\Psi_A$  and  $\Psi_B$ ?

The answer is –if we are interested in the ground state, this will arise by choosing for  $\Psi_A$  and  $\Psi_B$  the lowest atomic orbitals for a hydrogen atom, i. e. 1s orbitals from which  $\beta$  and  $S$  may be calculated for any inter nuclear distance  $R$  { the Hamiltonian for  $H_2^+$  is  $-\hbar^2/8\pi^2m \{ (\nabla^2 - e^2/r_a - e^2/r_b + e^2/R_{ab}) \}$ . In this way the electronic energy is obtained, and so by adding the nuclear Coulomb energy  $e^2/R$  we can determine the energy curve for the molecule (figure 6).

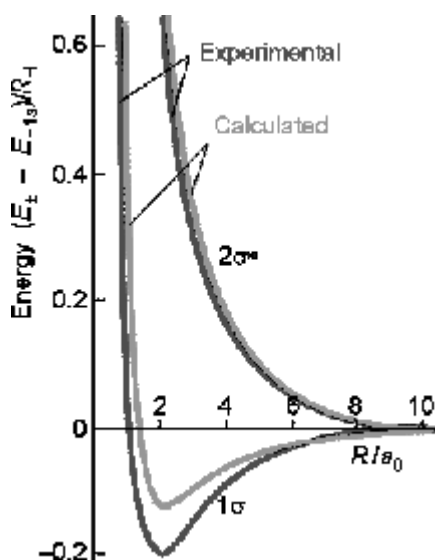


Figure 6

$\Psi_A + \Psi_B$  shows a minimum at an internuclear separation of about 2 Bohr radii (approximately 1 Å). This proves that the ion  $H_2^+$  must be stable. In fact  $H_2^+$  has been found in the discharge tube and Mass Spectrometer.

$\Psi_A - \Psi_B$  shows no minimum, so  $H_2^+$  is unstable in such a level.

The potential energy curves of these two kinds are called attractive and repulsive, respectively. The corresponding orbitals are called **Bonding and Anti-bonding Orbitals**. If we plot  $\Psi^2$  we get the following curves (figure 7).



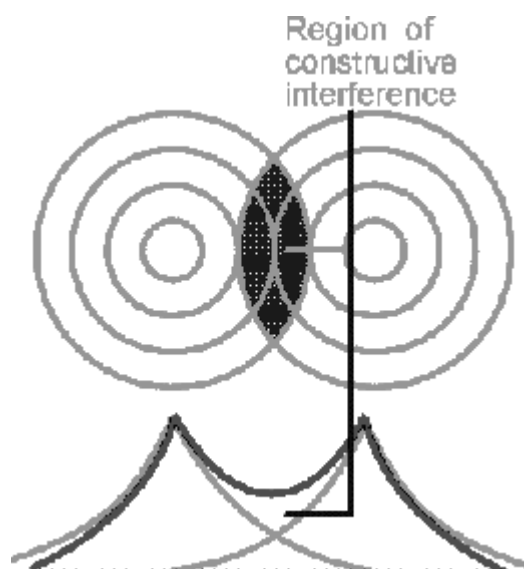


Figure 7

From the potential energy curves it is clear that in the bonding Orbitals

- (i) the electronic charge is concentrated in the internuclear region.
- (ii) The lateral spread is not very great so the effective thickness of the charge cloud is less than the internuclear distance.
- (iii) The orbital is symmetrical with respect to the center of the molecule.

In the antibonding orbital

- (i) The charge cloud is pushed away from between the nuclei, that is, there is a node.
- (ii) The orbital is unsymmetrical with respect to the center of the molecule.

*The qualitative explanation of the bonding that occurs when the electron occupies the MO  $\Psi_A + \Psi_B$ .*

The total energy with which we are concerned is the sum of the potential energy, kinetic energy and the nuclear repulsion energy. Concerning the potential energy, we may say that the electron is being simultaneously attracted to both nuclei and is correspondingly concentrated in the region between them. That means, its potential energy is much higher numerically, though of course negative in sign, than it would be around one single nucleus. But the kinetic energy, which is necessarily positive, is not much increased. As a result there is a gain in energy that is sufficient to offset the nuclear repulsion. The dominant effect from the energy point of view is the increase in magnitude of the electronic potential energy. With the MO  $\Psi_A - \Psi_B$ , the concentration of charge between the nuclei does not occur, so that there is no sufficient gain in potential energy to overcome the nuclear repulsion, and an antibonding state results.

### **Homonuclear Diatomics**

Let us now look at other homonuclear diatomic molecules. It is clear from the above discussion that, when we bring two similar atoms together, each atomic orbitals  $\Psi_A$  or  $\Psi_B$  from the two different atoms combine (LCAO) to give two MOs of the form  $\Psi_A + \Psi_B$  and  $\Psi_A - \Psi_B$ , one of these being bonding and another being antibonding. The difference in energy between the two is determined by resonance integral  $\beta$ . At large distance the energies of both the MOs tend to the energy of the AOs. The shape of the atomic orbitals and the corresponding MOs are shown below.

*Proper notation for the MOs*

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.

Orbitals that are symmetrical about the molecular axis are called  $\sigma$  orbitals. Those, which are formed by  $p_y$  and  $p_z$  orbitals, are  $\pi$  orbitals. The mathematical distinction between  $\sigma$  and  $\pi$  orbitals is that, a  $\sigma$  type MO has zero component of angular momentum around the bond axis and a  $\pi$  type orbital has unit component. The second classification arises from  $\pm$  signs in the LCAO form  $\Psi_A \pm \Psi_B$ . One of those (negative sign) is antibonding and is designated by an asterix, e. g.  $\sigma^*$   $\pi^*$  etc. The classification is closely related to the symmetrical or antisymmetrical nature of the MO. The suffix  $g$  and  $u$  is used in case of symmetrical and antisymmetrical with respect to its center, respectively.

$$\begin{aligned}\Psi_A(1s) + \Psi_B(1s) &\dots\dots g \\ \Psi_A(2p_z) + \Psi_B(2p_z) &\dots\dots u\end{aligned}$$

The third classification of MOs is in terms of AOs. Thus, the MO  $\Psi_A(1s) + \Psi_B(1s)$  is designated by  $\sigma_{1s}$  and  $\Psi_A(1s) - \Psi_B(1s)$  is by  $\sigma_{1s}^*$ .

The *Aufbau principle* may now be applied for homonuclear diatomics. All that we require now is the ordering of the various MO energies. For atoms in the first row of elements, the sequence is given by

$$\sigma_{1s} < \sigma_{1s}^* < \sigma_{2s} < \sigma_{2s}^* < \sigma_{2p} < \pi_y(2p) = \pi_z(2p) < \pi_y^*(2p) = \pi_z^*(2p) < \sigma_{2p}^*.$$

The energy level diagram is given below.

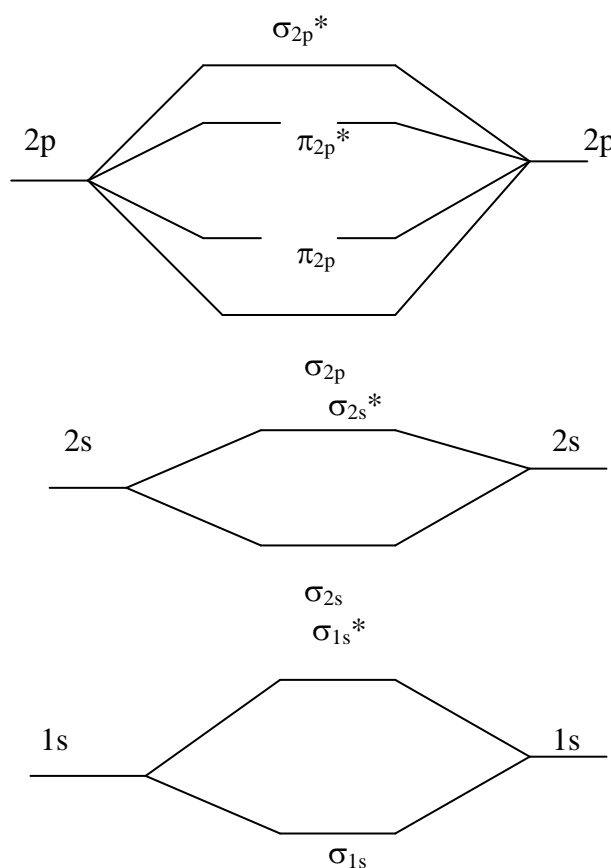


Figure 9

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. As we travel from right to left of the periodic table along the first period of the periodic table, the energy difference between the 2s and 2p orbitals increases. Thus from Li to at least N there is strong interaction between the 2s and 2p orbitals. This interaction causes slight modification of the energy level diagram. The  $\sigma_{2p}$  level is higher in energy than the  $\pi_{2p}$  level. The modified diagram is given below (figure10). This can explain paramagnetism of  $B_2$ . The modified diagram is applicable at least upto  $N_2$ . Both the diagram can explain the paramagnetism of  $O_2$ .

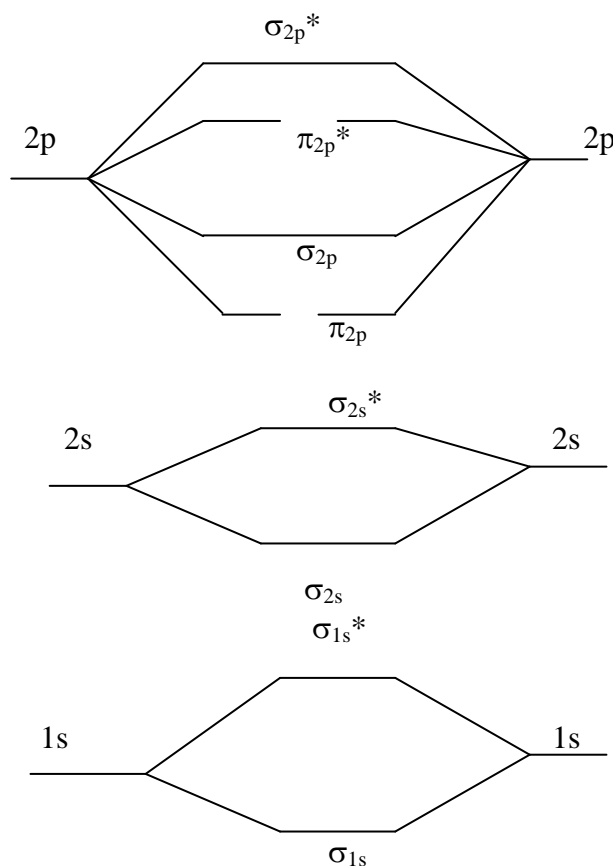


Figure 10

Some boundary surfaces of the molecular orbitals are shown below.

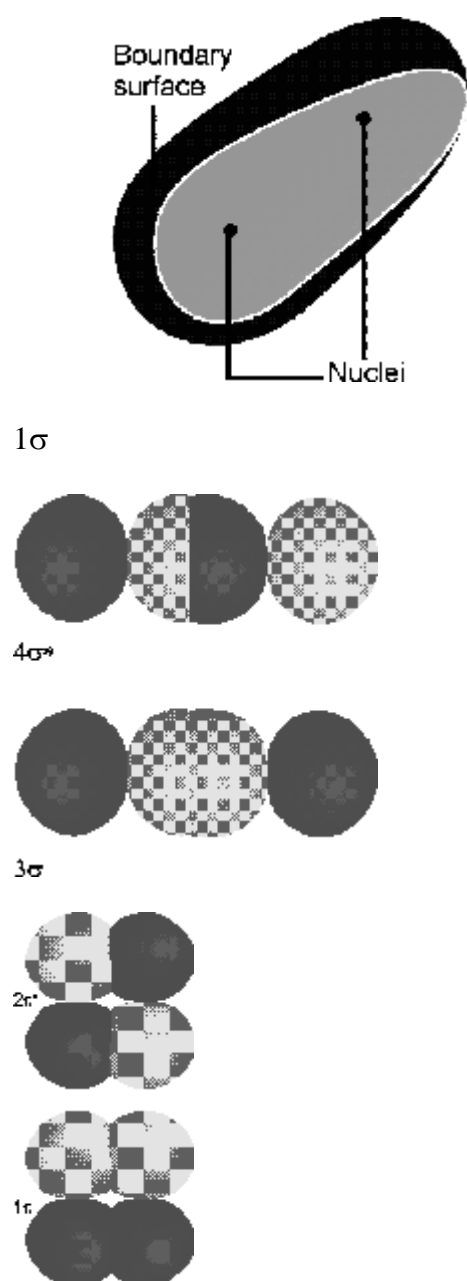


Figure 11