Basic Principles of Quantum Chemistry

- ✓ **Particle–Wave Duality:** Since light can behave both as a **wave** (it can be diffracted and it has a wavelength) and as a **particle** (it contains packets of energy hσ), de Broglie reasoned in 1924 that matter also can exhibit this wave–particle duality.

- ✓ Matter would obey the same equation for wavelength as light namely: $\boldsymbol{\lambda = (\frac{h}{p})}$

  where $\boldsymbol{p} = \boldsymbol{mv}$ is the linear momentum, as shown by Einstein.

- ✓ This relationship easily follows from the consideration that $E = h\nu$ for a photon

  and $\lambda = {}^{c}/_{\nu}$ for an electromagnetic wave.

- ✓ Simplest type of a wave is a plane monochromatic wave:

$$\psi(r,t)=e^{i[kr-wt]}$$

$$\boldsymbol{E}=\hbar\,\boldsymbol{\omega}\ \text{et}\ ,\ \mathbf{p}=\hbar\boldsymbol{k},$$

- ✓ for the energy and linear momentum, this equation may also be written as:

$$\psi(r,t)=e^{[\frac{i}{\hbar}(pr-Et]}$$

where $\omega=2\pi\nu$ and $k=(\frac{2\pi}{\lambda})$ are the angular frequency and wave vector of the plane wave, respectively.

- ✓ A **wave packet** is constructed by **superposition** of waves by Fourier relation. Thus, for one spatial dimension the wave packet is:

$$\psi(x,t)=\frac{1}{\sqrt{2\pi}}\int_{-\infty}^{+\infty}\boldsymbol{g}(\boldsymbol{k})e^{i[kx-wt]}dk$$

or in terms of energy and linear momentum, $\psi(x,t)=\frac{1}{\sqrt{2\pi\hbar}}\int_{-\infty}^{+\infty}\boldsymbol{A}(\boldsymbol{p})e^{i[kx-wt]}dp$

Schrödinger Wave Equation

✓ The time-dependent Schrödinger equation for particle wave for one spatial dimension is of the form:

$$-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\psi(x,t)+V(x)\psi(x,t)=i\hbar\frac{\partial\psi}{\partial t}(x,t)\;\ldots\ldots(1)$$

✓ Where $r\ (x,y,z)$the position ,$\nabla^2=\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}$ (Laplacian operator).

V(x): represents the potential field in which the particle moves.

✓ This equation may be derived from : $\psi(x,t)=\frac{1}{\sqrt{2\pi}}\int_{-\infty}^{+\infty}\boldsymbol{g}(\boldsymbol{p})e^{i[kx-wt]}dp\;\ldots\ldots(2)$

✓ by appropriate differentiation with respect to t gives:

$$\frac{\partial\psi}{\partial t}=\frac{1}{\sqrt{2\pi\hbar}}\int_{-\infty}^{+\infty}g(p)\left(-\frac{iE}{\hbar}\right)e^{\frac{i}{\hbar}[px-Et]}dp\;\ldots\ldots(3)$$

✓ and second differentiation with respect to x gives:

$$-\hbar^2\frac{\partial^2\psi}{\partial x^2}=\frac{1}{\sqrt{2\pi\hbar}}\int_{-\infty}^{+\infty}P^2g(p)\,e^{\frac{i}{\hbar}[px-Et]}\;\ldots\ldots(4)$$

✓ The total energy (E) of the particle, which in classical expression is the Hamiltonian (H), is given as:

$$H = E = \frac{p^2}{2m} + V(x) \;\ldots\ldots(5)$$

then, on using (3) and (2) with equation (5), we get Schrödinger wave (1)

For a free particle $V\ (x) = 0$ and hence Eq. (1) reduces to:

$$-\frac{\hbar^2}{2m}\ \frac{\partial^2}{\partial x^2}\ \psi(x,t) = \ i\hbar\frac{\partial\psi}{\partial t}(x,t)$$

- Here, $\psi(x,t)$ is called wavefunction of the particle wave.

✓ Differentiation of Eq. $\psi(r,t)$=$e^{\frac{i}{\hbar}(pr-Et)}$ with respect to position and time gives:

$$-\,i\hbar\frac{\partial\psi}{\partial x} = p\psi \quad , \quad i\hbar\frac{\partial\psi}{\partial t} = E\psi \quad \text{and} \quad -\,\hbar^2\frac{\partial^2\psi}{\partial^2 x} = p^2\psi$$

✓ From these equations it may be seen that the operator $-i\hbar\frac{\partial\psi}{\partial x}$ represents p_x.

the operator $i\hbar\frac{\partial\psi}{\partial t}$ represents the energy E.

Time-Independent Schrödinger Wave Equation

- ✓ When the **Hamiltonian** is independent of time the general solution of the Schrödinger can be expressed as a product of function of spatial position and time. Thus

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

- ✓ Substitution of this equation into $-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\psi(x,t)+V(x)\psi(x,t) = i\hbar\frac{\partial\psi}{\partial t}(x,t)$ ......(1)

We will then have : $\hat{H}\varphi(x)f(t) = i\hbar\frac{d}{dt}\varphi(x)f(t),$

therefore : $f(t)\left[\hat{H}\varphi(r)\right] = \varphi(r)[\, i\hbar\frac{d}{dt}f(t)]$

- Dividing on both sides by $\varphi(r)f(t)$ we obtain $\frac{\hat{H}\varphi(r)}{\varphi(r)} = \frac{i\hbar\frac{d}{dt}f(t)}{f(t)}$ =E

We can write : $\hat{H}\varphi(r) = \mathrm{E}f(t),$ and $i\hbar\frac{df(t)}{dt} = \mathrm{E}f(t),$

We find:

1. The time-independent stationary Schrödinger equation : $\hat{H}\varphi(r) = E\varphi(r)$

2. The time-dependent Schrödinger equation : $i\hbar\frac{df(t)}{dt} = Ef(t)$

- ✓ By solving the differential equation : $\frac{df(t)}{f(t)} = \frac{Edt}{i\hbar}$

one finds $f(t) = C\ e^{-i\frac{Et}{\hbar}}$

where C is a constant

- ✓ The total wavefunction is therefore : $\psi(x,t) = \varphi(x).e^{-i\frac{Et}{\hbar}}$

- Can also be written as : $\hat{H}\varphi(x) = E\varphi(x)$ is an eigenvalue equation and E is the energy eigenvalue.

- ✓ where the Hamiltonian : $H = E = \frac{p^2}{2m} + \mathrm{V(x)} = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x)$

❑ Schrödinger Equation in Three-Dimensions

- ✓ In a three-dimensional space the wave packet can be written as

$$\psi(r,t)=\frac{1}{\sqrt{(2\pi)^3}}\int_{-\infty}^{+\infty}\boldsymbol{g}(\boldsymbol{k})exp^{i[kr-\omega t]}dk$$

and the time-dependent Schrödinger equation is written:

$$-\frac{\hbar^2}{2m}\nabla^2\psi(r,t)+V(r)\psi(r,t)=\ i\hbar\frac{\partial\psi}{\partial t}(r,t)$$

where, $\Delta\equiv\nabla^2$ (laplacien operator), $\nabla^2=\frac{d^2}{dx^2}+\frac{d^2}{dy^2}+\frac{d^2}{dz^2}$

The time-independent Schrödinger equation is written as $-\frac{\hbar^2}{2m}\nabla^2\psi(r)+V(r)\psi(r)=E\psi(r)$

- ✓ For a three-dimensional problem, the Laplacian in spherical

$$\Delta=\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{d}{dr}\right)+\frac{1}{r^2 sin\theta}\frac{d}{d\theta}\left(sin\theta\frac{d}{d\theta}\right)+\frac{1}{r^2 sin^2\theta}\frac{d^2}{d\varphi^2}$$

- ✓ Describing it in spherical coordinates, we find the Schrödinger equation:

$$-\frac{\hbar^2}{2mr^2}\left[\left(\frac{d}{dr}\left(r^2\frac{d}{dr}\right)+\frac{1}{sin\theta}\frac{d}{d\theta}\left(sin\theta\frac{d}{d\theta}\right)+\frac{1}{sin^2\theta}\frac{d^2}{d\varphi^2}\right)\right]\psi(r,\theta,\varphi)+V(r)\psi(r,\theta,\varphi)=E\psi(r,\theta,\varphi)$$

- ➢ This is the form best suited for the study of the **hydrogen atom**.

- ✓ $\rho = \Psi^* \Psi$, defines the probability of finding a particle in unit volume element.
- ✓ the probability density ρ will be a constant in time.
- ✓ Such states are called stationary states and are independent of time.
- ✓ Since the probability of finding the particle somewhere in the region must be unity,

$\int_{-\infty}^{+\infty} \Psi^* (r, t)\Psi(r, t)d\tau = 1$ (the normalization condition)

- ✓ where $d\tau$ is the three-dimensional volume element $dxdydz$.

Postulates of Quantum Mechanics

✓ **Heisenberg** made some postulates in the development of quantum mechanics these are:

Postulate **1** : The state of a quantum mechanical system is represented by a mathematical function ψ (called **a state function** or a **wavefunction**).

- For a particle moving in a conservative field of force the **wavefunction** determines everything that can be known about the system.
- The **wavefunction** must be a single-valued function of **position** and **time.** as that is sufficient to guarantee an unambiguous value of probability of finding the particle at a particular position and time.

Postulate **2** : With every physical observable **a** there is associated an operator ***A*,** which is a linear hermetic operator acting in the space of wave functions.

✓ The only possible values which a single measurement of an observable $\hat{A}\,\phi = a\phi$

a are just numbers called eigenvalues of operator $\hat{A}$ corresponding to eigenfunction ϕ .

Postulate 3: Any operator Â associated with a physically measurable property a will be Hermitian.

- ✓ An operator is said to be Hermitian if for any two functions ϕ and ψ it satisfies the condition :

$$\int_{-\infty}^{+\infty} \phi^*(A\psi)d\tau = \int_{-\infty}^{+\infty} \psi(A^+\phi)^*\, d\tau$$

Postulate 4. The set of eigenfunctions of an operator Â form a complete set of linearly independent functions. If $\Psi_1, \Psi_2\ \Psi_3, \ldots\ \Psi_n$ are a complete set of linearly independent eigenfunctions of the operator Â representing a physical system, then these functions are said to be normal if

$$\int_{-\infty}^{+\infty} \Psi_i^*\, \Psi_i \mathrm{d}\tau = 1$$

and orthogonal, if

$$\int_{-\infty}^{+\infty} \Psi_i^*\, \Psi_j \mathrm{d}\tau = 0$$

- ✓ These two equations combined together may be written as :

$\int_{-\infty}^{+\infty} \Psi_i^*\, \Psi_j \mathrm{d}\tau = \delta_{ij}$ where $\begin{cases} \delta_{ij} = 1 \quad if\ i = j \\ \quad\ \ = 0\ if\ i \neq j \end{cases}$ [Represents the **orthonormality conditions** of the eigenfunctions]

Postulate **5** : the calculated " expectation value" of a measurable parameter in quantum mechanics can be related with its average value from a large number of physical measurements.

$$\langle x\rangle=\int_{-\infty}^{+\infty}\Psi^*(x,t)x\Psi(x,t)dx$$

- This integral can be interpreted as the average value of x that we would expect to obtain from a large number of measurements.

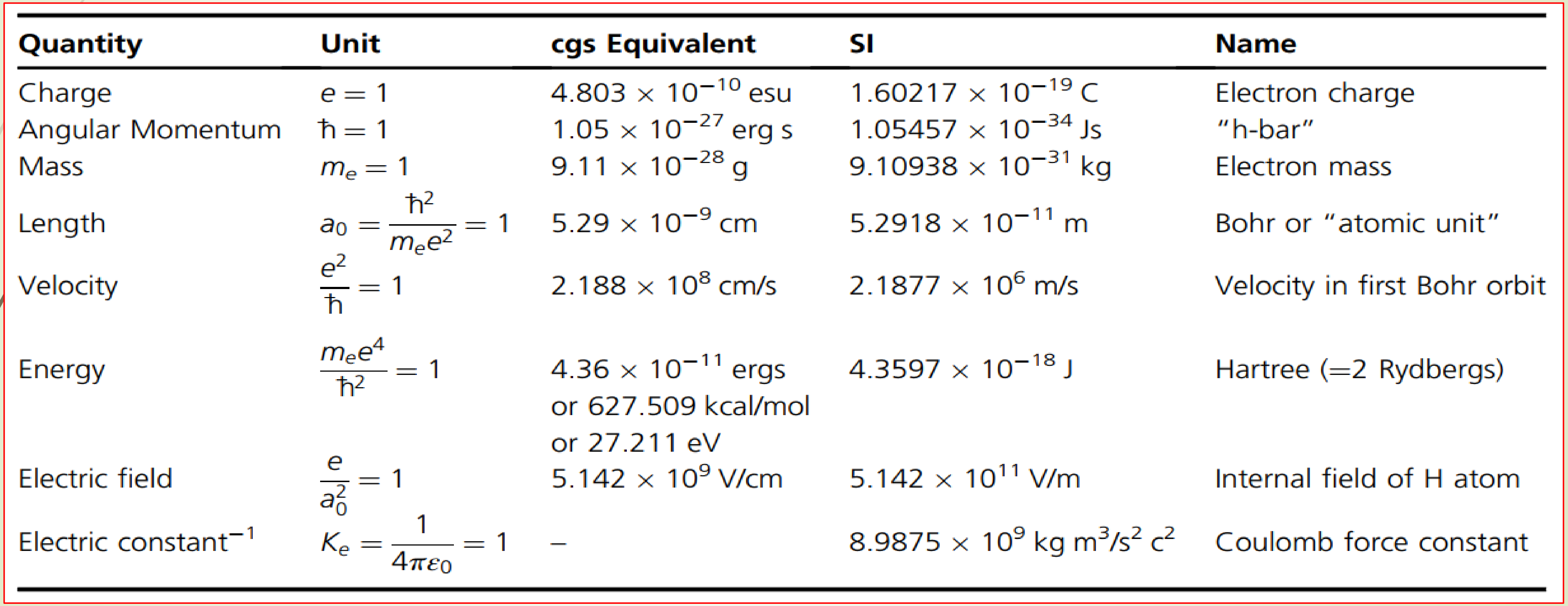
Atomic Units

- ✓ In order to simplify the representation of equations in quantum mechanics and to reduce the use of powers of 10, a set of units called atomic units (au or a. u.) are used.
- ✓ Two different kinds of atomic units: the Hartree atomic units (useful for quantum mechanical calculations) and Rydberg atomic units.
- ✓ four fundamental physical constants: electronic mass (me), electronic charge (e), reduced Planck's constant. $\hbar = \frac{h}{2\pi}$) and the Coulomb's constant $(k = \frac{1}{4\pi\varepsilon_0})$ are taken as **unity** by definition.

- ✓ In Hartree unity by definition atomic units:
- ➢ the unit of length is a_0 which is equal to the radius of first Bohr orbit of hydrogen atom (Bohr).
- ➢ the unit of energy is Hartree (EH) which is twice the energy of the ground state of the hydrogen atom. ($\frac{1}{4\pi\varepsilon_0}$, m_e, $\hbar = \frac{h}{2\pi}$ and e =1).
- ➢ The unit of length is a_0=1 Bohr radius.
- ➢ The unit of mass is m_e = 9, 11.10^{-31} kg, the mass of the electron.
  - ✓ The unit of charge is e = 1, 60.10^{-19} C, the charge of the electron.

✓ 1 Hartree= 27,21eV

- ✓ the Schrödinger equation for the hydrogen-like atom: $\left[-\frac{\hbar^2}{2m}\,\nabla^2-\frac{1}{4\pi\varepsilon_0}\frac{ze^2}{r}\right]\psi(r)=E\psi(r)$
- ✓ Can be rewritten in a simplified form as: $\left[-\frac{1}{2}\,\nabla^2-\frac{z}{r}\right]\psi(r)=E\psi(r)$ (a.u)
- ✓ The atomic units of some common physical quantities and their equivalents in **cgs** and **SI** units:



Quantity	**Unit**	**cgs Equivalent**	**SI**	**Name**
Charge	$e = 1$	4.803×10^{-10} esu	1.60217×10^{-19} C	Electron charge
Angular Momentum	$\hbar = 1$	1.05×10^{-27} erg s	1.05457×10^{-34} Js	"h-bar"
Mass	$m_e = 1$	9.11×10^{-28} g	9.10938×10^{-31} kg	Electron mass
Length	$a_0 = \frac{\hbar^2}{m_e e^2} = 1$	5.29×10^{-9} cm	5.2918×10^{-11} m	Bohr or "atomic unit"
Velocity	$\frac{e^2}{\hbar} = 1$	2.188×10^{8} cm/s	2.1877×10^{6} m/s	Velocity in first Bohr orbit
Energy	$\frac{m_e e^4}{\hbar^2} = 1$	4.36×10^{-11} ergs or 627.509 kcal/mol or 27.211 eV	4.3597×10^{-18} J	Hartree (=2 Rydbergs)
Electric field	$\frac{e}{a_0^2} = 1$	5.142×10^{9} V/cm	5.142×10^{11} V/m	Internal field of H atom
Electric constant^{-1}	$K_e = \frac{1}{4\pi\varepsilon_0} = 1$	–	8.9875×10^{9} kg m^3/s^2 c^2	Coulomb force constant

Many-Electron Atoms and Self-consistent Fields

Wavefunction of Many-Electron Atoms

- ✓ In a many-electron system, we need to include the electron repulsion in the potential energy term of the wave-equation.

Thus, the potential of a many-electron atom having nuclear charge Ze, in atomic unit representation is:

$$V = -\sum_{i=1}^{n} \frac{z}{r_i} - + \frac{1}{2} \sum_{i \neq j} \frac{1}{r_{ij}} \ldots..(1)$$

- ✓ Where r_i the distance of the i^{th} ith electron from the nucleus.

  r_{ij} is the interelectronic distance.

- ✓ A factor of $\frac{1}{2}$ in the second term is included to avoid each r_{ij} term being counted twice in the summation.

- The Hamiltonian, H, for this system is

$$V = -\frac{1}{2}\sum_{i}\nabla_i^2 - \sum_{i=1}^{n}\frac{z}{r_i} - + \frac{1}{2}\sum_{i\neq j}\frac{1}{r_{ij}} \ldots\ldots\ldots..(2)$$

- The first term in the equation is the kinetic energy operator for the electron.
- he second one-electron term corresponds to electron–nucleus attraction.
- the third term is sum of two electron repulsions.

The Schrödinger equation for an N-electron atom may then be written as:

$$H\psi(1,2,\ldots \mathrm{N}) = E\psi(1,2,\ldots N) \ \ldots\ldots\ldots.(3)$$

✓ The solution to this equation is not straightforward due to the presence of **electron repulsion** terms as, unlike hydrogen atom, Only if we assume that the electrons are independent of each other we can approximate the Hamiltonian, H, as the sum of one-electron Hamiltonians:

$$\hat{H} = \sum_i \hat{H}_i = -\frac{1}{2}\sum_i \nabla_i^2 - \sum_i V_i \ldots\ldots.(4)$$

- In order to guess a solution of **Eq 3** let us ignore the electron repulsion term. The equation may then be written as a sum of one-electron Hamiltonians,

$$(H_1 + H_1 \ldots . H_N)\ \psi\ (1 + 2 \ldots . N) = E\psi(1{,}2, \ldots N) \ldots\ldots .(5)$$

We can now solve the equation by the standard "Separation of variables" technique

$$\psi\ (1 + 2 \ldots . N) = \varphi_1(1)\varphi_2(2) \ldots . \varphi_N(N) \text{ (known as Hartree product) } \ldots . (6)$$

where $\boldsymbol{\varphi_1(1)\varphi_2(2) \ldots . \varphi_N(N)}$ are the one-electron orbitals. Substituting Eq. 6 into 5, we get,

$$\frac{1}{\varphi_1(1)} H_1\ \varphi_1(1) + \frac{1}{\varphi_2(2)} H_2\ \varphi_2(2) + \ldots + \frac{1}{\varphi_N(N)} H_N\ \varphi_N(N) = E$$

- Each term on the left-hand side is independently variable and so each of them must individually be equal to a constant:

$$\begin{gathered} H_1\ \varphi_1(1) = E_1\ \varphi_1(1) \\ H_2\ \varphi_2(2) = E_2\ \varphi_2(2) \\ \vdots \\ H_N\ \varphi_N(N) = E_N\ \varphi_N(N) \end{gathered}$$

Thus, $E = E_1 + E_2 + \ldots E_N$ and, $H\psi(1{,}2, \ldots \mathrm{N}) = (E_1 + E_2 + \ldots E_N)\ \psi(1{,}2, \ldots \mathrm{N})$

- A many-electron wavefunction can be given as a product of orbitals;

$$\psi\ (1+2\ \ldots.N) = \varphi_1(1)\varphi_2(2)\ \ldots.\varphi_N(N)$$ (Hartree product)

- However, since we cannot ignore the electron repulsion terms the many-electron Hamiltonian operator.
- Cannot be written simply as a sum of one-electron operators; due to the term $\frac{\mathbf{1}}{\boldsymbol{r_{ij}}}$ which depends on the instantaneous relative coordinates of the two electrons i and j.
- The total wavefunction cannot be written as a simple product of orbitals.
- While constructing many-electron wavefunction we need to include electron spin and thus use spin orbitals.

Spin Orbitals

- ✓ In a complete quantum mechanical description of the motion of an electron, both its position and spin coordinate must be considered.
- ✓ Thus, its wavefunction must be a function of x, y, z or r, θ, φ and s:

$$\Psi = (\mathrm{r},\ \theta,\ \varphi\ ,\mathrm{s})$$

- ✓ Taking cognizance of the independence of spatial and orbital motions, we can set up wavefunctions as products of the spatial $\Psi = (\mathrm{r},\ \theta,\ \varphi)$ and spin functions u_{m_s}.

$$\phi(\mathrm{r},\ \theta,\ \varphi\ ,\mathrm{s}) = \Psi_{nlm}(\mathrm{r},\ \theta,\ \varphi)\ u_{m_s}(\mathrm{s})$$

- ✓ Orbitals like $\phi(\mathrm{r},\ \theta,\ \varphi\ ,\mathrm{s})$ are known as **spin orbitals**.
- ✓ Since the quantum number m_s takes only two values $\frac{1}{2}$ and - $\frac{1}{2}$ we may have two spin functions $u_{1/2}(\mathrm{s})$ and $u_{-1/2}(\mathrm{s})$.
- ✓ Pauli defines : $\boldsymbol{u_{1/2}(\mathrm{s})} \equiv \boldsymbol{\alpha(s)}$ and $\boldsymbol{u_{-1/2}(\mathrm{s})} \equiv \boldsymbol{\beta(s)}$.

- ✓ we need to take into account the symmetry property of the **electronic wavefunction** under interchange of electron coordinates, also known as Pauli’s exclusion principle.
- ✓ Since electrons are essentially indistinguishable particles, no physical property of the system can be affected if we simply renumber or rename the electrons. If we consider the many-electron density function, $\rho(1, 2, . N)$.

$$\rho(1, 2, . \mathrm{N}) = |\psi\ (1,2 \ldots N)|^2$$

- It shall not be affected by the interchange of two electrons.
- The indistinguishability of the electrons also leads to symmetry properties of the wavefunction.
- Suppose P_{ij} is a permutation operator which interchanges all the coordinates (including spin coordinates) of electrons i and j, then

$$P_{ij}\psi\ (1, 2 \ldots \mathrm{i}, \mathrm{j} \ldots N) = \psi\ (1, 2 \ldots \mathrm{j}, \mathrm{i} \ldots N)$$

$$P_{ij}{}^2\ \psi\ (1, 2 \ldots \mathrm{i}, \mathrm{j} \ldots N) = P_{ij}\ \psi\ (1, 2 \ldots \mathrm{j}, \mathrm{i} \ldots N) = \psi\ (1, 2 \ldots \mathrm{i}, \mathrm{j} \ldots N)$$

Or, $P_{ij} \neq \pm 1$

Hence: $\psi\ (1, 2 \ldots \mathrm{i}, \mathrm{j} \ldots N) = \pm 1\ \psi\ (1, 2 \ldots \mathrm{j}, \mathrm{i} \ldots N)$

- ✓ Thus, on interchanging two electrons, the wavefunction, ψ, changes only by a factor of +1 or -1

In the former case, the wavefunction J is said to be symmetric with respect to interchange and in the latter case, it is antisymmetric.

- The antisymmetric property is appropriate for electrons, since it leads to the Pauli's exclusion principle which states that no two electrons can be assigned to identical spin orbitals.

- Since a single product function like: $\psi\ (1 + 2 \ldots.N) = \varphi_1(1)\varphi_2(2) \ldots.\varphi_N(N)$ (Hartree product)

  does not satisfy the antisymmetry principle, it cannot **be a suitable approximate form to use.**

- A combination of two functions can however, satisfy this criterion.

- ✓ If we consider the excited state of a two electron the atom, for example, helium atom He (Z=2, $1s^1\ 2s^1$) in which one electron is in 1s state and the other in 2s state, we can write :
- ✓ Since the electrons are identical any one of them can be either in 1s or 2s orbital.
  - ✓ If there is only one electron in each orbital, then on ignoring electron spin, the two electron wavefunction is: $\psi_1(1,2) = \phi_{1s}(1)\phi_{2s}(2)$

If we apply the two-electron permutation operator, then

$$P_{12}\psi_1(1,2) = \phi_{1s}(2)\phi_{2s}(1)$$

Clearly, $P_{12}\psi_1(1,2)$ is not the negative of $\psi_1(1,2)$.

- However, a combination of Hartree products may be constructed which has antisymmetry. Consider now a wavefunction like: $\psi_1(1,2) = \phi_{1s}(1)\phi_{2s}(2) - \phi_{1s}(2)\phi_{2s}(1)$

$$P_{12}\psi_1(1,2) = \phi_{1s}(2)\phi_{2s}(1) - \phi_{1s}(1)\phi_{2s}(2) = -[\phi_{1s}(1)\phi_{2s}(2) - \phi_{1s}(2)\phi_{2s}(1)] = -\psi_1(1,2)$$

The wavefunction, therefore, changes sign.

- The correct form of wavefunction for the **two-electron** system given by :

$$\boldsymbol{\psi_1(1,2) = \phi_{1s}(1)\phi_{2s}(2) - \phi_{1s}(2)\phi_{2s}(1)}$$

- ✓ If we now include electron spin and consider that the electron in 1s orbital has spin up ($\propto$) and in 2s orbital spin down (β) we may write:

$$\psi_1(1,2) = \phi_{1s}(1) \propto (1)\phi_{2s}(2)\beta(2)$$

and

$$\psi_1(2,1) = \phi_{1s}(2) \propto (2)\phi_{2s}(1)\beta(1)$$

We may then construct an antisymmetric function as:

$$\boldsymbol{\psi} = \phi_{1s}(1) \propto (1)\phi_{2s}(2)\beta(2) - \phi_{1s}(2) \propto (2)\phi_{2s}(1)\beta(1)$$

or in the normalized form $\boldsymbol{\psi} = \frac{1}{\sqrt{2}}[\phi_{1s}(1) \propto (1)\phi_{2s}(2)\beta(2) - \phi_{1s}(2) \propto (2)\phi_{2s}(1)\beta(1)\ ]$

- This will be the correct form of antisymmetric wavefunction inclusive of electron spin. The wavefunction can also written in matrix form as:

$$\boldsymbol{\psi}(1,2) = \frac{1}{\sqrt{2}}\begin{vmatrix} \phi_{1s}(1) \propto (1) & \phi_{2s}(1)\beta(1) \\ \phi_{1s}(2) \propto (2) & \phi_{2s}(2)\beta(2) \end{vmatrix}$$

- Example 1: Thus, for the ground state of hydrogen (H, z=1, $1s^1$) , the spin orbitals are:

$$\psi_{100} = 1s^1$$

$$\phi_{1s} = \Psi_{1s}(r) \propto (s) \qquad \text{or} \qquad \overline{\phi_{1s}} = \Psi_{1s}(r)\beta(s)$$

- Example 2 : He (Z=2), $\psi_{100} = 1s^2$

✓ The spin-orbitals of helium atom He (Z=2) are:

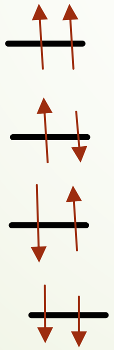
- We have four functions that can describe the ground state of the He atom.

$$\psi_1(1,2) = \phi_1(1)\phi_1(2)$$

$$\psi_2(1,2) = \phi_1(1)\overline{\phi_1}(2)$$

$$\psi_3(1,2) = \overline{\phi_1}(1)\phi_1(2)$$

$$\psi_4(1,2) = \overline{\phi_1}(1)\overline{\phi_1}(2)$$



$\widehat{P_{ij}}$: is a permutation operator:

$$\widehat{P_{12}}\,\psi_1 = \psi_1$$

$\widehat{P_{12}}\psi_2 = \psi_3$ **antisymmetric**

$\widehat{P_{12}}\psi_3 = \psi_2$ **antisymmetric**

$$\widehat{P_{12}}\psi_4 = \psi_4$$

Slater Determinants for Wavefunctions

- ✓ The form of wavefunction given by $\boldsymbol{\psi}(1,2) = \frac{1}{\sqrt{2}}\begin{vmatrix} \phi_{1s}(1) \propto (1) & \phi_{2s}(1)\beta(1) \\ \phi_{1s}(2) \propto (2) & \phi_{2s}(2)\beta(2) \end{vmatrix}$

  can be generalized to describe wavefunctions with any number of electrons.

- ✓ Thus, the general form for a 2N-electron system with two electrons per spatial orbital can be written as a determinant of 2N spin orbitals.

$$\Psi(1,2,\dots N) = \frac{1}{\sqrt{2N!}}\begin{vmatrix} \Phi_1(1)\alpha(1) & \Phi_1(1)\beta(1) & \Phi_2(1)\alpha(1) & \dots & \Phi_N(1)\beta(1) \\ \Phi_1(2)\alpha(2) & \Phi_1(2)\beta(2) & \dots & \dots & \dots \\ \vdots & \vdots & \vdots & \vdots & \vdots \\ \Phi_1(2N)\alpha(2N) & \dots & \dots & \dots & \Phi_N(2N)\beta(2N) \end{vmatrix}$$

$\frac{1}{\sqrt{2N!}}$ the normalization constant.

- ✓ The various spin orbitals appear in the rows and the various electrons in the columns.

✓ Several abbreviations are in common use in the literature for writing Slater determinants.

$$\Psi(1,2,\dots\ N) = \frac{1}{\sqrt{2N!}} \begin{vmatrix} \Phi_1(1) & \overline{\Phi}_1(1) & \Phi_2(1) & \dots & \overline{\Phi}_N(1) \\ \Phi_1(2) & \overline{\Phi}_1(2) & \dots & \dots & \dots \\ \vdots & \vdots & \vdots & \vdots & \vdots \\ \Phi_1(2N) & \overline{\Phi}_1(2N) & \dots & \dots & \overline{\Phi}_N(2N) \end{vmatrix}$$

✓ or in a notational form as $\Psi(1,2,\dots\ N) = \left|\Phi_1\overline{\Phi}_1\dots\Phi_N\overline{\Phi}_N\right|$

Example

- ✓ The spin-correct eigenfunctions for a 4-electron system Beryllium (Be) having configuration $1s^2 2s^2$ is

$$
{}^{1}\Psi(\mathrm{Be}) = \frac{1}{\sqrt{4!}} \begin{vmatrix} \Phi_{1s}(1) & \overline{\Phi}_{1s}(1) & \Phi_{2s}(1) & \overline{\Phi}_{2s}(1) \\ \Phi_{1s}(2) & \overline{\Phi}_{1s}(2) & \Phi_{2s}(2) & \overline{\Phi}_{2s}(2) \\ \Phi_{1s}(3) & \overline{\Phi}_{1s}(3) & \Phi_{1s}(3) & \overline{\Phi}_{2s}(3) \\ \Phi_{1s}(4) & \overline{\Phi}_{1s}(4) & \Phi_{1s}(4) & \overline{\Phi}_{2s}(4) \end{vmatrix}
$$

- ✓ where unbarred terms correspond to $\propto$ spin and barred to β spin.

In contracted notation, the orbital function is written as ${}^{1}\Psi(\mathrm{Be}) = \left|\Phi_{1s}(1)\overline{\Phi}_{1s}(2)\Phi_{2s}(3)\overline{\Phi}_{2s}(4)\right|$

Central Field Approximation

- ✓ The procedure used in quantum chemistry is to assume an initial charge distribution and then to solve the Schrödinger equation for one electron moving in the averaged field of all the other electrons.
- ✓ The functional solution for each electron is then used to recompute the average electron distribution.
- ✓ This procedure is repeated until a final distribution is obtained that agrees to some desired degree of accuracy with the preceding approximation.

Self-consistent Field (SCF) Approximation—Hartree Theory

- ✓ the Hartree theory which is a powerful method to calculate the energy and wavefunction using iterative process.
  - ✓ If we ignore Pauli's exclusion principle, the wavefunction can be written as a product of spatial orbitals $: \psi\ (1+2\ldots.N)=\varphi_1(1)\varphi_2(2)\ldots.\varphi_N(N)$
- ✓ The effective Hamiltonian associated with each electron is now the total Hamiltonian averaged over the other electrons.
- ✓ Each electron will have a kinetic energy, Coulomb attraction to the nucleus and repulsion by other electrons.
- ✓ The average repulsion by each electron (say, electron 1) due to charge distribution associated with another electron (say, electron j) is given by the integral of the product of $\frac{1}{r_{ij}}$ and the charge density of electron j. The charge density on electron j in atomic units is $\rho_j=\left|\boldsymbol{\phi}_j(j)\right|^2$

✓ The average repulsion induced in electron 1 by electron j is then

$$V_{1J} = \int \left|\boldsymbol{\phi}_j(j)\right|^2 \frac{1}{r_{ij}}\, \mathrm{d}\tau = J_j(1)$$

✓ where r_{1j} is the distance between the electrons 1 and j and Jj is called a Coulomb operator or Coulomb integral.

✓ The overall effective one-electron Hamiltonian for the electron 1 is then

$$\hat{H}_1^{eff} = -\frac{1}{2}\nabla_1^2 - \frac{Z}{r_1} + \sum_{j\neq 1}\int \frac{|\Phi_j(j)|^2}{r_{j1}}\, d\tau_j = -\frac{1}{2}\nabla_1^2 - \frac{Z}{r_1} + \sum_{j\neq 1} J_j(1)$$

✓ where $\boldsymbol{\phi}_j(j)$ is the spatial function for the jth electron.

Hartree–Fock Method

- ✓ Hartree–Fock (HF) method uses spin orbitals instead of the spatial orbitals in SCF theory proposed by Hartree.

- consider a two-electron system in which the wavefunction is expressed as an antisymmetrized product of spin orbitals, φ_1 and φ_2.

$$\Psi = \frac{1}{\sqrt{2}}[\Phi_1(1)\Phi_2(2) - \Phi_2(1)\Phi_1(2)] = \frac{1}{\sqrt{2}}\begin{vmatrix} \Phi_1(1) & \Phi_2(1) \\ \Phi_1(2) & \Phi_2(2) \end{vmatrix}$$

- ✓ The Schrödinger equation for the two-electron atom is

$$\hat{H}\Psi = E\Psi$$

$$E = \left\langle \Psi|\hat{H}|\Psi \right\rangle$$

$$\hat{H} = -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{r_{12}}$$

$$E = \left\langle \hat{H} \right\rangle = -\frac{1}{2}\langle \Phi_1|\nabla^2|\Phi_1\rangle - \frac{1}{2}\langle \Phi_2|\nabla^2|\Phi_2\rangle - Z\langle \Phi_1|1/r|\Phi_1\rangle - Z\langle \Phi_2|1/r|\Phi_2\rangle + \langle \Phi_1\Phi_2|1/r_{12}|\Phi_1\Phi_2\rangle - \langle \Phi_1\Phi_2|1/r_{12}|\Phi_2\Phi_1\rangle \qquad (**)$$

Generalization of the HF method to a many-electron atom

We shall now consider generalization of Eq. (**) to a many-electron atom for which the Slater determinant form of the wavefunction is given by

$$\Psi(1,2,3\ldots N)=\frac{1}{\sqrt{N!}}|\Phi_1(1)\Phi_2(2)\Phi_3(3)\ldots\Phi_N(N)|$$

✓ where φ_1 , φ_2, etc., are spin orbitals which form an orthonormal set.

The Hamiltonian for the N-electron atom is given as

$$\begin{aligned}\hat{H}&=\left\{-\frac{1}{2}\sum_{\mu}\nabla_{\mu}^{2}-\sum_{\mu}\frac{Z}{r_{\mu}}\right\}+\sum_{\mu<\nu}1/r_{\mu\nu}\\&=\sum_{\mu}h_{\mu}+\sum_{\mu<\nu}1/r_{\mu\nu}\end{aligned}$$

- where h_μ is the one-electron operator for electron μ and $\frac{1}{r\mu_v}$ is the electron repulsion term.
- the expectation value of $\hat{H}$ for the state ψ can be obtained from the relation
-

$$\left\langle\Psi\middle|\hat{H}\middle|\Psi\right\rangle=\left\langle\Psi\middle|\sum_{\mu}h_{\mu}+\sum_{\mu<\nu}1/r_{\mu\nu}\middle|\Psi\right\rangle$$

Thus, we get, $$\langle\Psi|H|\Psi\rangle = \sum_{i}\langle\Phi_i|h_\mu|\Phi_i\rangle + \sum_{i<j} J_{ij} - \sum\nolimits'_{i<j} K_{ij}$$

- Hartree–Fock method determines the set of spin orbitals which minimize the energy subject to the constraints of orthonormality of the spin orbitals.
- The Hartree–Fock strategy to find self-consistent solution to the N-electron Schrödinger equation lies in the use of the variational principle.
- Hence, Hartree–Fock can be simplified to give $\widehat{F}\Phi_j = \varepsilon_j\Phi_j$
- The total energy is given as $$E = \sum_{j}\varepsilon_j - \left(\sum_{i>j} J_{ij} - \sum\nolimits'_{i>j} K_{ij}\right)$$

Coulomb integral →

$$J_{ij} = \langle\Phi_j(\nu)|J_i|\Phi_j(\nu)\rangle$$

$$J_i = \left\langle\Phi_i(\mu)\left|\frac{1}{r_{\mu\nu}}\right|\Phi_i(\mu)\right\rangle$$

Exchange integral →

$$K_{ij} = \langle\Phi_i(\mu)|K_i|\Phi_j(\mu)\rangle$$

$$K_i = \left\langle\Phi_i(\nu)\left|\frac{1}{r_{\mu\nu}}\right|\Phi_j(\nu)\right\rangle$$

Calculating the atomic or molecular energy

- The HF equations is to express the energy of the molecule or atom in terms of the total wave function Ψ.
- The energy will then be minimized with respect to each of the component molecular (or atomic; an atom is a special case of a molecule) spin orbitals.

✓ It follows from the Schrödinger equation that the energy of a system is given by

$$E = \frac{\int \Psi^* \widehat{H}\, \Psi d\tau}{\int \Psi^{*\wedge} \Psi d\tau} \quad \ldots\ldots\ldots\ldots\ldots\ldots 1$$

Ψ^* is complex conjugate

Ψ is the total wavefunction

$d\tau$ means $dxdydz$

✓ usual normalized wavefunctions makes the denominator unity can then be written as $E{=}\int \Psi^* \widehat{H}\, \Psi d\tau$

or using the more compact Dirac notation for integrals $E{=}\langle \Psi | H | \Psi \rangle$............2

✓ A simple extension of the **helium** Hamiltonian to a molecule with 2n electrons and atomic nuclei (the nucleus has charge gives Z).

$$\hat{H} = \sum_{i=1}^{2n} -\frac{1}{2}\nabla_i^2 - \sum_{\text{all } \mu, i} \frac{Z_\mu}{r_{\mu i}} + \sum_{\text{all } i, j} \frac{1}{r_{ij}} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(3)$$

- The molecular Hamiltonian in this is composed (from left to right) of electron kinetic energy terms, nucleus-electron attraction potential energy terms, and electron–electron repulsion potential energy term.
- Substituting into Eq. 2 the Slater determinant and the molecular Hamiltonian gives, after much algebraic manipulation

$$E = 2\sum_{i=1}^{n} H_{ii} + \sum_{i=1}^{n}\sum_{j=1}^{n}(2J_{ij} - K_{ij})$$

- for the electronic energy of a 2n-electron molecule (the sums are over the n occupied spatial orbitals The terms in Eq. (5.17) have these meanings

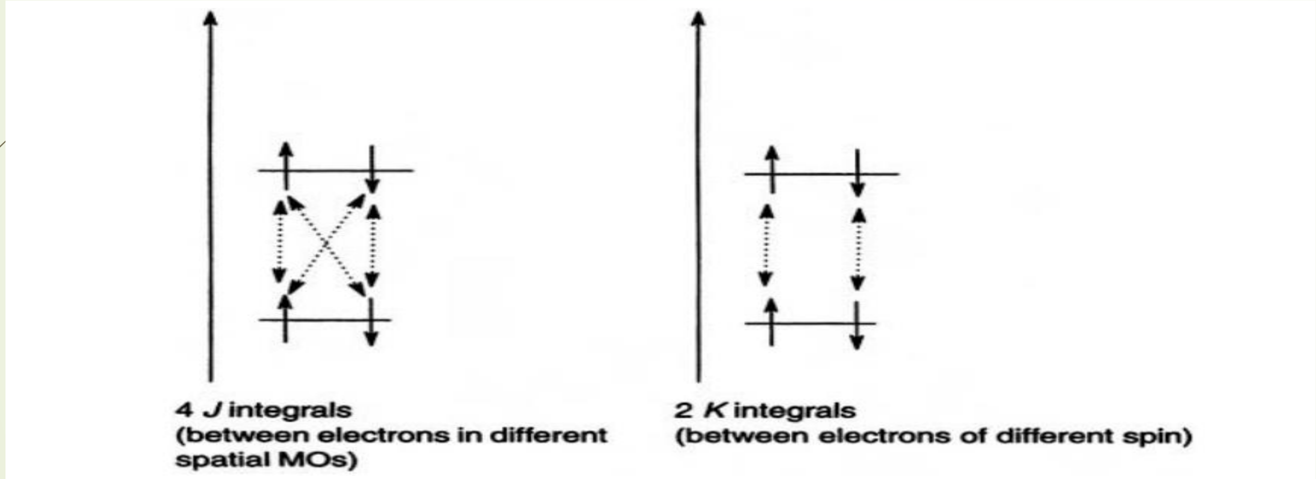
$$H_{ii} = \int \psi_i^*(1)\hat{H}^{\text{core}}(1)\psi_i^*(1)\,dv$$

- where

$$\hat{H}^{\text{core}}(1) = -\frac{1}{2}\nabla_1^2 - \sum_{\text{all } \mu} \frac{Z_\mu}{r_{\mu 1}}$$

- The coulomb integral can be written $J_{ij} = \int \psi_i^*(1)\psi_j^*(2)\left(\frac{1}{r_{12}}\right)\psi_i(1)\psi_j(2)\,dv_1\,dv_2$

- K is called an exchange integral $K_{ij} = \int \psi_i^*(1)\psi_j^*(2)\left(\frac{1}{r_{12}}\right)\psi_i(2)\psi_j(1)\,dv_1\,dv_2$



4 J integrals
(between electrons in different spatial MOs)

2 K integrals
(between electrons of different spin)

The J integrals represent interactions between electrons in different spatial orbitals

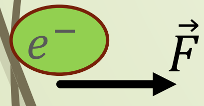
Self-consistent Field Molecular Orbital Theory

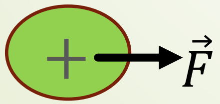
- ✓ The electron is now no more confined to individual atoms but is influenced by all the electrons and nuclei in the molecule.
- ✓ The molecule contains not only the moving electrons but also the moving nuclei.
- ✓ As such, while constructing the Hamiltonian one needs to take into account electron nuclear attraction, nuclear–nuclear repulsion, and electron–electron repulsion terms.
- ✓ The Hamiltonian now becomes very complex and in most cases the Schrödinger equation cannot be solved even by analytical methods.
- ✓ Exact solutions of the Schrodinger equation have been worked out only for small molecules like hydrogen molecular ion H_2^+ and hydrogen molecule (H_2).
  - Solving Schrodinger equation **for polyatomic molecules.**
- ✓ The two approaches that have historically emerged to solve the Schrödinger equation of molecules are (1) molecular orbital (MO) approximation and (2) valence bond (VB) approximation.

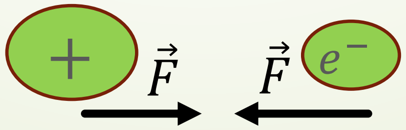
Born–Oppenheimer approximation (in 1927)

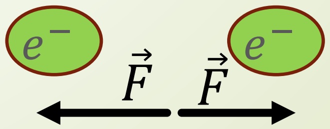
- ✓ In view of the fact that nuclear mass is very large in comparison with the electron mass (proton mass is 1836 times the electron mass), nuclei are expected to move much more slowly than the electrons.
- ✓ If we assume the nuclei and electrons in a molecule to be point masses and neglect spin–orbit.
- ✓ then the molecular Hamiltonian in atomic units can be written as

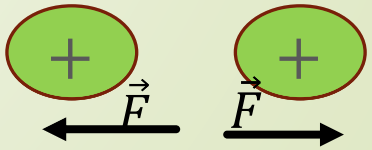
$$\hat{H} = \underbrace{-\frac{1}{2}\sum_{i=1}^{n}\nabla_i^2}_{\text{The kinetic energy of electrons.}} \underbrace{-\frac{1}{2}\sum_{A=1}^{N}\frac{1}{M_A}\nabla_A^2}_{\text{The kinetic energy of nuclei.}} \underbrace{-\sum_{i=1}^{n}\sum_{A=1}^{N}\frac{Z_A}{r_{iA}}}_{\text{the potential energy of attraction between the electrons and the nuclei.}} + \underbrace{\sum_{i=1}^{n}\sum_{j>i}^{n}\frac{1}{r_{ij}}}_{\text{the potential energy of repulsion between the electrons}} + \underbrace{\sum_{i=1}^{n}\sum_{B>A}^{n}\frac{Z_A Z_B}{r_{AB}}}_{\text{the potential energy of repulsion between the nuclei.}}$$











- ✓ The molecular Schrodinger equation is $\hat{H}\,\Psi\,(r_i, R_j,) = E_T\Psi\,(r_i, R_j,)$ ……. **1**

where r_i and R_j symbolize the electronic and nuclear coordinates, respectively.

in the Born–Oppenheimer approximation, the kinetic energy term for the nuclei is ignored and r_{AB} is taken to be a constant quantity so that the electron motion could be determined for a fixed position of the nuclei.

We try an approximate solution in the form

$$\Psi = \Psi_e(r_i, R_j)\,\Psi_N(R_j,)\text{……….}\mathbf{2}$$

where Ψ_e is a function of the electronic coordinates r_i.

And Ψ_N is a function of the nuclear coordinates R_j.

After substituting Eq. 2 in Eq. 1, where H is given

$$\hat{H} = -\frac{1}{2}\sum_{i=1}^{n}\nabla_i^2 - \cancelto{0}{\frac{1}{2}\sum_{A=1}^{N}\frac{1}{M_A}\nabla_A^2} - \sum_{i=1}^{n}\sum_{A=1}^{N}\frac{Z_A}{r_{iA}} + \sum_{i=1}^{n}\sum_{j>i}^{n}\frac{1}{r_{ij}} + \cancelto{\text{constant}}{\sum_{i=1}^{n}\sum_{B>A}^{n}\frac{Z_A Z_B}{r_{AB}}}$$

✓ The nuclei being fixed, their kinetic energy $\hat{T}_N = 0$, **et** $\hat{V}_{NN} = cte$ $\hat{H} = \hat{H}_e + \hat{V}_{NN}$

$$(\hat{H}_e + V_{NN})\Psi_e = (E_e + V_{NN})\,\Psi_e$$

✓ The electronic Hamiltonian ($\hat{H}_e$) associated with a fixed nuclear geometry is written:

$$\hat{H}_e = -\frac{1}{2}\sum_{i=1}^{n}\nabla_i^2 - \sum_{i=1}^{n}\sum_{A=1}^{N}\frac{Z_A}{r_{iA}} + \sum_{i=1}^{n}\sum_{j>i}^{n}\frac{1}{r_{ij}} \quad and \quad \hat{V}_{NN} = \sum_{i=1}^{n}\sum_{B>A}^{n}\frac{Z_A Z_B}{r_{AB}}$$

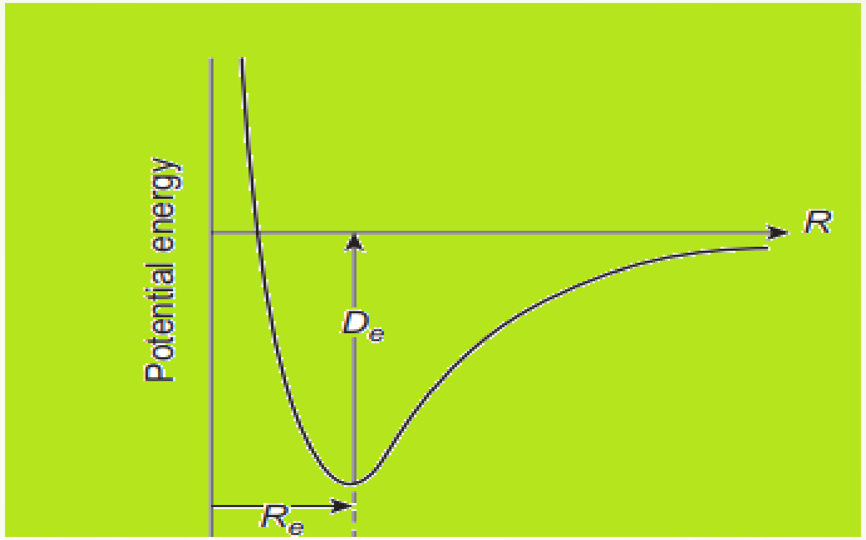
✓ In order to get the total electronic energy including nuclear repulsion $(E_e + V_{NN})$, we may first solve the equation $\hat{H}_e\Psi_e = E_e\Psi_e$

✓ to get the purely electronic energy E_e and then add to it the constant value V_{NN}.

✓ we use the electronic energy including nuclear repulsion $(E_e + V_{NN})$ as the potential energy in the Schrödinger equation for nuclear motion: $\hat{H}_N\Psi_N = E_N\Psi_N$

$$\hat{H}_N = -\frac{1}{2}\sum_{J=1}^{N}\frac{1}{2}\frac{1}{M_J}\nabla_J^2 + E_e + V_{NN}(R_J)$$

- ✓ The set of solutions for different internuclear distances can then be used to construct a potential energy curve for a diatomic molecule or a potential energy surface for a polyatomic molecule.



- De is the equilibrium dissociation energy of the molecule.

.

Potential energy curve of a diatomic molecule. The minimum energy point corresponds to equilibrium bond length of the molecule.

Molecular Orbitals as Linear Contribution of Atomic Orbitals (LCAO)

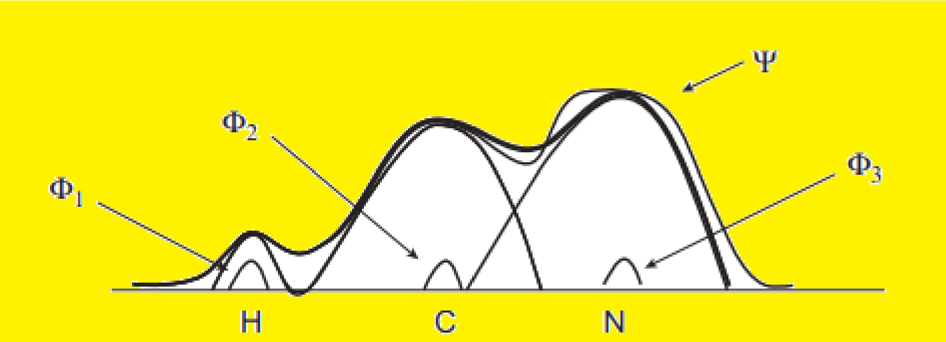
- ✓ The most generally applicable and useful representation of a MO is a linear combination of atomic orbitals (LCAOs).
- ✓ Each atom may contribute several atomic orbitals in the construction of MOs.

Thus, if $\varphi_1\ \varphi_2 \ldots \varphi_n$ are the atomic orbitals, then the MO shall have the form

$$\psi_i = \sum_{i=1}^{n} C_{ij}\varphi_j \quad \ldots 1$$

The functions $\varphi_1\ \varphi_2 \ldots \varphi_n$ are said to form a basis set of functions.

- ✓ The C_{ij} are the coefficients of the molecular orbitals expanded on the basis functions.
- ✓ n is the number of combined OAs.



Molecular Orbitals as Linear Contribution of Atomic Orbitals

- ✓ The optimal values of these coefficients are determined using the variational method so as to minimize the energy E of the system

$$E = \frac{\int \Psi^{*}\widehat{H}\Psi d\tau}{\int \Psi^{*\wedge}\Psi d\tau} \quad \ldots 2$$

The variational method leads to a set of equations

Where $H_{ij} = \int \Phi_i^* H \Phi_j d\tau$

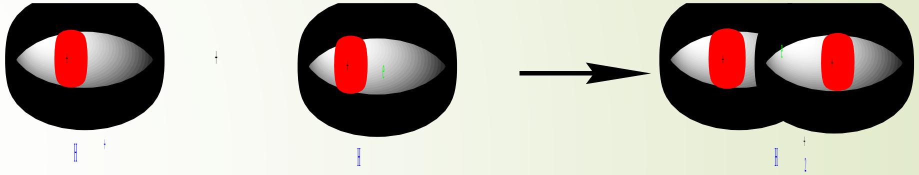
$S_{ij} = \int \Phi_i^* \Phi_j d\tau$

$$\begin{pmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} & \ldots & H_{1n} - ES_{1n} \\ H_{21} - ES_{21} & H_{22} - ES_{22} & \ldots & H_{2n} - ES_{2n} \\ \vdots & \vdots & \vdots & \vdots \\ H_{n1} - ES_{n1} & H_{n2} - ES_{n2} & \ldots & H_{nn} - ES_{nn} \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \\ \vdots \\ c_n \end{pmatrix} = 0 \quad \ldots 3$$

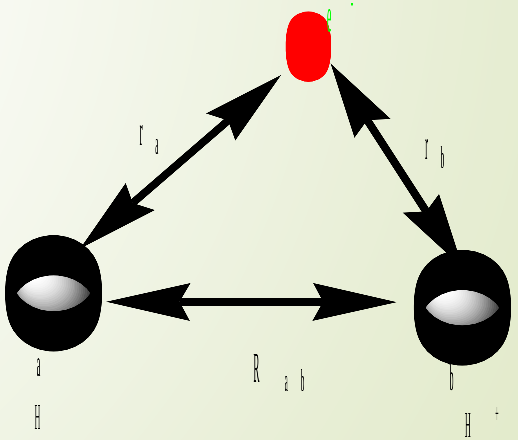
- ✓ the determinant $|H - ES|$ must be zero, which shall provide n-values of energy $E1, E2, \ldots En$.
- ✓ Substitution of these energies back into Eq.3 shall provide the corresponding values of coefficients $(c_{11}, c_{12},. c_{1n}), (c_{21}, c_{22} \ldots c_{2n}) \ldots (c_{n1}, c_{n2} \ldots c_{nn})$ and hence a set of wavefunctions from Eq. 1.
- ✓ Each value of energy Ei calculated from Eq. 3 is greater than or equal to the true energy of each n state. $E_i \gg E_{true}$ (This is known as MacDonald's theorem).

Molecular Orbital Treatment of H_2^+ Molecule

- ✓ The hydrogen molecule ion consists of two protons and an electron as shown in the Figure 1.1.
- ✓ If we take the two nuclei to be fixed with internuclear distance R_{AB} (a_0 Bohr's radius) then within the **Born–Oppenheimer** approximation the Hamiltonian can be written as :



$$\hat{H} = -\frac{1}{2}\nabla^2 - \frac{1}{r_a} - \frac{1}{r_b} + \frac{1}{R_{ab}} \quad \text{(in a.u.) ------}(1)$$



- ✓ The term $\frac{1}{R_{ab}}$ is a constant for a particular nuclear configuration.
- ✓ The Schrödinger equation can be written as:

$$\hat{H}\psi = E\psi$$

Figure 1.1. Relative positions of particles in H_2^+ molecule.

- ✓ The atomic orbitals ($\emptyset_a, \emptyset_b$) centered on each of the nuclei to construct MOs.
- ✓ When the electron is close to nucleus A, its distance from nucleus B (r_b) is very large and the potential due to nucleus B is negligible.
- ✓ In this case, the atomic orbital is very similar to that of hydrogen-like orbital around nucleus A.
- ✓ Similarly when electron is close to *nucleus B*, r_a is very large and the atomic orbital $\emptyset_b$ is similar to the hydrogen-like orbital around the *nucleus B*.
- ✓ We may therefore construct a MO as a LCAOs $\emptyset_a$ and $\emptyset_b$.

$$\psi = C_a\varphi_a + C_b\varphi_b \text{.....................} 2$$

- ✓ where c_a and c_b are variable parameters which indicate the magnitude of contribution of each atomic orbital to the **MO**.
- ✓ The optimal value of the coefficients c_a and c_b are obtained by using the variational theory.

$$\int \psi^* \hat{H} \psi d\,\tau = \boldsymbol{E} \int \psi^* \psi d\tau \text{ ....} 3$$

and on using Eq.(2), we get:

$$E\left[\int (c_a\varphi_a+c_b\varphi_b)^*(c_a\varphi_a+c_b\varphi_b)\,d\tau\right]=\int (c_a\varphi_a+c_b\varphi_b)^*\hat{H}\,(c_a\varphi_a+c_b\varphi_b)\,d\tau \text{……….(4)}$$

- If we use the notations :

$\int \varphi_a{}^*\varphi_a\, d\tau = s_{aa}$

$\int \varphi_a{}^*\varphi_b\, d\tau = s_{ab}$

$\int \varphi_a{}^*\hat{H}\varphi_a\, d\tau = H_{aa}$

$\int \varphi_a{}^*\hat{H}\varphi_b\, d\tau = H_{ab}$

- Eq (4) simplifies to: $[c_a^2 s_{aa}+c_ac_b(s_{ab}+s_{ba})+c_b^2 s_{bb}] = c_a^2 H_{aa} + c_ac_bH_{ab} + c_bc_aH_{ba} + c_b^2 H_{bb}$
- According to the variation principle, if the coefficients c_a, c_b, etc., can be chosen, so as to minimize the energy E, i.e. $\frac{\partial E}{\partial c_a} = \frac{\partial E}{\partial c_b} = 0$
- Differentiating E with respect to c_a and c_b respectively, and remembering that : $s_{aa} = s_{ba}$ and $H_{ab} = H_{ba}$ for real wavefunctions, we get:

$$\frac{\partial E}{\partial c_a}[c_a^2 s_{aa}+2c_ac_bs_{ab}+c_b^2 s_{bb}]+E[2c_as_{aa}+2c_bs_{ab}] = 2c_aH_{aa}+2c_bH_{ab} \text{……(5)}$$

- ✓ Since $\frac{\partial E}{\partial c_a} = 0$, Eq. 5 reduces to: $c_a(H_{aa} - E\,S_{aa}) + c_b(H_{ab} - ES_{ab}) = 0$.......6

- ✓ Similary for $\frac{\partial E}{\partial c_b} = 0$, we get: $c_a(H_{ba} - E\,S_{bb}) + c_b(H_{bb} - ES_{bb}) = 0$.........7

- ➢ If the atomic orbitals $\boldsymbol{\varphi_a}$ and $\boldsymbol{\varphi_b}$ are normalized: $S_{aa} = S_{bb} = 1$,

- ➢ but since FA and FB are centered on different atoms: $S_{ab} = S_{ba} \neq 0$.

- ✓ Further, if both the atomic orbitals are of the same type, e.g., both are 1s, then

$$\varphi_a = \varphi_b \quad , H_{aa} = H_{bb}, \; H_{ab} = H_{ba} \text{ and } S_{ab} = S_{ba} = S.$$

- ✓ Equations (6) and (7) can therefore be written as: $c_a(H_{aa} - ES_{aa}) + c_b(H_{ab} - ES_{ab}) = 0$........8

$c_a(H_{ba} - ES_{ba}) + c_b(H_{aa} - ES_{bb}) = 0$.......9

- ✓ The coefficients c_a and c_b are determined by solving the secular determinant :

$$\begin{vmatrix} H_{aa} - E & H_{ab} - ES \\ H_{ab} - ES & H_{aa} - E \end{vmatrix} = 0,$$

- ✓ which gives a quadratic equation in $\boldsymbol{E}$ and hence two values of energy:

$$\boldsymbol{E_1} = \frac{\boldsymbol{H_{aa}+H_{ab}}}{\boldsymbol{1+S}}$$ (represents symmetric bonding mode).

and $$\boldsymbol{E_2} = \frac{\boldsymbol{H_{aa}-H_{ab}}}{\boldsymbol{1-S}}$$ (represents antisymmetric or antibonding mode).

- ✓ Substituting the values of $\boldsymbol{E_1}$ and $\boldsymbol{E_2}$ in either Eq. 8 or 9, we get $c_a \pm c_b$

  and hence two possible MOs : $\Psi_1 = C_a(\varphi_a + \varphi_b)$, and $\Psi_2 = C_a(\varphi_a - \varphi_b)$

- ✓ The coefficients C_a can be determined by normalizing the two MOs.
- ✓ The normalized MOs Ψ_1 and Ψ_2 are given as :

$$\Psi_1 = \frac{1}{\sqrt{2(1+S)}}(\varphi_a + \varphi_b) \qquad \text{and} \qquad \Psi_2 = \frac{1}{\sqrt{2(1-S)}}(\varphi_a - \varphi_b)$$

- ✓ The lowest energy atomic orbitals 1s of the hydrogen atom can be used to determine the integrals, H_{aa}, H_{ab}, and S and hence the energies $\boldsymbol{E_1}$ and $\boldsymbol{E_2}$ of the $\boldsymbol{H_2^+}$ molecule.

✓ Using Eq. (1) for the Hamiltonian of the hydrogen ion, we get:

$$\hat{H} = -\frac{1}{2}\nabla^2 - \frac{1}{r_a} - \frac{1}{r_b} + \frac{1}{R_{ab}}$$

➢ $H_{aa} = \int \varphi_a{}^* H\, \varphi_a \, d\tau = \int \varphi_a{}^* \left(-\frac{1}{2}\nabla^2 - \frac{1}{r_a} - \frac{1}{r_b} + \frac{1}{R_{ab}}\right) \varphi_a \, d\tau$

$$= \int \varphi_a{}^* \left(-\frac{1}{2}\nabla^2 - \frac{1}{r_a}\right) \varphi_a \, d\tau - \int \varphi_a{}^* \frac{1}{r_b} \varphi_a \, d\tau + \int \frac{\varphi_a{}^* \varphi_a}{R_{ab}} \, d\tau.$$

➢ Since φ_a is the solution of the Schrödinger equation for the hydrogen atom,

$$\left(-\frac{1}{2}\nabla^2 - \frac{1}{r_a}\right) \varphi_a = E_H \varphi_a$$

we get: $H_{aa} = E_H \underbrace{\int \varphi_a{}^* \varphi_a \, d\tau}_{1} - \underbrace{\int \varphi_a{}^* \frac{1}{r_b} \varphi_a \, d\tau}_{J} + \frac{1}{R_{ab}} \underbrace{\int \varphi_a{}^* \varphi_a \, d\tau}_{1}$

✓ For normalized wavefunction φ_a, this gives

$$H_{aa} = E_H + J + \frac{1}{R_{ab}}$$

Where, $J = -\int \varphi_a{}^* \frac{1}{r_b} \varphi_a d\tau$

- ✓ J is called the **Coulomb integral** and represents the energy due to electrostatic attraction of one nucleus (charge +1 in au).
- ✓ Similarly, we get: $H_{ab} = \int \varphi_a{}^* H \varphi_b d\tau = E_H \int \varphi_a{}^* \varphi_b \, d\tau - \int \varphi_a{}^* \frac{1}{r_b} \varphi_b d\tau + \frac{1}{R_{ab}} \int \varphi_a{}^* \varphi_b \, d\tau$

$$H_{ab} = E_H S + K + \frac{S}{R_{ab}}$$

where, $S = \int \varphi_a{}^* \varphi_b \, d\tau$ is the overlap integral for the two 1s orbitals.

$$K = -\int \varphi_a{}^* \frac{1}{r_b} \varphi_b d\tau$$

- ✓ K is called a **resonance** or **exchange integral** (it has no simple *interpretation*).

- ✓ Substituting the values of H_{aa}, H_{ab}, and S in

$$E_1 = \frac{H_{aa}+H_{ab}}{1+S} \quad \text{and} \quad E_2 = \frac{H_{aa}-H_{ab}}{1-S}$$

we get,

$$E_1 = E_H + \frac{J+K}{1+S} + \frac{1}{R_{ab}}$$

$$E_2 = E_H + \frac{J-K}{1-S} + \frac{1}{R_{ab}}$$

- K has a negative value and so $E_1 < E_2$.

- ✓ The atomic energies E_H which were equal when the two hydrogen atoms were infinitely apart.

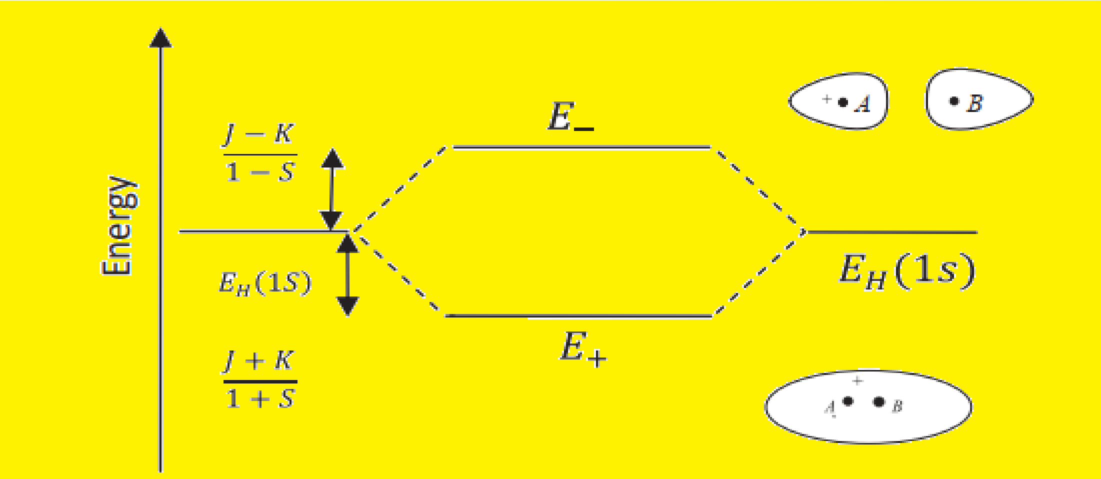
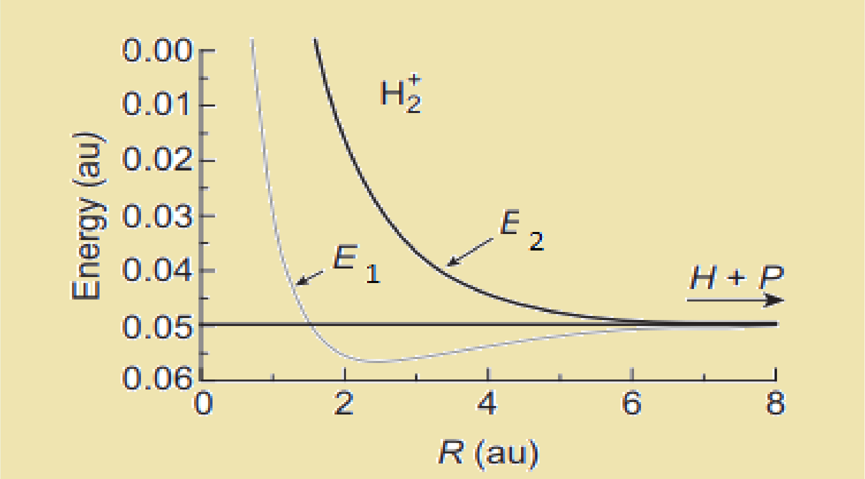
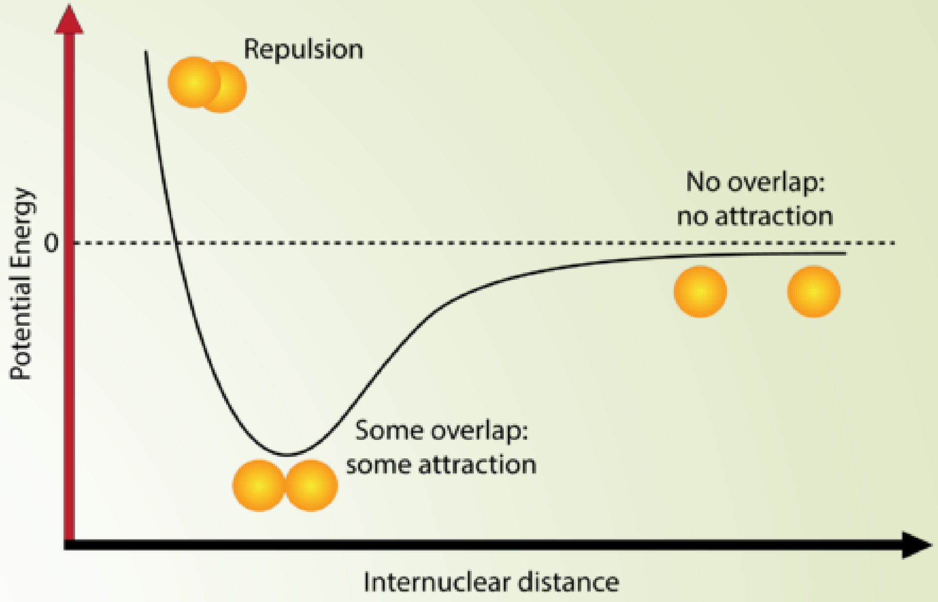


Figure.2 Energies and orbitals for the bonding and antibonding states of H_2^+.



Curves representing the total energy for the bonding E_1 and the antibonding E_2 MOs as a function of the internuclear distance R.



- ✓ The curve for E_1 (attractive) refers to the ground state of the molecule where a minimum energy is found for a nuclear distance of approximately $2a_0$ (1.32 $\dot{A}$). Thus the bond length of H_2^+ molecule is **1.320** $\dot{A}$.
- ✓ This value is higher than the experimental value of **1.06** $\dot{A}$.
- ✓ Since the H_2^+ has a potential energy minimum, it should exist as a stable molecule.
- ✓ The calculated **bonding energy** is **1.77 eV**, which is **lower** than the experimental value of **2.77** eV.
- ✓ The curve for E_2 (repulsive) shows **no minimum**.
- ✓ The molecule in this **state is instable** and with emission of energy, it splits simultaneously in one **hydrogen** atom and a proton $P(H^+)$.

- ✓ Using Eqs $\Psi_1 = \frac{1}{\sqrt{2(1+S)}}(\varphi_a+\varphi_b)$ and $\Psi_2 = \frac{1}{\sqrt{2(1-S)}}(\varphi_a-\varphi_b)$, the electron distributions in states Ψ_1 and Ψ_2 are given as,

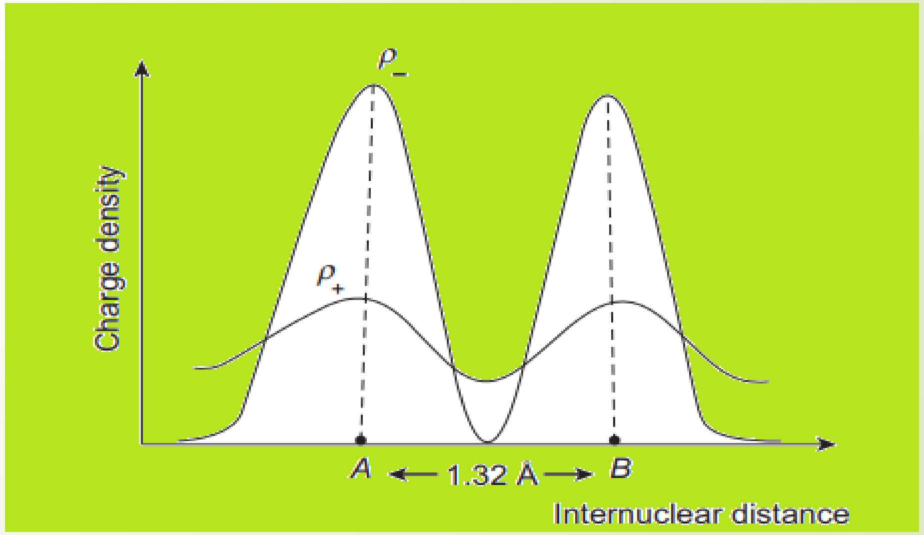
$$\rho_+ = \Psi_+^2 = \frac{1}{(2+2S)}(\varphi_a+\varphi_b)^2 = \frac{1}{(2+2S)}[1s_a^2+1s_b^2+2s_a s_b]$$

$$\rho_- = \Psi_-^2 = \frac{1}{(2-2S)}(\varphi_a-\varphi_b)^2 = \frac{1}{(2-2S)}[1s_a^2+1s_b^2\text{-}2s_a s_b]$$

- ✓ At a midpoint between the nuclei A and B, we have $1S_a=1S_b$, Hence

$$\rho_+ = \frac{4.1s_a^2}{(2+2S)} \quad \text{and} \quad \rho_- = 0$$

- ✓ Thus, in the bonding state Ψ_1 there is more electron density between the two nuclei.
- ✓ On the other hand, in the Ψ_2 state, the charge density at the center of the bond is zero less than sum of the electron densities of separate atoms.
- ✓ The electron has maximum probability of existing near the two protons leading to structures $(H^+ + \text{H})$.



Distribution of electron density along the molecular axis in H_2^+.