

COUNCIL OF SCIENTIFIC AND INDUSTRIAL RESEARCH
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CHEMICAL SCIENCES

CODE:01

2.4. Chemical bonding in diatomics

At a Glance

Atomic Orbitals, Energy levels of hydrogenic system, Shells, Subshells, Electronic spin, Radial Distribution Function, Valance Bond Theory, Hückel Approximation method,



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Key Statements

Basic Key Statements: Atomic orbitals (2.4.1), Hydrogenic energy levels (2.4.2), Shells, subshells and orbitals (2.4.3), Electron spin (2.4.4)

Standard Key Statements: The radial variation of atomic orbitals (2.4.5), Radial distribution function (RDF) (2.4.6), Symmetric and Antisymmetric wave functions of hydrogen molecule (2.4.7)

Advance Key Statements: Valence Bond Theory (2.4.8), Hückel Approximation method (2.4.10/11)



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2.4. Chemical bonding in diatomics

2.4.1. Atomic orbitals:

The wave function of an electron in an atom is called an orbital. Chemists use hydrogen atomic orbital to develop model status Central to the interpretation of inorganic chemistry and we will spend some time describing their shapes and significance.

2.4.2. Hydrogenic energy levels:

The energy of the bound electron is determined by n , the principal quantum number, in addition, l specifies the magnitude of the orbital angular momentum and m , specifies the orientation of the angular momentum.

Each of the wave functions obtained by solving the Schrödinger equation for hydrogenic atom is uniquely labeled by a set of 3 integers called Quantum numbers. These Quantum numbers are designated as n, l, m .

The allowed energies are specified by the principal quantum number, n . For a hydrogenic atom of atomic number, Z they are given by

$$E_n = -\frac{hcRZ^2}{n^2} \dots\dots\dots (i) \text{ [where } n = 1, 2, 3\dots]$$

$$\text{And } R = \frac{m_e e^4}{8h^3 c \epsilon_0^2} \dots\dots\dots (ii)$$

The calculated numerical value of R is $1.097 \times 10^7 m^{-1}$, in excellent agreement with the empirical value determined spectroscopically.

2.4.3. Shells, subshells and orbitals:

The principal Quantum number therefore defines a series of shells of the atom, or sets of orbitals with the same value of n and hence with the same energy and approximately the same radial extent. Shells with $n = 1, 2, 3, \dots$ are commonly referred to as K, L, M \dots shells.

The orbitals belonging to each shells are classified into subshells distinguished by a quantum number l . For a given value of n , the quantum number l can have the values 0 to $n-1$, giving n different values in all.

It is common practice to refer to each subshell by a symbol

Value of l	0	1	2	3	4	\dots
Subshell	s	p	d	f	g	\dots

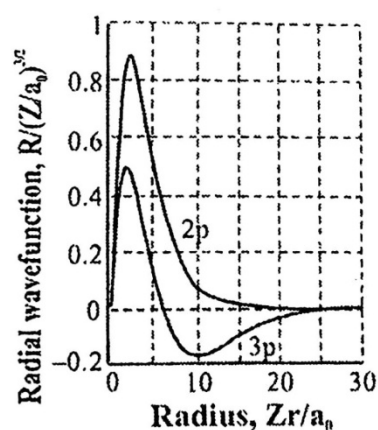
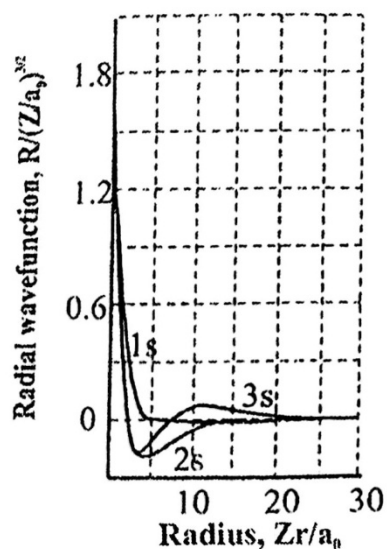
A subshell with quantum number l consists of $2l+1$ individual orbitals have different m value ranging from $-l$ to $+l$.

2.4.4. Electron spin:

In addition to the three Quantum numbers required to specify the spatial distribution of an electron in hydrogenic atom, two more Quantum numbers are needed to define state of an electron. Spin is a quantum mechanical property. Its value is $+\frac{1}{2}$ (anticlockwise spin) $-\frac{1}{2}$ (clockwise spin).

2.4.5. The radial variation of atomic orbitals:

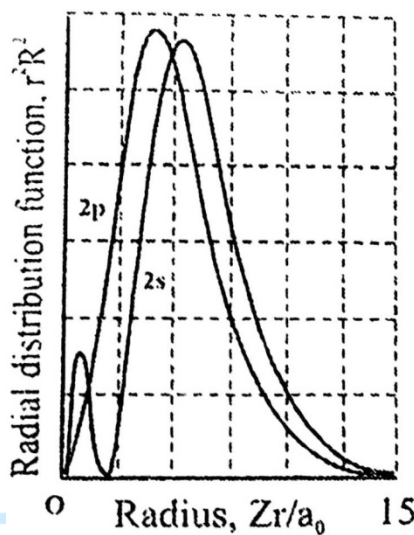
A 1s orbital the wave function with $n = 1$, $l = 0$ and $m = 0$, decays exponentially with distance from the nucleus and never passes through zero. All orbitals decay exponential at sufficiently great distance from the nucleus and this distance increases as n increases. Some orbitals oscillate through zero to close to the nucleus and thus have one or more radial nodes before beginning their final exponential decay.



2.4.6. Radial distribution function (RDF):

The radial distribution function is the probability that an electron will be found at a given distance from the nucleus, regardless of the direction.

$$P(r) = r^2 R(r)^2$$



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2.4.7. Symmetric and antisymmetric wave functions of hydrogen molecule:

When two H atoms meet a molecule is not always formed. The two atoms repel each other if the spins of two electrons are parallel ($\uparrow\uparrow$) and atoms attract each other if the spins of the two electrons are antiparallel ($\uparrow\downarrow$).

For two electrons the Schrödinger equation becomes

$$\nabla_1^2\psi + \nabla_2^2\psi + \frac{2m}{\hbar^2} \left(E - V_1 - V_2 - \frac{e^2}{r_{12}} \right) \psi = 0 \dots\dots(1)$$

For two electrons, there will be two spin functions $\alpha(1)$ and $\alpha(2)$. The total spin wave function is the product of two such spin functions. In all, we have for two electrons four spin functions:

	Electron 1	Electron 2
$\alpha(1)\alpha(2)$	\uparrow	\uparrow
$\beta(1)\beta(2)$	\downarrow	\downarrow
$\alpha(1)\beta(2)$	\uparrow	\downarrow
$\alpha(2)\beta(1)$	\downarrow	\uparrow

Each α describes the spin $+\frac{1}{2}$ and β describes the spin $-\frac{1}{2}$.

Since two electrons are indistinguishable from each other, so we choose linear combination of the four functions, $\alpha(1)\alpha(2)$ and $\beta(1)\beta(2)$ are already symmetrical. Instead of $\alpha(1)\beta(2)$ and $\alpha(2)\beta(1)$ we choose $\alpha(1)\beta(2) + \alpha(2)\beta(1)$ symmetrical function and $\alpha(1)\beta(2) - \alpha(2)\beta(1)$ anti symmetrical function.

Now four spin functions will be

$$\begin{array}{l} \alpha(1)\alpha(2) \\ \alpha(1)\beta(2) + \alpha(2)\beta(1) \\ \beta(1)\beta(2) \\ \alpha(1)\beta(2) - \alpha(2)\beta(1) \end{array} \quad \left. \begin{array}{l} +1 \\ 0 \\ -1 \\ 0 \end{array} \right\} \begin{array}{l} \text{with } S = 1 \\ \\ \\ \text{with } S = 0 \end{array}$$

The complete function of an electron is the product of the orbital wave function multiplied by one of the spin functions. As per Pauli exclusion principle only two product will be allowed.

$$[\psi_a(1)\psi_b(2) + \psi_a(2)\psi_b(1)]\alpha(1)\beta(2) - \alpha(2)\beta(1)$$

$$\text{And } [\psi_a(1)\psi_b(2) - \psi_a(2)\psi_b(1)] \begin{bmatrix} \alpha(1)\alpha(2) \\ \beta(1)\beta(2) \\ \alpha(1)\beta(2) + \alpha(2)\beta(1) \end{bmatrix}$$

Hence total wave function of two electrons is always antisymmetrical in the electrons, because symmetry orbital functions will be associated with the antisymmetric spin function ($S = 0$, singlet) and antisymmetric orbital function will be associated with symmetrical spin function ($S = 1$, triplet).

Therefore molecular orbital treatment of H_2 may be represented as

$$[\phi_A(1)\phi_B(1)][\phi_A(2)\phi_B(2)] = [1s_A(1)1s_B(1)][1s_A(2)1s_B(2)]$$

2.4.8. Valence Bond Theory:

Let the two electron of H_2 designated by (1) and (2) and the two nuclei a and b.

So, $\psi_{AB} = C_1\psi_1 + C_2\psi_2$; where $\psi_1 = \phi_a(1)\phi_b(2)$ and $\psi_2 = \phi_a(2)\phi_b(1)$

Bonding M.O = $\psi_+ = N_+[\phi_a(1)\phi_b(2) + \phi_a(2)\phi_b(1)]$

Antibonding M.O = $\psi_- = N_-[\phi_a(1)\phi_b(2) - \phi_a(2)\phi_b(1)]$

Applying normalization condition over ψ_+ we get,

$$\int N_+[\phi_a(1)\phi_b(2) + \phi_a(2)\phi_b(1)]N_+[\phi_a(1)\phi_b(2) + \phi_a(2)\phi_b(1)]d\tau = 1$$

$$\Rightarrow N_+^2 \left[\int \phi_a(1)\phi_a(1)d\tau \int \phi_b(2)\phi_b(2)d\tau + \int \phi_a(1)\phi_a(2)d\tau + \int \phi_b(1)\phi_b(2)d\tau + \int \phi_a(1)\phi_a(2)d\tau \int \phi_b(1)\phi_b(2)d\tau + \int \phi_b(1)\phi_b(1) \int \phi_a(2)\phi_a(2)d\tau \right] = 1$$

$$\Rightarrow N_+^2[1 + 2s^2 + 1] = 1$$

$$\Rightarrow \boxed{N_+ = \frac{1}{\sqrt{2(1+s^2)}}}$$

Similarly, we have $N_- = \frac{1}{\sqrt{2(1-s^2)}}$

$$\text{So, } \psi_+ = \frac{1}{\sqrt{2(1+s^2)}} [\phi_a(1)\phi_b(2) + \phi_a(2)\phi_b(1)]$$

$$\text{And, } \psi_- = \frac{1}{\sqrt{2(1-s^2)}} [\phi_a(1)\phi_b(2) - \phi_a(2)\phi_b(1)]$$

For, Antisymmetric function

$$\psi_1 = [\phi_1(1)\phi_2(2) + \phi_1(2)\phi_2(1)]$$

And for symmetric function,

$$\psi_2 = [\phi_1(1)\phi_2(2) - \phi_1(2)\phi_2(1)]$$

2.4.9. Spin and Spatial part:

Spin Part	Spatial Part
$\alpha(1)\alpha(2) \rightarrow \text{symmetric}$	$\phi_a(1)\phi_b(2) \rightarrow \text{symmetric}$
$\beta(1)\beta(2) \rightarrow \text{symmetric}$	$\phi_a(2)\phi_b(1) \rightarrow \text{symmetric}$
$\frac{1}{\sqrt{2}} [\alpha(1)\beta(2) + \beta(1)\alpha(2)] \rightarrow$ Symmetric	$\frac{1}{\sqrt{2}} [\phi_a(1)\phi_b(2) + \phi_a(2)\phi_b(1)] \rightarrow$ Symmetric
$\frac{1}{\sqrt{2}} [\alpha(1)\beta(2) - \beta(1)\alpha(2)] \rightarrow$ Antisymmetric	$\frac{1}{\sqrt{2}} [\phi_a(1)\phi_b(2) - \phi_a(2)\phi_b(1)] \rightarrow$ Antisymmetric

The wave function must be antisymmetric with respect to any interchange of electron.

$$\psi_{\text{total}} = \psi_{\text{spatial}} \times \psi_{\text{spin}} \rightarrow \text{Antisymmetric}$$

2.4.10. Hückel Approximation method:

This method is mainly used for organic molecules of linear secular equation.

As we know that conjugate diene are an alternative arrangement of single and double bond between carbon atoms.

These molecular orbitals may be constructed by the linear combination of carbon 2pz orbitals i.e., $\psi_n = \sum_{i=1}^n C_i \psi_{2p_z}(i) \dots \dots \dots (1)$

$$C_1(H_{11} - ES_{11}) + C_2(H_{12} - ES_{12}) + \dots + C_n(H_{1n} - ES_{1n}) = 0$$

$$\dots \dots \dots$$

$$C_1(H_{n1} - ES_{n1}) + C_2(H_{n2} - ES_{n2}) + \dots + C_n(H_{nn} - ES_{nn}) = 0$$

$\dots \dots \dots (2)$

For the non trivial roots we set $n \times n$ secular determinant equal to zero,

That is
$$\begin{vmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} & \dots & \dots & H_{1n} - ES_{1n} \\ H_{21} - ES_{21} & H_{22} - ES_{22} & \dots & \dots & H_{2n} - ES_{2n} \\ H_{31} - ES_{31} & H_{32} - ES_{32} & \dots & \dots & H_{3n} - ES_{3n} \\ \dots & \dots & \dots & \dots & \dots \\ H_{n1} - ES_{n1} & H_{n2} - ES_{n2} & \dots & \dots & H_{nn} - ES_{nn} \end{vmatrix} = 0 \dots \dots \dots (3)$$

$$\begin{vmatrix} \alpha - E & \beta & 0 & 0 & 0 & \dots \\ \beta & \alpha - E & \beta & 0 & 0 & \dots \\ 0 & 0 & \alpha - E & \beta & 0 & \dots \\ 0 & \beta & 0 & \alpha - E & 0 & \dots \\ \beta & 0 & 0 & 0 & \alpha - E & \dots \\ \dots & \dots & \dots & \dots & \dots & \dots \end{vmatrix} = 0$$

$S_{ii} = 1$; $S_{ij} = 0$; $H_{ij} = \alpha$ (coulomb integral)

$$\int \phi_i H \phi_i d\tau = \alpha$$

Exchange integral = $H_{ij} = \int \phi_i H \phi_j d\tau = \beta$

Overlap integral = $S_{ij} = \int \phi_i \phi_j d\tau$

2.4.11. **The approximations introduced by Hückel are:**

- (a) All overlap integrals S_{ij} are assumed to be equal to zero. Since the atomic orbitals are normalized, $S_{ij} = 1$.
- (b) H_{ij} is assumed to be the same for all the carbon atoms involved. It is usually represented by the symbol α and called as coulomb integral.
- (c) H_{ij} is assumed to have the constant value β if atom i and j are bounded directly, it is called exchange integral.

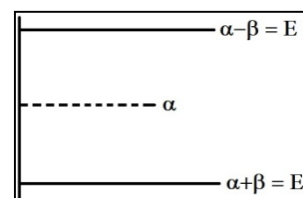
For ethylene: $H_2C=CH_2$:

The secular determinant will take form,

$$\begin{vmatrix} \alpha - E & \beta \\ \beta & \alpha - E \end{vmatrix} = 0$$

That is $\frac{\alpha - E}{\beta} = 1$, which gives $E_+ = \alpha + \beta$ and $E_- = \alpha - \beta$

Therefore the ground electronic energy is $2(\alpha + \beta)$.



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