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Introduction to Molecular Orbital

Now we shall move from atom to molecule for further study. This will require the understanding of electronic terms symbol for molecular orbital.

Terms Symbol for energy levels:

The atomic states are represented by spectral terms $^{(2S+1)}L_J$. Here **L**= total orbital angular momentum, **S** = total spin and **J** = **S** + **L** (vector addition).

In case of molecule, there are no law of conservation for total angular momentum. Because, electric field of several nuclei is not centrally symmetric. But for diatomic molecules, the electric field is axially symmetric about the axis passing through two nuclei. Hence it angular momentum component is conserved.

- The molecular energy levels can be classified according to the value of orbital angular momentum component. The quantum number for this component is denoted by Λ. For $\Lambda = 0,1,2\ldots$ the electronic terms will be denoted by $\Sigma, \Pi, \Delta \ldots$ etc. The total spin is denoted as $(2S+1)$ in upper left prefix as $^{(2S+1)}\Lambda$, where $S = s_1 + s_2$.

- There is also reflection symmetry about axis, denoted as $\pm$. The overall notation would be $^{(2S+1)}\Lambda^{\pm}$. There is another type of symmetry: the parity symmetry (Hamiltonian remains unchanged if all electrons coordinates change sign) at the center point bisecting the line joining the two nuclei. Even wave function denotes by g and odd denoted by u. The electronic term for such diatomic molecules are denoted as $^{2S+1}\Lambda^{\pm}_{u,g}$.

Molecular Orbitals

- Now under the Born Oppenheimer approximation, we shall try to solve Schrödinger equation for electrons in case of molecules.

- A possible approach is to form a trial function of the molecule by using atomic wave functions of each atom.

- For ground state and low-lying excited states, the linear combination of atomic ground state wave functions associated with different nuclei are considered in practice to form trial functions.

- These trail functions are referred as molecular orbitals. We here use variational method to obtain the ground state wave function and energy of a molecule. This method is known as linear variational method.

Let us consider a trail wave function ψ as given by a linear combination of atomic orbitals ϕ_i where i(=1,2,3....) denotes different nuclei,

$$\Psi = \sum_i c_i \phi_i ,$$

where, c_i are the parameters to be determined by variational method for a given molecular Hamiltonian.

Here we are introducing two special integrals:

$$\mathbf{H}_{ij} \equiv \langle \phi_i | \mathbf{H} | \phi_j \rangle \quad ; \quad \mathbf{S}_{ij} \equiv \langle \phi_i | \phi_j \rangle$$

Here, $\mathbf{H}_{ij}$= Hamiltonian matrix and $\mathbf{S}_{ij}$= overlap integrals

The energy expectation is given by :

$$E = \langle \hat{H} \rangle = \frac{\langle \Psi | \hat{H} | \Psi \rangle}{\langle \Psi | \Psi \rangle} = \frac{\sum_{i,j} c_i c_j H_{ij}}{\sum_{i,j} c_i c_j S_{ij}} \ .$$

Now we want to minimise the energy with respect to c_k, which requires that

$$\partial E / \partial c_k = 0$$

for all i. Hence differentiating the expectation energy equation:

$$\frac{\partial E}{\partial c_k} = \frac{\sum_j c_j H_{kj} + \sum_i c_i H_{ik}}{\sum_{i,j} c_i c_j S_{ij}} - \frac{\left(\sum_j c_j S_{kj} + \sum_i c_i S_{ik} \right) \sum_{i,j} c_i c_j H_{ij}}{\left(\sum_{i,j} c_i c_j S_{ij} \right)^2}$$

$$= \frac{\sum_j c_j \left[H_{kj} - E S_{kj} \right] + \sum_i c_i \left[H_{ik} - E S_{ik} \right]}{\sum_{i,j} c_i c_j S_{ij}} = 0 \ ,$$

This is satisfied if each term in numerator vanishes.

$$\sum_i c_i \left[H_{ik} - E S_{ik} \right] = 0 \; .$$

For all k, these equations are known as Secular Equations.

If the functions ϕ_is are orthonormal, then the secular equations reduces to the familiar eigen value form:

$$\Sigma_{i=1 \to N} \; c_i H_{ik} = E c_i$$

From the secular equations with orthonormal functions, we have k simultaneous secular equations in k unknowns. These equations can also be written in matrix notation. This is known as secular determinant.

For a non-trivial solution (i.e $c_i \neq 0$, for all i), the determinant of secular matrix must be equal to zero.

$$\det |H_{ik} - ES_{ik}| = 0$$

Therefore the basic procedure in molecular calculations is to first calculate the Hamiltonian matrix H_{ik} and overlap integral S_{ik}, and then to diagonalise the secular determinant to obtain eigenvalues E and coefficients c_i.

The procedure, we applied here is **linear variation theory.**

Problem 1: Solve it your self:
If our trial function ψ_{trial} for a molecule is a linear combination of two functions ϕ_1 and ϕ_2, then the secular determinant looks like

$$\begin{vmatrix} H_{11} - E_{trial}S_{11} & H_{12} - E_{trial}S_{12} \\ H_{12} - E_{trial}S_{12} & H_{22} - E_{trial}S_{22} \end{vmatrix} = 0$$

Molecular orbital of H$_2^+$ ion

•At first we have to consider hydrogen molecular ion where single electron moves in the field of two proton before we study a diatomic molecule.

•This approach is very similar to the atomic quantum mechanics where we study hydrogen atom and use its wavefunctions as basis for other atoms.

•Let two protons are fixed at position **±R/2** and then applying Born-Oppenheimer approximation, the single electron eigenequation becomes

$$\left(-\frac{\hbar^2}{2m}\nabla_r^2 - \frac{e^2}{4\pi\epsilon_0|\mathbf{r}-\mathbf{R}/2|} - \frac{e^2}{4\pi\epsilon_0|\mathbf{r}+\mathbf{R}/2|} + \frac{e^2}{4\pi\epsilon_0 R}\right)\psi(\mathbf{r},\mathbf{R}) = E(R)\psi(\mathbf{r},\mathbf{R})$$

where the 2nd and 3rd terms are attractive interactive between the electron and the two protons and the last term (constant) is the repulsive interaction between two protons. These two contributions combine to give total energy with a minimum at an equilibrium position R$_0$ (the size of the molecule), as shown in Fig. given next slide

From the figure we can conclude that
At large separation R → ∞, the electron will be bound to one of nucleus, the energy is about −13.6 eV.
When R → 0, the electron will be bound to Z = 2 nucleus with Energy $-13.6Z^2$ = −54.4 eV plus nuclear repulsion energy which goes to infinity as R → 0. The equilibrium minimum energy $E(R_0)$ is between these two positions.
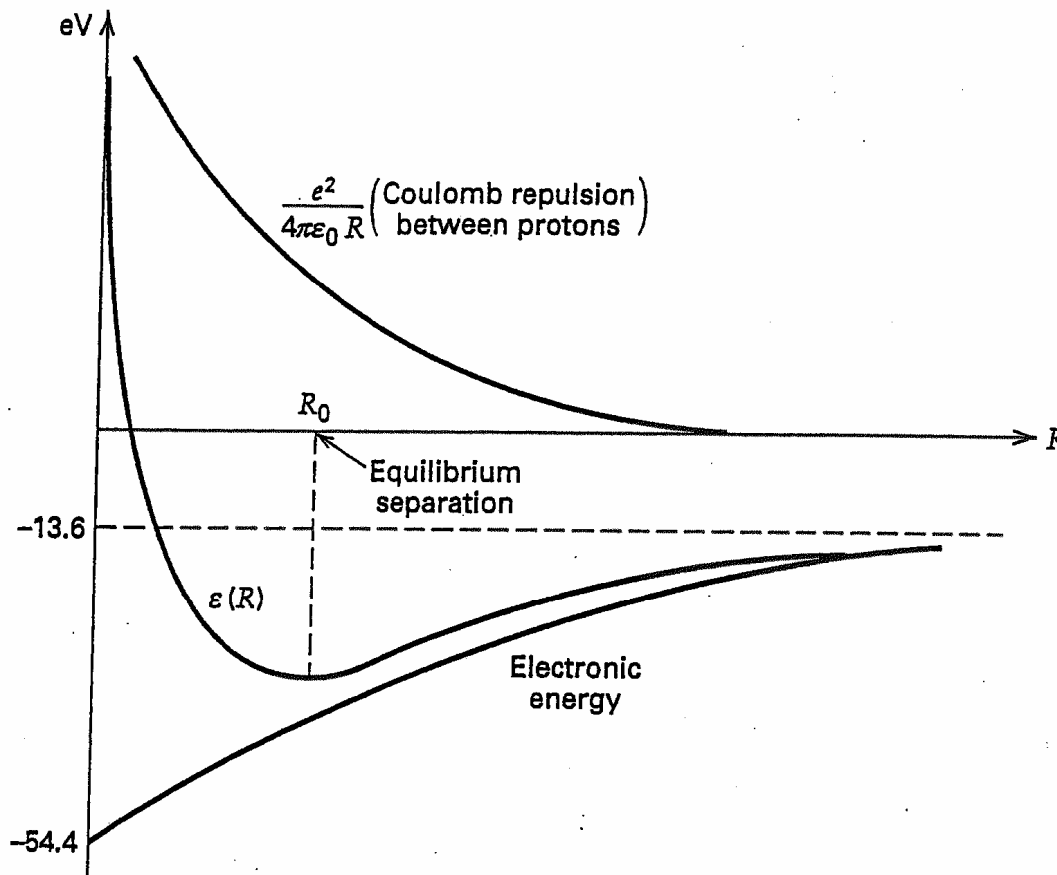

Fig. *Hydrogen ion energy as a function of separation of the two protons*

We follow the linear combination of atomic orbitals (LCAO) procedure to calculate the ground-state energy, using molecular orbital method.

We consider a trial wavefunction based on single hydrogen ground-state wavefunctions $\varphi = \varphi_{1s}$ centered at R/2 denoted as φ_1 and at −R/2 denoted as φ_2. Our trial wavefunction is a linear combination of these two hydrogen (1s) orbitals

$$\psi(r,R) = c_1\varphi_1 + c_2\varphi_2$$

Where $\qquad \phi_1 = \dfrac{1}{\sqrt{\pi a_0^3}} e^{-|\mathbf{r}-\mathbf{R}/2|/a_0}, \qquad \phi_2 = \dfrac{1}{\sqrt{\pi a_0^3}} e^{-|\mathbf{r}+\mathbf{R}/2|/a_0}$

The overlap integral S is, $S = S_{12} = S_{21} = \langle\varphi_1|\varphi_2\rangle$
Note that $S_{11} = S_{22} = 1$ due to normalization of 1s orbitals.
The Hamiltonian matrix
$\alpha = H_{11} = H_{22} = \langle\varphi_1|\mathbf{H}|\varphi_1\rangle$, $\beta = H_{12} = H_{21} = \langle\varphi_1|\mathbf{H}|\varphi_2\rangle$

The secular equation is

$$\begin{vmatrix} \alpha - E & \beta - ES \\ \beta - ES & \alpha - E \end{vmatrix} = (\alpha - E)^2 - (\beta - ES)^2 = 0, \quad \text{or} \quad \alpha - E = \pm(\beta - ES)$$

This equation has solutions, $\quad E_{\pm} = \dfrac{\alpha \pm \beta}{1 \pm S}$

The corresponding values for the coefficients

$$c_1 = c_2 = c_+ = \frac{1}{\sqrt{2(1 + S)}} \quad \text{for} \quad E_+$$

and

$$c_1 = -c_2 = c_- = \frac{1}{\sqrt{2(1 - S)}} \quad \text{for} \quad E_-$$

The actual values for S, α and β can be calculated exactly by using the so-called ellipsoidal coordinates. Here we just quote the results. The overlap integral is given by

$$S = \left[1 + \frac{R}{a_0} + \frac{1}{3} \left(\frac{R}{a_0} \right)^2 \right] e^{-R/a_0}$$

The diagonal Hamiltonian matrix element is

$$\alpha = E_{1s} - J + \frac{e^2}{4\pi\epsilon R}, \quad J \equiv \frac{e^2}{4\pi\epsilon} \langle \phi_1 | \frac{1}{r_2} | \phi_1 \rangle = \frac{e^2}{4\pi\epsilon R} \left[1 - \left(1 + \frac{R}{a_0} \right) e^{-2R/a_0} \right]$$

where the first term is the hydrogen ground-state energy, second term J > 0 corresponds to the electrostatic energy between electron with charge distribution φ_1^2 and the nucleus 2

The off-diagonal element is

$$\beta = \left(E_{1s} + \frac{e^2}{4\pi\epsilon R} \right) S - K \, , \quad K \equiv \frac{e^2}{4\pi\epsilon} \langle \phi_1 | \frac{1}{r_1} | \phi_2 \rangle = \frac{e^2}{4\pi\epsilon a_0} \left(1 + \frac{R}{a_0} \right) e^{-R/a_0}$$

where K > 0 has no direct classical analogue. It represents the interaction between the overlap charge $-e\varphi_1\varphi_2$ and the nucleus1. Notice that all three special integrals
S, J,K $\rightarrow$ 0 as R $\rightarrow$ ∞.
In summary, the two energies of hydrogen ion using MO are

$$E_+ = E_{1s} + \frac{e^2}{4\pi\epsilon R} - \frac{J+K}{1+S}$$

$$E_- = E_{1s} + \frac{e^2}{4\pi\epsilon R} - \frac{J-K}{1-S}$$

and the corresponding two states are
$$\psi_+ = c_+(\varphi_1 + \varphi_2) \, , \ \psi_1 = c_-(\varphi_1 - \varphi_2)$$

As both J and K are positive, E_+ is lower than E_-. Their behaviors as functions of separation R are shown in next figure given below. There is a clear minimum R_0 for E_+. We refer state ψ_+ as bonding orbital with lower energy and ψ_- as antibonding state with higher energy. Numerically, the bonding energy has a minimum at $R_0 = 130$ pm and the dissociation energy ($E_{1s} - E_+$) is about 170 kJ/mol. The experimental values are 106 pm and 251 kJ/mol. More accurate calculations reveal major bonding energy comes from further shrinkage of the orbitals on to the nuclei which is beyond the
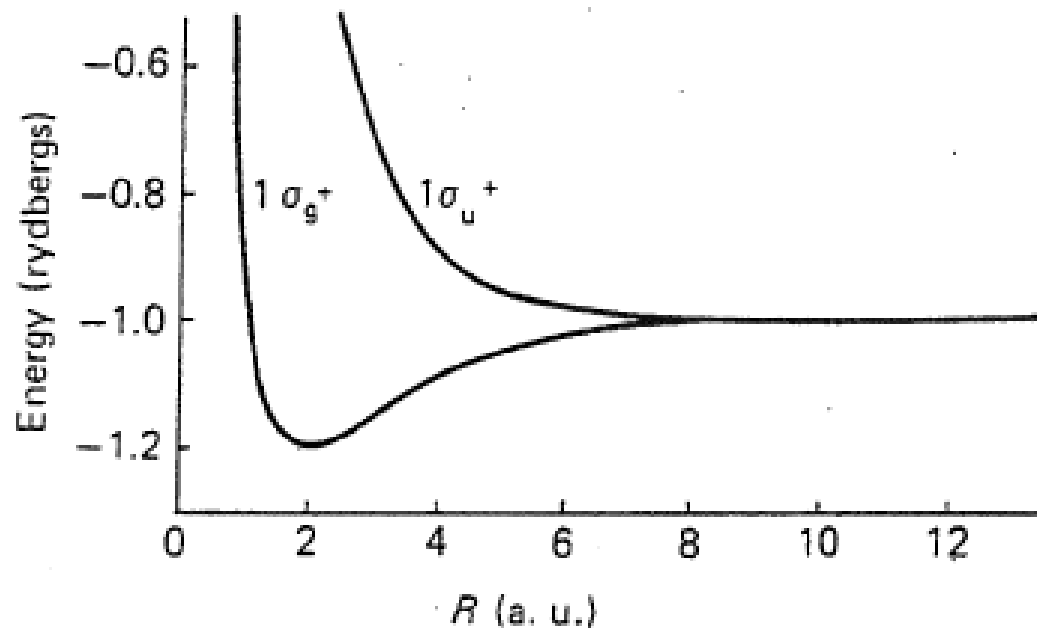simple approximation employed here.

Figure: Energy of bonding state ψ_+ (denoted as σ_g) and of antibonding state ψ_- (denoted σ_u) as function of separation R.
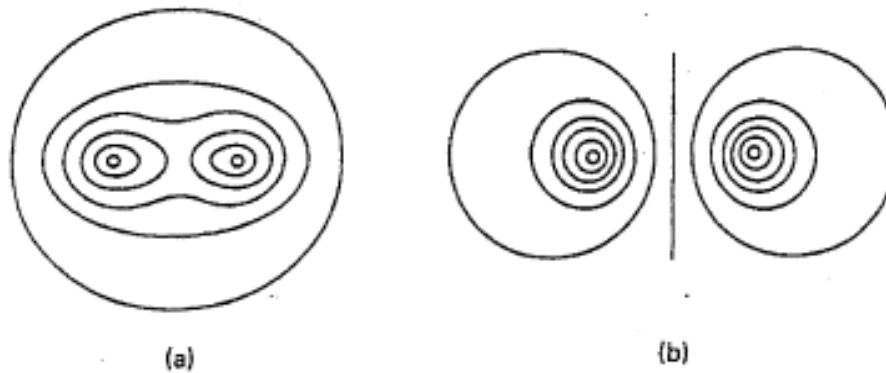
Figure: Charge distribution |ψ|² of H_2^+. (a) Bonding state. (b) Antibonding state.

Special integrals using ellipsoidal coordinates

For hydrogen molecule ion, we introduce ellipsoidal coordinates

$$\mu = \frac{r_1 + r_2}{R}, \quad \nu = \frac{r_1 - r_2}{R}$$

with volume element in integral

$$d^3r = \frac{1}{8}R^3(\mu^2 - \nu^2)d\mu \, d\nu \, d\phi, \quad 1 \le \mu < \infty, \quad -1 \le \nu \le 1, \quad 0 \le \phi \le 2\pi$$

Using the transformation

$$r_1 = \frac{1}{2}(\mu + \nu) , \quad r_2 = \frac{1}{2}(\mu - \nu)$$

the integrals become elementary. For example, the overlap integral

$$
\begin{aligned}
S &= \langle \psi_1 | \psi_2 \rangle = \frac{1}{\pi a_0^3} \int d^3 r \, e^{-(r_1+r_2)/a_0} = \frac{1}{\pi a_0^3} \int_0^{2\pi} d\phi \int_0^{\infty} d\mu \int_{-1}^{1} d\nu \frac{1}{8} R^8 (\mu^2 - \nu^2) e^{-\mu R/a_0} \\
&= \left[1 + \frac{R}{a_0} + \frac{1}{3} \left(\frac{R}{a_0} \right)^2 \right] e^{-R/a_0} .
\end{aligned}
$$

Note that S → 0 as R → ∞.

Reference:

1) Molecular Quantum mechanics, Atkins and Friedman, 4th edition

2) Physical Chemistry by K. L. Kapoor

3) Physical Chemistry by Levine