

COURSE CODE: CHM 441

COURSE TITLE: QUANTUM CHEMISTRY

CREDIT UNIT: 02

COURSE DURATION: TWO HOURS PER WEEK

COURSE DETAILS:

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COURSE CONTENT:

Section A

- Postulates of quantum mechanics
- Operator angular momentum
- Solution of the hydrogen atom problem

Section B

Quantum chemistry and chemical bonding

- Secular equation
- Variation principle
- Application of quantum chemistry
 - Valence theory of chemical bonding
 - Molecular theory of chemical bonding
 - Configuration interaction
 - Hybridization
- Computational aspect of chemical bonding
- Perturbation theory

COURSE REQUIREMENTS:

Students are expected to have a minimum of 75% attendance in this course before they could be allowed to write the examination.

READING LIST:

1. Gross, J.M. and Wiseall, B. *Principle of physical chemistry*. MacDonalD and Evans Handbook series, 1972
2. Atkins, P.W. *Physical chemistry*. Oxford University Press, sixth edition, 1999
3. Engel, T. and Ried, P. *Physical Chemistry*. Pearson Education Inc., 2006
4. Chandra, A.K. *Introductory quantum chemistry*, Tata McGraw-Hill company Ltd. 2nd edition, 1983
5. Roger Grinter . *The quantum in Chemistry: An Experimentalist's View*, John Wiley & sons, Ltd. 2005

6. George D.V. *Principles of Quantum Chemistry*.
Pergamon press Inc. 1976

7. Alberty, R.A. and Sibley, R.J. *Physical Chemistry*.
John Wiley & sons, Inc. 2nd edition, 1986

LECTURE NOTES

SECTION A

INTRODUCTION

Quantum mechanics is a clear replacement of classical mechanics. Plank in 1900 showed that the description of the distribution of energies of electromagnetic radiation in a cavity requires the quantization of energy. Modern Chemistry relies on quantum mechanics for the description of most phenomena. In the beginning of twentieth century, a number of experimental observations were made that could not be reconciled or explained by the laws of classical physics. E.g. Plank measured the emission of radiation from a hot mass (called blackbody radiation) and found that it did not fit the formula derivation from classical physics. To derive the right equation, he had to assume in contrast to classical physics ideas that radiation of frequency (ν) is absorbed and emitted only in multiples of $h\nu$ where h is a universal constant.

In another experiment, it was discovered that the energy of an electron ejected from metals by the absorption of radiation (the photoelectric effect) depended only on the frequency of the radiation and not on intensity, again in contrast with classical ideas. Einstein in 1905 explained this by suggesting that light of frequency (ν) consists of quanta of energy $h\nu$, called Photons. When one Photon strikes an electron in the metal, the electron is ejected with a kinetic energy that is, the difference between the energy of the photon and the minimum energy needed to eject the electron.

In 1911, Rutherford showed that an atom has all its positive charge in a tiny nucleus with the electrons surrounding it, but this could not be understood using classical mechanics which predicted that the electrons would radiate energy and fall into the nucleus.

Bohr in 1913 postulated the existence of stable orbits in atoms and the quantization of angular momentum which marks the beginning of quantum mechanics applied to atoms, but was unable to describe atoms with more than one electron.

The underlying problem that emerged from these and other experiments was that electromagnetic radiation shows properties that are both wavelike and particle-like. Experiments showing the interference of light must be explained with wave theory whereas that of photoelectric effect reveals particlelike principles.

De Broglie in 1924 developed an equation for the wavelength of a particle by reasoning in terms of light. In 1926 Schrodinger published the wave equation for atomic and molecular systems. In 1927 Heisenberg put forward an uncertainty principle implying that if the momentum of a particle is known precisely, the position of that particle is completely unknown. This is the new mechanics called quantum mechanics, It challenged classical mechanics which states that the position and momentum of a particle can be calculated precisely at all times from knowledge of the forces on the particle. Photons which have energies given by $E = h\nu$ are usual particles in that they have zero rest mass and travel with the speed of light. However, Einstein suggested that photons have a relative mass given by $E = mc^2$. Equating these two equations for the energy of a photon yields.

$$E = mc^2 = h\nu = hc/\lambda \text{ or } E = mc^2 = P = hc/\lambda \dots\dots\dots [1]$$

Where P = momentum of photon.

By analogy de Broglie [1924] suggested that the momentum of a particle with finite rest mass is given by $mv = P = h/\lambda$ or $\lambda = h/p = h/mv \dots\dots\dots [2]$

Where m = rest mass

$$V = \text{velocity and } V = P/m \dots\dots\dots [3]$$

Equation [2] shows that all particles have a wavelike property with wavelength that is inversely proportional to the momentum.

The energy of an electron is given as the product of elementary charge (e) and potential difference in Joules and the energy of an electron of mass (m) moving with a velocity v well below the velocity of light is given by

$$E = (1/2)mv^2 = P^2/2m \dots\dots\dots [4]$$

Total Energy of a Particle

The total energy E of a particle is equal to the sum of its kinetics energy $((1/2)mv^2)$ and its potential energy V.

$$E = (1/2)mv^2 + V = P^2/2m + V \dots\dots\dots (5)$$

The Heisenberg uncertainty principle

In 1927, Heisenberg formulated his principle that values of particular pairs of observables cannot be determined simultaneously with arbitrarily high precision in mechanics. Examples of pairs of observables that are restricted in this way are momentum and position, and energy and time; such pairs are referred to as ‘complementary’.

The quantitative expressions of the Heisenberg uncertainty principle can be derived by combining the de Broglie relation $P = h/\lambda$ and the Einstein relation $E = h\nu$ with properties of all waves.

The de Broglie wave for a particle is made up of a super position of an infinitely large number of waves of the form

$$\Psi_{(x,t)} = A \sin 2\pi(x/\lambda - \nu t) \\ = A \sin 2\pi(kx - \nu t) \dots\dots\dots (6)$$

Where A is amplitude and k is the reciprocal wavelength .Let’s consider one spatial dimension for simplicity. The waves that are added together have infinitesimal different wavelengths. This superposition of waves produces a wave packed as shown below:

Figures (a) and (b)

By the use of Fourier integral methods, it is possible to show that for wave motion of any type

$$\Delta_x \Delta_k = \Delta_x \Delta(1/\lambda) \geq 1/4\pi \dots\dots\dots (7)$$

$$\text{And } \Delta_t \Delta_\nu \geq 1/4\pi \dots\dots\dots (8)$$

Where Δ_x is the extent of the wave packed in space, Δ_k is the range in reciprocal wavelength, Δ_ν is the range in frequency, and Δ_t is a measure of the time required for the packed to pass a given point.

Note that the Δ 's are actually standard deviations if at a given time the wave packed extends over a short range of x values; there is a limit to the accuracy with which we can measure the wavelength. If a wave packed is of short duration, there is a limit to the accuracy with which we can measure the frequency.

One form of the Heisenberg uncertainty principle may be by substitution the de Broglie relation in equation [7]. Since $1/\lambda = P_x/h$ for motion i x direction, then by substitution,

$$\Delta_x \Delta P_x/h \geq 1/4\pi \dots\dots\dots (9)$$

$$\text{And } \Delta P_x \geq h/4\pi\Delta_x \dots\dots\dots (10)$$

$$\Delta_x \Delta P_x \geq \hbar/2 \dots\dots\dots (11)$$

Where $\hbar = h/2\pi$ and it is called ‘h bar’

The limitation to determine the simultaneous position and momentum of an electron is well understood. To determine the position of the electron at least photon would have to strike the electron, and momentum of the electron would inevitably be after in the process. This would definitely limit our ability to measure the momentum. If we use a photon of shorter wavelength to determine the position of the electron more accurately, the disturbance of the momentum is greater and Δp_x is greater according to equation [11]. This same uncertainty applies to $\Delta y \Delta p_y$ and $\Delta z \Delta p_z$.

Another form of the Heisenberg uncertainty principle may be derived by substituting $E = h\nu$ in equation [8].

These yields:

$$\Delta_t \Delta E/h \geq 1/4\pi \dots\dots\dots [12]$$

$$\Delta t \Delta E \geq \hbar/2 \dots\dots\dots [13]$$

The Schrödinger equation

The time independent Schrödinger equation is written as:

$$-(\hbar^2/8\pi^2m)(d^2/dx^2 + d^2/dy^2 + d^2/dz^2)\Psi_{(x,y,z)} + V_{(x,y,z)}\Psi_{(x,y,z)} = E\Psi_{(x,y,z)}$$

Or where Ψ = wave function in three dimension..... (14)

$$-(\hbar^2/8\pi^2m)\nabla^2 \Psi_{(x,y,z)} + V_{(x,y,z)}\Psi_{(x,y,z)} = E\Psi_{(x,y,z)} \dots\dots\dots (15)$$

$$\nabla^2 = \text{del square} = (d^2/dx^2 + d^2/dy^2 + d^2/dz^2)$$

The time independent Schrödinger equation provides a means for calculating the wave function Ψ for a quantum mechanical particle, and the probability density is given by the product of the wave function with its complex conjugate.

Note that the probability of finding the particle between x and x+dx is given by $\Psi^*_{(x)}\Psi_{(x)}dx$ where Ψ^* is the complex conjugate of Ψ (The complex conjugate is found by changing i to -i everywhere in Ψ). This means that $\Psi^*_{(x)}\Psi_{(x)}$ is a probability density.

For example, if Ψ is a complex number, it can be written as a+ib then $\Psi^* = a - ib$ and $\Psi^*\Psi = a^2 + b^2$, which is clearly positive and real. We often write $(\Psi)^2$ for $\Psi^*\Psi$. With the interpretation of Ψ ; the probability of finding the particle between x_1 and x_2 is probability

$$(x_1 \leq x \leq x_2) = \int \Psi^*_{(x)}\Psi_{(x)}dx \dots\dots\dots$$

(16) and since the probability of finding the particle anywhere on the x-axis must be 1.

$$(-\infty \leq x \leq +\infty) = \int \Psi^*_{(x)}\Psi_{(x)}dx = 1 \text{ in one dimension } \dots\dots\dots (17)$$

For this one-dimensional example, the units of Ψ are $m^{-1/2}$ to ensure that the probability is a pure number. If we were in considering a 3-dimensional system, the integral of $(\Psi)^2$ over 3-dimensional would be the probability of finding the particle anywhere in the space, which is 1.

Then the wave function would have unit's $m^{-3/2}$.

An atom or a molecule can be in any one of the stationary energy states e.g. nth, represented by its own wave function Ψ_n with energy E_n .

The wave function contains all the information we can have about a particle in quantum mechanics.

However for $(\Psi)^2$ to be a probability density, all the Ψ 's must be 'well behaved' that is, have certain general properties.

- [a] They are continuous,
- [b] They are finite
- [c] They are single valued
- [d] Their integral $\int \Psi^* \Psi dT$ over the entire range of variables is equal to unity.

Note also that the differential volume is represented by dT .

A wave function Ψ_i is said to be normalized if $\int \Psi_i^* \Psi_i dT = 1$ [18]

Two functions Ψ_i^* and Ψ_j are said to be orthogonal if $\int \Psi_i^* \Psi_j dT = 0$ [19]

These relations can be combined by writing

$$\int \Psi_i^* \Psi_j dT = \delta_{ij} \dots\dots\dots [20]$$

Where δ_{ij} = kroncker delta, which is defined by

$$\delta_{ij} = \begin{cases} 0 & \text{for } i \neq j \\ 1 & \text{for } i = j \end{cases} \dots\dots\dots [21]$$

And the wave functions that satisfy equation [21] is said to be orthonormal.

OPERATORS

An operator is a mathematical operation that is applied to a function and in quantum mechanics there is a linear operator for each classical mechanical observable. When two operators commute, the corresponding variables can be simultaneously measured to any precision and when they do not commute, the corresponding observables cannot be measured as arbitrary precision

e.g. d/dx is the operator that indicates that the function is to be differentiated with respect to x and \hat{x} is the operator that indicates that the function is to be multiplied by x . Operators are designated with caret. E.g. \hat{A} or \hat{x} . The symbol of the operator is placed to the left of the function to which it is applied. The operators of quantum mechanics are linear. A linear operator has the following properties:-

$$\hat{A}(f_1 + f_2) = \hat{A}f_1 + \hat{A}f_2 \dots\dots\dots (22)$$

$$\hat{A}(cf) = c\hat{A}f \dots\dots\dots (23)$$

Where c is a number. The simplest operator is the identity operator \hat{E} for which $\hat{E}f = f$

An algebra linear operator will give $\hat{A}_3 = \hat{A}_1 + \hat{A}_2$ or $\hat{A}_4 = \hat{A}_1\hat{A}_2$

Note that operator multiplication is different from the multiplication of numbers.

Example:-

Suppose $\hat{p} = d/dx$, $\hat{x} = x$ and $f(x) = x^3$; do the operators commute?

Example 1:

- (a) Apply the operator $\hat{A} = d/dx$ to the function x^2
- (b) Apply the operator $\hat{A} = d^2/dx^2$ to the function $4x^2$
- (c) Apply the operator $\hat{A} = (d/dy)x$ to the function xy^2
- (d) Apply the operator $\hat{A} = -i\hbar d/dx$ to the function e^{-ikx}
- (e) Using the same operators as in (d) apply the operator $\hat{A}\hat{A} = \hat{A}^2 = (-i\hbar d/dx)(-i\hbar d/dx) = \hbar^2 d^2/dx^2$ to the function e^{-ikx}

Solutions:

- (a) $\hat{A}(x^2) = d/dx(x^2) = 2x$
- (b) $\hat{A}(4x^2) = d^2/dx^2(4x^2) = d/dx(8x) = 8$
- (c) $\hat{A}(xy^2) = [d/dy(xy^2)]x = 2xy$
- (d) $\hat{A}(e^{-ikx}) = -i\hbar d/dx(e^{-ikx}) = i^2\hbar k e^{-ikx} = -\hbar k e^{-ikx}$
- (e) $\hat{A}^2(e^{-ikx}) = -\hbar^2 d^2/dx^2(e^{-ikx}) = \hbar^2 d/dx(-ik e^{-ikx}) = -i^2\hbar^2 k^2 e^{-ikx} = \hbar^2 k^2 e^{-ikx}$

Example:- Given $(\hat{A}\hat{B} - \hat{B}\hat{A}) = (\hat{A}, \hat{B})$, when $(\hat{A}, \hat{B}) = 0$ the operators are said to commute.

If $\hat{A} = d/dx$ and $\hat{B} = x$ show whether or not \hat{A} and \hat{B} commute.

Ans: $AB\Psi = d/dx(1/x)\Psi = d/dx(4/x) = d/dx(4x^{-1})$ [$d(u/v) = \{vdu - udv\}$]

Schrodinger's Equation and Operators

Let's rewrite the Schrödinger's equation in equation [15] in the form.

$$-(\hbar^2/8\pi^2m)\nabla^2\Psi_{(x,y,z)} + V_{(x,y,z)}\Psi_{(x,y,z)} = E\Psi_{(x,y,z)} \dots \dots \dots (24)$$

Where the quantity in square brackets is called Hamiltonian operator \hat{H} .

When an operator e.g. \hat{A} , operating on a function e.g. ϕ_n yields a constant, Q_n , multiply by that function i.e. $\hat{A}\phi_n = Q_n\phi_n \dots \dots \dots [25]$

We say that ϕ_n is Eigen function of \hat{A} ; with Eigen value Q_n . Thus for the Schrödinger equation [24] $\Psi_{(x,y,z)}$ is the Eigen function of \hat{H} with Eigen value E

Example: what are the Eigen functions and Eigen value of the operator d/dx ?

$$d/dx f(x) = kf(x), df(x)/f(x) = kdx, \ln f(x) = kx+c$$

$$f(x) = e^c e^{kx} = c e^{kx}$$

Where c and c' are constants. For each difference value of k , there is an Eigen function. $C'e^{kx}$ or, to put it another way, the Eigen function $c'e^{kx}$ has the Eigen value k where k can be a complex number.

The Black body Radiation (by plank)

The blackbody radiation is an evidence that light exist as a form of particle.

The body is a hollow object painted black, when the body is heated up, the electrons gain energy and emit radiation till the radiation comes out which we can measure. The intensity of the radiation increases with temperature, and also to the number of photons emitted while the energy is proportional to the frequency.

$$E = hv = hc/\lambda$$

$$\text{And } h = E\lambda/c \text{ in Js}$$

The photo electric effect- by Hertz

Hertz found that if one illuminates one of the electrodes of electric discharge system with light, the electric discharged increases. The intensity of current increases irrespective of the material of the electrode.

The energy of the light is converted to discrete particles there is the pot energy to remove the electron on the nucleus of the metal surface and energy is also needed to move the electron. This is called photoelectron effect which is an evidence that light exist in waves.

The total energy applied in converted into

1. Energy to remove the metal from the surface which is termed work function = ϕ
2. The energy due to kinetic energy

$$E_{\text{total}} = \phi_{\text{Workfunction}} + E_{\text{kinetic}}$$

$$hv = hv_0 + 1/2mc^2$$

The energy responsible for the attraction of electron to the nucleus is a quantum which can be replaced by a radiation of light.

A time will come when the kinetic Energy of electron will be equal to the voltage of meter and the energy will be eV_0 .

Note that the threshold frequency is the minimum energy required to remove an electron from the surface of the metal.

$$\text{Therefore, } hv = hv_0 + 1/2mc^2$$

Where $hv_0 =$ work function

$$hv = hv_0 + eV_0$$

$$eV_0 = hv - hv_0$$

A plot of eV_0 against v gives a straight line, the slope = h and $-hv_0$ is the intercept.

Example:- A particular metal surface has a work function of 2.0eV. Calculate the expected maximum K.E of the electron if the wavelength of the incident photon is 4500Å, calculate also the threshold frequency.

COMPTON EFFECT

J.J. Thompson observed that whenever X-ray is allowed to strike a matter, the X-ray is scattered into

- (1) light that have the same wavelength with the incident photon with energy hv.
- (2) Light with shorter wavelength with that of the incident photon.

This means that light wave is elastic and that electron in matter is bounded but moves about in stationery state in the matter.

J.J. Thompson came up with the equation.

$$\lambda^1 - \lambda = h/m_0C [1 - \text{Cos}\theta] \dots\dots\dots (26)$$

Which relates the scattered light, incident angle and the Cosθ. The m₀ is n k by plotting λ¹ - λ versus Cosθ, intercept = h/m₀C and slope = - h/m₀C.

$$h/m_0C = 6.625 \times 10^{-34} / 9.11 \times 10^{-31} \times 3 \times 10^8$$

$$= 2.4241 \times 10^{-12} \text{m}$$

Example

If a photon of wavelength 0.2Å is scattered through an angle of 45°. What is the wavelength of the scatted light in Å and in metre?

Particle in a one Dimensional Box

An important problem to treat in quantum mechanics is that of a particle of mass m constrained to move in a one-dimensional box of length a. The potential energy V_(x) is taken to be 0 for 0 ≤ x ≤ a and infinite outside this region in the figure 1. below (not shown). We can see that this leads to quantized energy levels.

In the region between x = 0 and x =a, then Schrödinger in equation (24) can be written as

$$-(\hbar^2 d^2\Psi/2mdx^2) = E\Psi \text{ or } d^2\Psi/dx^2 = -2mE\Psi/\hbar^2 = -k^2\Psi$$

$$\text{Where } k = (2mE/\hbar^2)^{1/2}$$

Figure 1 (not here): Potential for a particle in a one-dimensional box. The potential becomes infinite for x ≥ a and x ≤ 0, and is zero for 0 ≤ x ≤ a.

$$E_n = h^2 n^2 / 8ma^2, n = 1, 2 \dots\dots\dots (26).$$

Therefore, a particle constrained to be between x = 0 and x = a, has quantised energy levels given by eqn. (26). As a gets large, the energy levels get closer together. In the limit of a very large box (or a very heavy particle), the energy levels are so close that the quantization may be unnoticeable. In the that a becomes very large, all energies becomes allowed (i.e. the allowed energies get very close together so that any energy is an Eigen value), together so the perfectly free particle can have any energy.

A particle in a box cannot have zero energy because the lowest energy h²/8ma² is given by equation (26) for n = 1. Although n = 0 satisfies the boundary conditions, the corresponding wave function is zero everywhere. The zero-point energy associated with the state n = 1 is found whenever a particle is constrained to a finite region; if this were not so the uncertainty principle would be violated. The next higher energy levels are at a four time (n=2) and nine time (n=3) this energy, as shown in fig.2. The wave functions are superimposed on this plot, and we can see that the wavelength is equal 2a/n.

FIGURE 2 is not here

Figure 2(a): Wave function Ψ and (b) Probability density function Ψ*Ψ for the lowest three energy levels for particle in a box. The plots are placed at vertical heights that correspond to

the energies of the levels. As the number of nodes goes up, the energy goes up (c) The product of wave functions $\Psi_1 * \Psi_2$ and $\Psi_1 * \Psi_3$ plotted against x.

Note that the normalized wave function for a particle in a one-dimensional box is

$$\Psi_n = (2/a)^{1/2} \sin(n\pi x/a) \dots \dots \dots (27)$$

Note that the probability density at point x is given by the square figure 2b of the wave function $\Psi^2 = (2/a) \sin^2(\pi x/a)$ given the probability densities $\Psi * \Psi$ for a particle in an infinitely deep box. These are the probabilities per unit distance that the particle will be found at a given position. The most probable position for a particle in the zero-point level (n = 1) is in the centre of the box. Note that the Ψ_n are waves with wavelength $\lambda_n = 2a/n$, this means that Ψ_n is zero at value of x equal to an integral number of $\lambda_n/2$. These zeros are called nodes of the wave function. The more nodes in an eigen function, the higher its Eigen value of energy. For one-dimensional problem the number of nodes is n-1.

As the value of n is increases, the probability density increases more and more, for very high values of n, there so many oscillations that the probability density becomes constant. Particles in a box wave functions are orthonormal i.e.

$$(-\infty \leq x \leq +\infty) = \int \Psi_i * \Psi_j dx = 0 \text{ if } i \neq j.$$

Which can be seen if we plot $\Psi_i * \Psi_j$ for $i \neq j$ as a function of x in figure 2(c). We can see that the most probable position for the particles is in the middle of the box if the system is in the ground state, but it is more likely to be at a/4 or 3a/4 in the first excited state (n = 2) If we measure the position of a particle in a box, we would yet different answers in different trials.

$$\text{Lets define } E = n^2 h^2 / (8ma^2) \dots \dots \dots (28)$$

Where n = 1, 2, 3..... is quantum number. The energy, E, can only have discrete values as shown in the above equation. This is an important result since the imposition of boundary conditions on the solution to the S.E results in the appearance of quantum numbers that restrict the energies to discrete values. This is then the source of the term quantum mechanics; the energies of the system are quantized.

$$\text{The solution we obtained now is } \Psi_{(x)} = A \sin(2mE/\hbar^2)^{1/2} x$$

This is not yet complete since we still need to determine the value of A. To solve this problem we normalise $\Psi_{(x)}$ because the probability of finding a particle, somewhere in space is one, for our case, all space is the dimension of the box because the particle is not allowed outside this region.

$$(0 \leq x \leq a) = \int \Psi * \Psi dx = \int [A \sin(2mE/\hbar^2)^{1/2} x]^2 dx = 1$$

$$\Psi^* = \Psi \text{ because } \Psi \text{ is real in this case where } \hbar^2 = h^2 / 4\pi^2, E = n^2 h^2 / 8ma^2$$

$$A^2 / 2 \int (1 - \cos(2n\pi/a)x) dx = 1$$

$$A^2 / 2 [x - a/2n\pi \sin(2n\pi/a)x] (0 \leq x \leq a) = 1$$

$$A^2 / 2 [a - 0 + a/2n\pi \sin(2n\pi/a) 0 + 0] = 1$$

$$A^2 = 2/a,$$

$$\text{Hence } \Psi_{(x)} = (2/a)^{1/2} \sin(n\pi x/a) \dots \dots \dots (29)$$

Equation (29) is now the desired solution. We can now calculate the probability of finding the particle at any point, x, once the values of n, x and a are known.

Note also that we can now calculate ΔE for n equals two different values e.g. 2 and 3 from equation (28)

The probability is $[\Psi_{(x,n)}]$ so if the value of n, x and a are known, then it can be evaluated.

Particle in a Three Dimensional Box

We have been dealing with particle in a box. Here we want to expand the box to three dimensions. The particle is confined to a regular shape with sides of a, b, and c by having an infinite potential outside the box.

The time-independent Schrodinger equation for a single particle of mass m, moving in three dimensions is

$$\square \Psi_{(x,y,z)} = E\Psi_{(x,y,z)} \dots \dots \dots (32)$$

Where the Hamittonian operator is $\square = -(\hbar^2/2m) \nabla^2 \Psi + V_{(x,y,z)} \dots \dots \dots (33)$

And $\nabla^2 = d^2/dx^2 + d^2/dy^2 + d^2/dz^2 \dots \dots \dots (34)$

Where $\nabla^2 =$ laplacian operator or Del square.

The wave function is normalized so that $(-\infty \leq x \leq +\infty) = \int \Psi^*_{(x,y,z)} \Psi_{(x,y,z)} dx dy dz = 1 \dots \dots \dots (35)$

If a particle can move in three dimensions, its probability density P(x,y,z) is given by

$$P_{(x,y,z)} = \Psi^*_{(x,y,z)} \Psi_{(x,y,z)} \dots \dots \dots (36)$$

The probability that x coordinate is between x and x + dx, the y coordinate is between y + dy and the z coordinate is between z + dz is $P_{(x,y,z)} dx dy dz = \Psi^*_{(x,y,z)} \Psi_{(x,y,z)} dx dy dz$ which can be shortened to $\Psi^* \Psi dT$ where dT represents the differential element of volume dx dy dz.

Since the potential within the box is zero, the following partial differential equation for the region inside the box is obtained as $-\hbar^2/2m(d^2/dx^2 + d^2/dy^2 + d^2/dz^2)\Psi = E\Psi \dots \dots \dots (37)$

If we assume that the wave function Ψ is the product of three functions each depending on just one coordinate we will have;

$$\Psi_{(x,y,z)} = X_{(x)} Y_{(y)} Z_{(z)} \dots \dots \dots (38)$$

By substituting this for Ψ in equation (37) and then divide by $X_{(x)} Y_{(y)} Z_{(z)}$ we obtained $-\hbar^2/2m(1/X_{(x)}[d^2X_{(x)}/dx^2] + 1/Y_{(y)}[d^2Y_{(y)}/dy^2] + 1/Z_{(z)}[d^2Z_{(z)}/dz^2]) = E\Psi \dots \dots \dots (39)$

Since the terms on the left hand side of the equation are a function of different independent variable and this can be varied independently of one another, each must equal a constant in order that the sum of the three terms equals a constant for all values of x, y and z.

$$E_x + E_y + E_z = E \dots \dots \dots (40)$$

This coverts the partial differential equation (39) into three ordinary differential equations that can be easily solved

$$-\hbar^2/2m(1/X_{(x)}[d^2X_{(x)}/dx^2]) = E_x \dots \dots \dots (41)$$

$$-\hbar^2/2m(1/Y_{(y)}[d^2Y_{(y)}/dy^2]) = E_y \dots \dots \dots (42)$$

$$-\hbar^2/2m(1/Z_{(z)}[d^2Z_{(z)}/dz^2]) = E_z \dots \dots \dots (43)$$

These equations are just like equation (27) and may be solved in the same way to obtain

$$X_{(x)} = A_{(x)} \text{Sin } n_x \pi x/a = A_{(x)} \text{Sin } (2mE_x/\hbar^2)^{1/2} x \dots \dots \dots (44)$$

$$Y_{(y)} = A_{(y)} \text{Sin } n_y \pi y/b = A_{(y)} \text{Sin } (2mE_y/\hbar^2)^{1/2} y \dots \dots \dots (45)$$

$$Z_{(z)} = A_{(z)} \text{Sin } n_z \pi z/c = A_{(z)} \text{Sin } (2mE_z/\hbar^2)^{1/2} z \dots \dots \dots (46)$$

Where a, b and c are the lengths of the sides in the x, y and z directions respectively, n_x , n_y and n_z are non-zero integers called quantum numbers and $E_x = \hbar^2 n_x^2 / 8ma^2$ and so on.

Thus there is a quantum number for each coordinate. When the wave function is normalized, we obtained $\Psi_{(x,y,z)} = (8/abc)^2 \text{Sin } n_x \pi x/a \text{Sin } n_y \pi y/b \text{Sin } n_z \pi z/c \dots \dots \dots (47)$

When the Eigen function is substituted in eqn (37) we obtained:

$$E = \hbar^2/8m(n_x^2/a^2 + n_y^2/b^2 + n_z^2/c^2) \dots \dots \dots (48)$$

The three quantum numbers are independent and for a given set of three quantum numbers there is in general, a unique value for the $a \neq b \neq c$.

If the sides of the box are equal; if $a = b = c$, the energy levels are given by

$$E = \hbar^2/8ma^2 (n_x^2 + n_y^2 + n_z^2) \dots \dots \dots (49)$$

If $a \neq b \neq c$, there may be several combinations (n_x , n_y , n_z) that yield the same energy for example (2,1,1), (1,2,1) and (1,1,2) have the same energy. These three states of the system (with different wave function) make up a level that we can refer to as the 211 level. Such an energy level is said to be degenerate and the degeneracy is equal to the number of independent wave functions associated with a given energy level as shown below. Note that 111 level is non-degenerate.

n_x, n_y, n_z	111	211	221	311	222	321	322	411	331
-----------------	-----	-----	-----	-----	-----	-----	-----	-----	-----

Degeneracy	1	3	3	3	1	6	3	3	3
------------	---	---	---	---	---	---	---	---	---

The degeneracy of a translational energy level increases rapidly with energy. If $n^2 = n_x^2 + n_y^2 + n_z^2$, the $E = h^2/(8ma^2) \cdot n^2$

If we think of allowed values of n_x , as point along x-axis, n_y along the y-axis and n_z along the z-axis, then n can be thought of as the length of a vector in this three dimensional space. All such vectors with the same length have the same energy they represents degenerate states.

The Degeneracy of quantum levels at thermal energy

The most probable translational energy for an atom in a gas at temperature T . is equal to $3/2KT$. Where $K = R/N_A =$ Boltzman constant.

Reduced Mass and Moment of Inertial of Molecules

Let define μ as the reduced mass $= m_1m_2/m_1+m_2$ (50)

Where m are the molar mass in kg. E.g. The reduced mass for CO is given by $\mu = m_1m_2/m_1+m_2 = (12 \times 10^{-3})(16 \times 10^{-3})/(12+16) \times 10^{-3} = 6.022 \times 10^{-26} = 1.139 \times 10^{-26}$ kg

The moment of Inertia (I) is defined by the equation $I = \mu R_e^2$ for the rotation of a classical particle about the axis. Where R_e is the equilibrium inter-nuclear distance between the nuclei of a molecules.

Rotational energy levels of Molecules

A rotating molecule has quantized angular momentum. In considering the rotational energy levels of molecules, the rotational quantum number is denoted by J so that

$$E = h^2/2I \cdot J(J+1)..... (51)$$

The square of the total angular momentum is given by $L^2 = J(J+1) \hbar$ where $J = 0, 1, 2$.

The angular momentum vector L with respect to a particular direction is defined as $L_z = - \hbar, 0, \hbar$

Where the choice of the z axis is entirely arbitrary.

Calculate the reduced mass and the moment of inertia of CO the equilibrium internuclear distance is 123.5×10^{-12} . What are the values of L_z given that $J = 1, C = 12, O = 16$.

Summary Particle in a Three-Dimensional Box

Consider a particle constrained to move in a rectangular box of dimensions $a, b,$ and c in length. Within the box (i.e. between $x = 0$ and $a; y = 0$ and b and $z = 0$ and c), the potential energy is zero at the walls and everywhere outside the box, the potential is ∞ .

Recall S.E for 3-dimensional box

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

Where Ψ and V are $f(x, y, z)$. Since $V = 0$ inside the box, then the last equation becomes

$$d^2\Psi/dx^2 + d^2 \Psi/dy^2 + d^2\Psi/dz^2 + 8\pi^2m/h^2 E\Psi = 0..... (52)$$

Equation (52) may be solved by writing the wave function as the product of three functions each depending on one coordinate

$$\Psi_{(x,y,z)} = X_{(x)} Y_{(y)} Z_{(z)}..... (53)$$

Differentiating equation (7)

$$d\Psi/dx = Y_{(y)} Z_{(z)} dX/dx$$

$$d^2\Psi/dx^2 = Y_{(y)} Z_{(z)} d^2X/dx^2..... (54a)$$

and by a similar reasoning

$$d^2\Psi/dy^2 = X_{(x)} Z_{(z)} d^2Y/dy^2..... (54b)$$

$$d^2\Psi/dz^2 = X_{(x)} Y_{(y)} d^2Z/dz^2..... (54c)$$

Substituting equations 54a, 54b and 54c into equation (52)

$$Y_{(y)} Z_{(z)} d^2X/dx^2 + X_{(x)} Z_{(z)} d^2Y/dy^2 + X_{(x)} Y_{(y)} d^2Z/dz^2 + 8\pi^2m/h^2 E X_{(x)} Y_{(y)} Z_{(z)} = 0 \dots (56)$$

$$-h^2/8\pi^2m (1/X_{(x)}[d^2X_{(x)}/dx^2] + 1/Y_{(y)}[d^2Y_{(y)}/dy^2] + 1/Z_{(z)} d^2Z_{(z)}/dz^2) = E \dots (57)$$

We can write the energy level as the sum of three contributions associated with the coordinates

$$E = E_x + E_y + E_z \dots (58)$$

Using eqn (57) in (58) we can separate the expression obtained into three equations

$$-h^2/8\pi^2m (1/X_{(x)}[d^2X_{(x)}/dx^2]) = E_x \dots (59)$$

$$-h^2/8\pi^2m (1/Y_{(y)}[d^2Y_{(y)}/dy^2]) = E_y \dots (60)$$

$$-h^2/8\pi^2m (1/Z_{(z)}[d^2Z_{(z)}/dz^2]) = E_z \dots (61)$$

Each of eqns 59, 60, 61 is similar to the expression for the particle in a one dimensional box.

Hence their solutions are

$$X_{(x)} = (2/a)^{1/2} \text{Sin}(n_x\pi x/a) E_{n,x} = n_x^2 h^2/8ma^2$$

$$Y_{(y)} = (2/b)^{1/2} \text{Sin}(n_y\pi y/b) E_{n,y} = n_y^2 h^2/8mb^2$$

$$Z_{(z)} = (2/c)^{1/2} \text{Sin}(n_z\pi z/c) E_{n,z} = n_z^2 h^2/8mc^2$$

Where a,b,c are lengths in x,y,z direction respectively and n_x, n_y, n_z are quantum numbers.

Since $\Psi_{(x,y,z)} = X_{(x)} Y_{(y)} Z_{(z)}$ and $E = E_x + E_y + E_z$, then

$$\Psi_{(x,y,z)} = (8/V)^{1/2} \text{Sin} n_x\pi x/a \text{Sin} n_y\pi y/b \text{Sin} n_z\pi z/c \dots (62)$$

Where V is the volume of the box,

$$E_{x,y,z} = h^2/8m(n_x^2/a^2 + n_y^2/b^2 + n_z^2/c^2) \dots (63)$$

Whenever the 3-dimensional box has geometrical symmetry, more interesting results are often obtained, in a cubic box, $a = b = c$ thus eqn (63) becomes

$$E = h^2/8m(n_x^2 + n_y^2 + n_z^2) \dots (64)$$

Suppose $n_x = 3, n_y = n_z = 2$ then

$$\Psi_{(x,y,z)} = (8/V)^{1/2} \text{Sin} 3\pi x/a \text{Sin} 2\pi y/b \text{Sin} 2\pi z/c \dots (65)$$

$$E = h^2/8m(3^2 + 2^2 + 2^2) = 17h^2/8ma^2 \dots (66)$$

Assuming we have another set of values $n_x = 2, n_y = 3, n_z = 2$ then

$$\Psi_{(x,y,z)} = (8/V)^{1/2} \text{Sin} 2\pi x/a \text{Sin} 3\pi y/b \text{Sin} 2\pi z/c \dots (67)$$

$$E = h^2/8m(2^2 + 3^2 + 2^2) = 17h^2/8ma^2 \dots (68)$$

Suppose $n_z = 3, n_y = n_x = 2$ then

$$\Psi_{(x,y,z)} = (8/V)^{1/2} \text{Sin} 2\pi x/a \text{Sin} 2\pi y/b \text{Sin} 3\pi z/c \dots (69)$$

$$E = h^2/8m(2^2 + 2^2 + 3^2) = 17h^2/8ma^2 \dots (70)$$

Even though these states are different, their energies (eqn 59, 60, 61) are the same. The three states are said to be degenerate because they have equal energy.

For a situation where $n_x = n_y = n_z = 1$ it corresponds to only one state of the system. The same is true of $n_x = n_y = n_z = 2$ but for the situation such as $n_i = 2, 2, 1$ or $3, 1, 1$, three degenerate states are obtained (figure 5 not shown): Quantized energy levels of a particle in a cubic box

Suppose we wish to calculate the transition energy between the level $E_{2,2,2}$ and $E_{3,2,1}$ the,

$$\Delta E = 14h^2/8ma^2 + 12h^2/8ma^2 = hv$$

$$hv = 2h^2/8ma^2 = h^2/4ma^2$$

Given appropriate data, it should be possible for us to evaluate v. If the value of a, is known, the transition energy can be evaluated.

Zero Point Energy

According to the old quantum theory the energy level of a harmonic oscillator is $E = nhv$

The lowest energy level with $n = 0$ would have zero energy. Based on the wave treatment of the system, the energy level corresponds to the state with quantum numbers $n_x = n_y = n_z = 1$.

The difference between these two values is called the zero point energy.

Free Electron Model

The simple calculation done for the particle in a one-dimensional box can be applied to estimate the absorption frequency of some organic molecules, presumably conjugated dienes. The method often employed is the free electron model. For the π electrons of these molecules, the energy for the lowest electronic transition is that required to raise an electron from the highest filled level (HOMO) to the lowest unfilled level (LUMO). For molecules with conjugated dienes, it has been found that the electronic absorption bands shift to longer wavelengths (Bathochromic or red shift) as the number of conjugated dienes is increased each carbon atom contributes one electrons are free to move the entire length of the series of π -orbitals and are not localized on a given carbon atom. In the free electron model, it is assumed that π -system is a region of uniform potential and that P.E rises sharply to infinity at the end of the system.

Hence the energy level, E , available to the following electron would be expected to be analogous to that of particle restricted to move in one direction. The π -electrons are assigned to orbitals so that there are two in each level (with opposite spin) starting with the lowest, for completely conjugated hydrocarbon, the no of π -electrons is even and the quantum number of the HOMO is $n = N/2$ where N is the number of π -electrons involved and parallels the number of carbon atoms in the system. In absorption, an electron from the HOMO is excited to the LUMO with quantum no $n^1 = (N/2 + 1)$. The difference in energy between these levels is $\Delta E = h^2/8ma^2(n^{12} - n^2) = h^2/8ma^2[(N/2 + 1)^2 - (N/2)^2]$

The absorption frequency in wave number is $\Delta E = hv$, $c = \lambda\nu$, $\Delta E = hc/\lambda = hc\bar{\nu}$

$$\bar{\nu} = \Delta E/hc = h(N+1)/8ma^2c \dots \dots \dots (71)$$

let us consider butadiene with the structure $C=C-C=C$, if the 4π -electrons are removed, we have $C^+-C^+-C^+-C^+$ at the boundary, the potential is infinitely large. The first transitions for the system corresponds to electron from $E_2^{4/2}$ to $E_3^{4/2+1}$

$$\begin{aligned} \Delta E &= E_3 - E_2 \\ &= 9h^2/8ma^2 - 4h^2/8ma^2 \end{aligned}$$

To estimate a , two methods are used;

When end effects are not neglected, a equals the sum of bond lengths and $1/2$ bond length of the extensions at both extremes $1/2b.LC=C-C=C1/2b.L$

When end effects are neglected (better because $V = \infty$ at the extremes)

$$a = 1.54 (N-1)\text{\AA}, \text{ where } N = \text{number of carbon atoms.}$$

Examples: Calculate the lowest absorption wave number for octatetraene neglecting end effects.

Solution: First draw the structure end effect– $C=C-C=C-C=C-C=C$ - end effect

$$a = 1.54 (8-1)\text{\AA} = 10.78\text{\AA}$$

Draw the energy-level diagram to determine the quantum levels involved in the transition

$$\begin{aligned} \Delta E &= 5^2h^2/8ma^2 - 4^2h^2/8ma^2 \\ &= 9h^2/8ma^2 \end{aligned}$$

But $\Delta E = hv = hc\bar{\nu}$

$$hc\bar{\nu} = 9h^2/8ma^2, \quad \bar{\nu} = 9h/8ma^2c$$

$$\begin{aligned} \bar{\nu} &= 9 \times 6.626 \times 10^{-34} / 8 \times 9.11 \times 10^{-31} \times (10.78 \times 10^{-10})^2 \times 3 \times 10^8 \\ &= 2.347 \times 10^6 \text{ m}^{-1} \\ &= 2.347 \times 10^4 \text{ cm}^{-1} \end{aligned}$$

$$\begin{aligned} \text{If it is energy, } \Delta E &= hv = 9h^2/8ma^2 \\ &= 9 (6.626 \times 10^{-34})^2 / 8 \times 9.11 \times 10^{-31} (10.78 \times 10^{-10})^2 \\ &= 4.67 \times 10^{-19} \text{ J or } 2.91 \text{ eV} \end{aligned}$$

The Hydrogen Molecule Ion

The hydrogen molecule ion, H_2^+ consist of 2 protons and 1 electron and is thus the simplest molecular system that can be encountered in nature. The hydrogen molecule ios often represented as shown below:

We have one proton each at A and B. The potential energy for a hydrogen atom is $u = -e^2/r_A$. Similarly, the P.E for the hydrogen molecule ion is $u = -e^2/r_A - e^2/r_B + e^2/r_{AB}$ (72)

The first two terms in eqns 72 represent the electrostatic attraction between the nuclei and electron while the last term represent the repulsion between the nuclei. The kinetic energy for molecule is $K.E = P^2/2m = 1/2m (P_x^2 + P_y^2 + P_z^2)$

Where P = momentum of the electron, m = mass of the electron, and the electron is assumed to be moving in three directions. Note that we have assumed r_{AB} fixed which implies that only K.E term need be considered: the K.E due to the electron motion.

Recall S.E for a 3-dimensional system which is

$$\nabla^2 \Psi / dx^2 + d^2 \Psi / dy^2 + d^2 \Psi / dz^2 + 8\pi^2 m / h^2 (E - V_{(x,y,z)}) \Psi = 0$$

which can be written as $\square \Psi = E\Psi$ (73)

where $\square = -h^2/8\pi^2 m (d^2/dx^2 + d^2/dy^2 + d^2/dz^2)$ $\Psi + V_{(x,y,z)}$ is known as the Hamittonian operator and $\nabla^2 = d^2/dx^2 + d^2/dy^2 + d^2/dz^2$ is a Laplacian operator. Equation 73 is known as the Hamittonian form of the Schrodinger equation.

Note that $\hbar = h/2\pi$ and $\square = -\hbar^2/2m \nabla^2 + u_{(x,y,z)}$ (74)

The Schrodinger eqn for the hydrogen molecule ion is $(-\hbar^2/2m \nabla^2 + e^2/r_{AB} - e^2/r_A - e^2/r_B)\Psi = E\Psi$ (74)

The wave eqn is simple and it is possible to get an exact solution. We now attempt to set up S.E for the hydrogen molecule which has two electrons and 2 nuclei as shown the figure below:

We are to write expression for the K.E, write expression for the P.E and put both expression in the S.E.

$$\text{The total K.E} = (K.E)_1 + (K.E)_2 = P_1^2/2m + P_2^2/2m$$

Where 1,2 stand for 1st and 2nd electrons

$$\text{The total K.E} = 1/2m (P_{x1}^2 + P_{y1}^2 + P_{z1}^2) + 1/2m (P_{x2}^2 + P_{y2}^2 + P_{z2}^2)$$

The P.E for the system is

$$U_{(x,y,z)} = -e^2/r_{1A} - e^2/r_{1B} - e^2/r_{2A} - e^2/r_{2A} + e^2/r_{AB} + *e^2/r_{12}..... (75)$$

* represents repulsion between the two electrons

The S.E for the hydrogen molecule is

$$[-\hbar^2/2m(\nabla^2 + \nabla^2) - e^2/r_{1A} - e^2/r_{1B} - e^2/r_{2A} - e^2/r_{2B} + e^2/r_{AB} + e^2/r_{12}]\Psi = E\Psi$$

Which transform to

$$(\nabla_1^2 + \nabla_2^2)\Psi + 8\pi^2 m/h^2 [E + e^2/r_{1A} + e^2/r_{1B} + e^2/r_{2A} + e^2/r_{2B} - e^2/r_{AB} - e^2/r_{12}]\Psi = 0..... (78)$$

This is the required equation. Whereas it is possible to get an exact solution to eqn 2.8 by separating into any other coordinates (e.g. polar or spherical). We cannot solve eqn 3.0 exactly because of the presence of the repulsive term e^2/r_{12} . In this situation, we use an approximate method to get solution to the S.E. we always aim at the energy of the system in joint form compared with when the atoms are far apart. We have assumed that both nuclei A and B are fixed meaning that their K.E will be almost zero. Thus instead of the K.E being:

$$K.E = K_A + K_B + K.E_1 + K.E_2$$

We have neglected that due to the nucleus both eqns 2.8 and 3.0 giving us $K.E = K.E_1 + K.E_2$ for the hydrogen molecule. The justification for doing this is that the motions of nuclei in ordinary molecular vibrations are so slow compared to the motions of the electrons that it is possible to calculate the electronic states on the assumption that the nuclei are held in fixed position. Thus is the Borh-oppenheimer approximation. What this means is that in eqn 3.0 for instance, we consider r_{AB} constant. We can therefore calculate E for the fixed values of r_{AB} . If

we change the value of r_{AB} , a corresponding value of $E(r_{AB})$ can be got. Thus it should be possible to make a plot of $E(r_{AB})$ against r_{AB} in the figure below (Figure (x); NOT SHOWN) potential energy curve showing the variation of the total energy of the system with the internuclear distance, r_{AB} .

Figure (x) is known as the potential energy curve. In this figure, the equilibrium inter nuclear distance is r_{eq} and it corresponds to the region where the total energy of the system is a minimum (i.e. the system is stable there). It is called the bond length. When r , is small the molecule is unstable and also when r , is large, it is unstable because the attractive force may not be large enough to offset the repulsive force. In between A and B, the molecule is stable but it is most stable at r_{eq} .

The attractive state leads to bonding molecular orbitals whereas the repulsive state leads to antibonding M.O.

We cannot obtain exact value of E for the hydrogen molecule because of the presence of the repulsive term which made it impossible for us to separate the molecule into hydrogen atoms for which two electrons are involved. Also the presence of ∇_1^2 and ∇_2^2 in the S.E for the hydrogen molecule suggests that we should look for another way of solving the equation. The approximate method known as the variation method is often employed.

Quantum chemistry and chemical bonding

Secular equation

van der Waal bonding is a transient/temporary with δ^+ and δ^- becoming attracted. However, in chemical bonding, there is actual sharing of electrons by atomic orbitals to form molecular orbital.

Consider a bonded system, the total energy of the

System = kinetic + potential

i.e $H = T + V$

Let's represent the atomic orbital by ϕ (phi) and molecular orbital by ψ (psi)

From the Schrodinger wave equation

$$H = \frac{P^2}{2m} + V$$

$$H\psi - E\psi = \text{total energy of system} \quad (1)$$

$$(H - E)\psi = 0 \quad (2)$$

$$\psi = C_1\phi_1 + C_2\phi_2 + \dots + C_n\phi_n$$

$$\sum_{i=1}^n C_i\phi_i \quad (3)$$

Where ϕ_i is the number of atoms in a molecule

$$\psi = \sum_{i=1}^n C_i(H - E)\phi_i = 0 \quad (4)$$

Adding to 2 atoms;

$$C_1(H - E)\phi_1 + C_2(H - E)\phi_2 = 0 \quad (5)$$

A secular equation can be devp. mult. by ϕ_1 and integ. all over config.

$$C_1 \int \phi_1(H - E)\phi_1 d\tau + C_2 \int \phi_1(H - E)\phi_2 d\tau = 0$$

$$C_1 \left[\int \phi_1 H \phi_1 d\tau - E \int \phi_1 \phi_1 d\tau \right] + C_2 \left[\int \phi_1 H \phi_2 d\tau - E \int \phi_1 \phi_2 d\tau - E S_{12} \right] \quad (5)$$

$$C_1[H_{11} - ES_{11}] + C_2(H_{12} - ES_{12}) = 0 \quad (6)$$

Multiplying from L.H.S. with ϕ_2 and integrate over all configurational space gives

$$C_1 \left[\int \phi_2 H \phi_1 d\tau - E \int \phi_2 \phi_1 d\tau \right] + C_2 \left[\int \phi_2 H \phi_2 d\tau - E \int \phi_2 \phi_2 d\tau - E S_{22} \right]$$

$$C_1(H_{21} - ES_{21}) + C_2(H_{22} - ES_{22}) = 0 \quad (7)$$

$$\text{Note } C_1 (H_{11} - ES_{11}) + C_2 (H_{12} - ES_{12}) = 0$$

$$C_1 (H_{21} - ES_{21}) + C_2 (H_{22} - ES_{22}) = 0$$

$$\begin{pmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} \\ H_{21} - ES_{21} & H_{22} - ES_{22} \end{pmatrix} \begin{pmatrix} C_1 \\ C_2 \end{pmatrix} = 0$$

To know the determinant; $C_i \neq 0$ otherwise there's no molecular orbital

$$\begin{vmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} \\ H_{21} - ES_{21} & H_{22} - ES_{22} \end{vmatrix} = 0$$

$$(H_{11} - ES_{11})(H_{22} - ES_{22}) - (H_{21} - ES_{22})(H_{12} - ES_{12}) = 0$$

$$\left[x = \frac{c + bE + aE^2}{2a} \right]$$

$$H_{11}(H_{22} - ES_{22}) - ES_{11}(H_{22} - ES_{22}) - H_{21}(H_{12} - ES_{12}) + ES_{21}(H_{12} - ES_{12}) = 0$$

$$H_{11}H_{22} - ES_{22}H_{11} - ES_{11}H_{22} + E^2S_{22}S_{11} - H_{21}H_{12} + ES_{12}H_{21} + ES_{21}H_{12} - E^2S_{12}S_{21} = 0$$

$$H_{11}H_{22} - H_{21}H_{12} - E(S_{22}H_{11} + S_{11}H_{22} - S_{12}H_{21} - S_{21}H_{12}) + E^2(S_{22}S_{11} - S_{12}S_{21}) = 0$$

$$c = H_{11}H_{22} - H_{21}H_{12}, \quad b = -(S_{22}H_{11} + S_{11}H_{22} - S_{12}H_{21} - S_{21}H_{12}), \quad a = S_{22}S_{11} - S_{12}S_{21}$$

$$E = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

$$E = \frac{+(S_{22}H_{11} + S_{11}H_{22} - S_{12}H_{21} - S_{21}H_{12}) \pm \sqrt{-(S_{22}H_{11} + S_{11}H_{22} - S_{12}H_{21} - S_{21}H_{12})^2 - 4(S_{22}S_{11} - S_{12}S_{21})(H_{11}H_{12} - H_{21}H_{12})}}{2(S_{22}S_{11} - S_{12}S_{21})}$$

$$2(S_{22}S_{11} - S_{12}S_{21})$$

note: $c + bE + aE^2$

$c - bE + aE^2$

$$\begin{aligned}
H_{ii} &= \int \phi_i H \phi_i d\tau \text{ coulomb} \Rightarrow \alpha \\
H_{ij} &= H_{ij} = \int \phi_i H \phi_j d\tau \text{ resonance} \Rightarrow \beta \\
S_{ii} &= 1 \text{ maximum overlap} \\
S_{ij} &= S \text{ if } |i-j| = \pm 1 \text{ adjacent atom} \\
&= 0 \text{ if } |i-j| \geq 2
\end{aligned}$$

Ass: Use these expressions to solve for E

For more than 2 atoms, there's no need to derive again the secular equations after pattern which is quite clear is similarly

$$2 (S_{11}S_{22} - S_{21}S_{12})$$

$$2 (1 - S^2)$$

$$\begin{pmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} + \dots H_{1n} - ES_{1n} \\ H_{12} - ES_{12} & H_{22} - ES_{22} + \dots H_{2n} - ES_{2n} \\ \dots & \dots & \dots \\ H_{1n} - ES_{1n} & H_{2n} - ES_{2n} + \dots H_{nn} - ES_{nn} \end{pmatrix} \begin{pmatrix} C_1 \\ C_2 \\ \dots \\ C_n \end{pmatrix} = 0$$

For diatomic molecule; homo-nuclear

$$C_1 (H_{11} - ES_{11}) + (H_{12} - ES_{12}) C_2 = 0$$

$$(H_{21} - ES_{21}) C_1 + (H_{22} - ES_{22}) C_2 = 0$$

$$\begin{vmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} \\ H_{21} - ES_{21} & H_{22} - ES_{22} \end{vmatrix} = 0$$

Since homonuclear H_{12} and H_{21} are same, then

ES_{12} and ES_{21} are the same

Divide through by $H_{12} - S_{12}$

$$\begin{vmatrix} H_{11} - ES_{11} & \\ H_{12} - ES_{12} & \\ 1 & \frac{H_{22} - S_{22}}{H_{12} - ES_{12}} \end{vmatrix} = 0 \quad \text{i.e.} \quad \begin{vmatrix} x & 1 \\ 1 & x \end{vmatrix} = 0$$

$$x^2 - 1 = 0 \quad ; \quad x^2 = 1 \quad ; \quad x = \pm 1 \quad x = \frac{H_{ij} - ES_{ij}}{H_{ij} - ES_{ij}}$$

$$x = \frac{H_{11} - E}{H_{12} - ES} = +1$$

$$\therefore H_{11} - E = H_{12} - ES - ES = H_{11} - H_{12}$$

$$E + = \frac{H_{11} - H_{12}}{1 - S}$$

$$\text{For } E = H_{11} - E = -(H_{12} - ES) = H_{11} + E = H_{12} - ES$$

$$\text{i.e. } x = 1 \quad E - = \frac{H_{11} - H_{12}}{(1 + S)}$$

$$E_t = \frac{\alpha - \beta}{1 - S} \quad E - = \frac{\alpha + \beta}{(x - 1) 1 + S}$$

$$\text{if } \alpha = -5 \quad \alpha\beta = -2 \quad E_+ = -3, E - = - >$$

Variation Method

According to Schrödinger equation $H\psi = E\psi$(1)

$E\psi = H\psi$ multiply by ψ and integrate over configurational space.

$$\int \psi E \psi d\tau = \int \psi H \psi d\tau \dots\dots\dots(2)$$

$$\int \psi E \psi d\tau = \int \psi H \psi d\tau \div L.H.S. \& R.H.S. \text{ by integral}$$

$$\int \psi \psi d\tau = \int \psi \psi d\tau \dots\dots\dots(3)$$

$$\langle E \rangle = \frac{\int \psi H \psi d\tau}{\int \psi \psi d\tau} \dots\dots\dots(4)$$

$$\psi = C_1\phi_1 + C_2\phi_2$$

$$\Psi = C_1\phi_1 + C_2\phi_2 \dots \dots \dots (5)$$

subs. (5) into (4)

The energy of system;

$$E = \frac{C_1^2 \phi_1 H \phi_1 d\tau + C_2^2 (\phi_2 H \phi_2 d\tau) + 2C_1 C_2 (\phi_1 H \phi_2 d\tau)}{(C_1 \phi_1 + C_2 \phi_2)(C_1 \phi_1 + C_2 \phi_2) d\tau}$$

transient events \Rightarrow momentum

stability \Rightarrow energy

$$E = \frac{C_1^2 (\phi_1 H \phi_1 d\tau + C_2^2 (\phi_2 H \phi_2 d\tau) + 2C_1 C_2 (\phi_1 H \phi_2 d\tau)}{C_1^2 (\phi_1 \phi_1 d\tau) + C_2^2 \int \phi_2 \phi_2 d\tau + 2C_1 C_2 \int \phi_1 \phi_2 d\tau}$$

$$= \frac{C_1^2 H_{11} + C_2^2 H_{22} + 2C_1 C_2 H_{12}}{C_1^2 S_{11} + C_2^2 S_{22} + 2C_1 C_2 S_{12}}$$

$$E = \frac{\text{Numerator, N}}{\text{Dnominator, D}} \quad E = \frac{U}{V} \therefore dE = \frac{VdU - UdV}{V^2}$$

$$\frac{dE}{dC_1} = \frac{DdN - NdD}{D^2} = 0$$

Use D^2 as $D \times D$

$$dN - \frac{NdD}{D} = 0$$

$$\frac{dE}{dG} = dN - EdD$$

$$\frac{dE}{dc_1} = 2C_1 H_{11} + 2C_2 H_{12} - 2E(2C_1 S_{11} + 2C_2 S_{12}) = 0$$

$$= (H_{11} - ES_{11})C_1 + CH_{12} - ES_{12})C_2 = 0$$

$$\text{For } \frac{dE}{dC_2} = 0 + 2C_2 H_{22} + 2C_1 H_{12} - E(2C_2 S_{22} + 2C_1 S_{12}) = 0$$

$$(H_{12} - ES_{12})C_1 + (H_{22} - ES_{22})C_2 = 0$$

$$\text{Going back } \begin{vmatrix} x & x \\ 1 & 1 \end{vmatrix} = 0 \quad \frac{H_{11} - ES_{11}}{H_{12} - ES_{12}} = \pm 1$$

$$(H_{11} - ES_{11})C_1 + (H_{12} - ES_{12})C_2 = 0$$

excited state

$$(H_{11} - ES_{11}) = (H_{12} - ES_{11})(C_1 + C_2) = 0$$

$$\therefore C_1 = -C_2 \text{ or } C_1 = C_2$$

$$\psi_+ = C_1 (\phi_1 - \phi_2)$$

$$C_1 = C_2 \text{ ground state}$$

$$\text{and } \psi_- = C(\phi_1 + \phi_2)$$

$$\psi_- = C_1(\phi_1 + \phi_2)$$

$$\psi_- = C_1\phi_1 + C_2\phi_2$$

$$C_1\phi_1 - C_1\phi_2$$

$$C_1(\phi_1 - \phi_2)$$

$$E_+ \frac{\psi_+}{\psi_+} = C_1(\phi_1 + \phi_2)$$

$$E_- \frac{\psi_-}{\psi_-} = C_1(\phi_1 + \phi_2)$$

C_i affect the probability of finding an e^- in configuration specie but are not probability-coefficient because one C_i is -ve

$$\int \psi_1 \psi_2 d\tau = \langle \psi_+ \psi_- \rangle = 1$$

$$\langle C_1\phi_1 + C_2\phi_2 | C_1\phi_1 + C_2\phi_2 \rangle = 1$$

$$C_1^2 \langle \phi_1 | \phi_1 \rangle + C_2^2 \langle \phi_2 | \phi_2 \rangle + 2C_1C_2 \langle \phi_1 | \phi_2 \rangle = 1$$

By normalization $\langle \phi_1 | \phi_1 \rangle = 1$; also, $\langle \phi_2 | \phi_2 \rangle = 1$

$$\therefore C_1^2 + C_2^2 + 2C_1C_2S = 1$$

$$C_1 = C_2 = 0; \quad C_1^2(1+1+2S) = 1$$

$$C_1^2 2(1+S) = 1$$

$$C_1 = \frac{1}{\sqrt{2(1+S)}}; \text{ if } S = 0; C_1 = \frac{1}{\sqrt{2}}$$

$$\text{if } C_2 = -C_1; (C_1^2 + C_1^2 - 2C_1^2S) = 0$$

$$C_1^2 C_2 (1-S) = 1$$

$$C_1 = \frac{1}{\sqrt{2(1-S)}}; \text{ if } S \text{ is so small } = 0; C_1 = \frac{1}{\sqrt{2}}$$

$$\therefore \psi_+ = \frac{1}{\sqrt{2(1-S)}}(\phi_1 - \phi_2)$$

$$\psi_- = \frac{1}{\sqrt{2(1+S)}}(\phi_1 - \phi_2)$$

what of heteronuclear diatomic?

$$\text{Homo nuclear} \quad \begin{vmatrix} H_{11}^\circ - ES_{11}^\circ & H_{12}^\circ - ES_{12}^\circ \\ H_{21}^\circ - ES_{21}^\circ & H_{22}^\circ - ES_{22}^\circ \end{vmatrix} = 0$$

$$\text{hetero nuclear} \quad \begin{vmatrix} H_{11}^* - ES_{11}^* & H_{12}^\circ - ES_{12}^\circ \\ H_{21}^* - ES_{21}^* & H_{22}^\circ - ES_{22}^\circ \end{vmatrix} = 0 \text{ i.e. } \begin{vmatrix} H_{11}^\circ - ES_{11}^* & \gamma H_{12}^\circ - E\Delta_{12} \\ \gamma H_{21}^\circ - ES_{21}^* & wH_{22}^\circ - E\Delta_{22} \end{vmatrix} = 0$$

note if $x = H$ overlap of $H-Cl$ is larger than $H-H$

$y = Cl$ hence $H-Cl$ is $>$ $H-H$ by a factor e.g. α

$$\therefore \begin{vmatrix} H_{11}^\circ - ES_{11}^\circ & \gamma H_{12}^\circ - ES_{11}^\circ \\ \gamma H_{21}^\circ - ES_{21}^\circ & \gamma H_{22}^\circ - ES_{22}^\circ \end{vmatrix} = 0$$

$$\begin{vmatrix} H_{11}^\circ - ES_{11}^\circ & wH_{22}^\circ - H_{22}^\circ + H_{22}^\circ - ES_{22}^\circ \\ \alpha H_{21}^\circ - H_{21}^\circ + H_{21}^\circ - ES_{21}^\circ & \gamma H_{21}^\circ - ES_{22}^\circ \\ H_{21}^\circ(\alpha - 1) & H_{22}^\circ(w - 1) \end{vmatrix} = 0$$

$$\begin{vmatrix} \frac{H_{11}^\circ - ES_{11}^\circ}{1 + E} & \frac{1 + E}{H_{12}^\circ - ES_{12}^\circ} + \delta \end{vmatrix} = 0 \quad \text{where } E = \frac{H_{12}^\circ - (\alpha - 1)}{H_{12}^\circ - ES_{12}^\circ} \\ \delta = \frac{H_{22}^\circ - (w - 1)}{H_{12}^\circ - ES_{12}^\circ}$$

$$\begin{vmatrix} x & 1 + E \\ 1 + E & x + \delta \end{vmatrix} = 0$$

$$(x)(x + \delta) - (1 + E)(1 + E) = 0$$

$$x^2 + x\delta - (1 + E)^2 = 0$$

$$x = \frac{-\delta \pm \sqrt{\delta^2 - 4ac}}{2a}$$

$$x = \frac{-\delta \pm \sqrt{\delta^2 + 4(HE)^2}}{2}$$

when δ and $E = 0$; $x = \pm 1$

solve for the system where $\delta = 0.2x$ and $E = x = \frac{2}{5}$

Nature of H_{ii} and H_{ij}

Considering H atom

Atom a

$$\frac{1}{\mu} = \frac{1}{m_n} + \frac{1}{m_e} = \frac{m_e + m_n}{m_n m_e}$$

$$\mu = \frac{m_n m_e}{m_e + m_n} \text{ but } m_e \text{ is negligible so } \mu = \frac{m_n m_e}{m_n}$$

$$H = \frac{-\hbar^2 \nabla_a^2}{2\mu} - \frac{\ell^2}{dr_a} |a\rangle = E_a |a\rangle$$

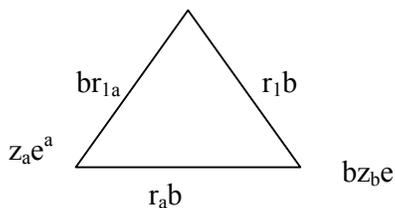
$$\langle a|H|a\rangle = \langle a| \left[\frac{-\hbar^2 \nabla_a^2}{2\mu} - \frac{\ell^2}{dr_a} \right] |a\rangle = E_a \langle a|a\rangle$$

note $\langle a|a\rangle = 1$

overlap integral

but for 2 atoms e.g. $x_2^+; H_2^+$

(z = atomic no)



$$H = \frac{-\hbar^2 \nabla^2}{2\mu} - \frac{Zae^2}{dr_{1a}} - \frac{Zbe^2}{dr_{1b}} + \frac{ZaZbe^2}{dr_{ab}}$$

$$H|a\rangle = \left[\frac{-\hbar^2 \nabla^2}{2\mu} - \frac{Zae^2}{dr_{1a}} - \frac{Zbe^2}{dr_{1b}} + \frac{ZaZbe^2}{dr_{ab}} \right] |a\rangle$$

$$\langle a|H|a\rangle = \langle a| \left[\frac{-\hbar^2 \nabla^2}{2\mu} - \frac{Zae^2}{dr_{1a}} \right] |a\rangle + \langle a| \left[-\frac{Zbe^2}{dr_{1b}} + \frac{ZaZbe^2}{dr_{ab}} \right] |a\rangle$$

$$Ea + \frac{Zabe^2}{drab} \langle a|a \rangle$$

For H_{ij}

$$\langle b|H|a \rangle = \langle b| -\frac{\hbar^2}{2\mu} \nabla^2 - \frac{Zae^2}{dr_1a} |a \rangle + \langle b| -\frac{Zbe^2}{dr_1b} |a \rangle + \frac{Zabe^2}{dr_1ab} \langle b|a \rangle$$

$$H_{11} = E_a + J + R$$

$$Ea + \langle b|a \rangle + \langle b| -\frac{Zbe^2}{dr_1b} |a \rangle + R \langle b|a \rangle$$

$$\langle b|Ha \rangle = H_{12} = EaS + K + RS$$

$$E_1 = \frac{H_{11} - H_{12}}{1 - S} = E + \frac{J - K}{1 - S} + R$$

$$E_- = \frac{H_{11} - H_{12}}{1 + S} = \frac{Ea(1 + S) + J + K + R(1 + S)}{1 + S} = E + \frac{J + K}{1 + S} + R$$

K determines the extent of bonding or contribution of stability to the system as R and J are equal but opposite

$$\psi = C_1\phi_a + C_2\phi_b; \quad \text{set } C_1 = C_2 = 1$$

$$\psi = \phi_a\phi_b$$

$$H\Psi = (E_a + E_b)\Psi_{TOT}$$

$$(H_a + H_b)(\phi_a + \phi_b) = H_a\phi_a + H_b\phi_b + H_a\phi_b + H_b\phi_a$$

$$E_a\phi_a \quad E_b\phi_b$$

OR

$$(H_a + H_b)\phi_a + \phi_b = E_a\phi_a\phi_b + E_b\phi_a\phi_b$$

$$= (E_a + E_b)\phi_a\phi_b \text{ (obey's rule)}$$

It is not always that either linear/product form is convenient

For the 2 molecule system

$$\begin{aligned}
& H \frac{-\hbar^2}{2\mu} (\nabla_a^2 + \nabla_b^2) + \frac{-Zae^2}{dr_a} + \frac{-Zae^2}{dr_b} + \frac{-Zb^2}{dr_b} + \frac{-Zb^2}{dr_b} + \frac{-ZaZbe^2}{dr_b} + \frac{e^2}{r_{12}} \\
& = \left(\frac{-\hbar^2}{2\mu} \nabla_a^2 + \frac{-Zae^2}{dr_a} \right) f \left(\frac{-\hbar^2}{2\mu} \nabla_b^2 + \frac{-Zb^2}{dr_b} \right) + \frac{-Zae^2}{dr_a} + \frac{-Zb^2}{dr_b} + \frac{-ZaZbe^2}{dr_b} + \frac{e^2}{dr_{12}} \\
& \langle \phi_a \phi_b | H_a \phi_a \phi_b = \phi_a \phi_b \left(\frac{-\hbar^2}{2\mu} \nabla_a^2 + \frac{-Zae^2}{dr_a} \right) \phi_a \phi_b = \langle \phi_a \phi_b | E_a \phi_a \phi_b \rangle \\
& = E_a \langle a|a \rangle \langle b|b \rangle \\
& = \langle b|E_b|b \rangle \langle a|a \rangle = E_b
\end{aligned}$$

$$\langle \phi_a \phi_b | \frac{-Zae^2}{dr_a} | \phi_a \phi_b \rangle$$

$$\langle \phi_a \phi_b | \frac{-Zbe^2}{dr_b} | \phi_a \phi_b \rangle$$

$\psi = \phi_a(1) \phi_b(2) + \phi_a(2) \phi_b(1)$ Labeling diction

$$\begin{aligned}
& \langle \psi | H_a | \psi \rangle = \langle \phi_a(1) \phi_b(2) + \phi_a(2) \phi_b(1) | H_a | \phi_a(1) \phi_b(2) + \phi_a(2) \phi_b(1) \rangle \\
& = \langle \phi_a(1) \phi_b(2) + H_a | \phi_a(1) \phi_b(2) + \phi_a(1) \phi_b(2) | H_a | \phi_a(2) \phi_b(1) \rangle \\
& = \langle \phi_a(2) \phi_b(1) + H_a | \phi_a(1) \phi_b(2) + \phi_a(2) \phi_b(1) | H_a | \phi_a(2) \phi_b(1) \rangle \\
& \quad E_a \langle a|b \rangle^2 \\
& \quad E_a S^2
\end{aligned}$$

\therefore total of this integral = $2E_a (1 + S^2)$

$$\langle \phi_a(1) \phi_b(2) + \phi_a(2) \phi_b(1) | \frac{-Zbe^2}{dr_b} | \phi_a(1) \phi_b(2) + \phi_a(2) \phi_b(1) \rangle$$

$$\langle \phi_a(1) \phi_b(2) + H | \phi_a(1) \phi_b(2) + \phi_a(1) \phi_b(2) | H_a | \phi_a(2) \phi_b(1) \rangle$$

$$\langle \phi_a(2) \phi_b(1) + H | \phi_a(1) \phi_a(1) \phi_b(2) + \langle \phi_a(2) \phi_b(1) | H | \phi_a(2) \phi_b(1) \rangle$$

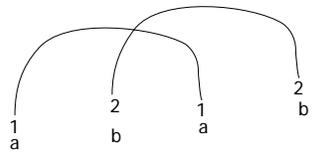
e' inter of e' density on b without nucleus of b

$$\langle \phi_b(2) | \frac{-Zbe^2}{dr_b} | \phi_b(2) \rangle \langle a|a \rangle$$

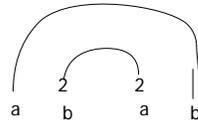
$$\langle \phi_a(1) | \frac{-Zbe^2}{dr_b} | 0$$

my personal rule

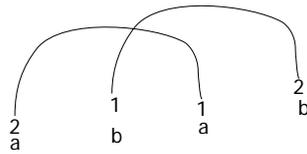
$$\psi = \phi_a(1) \phi_b(2) + \phi_a(2) \phi_b(1)$$



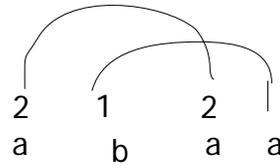
$$\dot{i}.e. Ea \langle a|a \rangle \langle b|b \rangle Ea$$



$$Ea \langle b|a \rangle \langle b|a \rangle CaS^2$$



$$\dot{i}.e. Ea \langle b|a \rangle \langle b|a \rangle EaS^2$$



$$Ea \langle a|a \rangle \langle b|b \rangle Ea$$

$$\therefore \text{Total} = 2Ea (1 + S^2)$$

$$\frac{H_{11} + H_{12}}{(1 + S^2)} = \frac{2(Ea + E_b)(1 + S^2) + 2(2J + 2KS) + 2(R + Q)(1 + S^2)}{2(1 + S^2)}$$

$$\therefore E = Ea + E_b + \frac{2J + 2KS}{(1 + S^2)} + R + Q$$

Before $\phi = C_1\phi_1 + C_2\phi_2$

But for this system $C_1\phi_a(1)\phi_b(2) + C_2\phi_a C_2\phi_b(1)$

$$\begin{aligned} \langle \psi | \psi \rangle &= \langle C_1 \psi_1 + C_2 \psi_2 | C_1 \psi_1 + C_2 \psi_2 \rangle = 1 \\ C_1^2 \langle \psi_1 | \psi_1 \rangle &+ \langle C_2 \psi_2 + C_2 \psi_2 | \psi \rangle + 2C_1 C_2 \langle \psi_1 | \psi_2 \rangle \\ 1 &= C_1^2 \langle \phi_a(1) \phi_b(2) | \phi_a(1) \phi_b(2) \rangle + C_2^2 \langle \phi_a(2) \phi_b(1) | \phi_a(2) \phi_b(1) \rangle + 2C_1 C_2 \langle \phi_a(1) \phi_b(2) | \phi_a(2) \phi_b(1) \rangle \\ 1 &= C_1^2 \langle a | a \rangle \langle b | b \rangle + C_2^2 C_2 \langle a | a \rangle \langle b | b \rangle + 2C_1 C_2 \langle a | b \rangle \langle a | b \rangle \\ C_1^2 &+ C_2^2 & 2C_1 C_2 S^2 &= 1 \end{aligned}$$

$$\text{Set } C_2 = C_1$$

$$\therefore C_1^2 (1 + 1 + 2S^2) = 1$$

$$C_1^2 (2 + 2S^2) = 1$$

$$C_1 = \frac{1}{\sqrt{2(1+S^2)}}$$

$$\text{Similarly if } C_2 = -C_1; \text{ then } C_1 = \frac{1}{\sqrt{2(1+S^2)}}$$

$n!$ = normalization constant for n atoms

$$\frac{1}{n!} \begin{vmatrix} \phi_a(1) & \pm \phi_b(1) \\ \phi_a(2) & \phi_b(2) \end{vmatrix}$$

$$\psi = N(\phi_b C_1)(\phi_b(2) \pm \phi_a(2) \phi_b(C_1)) \text{ where } N = C_1 = C_2$$

From the molecular theory, $\psi = (\phi_a C_1) \phi_b C_2 + \phi_a C_2) \phi_b(1)$

Taking H_a ,

$$\begin{aligned} \langle \psi | H_a | \psi \rangle &= \langle \phi_a(1) \phi_b(2) + \phi_a(2) \phi_b(1) | H_a | \phi_a(1) \phi_b(2) + \phi_a(2) \phi_b(1) \rangle \\ &= \langle \phi_a(2) \phi_b(1) | H_a | \phi_a(1) \phi_b(2) \rangle + \langle \phi_a(2) \phi_b(1) | H_a | \phi_a(2) \phi_b(1) \rangle \\ &+ \langle \phi_a(1) \phi_b(2) | H_a | \phi_a(1) \phi_b(2) \rangle + \langle \phi_a(1) \phi_b(2) | H_a | \phi_a(2) \phi_b(1) \rangle \end{aligned}$$

$$E_a \langle a | a \rangle \langle b | b \rangle = E_a$$

$$E_a \langle a | a \rangle \langle b | b \rangle = E_a$$

$$E_a \langle a | b \rangle^2 = E_a S^2 \quad a \neq b \Rightarrow J_a, J_b$$

$$E_a \langle b | a \rangle^2 = E_a S^2 \quad \text{Total} = E_a (HS^2)$$

$$\text{For (4)} \quad \phi_a(1) \phi_b(2) | H_a | \phi_a(1) \phi_b(2) + \langle \phi_a(1) \phi_b(2) | H_a | \phi_a(2) \phi_b(1) \rangle$$

$$\langle \phi_a(1) \phi_b(2) | \phi_a(1) \phi_b(2) \rangle + \langle \phi_a(1) \phi_b(2) | \phi_a(2) \phi_b(1) \rangle + \langle \phi_a(2) \phi_b(1) | \phi_a(1) \phi_b(2) \rangle$$

$$\text{contd } \langle \phi_a(1) \phi_b(2) \rangle + \langle \phi_a(2) \phi_b(1) | \phi_a(2) \phi_b(1) \rangle$$

$$N (\langle \phi_a(1) + \phi_b(1) \rangle + \langle \phi_a(2) + \phi_b(2) \rangle$$

$$= (\langle \phi_a(1) \phi_a(2) \rangle + \langle \phi_a(1) \phi_b(2) \rangle + \langle \phi_b(1) \phi_a(2) \rangle + \langle \phi_b(1) \phi_b(2) \rangle$$

$$-A_a - A_b^+ \quad A_a - A_b \quad A_a - A_b \quad A_a^+ - A_b^-$$

← equal contributions →

purely covalent in nature

Suppose we reverse the order taking the product combination the linear combination

$$\Psi = N \Psi_1 \Psi_2$$

$$N (\langle \phi_a(1) \phi_b(1) \rangle + \langle \phi_a(1) \phi_a(2) \rangle + \langle \phi_b(2) \rangle$$

$$= (\langle \phi_a(1) \phi_a(2) \rangle + \langle \phi_a(1) \phi_b(2) \rangle + \langle \phi_b(1) \phi_a(2) \rangle + \langle \phi_b(1) \phi_b(2) \rangle$$

$$-A_a - A_b^+ \quad A_a - A_b \quad A_a - A_b \quad A_a^+ - A_b^-$$

← equal contributions →

purely covalent

Proposal thus takes case of not only the covalent but also the possible ionic bonding

Configuration interaction theory

Another theory supposes the ground state is actually mixed with some amount of the excited state. Thus, the wave function observed are slightly mixed from one perspective

$$\therefore \Psi = \Psi_1 \Psi_2 + \text{just } \Psi_1 \Psi_2$$

$$\Psi = \Psi_1 \Psi_2 + f \text{ just } \Psi_1 \Psi_2$$

Excited state = $(\langle \phi_a(1) \phi_b(1) \phi_a(2) \phi_b(2) \rangle + \langle \phi_b(2) \rangle + f$
 $(\phi_a(1) - \phi_b(1) (\phi_a(2) (\phi_b(2))$ the excited state must have a
 -ve sign

$$= (\langle \phi_a(1) \phi_a(2) + \phi_a(1) \phi_b(2) + (\phi_b(1) + \phi_a(2) + \phi_b(1)) \phi_b(2) \rangle)$$

Note

$$\Psi = C_1 \phi_1 + C_2 \phi_2$$

$$\Psi = \phi_a \phi_b$$

$$\Psi = N[\psi_1 + \psi_2]$$

$$\begin{array}{cc} \phi(1)\phi_b(2) & \phi(2)\phi(1) \\ a & b \end{array}$$

$$\Psi = \psi_1 \psi_2 = \phi_a(1) \phi_b(2) \text{ just } \psi_1 \psi_2$$

$$\Psi = \psi_1 \psi_2 = \phi_a(1) \phi_b(1) \phi_a(2) + \phi_b(2)$$

$$\Psi = \psi_1 \psi_2 + f \psi_1 \psi_2$$

$$= \phi_a(1) \phi_b(1) \phi_a(2) + \phi_b(2) + f \phi_a(1) - \phi_b(1) \phi_a(2) - \phi_b(2)$$

$$= \phi_a(1) \phi_a(2) + \phi_b(1) \phi_b(2) + \phi_a(1) \phi_b(2) + \phi_a(2) \phi_b(1)]$$

$$f [\phi_a(1) \phi_a(2) + \phi_b(1) \phi_b(2) - \phi_a(1) \phi_b(2) + \phi_a(2) \phi_b(1)]$$

$$= 1 + \phi_a(1) \phi_a(2) + \phi_b(1) \phi_b(2) + (1 - f) (\phi_a(1) \phi_b(2) + \phi_a(2) \phi_b(1)]$$

f can be 0, +1, -1

$$\bar{A}_a - A_a^+ \quad A_b^+ - A_b^- \quad A_a - A_b$$

By setting $f = 0$, essentially you're dealing with the M. O. theory. If $f = -1$, you get M. O. theory, which is a covalent contribution.

If $f = +1$, describes a totally ionic condition.

Putting an atom in the centre of coordination,

$$\Psi = R(r) \Theta(\theta) \Phi(\phi)$$

$n \quad l \quad m$

R is a function of Radius itself, angle with Z axis and angle with x axis respectively.

E_{m_l}	0	± 1	± 2	± 3	(magnetic quantum nos)
	S	P	D	F	

Where $C_n = \infty$ and $C_{m_l} = \infty$

You have $D_n = \infty$

$\Psi = \text{const } e^{\pm i \lambda \phi}$

0 +1 +2 +3

σ π δ ω

$\lambda = 0, \quad +1, \quad +2 \quad +3$

σ π δ ϕ

Σ π Δ Φ Term symbol

$\Psi = \Psi_1 \Psi_2 = 1s/s$

There are 2 ways of classifying this mol orb

(1) Origin = H atomic orbitals f/qch they emerge e.g.

$\sigma_g (1s)$ (it could have w i.e. f/ 35 atom)

(2) Position in energy scale e.g. $1\sigma_g, 2\sigma_g, 3\sigma_g$

The atomic orbitals f/quenching these m. o. occur can be linked or correlated to them in 2 form i.e.

(1) In terms of energies

(2) In terms of the symmetries of origin atomic orbitals qch can be correlated to the symmetries of m. o.

If they are of the same symmetry, they're correlated. If

not they're not correlated. To change symmetry to correlate involves use of a large amount of energy.

The concept of correlation diagram of A. O. and M. O. is found on these 2 term i.e. " " in terms of energy (easier to perceive) and " " " " " symmetry

M .O. has lower energy than A. O.

The energy correlation diagram req. that certain atomic orbital combine to form mol orb.

At the third level, the sequence change. The size of splitting

$$= \Delta E = \Delta E = a \frac{1}{E(2p) - E(2s)}, \quad \text{there'll be a}$$

When $E(2p) - E(2s)$ is small; ΔE is large

Repulsion between $2\sigma_u$ and $3\sigma_g$ such that $1\pi_u$ is really nearer to $2\sigma_u$

Then u fill in the orbital with the available e^- . Only $2e^-$ can occupy an orbital and they should be of opp..... An excited will have an e^- in a higher orbital when the lower orbital still has only e^-

e.g. $1\sigma_g^2 =$ hydrogen molecule; $1\sigma_g^1 1\sigma_u^1 \Rightarrow$ excited state

Helium He₂ molecule - $1\sigma_g^2 \sigma_u^{*2}$, but molecule is not stable

viz $\Rightarrow 1\sigma_g^2 1\sigma_u^{*2} 2\sigma_g^2$ (behaves like H₂)

Term symbol of H₂ = Σ

Multiplicity $(2S + 1) = 1$ because $S = 0$ i.e. $^1\Sigma_{g,u}$ + mirror

Net no of bonding to antibonding (i.e. bonding - antibonding)

Molecule	Spin	#	σ_g	σ_u^*	$2\sigma_g$	$2\sigma_u^*$	$1\pi_u$	$3\sigma_g$	$1\pi_g^*$	$3\sigma_u^*$	Energy		
			$\sigma_g(1s)$	$\sigma_u^*(1s)$	$\sigma_g(2s)$	$\sigma_u^*(2s)$	π_u	$\sigma_g(2p)$	$\pi_g^*(2p)$	$\sigma_u^*(2p)$	(Symmetry)		
+2	$\frac{1}{2}$	1	\uparrow								Bonding 2.65	Bond length 1.06	Ground state terms $2\Sigma^+_g$
+2	0	2	$\uparrow\downarrow$								4.48	0.78	$1\Sigma^+_g$
+2	$\frac{1}{2}$	1	$\uparrow\downarrow$								(3.1)	1.08	$1\Sigma^+_g$
+2	0	0	$\uparrow\downarrow$								-	-	$1\Sigma^+_g$
+2	0	2	$\uparrow\downarrow$								1.0	2.67A	$1\Sigma^+_g$
+2	0	0	$\uparrow\downarrow$								not stable	-	$1\Sigma^+_g$
+2	1	2	$\uparrow\downarrow$								3.6	1.54	$3\Sigma^-_g$

The higher the net bonding to anti-bonding; the more stable because the bond energy is more:
 Look at He_2^+ is theoretically computed that's why bond energy is put in bracket for He_2^+
 Bond energy is also called dissociation energy
 Electronic configuration of Be_2 is $1\sigma_g^2 1\sigma_u$ etc but for $\text{Be} - 1s^2 2s^2$ etc.

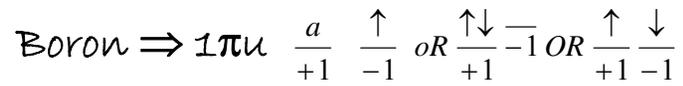
Molecule

+2	0	4	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$				6.2	1.24A	$1\Sigma^+_g$
+2	$\frac{1}{2}$	5	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	\uparrow			8.73	Not known	$2\Sigma^+_g$
+2	0	6	$\uparrow\downarrow$			9.76	1.09	$1\Sigma_g$						
+2	$\frac{1}{2}$	5	$\uparrow\downarrow$	\uparrow		6.48	1.12							

Σ^- : symmetry operation of reflection

N_2^+ is very stable

	$1\sigma_g$	$1\sigma_u^*S$														
O ₂	4		↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑	↑↓	↑↓		5.08	1.21	$2\Sigma^-$ g+	
Fe	2		↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓		1.6	1.44	$1\Sigma_g$	
Ne	0		↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	-	-		



For case L; $\Omega = 0 \therefore$ Term symbol is Σ_g

For case A; ${}^3\Sigma_g$ ($\Omega = 0$)

For case B; $\Omega = 2$, Term symbol ${}^1\Delta_g$

If two multiplicities are equal; the largest value of L, angular momentum is next stable \therefore in order of stability we have

${}^1\Sigma_g$

\downarrow stability i.e. why the intensity of oxygen is low because of the spin is not the same and thus forbidden

${}^3\Sigma_g$

Morse's potential energy for the formation of a molecule, the electron sit inside the vibrational levels (in each are also the rotational levels)

Vibration is determined by "a" in the equation

Expanding the equation

$$EP = D[1 - e^{-a(r-r_0)}]^2 - D$$

$$EP = D(1 + e^{-2a(r-r_0)} - 2e^{-a(r-r_0)}) - D$$

M. P. E. curve describes the bonding between molecules

The slope at any point = $\frac{dE_p}{dr}$

$$\frac{dE_e}{dr} = 2ae^{-2a(r-r_0)} + 2ae^{-a(r-r_0)} = 0 \text{ at bottom of curve}$$

Because at bottom of curve $\frac{dE_p}{dr} = 0$

$$2ae^{-a(r-r_0)} + 1 - e^{-a(r-r_0)} = 0$$

This is not zero therefore the one in bracket must be set in 0

$$\therefore e^{-a(r-r_0)} = 1 \quad \therefore r - r_0 = 0$$

At the minimum of curve where $r = r_0$; the curve is assigned a value of $-D$ where $r = \infty$ i.e. infinite then $e^{-a(r-r_0)}$ can be $\frac{1}{e^{\infty}}$

which is 0;

$$\therefore Ep = 0 \text{ where } r = \infty$$

If $-D$ is removed from the initial equation then $r = r_0$ will yield $Ep = 0$ and $r = \infty$ will yield $Ep = D$ and the change in Ep will still be D on the graph

Writing the equation in another way;

$$Ep = D [1 - e^{-x}]^2 - D$$

Any exponential term can be expanded

$$e^{-x} = \sum_{r=0}^{\infty} \frac{c - D^r x^r}{r!}$$

Therefore for some terms up to $n = 3$ $e^{-x} = 1 - x +$

$$\frac{x^2}{2!} - \frac{x^3}{3!}; Ep = \left[1 - \left[1 - x + \frac{x^2}{2!} - \frac{x^3}{3!} \right] \right]^2$$

$$Ep = \left[1 - \left[1 - x + \frac{x^2}{2} - \frac{x^3}{6} \right] \right]^2$$

$$\left(x - \frac{x^2}{2} + \frac{x^3}{6} \right) \left(x - \frac{x^2}{2} + \frac{x^3}{6} \right)$$

$$x^2 - x \frac{3}{2} + \frac{x^4}{6}$$

$$-x \frac{3}{2} + \frac{x^4}{4}$$

$$+ \frac{x^4}{6}$$

$$x^2 + \frac{7}{12x^4}$$

$$E_p = D(x^2 + \frac{7}{12}x^4 + \dots) - D$$

Then u can differentiate wrt x and D will disappear

A vibrating diatomic molecule is held by its bond strength and by hooke's law, this force; $-F = Ky$ (y = distance of expansion $r - r_0$).

$$E_p = \int -F(y) dy = K \int y dy = \frac{1}{2}ky^2$$

$$\text{i.e. } x^n dx = \frac{1}{n+1} x^{n+1}$$

Hooke's law deals only with the 1st approximation

$$E_p = \frac{1}{2}ky^2 = Dx^2$$

$$E_p = \frac{1}{2}ky^2 = Da^2(r - r_0)^2$$

$$= \frac{1}{2}k(r - r_0)^2 = Da^2(r - r_0)^2$$

$$a = \sqrt{\frac{k}{2D}}$$

$$f(x) = \mu x + \delta x + Kx = 0$$

$$= \frac{\infty}{x} + \frac{\alpha}{\mu} + \frac{kx}{\mu} = 0 +$$

w = circular frequency = $2\pi y \rightarrow$ (linear frequency cycle/s)

$$\therefore k = \mu \omega_0^2 \text{ where } w = 2\pi v$$

$$a = \sqrt{\frac{(2\pi y)^2 \mu}{2D}} = \sqrt{\frac{(w_0^2) \mu}{2D}}$$

The dissociation constant is inversely..... bond

HYBRIDISATION

Hybridisation is the mixing of orbitals which overlap when forming bonds. The sum of the starting hybridized orbitals = sum of hybridized orbitals. The energies of hybridized orbitals are equivalent.

For sp, angle is 180° to minimize repulsion. The best way to arrange 2 hybridized volume in space such that the e - e repulsion is minimal is at 180° i.e. $360/n$ where n = no of orbitals. But for 4 orbitals, $360/n$ is no longer applied because of too much repulsion. The array is that of a tetrahedral

Correction $f(x) = \mu \ddot{X} + \alpha \dot{X} + kx$; $\ddot{X} = \text{acc}$ $\dot{X} = \text{vel}$

μ = reduced mass; α = frictional coeff; x ; displacement
calculation of angle of hybridized orbitals

$\phi = as + bp$ (a and b are mixing coefficient of S and P orbitals

$$\begin{aligned} \langle \phi_1 | \phi_1 \rangle &= \langle as + bp | as + bp \rangle = 1 \\ &= a^2 \langle s | s \rangle + b^2 \langle p | p \rangle + 2ab \langle s | p \rangle = 1 \end{aligned}$$

They don't belong to same symmetry i.e. $\langle s | p \rangle = 0$

$$\therefore a^2 + b^2 = 1$$

For Sp^3 ; $\frac{1}{4}s$ $\frac{3}{4}p$

$$\therefore a^2 = \frac{1}{4} \quad b^2 = \frac{3}{4}$$

$$= \frac{1}{2} \quad \frac{\sqrt{3}}{2}$$

$$\therefore \phi_1 = as + bp = \frac{1}{2}s + \frac{\sqrt{3}}{2}p$$

Two hybridized orbitals where orientations of P orbitals are different

$$\phi_1 = as + bp_1$$

$$\phi_2 = as + bp_2$$

$$\langle \phi_1 | \phi_2 \rangle = \langle as + bp_1 | as + bp_2 \rangle = 0$$

$$a^2 \langle s | s \rangle + b^2 \langle p_1 | p_2 \rangle + ab \langle s | p_1 \rangle + \langle s | p_2 \rangle = 0$$

$$a^2 + b^2 \langle p_1 | p_2 \rangle$$

$$a^2 + b^2 \langle p_1 | p_1 \rangle \cos \theta$$

$$\cos \theta = \frac{-a^2}{b^2}$$

$$\text{For } sp^3 \cos \theta = \frac{1}{4} \cdot \frac{4}{3} = -\frac{1}{3}; \theta = 109.45^\circ$$

$$\text{For } sp^2 \text{ hybridisation; } a^2 + b^2 = 1$$

$$sp = \frac{1}{3}s + \frac{2}{3}p$$

$$\cos \theta = \frac{-a^2}{b^2} = -\frac{1}{3} \times \frac{3}{2} = -\frac{1}{2}; \theta = 120^\circ$$

$$sp = \frac{1}{2}s + \frac{1}{2}p$$

$$a = \frac{1}{\sqrt{2}}; a^2 = \frac{1}{2}$$

$$b = \frac{1}{\sqrt{2}}; b^2 = \frac{1}{2}$$

$$\cos \theta = -\frac{a^2}{b^2} = -\frac{1}{2} - \frac{2}{1} = -1; \theta = 180^\circ$$

Monovalent elements can easily combined with the tetrahedron e.g. CCl_4 , CF_4 , CH_2Cl_2 , CH_3Cl , the tetrahedron can react with its type

By virtue of hybridization; carbon not only changes its valence, it also forms homologous series

For sp^3d^2 (square planar) e.g. XeF_4

3d

sp

3s

sp^3d^3 : 7 orbitals destroy orbital balance. It will be a distorted octahedron

Computational aspect

Conjugated system

Looking at a 2-atom system

$$\begin{pmatrix} x & 1 \\ 1 & x \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = 0 \quad x = \pm 1$$

mount c_1 c_2 into the rows

$$xc_1 + c_2 = 0 \text{ implies } c_2 = -xc_1$$

$$c_1 + xc_2 = 0$$

$$\frac{H_{11} - ES_{11}}{H_{12} - ES_{12}} = \frac{\alpha - E}{\beta - Es}$$

$$x\beta - E \times s = \alpha - E$$

$$E(1 - xs) = \alpha - x\beta$$

$$E = \frac{\alpha - \beta}{1 - xs}$$

$$E_+ = \frac{\alpha - \beta}{1 - S} \quad E_- = \frac{\alpha + \beta}{1 + S}$$

can only be obtained for this kind of cpd (i.e. x varies for others)

To give the coefficient values, normalize the ψ

$$\sum C_n^2 = 1 \quad \{c_1^2 + c_2^2 + 2c_1c_2S = 1\}$$

$$\text{so small } = 0$$

$$c_1^2 + c_2^2 = 1 \text{ for 2 atomic system (11)}$$

$$c_2 = -xc_1 \dots (1)$$

substitute (1) into (2)

$$c_1^2 + x^2c_1^2 = 1$$

$$c_1^2(1 + x^2) = 1$$

$$c_1 = \frac{1}{\sqrt{1+x^2}}$$

$$\text{when } x = -1$$

$$c_1 = \frac{1}{\sqrt{2}}; c_2 = -1 \times c_1 = \left(-1 \frac{1}{\sqrt{2}}\right) = -\frac{1}{\sqrt{2}}$$

$$\text{when } x = +1$$

$$c_1 = \frac{1}{\sqrt{2}}; c_2 = \left(-1 \frac{1}{\sqrt{2}}\right) = -\frac{1}{\sqrt{2}}$$

It's the ground state that has pluses through out

	X	c_1	c_2	E
Ψ_+ Ψ_2	+	$\frac{1}{\sqrt{2}}$	$\frac{1}{\sqrt{2}}$	$\frac{\alpha - \beta}{1 - S}$
	1			
		$\frac{1}{\sqrt{2}}$	$\frac{1}{\sqrt{2}}$	$\frac{\alpha - \beta}{1 - S}$
Ψ_- Ψ_1	-1			

$\uparrow\downarrow$ (i.e. from each carbon, $c = c$)

$$\Psi_2 = \frac{1}{\sqrt{2}} \phi_1 - \frac{1}{\sqrt{2}} \phi_2$$

$$\Psi_1 = \frac{1}{\sqrt{2}} \phi_1 + \frac{1}{\sqrt{2}} \phi_2$$

To calculate the charges on each atom

c_1, c_2 are the i 's. The molecular orbitals are the j 's

electron density is defined as $q_j = \sum_i n_j c_i^2$

$$\therefore \text{for } q_i \text{ in ground state} = 2 \left(\frac{1}{\sqrt{2}} \right)^2 + 0 \left(-\frac{1}{\sqrt{2}} \right)^2 = 1$$

For excited state, e^- - e^- /nuclear - nuclear repulsion is not taken into account hence result is the same

Charge density, $\sum_1 = 1 - q$

If q is 1; then $\sum_1 = 0$ which means

Because atoms of molecule has a charge

unless sth is done to move electrons

$$B.O. \propto \frac{1}{B.L}$$

$$P = n_j c_i c_k$$

$$e_{12} = 2 \left(\frac{1}{\sqrt{2}} \right) \left(\frac{1}{\sqrt{2}} \right) = 1.0 \text{ for ground state}$$

slope

$$B.L = A - XB O$$

For 3 atom

$$\begin{pmatrix} x & 1 & 0 \\ 1 & x & 1 \\ 0 & 1 & x \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \\ c_3 \end{pmatrix} = 0$$

$$\begin{vmatrix} x & 1 & 0 \\ 1 & x & 1 \\ 0 & 1 & x \end{vmatrix} = x(x^2 - 1) - 1(x - 0) = 0$$

$$x^3 - 2x = 0$$

$$x(x^2 - 2) = 0$$

$$\therefore x = 0, +\sqrt{2}, -\sqrt{2}$$

$$E = \frac{\alpha - x\beta}{1 - xS}$$

$$E_3 = \frac{\alpha - \sqrt{2}\beta}{1 - \sqrt{2}S} \quad \Psi_3$$

$$E^2$$

$$x=0 \quad \alpha \quad \Psi_2$$

$$E_1 = \alpha + \frac{\sqrt{2}\beta}{1 + \sqrt{2}S}$$

$$xC_1 + C_2 = 0 \text{ ----- (i) } C_2 = -xC_1$$

$$C_1 + xC_2 + C_3 = 0 \text{ ----- (ii) } C_3 = C_1 - xC_2$$

$$C_2 + xC_3 = 0 \text{ ----- (iii) } -C_1 + x^2 C_1 = C_1(x^2 - 1)$$

$$C_1^2 + C_2^2 + C_3^2 = 1$$

$$C_1^2 (1 + x^2 + x^2 - 1) = 1$$

$$C_1 = \frac{1}{1 + x^2 + (x^2 - 1)^2}$$

$$\psi_3 \quad \begin{array}{cccc} x & c_1 & c_2 & c_3 \\ +\sqrt{2} & \frac{1}{2} & \frac{\sqrt{-1}}{2} & \frac{1}{2} \\ 0 & \frac{1}{\sqrt{2}} & 0 & \frac{1}{\sqrt{2}} \end{array}$$

$$\psi_3 \quad \begin{array}{cccc} x & c_1 & c_2 & c_3 \\ +\sqrt{2} & \frac{1}{2} & \frac{\sqrt{-1}}{2} & \frac{1}{2} \\ 0 & \frac{1}{\sqrt{2}} & 0 & \frac{1}{\sqrt{2}} \end{array}$$

$$\psi_1 \quad \begin{array}{cccc} -\sqrt{2} & \frac{1}{2} & \frac{\sqrt{2}}{2} & \frac{1}{2} \end{array}$$

$$x c_1 + c_2 = 0; \quad c_2 = -x c_1$$

$$c_1 + x c_2 + c_3 = 0; \quad c_3 = -c_1 - x c_2 \text{ or } c_3 = c_1 + x^2$$

If you use equation 3 to get c_3 for ψ for $x = \frac{1}{\sqrt{2+x^2}}$

$$E_3 = \frac{\alpha - \sqrt{2}\beta}{1 - \sqrt{2}S}$$

$$E_2 = \alpha$$

$$E_1 = \frac{\alpha - \sqrt{2}\beta}{1 - \sqrt{2}S}$$

$E_2 - E_1 = \sqrt{2}\beta$ if S is set to 0, B is -ve therefore the transition energy is a +ve value

$$\lambda\nu = \alpha - \frac{\alpha + \sqrt{2}\beta}{1+S}; \quad \alpha - \frac{\alpha + \sqrt{2}\beta}{1+\sqrt{2}S} - \alpha$$

e-e repulsion is not taken into account. So, the 2nd and 3rd are equivalent coulombic integral being dealt with.

$E_{\text{resonance}} = E_{\text{allyl}} - E_{\text{q ethane}}$ ($E_{\text{equiv}} = E_{\text{equiv}} - E_{\text{q ethane}}$)

To cal; E for allyl cat; multiply the no of E by every energy level. Total energy = E_1 set $S = 0$

$$\text{Ethene} = \alpha - \alpha + \beta \quad E_1 \frac{\alpha + \beta}{1 + S}$$

$$E_{\text{cation}} = 2(\alpha + \sqrt{2}\beta) - 2(\alpha + \beta)$$

$$2(\alpha - \alpha + (\sqrt{2} - 1)\beta)$$

$$2 \times 0.414 \times \beta = 0.820\beta \quad \beta = -2.3 \text{ eV}$$

$$\text{Allyl radical; } E_{\pi_r} = 2(\alpha + \sqrt{2}\beta) + \alpha - 2(\alpha + \beta) - \alpha$$

$$2(\sqrt{2} - 1)\beta = 0.828\beta$$

All have the same stabilization energy; it should not be because of repulsion

$$\text{Anion, } E = 2(\alpha + \sqrt{2}\beta + 2\alpha - 2(\alpha + \beta) - 2\alpha$$

$$= 2(\sqrt{2} - 1)\beta = 0.828\beta$$

$$q_1 = \sum n_{ij}^2 \text{ when } n_i = \text{ground state}$$

$$q_1 = 2 \left(\frac{1}{2}\right)^2 + 0\left(\frac{1}{2}\right)^2 + 0\left(\frac{1}{2}\right)^2 + 0\left(\frac{1}{2}\right)^2 = \frac{1}{2}$$

$$q_2 = 2 \left(\frac{\sqrt{2}}{2}\right)^2 + 0(0)^2 + 0\left(-\frac{\sqrt{3}}{2}\right)^2 = 1$$

$$q_3 = 2 \left(\frac{1}{2}\right)^2 + 0\left(-\frac{1}{\sqrt{2}}\right)^2 + 0\left(-\frac{1}{2}\right)^2 = \frac{1}{2}$$

According to resonance theory of organic chemistry, there is an oscillation of charge

Molecular orb theory says no; that the charges are permanently on 1 and 3, and that these ext with nucleophiles

The resonance theory is not supported by experiment

X-ray supports M - OT

Excitation of the electron from E_1 to either E_2 or E_3 changes the q of the relative of the difference ext. st cannot be compared relative to the g.s.

Calculate excited states for cation

Allyl cation $\Rightarrow \psi_1^2 \psi_2^0 \psi_3^0$

$$\psi_1^1 \psi_2^1 \psi_3^0$$

$$\psi_1^1 \psi_2^0 \psi_3^1$$

	ψ	x	c_1	c_2	c_3
0	$(P_{12}) \psi_3$	$+\sqrt{2}$	$\frac{1}{2}$	$\frac{-\sqrt{2}}{2}$	$\frac{1}{2}$
1	$(P_{12}) \psi_2$	0	$\frac{1}{\sqrt{2}}$	0	$\frac{-1}{\sqrt{2}}$
2	$(P_{12}) \psi_1$	$-\sqrt{2}$	$\frac{1}{2}$	$\frac{\sqrt{2}}{2}$	$\frac{1}{2}$

Allyl radical

$$q_1 = 2\left(\frac{1}{2}\right)^2 + 1\left(\frac{1}{\sqrt{2}}\right)^2 + 0\left(\frac{1}{2}\right)^2 = 1.0$$

$$q_2 = 2\left(\frac{1}{2}\right)^2 + 1(0)^2 + 0\left(-\frac{\sqrt{2}}{2}\right)^2 = 1.0$$

$$q_3 = 2\left(\frac{1}{2}\right)^2 + 2\left(-\frac{1}{\sqrt{2}}\right)^2 + 0\left(\frac{1}{2}\right)^2 = 1.0$$

\therefore we have reactive to an electron seeking reagent the charges are spread from 1 and 3 and the activity is thus centered.

Bond order for Allyl radical

$$P_{12} = 2\left(\frac{1}{2}\right)\left(\frac{\sqrt{2}}{2}\right) + 1\left(\frac{1}{\sqrt{2}}\right)(0) + (0) = \left(\frac{1}{2}\right)\left(-\frac{\sqrt{2}}{2}\right) = \frac{\sqrt{2}}{2}$$

$$P_{23} = 2\left(\frac{\sqrt{2}}{2}\right)\left(\frac{1}{2}\right) + 1(0) = \left(-\frac{1}{2}\right) + 0\left(-\frac{\sqrt{2}}{2}\right)\frac{1}{2} = \frac{\sqrt{2}}{2}$$

For cation, B. O.

$$P_{12} = 2\left(\frac{1}{2}\right)\left(\frac{\sqrt{2}}{2}\right) + 0\left(\frac{1}{\sqrt{2}}\right)(0) + (0)\left(\frac{1}{2}\right)\left(-\frac{\sqrt{2}}{2}\right) = \frac{\sqrt{2}}{2}$$

$$P_{23} = 2 \left(\frac{\sqrt{2}}{2}\right) \left(\frac{1}{2}\right) + 0(0) \left(-\frac{1}{\sqrt{2}}\right) + 0 \left(-\frac{\sqrt{2}}{2}\right) \frac{1}{2} = \frac{\sqrt{2}}{2}$$

Rb. BL = A - D.BO (Since BL will be the same is allowed not)

But all the BL ought not to be the same because there're different no of e's in the system, but there're the same because e-e repulsion is ignored

The wave defines the nature of x

Cyclopropene

$$\begin{pmatrix} x & 1 & 1 \\ 1 & x & 1 \\ 1 & x & x \end{pmatrix} \begin{pmatrix} C_1 \\ C_2 \\ C_3 \end{pmatrix} = 0$$

$$\begin{vmatrix} x & 1 & 1 \\ 1 & x & 1 \\ 1 & x & x \end{vmatrix} = 0$$

$$x(x^2 - 1) - 1(x-1)1(x-1)$$

$$x(x-1)(x+1) - (x-1) - (x-1) = 0$$

$$(x-1)(x^2 + x - 2) = 0$$

$$(x-1)(x+2)(x-1) = 0$$

$$x = 1, 1, -2 \text{ most stable}$$

$$\text{Rb. } \epsilon = \frac{\alpha - x\beta}{1 - xS}$$

$$E_3 = E_2 \frac{\alpha - x\beta}{1 - S}$$

$$E_1 = E_2 \frac{\alpha - 2\beta}{1 - 2S}$$

If S is 0; $\epsilon = \alpha\beta$ and $\alpha + 2\beta$

$$\Delta E\pi_{\text{cation}} = 2(\alpha + 2\beta) - 2(\alpha + \beta)$$

$$2\alpha + 4\beta - 2\alpha - 2\beta = 2\beta$$

$$\Delta E\pi_{\text{res}}^{\text{radical}} = 2(\alpha + 2\beta) + (\alpha - \beta) - 2(\alpha + \beta) - \alpha$$

$$2\alpha + 4\beta + \alpha - \beta - 2\alpha - 2\beta - \alpha$$

$$\Delta E_{\text{res}}^{\text{anion}} = 2(\alpha + 2\beta) + 2(\alpha - \beta) - 2(\alpha + \beta) - 2\alpha$$

$$2\alpha + 4\beta + 2\alpha - 2\beta - 2\alpha - 2\beta - 2\alpha$$

ψ	x	c_1	c_2	c_3
ψ_3	1	$\frac{1}{\sqrt{6}}$	$\frac{-2}{\sqrt{6}}$	$\frac{1}{\sqrt{6}}$
ψ_2	1	$\frac{1}{\sqrt{6}}$	$\frac{-2}{\sqrt{6}}$	$\frac{1}{\sqrt{6}}$
ψ_1	-3	$\frac{1}{\sqrt{3}}$	$\frac{1}{\sqrt{3}}$	$\frac{1}{\sqrt{3}}$

$$xC_1 + C_2 + C_3 = 0$$

$$C_1 + xC_2 + C_3 = 0$$

$$C_1 + C_2 + xC_3 = 0$$

$$(x+1)C_1 - (x-1)C_3$$

$$(x-1)C_1 - C_3 = 0$$

$$C_1 = C_3$$

Multiply (1) by x to give

i.e. $x^2C_1 + xC_2 + xC_3$; then (1) (3)

$$C_1 + C_2 + xC_3$$

$$(x^2 - 1)C_1 + (x - 1)C_2 = 0 \quad (x + 1)(x - 1)C_1 + (x - 1)C_2 = 0$$

$$(x - 1)\{(x + 1)C_1 + C_2\} = 0$$

$$C_2 = -(x + 1)C_1$$

$$\text{Rb } C_1^2 + C_2^2 + C_3^2 = 1$$

$$\text{i.e. } C_1^2 + (x+1)^2 C_1^2 + C_1^2 + C_1^2 = 1$$

$$C_1 = \frac{1}{\sqrt{(x-1)^2 + 2}}$$

$$\text{when } x \text{ is } -2; C_1 = \frac{1}{\sqrt{3}}, C_3 = \frac{1}{\sqrt{3}} \text{ and } C_2 = \frac{1}{\sqrt{3}}$$

cation radical anion

$$\psi_1^2 \psi_2^0 \psi_3^0$$

$$\psi_1^2 \psi_2^1 \psi_3^0$$

$$\psi_1^2 \psi_2^1 \psi_3^1$$

For anion, excitation $\psi_1^2 \psi_2^2 \psi_3^1$

How can you distinguish g.s. and exc st. by e' spin resonance since the same unpelied e' s are present they do not distinguishable by e' spin res- because they will have the same intensity and magnetic moment. However, if e' density is carried out, it will be distinguish.

Electron density for cation

$$q_1 = 2\left(\frac{1}{\sqrt{3}}\right)^2 + 0\left(\frac{1}{\sqrt{6}}\right)^2 + 0\left(\frac{1}{\sqrt{6}}\right)^2 = \frac{2}{3}\Sigma_1 = +\frac{1}{3}$$

$$q_2 = 2\left(\frac{1}{\sqrt{3}}\right)^2 + 0\left(-\frac{2}{\sqrt{6}}\right)^2 + 0\left(-\frac{2}{\sqrt{6}}\right)^2 + 0\left(-\frac{2}{\sqrt{6}}\right)^2 = \frac{2}{3}\Sigma_1 = +\frac{1}{3}$$

$$q_3 = 2\left(\frac{1}{\sqrt{3}}\right)^2 + 0\left(-\frac{1}{\sqrt{6}}\right)^2 + 0\left(-\frac{2}{\sqrt{6}}\right)^2 + 0\left(-\frac{1}{\sqrt{6}}\right)^2 = \frac{2}{3}\Sigma_1 = +\frac{1}{3}$$

$$p_{12} = 2\left(\frac{1}{\sqrt{3}}\right)\left(\frac{1}{\sqrt{3}}\right) + 0\left(\frac{1}{\sqrt{6}}\right) + 0\left(-\frac{2}{\sqrt{6}}\right)\left(-\frac{2}{\sqrt{6}}\right) + 0\left(\frac{1}{\sqrt{6}}\right)\left(-\frac{2}{\sqrt{6}}\right) = \frac{2}{3}$$

$$p_{23} = 2\left(\frac{1}{\sqrt{3}}\right)\left(\frac{1}{\sqrt{3}}\right) + 0\left(-\frac{2}{\sqrt{6}}\right)\left(\frac{1}{\sqrt{6}}\right) + 0\left(-\frac{2}{\sqrt{6}}\right)\left(\frac{1}{\sqrt{6}}\right) = \frac{2}{3}$$

$$p_{13} = 2\left(\frac{1}{\sqrt{3}}\right)\left(\frac{1}{\sqrt{3}}\right) + 0\left(\frac{1}{\sqrt{6}}\right)\left(\frac{1}{\sqrt{6}}\right) + 0\left(\frac{1}{\sqrt{6}}\right)\left(\frac{1}{\sqrt{6}}\right) = \frac{2}{3}$$

For radical exc. State is $\psi_1^1 \psi_2^1 \psi_3^1$

For anion exc. State is $\psi_1^1 \psi_2^2 \psi_3^1$

Electron density for radical g.s. Σ_1

$$q_1 = 2\left(\frac{1}{\sqrt{3}}\right)^2 + \left(\frac{1}{\sqrt{6}}\right)^2 + 0\left(\frac{1}{\sqrt{6}}\right)^2 = \frac{5}{6} + \frac{1}{6}$$

$$q_2 = 2\left(\frac{1}{\sqrt{3}}\right)^2 + 1\left(-\frac{2}{\sqrt{6}}\right)^2 + 0\left(-\frac{2}{\sqrt{6}}\right)^2 = \frac{4}{3} - \frac{1}{3}$$

$$q_3 = 2\left(\frac{1}{\sqrt{3}}\right)^2 + 1\left(\frac{1}{\sqrt{6}}\right)^2 + 0\left(\frac{1}{\sqrt{6}}\right)^2 = \frac{5}{6}$$

$$p_{12} = 2\left(\frac{1}{\sqrt{3}}\right)\left(\frac{1}{\sqrt{3}}\right) + 1\left(-\frac{2}{\sqrt{6}}\right)\left(-\frac{2}{\sqrt{6}}\right) + 0\left(\frac{1}{\sqrt{6}}\right)\left(-\frac{2}{\sqrt{6}}\right) = \frac{1}{3}$$

$$p_{23} = 2\left(\frac{1}{\sqrt{3}}\right)\left(\frac{1}{\sqrt{3}}\right) + 1\left(-\frac{2}{\sqrt{6}}\right)\left(\frac{1}{\sqrt{6}}\right) + 0\left(-\frac{2}{\sqrt{6}}\right)\left(\frac{1}{\sqrt{6}}\right) = \frac{1}{3}$$

$$p_{13} = 2\left(\frac{1}{\sqrt{3}}\right)\left(\frac{1}{\sqrt{3}}\right) + 1\left(\frac{1}{\sqrt{6}}\right)\left(\frac{1}{\sqrt{6}}\right) + 0\left(\frac{1}{\sqrt{6}}\right)\left(\frac{1}{\sqrt{6}}\right) = \frac{5}{6}$$

B. O. for anion

$$p_{12} = 2\left(\frac{1}{\sqrt{3}}\right)\left(\frac{1}{\sqrt{3}}\right) + 1\left(\frac{2}{\sqrt{6}}\right)\left(-\frac{1}{\sqrt{6}}\right) - \frac{2}{\sqrt{6}} + 1\left(\frac{1}{\sqrt{6}}\right)\left(-\frac{2}{\sqrt{6}}\right) = 0.0$$

$$p_{23} = 2\left(\frac{1}{\sqrt{3}}\right)\left(\frac{1}{\sqrt{3}}\right) + 1\left(-\frac{2}{\sqrt{6}}\right)\left(\frac{1}{\sqrt{6}}\right) + 1\left(-\frac{2}{\sqrt{6}}\right)\left(\frac{1}{\sqrt{6}}\right) = 0.0$$

$$p_{13} = 2\left(\frac{1}{\sqrt{3}}\right)\left(\frac{1}{\sqrt{3}}\right) + 1\left(\frac{1}{\sqrt{6}}\right)\left(\frac{1}{\sqrt{6}}\right) + 1\left(\frac{1}{\sqrt{6}}\right)\left(\frac{1}{\sqrt{6}}\right) = 1.0$$

B. L. = A - D B. O. \therefore If B. O. = 0.0, B. L. = A

A is often 1.517 i.e. $BL(A^0) = 1.517 - 0.18 \times B. O.$

For 4 atoms

$$\begin{pmatrix} x & 1 & 0 & 0 \\ 1 & x & 1 & 0 \\ 0 & 1 & x & 1 \\ 0 & 0 & 1 & x \end{pmatrix} \begin{pmatrix} C_1 \\ C_2 \\ C_3 \\ C_4 \end{pmatrix} = 0$$

$$\begin{pmatrix} x & 1 & 0 & 0 \\ 1 & x & 1 & 0 \\ 0 & 1 & x & 1 \\ 0 & 0 & 1 & x \end{pmatrix} = x \begin{vmatrix} x & 1 & 0 \\ 1 & x & 1 \\ 0 & 1 & x \end{vmatrix} - 1 \begin{vmatrix} 1 & 1 & 0 \\ 0 & x & 1 \\ 0 & 1 & x \end{vmatrix} + 0 \begin{vmatrix} 1 & 1 & 0 \\ 0 & x & 1 \\ 0 & 1 & x \end{vmatrix} + 0 \begin{vmatrix} 1 & 1 & 0 \\ 0 & x & 1 \\ 0 & 1 & x \end{vmatrix} = 0$$

$$= x \{x(x^2 - 1) - 1(x - 0)\} - 1 \{1(x^2 - 1) - 1(0 - 0)\} = 0$$

$$= x \{x^3 - x\}$$

$$= x^4 - x^2 - x^2 - x^2 + 1 = 0$$

$$= x^4 - 3x^2 + 1 = 0$$

$$= x^4 - 3x^2 + 1 = 0$$

$$\text{let } y = \pm x^2$$

$$y^2 - 3y + 1 = 0$$

$$y = \pm \frac{(-b \pm \sqrt{b^2 - 4ac})}{2a}$$

$$= \frac{3 \pm \sqrt{9-4}}{2a} = \frac{-3 \pm \sqrt{5}}{2}$$

$$y = x^2 = \frac{3 \pm \sqrt{5}}{2} \text{ or } \frac{3 - \sqrt{5}}{2}$$

$$x = \pm \sqrt{\frac{3 \pm \sqrt{5}}{2}} \text{ or } x = \pm \sqrt{\frac{3 - \sqrt{5}}{2}}$$

$$x = \pm 1.618 \text{ or } x = \pm 0.618$$

$$\frac{\alpha - 1.618 \beta}{1 - 1.6185}$$

$$\frac{\alpha - 0.618 \beta}{1 - 0.6185}$$

$$\frac{\alpha + 0.618 \beta}{1 + 0.6185}$$

$$\frac{\alpha + 1.618 \beta}{1 + 1.6185}$$

$$G.S. \psi_1^2 \psi_2^2 \psi_3^0 \psi_4^0$$

Possibilities of excitation are:

$$\psi_1^2 \psi_2^1 \psi_3^0 \psi_4^1 \quad \psi_1^2 \psi_2^1 \psi_3^1 \psi_4^0 \quad \psi_1^1 \psi_2^2 \psi_3^1 \psi_4^0 \quad \psi_1^1 \psi_2^2 \psi_3^0 \psi_4^1$$

For 2 transition Energy

$$E_3 - E_2 = \alpha - 0.618\beta - \alpha - 0.618\beta = -1.236\beta \text{ But}$$

$$\beta = -2.3e$$

$$\text{So } E_3 - E_2 = -1.236 \times -2.3eV = +$$

(+ve E = absorption; -ve is emission)

$$E_3 - E_2 = h\nu = \frac{hc}{\lambda} \quad \therefore \lambda \text{ can be determined}$$

$$\alpha = -5.0 \text{ eV}$$

$$\beta = -2.3eV \quad \text{Rb } 1 \text{ eV} = 1.6 \times 10^{19} \text{ J}$$

For weighing coefficients

$$xC_1 + C_2 = 0$$

$$C_1 + xC_2 + C_3 = 0$$

$$C_2 + xC_3 + C_4 = 0$$

(4) is not used to determine because $C_4 = \frac{-3}{x}$ and if $x = 0$,

$$C_4 = \phi$$

$$\text{From (1) } C_2 = -xC_1$$

$$\text{From (2) } C_3 = -(C_1 + x^2C_1) = -C_1(1 + x^2) = C_1(x^2 - 1)$$

$$\begin{aligned} \text{From (3) } C_4 &= -(C_2 + xC_3) = -(-xC_1 + x(C_1(x^2 - 1))) \\ &= xC_1 - xC_1(x^2 - 1) \end{aligned}$$

$$= C_1(x - x(x^2 - 1))$$

$$= C_1(x - x^3 + x) = (2x - x^3) C_1$$

$$C_1 = \frac{1}{(1+x^2+(x^2-1)^2+(2x-x^3)^2)} = 1$$

	x	C_1	C_2	C_3	C_4	
ψ_4	1.618	+0.3718	-0.6015	-0.6015	-0.3718	
ψ_3	+0.618	+0.6015	-0.3718	-0.3718	+0.6015	
ψ_2	-0.618	+0.6015	+0.3718	-0.3718	-0.6015	$\uparrow\downarrow$
ψ_1	-1.618	+0.3718	+0.6015	+0.6015	+0.3718	$\uparrow\downarrow$
						$\psi_1^2 \psi_2^1 \psi_3^0 \psi_4^0$

But practically

$$\begin{pmatrix} x & 1 & 0 & 1 \\ 1 & x & 1 & 0 \\ 0 & 1 & x & 1 \\ 1 & 0 & 1 & x \end{pmatrix} \begin{pmatrix} C_1 \\ C_2 \\ C_3 \\ C_4 \end{pmatrix} = 0$$

A new matrix develops

$$\begin{pmatrix} x & 1 & 0 & 1 \\ 1 & x & 1 & 0 \\ 0 & 1 & x & 1 \\ 1 & 0 & 1 & x \end{pmatrix} \begin{pmatrix} C_1 \\ C_2 \\ C_3 \\ C_4 \end{pmatrix} = 0 \quad x \begin{vmatrix} x & 1 & 0 \\ 1 & x & 1 \\ 0 & 1 & x \end{vmatrix} - 1 \begin{vmatrix} 1 & 1 & 0 \\ 0 & x & 1 \\ 1 & 1 & x \end{vmatrix} + 0 \begin{vmatrix} x & 1 & 1 \\ 0 & 1 & x \\ 1 & 0 & 1 \end{vmatrix} - 1 \begin{vmatrix} x & 1 & 1 \\ 0 & 1 & x \\ 1 & 0 & 1 \end{vmatrix} = 0$$

$$x(x^2 - 1) - 1(x - 0) + \{1(x^2 - 1) - 1(0 - 1)\}$$

$$- 1\{1 - 0 - x(0 - x) + (0 - 1)\}$$

$$x^4 - x^2 - x^2 - x^2 + 1 - 1 - 1 - x^2 + 1$$

$$x^4 - 4x^2 = 0$$

$$\text{Let } y = x^2$$

$$y^2 - 4y = y(y - 4) = 0$$

$$y = x^2 = 0 \Rightarrow x = 0, 0$$

$$y = x^2 = 4 \Rightarrow x = \pm 2$$

$$\begin{array}{lll}
 +2, & \frac{\alpha - 2\beta}{1 - 2S} & \psi_4 \\
 0, & \alpha & \psi_2, \psi_3 \\
 -2, & \frac{\alpha - 2\beta}{1 - 2S} & \psi_1
 \end{array}$$

$$\psi_1^2 \psi_2^1 \psi_3^1 \psi_4^0$$

$$\Delta E_{\pi_{res}} = 2(\alpha + 2\beta) + 2\alpha - \text{the equivalent in ethane} = 2(\alpha + 2\beta) + 2\alpha - 2(\alpha + \beta) - 2\alpha$$

More stable than butadiene because of limitation in theory being used. Butadiene because of strain relief should be more stable

Rb - n - nuclear repulsion is not considered only n - e interact

$$x C_1 + C_2 + C_4 = 0 \quad (i)$$

$$C_1 + x C_2 + C_3 = 0 \quad (ii)$$

$$C_2 + x C_3 + C_4 = 0 \quad (iii)$$

$$C_1 + C_3 + x C_4 = 0 \quad (iv)$$

$$\text{Rewrite (i)} \quad 2C_2 = -x C_1 ;$$

$$C_1^2 + C_2^2 + C_3^2 + C_4^2 = 1$$

$$2C_1^2 + 2C_2^2 = 1$$

$$\text{note } C_2 = -\frac{x C_1}{2}$$

$$\therefore C_1^2 \left[2 \left(1 + \frac{x^2}{4} \right) \right] = 1$$

Multiply by 4

$$C_1 = \frac{1}{\sqrt{\frac{4+x^2}{2}}}$$

x	C_1	C_2	C_3	C_3
$+2$	$\frac{-1}{2}$	$\frac{1}{2}$	$\frac{-1}{2}$	$\frac{-1}{2}$
$0,0$	$\frac{1}{2}$	0	$\frac{1}{2}$	0
-2	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$

$$q_1 = 2\left(\frac{1}{2}\right)^2 + 1\left(\frac{1}{2}\right)^2 + 1\left(\frac{1}{2}\right)^2 + 0\left(\frac{1}{2}\right)^2 = \frac{3}{2} \quad -\frac{1}{2}$$

$$q_2 = 2\left(\frac{1}{2}\right)^2 + 1(0)^2 + 1(0)^2 + 0\left(-\frac{1}{2}\right)^2 = \frac{1}{2} \quad +\frac{1}{2}$$

$$q_3 = 2\left(\frac{1}{2}\right)^2 + 1\left(\frac{1}{2}\right)^2 + 1\left(\frac{1}{2}\right)^2 + 0\left(\frac{1}{2}\right)^2 = \frac{3}{2} \quad -\frac{1}{2}$$

$$q_4 = 2\left(\frac{1}{2}\right)^2 + 1(0)^2 + 1(0)^2 + 0\left(\frac{1}{2}\right)^2 = \frac{1}{2} \quad +\frac{1}{2}$$

$$P_{12} = 2\left(\frac{1}{2}\right)^2 + 1\left(\frac{1}{\sqrt{2}}\right)(0) + 1\left(\frac{1}{2}\right)(0) + 0\left(\frac{1}{\sqrt{2}}\right)\left(-\frac{1}{\sqrt{2}}\right) = \left(\frac{1}{\sqrt{2}}\right)$$

$$P_{23} = 2\left(\frac{1}{2}\right)^2 + (1(0)\left(\frac{1}{2}\right) \times 2 + 0\left(-\frac{1}{\sqrt{2}}\right)\left(\frac{1}{\sqrt{2}}\right)) = \left(\frac{1}{\sqrt{2}}\right)$$

$$P_{34} = 2\left(\frac{1}{2}\right)^2 + 1\left(\frac{1}{\sqrt{2}}\right)0 + 1\left(\frac{1}{2}\right)0 + 0\frac{1}{\sqrt{2}}\left(-\frac{1}{\sqrt{2}}\right) = \left(\frac{1}{\sqrt{2}}\right)$$

$$P_{14} = 2\left(\frac{1}{2}\right)^2 + 1(0)\left(\frac{1}{2}\right) \times 2 + 0\left(-\frac{1}{\sqrt{2}}\right)\frac{1}{\sqrt{2}} = \frac{1}{\sqrt{2}}$$

$$\begin{pmatrix} x & 1 & 0 & 1 \\ 1 & x & 1 & 1 \\ 0 & 1 & x & 1 \\ 0 & 1 & 1 & x \end{pmatrix} \begin{pmatrix} C_1 \\ C_2 \\ C_3 \\ C_4 \end{pmatrix}$$

Frontier Electron hypothesis states that for a given molecule, the terminal atomic orbital will determine the stereochemistry of the molecule

Homo of butadiene is

ψ_4

ψ_3

ψ_2 $\uparrow\downarrow$

ψ_1 $\uparrow\downarrow$

Suppose we excite to ψ_3

ψ_3 \downarrow

ψ_2 $\uparrow\downarrow$

ψ_1 \uparrow

Cyclo propene

$$\psi_3 = \frac{1}{2} \phi_1 - \frac{\sqrt{2}}{2} \phi_2 + \frac{1}{2} \phi_3$$

$$\psi_2 = \frac{1}{2} \phi_1 - \frac{1}{\sqrt{2}} \phi_3$$

$$\psi_1 = \frac{1}{2} \phi_1 - \frac{\sqrt{2}}{2} \phi_2 + \frac{1}{2} \phi_3$$

$$\psi_3 = Ae^{kx} + Be^{-kx} \text{ (note } \alpha = k \text{ ; } k = \frac{2\pi}{\lambda} \text{)}$$

$$k\hbar = \sqrt{2m(E - v)} \quad \text{but } v = 0$$

$$\alpha\hbar = \sqrt{2m(E - v)} \quad (\text{note } \hbar = \frac{h}{2\pi})$$

$$\therefore \alpha\hbar = \sqrt{2\mu\mu}$$

$$\alpha = \frac{2\pi}{h} \sqrt{2\mu\mu}$$

For B; $v \neq 0$

$$\therefore B = \frac{2\pi}{h} \sqrt{2\mu\mu_1 - V_r}$$

PERTURBATION THEORY

Exact solution of Schrödinger's equation is possible for only a very small proportion of the problems of interest in the physical sciences. Great importance therefore attaches to approximate methods of solution and among these methods perturbation theory, which is also extensively used in classical mechanics, occupies a very important place. The technique can be applied where the Hamiltonian can be written as a sum of two parts, a simple part which if present alone would generate a soluble Schrodinger equation, and a second part consisting of one or more relatively small additional terms. The approximate behaviour of the system can then be obtained by considering the soluble part as giving the dominant behaviour and treating the actual behaviour as a relatively minor deviation, or *perturbation*, from this calculable behaviour. The perturbation can be estimated by studying the small, complicating additional terms in the second part of the Hamiltonian.

The analysis of time-independent and time-dependent perturbations is different and we treat only the former type of problem here.

Time-independent perturbation theory

We have a Hamiltonian operator of the form:

$$\hat{H} = \hat{H}(0) + \hat{H}_- \quad (1)$$

where the energy associated with $\hat{H}(0)$ is large compared with that derived from \hat{H}_- .

In order to facilitate the algebra we write Equation (1) in the form:

$$\hat{H} = \hat{H}(0) + \lambda \hat{H}_- \quad (2)$$

λ is an arbitrary parameter, which we use to keep track of the order of the perturbation,

i.e. the degree to which our approximate Hamiltonian ($\hat{H}(0) + \lambda \hat{H}_-$) approaches the true Hamiltonian (\hat{H}).

Once it has performed its labelling duty λ is simply set equal to 1.

We seek eigenfunctions $|\psi_k\rangle$ and energies E_k which satisfy the Schrödinger equation:

$$\hat{H}|\psi_k\rangle = (\hat{H}(0) + \lambda \hat{H}_-)|\psi_k\rangle = E_k|\psi_k\rangle \quad (3)$$

In addition to the assumption concerning the relative magnitudes of the energies associated

with $\hat{H}(0)$ and \hat{H}_- we also assume the following:

i) \hat{H} does not depend explicitly on the time.