

# Quant mech Chem: T2 T1, Yr 2.

Postulates: a stipulation, assumption, a fundamental principle

(1)

State State of the system is fully described by a mathematical  $\Psi$

Probability that a particle will be found between  $x$  and  $x+dx$

$$|\Psi(x)|^2 = \Psi(x)\Psi^*(x) dx \rightarrow \text{real}$$

→ always non-negative

Born interpretation  $\Rightarrow$  probabilistic interpretation of  $\Psi$

2) assuming that the  $\Psi$  is normalized

$$\int_{-\infty}^{\infty} \Psi(x)\Psi^*(x) dx = \langle \Psi | \Psi \rangle = 1$$

↳ i.e. probability of finding the particle somewhere along dir-x = 1

$\langle \cdot \rangle \Rightarrow$  bracket "braket" notation  
introduced by Paul Dirac.

~~if~~  $\Psi$  has no physical meaning. ~~then~~ It may, at any given pt in space, be +ve/-ve, R or C

†††

Operators & Hamiltonian,

(2)

Observable: measurable property, such as bond length, dipole moment, KE

Every observable  $B$  is represented by an operator.

↳ all operators can be built from the operators for position ( $\hat{x}$ ) and momentum ( $\hat{p}$ )

e.g. Operator for position in the  $x$  direction  $\Rightarrow \hat{B} = \hat{x}$

$$\text{momentum in the } x \text{ direction } \Rightarrow \hat{p}_x = \hat{p}_x = -i\hbar \frac{\partial}{\partial x}$$

$$\hat{H} = \hat{T} + \hat{V}$$

(1) Ham. operator

$$\hat{T} = \frac{1}{2}mv^2 = \frac{\hat{p}^2}{2m}$$

$$\hat{p}_x^2 = \frac{\hat{p}_x^2}{2m}$$

$$= -\frac{\hbar^2}{2m} \frac{d^2}{dx^2}$$

The role of the operator is to "operate" on a wave function

to yield information associated w/ the observable that the operator represents

## Eigenvalue eq<sup>n</sup>

2.

- eq<sup>n</sup> has a general form:

somewhat similar to Matrices:

$$\hat{B}f = bf$$

operator      function

operator acts on a function, stays the same  
function is invariant upon action of an operator

just like  $Ax = \lambda x$

eg:

$$\hat{B} = \frac{d}{dx}$$

$$f = e^{\alpha x}$$

$$\hat{B}f = \alpha e^{\alpha x}$$

eigenfunction  
Eigenvalue

like eigenvectors:  $Ax = \lambda x$

if vector  $x$  is invariant upon

linear transformation by  $AA$ , w/  $\lambda$  as the eigenvalue, which is the value of which the vector scales i.e. scaling factor of the eigenvector

## Strong Schrödinger Eq<sup>n</sup>

if  $\psi$  is an eigenfunction of  $\hat{A}$

$$\hat{A}\psi(x) = E\psi(x)$$

$$\hat{H} = \hat{T} + \hat{V}$$

$$= -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \psi(x) + V(x)\psi(x)$$

$E$ : Energy of the system  $\Rightarrow$  eigenvalue of the

There may be more than one wavefunction which are eigenfunctions of  $\hat{A}$

$\Rightarrow$  Any non-degenerate solutions [sol<sup>n</sup> of diff. energy] are orthogonal

$$\int_{-\infty}^{\infty} \psi_j(x) \psi_k^*(x) dx = \langle \psi_j | \psi_k \rangle = 0$$

有  $\langle \psi_j | \psi_k \rangle = 0 \Rightarrow$  orthogonal

Two wavefunctions are orthogonal if:

$$\langle \psi_j | \psi_k \rangle = \delta_{jk} \quad j \neq k \Rightarrow 0 \quad (\text{orthogonal}) \Rightarrow \langle \psi_j | \psi_k \rangle = 0$$

$$= \delta_{jk} \left\{ \begin{array}{l} j \neq k \Rightarrow 0 \\ j = k \Rightarrow 1 \end{array} \right. \quad (\text{normalised}) \Rightarrow \langle \psi_j | \psi_j \rangle = 1$$

Expectation values:

$\langle B \rangle =$  expectation value of an operator  $\hat{B}$  of a wavefunction

if  $\psi$  is an exact  $\hat{H}$  wavefunction, it is also an eigenfunction of  $\hat{B}$ , such that  $\hat{B}\psi = b\psi$

$$\langle B \rangle = \int \frac{\psi^* \hat{B} \psi dx}{\psi^* \psi dx} = \frac{\langle \psi | \hat{B} | \psi \rangle}{\langle \psi | \psi \rangle}$$

$$\langle B \rangle = \langle \psi | \hat{B} | \psi \rangle = \int_{-\infty}^{+\infty} \psi^* b \psi dx = \int_{-\infty}^{+\infty} \psi^* \psi dx = b$$

when we attempt to measure the value of observable  $B$

$\Leftarrow$  if  $\psi$  is normalized to 1, simplifies to

$\Leftarrow$  A series of identical expt. will all yield  $b \rightarrow$  single value

$$\langle B \rangle = \langle \psi | \hat{B} | \psi \rangle = \int_{-\infty}^{+\infty} \psi^* \hat{B} \psi dx$$

$\Leftarrow$   $\psi$  is an exact wavefunction and an eigenfunction of  $\hat{B}$

3

(3) When a system is described by a wavefunction  $\Psi$ .

$\Rightarrow$  avg value of the observable  $B$  in a series of measurements

$\#$  is equal to the expectation value of the corresponding operator  $\hat{B}$  i.e.  $\langle B \rangle$

$\Rightarrow$  When  $\Psi$  is an eigenfunction of  $\hat{B}$ , determination of  $B$  always yield one result, b

$\Rightarrow$  x when  $\Psi$  is NOT an eigenfunction of  $\hat{B}$ ,  $\hat{B}$  has multiple eigenvalues of  $B$

$\hookrightarrow$   $\Psi$  is a linear combination of eigenfunctions of  $\hat{B}$   $\Rightarrow \langle B \rangle$

Leading to the variation principle

- for the computational treatment of many-e<sup>-</sup> atoms & molecules

- foundation for the approximate methods for determining molecular orbitals

for many-e<sup>-</sup> systems

$\Rightarrow$  exact  $\Psi$  are not known

$\hookrightarrow$  employ an approximate wavefunction,  $\Psi_{\text{trial}}$ , which is not exact

$$\hat{H}\Psi_{\text{trial}} \neq E\Psi_{\text{trial}}$$

if we were to measure the energy of the hypothetical system, described by  $\Psi_{\text{trial}}$

$\hookrightarrow$  identical experiments would give same answer, but will give any one of the eigenvalues

$\Rightarrow$  expectation value of  $\hat{H}$

$$\langle H \rangle = E_{\text{trial}} = \int \Psi_{\text{trial}}^* \hat{H} \Psi_{\text{trial}} dt$$

Best trial wavefunction minimises  $\langle E \rangle$

$$\hookrightarrow \frac{\partial \langle E \rangle}{\partial c_i} = \frac{\partial \langle E \rangle}{\partial c_2} = 0$$

# The Harmonic Oscillator

- occurs when a system experiences a restoring force  $\propto (F) \propto$  displacement from Eq<sup>M</sup>

e.g. Pendulum / vibrating springs

$$F = -kx$$

$$F = -kx = -\frac{dV}{dx}$$

$$\frac{dV}{dx} = -F$$

$$\int dV = \int F dx$$

$$dV = \int kx$$

$$V_{(n)} = \frac{kx^2}{2} + C$$

$$\text{when } x=0, V(n)=0$$

$$\hookrightarrow V_{(n)} = \frac{kx^2}{2} \Rightarrow \hat{V} = \frac{kx^2}{2}$$

Hamiltonian

$$\hat{H} = \hat{T} + \hat{V} = \hat{T} = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + \frac{kx^2}{2}$$

Schrödinger Eq<sup>M</sup>

$$\hat{E} = \hat{T} + \hat{V}$$

$$\hat{H} \Psi(n) = E \Psi$$

$$\hat{H} \Psi(n) = \left( -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + \frac{kx^2}{2} \right) \Psi(n)$$

finding a sol<sup>n</sup> beginning w/ an ansatz:

$$\Psi = A e^{-an^2}$$

$$\hookrightarrow \frac{d\Psi}{dx} = -2anAe^{-an^2}$$

$$\frac{d^2\Psi}{dx^2} = (-2a + 4a^2n^2)Ae^{-an^2}$$

$$\text{S.E. } \hat{H}\Psi = \left( -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} (-2a + 4a^2n^2) + \frac{kx^2}{2} \right) \Psi(n)$$

$$\hookrightarrow E = -\frac{\hbar^2}{2m}(-2a + 4a^2n^2) + \frac{kx^2}{2} = \frac{\hbar^2a}{m} - \underbrace{\frac{\hbar^2}{2m}4a^2n^2 + \frac{kx^2}{2}}_{=0}$$

$E$  is constant only if  $E$  is independent of  $x$

→ we want  $x$  to cancel out

$$\hookrightarrow \frac{\hbar^2}{2m} - \frac{2\hbar^2a^2x^2}{m} - \frac{kx^2}{2}$$

~~a<sup>2</sup>~~

$$a^2 = \frac{kx^2 m}{2(2)\hbar^2}$$

$$a = \frac{\sqrt{m}}{2m\hbar}$$

$\Psi = A e^{-an^2}$  is the exact wave function

$\Psi = A e^{-an^2}$  ⇒ first in series which satisfies S.E. for th. H.O.

2) general formula:

$$\Psi_n = H_n(x) e^{-ax^2}$$

H<sub>n</sub>: Hermite polynomial

$$H_0(x) = 1$$

$$H_1(x) = x$$

$$H_2(x) = (4ax^2 - 1)$$

# Wavefunctions for the harmonic oscillator

$\Psi$

$$\Psi_0 = A_0 e^{-\alpha x^2}$$

$$\Psi_1 = A_1 x e^{-\alpha x^2}$$

$$\Psi_2 = A_2 (1 - \alpha x^2) e^{-\alpha x^2}$$

$$\Psi_v = A_v H_v(n) e^{-\alpha x^2}$$

Energy

$$E_0 = \frac{\hbar \omega}{2}$$

$$E_1 = \frac{3\hbar \omega}{2}$$

$$E_2 = \frac{5\hbar \omega}{2}$$

$$E_v = \left(v + \frac{1}{2}\right)\hbar \omega$$

$v$  = a quantum number

→ corresponds to

$$x^v \rightarrow v$$

- Eigenvalue of ground state  $E_0 \neq 0$

[zero-pt energy]

- Energy spacing  $\Rightarrow \Delta E = \hbar \omega$

e.g. for force constants,  $k \uparrow \uparrow$ ,  $\omega \uparrow \uparrow$ ,  $\Delta E \uparrow \uparrow$

or mult.  $\Delta E \uparrow \uparrow$

- Max expansion:

when  $E_{n=1} = V$

$$\frac{1}{2}kx_{\max}^2 = E = V = \left(v + \frac{1}{2}\right)\hbar \sqrt{\frac{k}{m}}$$

↳ end edges of the potential well

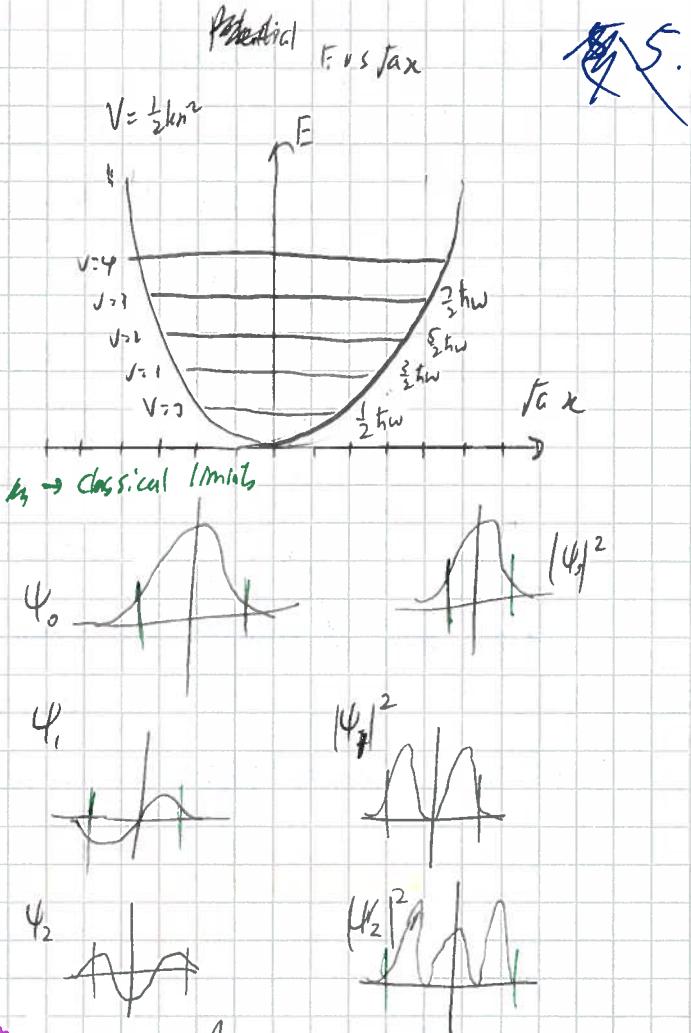
correspond to  $x_{\max}$ , the classical limit

→ quantum tunnelling regions of -ve KE

-  $v \uparrow \uparrow$  →  $|\Psi_v|^2$  increasing peaks towards

the edge of the well

i.e. classical limit



As you go up,

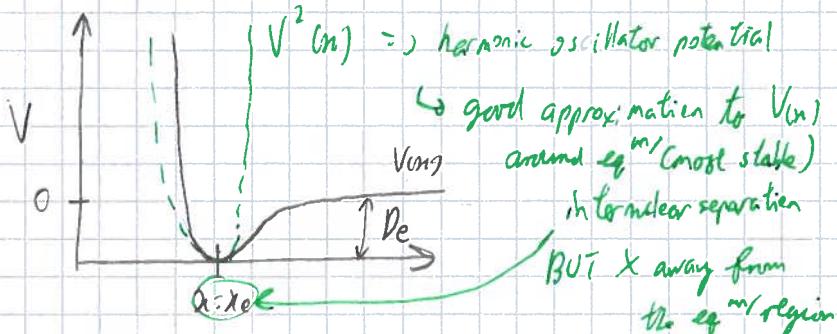
the  $\Psi$  that goes beyond  
the classical limit

## 6

### Application to spectroscopy

potential between 2 atoms  $\Rightarrow$  in a diatomic molecule

$\Rightarrow$  represented by  $V(r)$  against  $r$



$\rightarrow$  not most accurate for ground state energy ( $V=0$ )  
or  
zero-point energy

$\rightarrow$  Morse potential  $\Rightarrow$  treating diatomic molecules more realistically

$$V(n) = hcD_e \left(1 - e^{-\alpha(x-n_e)}\right)^2$$

$\alpha = \sqrt{\frac{k}{2hcD_e}}$

De: depth of the minimum of the potential curve  
[dissociation energy of bond, ignoring vibrational energy]

L.S.E.

$$E_v = \left(v + \frac{1}{2}\right)\hbar\omega - \left(v + \frac{1}{2}\right)^2 \hbar\omega \chi_e \quad v = 0, 1, 2, 3, \dots$$

$$\omega = \sqrt{\frac{k}{\mu}} \quad \chi_e = \frac{\alpha^2 h}{2\mu\omega} \Rightarrow \text{anharmonicity constant}$$

$$\mu = \frac{m_A m_B}{m_A + m_B}$$

- reduces energy from H.O. value  
 $\hookrightarrow$  PT important as  $v$  becomes large

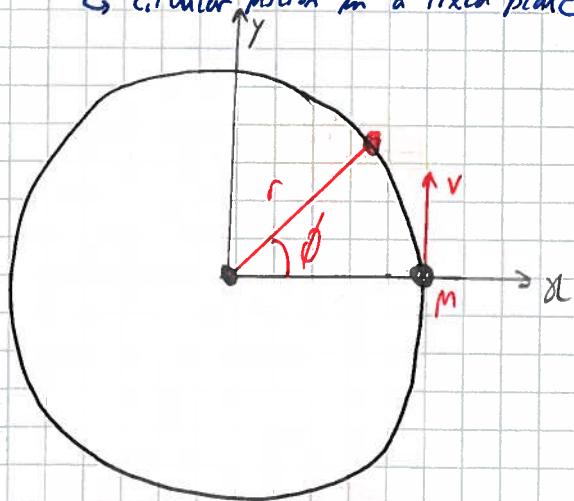
$\hookrightarrow$  vibrational energy  $\hbar\omega$  separation  $\times$  constant  
for H.O.

$\rightarrow$  converge as  $v$  gets larger

$\rightarrow$  molecule dissociates as  $v \rightarrow \infty$

# Particle on a ring

↳ circular motion in a fixed plane



-constant velocity

$$\hookrightarrow (\hat{v} = 0)$$

$$\hookrightarrow \hat{H} = \hat{T} + \hat{V}$$

$$= -\frac{\hbar^2}{2m} \nabla^2$$

$$= -\frac{\hbar^2}{2m} \left( \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} \right)$$

using polar coordinates  $r(x,y) \Rightarrow r(\theta, \phi)$

$$x = r \cos \phi$$

$$y = r \sin \phi$$

$$\frac{\partial x}{\partial r} = \cos \phi \quad \frac{\partial y}{\partial r} = \sin \phi$$

$$\frac{\partial x}{\partial \phi} = -r \sin \phi \quad \frac{\partial y}{\partial \phi} = r \cos \phi$$

$\Rightarrow$  using chain rule

$$\frac{\partial}{\partial r} = \cos \phi \frac{\partial}{\partial x} + \sin \phi \frac{\partial}{\partial y} \quad (1)$$

$$\frac{\partial}{\partial \phi} = -r \sin \phi \frac{\partial}{\partial x} + r \cos \phi \frac{\partial}{\partial y} \quad (2)$$

Isolating  $\frac{\partial}{\partial n}$ :

(1)  $\times r \cos \phi$ :

$$\cos \phi \frac{\partial}{\partial r} = r \cos^2 \phi \frac{\partial}{\partial x} + r \cos \phi \sin \phi \frac{\partial}{\partial y} \quad (3)$$

(2)  $\times \sin \phi$ :

$$\sin \phi \frac{\partial}{\partial \phi} = -r \sin^2 \phi \frac{\partial}{\partial x} + r \sin \phi \cos \phi \frac{\partial}{\partial y} \quad (4)$$

(3) - (4)

$$r \cos \phi \frac{\partial}{\partial r} - \sin \phi \frac{\partial}{\partial \phi} = r \cos^2 \phi \frac{\partial}{\partial x} + r \sin^2 \phi \frac{\partial}{\partial y} \\ = r \frac{\partial}{\partial x}$$

$$\Rightarrow \frac{\partial}{\partial x} = \cos \phi \frac{\partial}{\partial r} - \frac{\sin \phi}{r} \frac{\partial}{\partial \phi}$$

Isolating  $y$

(1)  $\times r \sin \phi$ :

$$r \sin \phi \frac{\partial}{\partial r} = r \sin \phi \cos \phi \frac{\partial}{\partial x} + r \sin^2 \phi \frac{\partial}{\partial y} \quad (5)$$

(2)  $\times \cos \phi$ :

$$\cos \phi \frac{\partial}{\partial \phi} = -r \sin \phi \cos \phi \frac{\partial}{\partial x} + r \cos^2 \phi \frac{\partial}{\partial y} \quad (6)$$

(1) + (2) =

$$r \sin \phi \frac{\partial}{\partial r} + \cos \phi \frac{\partial}{\partial \phi} = r \frac{\partial}{\partial y}$$

$$\frac{\partial}{\partial y} = \sin \frac{\partial}{\partial r} + \frac{\cos \phi}{r} \frac{\partial}{\partial \phi}$$

$$\Rightarrow \left( \frac{\partial}{\partial r} \right)^2 + \left( \frac{\partial}{\partial \phi} \right)^2 = \cos^2 \phi \frac{\partial^2}{\partial r^2} + 2 \cos \phi \frac{\partial}{\partial r} \frac{\sin \phi}{r} \frac{\partial}{\partial \phi} + \sin^2 \phi \frac{\partial^2}{\partial \phi^2} \\ = \frac{\partial^2}{\partial r^2} + \frac{\partial^2}{\partial \phi^2}$$

$$\left( \frac{\partial}{\partial r} \right)^2 = \left( \cos \phi \frac{\partial}{\partial r} - \frac{\sin \phi}{r} \frac{\partial}{\partial \phi} \right)^2 \left( \cos \phi \frac{\partial}{\partial r} + \frac{\sin \phi}{r} \frac{\partial}{\partial \phi} \right) \\ = \cos^2 \phi \frac{\partial^2}{\partial r^2} - \frac{\sin^2 \phi}{r^2} \frac{\partial^2}{\partial \phi^2} = \frac{\sin^2 \phi}{r^2} \frac{\partial^2}{\partial r^2} + \frac{\cos^2 \phi}{r^2} \frac{\partial^2}{\partial \phi^2}$$

$$\left( \frac{\partial}{\partial \phi} \right)^2 = \left( \sin \phi \frac{\partial}{\partial r} + \frac{\cos \phi}{r} \frac{\partial}{\partial \phi} \right)^2 \left( \sin \phi \frac{\partial}{\partial r} - \frac{\cos \phi}{r} \frac{\partial}{\partial \phi} \right) \\ = \frac{\sin^2 \phi}{r^2} \frac{\partial^2}{\partial r^2} + \frac{\sin^2 \phi}{r^2} \frac{\partial^2}{\partial \phi^2} + \frac{\cos^2 \phi}{r^2} \frac{\partial^2}{\partial r^2} - \frac{\cos^2 \phi}{r^2} \frac{\partial^2}{\partial \phi^2}$$

$$\left(\frac{\partial}{\partial r}\right)^2 = \left(\cos\phi \frac{\partial}{\partial r} - \frac{\sin\phi}{r} \frac{\partial}{\partial \phi}\right)^2 \left(\cos\phi \frac{\partial}{\partial r} - \frac{\sin\phi}{r} \frac{\partial}{\partial \phi}\right)$$

$$= \cos^2\phi \frac{\partial^2}{\partial r^2} - \frac{\sin^2\phi}{r^2} \left(\cos\phi \frac{\partial}{\partial r}\right) - \cos\phi \frac{\partial}{\partial r} \left(\frac{\sin\phi}{r} \frac{\partial}{\partial \phi}\right) + \sin^2\phi \frac{\partial^2}{\partial \phi^2}$$

$$= \cos^2\phi \frac{\partial^2}{\partial r^2} - \frac{\sin^2\phi}{r} \left(-\frac{\sin\phi}{r} \frac{\partial}{\partial r} + \frac{\cos\phi}{r} \frac{\partial^2}{\partial \phi^2}\right) - \sin\phi \cos\phi \left(-\frac{\sin\phi}{r^2} \frac{\partial}{\partial \phi} + \frac{\sin\phi}{r} \frac{\partial^2}{\partial \phi^2}\right) + \sin^2\phi \frac{\partial^2}{\partial \phi^2}$$

$$\left(\frac{\partial}{\partial \phi}\right)^2 = \left(\sin\phi \frac{\partial}{\partial r} + \frac{\cos\phi}{r} \frac{\partial}{\partial \phi}\right) \left(\sin\phi \frac{\partial}{\partial r} + \frac{\cos\phi}{r} \frac{\partial}{\partial \phi}\right)$$

$$= \sin^2\phi \frac{\partial^2}{\partial r^2} + \cos^2\phi \frac{\partial^2}{\partial \phi^2} + \frac{\cos\phi}{r} \frac{\partial}{\partial \phi} \left(\sin\phi \frac{\partial}{\partial r}\right) + \sin\phi \frac{\partial}{\partial r} \left(\frac{\cos\phi}{r} \frac{\partial}{\partial \phi}\right)$$

$$= \sin^2\phi \frac{\partial^2}{\partial r^2} + \frac{\cos^2\phi}{r^2} \frac{\partial^2}{\partial \phi^2} + \frac{\cos\phi}{r} \left(\frac{\cos\phi}{r} \frac{\partial}{\partial r} + \frac{\sin\phi}{r} \frac{\partial^2}{\partial \phi^2}\right)$$

$$\left(\frac{\partial}{\partial x}\right)^2 + \left(\frac{\partial}{\partial y}\right)^2 = \frac{\partial^2}{\partial r^2} + \frac{1}{r} \frac{\partial}{\partial r} + \frac{1}{r^2} \frac{\partial^2}{\partial \phi^2}$$

( $\frac{\partial^2}{\partial \phi^2}$  is not prop expand dim.)

$$\nabla^2 = \frac{\partial^2}{\partial r^2} + \frac{1}{r} \frac{\partial}{\partial r} + \frac{1}{r^2} \frac{\partial^2}{\partial \phi^2}$$

$r$  is constant

$$\hat{H} = -\frac{\hbar^2}{2m} \nabla^2$$

$$= -\frac{\hbar^2}{2mr^2} \frac{\partial^2}{\partial \phi^2}$$

Moment of Inertia,  $I$

$$I = mr^2$$

$$\Rightarrow \hat{H} = -\frac{\hbar^2}{2I} \frac{\partial^2}{\partial \phi^2}$$

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

$$-\frac{\hbar^2}{2I} \frac{\partial^2 \Psi}{\partial \phi^2} = E \Psi$$

$$\Psi = N e^{\pm im_2 \phi} = N (\cos(m_2 \phi) \pm i \sin(m_2 \phi))$$

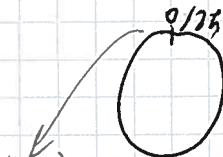
$$\Psi' = \pm N \pm i m_2 N e^{\pm im_2 \phi}$$

$$\Psi'' = -m_2^2 N e^{\pm im_2 \phi}$$

$$E = \frac{\hbar^2 m_2^2}{2I}$$

( $m_2$  is a constant, a quantum number)

Boundary conditions



$$\Psi(\phi + 2\pi) = \Psi(\phi) \Rightarrow \text{has to go to}$$

$$- \cos m_2 \phi = \cos(m_2 \phi + m_2 2\pi) \quad \text{zero at end of the box}$$

$$- \sin m_2 \phi = \sin(m_2 \phi + m_2 2\pi)$$

↳ for imaginary part = 0

$$\begin{aligned} \sin m_2 \phi &= 0 \\ m_2 \phi &= n\pi \end{aligned} \quad \Rightarrow \quad m_2 = 0 \text{ or an integer}$$

$$\Psi(\phi) = N e^{\pm im_2 \phi} \quad (m_2 = 0, \pm 1, \pm 2, \pm 3, \dots)$$

$\rightarrow$  antidiagonal around the ring  
 $\pm m_2 \quad \begin{cases} + \rightarrow \text{anticlockwise} \\ - \rightarrow \text{clockwise} \end{cases} \text{ around the ring}$  But still no diff.

Normalization constants:

$$\int_0^{2\pi} \Psi^*(\phi) \Psi(\phi) d\phi = 1$$

$$\int_0^{2\pi} d\phi = \frac{1}{N^2}$$

$$\Psi(\phi) = \frac{1}{\sqrt{2\pi}} e^{\pm im_2 \phi}$$

$$N = \frac{1}{\sqrt{2\pi}} \quad \therefore m_2 = 0, \pm 1, \pm 2, \pm 3, \dots$$

$$E = \frac{\hbar^2 m_2^2}{2I}$$

For linear momentum

$$\hat{p}_x = -i\hbar \frac{\partial}{\partial x}$$

$$\frac{\hat{p}_x^2}{2m} = \frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2}$$

Rewriting the Hamiltonian

$$\hat{H} = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial p^2}$$

$$\hat{H} = -\frac{\hbar^2}{2I} \frac{\partial^2}{\partial \phi^2} = \frac{\hat{L}_z^2}{2I}$$

$$\Rightarrow \hat{L}_z = -i\hbar \frac{\partial}{\partial \phi}$$

Eigenvalue for the  $\Psi$

$$\begin{aligned}\hat{L}_z \Psi(r) &= i\hbar \frac{\partial}{\partial \phi} (Nr^{im\phi}) \\ &= (-i\hbar)(\pm im) N e^{-im\phi} \\ &= \pm m_2 \hbar \Psi(\theta)\end{aligned}$$

$$\hat{L}_z \Psi(\theta) = \pm m_2 \hbar \Psi(\theta)$$

-  $\hat{L}_z$  component of angular momentum of a particle

moving @ constant velocity in a circle [by  $L_z = \pm m_2 \hbar$ ]

↳ can only have values which are multiples of  $\hbar$

↳ angular momentum is quantized

Particle on a sphere

9.

from MM III

$$\Rightarrow E = -\frac{\hbar^2}{2m} \nabla^2$$

$$= -\frac{\hbar^2}{2m} \left( \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right)$$

$$\begin{aligned}= -\frac{\hbar^2}{2m} \left[ \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \right) + \right. \\ \left. + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right]\end{aligned}$$

∴  $r$  is constant

$$E = -\frac{\hbar^2}{2mr^2} \left[ \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right]$$

$$= -\frac{\hbar^2}{2m} \left[ \frac{1}{r^2} \left( \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right) \right]$$

$\Delta^2$  (Legendrian)

$$\Rightarrow -\frac{\hbar^2}{2I} \Delta^2 \Psi(\theta, \phi) = E \Psi(\theta, \phi)$$

{ MM AD E stuff }

$$\Psi(\theta, \phi) = \Theta(\theta) \Phi(\phi)$$

⇒ which is spherical harmonics

$$Y_{l,m_l}(\theta, \phi) = \Theta(\theta) \cdot \Phi(\phi)$$

for  $\Phi$ :

$$\Phi(\phi) = N e^{\pm im_2 \phi} \quad m_2 = 0, \pm 1, \pm 2, \dots$$

for  $\Theta(\theta)$ : → depend on  $2\theta m$

Allowed values of  $2\theta m$  are:

$$m_2 = -2, -2+1, -2+2, \dots, 2-2, 2-1, 2$$

More on spherical harmonics :

$$\hookrightarrow \nabla^2 Y_{l,m_l} = -2(l+1) Y_{l,m_l}(\theta, \phi)$$

$\Rightarrow$  Subbing into ~~TF TISE~~ for particle on a sphere

$$\hat{H}\Psi(\theta, \phi) = -\frac{\hbar^2}{2m} \nabla^2 Y_{l,m_l}(\theta, \phi)$$

$$= E_{l,m_l} Y_{l,m_l}(\theta, \phi) = E_{l,m_l} \Psi(\theta, \phi)$$

$$\Rightarrow E_{l,m_l} = \frac{\hbar^2}{2m} l(l+1), \quad l=0, 1, 2, 3, 4, \dots$$

- energy independent of  $m_l$

$\hookrightarrow$  for every value of  $l$ , there are

$(2l+1)$  states which are degenerate

First 9 spherical harmonics:

$l$	$m_l$	$Y_{l,m_l}(\theta, \phi)$	Real?
①	0	constant	✓
③	1	$\cos\theta$	✓
③	+1	$\sin\theta e^{i\phi}$	✗
④	-1	$\sin\theta e^{-i\phi}$	✗
2	0	$3\cos^2\theta - 1$	✓
2	+1	$\cos\theta \sin\theta e^{i\phi}$	✗
2	-1	$\cos\theta \sin\theta e^{-i\phi}$	✗
2	+2	$\sin^2\theta e^{2i\phi}$	✗
2	-2	$\sin^2\theta e^{-2i\phi}$	✗



for degenerate wavefunctions VS

$\Rightarrow$  any linear combination of them will give the same energy

e.g. for  $Y_{2,+2}$   $\underbrace{Y_{2,+2}}$ ,  $\underbrace{Y_{2,-2}}$

$$\Rightarrow A+B = 2\sin\theta\cos\phi = \text{Re}(A+B) = Y_{2,0} \quad ] \text{ Same energy}$$

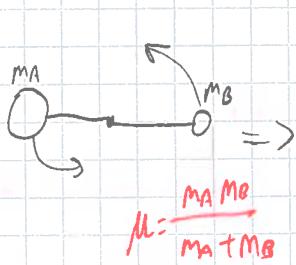
$$\Rightarrow A-B = 2i\sin\theta\sin\phi = \text{Im}(A-B) = Y_{2,1} \quad ] \text{ as origin}$$

angular dependence is either real or imaginary

Rigid rotor - rotation of diatomic molecule

[for rotational spectroscopy]

- using spherical harmonics



$$\mu = \frac{m_A m_B}{m_A + m_B}$$

Energies:

$$E = \frac{\hbar^2}{2I} J(J+1)$$

$\Rightarrow$  using  $J=J$  in rotational spectroscopy:

$\Rightarrow$  allowed rotational energies

for a diatomic molecule:

$$E = \frac{\hbar^2}{2I} J(J+1) \quad \text{where } J=0, 1, 2, 3, \dots$$

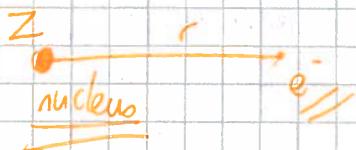
$$\text{where } I = \mu r^2$$

# The hydrogen atom:

consider to the general case

→ can be extended to  $\text{He}^+$  &  $\text{Li}^{2+}$

$$V(r) = -\frac{Z e^2}{4\pi \epsilon_0 r} \quad (\text{Coulomb's law})$$



using atomic units! (why?)

$$e = 1$$

$$m_e = 1$$

$$\hbar = 1$$

$$4\pi \epsilon_0 = 1$$

$$a_0 = 1 \quad [5.2918 \times 10^{-10} \text{ m}] \\ (\text{half an Angstrom})$$

=> atomic units of P.S. operator

$$\hat{V}(r) = -\frac{Z}{r}$$

$$\hat{H} = -\frac{1}{2} \left[ \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right) + \frac{1}{r^2 m_e \hbar^2} \right. \\ \left. + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right] - \frac{Z}{r} \quad \Psi = R \Theta \Phi$$

↓ Proof is left to the reader  
as an exercise

Solution:  $R_{n,l}(r) = L_{n,l}(r) (r^2) e^{-Zr/a_0}$

$$l = 1, 2, 3, \dots$$

Laguerre polynomials

→  $r$  is in atomic units

- Exponential decay of  $\Psi$ :  $e^{-Zr/a_0}$

$$a_0 = \frac{4\pi \epsilon_0 \hbar^2}{m_e e^2}$$

$$E = -Z^2 \frac{m_e e^4}{32 n^2 \pi^2 \epsilon_0^2 \hbar^2} = -\frac{Z^2}{2n^2} (E_h)$$

★ energy depends on quantum number  $n$

↳ true only for Hydrogen, or any other atom in w/ only one  $e^-$

$$\alpha = Z/a_0$$

$$\Psi(r, \theta, \phi) = R_{n,l}(r) Y_{l,m_l}(\theta, \phi)$$

$$E = -\frac{Z^2}{2n^2} (E_h)$$

- See 3.5 video for sol'n & graphs

11

# Hamiltonian for a Helium atom

using atomic units:

$$\hat{H} = \hat{T} + \hat{V} = -\frac{\nabla^2}{2} - \frac{Z}{r} \text{ for Hydrogen}$$

## Adapting for He atom

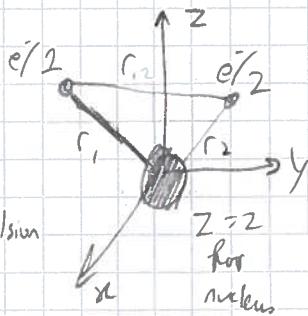
$$\hat{H} = -\frac{1}{2}\hat{\nabla}_1^2 - \frac{1}{2}\hat{\nabla}_2^2 - \frac{2}{r_1} - \frac{2}{r_2} + \frac{1}{r_{12}}$$

KE of  
e<sup>-</sup>s

nucleus

e<sup>-</sup> attraction

e<sup>-</sup> repulsion



$$\hat{\nabla}_i^2 = \frac{\partial^2}{\partial r_i^2} + \frac{\partial^2}{\partial \theta_i^2} + \frac{\partial^2}{\partial \phi_i^2} \text{ for each } e^-/i$$

本来有  
幾隻？

1. Assuming the repulsion between 2 e<sup>-</sup>s can be mathematically, if somehow absorbed into

un effective potential  $\Rightarrow$  How?

2. Assuming the e<sup>-</sup>s move independently of one another

$\hookrightarrow$  we can assign each e<sup>-</sup> its own hydrogenic wavefunction,  $\Psi_{1s}(1)$  &  $\Psi_{2s}(2)$

[one e<sup>-</sup> or orbital approximation]

To fix approximations  $\hookrightarrow$  you approximation

$\Rightarrow$  fit parameters to experimental data

$\hookrightarrow$  hope that fits the absorbing effect to some extent.

$\Rightarrow$  Computational  $\Rightarrow$  self-consistent field (starting at)

Matrix?

iterating  $\Rightarrow$  each e<sup>-</sup> "feels" other average effect of other e<sup>-</sup>s in their molecular orbitals

$\rightarrow$  getting the best possible atom? and orbitals

## Electron spin and

### the Pauli Exclusion principle

**Remember:**

2 component of the orbital angular momentum is restricted to be  $L_z = \pm m_l \hbar$

$\hookrightarrow$  ie. Component of the spin angular momentum in the z-direction

$$\Rightarrow S_z = \pm m_s \hbar$$

$\rightarrow m_s$  can only take  $+\frac{1}{2}$  or  $-\frac{1}{2}$   $\alpha$  or  $\beta$

Pauli Exclusion Principle states:

No e<sup>-</sup>s in an atom may have the same set of quantum numbers,  $n, l, m_l, m_s$

$\hookrightarrow$  why this, math & consider the effect of interchanging the two e<sup>-</sup>s  $\Psi(1,2) \Rightarrow \Psi(2,1)$

$\hookrightarrow$  e<sup>-</sup>s are indistinguishable  $\Rightarrow$  why is it a problem?

$\hookrightarrow$  cannot affect the physical properties of the system

$\hookrightarrow |\Psi|\Psi|$  must remain unchanged

$\hookrightarrow \Psi(1,2)\Psi(2,1)$  or  $\Psi(1,2) = -\Psi(2,1)$  [which is the correct restriction]

More fundamental statement  $\hookrightarrow$  why two

$\Rightarrow$  Total wavefunction of a system must change sign when any two e<sup>-</sup>s are interchanged

$\Rightarrow$  Total wavefunction is antisymmetric

if  $\Psi(1,2) = \Psi(2,1)$  both are zero

$$\therefore \Psi(1,2) = \Psi(2,1) : 0$$

$\Rightarrow$  only way will be

$$\Rightarrow \Psi(1,2) = -\Psi(2,1)$$

$\therefore$  total wave function should be antisymmetric

# Ground state of the helium atom

$$\Rightarrow \alpha = \beta = 1 \quad \beta \Rightarrow \downarrow$$

spin possibilities:

$$\alpha(1)\alpha(2) \quad \checkmark \quad \beta(1)\beta(2) \quad \checkmark$$

$$\cancel{\alpha(1)\beta(2)} \quad \cancel{\alpha(2)\beta(1)}$$

~~•~~ electrons are indistinguishable

$\Rightarrow$  we cannot say for sure

$e^-/1$  has  $\alpha$  spin

and

$e^-/2$  has  $\beta$  spin & vice versa

~~•~~ when  $e^-/s$  have opposite spins

↳ there must be equal probabilities of

$$\alpha(1)\beta(2) \& \alpha(2)\beta(1)$$

$\Rightarrow$  taking linear arrangements - combination of these spin arrangements

$$-\alpha(1)\beta(2) + \alpha(2)\beta(1)$$

and

$$-\alpha(1)\beta(2) - \alpha(2)\beta(1)$$

for Helium atom:

$$\Psi(1,2) = \psi_{1s}(1)\psi_{2s}(2)$$

Now combining spatial  $\Psi$  with spin wavefunctions

$$① \Psi(1,2) = \psi_{1s}(1)\psi_{1s}(2)\alpha(1)\beta(2)$$

$$② \Psi(1,2) = \psi_{1s}(1)\psi_{1s}(2)\beta(1)\alpha(2)$$

$$③ \Psi(1,2) = \psi_{1s}(1)\psi_{1s}(2)(\alpha(1)\beta(2) + \alpha(2)\beta(1))$$

$$④ \Psi(1,2) = \psi_{1s}(1)\psi_{1s}(2)(\alpha(1)\beta(2) - \alpha(2)\beta(1))$$

Which satisfies the Pauli Exclusion Principle?

Upon interchanging of 2  $e^-/s$

$\rightarrow$  spatial  $\Psi$  is symmetric

$\rightarrow$  spin  $\Psi$  is antisymmetric,  $\therefore$  only ④

$$\Rightarrow \Psi(1,2) = \psi_{1s}(1)\psi_{1s}(2) \frac{1}{\sqrt{2}}(\alpha(1)\beta(2) - \alpha(2)\beta(1))$$

$\Psi(1,2)$  in determinant form:

$$\Psi(1,2) = \frac{1}{\sqrt{2}} \begin{vmatrix} \psi_{1s}(1)\alpha(1) & \psi_{1s}(1)\alpha(1) \\ \psi_{1s}(2)\alpha(2) & \psi_{1s}(2)\beta(2) \end{vmatrix}$$

$$= \frac{1}{\sqrt{2}} (\psi_{1s}(1)\alpha(1)\psi_{1s}(2)\beta(2) - \psi_{1s}(1)\beta(1)\psi_{1s}(2)\alpha(2))$$

$$- \psi_{1s}(1)\beta(1)\psi_{1s}(2)\alpha(2)]$$

$\Rightarrow$  Slater's determinant

$\rightarrow$  each term has a hydrogenic spatial orbital

multiplied by a spin function

$\rightarrow$  spin orbitals

## Excited states of the helium atom

$\rightarrow$  promoting an  $e^-/1$  from the  $1s$  orbital

to the  $2s$  one  $\Rightarrow (1s^1 2s^1)$

$\rightarrow$  excited spatial wavefunction

$$\Psi_{\text{spatial}}(1s, 2s) = \psi_{1s}(1)\psi_{2s}(2)$$

$\rightarrow$  satisfactory spatial wavefunctions:

$$\Psi^S(1s, 2s) = \frac{1}{\sqrt{2}}(\psi_{1s}(1)\psi_{2s}(2) + \psi_{1s}(2)\psi_{2s}(1)) - \cancel{\Psi^A} \quad (A)$$

$$\text{or} \quad \frac{1}{\sqrt{2}}(\psi_{1s}(1)\psi_{2s}(2) - \psi_{1s}(2)\psi_{2s}(1)) - \cancel{\Psi^S} \quad (B)$$

$\rightarrow$  combining w/ the antisymmetric spin wavefunction

$\rightarrow$  to satisfy the Pauli principle:

$$A \cancel{\Psi^A} \Rightarrow \Psi(1s, 2s) = \frac{1}{\sqrt{2}}(\psi_{1s}(1)\psi_{2s}(2) + \psi_{1s}(2)\psi_{2s}(1))$$

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

$\Rightarrow$  which is a singlet state

[there is only one contributing wavefunction]

13

Using (B), which is antisymmetric

to satisfy the P.Ex.Principle.

We can use (D), (O) symmetric spin wavefunctions

$$\textcircled{B} \quad 1 \quad \Psi_{(1s2s)} = \frac{1}{\sqrt{2}} [\psi_{1s}(1)\psi_{2s}(2) - \psi_{1s}(2)\psi_{2s}(1)] [\alpha(1)\alpha(2)]$$

$$\textcircled{B} \quad 2 \quad = \frac{1}{\sqrt{2}} [\psi_{1s}(1)\psi_{2s}(2) - \psi_{1s}(2)\psi_{2s}(1)] [\beta(1)\beta(2)]$$

$$\textcircled{B} \quad 3 \quad = \frac{1}{\sqrt{2}} [\psi_{1s}(1)\psi_{2s}(2) - \psi_{1s}(2)\psi_{2s}(1)] [\alpha(1)\beta(2) + \alpha(2)\beta(1)]$$

$\Rightarrow$  triplet state [ contributing 3 wavefunctions ]

- There's a difference in energy between the

singlet & triplet states of  $2K$

$\rightarrow$  Triplet state is more stable

: exchange integral  $K > 0$

[ Hund's rule of maximum multiplicity ]

for normalised wavefunctions:

$$E = \langle \Psi_{(1s2s)} | \hat{H} | \Psi_{(1s2s)} \rangle$$

Singlet state:

$$E^{\text{sing}} = \frac{1}{2} \langle \psi_{1s}(1)\psi_{2s}(2) + \psi_{1s}(2)\psi_{2s}(1) | \hat{H}_1 + \hat{H}_2 + \frac{1}{r_{12}} |$$

$$\psi_{1s}(1)\psi_{2s}(2) + \psi_{1s}(2)\psi_{2s}(1) \rangle$$

$$E^{\text{sing}} = \frac{1}{2} \left[ \langle \psi_{1s}(1)\psi_{2s}(2) | \hat{H}_1 + \hat{H}_2 | \psi_{1s}(1)\psi_{2s}(2) \rangle - \textcircled{1} \right. \\ \left. + \langle \psi_{1s}(2)\psi_{2s}(1) | \hat{H}_1 + \hat{H}_2 | \psi_{1s}(2)\psi_{2s}(1) \rangle - \textcircled{2} \right] \\ + \frac{1}{2} \left[ \langle \psi_{1s}(1)\psi_{2s}(1) | \frac{1}{r_{12}} | \psi_{1s}(1)\psi_{2s}(2) \rangle \right. \\ \left. + \langle \psi_{1s}(2)\psi_{2s}(1) | \frac{1}{r_{12}} | \psi_{1s}(2)\psi_{2s}(1) \rangle \right] \text{JK}$$

Considering first terms:  $\textcircled{1}$

$$\langle \psi_{1s}(1)\psi_{2s}(2) | \hat{H}_1 | \psi_{1s}(1)\psi_{2s}(2) \rangle$$

$$+ \langle \psi_{1s}(1)\psi_{2s}(2) | \hat{H}_2 | \psi_{1s}(1)\psi_{2s}(2) \rangle$$

$$= \langle \psi_{1s}(1)\psi_{2s}(2) | E_{1s} \psi_{1s}(1)\psi_{2s}(2) \rangle$$

$$+ \langle \psi_{1s}(1)\psi_{2s}(2) | E_{2s} \psi_{1s}(1)\psi_{2s}(2) \rangle = E_{1s} + E_{2s}$$

$$\therefore \langle \psi_{1s}(1) | \psi_{1s}(1) \rangle = 1$$

$\hat{H}_1$  only acts on  $e/\ell 1$

Considering 2nd term:  $\textcircled{2}$

$$\langle \psi_{1s}(2)\psi_{2s}(1) | \hat{H}_1 | \psi_{1s}(1)\psi_{2s}(2) \rangle$$

$$+ \langle \psi_{1s}(2)\psi_{2s}(1) | \hat{H}_2 | \psi_{1s}(1)\psi_{2s}(2) \rangle$$

$$= \langle \psi_{1s}(2)\psi_{2s}(1) | E_{1s} \psi_{1s}(1)\psi_{2s}(2) \rangle$$

$$+ \langle \psi_{1s}(2)\psi_{2s}(1) | E_{2s} \psi_{1s}(1)\psi_{2s}(2) \rangle = 0 + 0 = 0$$

$$\therefore \langle \psi_{1s}(1) | \psi_{2s}(1) \rangle = 0$$

$\hat{H}_1$  only acts on  $e/\ell 1$

$$\hookrightarrow E^{\text{sing}} = E_{1s} + E_{2s} + J + K$$

Labels 1 & 2 refer to the  $e/\ell$ 's  
 $\rightarrow r_1$ : radial coordinate of  $e/\ell 1$   
 $r_{12}$ : distance between 2  $e/\ell$ 's

for singlet spatial wavefunction

$$\Psi_{(1s2s)} = \frac{1}{\sqrt{2}} [\psi_{1s}(1)\psi_{2s}(2) + \psi_{1s}(2)\psi_{2s}(1)]$$

for triplet spatial wavefunction

$$\Psi_{(1s2s)} = \frac{1}{\sqrt{2}} [\psi_{1s}(1)\psi_{2s}(2) - \psi_{1s}(2)\psi_{2s}(1)]$$

for triplet state:

$$\begin{aligned} E^{\text{trip}} &= \langle \Psi(1s, 2s) | \hat{H} | \Psi(1s, 2s) \rangle \\ &= \frac{1}{2} \left[ \langle \psi_{1s}(1) \psi_{2s}(2) - \psi_{1s}(2) \psi_{2s}(1) | \hat{H}_1 + \hat{H}_2 + \frac{1}{r_{12}} \right] \\ &\quad \left[ \psi_{1s}(1) \psi_{2s}(2) - \psi_{1s}(2) \psi_{2s}(1) \right] \\ &= \frac{1}{2} \left[ \langle \psi_{1s}(1) \psi_{2s}(2) | \hat{H}_1 + \hat{H}_2 | \psi_{1s}(1) \psi_{2s}(2) \rangle \right] \\ &\quad - \frac{1}{2} \left[ \langle \psi_{1s}(2) \psi_{2s}(1) | \hat{H}_1 + \hat{H}_2 | \psi_{1s}(2) \psi_{2s}(1) \rangle \right] \\ &\quad + \frac{1}{2} \left[ \langle \psi_{1s}(1) \psi_{2s}(2) | \frac{1}{r_{12}} | \psi_{1s}(1) \psi_{2s}(2) \rangle \right] \\ &\quad - \frac{1}{2} \left[ \langle \psi_{1s}(2) \psi_{2s}(1) | \frac{1}{r_{12}} | \psi_{1s}(2) \psi_{2s}(1) \rangle \right] \end{aligned}$$

Similarly  $\underline{E} = E_{1s} + E_{2s} + J - K$

$$E^{\text{trip}} = E_{1s} + E_{2s} + J - K$$

$$\therefore \text{Energy difference: } E^{\text{sing}} - \underline{E^{\text{trip}}} = 2K$$

J: Coulomb integral

K: Exchange integral  $K > 0$ , & hence the triplet state is more stable

(using Hund's rule of maximum multiplicity)

↳ ?

$$\langle \hat{A}_{ee} \rangle = \frac{e^2}{4\pi\epsilon_0} \langle \frac{1}{r_{12}} \rangle$$

$$\begin{aligned} E &= J \pm K \\ &\uparrow \\ &\text{Total (symm)} \end{aligned}$$

15

# Molecular Orbitals

## 5.1 Born Oppenheimer approximation (B.O. Approx)

can

- Why can the electronic motion be separated from the nuclear motion? (translations, rotations, vibrations)

- e/s are much more less massive than nuclei

↳ We can assume that the nuclei are fixed in space

~~B.O.~~ determine the energy of e/s for these fixed nuclear positions

⇒ Hence the B.O. Approx

which states: The total wavefunction for a molecule

can be approximated as:  $\Psi_{\text{mol}} = \Psi_{\text{nuc}} \Psi_{\text{elec}}$

where  $\Psi_{\text{elec}}$  can be determined by the following

electronic Hamiltonian [w/ comparison to that of an atom]

$$\hat{H} = -\sum_i \frac{\nabla_i^2}{2} - \sum_{i>j} \frac{2e^2}{r_{ij}} + \sum_{i>j} \frac{Z_i Z_j}{R_{ij}}$$

[No. of nuclei]   
 for nuclei,   
 - of electron   
 B.O. Approx KE

Coulombic attraction between e/s & nuclei   
 Coulombic repulsion between e/s   
 Coulombic repulsion between nuclei

- i & j refer to e/s

-  $\hat{H}$  is in atomic units

-  $k \propto 1/r$  refers to the nucleus

-  $r_{ik}$ : distance between

e/s & nucleus

w/ charge  $Z_k$

-  $R_{ij}$  ⇒ fixed nuclear distance



A Potential Energy surface can

be obtained

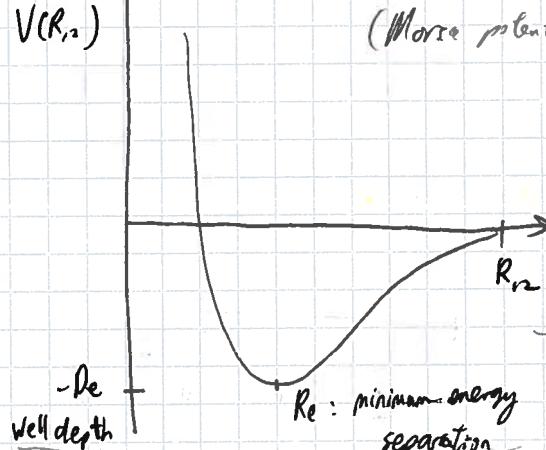
- By calculating over a range of nuclear geometries

- For a diatomic molecule,

P.E. surface depends only on  $R_{12} = R_{1,2}$

$$V(R_{12})$$

(Morse potential)



## 5.2 Linear Combination of Atomic Orbitals (LCAO)

For the ground state wavefunction,

we had:

$$\Psi(1,2) = \frac{1}{\sqrt{2}} \begin{vmatrix} \Psi_{1s}(1)\alpha(1) & \Psi_{1s}(1)\beta(1) \\ \Psi_{1s}(2)\alpha(2) & \Psi_{1s}(2)\beta(2) \end{vmatrix}$$

⇒ simplifying it - [leading diagonal is sufficient to define the det]

- [  $\frac{1}{\sqrt{2}}$  ] : n in just the number of electrons]

∴ We can write

$$\Psi(1,2) = \Psi_{1s}(1)\alpha(1)\Psi_{1s}(2)\beta(2)$$

∴ spins of e/s are implied by the det

$$\Rightarrow \Psi(1,2) = \Psi_{1s}(1)\Psi_{1s}(2)$$

- Same approach is taken when writing molecular wavefunctions

• electronic wavefunction for a molecule with  $n$ -electrons is written as a product of one electron wavefunctions [actually not a product wavefunction, but the leading diagonal of a Slater Det.]

$$\Psi = \Psi_1(1) \Psi_2(2) \Psi_3(3) \Psi_4(4) \dots \Psi_n(n)$$

→ Each molecular orbital  $\Psi_i$  as a linear combination of atomic orbitals  $\phi_k$

i.e.

$$\Psi_i = \sum_k c_{ik} \phi_k$$

expansion coefficients

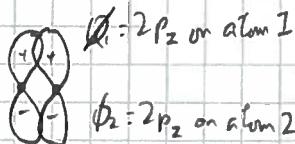
Basis set = set of atomic orbitals  $\phi_k$

• 有幾多  $\phi_k$ , 就有幾多  $\Psi_i$  molecular orbitals,  $\Psi_i$



$\phi_1$ : 1s on atom 1

$\phi_2$ : 2s on atom 2



$\phi_1$ :  $2p_z$  on atom 1

$\phi_2$ :  $2p_z$  on atom 2

• solve by computer

### 5.3 The secular Eq'y, 6.7

Consider a diatomic orbital using BO approach as well

$\phi_1$ ,  $\phi_2$ , separated at distance  $R$

$$\Psi_{\text{trial}} = c_1 \phi_1 + c_2 \phi_2$$

- Determining  $c_1$  &  $c_2$

$$\langle E \rangle = \frac{\langle \Psi_{\text{trial}} | \hat{H} | \Psi_{\text{trial}} \rangle}{\langle \Psi_{\text{trial}} | \Psi_{\text{trial}} \rangle}$$

Assuming the atomic orbitals are real:  $\hat{V}_e = V_e$

$$\Rightarrow \langle E \rangle = \frac{\int (c_1 \phi_1 + c_2 \phi_2) \hat{H} (c_1 \phi_1 + c_2 \phi_2) d\tau}{\int (c_1 \phi_1 + c_2 \phi_2) (c_1 \phi_1 + c_2 \phi_2) d\tau}$$

$$\rightarrow H_{11} = \int \phi_1 \hat{H} \phi_1 d\tau \quad \text{simplifying the relation} \quad S_{11} = \int \phi_1 \phi_1 d\tau$$

$$H_{22} = \int \phi_2 \hat{H} \phi_2 d\tau \quad \Rightarrow \quad S_{22} = \int \phi_2 \phi_2 d\tau$$

$$H_{12} = \int \phi_1 \hat{H} \phi_2 d\tau \quad S_{12} = \int \phi_1 \phi_2 d\tau$$

$$= \int \phi_2 \hat{H} \phi_1 d\tau \quad = \int \phi_2 \phi_1 d\tau$$

$$= H_{21} \quad = S_{21}$$

Coulomb integrals      Resonance integrals

$$\text{Hence: } \Rightarrow \langle E \rangle = \frac{c_1^2 H_{11} + c_2^2 H_{22} + 2c_1 c_2 H_{12}}{c_1^2 S_{11} + c_2^2 S_{22} + 2c_1 c_2 S_{12}}$$

Assuming  $S_{11}$  &  $S_{22}$  are normalized

i.e.  $S_{11} = S_{22} = 1$

$$\Rightarrow \langle E \rangle (c_1^2 + c_2^2 + 2c_1 c_2 S_{12}) = c_1^2 H_{11} + c_2^2 H_{22} + 2c_1 c_2 H_{12}$$

From variation principle

[Best trial wavefunction minimises  $\langle E \rangle$ ]

$$\text{i.e. } \frac{\partial \langle E \rangle}{\partial c_i} = \frac{\partial \langle E \rangle}{\partial c_1} = 0$$

$$\frac{\partial E}{\partial c_1} \propto \left[ \langle E \rangle (c_1^2 + c_2^2 + 2c_1 c_2 S_{12}) \right] / \left[ c_1^2 H_{11} c_2^2 H_{22} + 2c_1 c_2 H_{12} \right]$$

$$\frac{\partial E}{\partial c_1} (c_1^2 + c_2^2 + 2c_1 c_2 S_{12}) + \langle E \rangle (2c_1 + 2c_2 S_{12})$$

$$= 2c_1 H_{11} + 2c_2 H_{12} - 0$$

Similarly:

$$\frac{\partial E}{\partial c_2} (c_1^2 + c_2^2 + 2c_1 c_2 S_{12}) + \langle E \rangle (2c_2 + 2c_1 S_{12})$$

$$= 2c_2 H_{22} + 2c_1 H_{12} - 0$$

$$\therefore \frac{\partial c_1 \langle E \rangle}{\partial c_1} = \frac{\partial c_2 \langle E \rangle}{\partial c_2} = 0$$

$$\Rightarrow 0 = 0$$

$$0 = \frac{\partial E}{\partial c_1} = \frac{2c_1 H_{11} + 2c_2 H_{12} - \langle E \rangle (2c_1 + 2c_2 S_{12})}{(c_1^2 + c_2^2 + 2c_1 c_2 S_{12})}$$

$$0 = \frac{\partial E}{\partial c_2} = \frac{2c_2 H_{22} + 2c_1 H_{12} - \langle E \rangle (2c_2 + 2c_1 S_{12})}{(c_1^2 + c_2^2 + 2c_1 c_2 S_{12})}$$

$$\Rightarrow 2c_1 H_{11} + 2c_2 H_{22} - \langle E \rangle (2c_1 + 2c_2 S_{12})$$

$$2c_1 H_{12} + 2c_2 H_{12} = \langle E \rangle (2c_1 + 2c_2 S_{12})$$

$$0 = c_1 H_{11} + c_2 H_{22} - \langle E \rangle (c_1 + c_2 S_{12})$$

$$= c_1 H_{11} + c_2 H_{22} - \langle E \rangle (c_2 + c_1 S_{12})$$

$\langle E \rangle - E$  : This is the best energy we can determine using the variation principle

$$c_1 H_{11} + c_2 H_{22} = E_{c_1} + E_{c_2} S_{12}$$

$$\Rightarrow c_1 (H_{11} - E) + c_2 (H_{22} - E S_{12}) = 0 \quad (A)$$

$$\Rightarrow c_2 H_{22} + c_1 H_{12} = E c_2 + E c_1 S_{12}$$

$$c_2 (H_{22} - E) + c_1 (H_{12} - E S_{12}) = 0 \quad (B)$$

Secular Eqn

18

$$c_1 (H_{11} - E) + c_2 (H_{22} - E S_{12}) = 0$$

$$c_2 (H_{22} - E) + c_1 (H_{12} - E S_{12}) = 0$$

or

$$\begin{bmatrix} H_{11} - E & H_{12} - E S_{12} \\ H_{22} - E S_{12} & H_{22} - E \end{bmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = 0$$

→ non trivial sol'n when det

the secular determinant  $\neq 0$

$$\det[S] = 0$$

→ trivial sol'n when  $c_1$ ,  $c_2$  both equal zero.

5.4 Two orbital systems :

[identical orbitals]

→ considering the 2 identical orbitals on zero overlap  
different atoms/adjacent atoms

[e.g. homonuclear diatomics or  $\pi$  orbitals of ethene]

$\Rightarrow \phi_1, \phi_2$  are each  $2p_z$  orbitals  
on the carbon atoms]

-  $\phi_1, \phi_2$  are assumed real

$\Rightarrow$  replace the Coulomb integral & resonance integral by  $\alpha$  &  $\beta$  respectively

$$\int \phi_1 \hat{H}_1 \phi_1 = H_{11} = H_{22} = \alpha$$

$$\int \phi_1 \hat{H}_2 \phi_2 = H_{12} = H_{21} = \beta$$

- Assume zero overlap between  $\phi_1$  &  $\phi_2$

$\int \phi_1 \phi_2 dz = S_{12} S_{21} = 0$ ;  $S_{11} = S_{22} = 1$   $\because$  normalized  
Secular Eqn & determinant become:

$$\begin{bmatrix} \alpha - \beta & \beta \\ \beta & \alpha - \beta \end{bmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix}$$

$$\begin{vmatrix} \alpha - \beta & \beta \\ \beta & \alpha - \beta \end{vmatrix} = 0 \Rightarrow (\alpha - \beta)^2 - \beta^2 = 0$$

$$\beta = \alpha \pm \beta$$

Substituting Back into Scalar Eq<sup>b</sup>'s

$$\tilde{E}^2 \alpha + \beta:$$

$$\begin{pmatrix} -\beta & \beta \\ \beta & -\beta \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix}$$

$$\therefore -\beta c_1 + \beta c_2 = 0$$

$$\Rightarrow c_1 = c_2$$

$$\rightarrow \text{normalizing } c_1^2 + c_2^2 = 1$$

$$\Rightarrow c_1 = c_2 = \frac{1}{\sqrt{2}}$$

$$\therefore \text{for } E_T = \alpha + \beta$$

$$\Psi_T = \frac{1}{\sqrt{2}}(\phi_1 + \phi_2)$$

$\rightarrow$  bonding

for  $E_B$ :

$$E = \alpha - \beta$$

$$\begin{pmatrix} \alpha & \beta \\ \beta & \alpha \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix}$$

$$\beta c_1 + \alpha c_2 = 0$$

$$c_1 = -c_2$$

$$\rightarrow \text{normalizing: } c_1^2 + c_2^2 = 1$$

$$c_1 = \frac{1}{\sqrt{2}}, c_2 = -\frac{1}{\sqrt{2}}$$

$$\therefore \text{for } E_B = \alpha - \beta$$

$$\Psi_B = \frac{1}{\sqrt{2}}(\phi_1 - \phi_2)$$

$\rightarrow$  anti-bonding

Assuming  $S_{1,2} = 0$

i.e., no overlap

$$\alpha - \beta$$

$$\Psi_B = \frac{1}{\sqrt{2}}(\phi_1 - \phi_2) \quad (\text{no overlap})$$

$$\alpha + \beta$$

$$\Psi_T = \frac{1}{\sqrt{2}}(\phi_1 + \phi_2) \quad (\text{full overlap})$$

$\Psi$  bonding orbital is stabilised  
as much as

19

anti-bonding orbital is destabilised.

Coulomb integrals:  $\alpha$

In representing the e<sup>-</sup> would have in the molecule  
if it occupied either atomic orbital,  $\phi_1$  or  $\phi_2$

$\rightarrow$  of Coulomb attractions between

the e<sup>-</sup> & the second nucleus

$\rightarrow \alpha$  will be more negative than  
the energy an electron would have,  
if it occupied either  $\phi_1$  or  $\phi_2$

$\rightarrow$  resonance  $\pi$  integrals,  $\beta$

$\hookrightarrow$  associated w/ the energy of interaction  
between  $\phi_1$  &  $\phi_2$  in the molecule

$\rightarrow$  normally -ve,

$\rightarrow$  5 times smaller than  $\alpha$   
for adjacent identical orbitals

$\rightarrow$  as bond length  $\uparrow\uparrow$ ,

approximation for overlap more accurate,

$\hookrightarrow \beta \downarrow\downarrow$   $\because$  involved in overlap  
of exponentially decaying orbitals

## Identical orbitals & non-zero overlap

- a more realistic case,

$$\rightarrow \text{overlap between } \phi_1 \text{ & } \phi_2 \Rightarrow \int \phi_1 \phi_2 d\tau = S_{12} \\ \neq S_{21} \neq 0$$

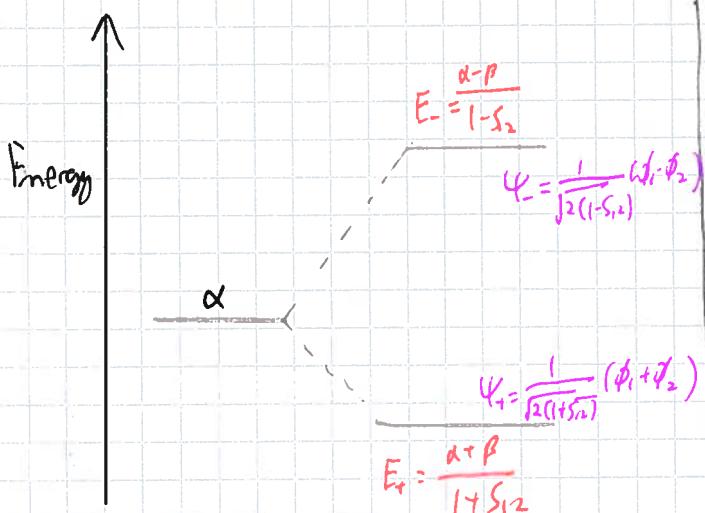
$$\Rightarrow \begin{pmatrix} \alpha - E & \beta - ES_{12} \\ \beta - ES_{21} & \alpha - E \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix}$$

$$\hookrightarrow \begin{vmatrix} \alpha - E & \beta - ES_{12} \\ \beta - ES_{21} & \alpha - E \end{vmatrix} = 0$$

$$\alpha^2 + E^2 - 2\alpha E - \beta^2 + 2\beta E S_{12} - E^2 S_{12}^2 = 0$$

$$\Rightarrow E^2(1 - S_{12}^2) + E(2\beta S_{12} - 2\alpha) + (\alpha^2 - \beta^2) = 0$$

hence giving energies & molecular orbitals:



\* Signs

- anti-bonding is destabilized by the more resonance integral  $S_{12}$

bonding orbital is stabilized

bonding orbital is less bonding than

antibonding orbital is antibonding

→ explaining why H<sub>2</sub> is not stable

∴ Both e<sup>-</sup>s in bonding & antibonding orbital

→ energy: 2E<sub>B</sub> & 2E<sub>A'</sub>

→ less stable than the isolated atoms

at all separations

## Different orbitals & zero overlap

20.

$$\phi_1 \text{ & } \phi_2$$

Re simplifying:

$$H_{11} = \int \phi_1 \phi_1 d\tau = \alpha_1$$

$$S_{11} = \int \phi_1 \phi_1 d\tau$$

$$= \int \phi_2 \phi_2 d\tau$$

= 1

$$H_{22} = \int \phi_2 \phi_2 d\tau = \alpha_2$$

$$S_{22} = S_{21}$$

$$= \int \phi_1 \phi_2 d\tau$$

$$= H_{12} = \beta$$

≈ 0

Scalar Eq's

$$\begin{pmatrix} \alpha_1 - E & \beta \\ \beta & \alpha_2 - E \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix}$$

| | (proof as Exercise)

⇒ Energies will be

$$E_{\pm} = \frac{1}{2}(\alpha_1 + \alpha_2) \pm \sqrt{\beta^2 + (\alpha_1 - \alpha_2)^2} \quad | \quad \delta = \frac{1}{2}(\alpha_1 - \alpha_2)$$

Considering  $\phi_1$  &  $\phi_2$  have different energies

⇒  $\alpha_1, \alpha_2$  will be different to one another

$$\Rightarrow \delta^2 \gg \beta^2$$

$$\Rightarrow E_I \approx \frac{1}{2}(\alpha_1 + \alpha_2) \pm \frac{1}{2}(\alpha_1 - \alpha_2)$$

$$\rightarrow E_I \approx \alpha_1$$

$$\rightarrow E_A \approx \alpha_2$$

i.e. ~~M.O.~~ Atom orbitals will mix strongly tgt,

to form M.O. only if  $|\alpha_1 - \alpha_2| \approx |\beta|$

→ if 2 A.O. have different energies ( $\alpha_1, \alpha_2$  v. diff.)

↳ they will not mix together strongly

∴ 2s & 2p orbitals of C, N, O all have similar energies to that of the 1s orbital of H,

∴ they mix well tgt if on adjacent atoms in a molecule



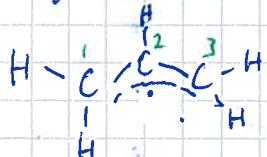
$\lambda$  e<sup>-</sup>s for an uncharged molecule  
w/  $n$  C atoms contributing to the  $\pi$  system  
↳ can be put in pairs in the MOs

$\Rightarrow$  total energy:  $| n_i: \text{occupation number of the } i^{\text{th}} \text{ MO} |$

$$E_{\text{tot}}^{\pi} = \sum_i n_i E_i \quad \begin{array}{l} \text{occupation number} \\ \text{of the } i^{\text{th}} \text{ MO} \\ \text{e<sup>-</sup>s in the} \\ \text{MO } n_i \end{array}$$

$$i = 1, 2, 3, \dots$$

Example: the allyl radical  $\text{CH}_2\text{CHCH}_2$



$\Rightarrow$  3  $2p$  orbitals, one on each carbon atom, contributing to the  $\pi$  MOs,  $\perp$  to molecular plane

$\Rightarrow$  3 atomic orbitals, 3  $\pi$  MOs:

Secular det!  $\Rightarrow$  using Hückel Approach

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

for non-trivial solns

$$(\alpha - E) \left[ (\alpha - E)^2 - \beta^2 \right] - \beta [ \beta (\alpha - E) - 0 ] + 0 = 0$$

$$(\alpha - E)^3 - 2\beta^2 (\alpha - E) = 0$$

$$(\alpha - E) \left[ (\alpha - E)^2 - 2\beta^2 \right] = 0$$

↳  $E = \alpha$ ;  $E = \alpha + \sqrt{2}\beta$ ;  $E = \alpha - \sqrt{2}\beta$

$\Rightarrow$  MO coefficients are found by subbing each value of  $E$  back to the secular eqn

$$\begin{pmatrix} \alpha - E & \beta & 0 \\ \beta & \alpha - E & \beta \\ 0 & \beta & \alpha - E \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \\ c_3 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ 0 \end{pmatrix}$$

When  $E = \alpha$ :

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

$$\beta c_1 + \beta c_3 = 0 \quad \boxed{c_3 = -c_1}$$

$$\therefore \Psi_{E=\alpha}^{\pi} = c_1 \phi_1 - c_3 \phi_3$$

$= \frac{1}{\sqrt{2}} (\phi_1 - \phi_3)$  after normalization

When  $E = \alpha + \sqrt{2}\beta$ :

$$\begin{pmatrix} -\sqrt{2}\beta & \beta & 0 \\ \beta & -\sqrt{2}\beta & \beta \\ 0 & \beta & -\sqrt{2}\beta \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \\ c_3 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ 0 \end{pmatrix}$$

$$\sqrt{2} c_1 = c_2 = \sqrt{2} c_3$$

$$\Psi_{E=\alpha+\sqrt{2}\beta}^{\pi} = \frac{1}{2} (\phi_1 + \sqrt{2}\phi_2 + \phi_3)$$

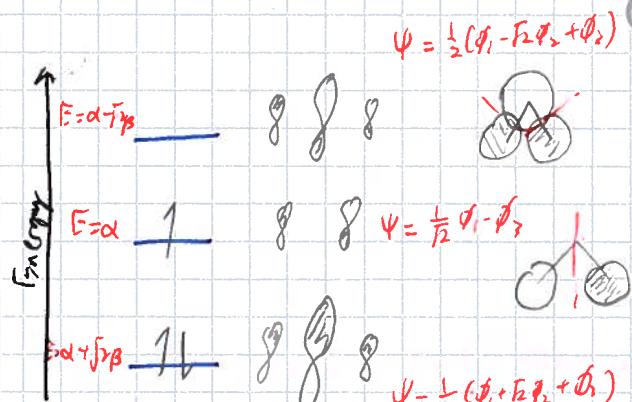
When  $E = \alpha - \sqrt{2}\beta$ :

$$\begin{pmatrix} \sqrt{2}\beta & \beta & 0 \\ \beta & \sqrt{2}\beta & \beta \\ 0 & \beta & \sqrt{2}\beta \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \\ c_3 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ 0 \end{pmatrix}$$

$$\sqrt{2} c_1 = -c_2 = \sqrt{2} c_3$$

$$\Psi_{E=\alpha-\sqrt{2}\beta}^{\pi} = \frac{1}{2} (\phi_1 - \sqrt{2}\phi_2 + \phi_3)$$

M.O. Diagram



Total electron energy:

$$E_{\text{total}}^{\pi} = 2(\alpha + \sqrt{2}\beta) + \alpha = 3\alpha + 2\sqrt{2}\beta$$

for  $(\phi_p - \phi_p, \beta \approx 75 \text{ kJ mol}^{-1})$

$\therefore$  the  $\pi$  orbital bonding stabilizes

the radical by about  $200 \text{ kJ mol}^{-1}$

### 6.3 FCF Population & bond orders

$e^-$  population on atom k

$$\text{In } e^- \text{ density: } Q_k = \sum_i n_i c_{ik}^2$$

→ for an uncharged molecule:

total charge on each atom

$$\hookrightarrow q_k = 1 - Q_k$$

[ $\therefore$  each atom k has a residual nuclear charge of +1]

- useful for determining most likely position for electrophilic or nucleophilic attack

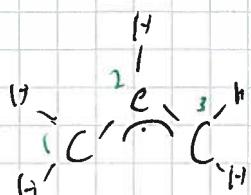
→ Bond order between atoms j & k:

$$P_{jk} = \sum_i n_i c_{ij} c_{ik}$$

⇒ there is an approximate correlation between the calculated bond order & bond length, found experimentally

Reducing now, the  $e^-$  population &

bond orders for the allyl radical



In  $e^-$  densities:  $Q_k > \sum_i n_i c_{ik}^2$

23

$$Q_1 = 2\left(\frac{1}{2}\right)^2 + 1\left(\frac{1}{2}\right)^2 + 0\left(\frac{1}{2}\right)^2 = 1 = 2$$

$$Q_2 = 2\left(\frac{1}{2}\right)^2 + 1 \cdot 0 + 0\left(-\frac{1}{2}\right)^2 = 1$$

$$q_k = 1 - Q_k = 0$$

↳ neutral  $\Rightarrow$  each C has same charge

Bond order:  $P_{jk} = \sum_i n_i c_{ij} c_{ik}$

$$P_{12} = 2\left(\frac{1}{2}\left(\frac{1}{2}\right)\right) + 1\left(\frac{1}{2}\right) + 0\left(\frac{1}{2}\left(\frac{1}{2}\right)\right) \\ = \frac{1}{2} = P_{32} \approx 0.7$$

$$P_{13} = 2\left(\frac{1}{2}\right) + 1\left(\frac{1}{2}\left(\frac{1}{2}\right)\right) + 0\left(\frac{1}{2}\right) = 0$$

→ two bonds equal in length

↳ delocalization makes them slightly shorter than in benzene

$\Rightarrow$  no bond between C & C<sub>3</sub>

[C<sub>3</sub> assumed in the secular eqn]

M <sub>i</sub> , (E <sub>i</sub> )	E <sub>i</sub>	n <sub>i</sub>	c <sub>11</sub>	c <sub>12</sub>	c <sub>13</sub>
1	$\alpha + \sqrt{2}\beta$	2	$\frac{1}{2}$	$\frac{1}{\sqrt{2}}$	$\frac{1}{2}$
2	$\alpha$	1	$\frac{1}{\sqrt{2}}$	0	$-\frac{1}{\sqrt{2}}$
3	$\alpha - \sqrt{2}\beta$	0	$\frac{1}{2}$	$-\frac{1}{\sqrt{2}}$	$\frac{1}{2}$

$$\tanh\left(\frac{k}{T}\right) = \frac{\sinh\left(\frac{k}{T}\right)}{\cosh\left(\frac{k}{T}\right)} = \frac{e^{\frac{k}{T}} - e^{-\frac{k}{T}}}{e^{\frac{k}{T}} + e^{-\frac{k}{T}}} \\ = \frac{1}{1 + e^{-\frac{2k}{T}}}$$

↗

Random stat mech calculation

