

Atomic Units

It is often convenient to write equations and carry out calculations in atomic units.

quantity	atomic unit	symbol	S.I.
mass	electron mass	m_e	9.109×10^{-31} kg
length	Bohr radius	a_0	52.92×10^{-12} m
charge	electron charge	e	1.602×10^{-19} C
energy	Hartree	H	2625 kJ mol ⁻¹ 27.2 eV
velocity	speed of light	c	2.998×10^8 m s ⁻¹
angular momentum		\hbar	1.0546×10^{-34} J s

e.g for the H atom

$$\hat{H} = -\frac{\hbar^2}{2\mu} \nabla^2 - \frac{Ze^2}{4\pi\epsilon_0 r} \Rightarrow -\frac{1}{2} \nabla^2 - \frac{Z}{r} \text{ a.u.}$$

$$E_n = -\frac{Ze^4\mu}{2\hbar^2(4\pi\epsilon_0)^2} \cdot \frac{1}{n^2} \Rightarrow -\frac{1}{2} \cdot \frac{Z}{n^2} \text{ a.u.}$$

The Born-Oppenheimer Approximation

$$\hat{H}_{\text{TOT}} = -\frac{1}{2} \sum_i \nabla_i^2 - \frac{1}{2} \sum_k \frac{m}{M_k} \nabla_k^2 - \sum_i \sum_k \frac{Z_k}{r_{ik}} + \sum_i \sum_{j>i} \frac{1}{r_{ij}} + \sum_{k_1} \sum_{k_2>k_1} \frac{Z_{k_1} Z_{k_2}}{r_{k_1 k_2}} = \hat{T}_e + \hat{T}_N + V_{eN} + V_{ee} + V_{NN}$$

electrons
nuclei
el-nucl.
pairs
electron
pairs
pairs of
nuclei

Ψ_{int} has $3(n+N-1)$ coordinates – impossible to solve the Schrödinger equation exactly.

The Born-Oppenheimer Approximation states that electronic motion is so fast that nuclei can be considered fixed.

The Schrödinger equation can then be solved (usually approximately) for the *electronic* wavefunction for fixed nuclear distances. The plot of *electronic* energy as a function of *nuclear* distances is called the **potential energy surface**.

The P.E. surface represents the potential within which the nuclei move. Motion of nuclei on this surface corresponds to molecular vibration. (Rotation is considered as a special case of vibration in which internuclear distances are fixed.)

The B.O. Approximation is another example of simplifying a Q.M. problem by **separation of variables**.

$$\Psi_{\text{tot}} = \Psi_{\text{el}} \Psi_{\text{vib}} \Psi_{\text{rot}} \qquad E_{\text{tot}} = E_{\text{el}} + E_{\text{vib}} + E_{\text{rot}}$$

1-D Reaction Coordinate

The **potential energy** V is the internal energy U from thermodynamics.

In the **Born-Oppenheimer Approximation** the nuclear and electronic parameters are separable: **product of wavefunctions, sum of energies.**

The potential energy surface then corresponds to a plot of the energy of the system as a function of nuclear coordinates.

The simplest reaction “surface” has 1 dimension, such as the interatomic distance in the dissociation of a diatomic. **e.g.** $AB \rightarrow A + B$

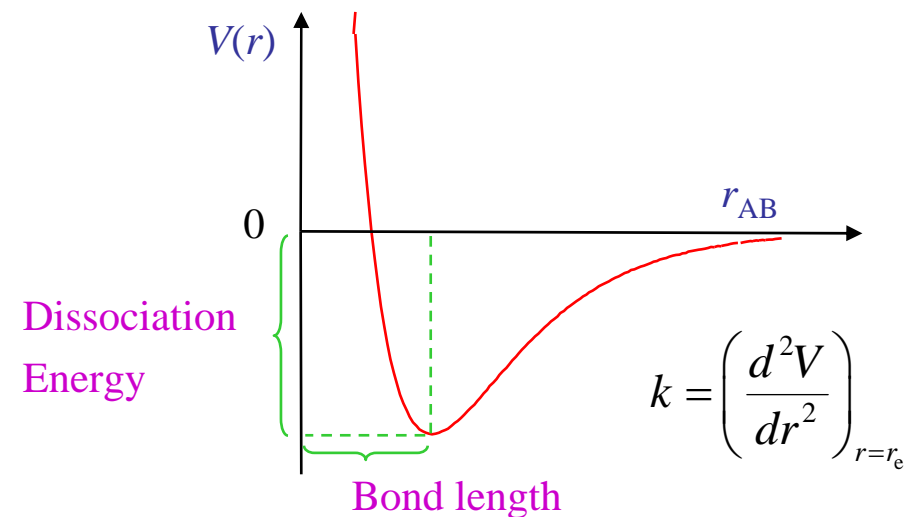
For $r \approx r_e$ the potential can be modelled by the simple harmonic oscillator.

$$V(r) = V(r_e) + \frac{1}{2}k(r - r_e)^2$$

But extreme anharmonicity is needed to model dissociation:

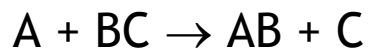
The Morse Potential

$$V(r) = D_e \left[1 - e^{-\alpha(r-r_e)} \right]^2 - D_e$$

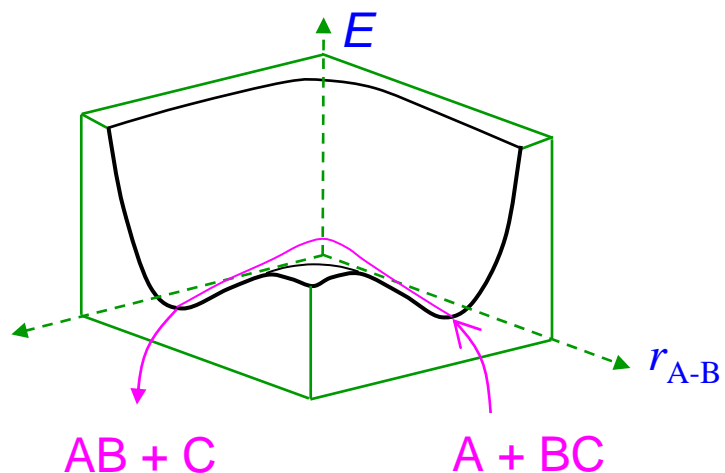


2-D Potential Energy Surface

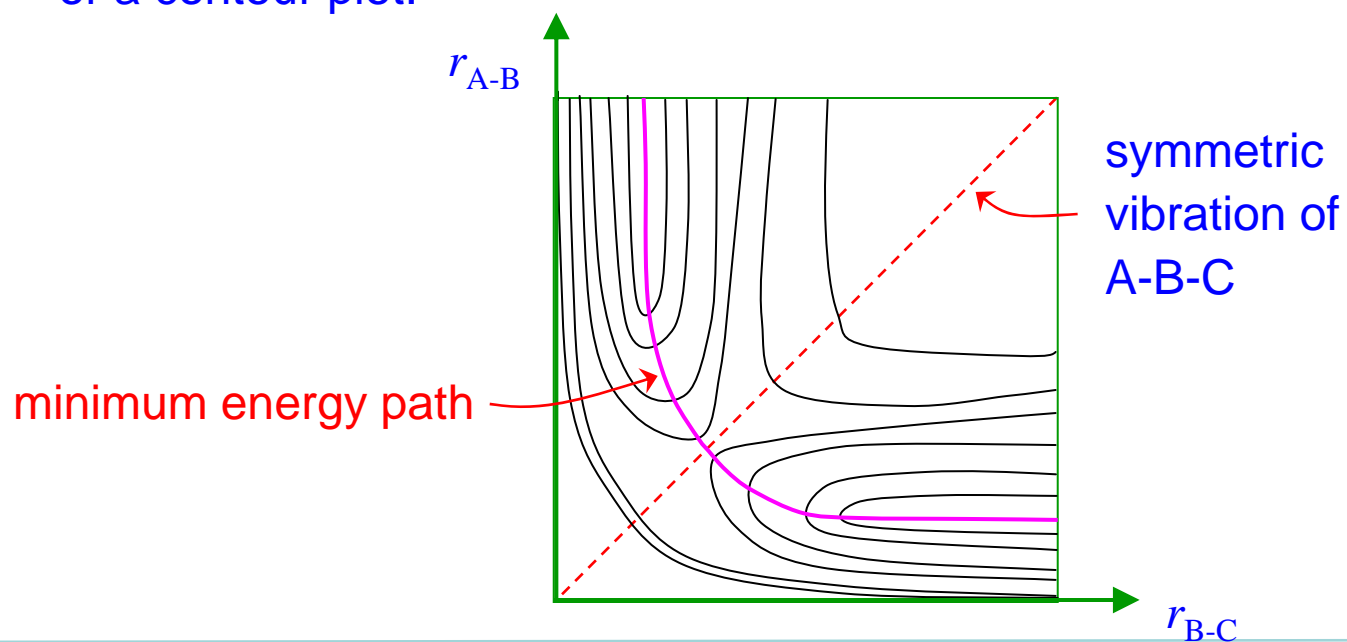
A collinear triatomic
reaction such as



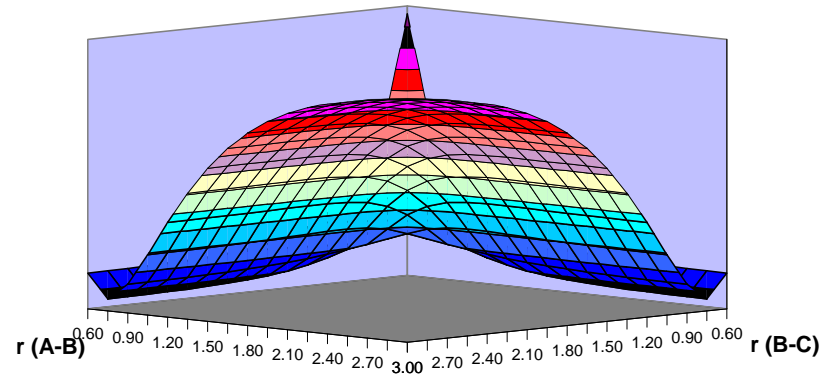
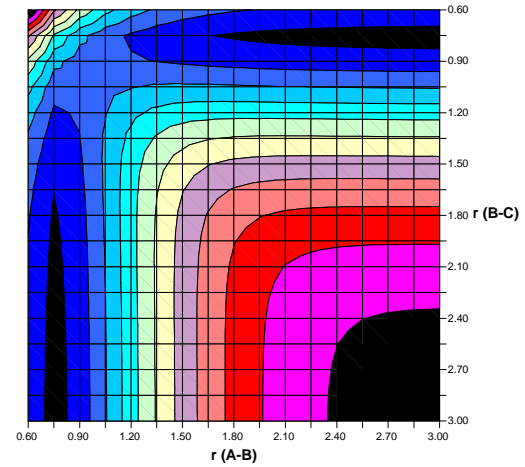
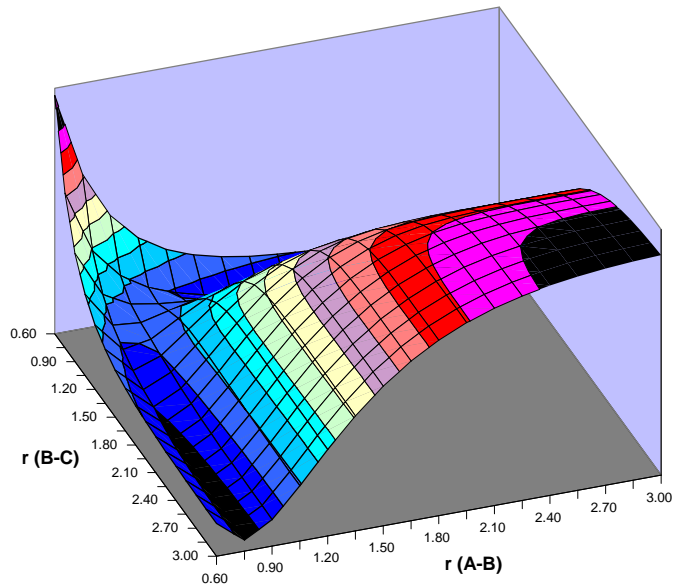
needs a 3-D plot:



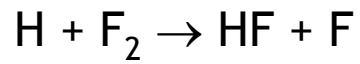
or a contour plot:



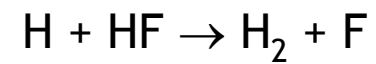
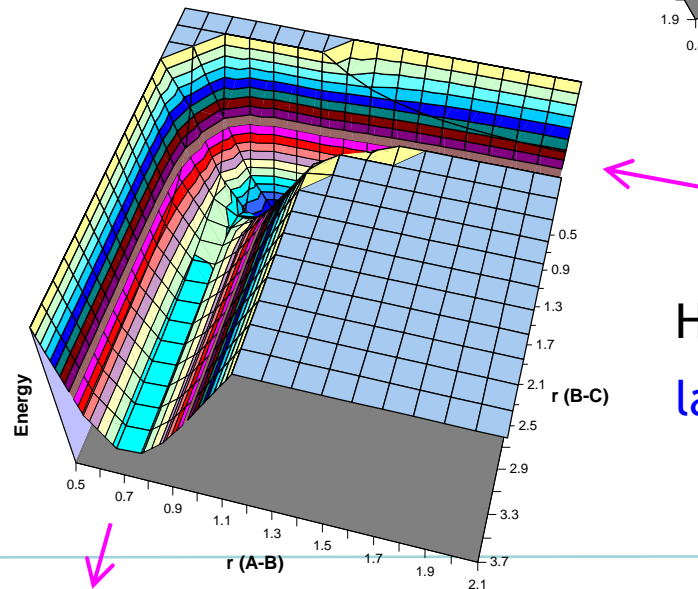
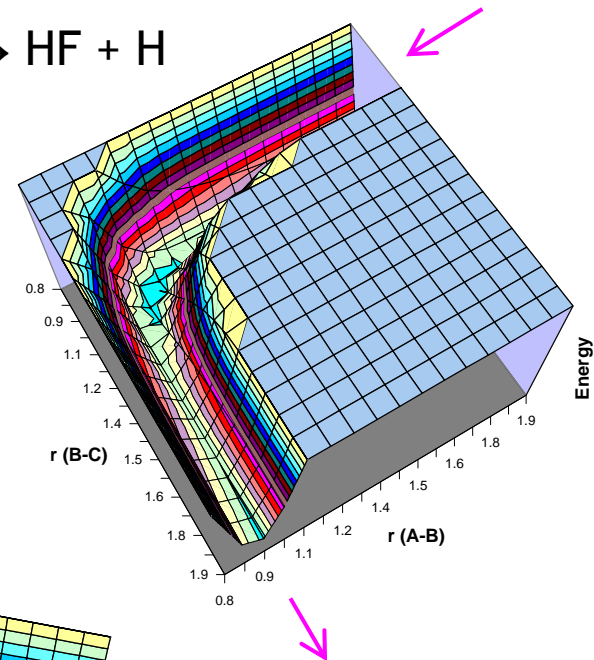
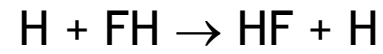
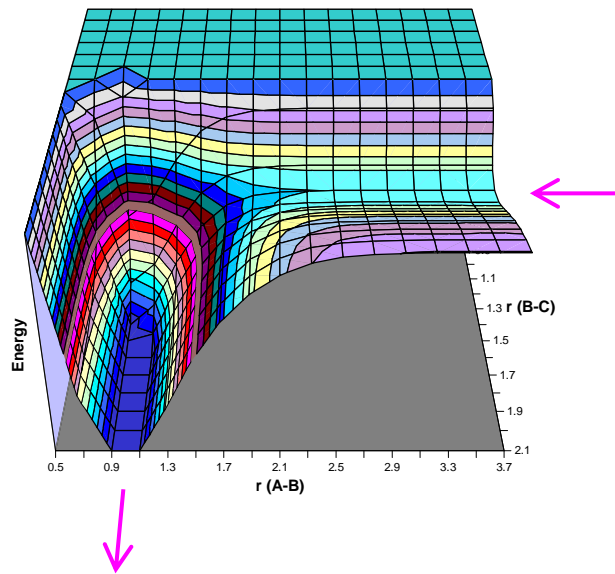
Views of a Potential Energy Surface



Miscellaneous Reaction Surfaces



early barrier



late barrier

The Electron Pair Bond

Consider two independent electrons with wavefunctions $\psi_a(1), \psi_b(2)$; and $E = E_a + E_b$.

electron repulsion ignored

Since $\psi_a(1)\psi_b(2)$ is indistinguishable from $\psi_b(1)\psi_a(2)$

possible molecular wavefunctions are: $\Psi_S = \frac{1}{\sqrt{2}}[\psi_a(1)\psi_b(2) + \psi_b(1)\psi_a(2)]$

$$\Psi_A = \frac{1}{\sqrt{2}}[\psi_a(1)\psi_b(2) - \psi_b(1)\psi_a(2)]$$

For any point between the nuclei where $\vec{r}(1) \approx \vec{r}(2)$, $\psi_a(1) \approx \psi_a(2)$, $\psi_b(1) \approx \psi_b(2)$

$$\Rightarrow \Psi_A \approx 0, \quad \Psi_S \approx \sqrt{2} \psi_a(1)\psi_b(2)$$

For points outside the internuclear region, either $\psi_a \approx 0$ or $\psi_b \approx 0$

$$\Rightarrow \Psi_S \approx 0$$

i.e. Ψ_S represents bond formation with a pair of electrons between nuclei.

To satisfy the **Pauli Principle** the total wavefunction, including the spin part ϕ , must be **antisymmetric**. Thus, $\Psi_0 = \Psi_S \phi_A = \frac{1}{2}[\psi_a\psi_b + \psi_b\psi_a][\alpha\beta - \beta\alpha]$

The spins are paired in the bond. This is the essence of the **Valence Bond Method**.

H₂ : Valence Bond Approach

For an electron pair in the bonding orbital,

$$\Psi_0 = \Psi_S \phi_A = \frac{1}{2}[a(1)b(2) + b(1)a(2)][\alpha\beta - \beta\alpha]$$

where a and b represent the 1s wavefunctions in H atoms A and B.

$$\begin{aligned}\hat{H} &= \underbrace{-\frac{1}{2}\nabla_1^2 - \frac{1}{r_{a1}} - \frac{1}{r_{b1}}}_{\hat{H}_a(1)} - \underbrace{\frac{1}{2}\nabla_2^2 - \frac{1}{r_{b2}} - \frac{1}{r_{a2}}}_{\hat{H}_b(2)} + \frac{1}{r_{12}} \left\{ + \frac{1}{R_{ab}} \right\} \\ &= \hat{H}_a(1) + \hat{H}_b(2) + \hat{H}_{ab}(1,2) \\ &= E_{1s} + E_{1s} + E_{12}\end{aligned}$$

$$E_{12} = \frac{\langle \Psi | \hat{H}_{ab} | \Psi \rangle}{\langle \Psi | \Psi \rangle} = \frac{J + K}{1 + S^2}$$

where

- Coulomb integral $J = \langle ab | \hat{H}_{ab} | ab \rangle$
- exchange integral $K = \langle ab | \hat{H}_{ab} | ba \rangle$
- overlap integral $S = \langle a | b \rangle$

Note: $\langle ab | ba \rangle \equiv \int a(1)^* b(2)^* b(1) a(2) d\tau_1 d\tau_2 = \int a(1)^* b(1) d\tau_1 \cdot \int b(2)^* a(2) d\tau_2 = S^2$

Bra(c)ket Notation

Enrichment

Dirac proposed the bra-ket notation:

$$\langle \text{bra} | \text{c} | \text{ket} \rangle$$

$$|n\rangle = \text{ket} \equiv \psi_n$$

$$\langle m| = \text{bra} \equiv \psi_m^*$$

$$\langle m|n\rangle \equiv \int \psi_m^* \psi_n d\tau$$

$$\langle m|\hat{\Omega}|n\rangle \equiv \int \psi_m^* \hat{\Omega} \psi_n d\tau$$

Kets may be interpreted as vectors in Hilbert space.

Operators behave like matrices.

$\Omega_{mn} \equiv \langle m|\hat{\Omega}|n\rangle$ can be regarded as a matrix element.

Heisenberg developed a formulation of quantum mechanics using the language of matrix algebra.

Extensions to the Valence Bond Method

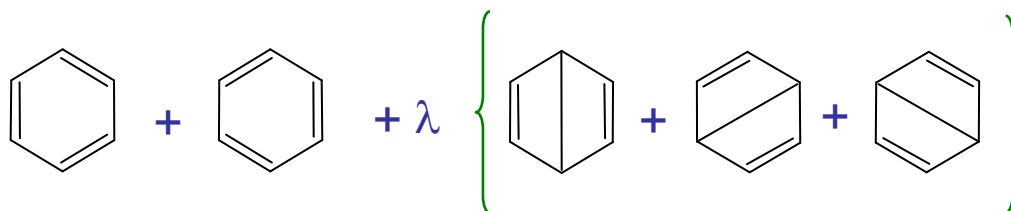
The pure valence bond wavefunction is covalent – each atom contributes one electron to the bond between them, and these atoms are shared equally.

An improved wavefunction has some “ionic” terms:

$$\Psi_{\text{space}} = N \{ ab + ba + \lambda [aa + bb] \} \quad \text{where } \lambda \text{ is a variational parameter.}$$

This concept can be generalized to include all possible arrangements of electron pairs, including other covalent structures.

e.g. benzene

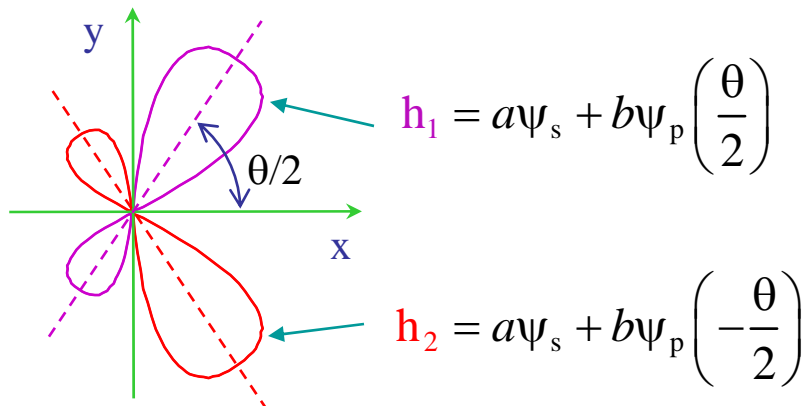


Often it is useful to make an electron pair bond from atomic orbitals that are themselves combinations of atomic orbitals centred on the *same* atom. These are called **hybrid orbitals**.

Hybrid Orbitals

A **hybrid orbital** contains contributions from more than one atomic orbital centred on the same atom.

e.g. Construct hybrids from oxygen s, p_x and p_y orbitals in H_2O :



where
$$\psi_p\left(\frac{\theta}{2}\right) = \psi_{p_x} \cos\left(\frac{\theta}{2}\right) + \psi_{p_y} \sin\left(\frac{\theta}{2}\right)$$

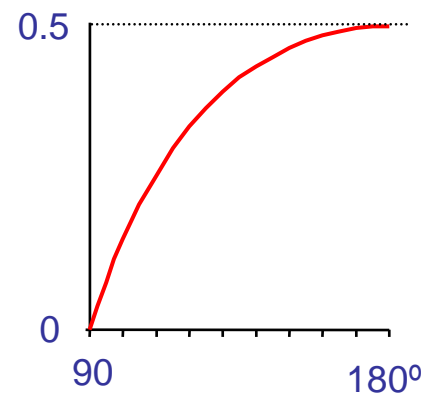
$$\psi_p\left(-\frac{\theta}{2}\right) = \psi_{p_x} \cos\left(\frac{\theta}{2}\right) - \psi_{p_y} \sin\left(\frac{\theta}{2}\right)$$

but from $\langle \mathbf{h}_1 | \mathbf{h}_1 \rangle = 1$ and $\langle \mathbf{h}_1 | \mathbf{h}_2 \rangle = 0$,

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

$$a^2 + b^2 \cos^2(\theta/2) - b^2 \sin^2(\theta/2) = 0$$

$$\Rightarrow a^2 = \frac{\cos \theta}{(\cos \theta) - 1}$$



The s character of the hybrid increases as the bond angle changes from 90° to 180° .

Hybridization – Special Cases

sp

$$\left. \begin{aligned} \mathbf{h}_1 &= a\psi_{2s} + b\psi_{2px} \\ \mathbf{h}_2 &= a'\psi_{2s} + b'\psi_{2px} \end{aligned} \right\} \begin{aligned} \langle \mathbf{h}_1 | \mathbf{h}_1 \rangle &= 1 & \Rightarrow & a^2 + b^2 = 1 \\ \langle \mathbf{h}_1 | \mathbf{h}_2 \rangle &= 0 & \Rightarrow & aa' + bb' = 0 \end{aligned} \Rightarrow a = a' = b = -b' = \frac{1}{\sqrt{2}}$$

$$\left. \begin{aligned} \mathbf{h}_1 &= \frac{1}{\sqrt{2}}(\psi_{2s} + \psi_{2px}) \\ \mathbf{h}_2 &= \frac{1}{\sqrt{2}}(\psi_{2s} - \psi_{2px}) \end{aligned} \right\}$$

sp²

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

$$\left. \begin{aligned} \mathbf{h}_1 &= \frac{1}{\sqrt{3}}\psi_{2s} - \sqrt{\frac{2}{3}}\psi_{2px} \\ \mathbf{h}_2 &= \frac{1}{\sqrt{3}}\psi_{2s} + \frac{1}{\sqrt{6}}\psi_{2px} - \frac{1}{\sqrt{2}}\psi_{2py} \\ \mathbf{h}_3 &= \frac{1}{\sqrt{3}}\psi_{2s} + \frac{1}{\sqrt{6}}\psi_{2px} + \frac{1}{\sqrt{2}}\psi_{2py} \end{aligned} \right\} \begin{aligned} &\text{aligned along } x \\ &\text{angled} \\ &\text{angled} \end{aligned}$$

sp³

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

$$\mathbf{h}_1 = \frac{1}{2}\psi_{2s} - \frac{\sqrt{3}}{2}\psi_{2px} \quad \text{etc. OR} \quad \left. \begin{aligned} \mathbf{h}_1 &= \frac{1}{2}[\psi_{2s} + \psi_{2px} + \psi_{2py} + \psi_{2pz}] \\ \mathbf{h}_2 &= \frac{1}{2}[\psi_{2s} - \psi_{2px} - \psi_{2py} + \psi_{2pz}] \\ \mathbf{h}_3 &= \frac{1}{2}[\psi_{2s} + \psi_{2px} - \psi_{2py} - \psi_{2pz}] \\ \mathbf{h}_4 &= \frac{1}{2}[\psi_{2s} - \psi_{2px} + \psi_{2py} - \psi_{2pz}] \end{aligned} \right\} \begin{aligned} &\text{aligned towards} \\ &\text{corners of a} \\ &\text{cube} \end{aligned}$$

The Variation Principle

The variational method

The energy calculated using an approximate wave function cannot be less than the true energy of the system.

For the exact wave function ψ

$$E = \frac{\langle \psi | \hat{H} | \psi \rangle}{\langle \psi | \psi \rangle}$$

but for a trial wave function χ

$$\frac{\langle \chi | \hat{H} | \chi \rangle}{\langle \chi | \chi \rangle} = E \geq E$$

If χ is a function of one or more adjustable parameters these can be optimized to give a minimum value for E .

If χ has the same form as ψ then E can be optimized to give the true E .

Slater-type orbitals (STO):

$$\phi_{nlm} = Nr^{n^*-1} e^{-(Z-\sigma)r/(n^*a_0)} Y_{lm} \quad \phi_{nlm} = Nr^{n-1} e^{-Z^*r/a_0} Y_{lm}$$

Gaussian-type orbitals (GTO):

$$\phi_{ijk} = Nx^i y^j z^k e^{-\alpha r^2}$$

Linear combination of atomic orbitals (LCAO):

$$\chi = \sum_i c_i \phi_i$$

H₂⁺ : LCAO-MO Approach

Linear Combination of Atomic Orbitals

H₂⁺: $\hat{H} = -\frac{1}{2}\nabla^2 - \frac{1}{r_a} - \frac{1}{r_b} + \frac{1}{R_{ab}}$ only one electron

Assume $\Psi = c_a a + c_b b$ where a, b are H 1s wavefunctions

$$E = \frac{\langle \Psi | \hat{H} | \Psi \rangle}{\langle \Psi | \Psi \rangle} = \frac{c_a^2 \langle a | \hat{H} | a \rangle + 2c_a c_b \langle a | \hat{H} | b \rangle + c_b^2 \langle b | \hat{H} | b \rangle}{c_a^2 \langle a | a \rangle + 2c_a c_b \langle a | b \rangle + c_b^2 \langle b | b \rangle} = \frac{c_a^2 \alpha + 2c_a c_b \beta + c_b^2 \alpha}{c_a^2 + 2c_a c_b S + c_b^2}$$

where $\alpha = \langle a | \hat{H} | a \rangle = \langle b | \hat{H} | b \rangle$ a Coulomb integral
 $\beta = \langle a | \hat{H} | b \rangle = \langle b | \hat{H} | a \rangle$ a resonance integral
 $S = \langle a | b \rangle = \langle b | a \rangle$ the overlap integral

Coulomb integral $\alpha = \langle a | -\frac{1}{2}\nabla^2 - \frac{1}{r_a} - \frac{1}{r_b} + \frac{1}{R_{ab}} | a \rangle$
 $= E_{1s} - \langle a | \frac{1}{r_b} | a \rangle + 1/R_{ab}$
 H atom el.-nucl. nuclear
 energy attraction repulsion

Resonance integral $\beta = (E_{1s} + 1/R_{ab})S - \langle a | \frac{1}{r_b} | b \rangle < 0$

H₂⁺ : LCAO-MO Approach– 2

The **Variation Principle** is used to find the optimum c_a and c_b :

$$\text{Setting } \frac{\partial E}{\partial c_a} = 0 \quad \text{and} \quad \frac{\partial E}{\partial c_b} = 0 \quad \Rightarrow \quad \begin{aligned} c_a(\alpha - E) + c_b(\beta - SE) &= 0 \\ c_a(\beta - SE) + c_b(\alpha - E) &= 0 \end{aligned}$$

This requires that $\begin{vmatrix} \alpha - E & \beta - SE \\ \beta - SE & \alpha - E \end{vmatrix} = 0$ **Secular Determinant**

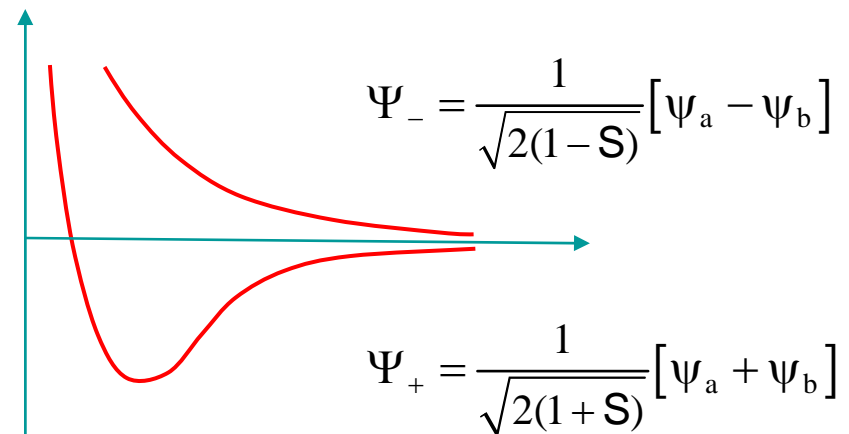
$$(\alpha - E)^2 - (\beta - SE)^2 = 0$$

$$E^0 = \frac{\alpha + \beta}{1 + S} \qquad E^* = \frac{\alpha - \beta}{1 - S}$$

$$c_a = c_b \qquad c_a = -c_b$$

These equations can be solved by using the normalization condition:

$$\langle \Psi | \Psi \rangle = c_a^2 + 2c_a c_b S + c_b^2 = 1$$



H₂ : LCAO-MO Approach

$$\hat{H} = -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{1}{r_{a1}} - \frac{1}{r_{b2}} - \frac{1}{r_{b1}} - \frac{1}{r_{a2}} + \frac{1}{r_{12}} + \frac{1}{R_{ab}} = \hat{h}_0(1) + \hat{h}_0(2) + \frac{1}{r_{12}} - \frac{1}{R_{ab}}$$

Start by ignoring $1/r_{12}$ (independent electron approach):

$$\Psi \approx \psi_i(1)\psi_j(2)\Phi_{\text{spin}} \quad \text{where } \psi_i \text{ are } H_2^+ \text{ functions.}$$

e.g. for ground state H₂, $\Psi_0 = \psi_+(1)\psi_+(2)\frac{1}{\sqrt{2}}[\alpha\beta - \beta\alpha]$

$$\text{where } \psi_+ \psi_+ = \frac{1}{2(1+S)} [\psi_a \psi_a + \psi_b \psi_b + \underbrace{\psi_a \psi_b + \psi_b \psi_a}_{\text{covalent}}]$$

ionic H-H⁺ H⁺H⁻ covalent

Ionic configurations are weighted too highly!

Configuration Interaction corrects this by mixing in some excited states, such as $\sigma^*\sigma^*$

$$\Psi_{\text{C.I.}} = \frac{1}{2(1+S)} [\psi_+ \psi_+ + \lambda \psi_- \psi_-] \Phi_{\text{spin}}$$

Treat $1/r_{12}$ as a perturbation to the simplified problem.

$$E = 2E(H_2^+) + \langle \Psi_0 | \frac{1}{r_{12}} | \Psi_0 \rangle - 1/R_{ab}$$

Bond Formation in M.O. Theory

The results of calculations on simple molecules can be extended as general rules to more complicated systems. Thus, to form a strong bond:

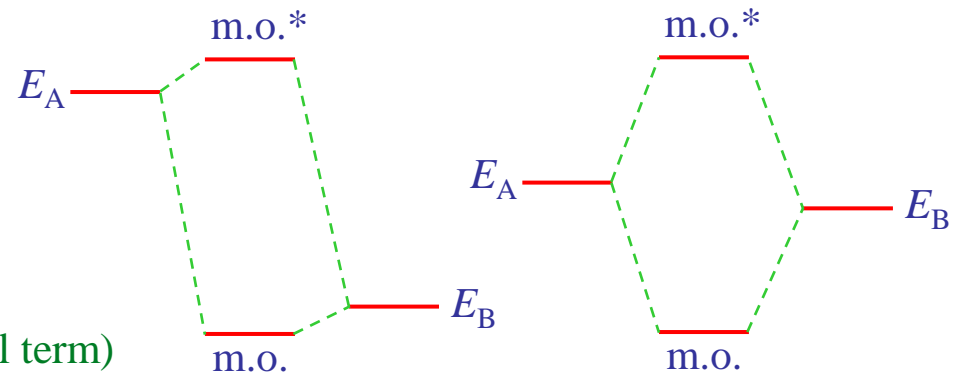
- ◆ Orbitals must have the same symmetry with respect to rotation about the internuclear axis. Otherwise $S = 0$
- ◆ Orbitals must not be too small or too diffuse. Otherwise S will be too small. Valence shell electrons are most effective, with strengths roughly $\sigma > \pi > \delta$
- ◆ Orbitals must be of similar energy. Otherwise...

If $|\alpha_A - \alpha_B|$ is large, and S is small,

$$\begin{vmatrix} \alpha_A - E & \beta - SE \\ \beta - SE & \alpha_B - E \end{vmatrix} = 0$$

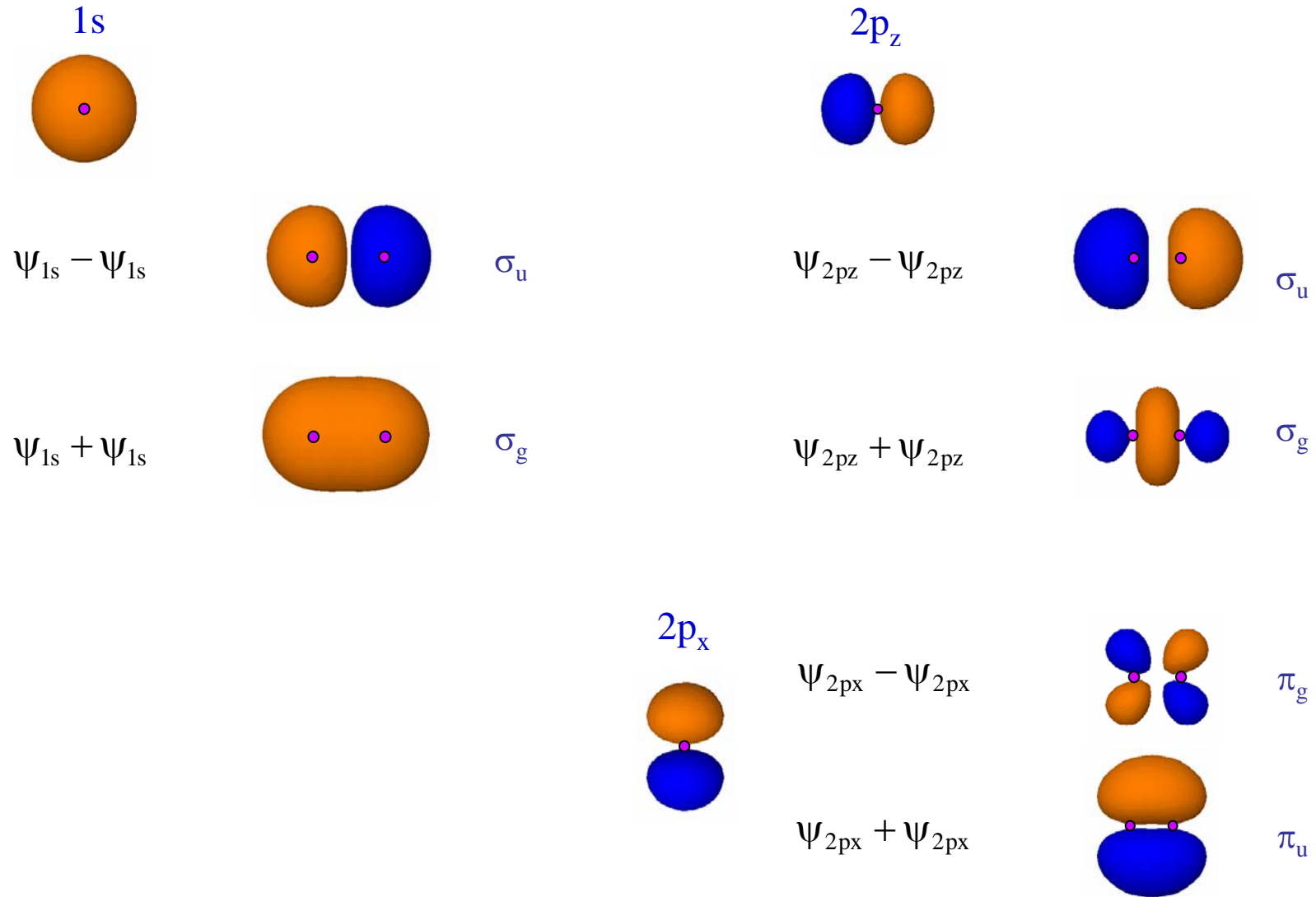
$$E \approx \alpha_A + \frac{\beta^2}{\alpha_A - \alpha_B}, \quad \alpha_B - \frac{\beta^2}{\alpha_A - \alpha_B}$$

$$\approx E_A + (\text{small term}), \quad E_B + (\text{small term})$$



strong bond

Molecular Orbitals of Diatomics



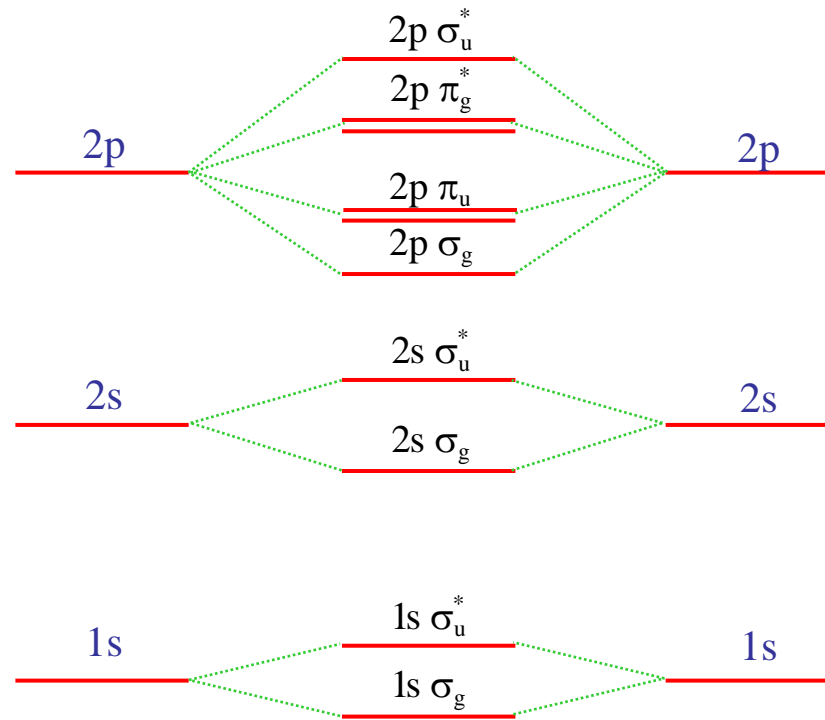
Homonuclear Diatomics

Molecular orbitals are classified as σ , π , δ , ϕ according to their symmetry as viewed along the internuclear axis.

If the wavefunction changes sign upon inversion through a centre of symmetry, the orbital is labelled **u ungerade**; If the wavefunction does not change sign it is **g gerade**.

An atomic orbital that remains relatively unperturbed in a molecule (e.g. a lone pair) is labelled **n non-bonding**.

Relative energies:



Homonuclear Diatomics – 2

