

VALENCE

Hilary Term 2021

8 Lectures

Prof M. Brouard

Valence is the theory of the chemical bond

Outline plan

1. *The Born-Oppenheimer approximation*
2. *Bonding in H_2^+*
 - the LCAO approximation
3. *Many electron molecules*
 - the orbital approximation, its strengths and weaknesses
 - binding in H_2
 - splitting of degenerate configurations
 - dissociation of H_2
4. *Application of the variation principle to find LCAO's*
 - the secular equations

5. *Binding of the first row diatomics*

- splitting into terms, and
- levels

6. *Walsh diagrams*

- bond angles in AH₂ systems

7. *Hückel theory*

- use of symmetry
- aromaticity
- bond order, electron densities and organic reactivity

8. *Correlation Diagrams*

- predicting chemical reactivity

Links with other lecture courses

Quantum Mechanics
Spectroscopy

Statistical Mechanics
Reaction Rates

Photochemistry (Year 3)

1: The Born-Oppenheimer approximation

General Schrödinger equation for molecules

For a molecular system the Hamiltonian is

$$\hat{H} = \hat{T}_e + \hat{T}_n + \hat{V}_{en} + \hat{V}_{nn} + \hat{V}_{ee}$$

\hat{T} — Kinetic energy terms for the electrons (e) and nuclei (n);

\hat{V} — Potential energy terms; the various Coulomb interactions between the electrons and the nuclei.

The Schrödinger equation for a molecule can be written

$$\hat{H}\Psi(\mathbf{r}, \mathbf{R}) = E\Psi(\mathbf{r}, \mathbf{R})$$

where \mathbf{r} and \mathbf{R} represent collectively the position vectors (with respect to the centre-of-mass) of the electrons and nuclei, respectively.

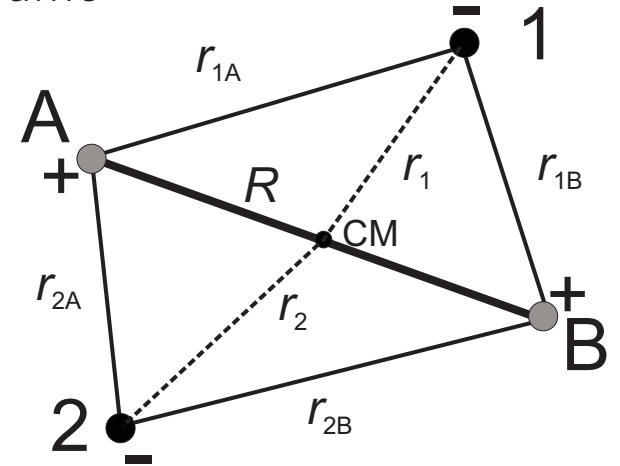
This equation is simple to write down, but too complex to solve.

We need to make a sequence of approximations.

The Schrödinger equation for H₂

- Use coordinates expressed in the centre-of-mass (CM) frame (i.e. factor out kinetic energy of the CM)
- Use atomic units ($e = 1$, $\hbar = 1$, $m_e = 1$)

$$\hat{H} = \hat{T}_e + \hat{T}_n + \hat{V}_{en} + \hat{V}_{nn} + \hat{V}_{ee}$$



$$\hat{T}_n = -\frac{1}{2\mu} \nabla_R^2 \quad \text{with} \quad \mu = \frac{M_A M_B}{M_A + M_B}$$

$$\hat{T}_e = -\frac{1}{2} \nabla_{\mathbf{r}_1}^2 - \frac{1}{2} \nabla_{\mathbf{r}_2}^2$$

$$\hat{V}_{en} = \frac{1}{r_{1A}} - \frac{1}{r_{1B}} - \frac{1}{r_{2A}} - \frac{1}{r_{2B}}$$

$$\hat{V}_{nn} = \frac{1}{R}$$

$$\hat{V}_{ee} = \frac{1}{r_{12}} \equiv \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|}$$

The approximation: the electronic problem

Electrons move much faster than nuclei, for the same force. Therefore, they adapt quickly to changes in nuclear motion.

The Born-Oppenheimer approximation assumes that nuclei are stationary on the timescale of electron motion.

We can therefore write the total wavefunction in a separable product form

$$\Psi(\mathbf{r}, R) = \chi_n(R) \Psi_e(\mathbf{r}|R) .$$

$\chi_n(R)$ — wavefunction describing the motion of the nuclei;

$\Psi_e(\mathbf{r}|R)$ — the electronic wavefunction (depends *parametrically* on the coordinates of the nuclei).

This separation is known as an **adiabatic separation**, and leads to adiabatic electronic states (see below).

Define an electronic Hamiltonian

$$\hat{H}_e = \hat{H} - \hat{T}_n ,$$

which is a Hamiltonian for **stationary nuclei**.

Cont.

Solution of the simplified Schrödinger equation for the electronic motion at fixed R ,

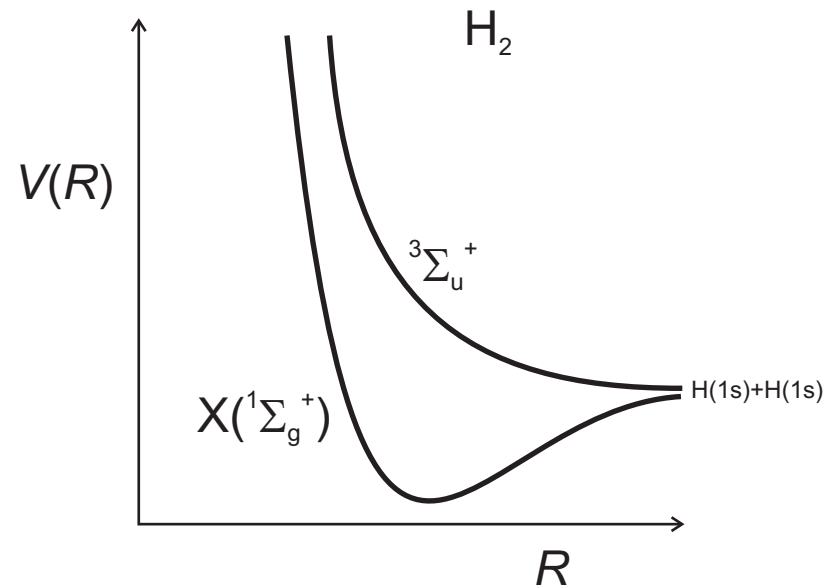
$$\hat{H}_e \Psi_e(\mathbf{r}|R) = E_e(R) \Psi_e(\mathbf{r}|R)$$

yields a set of **electronic states**, with energies $E_e(R)$ that depend on the positions of the nuclei, R .

This is the equation on which we will focus for most of the remaining lectures.

The electronic states with energies $E_e(R)$ represent the potential energy functions (curves), $V(R)$, that nuclei experience at a given separation, R .

Note that $E_e(R) \equiv V(R)$ includes the Coulomb repulsion between the (fixed) nuclei \hat{V}_{nn} .



The approximation: the nuclear problem

For each electronic state, $E_e(R)$, we can now attempt to solve the Schrödinger equation for the nuclear motion:

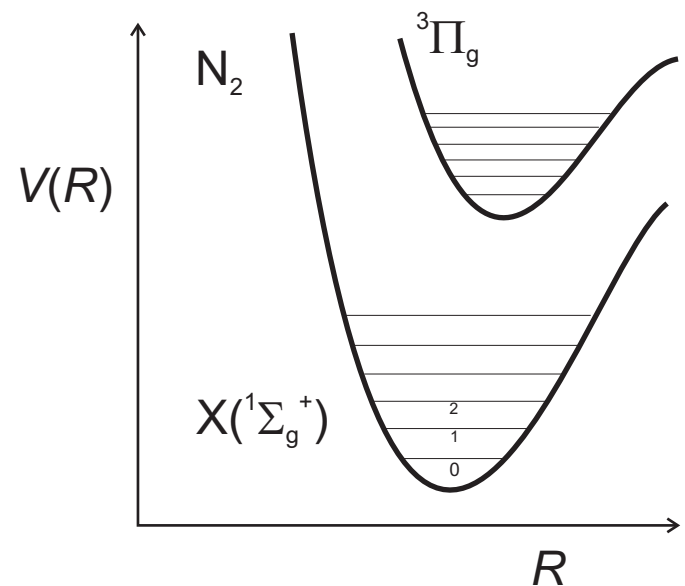
$$\hat{H}_n \chi_n(R) = [\hat{T}_n + E_e(R)] \chi_n(R),$$

The electronic energies, $E_e(R)$, play the role of the potential energy, $V(R)$, experienced by the nuclei at a given separation:

$$= [\hat{T}_n + V(R)] \chi_n(R) = E_n \chi_n(R).$$

E_n , are a set of energy levels associated with the vibrational and rotational motion of the nuclei in a specific electronic state.

Each electronic state is described by a different potential energy curve, with its own set of rotation-vibration states, obtained from the solution of the above Schrödinger for the nuclear motion.



Why is it an approximation?

Write the full Schrödinger equation

$$\hat{H}\Psi(\mathbf{r}, R) = E\Psi(\mathbf{r}, R) \quad \text{where } E \equiv E_n$$

as

$$\begin{aligned}\hat{H}\Psi(\mathbf{r}, R) &= (\hat{H}_e + \hat{T}_n)\chi_n(R)\Psi_e(\mathbf{r}|R) \\ &= \hat{H}_e\chi_n(R)\Psi_e(\mathbf{r}|R) + \hat{T}_n\chi_n(R)\Psi_e(\mathbf{r}|R)\end{aligned}$$

Term 1

Term 2

Look at **Term 1**

$$\begin{aligned}\hat{H}_e\chi_n(R)\Psi_e(\mathbf{r}|R) &= \chi_n(R)\hat{H}_e\Psi_e(\mathbf{r}|R) \\ &= \chi_n(R)E_e(R)\Psi_e(\mathbf{r}|R) = \Psi_e(\mathbf{r}|R)V(R)\chi_n(R).\end{aligned}$$

Note that the *electronic* Hamiltonian does not operate on $\chi_n(R)$.

Look at **Term 2**

$$\hat{T}_n\chi_n(R)\Psi_e(\mathbf{r}|R) = \chi_n(R)\hat{T}_n\Psi_e(\mathbf{r}|R) + \Psi_e(\mathbf{r}|R)\hat{T}_n\chi_n(R)$$

This term is more complicated.

Term 2 in more detail - an aside

$$\hat{T}_n \chi_n(R) \Psi_e(\mathbf{r}|R) = \chi_n(R) \hat{T}_n \Psi_e(\mathbf{r}|R) + \Psi_e(\mathbf{r}|R) \hat{T}_n \chi_n(R)$$

Note: A cross term in the derivatives has been neglected. It turns out not to contribute to the energy of the system $E = \langle \Psi | \hat{H} | \Psi \rangle$.

$$\begin{aligned} \hat{T}_n [\chi_n(R) \Psi_e(\mathbf{r}|R)] &\propto \frac{d^2 [\chi_n \Psi_e]}{dR^2} \\ &= \frac{d [\chi_n \Psi_e' + \chi_n' \Psi_e]}{dR} \\ &= \chi_n \Psi_e'' + 2\chi_n' \Psi_e' + \chi_n'' \Psi_e \end{aligned}$$

When considering the energy of the system the middle term (in green) is zero:

$$\begin{aligned} E &= \langle \Psi(\mathbf{r}, R) | \hat{H} | \Psi(\mathbf{r}, R) \rangle = \langle \Psi(\mathbf{r}, R) | \hat{H}_e + \hat{T}_n | \Psi(\mathbf{r}, R) \rangle \\ &= + \dots + \langle \chi_n \Psi_e | \hat{T}_n | \chi_n \Psi_e \rangle \\ &= + \dots + \dots + 2\langle \chi_n \Psi_e | \chi_n' \Psi_e' \rangle \end{aligned}$$

However,

$$\frac{d\langle \Psi_e | \Psi_e \rangle}{dR} = \frac{d1}{dR} = 0 = \langle \Psi_e' | \Psi_e \rangle + \langle \Psi_e | \Psi_e' \rangle = 2\langle \Psi_e | \Psi_e' \rangle$$

So the term in green goes to zero when considering the energy of the system.

Neglect of $\chi_n(R)\hat{T}_n\Psi_e(\mathbf{r}|R)$ Term

Neglect of the term in **red** is the essence of the Born-Oppenheimer approximation. Term 2 then becomes

$$\hat{T}_n\chi_n(R)\Psi_e(\mathbf{r}|R) \simeq \Psi_e(\mathbf{r}|R)\hat{T}_n\chi_n(R)$$

So combining remaining terms in 1 and 2 for the total energy gives

$$\begin{aligned}\hat{H}\Psi(\mathbf{r}, R) &= \Psi_e(\mathbf{r}|R)V(R)\chi_n(R) + \Psi_e(\mathbf{r}|R)\hat{T}_n\chi_n(R) \\ &= \Psi_e(\mathbf{r}|R) [\hat{T}_n + V(R)] \chi_n(R) \\ &= E\chi_n(R)\Psi_e(\mathbf{r}|R)\end{aligned}$$

This all works *provided* $\chi_n(R)\hat{T}_n\Psi_e(\mathbf{r}|R)$ is a relatively small term.

Neglect of the term $\chi_n(R)\hat{T}_n\Psi_e(\mathbf{r}|R)$ is reasonable provided $\Psi_e(\mathbf{r}|R)$ is a **slowly varying** function of the nuclear positions, R .

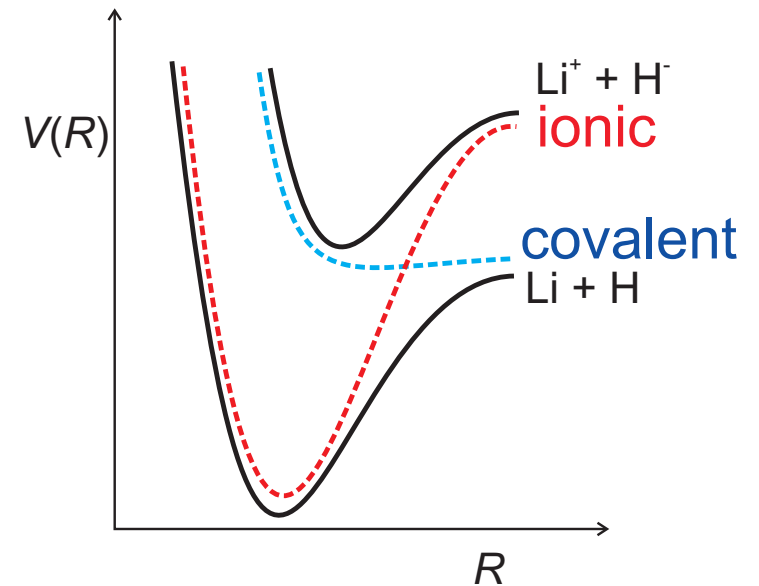
Note further that $\hat{T}_e\Psi_e(\mathbf{r}|R) \approx \mu/m_e\hat{T}_n\Psi_e(\mathbf{r}|R)$. Because nuclei are much heavier than electrons, $\hat{T}_e\Psi_e(\mathbf{r}|R)$ is usually much greater than $\hat{T}_n\Psi_e(\mathbf{r}|R)$.

Breakdown of the Born-Oppenheimer approximation.

The Born-Oppenheimer approximation may break down (*non-adiabatic* behaviour) when

- the nuclear motion is very fast (e.g., close to dissociation), or
- two electronic states have the same energy (e.g., at a **curve crossing**).

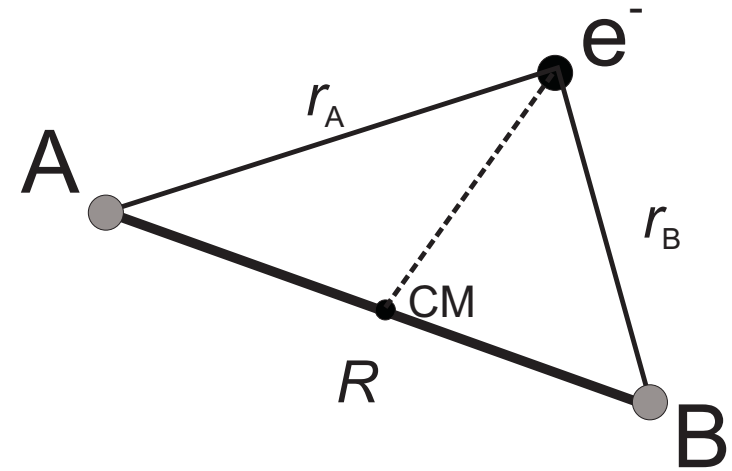
In the region of the crossing, the adiabatic electronic wavefunctions $\Psi_e(\mathbf{r}|R)$ (represented by the black lines) change rapidly in character.



[See Problem sheet 1, question 5.]

2: Solving the electronic problem

Low lying states of H_2^+



Within the Born-Oppenheimer approximation, the Schrödinger equation for the electronic motion in the H_2^+ molecular ion can be written

$$\hat{H}_e \Psi_e(\mathbf{r}|R) = E_e(R) \Psi_e(\mathbf{r}|R)$$

with

$$\hat{H}_e = \hat{T}_e + \hat{V}_{en} + \hat{V}_{nn}$$

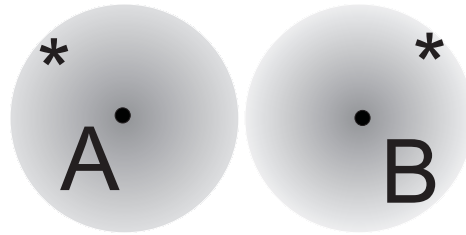
and

$$\hat{V}_{en} = -\frac{1}{r_A} - \frac{1}{r_B}$$

This equation can be solved exactly for H_2^+ .

However, we need to develop a treatment suitable for larger systems.

LCAO approximation



Suppose that the wavefunction (call it a *molecular orbital*) can be written as a **linear combination of atomic orbitals** (LCAOs) localized on atom A and B:

$$\Psi_e = c_A \phi_A + c_B \phi_B .$$

In this example take the atomic orbitals ϕ_i to be the $1s$ orbitals on atom i , although other orbitals could (should) be included in the summation. c_i are the weighting coefficients.

For H_2^+ , and other homonuclear diatomics, the electron density

$$\rho(\mathbf{r}) = |\Psi_e|^2 = c_A^2 \phi_A^2 + c_B^2 \phi_B^2 + 2c_A c_B \phi_A \phi_B$$

must be equal at all points related by symmetry (\star). This requires that

$$c_A^2 = c_B^2$$

$$c_A = \pm c_B = c$$

Normalization

The wavefunction for the electron in H_2^+ must be normalized, *i.e.*

$$\int \rho(\mathbf{r}) \, d\mathbf{r} = c^2 \left[\int \phi_A^2 \, d\mathbf{r} + \int \phi_B^2 \, d\mathbf{r} \pm 2 \int \phi_A \phi_B \, d\mathbf{r} \right] = 1.$$

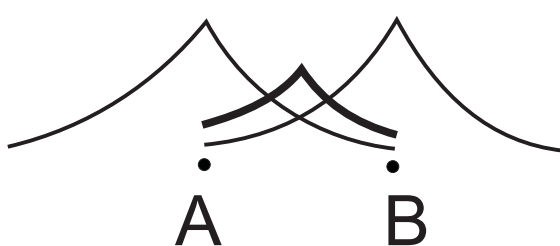
However, the $1s$ atomic orbitals are already normalized individually

$$\int \phi_A^2 \, d\mathbf{r} = \int \phi_B^2 \, d\mathbf{r} = 1,$$

such that the normalization constraint can be written

$$c = \left[\frac{1}{2(1 \pm S_{AB})} \right]^{1/2}.$$

S_{AB} is known as the **overlap integral**, defined as

$$S_{AB} = \int \phi_A \phi_B \, d\mathbf{r}$$


The diagram shows two overlapping wavefunctions, labeled A and B, represented by curves. The overlap region is shaded, illustrating the integral of the product of the two wavefunctions, S_{AB} .

The overlap integral is positive.

Wavefunctions

Given the constant, c , the approximate wavefunctions for H_2^+ can be written

$$\psi_e^+ = \frac{\phi_A + \phi_B}{[2(1 + S_{AB})]^{1/2}} \quad \psi_e^- = \frac{\phi_A - \phi_B}{[2(1 - S_{AB})]^{1/2}} .$$

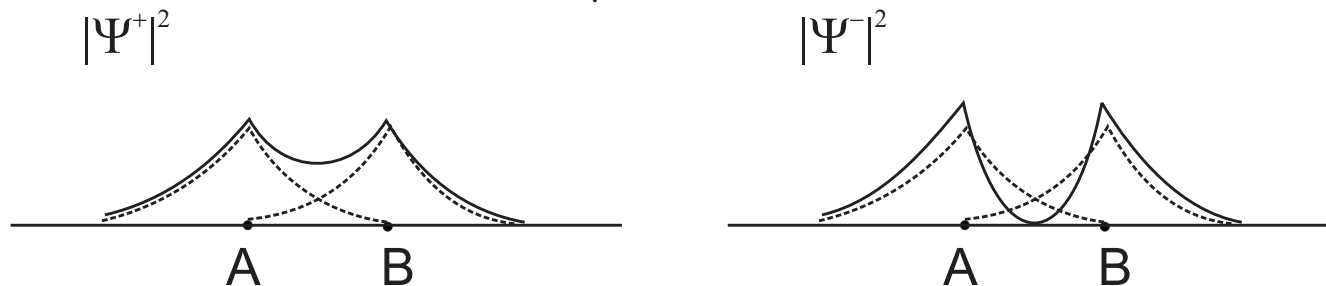
Two molecular wavefunctions are generated from the in-phase and out-of-phase superposition of the two atomic orbitals.

The electron densities for the two states can be written

$$\rho^\pm(\mathbf{r}) = |\psi_e^\pm|^2 = \frac{\phi_A^2 + \phi_B^2 \pm 2\phi_A\phi_B}{2(1 \pm S_{AB})}$$

$\frac{(\phi_A^2 + \phi_B^2)}{2}$ — the sum of atomic electron densities.

$\phi_A\phi_B$ — large where the orbitals overlap.



In ψ_e^+ the electron density is focussed between the nuclei (and reduced elsewhere by $(1 + S_{AB})$).

In ψ_e^- the electron density is reduced between the nuclei (and increased elsewhere by $(1 - S_{AB})$).

Orbital energies

The molecular orbital energies can be obtained by evaluating the expression

$$\langle E_e^\pm \rangle \equiv E_e^\pm(R) = \langle \Psi_e^\pm | \hat{H}_e | \Psi_e^\pm \rangle.$$

Substituting for the wavefunctions yields

$$E_e^\pm(R) = \frac{H_{AA} \pm H_{AB} \pm H_{BA} + H_{BB}}{2(1 \pm S_{AB})},$$

where we have defined the integrals

$$H_{ij} = \int \phi_i \hat{H} \phi_j \, d\mathbf{r}.$$

Because ϕ_A and ϕ_B are identical $1s$ orbitals,

$$H_{AA} = H_{BB} \quad \text{and} \quad H_{AB} = H_{BA}.$$

Therefore, the energy reduces to

$$E_e^\pm(R) = \frac{H_{AA} \pm H_{AB}}{(1 \pm S_{AB})}.$$

Cont.

Let's look at the integrals more closely:

$$H_{AA} =$$

$$\int \phi_A \left[\hat{T}_e - \frac{1}{r_A} \right] \phi_A d\mathbf{r} \quad \epsilon_{1s}$$

Coulomb integral

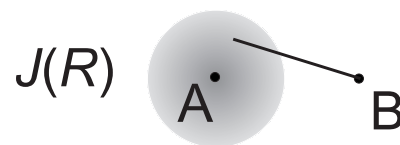
1s orbital energy of H atom A

$$+ \int \phi_A \left[-\frac{1}{r_B} \right] \phi_A d\mathbf{r} \quad J(R)$$

attraction of 1s electron density on A to the B nucleus

$$+ \int \phi_A \left[\frac{1}{R} \right] \phi_A d\mathbf{r} \quad \frac{1}{R}$$

Coulomb repulsion between nuclei



Note that $J(R)$ is negative.

So

$$H_{AA} = H_{BB} = \epsilon_{1s} + \frac{1}{R} + J(R)$$

H_{AA} can be thought of as the energy of the electron localized on A in the presence of B.

Similarly

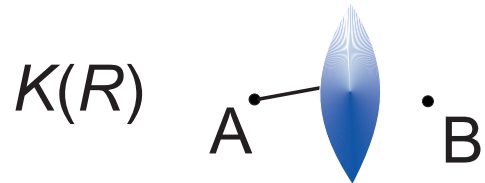
$$H_{AB} =$$

Resonance integral

$$\int \phi_A \left[\hat{T}_e - \frac{1}{r_B} \right] \phi_B \mathrm{d}\mathbf{r} \quad \epsilon_{1s} S_{AB}$$

$$+ \int \phi_A \left[-\frac{1}{r_A} \right] \phi_B \mathrm{d}\mathbf{r} \quad K(R) \quad \text{attraction of overlap density to nucleus A}$$

$$+ \int \phi_A \left[\frac{1}{R} \right] \phi_B \mathrm{d}\mathbf{r} \quad \frac{1}{R} S_{AB}$$



$K(R)$ is also negative.

So

$$H_{AB} = H_{BA} = S_{AB} \left(\epsilon_{1s} + \frac{1}{R} \right) + K(R)$$

There is no classical equivalent to $K(R)$.

Cont.

Adding up the terms yields

$$E_e^\pm(R) = \epsilon_{1s} + \frac{1}{R} + \frac{J \pm K}{1 \pm S_{AB}} .$$

The integrals are performed explicitly in Green QM2

$$S_{AB}(R) = e^{-R} \left(1 + R + \frac{R^2}{3} \right)$$

$$J(R) = - \left[\frac{1}{R} - e^{-2R} \left(1 + \frac{1}{R} \right) \right]$$

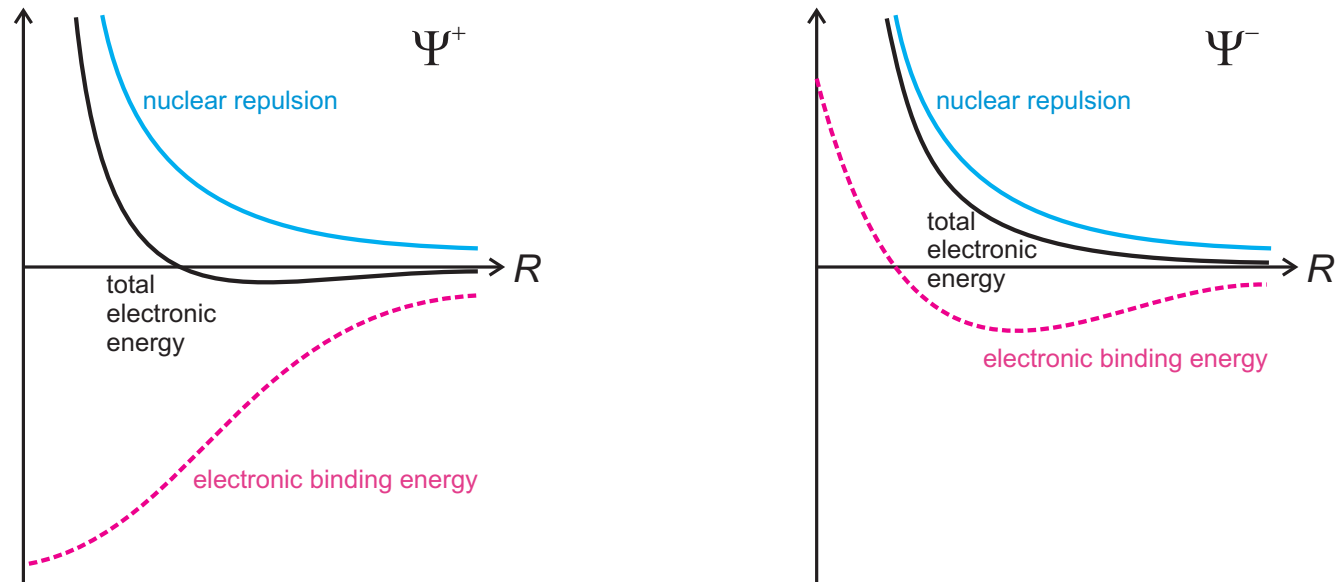
$$K(R) = -e^{-R} (1 + R)$$

In terms of bonding $K(R)$ must dominate.

Contributions to bonding ...

$$E_e^\pm(R) = \epsilon_{1s} + \frac{1}{R} + \frac{J \pm K}{1 \pm S_{AB}} .$$

In terms of bonding $K(R)$ must dominate.



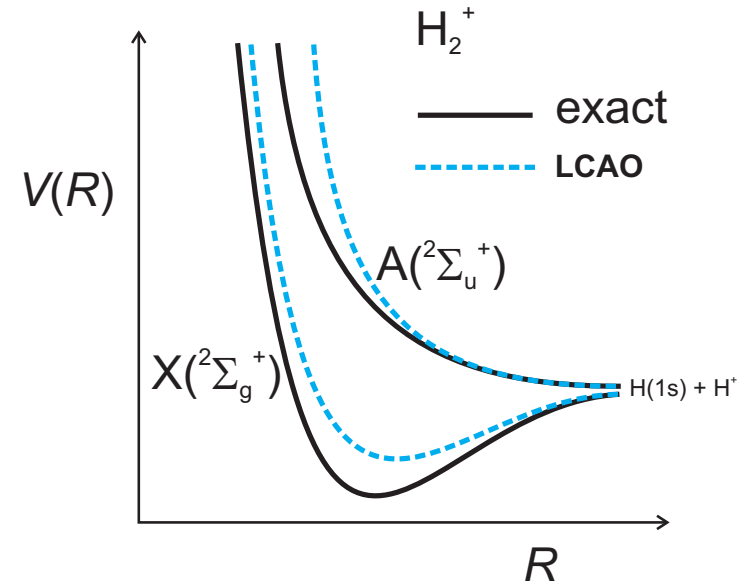
The $1 \pm S_{AB}$ term in E_e^\pm ensures that antibonding orbitals are more antibonding than bonding orbitals are bonding.

How bad is the LCAO approximation?

Compare with the exact solution (within the Born-Oppenheimer approximation) for H_2^+ .

$\sim 8\%$ error in R_e

$\sim 46\%$ error in D_e (for the ground electronic state)



Provides a qualitative guide to the nature of the binding and order of the electronic states.

Improve by increasing the number of basis functions in Ψ_e , e.g., write

$$\Psi_e = c_1\phi_{1s_A} + c_2\phi_{1s_B} + c_3\phi_{2s_A} + c_4\phi_{2s_B} + c_5\phi_{2p_{z_A}} + \dots$$

Optimize the coefficients, c_i , using the *variation principle* to *minimize* the energy. This would give the exact result in the limit of an infinite (or *complete*) basis set of orbitals.

In addition, one can also improve the basis functions themselves,

$$\phi_{1s} = e^{-\xi r}.$$

Again, ξ can be optimized to minimize the energy.

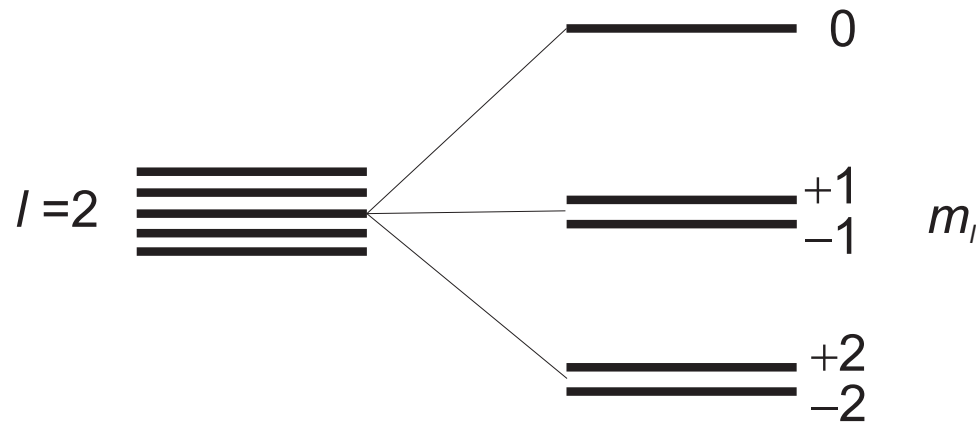
3: Many electrons

Orbital symmetries

Atomic orbitals are labelled according to the principal quantum number, n , and the orbital angular momentum quantum number, l .

Electrons in a diatomic molecule experience a cylindrically symmetric electric field.

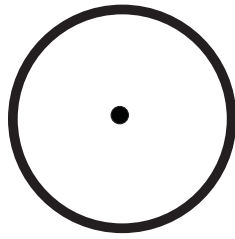
This leads to a **Stark splitting** of the atomic l states into components with $m_l = 0$ and $m_l = \pm 1$, etc., where m_l is the *component* of l along the symmetry axis of the field (the bond axis).



Cont.

The symmetries of the orbitals in diatomic molecules are labelled by the magnitude of the **component of the angular momentum along the internuclear axis, $\lambda\hbar$** .

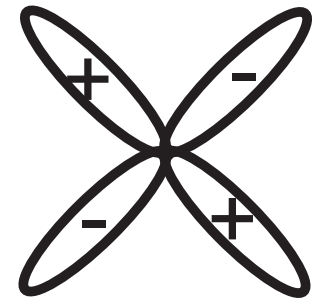
Looking down the symmetry axis



$$|\lambda| = 0 (\sigma)$$



$$|\lambda| = 1 (\pi)$$



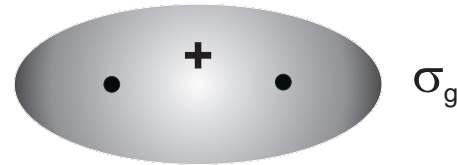
$$|\lambda| = 2 (\delta)$$

(cf. particle on a ring - see Problem sheet 2, question 3)

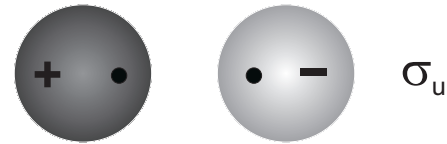
Cont.

For H_2^+

ψ_e^+ is the $1\sigma_g$ orbital



ψ_e^- is the $1\sigma_u$ orbital



The '1' indicates that ψ_e^+ is the lowest orbital of that symmetry.

The g and u symmetry labels refer to the **inversion symmetry**, \hat{I} , with respect to the molecular frame

$$\hat{I}\psi_e(x, y, z) = \pm\psi_e(-x, -y, -z)$$



The orbital approximation

Treat many electron molecules in same way as many electron atoms.

Define a molecular orbital (MO) as a one-electron wavefunction in a molecule.

In some cases these MO's may be constructed from eigenfunctions of some effective one-electron Hamiltonian.

Write the total wavefunction in the many electron case as a product of one electron MOs

$$\Psi_{\text{tot}}(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = (\phi_a(\mathbf{r}_1)\phi_b(\mathbf{r}_2) \dots \phi_n(\mathbf{r}_N))_{\text{space}} \times [\Phi(1)\Phi(2) \dots \Phi(N)]_{\text{spin}} .$$

Here, the ϕ_i are the molecular orbitals (e.g., the $1\sigma_g$ orbital of H_2^+ just discussed).

The total wavefunction is associated with a particular electron configuration.

Ψ_{tot} is a product of a *spatial wavefunction* (which describes where the electrons are) and a *spin part* (which tells us whether the spin of each electron is 'up' or 'down').

Pauli exclusion principle

The total wavefunction must be constructed so that it satisfies the Pauli exclusion principle.

It must be *antisymmetric* with respect to exchange of any two identical electrons.

For example, the ground state of the H₂ molecule has an electron configuration 1σ_g². The Pauli principle can only be satisfied if the electron spins are paired. The total wavefunction can be written, approximately

$$\Psi_{\text{tot}}(\mathbf{r}_1, \mathbf{r}_2) = (\phi_{1\sigma_g}(\mathbf{r}_1)\phi_{1\sigma_g}(\mathbf{r}_2)) \times \frac{1}{\sqrt{2}} [\alpha(1)\beta(2) - \alpha(2)\beta(1)] .$$

In this case the spatial wavefunction is symmetric, and the spin function is antisymmetric:

$$\begin{aligned}\Psi_{\text{tot}}(\mathbf{r}_2, \mathbf{r}_1) &= (\phi_{1\sigma_g}(\mathbf{r}_2)\phi_{1\sigma_g}(\mathbf{r}_1)) \times \frac{1}{\sqrt{2}} [\alpha(2)\beta(1) - \alpha(1)\beta(2)] \\ &= \Psi_{\text{space}} \times -\Phi_{\text{spin}} \\ &= -\Psi_{\text{tot}}(\mathbf{r}_1, \mathbf{r}_2)\end{aligned}$$

In general, a total (anti-symmetrized) wavefunction satisfying the Pauli Principle can be constructed using a *Slater* determinant (see Atkins MQM), which generates an antisymmetric sum of product terms in Ψ_{tot} , rather than a single product.

Labelling of molecular states

Recall that molecular *orbitals* are labelled according to $|\lambda|$.

In the many electron case, different electronic states are generated according to how the electrons fill up the available orbitals.

Molecular states are labelled with a term symbol:

$$2S+1|\Lambda|.$$

$|\Lambda|$ is the magnitude of the component of the total electronic orbital angular momentum along the internuclear axis.

The total component of the orbital angular momentum is obtained from the sum

$$\Lambda = \lambda_1 + \lambda_2 + \lambda_3 + \dots$$

S is the total spin angular momentum quantum number, obtained from the *vector sum*

$$S = s_1 + s_2 + s_3 + \dots$$

Note that the spin angular momentum is not coupled to the internuclear axis (*i.e.* is not affected so strongly by the electric field gradient) in the molecule.

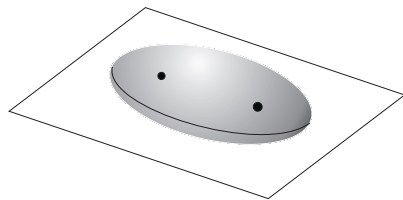
Predictions of the orbital approximation

Ground electronic states

Molecule	Config ⁿ	Term Symbol	No. of bonding e's	$R_e/\text{\AA}$	$D_e/\text{kJ mol}^{-1}$
H_2^+	$(1\sigma_g)^1$	$2\Sigma_g^+$	1	1.06	256
H_2	$(1\sigma_g)^2$	$1\Sigma_g^+$	2	0.74	432
He_2^+	$(1\sigma_g)^2(1\sigma_u)^1$	$2\Sigma_u^+$	1	1.08	300
He_2	$(1\sigma_g)^2(1\sigma_u)^2$	$1\Sigma_g^+$	0	see	below

MO picture provides qualitative rationale for experimental observations.

Note: The electronic states are also labelled according to their inversion symmetry (*i.e.* g/u), and their symmetry ($+/-$) with respect to reflection in the molecular plane see Problem sheet 2, question 3).



σ orbitals, and therefore the states they lead to when occupied, are symmetric with respect to this operation.

Doubly occupied orbitals are also totally symmetric (*i.e.* $(g \times g) = g$, $(u \times u) = g$, $(+ \times +) = +$, and $(- \times -) = +$).

Nature of the orbital approximation

Does the orbital approximation for Ψ_{tot} satisfy the Schrödinger equation?

Look at H_2 ground state again

$$\hat{H}\Psi_{\text{tot}} = \left(\hat{h}_1 + \hat{h}_2 + \frac{1}{r_{12}} \right) \Psi_{\text{space}} \Phi_{\text{spin}} .$$

\hat{h}_i is the Hamiltonian for electron i in H_2^+ , and $1/r_{12}$ is the electron-electron Coulomb repulsion.

The Hamiltonian does not operate directly on the spin function, so we can write

$$\hat{H}\Psi_{\text{space}} = \left(\hat{h}_1 + \hat{h}_2 + \frac{1}{r_{12}} \right) \phi_{1\sigma_g}(\mathbf{r}_1) \phi_{1\sigma_g}(\mathbf{r}_2) .$$

This yields

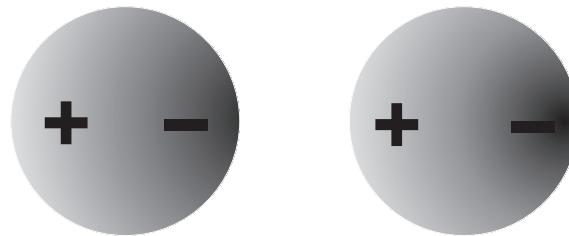
$$\hat{H}\Psi_{\text{space}} = (\epsilon_{1\sigma_g} + \epsilon_{1\sigma_g}) \Psi_{\text{space}} + \frac{1}{r_{12}} \Psi_{\text{space}} .$$

The last term is not a constant $\times \Psi_{\text{space}}$.

Cont.

To allow for this electron-electron repulsion term Ψ_{space} must depend on r_{12} , the electron-electron separation.

The electron positions described by Ψ_{space} must be correlated - the orbital approximation does not allow for this electron correlation.



Note: Some improvements can be made by optimizing the orbitals so as to minimize the *average* inter-electron repulsion using the variation principle.

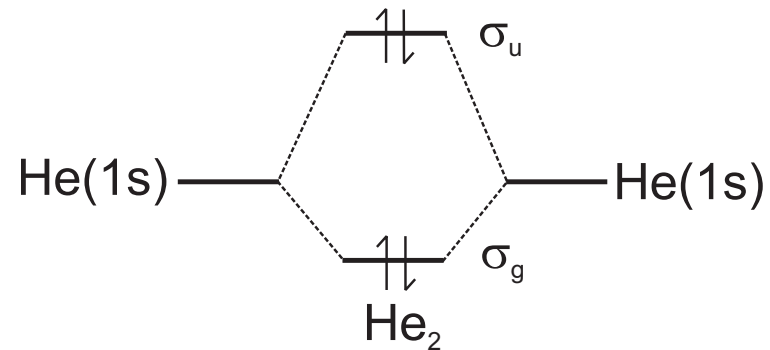
This leads to the *self-consistent field* or *Hartree-Fock* orbitals (see below).

However, these procedures do *not* eliminate problems associated with the neglect of electron correlation.

Consequences of the orbital approximation

A. Dispersion forces

He₂ is predicted to be *unbound* because anti-bonding orbitals are more antibonding than bonding orbitals are bonding.



In reality the electron positions are *correlated*, leading to the **van der Waals (dispersion) interaction**, $V(R) \propto 1/r^6$.

Leads to a binding energy of $\epsilon/k_B \sim 11$ K.

Within the orbital approximation, for example the ground state of H₂ is represented

$$P(\mathbf{r}_1, \mathbf{r}_2) = |\Psi_e|^2 = P_{1\sigma_g}(\mathbf{r}_1)P_{1\sigma_g}(\mathbf{r}_2)$$

i.e. a product of probabilities. The electron positions are intrinsically independent.

B. Dissociation

Examine the large R behaviour of the electron density in the molecular orbital wavefunction for H_2

$$|\phi_{1\sigma_g}(\mathbf{r}_1)\phi_{1\sigma_g}(\mathbf{r}_2)|^2 \stackrel{R \rightarrow \infty}{\equiv}$$

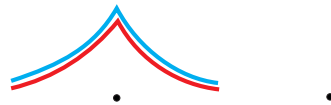
$$|1s_A(\mathbf{r}_1)|^2|1s_B(\mathbf{r}_2)|^2$$



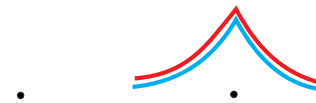
$$+ |1s_B(\mathbf{r}_1)|^2|1s_A(\mathbf{r}_2)|^2$$



$$+ |1s_A(\mathbf{r}_1)|^2|1s_A(\mathbf{r}_2)|^2$$



$$+ |1s_B(\mathbf{r}_1)|^2|1s_B(\mathbf{r}_2)|^2$$



(note that the cross terms vanish as $R \rightarrow \infty$)

i.e. dissociation products are $H + H + H^+ + H^-$, and the estimate of the dissociation energy is very poor.

Valence bond description

An alternative is to write a *valence bond* wavefunctions for the ground electronic state of H₂

$$\Psi_{\text{VB}}(\mathbf{r}_1, \mathbf{r}_2) = N [1s_{\text{A}}(\mathbf{r}_1)1s_{\text{B}}(\mathbf{r}_2) + 1s_{\text{A}}(\mathbf{r}_2)1s_{\text{B}}(\mathbf{r}_1)]$$

This is not an orbital approximation.

This completely removes the ionic terms in the wavefunction, leading to a more accurate description at the dissociation limit.

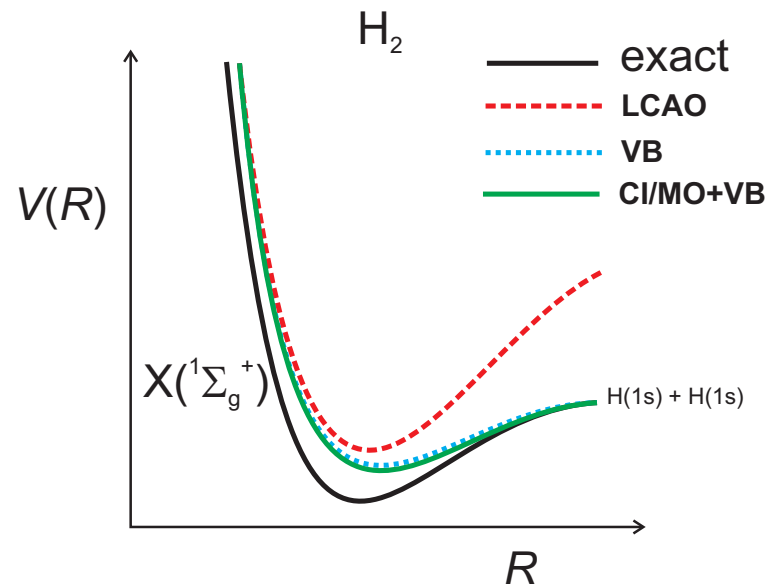
However, the description of the molecule is poor for the same reason: the valence bond wavefunction is *over-correlated*.

Cont.

A better approach is to mix the MO and VB wavefunctions

$$\Psi_e = N(\lambda) [\Psi_{\text{MO}} + \lambda \Psi_{\text{VB}}] ,$$

where λ is optimized, using the variation principle, at each value of R .



In this way the optimum mix of covalent and ionic character can be obtained at each R .

Configuration interaction

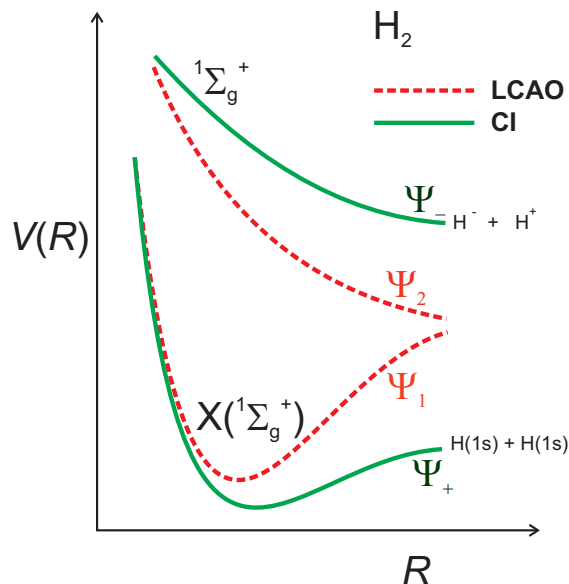
The same wavefunction is obtained using the MO wavefunction with *configuration interaction*.

The configurations $(1\sigma_g)^2$ and $(1\sigma_u)^2$ both lead to electronic states of $^1\Sigma_g^+$ symmetry.

$$\Psi_1 = \phi_{1\sigma_g}(\mathbf{r}_1)\phi_{1\sigma_g}(\mathbf{r}_2)$$

$$\Psi_2 = \phi_{1\sigma_u}(\mathbf{r}_1)\phi_{1\sigma_u}(\mathbf{r}_2)$$

Both of these electronic states correlate to the same $H + H + H^+ + H^-$ products.



Better trial wavefunctions for these two $^1\Sigma_g^+$ states are obtained by mixing the two configurations

$$\Psi_{\pm} = \Psi_1 \pm \lambda' \Psi_2.$$

The optimized ground state wavefunction is the same as that obtained using the mixed valence bond/MO wavefunction. More details can be found in Green QM2.

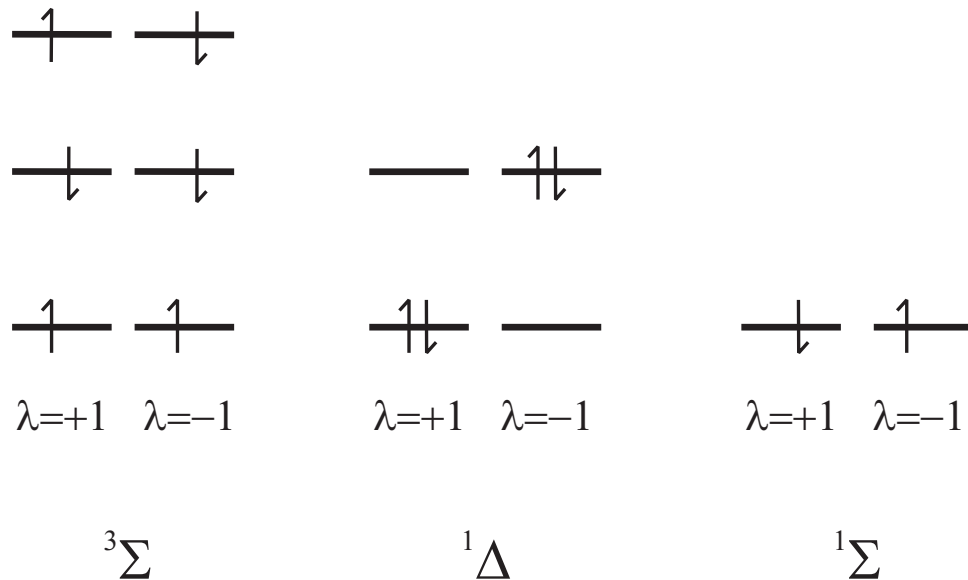
C. Configurations and terms

The orbital approximation predicts that all terms arising from a given configuration will be degenerate.

In reality, they can be split into different terms.

The energy of a configuration is not obtained simply as the sum of the occupied orbital energies!

Consider a $(\pi)^2$ configuration (see later for more discussion of B_2 and O_2). The π orbitals are two-fold degenerate, corresponding to an electron rotating about the bond axis in opposite directions, leading to $m_l = \pm 1$.



In reality, the above arrangements of the two electrons have different energies, because of differences in the *inter-electron repulsion*.

4: Applications of the variation principle

Secular equations

Provides a general route to approximate molecular wavefunctions and orbital energies.

Let Ψ be some trial (approximate) wavefunction. Then, according to the variation principle

$$\langle E \rangle \equiv E = \frac{\langle \Psi | \hat{H} | \Psi \rangle}{\langle \Psi | \Psi \rangle} \geq E_0,$$

where E_0 is the true ground state.

Apply this to LCAO molecular orbitals

$$\Psi = N \sum_{n=1}^m c_n \phi_n,$$

where N is a normalization constant, and c_n is the (real) coefficient for the n th basis function, ϕ_n .

Assume also that the basis functions, ϕ_n , are normalized.

For example, for the first row diatomics the ϕ_n might be the **basis set** comprised of the $1s$, $2s$, $2p_x$, etc. orbitals on each atom.

Introduce simplifying notation

$$\langle \Psi | \Psi \rangle = \int \left(\sum_n c_n \phi_n \right) \left(\sum_m c_m \phi_m \right) d\tau = \sum_{n,m} c_n c_m S_{nm},$$

where the **overlap integral** is defined

$$S_{nm} = \int \phi_n \phi_m d\tau.$$

Note that $S_{nm} = S_{mn}$.

The numerator can be written

$$\langle \Psi | \hat{H} | \Psi \rangle = \int \left(\sum_n c_n \phi_n \right) \hat{H} \left(\sum_m c_m \phi_m \right) d\tau = \sum_{n,m} c_n c_m H_{nm},$$

where the **matrix elements** are defined

$$H_{nm} = \int \phi_n \hat{H} \phi_m d\tau.$$

The Hermitian properties of \hat{H} ensure that $H_{nm} = H_{mn}$.

Cont.

To find the best estimate of E_0 , minimize E with respect to the coefficients, c_k .

$$\frac{\partial E}{\partial c_k} = \frac{1}{\langle \Psi | \Psi \rangle} \frac{\partial \langle \Psi | \hat{H} | \Psi \rangle}{\partial c_k} - \frac{\langle \Psi | \hat{H} | \Psi \rangle}{\langle \Psi | \Psi \rangle^2} \frac{\partial \langle \Psi | \Psi \rangle}{\partial c_k} = 0$$

or

$$\frac{\partial \langle \Psi | \hat{H} | \Psi \rangle}{\partial c_k} - \frac{\langle \Psi | \hat{H} | \Psi \rangle}{\langle \Psi | \Psi \rangle} \frac{\partial \langle \Psi | \Psi \rangle}{\partial c_k} = 0.$$

The partial derivatives can be written explicitly

$$\frac{\partial \langle \Psi | \hat{H} | \Psi \rangle}{\partial c_k} = 2 \sum_m c_m H_{km}$$

and

$$\frac{\partial \langle \Psi | \Psi \rangle}{\partial c_k} = 2 \sum_m c_m S_{km},$$

where the factor of 2 arises from the double summations in $\langle \Psi | \Psi \rangle$ and $\langle \Psi | \hat{H} | \Psi \rangle$.

Therefore

$$\sum_m (H_{km} - ES_{km}) c_m = 0 \quad \text{for all } k = 1 \rightarrow m.$$

In matrix notation this can be written

$$(\mathbf{H} - E\mathbf{S})\mathbf{c} = 0,$$

which are known as the **secular equations**. The non-trivial solutions are given by

$$\det |\mathbf{H} - E\mathbf{S}| = 0.$$

Solution yields a polynomial with m roots, or eigenvalues, i.e. m MO energies, E , the lowest of which is the best estimate of the ground state energy.

Once the eigenvalues, E , are known, the coefficients, c_m , can be calculated by back-substitution into the secular equations. For the lowest root one obtains the best estimate of Ψ_0 .

Illustration for two orbitals

Consider a heteronuclear diatomic molecule, e.g., a simple model of the HOMO of LiH

$$\Psi \approx c_1 \phi_{\text{Li}} + c_2 \phi_{\text{H}},$$

where ϕ_{Li} could be the $2s$ orbital on Li, and ϕ_{H} could be the $1s$ orbital on the H atom.

The secular equation reduces to

$$\begin{pmatrix} H_{11} - E & H_{12} - ES_{12} \\ H_{21} - ES_{21} & H_{22} - E \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix}$$

$H_{11} = \alpha_{\text{A}}$ and $H_{22} = \alpha_{\text{B}}$ are approximately the energies of the $2s$ orbital on Li ($-5 \text{ eV} \cong -\text{I.P. of Li}$) and the $1s$ orbital on H ($-13 \text{ eV} \cong -\text{I.P. of H}$).

$H_{12} = H_{21} = \beta \sim -2 \text{ eV}$ at R_e , known as the resonance integral, is the energy associated with the overlap density.

$S_{12} = S_{21} = S \sim 0.4$ at R_e . Note that $S_{11} = S_{22} = 1$

Solving to get the energy levels.

Multiplying out the secular determinant gives

$$(\alpha_A - E)(\alpha_B - E) - (\beta - ES)^2 = 0,$$

the solution of which is

$$E = \frac{\alpha_A + \alpha_B - 2\beta S \pm \sqrt{(\alpha_A + \alpha_B - 2\beta S)^2 - 4(1 - S^2)(\alpha_A\alpha_B - \beta^2)}}{2(1 - S^2)} \quad (1)$$

To progress further, either

1. Stick the numbers into a computer
2. Set $S = 0$ (provides a useful guide to the general behaviour — see below)
3. **Set $\alpha_A = \alpha_B = \alpha$ and check that we get the homonuclear H_2^+ case.**

Check for the H_2^+ case...

$$E_{\pm} = \frac{\alpha \pm \beta}{1 \pm S}.$$

This equation agrees with that for H_2^+ , when explicit results for α ($= H_{AA}$) and β ($= H_{AB}$) are substituted.

.... and solving to get the wavefunctions.

To get the orbitals substitute back into the secular equations. For example, for the ground state (Ψ_+)

$$\left(\alpha - \frac{\alpha + \beta}{1 + S}\right) c_A + \left(\beta - \frac{(\alpha + \beta)S}{1 + S}\right) c_B = 0,$$

$$\therefore c_A = c_B.$$

Normalization, as before (see p11), leads to

$$c_A = c_B = \frac{1}{[2(1 + S)]^{1/2}},$$

as produced before using symmetry arguments. The same procedure can be used for the other root (i.e. Ψ_-).

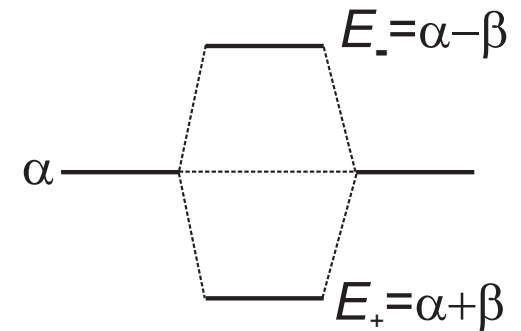
The two orbital case without overlap

Using equation 1, setting $S = 0$

$$E = \frac{1}{2} \left(\alpha_A + \alpha_B \pm \sqrt{(\alpha_A + \alpha_B)^2 - 4(\alpha_A \alpha_B - \beta^2)} \right).$$

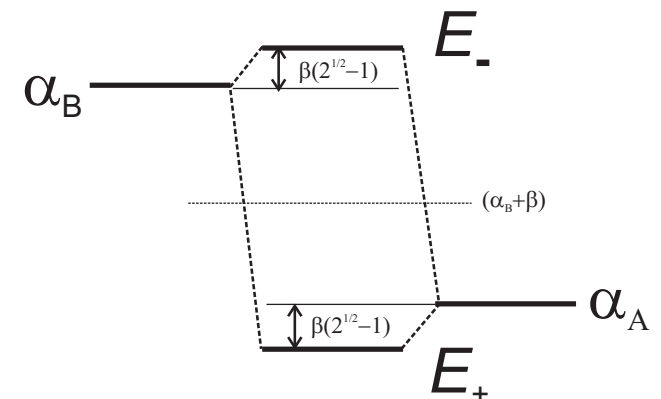
When $\alpha_A = \alpha_B = \alpha$

$$E_{\pm} = \alpha \pm \beta$$



When $\alpha_A \neq \alpha_B$

$$E_{\pm} = \frac{\alpha_A + \alpha_B}{2} \pm \frac{\alpha_A - \alpha_B}{2} \left(1 + \frac{4\beta^2}{(\alpha_A - \alpha_B)^2} \right)^{1/2}$$



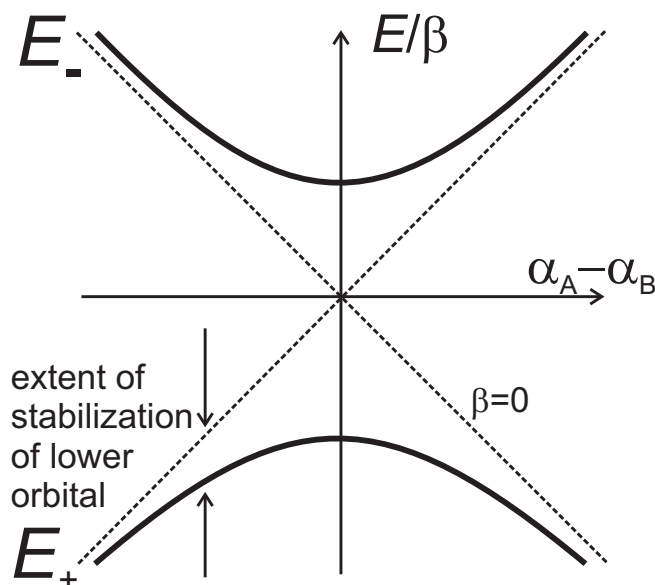
If $|\alpha_A - \alpha_B| = 2|\beta|$

Energies

For small $\beta/|\alpha_A - \alpha_B|$ the energies E_{\pm} can be approximated

$$E_{\pm} = \begin{cases} \alpha_A + \frac{\beta^2}{\alpha_A - \alpha_B} + \dots \\ \alpha_B - \frac{\beta^2}{\alpha_A - \alpha_B} + \dots \end{cases}$$

Plot the MO energies versus $(\alpha_A - \alpha_B)$ at fixed β .



This reveals that atomic orbitals of very different energies do not mix.

Wavefunctions

For $\alpha_A \leq \alpha_B$ (so that orbital of A is lower than that of B), with

$$\psi^+ = c_A^+ \phi_A + c_B^+ \phi_B$$

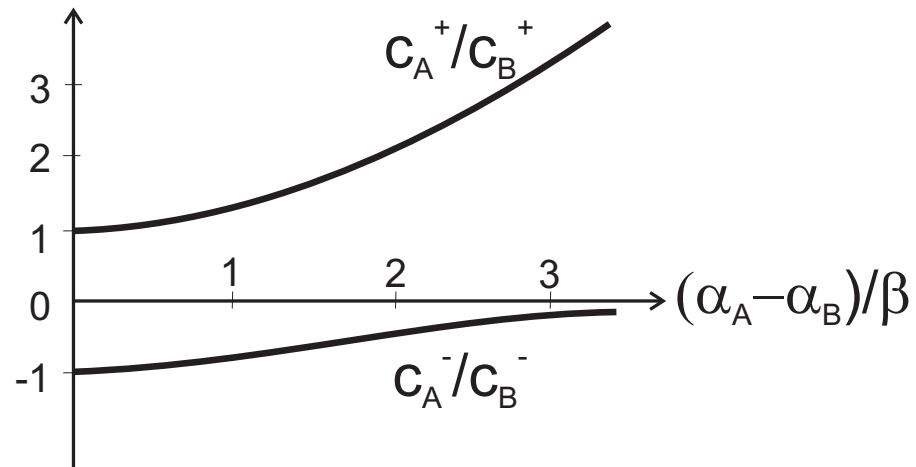
and

$$\psi^- = c_A^- \phi_A + c_B^- \phi_B,$$

then

$$\frac{c_A^+}{c_B^+} = \frac{\sqrt{\Delta^2 + 4\beta^2} + \Delta}{2\beta} \quad \text{with } \Delta = \alpha_A - \alpha_B.$$

For LiH $\Delta/\beta \sim 4$.



5: Bonding in diatomic molecules

General observations

- **Orbitals of different symmetry do not mix**

since

$$H_{ij} = \int \phi_i \hat{H} \phi_j d\tau = \beta = 0$$

$$S_{ij} = \int \phi_i \phi_j d\tau = 0$$

- **Orbitals of very different energies do not mix**

since then Δ/β is large (see above).

- **The non-crossing rule.**

The energies of two states *of the same symmetry* can never be equal (since $\beta \neq 0$ - see later).

First row homonuclear diatomics

Expect the MO's to be made up of combinations of $1s$, $2s$, $2p_x$, $2p_y$, $2p_z$ atomic orbitals (with z lying along the bond).

However,

Rule 1:

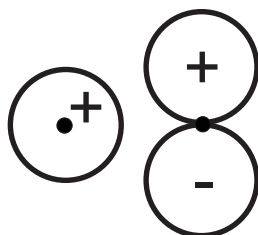
Two atomic orbitals will only both make a large contribution to an MO if their atomic energies are similar.

Ignore mixing of $1s$ with $2s$ and $2p$,

and mixing of $2s$ with $2p_z$ (depending on the $2s$ - $2p$ atomic separation, see below),

Rule 2:

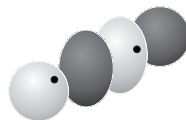
Orbitals on different atoms with zero overlap do not contribute to the same MO.



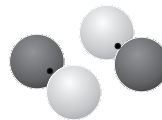
Hence, ignore mixing of $2s_A$, $2p_{z,A}$ with $2p_{x,B}$ and $2p_{y,B}$.

Leads to the following orbitals:

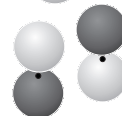
$$3\sigma_u = 2p_{z,A} + 2p_{z,B}$$



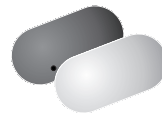
$$1\pi_{y,g} = 2p_{y,A} - 2p_{y,B}$$



$$1\pi_{x,g} = 2p_{x,A} - 2p_{x,B}$$



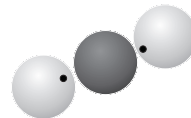
$$1\pi_{y,u} = 2p_{y,A} + 2p_{y,B}$$



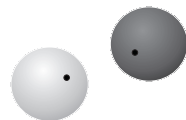
$$1\pi_{x,u} = 2p_{x,A} + 2p_{x,B}$$



$$3\sigma_g = 2p_{z,A} - 2p_{z,B}$$



$$2\sigma_u = 2s_A - 2s_B$$



$$2\sigma_g = 2s_A + 2s_B$$

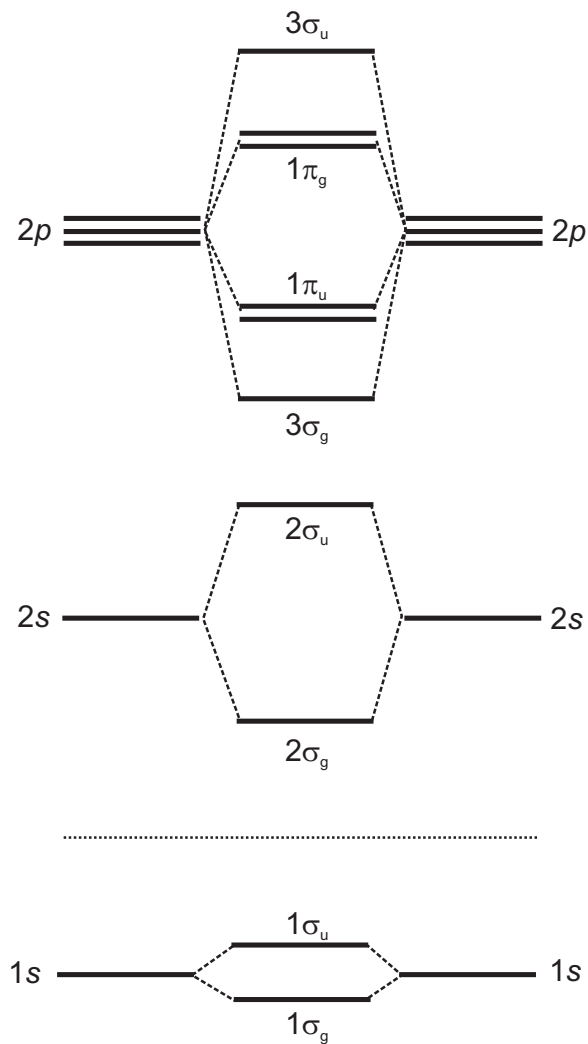


$1s$ overlap is negligible at the optimum bond length for overlap of $2s$ and $2p$.

Expect overlap of $2s$ and $2p_z$ orbitals to decrease less rapidly with R than for the $2p_{x,y}$ orbitals.

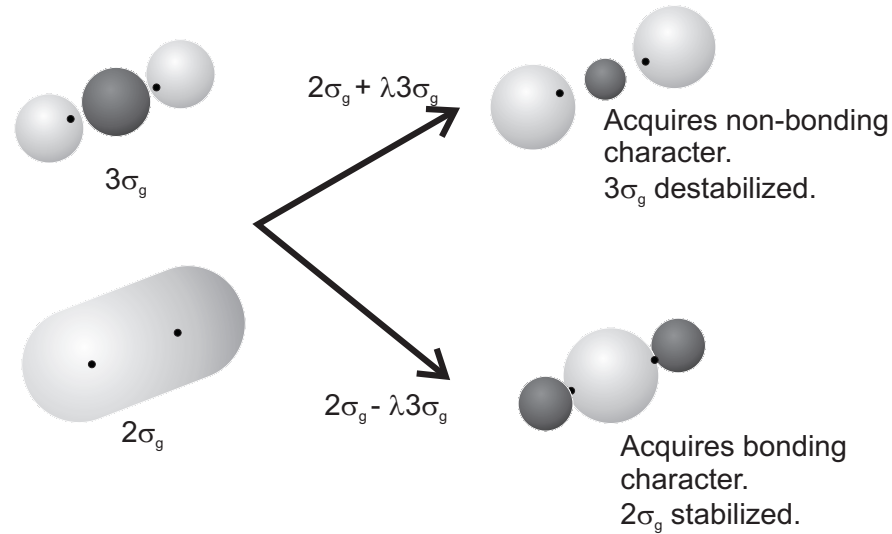
MO diagram for O₂ and upwards

If $2s$ and $2p_z$ energy separation is large (i.e. $E_{2p} - E_{2s} \gg$ bonding interaction) - limit of large penetration - obtain following MO diagram.



Mixing or hybridization of MOs

Mixing of $2\sigma_g$ and $3\sigma_g$, such that



$$\psi_g^- = 2\sigma_g - \lambda 3\sigma_g$$

develops bonding character

$$\psi_g^+ = 3\sigma_g + \lambda 2\sigma_g$$

develops non-bonding character

and

$$\psi_u^- = 2\sigma_u - \lambda 3\sigma_u$$

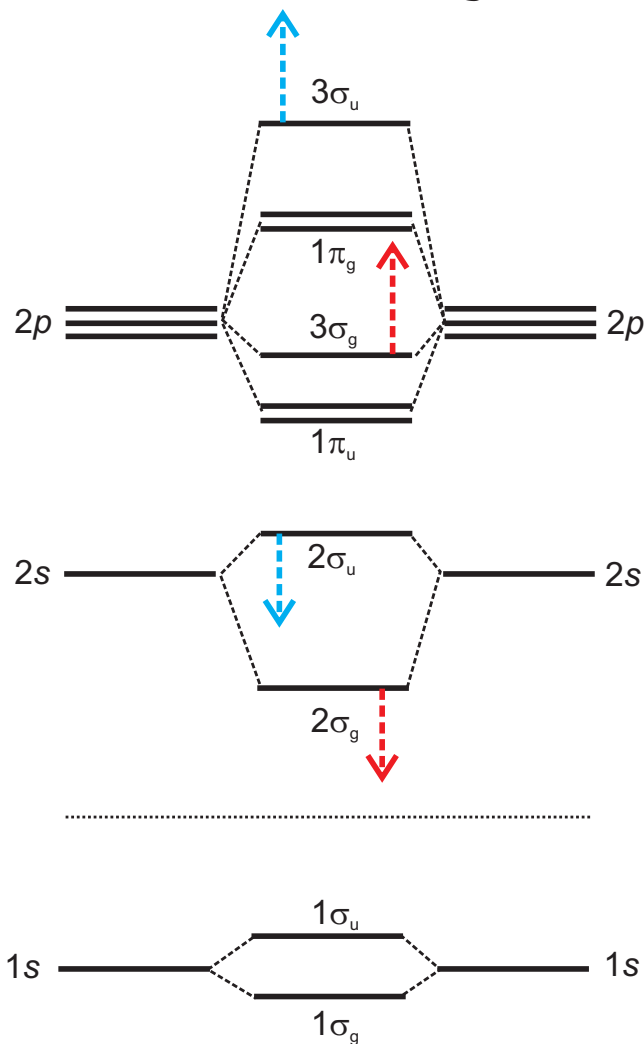
develops non-bonding character

$$\psi_u^+ = 3\sigma_u + \lambda 2\sigma_u$$

develops anti-bonding character

Light atom picture

If $2s$ and $2p_z$ energy separation is small (*i.e.* $E_{2p} - E_{2s} \sim$ bonding interaction) - limit of small penetration - this interaction leads to the 'light atom' MO picture:



An alternative, but equivalent description is to mix, or hybridize, the atomic orbitals before forming bond.

Properties of homonuclear diatomics

	Electron config.	Excess bonding e's	Number unpaired e's	Bond length/ Å	Diss ⁿ energy/ kJ mol ⁻¹	Term Symbol
Li ₂	(2σ _g) ²	2	0	2.67	107	1Σ _g ⁺
Be ₂	(2σ _g) ² (2σ _u) ²	0	0	2.45	9	1Σ _g ⁺
B ₂	[Be](1π _u) ²	2	2	1.59	291	3Σ _g ⁻
C₂	[Be](1π _u) ⁴	4	0	1.24	590	1Σ _g ⁺
N ₂ ⁺	[C](3σ _g) ¹	5	1	1.12	841	2Σ _g ⁺
N ₂	[C](3σ _g) ²	6	0	1.09	942	1Σ _g ⁺
O ₂ ⁺	[N](1π _g) ¹	5	1	1.12	644	2Π _g
O₂	[N](1π _g) ²	4	2	1.21	494	3Σ _g ⁻
F ₂	[N](1π _g) ⁴	2	0	1.44	154	1Σ _g ⁺

Bonding determined by mix of occupied orbitals.

Note: [Be], etc. stands for the ground state electronic configuration of Be₂, etc..

See Problem sheet 2.

Splitting into terms - revisited

	r/pm	ω_e/cm^{-1}	D_e/eV	E^*/eV	I/eV
N_2	110	2359	9.76	6.22	15.58
N_2^+	112	2207	8.71	1.14	
NO	115	1904	6.50	0.015	9.26
NO^+	106	2376	10.84	6.47	
O₂	121	1580	5.12	0.98	12.07
O_2^+	112	1905	6.66	0.024	

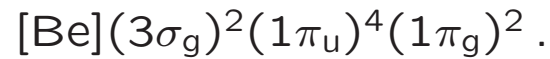
[ω_e is the harmonic vibrational wavenumber, D_e the bond dissociation energy, E^* the energy of the first excited electronic state, and I is the first ionization energy.]

Problem Sheet 2, Question 1

Splitting into terms - revisited

Oxygen

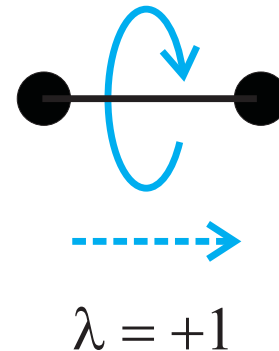
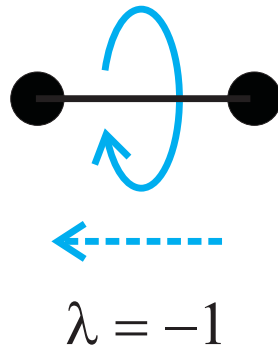
The ground electronic configuration of O_2 is



It is split in energy into three electronic states due to the effects of inter-electron repulsion.

The states arising from the $(\pi_g)^2$ configuration can be worked out as follows:

$$S = s_1 + s_2, s_1 + s_2 - 1, \dots |s_1 - s_2| = 0 \text{ or } 1$$



$$|\Lambda| = |\lambda_1 + \lambda_2|, |\lambda_1 - \lambda_2| = 0 (\Sigma) \text{ or } 2 (\Delta)$$

In principle there will be singlet and triplet Σ and Δ states, but not all of these satisfy the Pauli exclusion principle.

Look at wavefunctions in more detail.

For the Δ state the electrons orbit about the bond in the same direction

$$\Psi_{\Delta} = \pi_{+1}(1)\pi_{+1}(2)\Psi_{\text{spin}}$$

or

$$\Psi_{\Delta} = \pi_{-1}(1)\pi_{-1}(2)\Psi_{\text{spin}}.$$

Exchange of the labels for electrons (1) and (2) tells us that the spatial part of the above wavefunctions are symmetric with respect to exchange of the electrons.

To satisfy the Pauli exclusion principle, the spin functions must be anti-symmetric:

$$\Psi_{\text{spin}} = \frac{1}{\sqrt{2}} [\alpha(1)\beta(2) - \beta(1)\alpha(2)]$$

The only possibility is that the Δ state is a singlet state.

In the case of Σ , both singlet and triplet states are allowed

$$\Psi_{3\Sigma} = \frac{1}{\sqrt{2}} [\pi_{+1}(1)\pi_{-1}(2) - \pi_{-1}(1)\pi_{+1}(2)] \begin{cases} \alpha(1)\alpha(2) \\ \frac{1}{\sqrt{2}}[\alpha(1)\beta(2) + \beta(1)\alpha(2)] \\ \beta(1)\beta(2) \end{cases}$$

$$\Psi_{1\Sigma} = \frac{1}{\sqrt{2}} [\pi_{+1}(1)\pi_{-1}(2) + \pi_{-1}(1)\pi_{+1}(2)] \left\{ \frac{1}{\sqrt{2}}[\alpha(1)\beta(2) - \beta(1)\alpha(2)] \right\}$$

The full term symbols are $^3\Sigma_g^-$, $^1\Delta_g$, and $^1\Sigma_g^+$.

Symmetry (direct product) tables can also be used to work most of this out

$$\pi \times \pi = \Sigma^+ + [\Sigma^-] + \Delta$$

The square brackets indicate that the spatial wavefunction for the Σ^- state is *antisymmetric* with respect to electron exchange.

The $+/-$ reflection symmetry label is determined using the procedures illustrated in problem sheet 2, question 3.

Energy ordering of the states

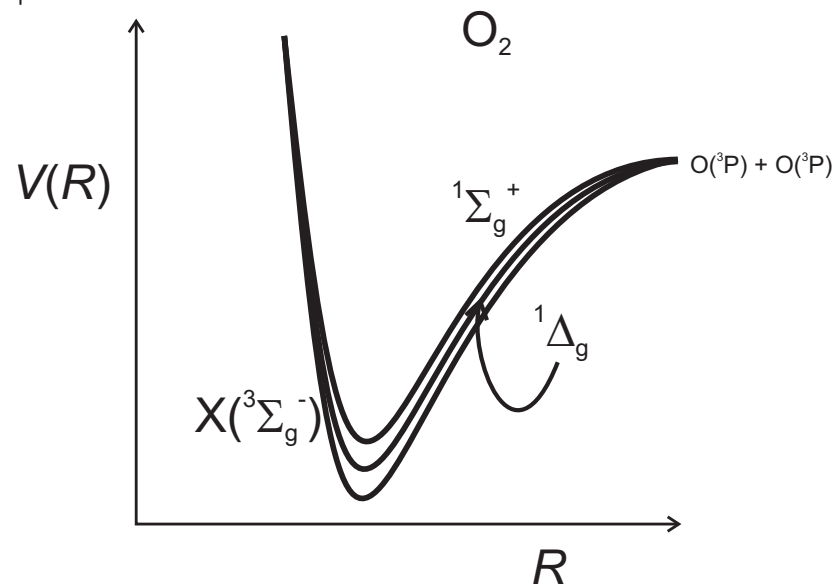
The relative energies of the states can be worked out by applying *Hund's rules*, although the latter were really devised for atoms.

The triplet state is lowest because of the formation of a **Fermi hole** in the triplet state. Notice that the spatial part of the wavefunction is zero when the coordinates of the two unpaired electrons are the same,

$$\psi_{3\Sigma \text{ space}} = \frac{1}{\sqrt{2}} [\pi_{+1}(1)\pi_{-1}(2) - \pi_{-1}(1)\pi_{+1}(2)] .$$

This spatial wavefunction therefore gives rise to reduced repulsion between the unpaired electrons. This effect is known as **spin-correlation**.

The $^1\Delta$ state lies lower than $^1\Sigma$ because the electrons are able to avoid one another more in a state of high $|\Lambda|$.



Splitting into terms - continued

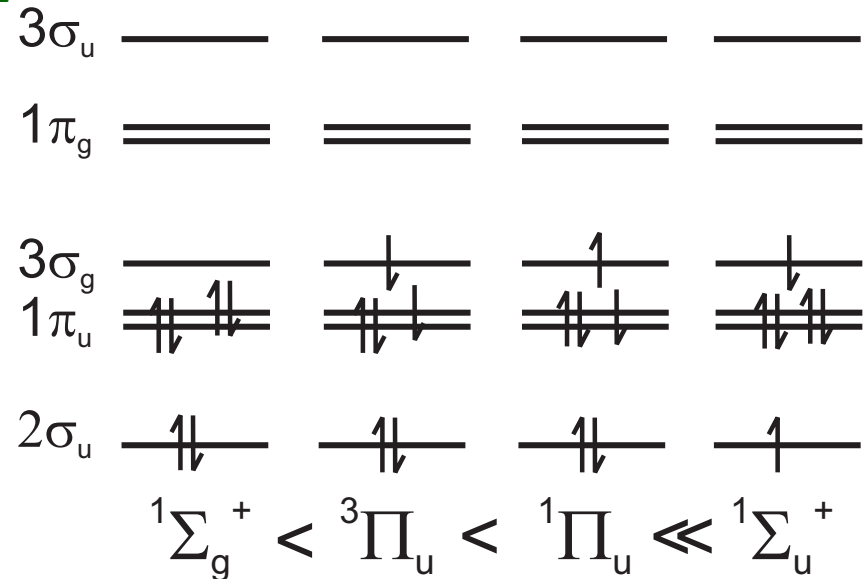
The low lying electronic states of C_2

Term symbol	Energy/ cm^{-1}	Vibrational frequency/ cm^{-1}	Bondlength/ \AA
$1\Sigma_g^+$	0	1856	1.242
$3\Pi_u$	610	1641	1.311
$1\Pi_u$	8392	1608	1.318
$1\Sigma_u^+$	43240	1830	1.238

Problem Sheet 2, Question 2

Splitting into terms - continued

Low lying states of C_2



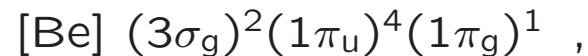
Things to note:

- The ${}^3\Pi_u$ and ${}^1\Pi_u$ states have similar properties (same electron configuration);
- The energy separation between the ${}^3\Pi_u$ and ${}^1\Pi_u$ states reflect the spin correlation energy (Fermi hole and Fermi heap);
- The ${}^1\Sigma_u^+$ state lies very high in energy;
- The ground ${}^1\Sigma_g^+$ and excited ${}^1\Sigma_u^+$ states have similar properties (suggesting that the σ_g orbitals are largely non-bonding in character);
- The ground ${}^1\Sigma_g^+$ and excited ${}^3\Pi_u$ states are very close in energy (due to the small gap between the $1\pi_u$ and $3\sigma_g$ and the reduced electron repulsion in the triplet state).

Splitting into terms - continued

NO and O_2^+

The ground state electronic configuration of NO (and O_2^+) is (*nb.*, for NO drop the g/u labels)



leading to a ${}^2\Pi$ term (*i.e.* $S = 1/2$, $|\Lambda| = 1$).

This state is split into two levels by the **spin-orbit** interaction:



The coupling arises from the coupling between intrinsic magnetic moment of the electron and that generated by the orbital motion of the electron.

Label states according to the full term symbol:

$$2S+1|\Lambda||\Omega| ,$$

where

$$\Omega = \Lambda + \Sigma .$$

Ω is the component of the total electronic angular momentum along the inter-nuclear axis. Each spin-orbit state is therefore two-fold degenerate.

For NO we have ${}^2\Pi_{3/2}$ or ${}^2\Pi_{1/2}$ spin-orbit states. The $|\Omega| = 1/2$ state is the lowest in energy because the molecular orbital is less than half full (Hund's 3rd rule).

6: The shapes of polyatomic molecules

Symmetry adapted linear combinations (SALCs)

AH₂ at linearity.



For 1st row element A, the valence MO's will involve $2s_A$, $2p_{x,A}$, $2p_{y,A}$, $2p_{z,A}$ and two $1s$ orbitals on the H atoms.

Only orbitals of the same symmetry mix. In $D_{\infty h}$ it's easy to write down the symmetry of the $2s$ and $2p$ orbitals of A (see below).

$1s$ orbitals of H have no symmetry in the $D_{\infty h}$ point group.

Take linear combination of H $1s$ functions to 'symmetrize' the H atom $1s$ basis functions:


$$\phi(\sigma_g) = 1s_1 + 1s_2$$

$$\phi(\sigma_u) = 1s_1 - 1s_2$$

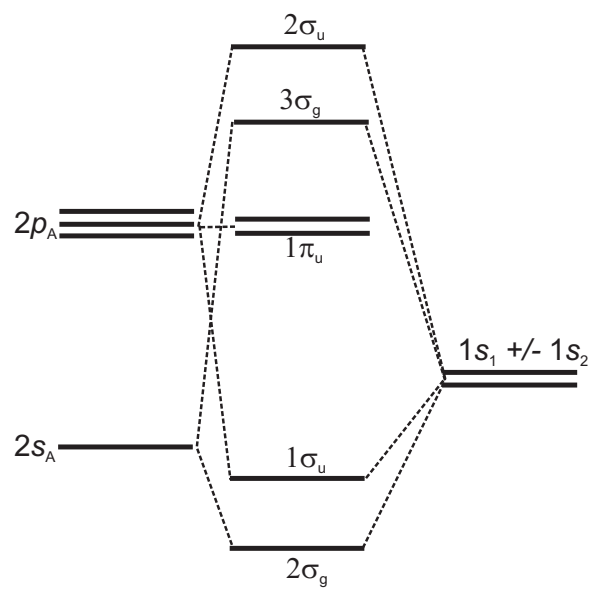
See butadiene example later.

MO diagram for AH₂ molecules

At linearity ($D_{\infty h}$) the atomic orbitals have the symmetries

$2s_A$	σ_g	$\cdot \circ \cdot$
$2p_{x,A}, 2p_{y,A}$	π_u	
$2p_{zA}$	σ_u	$\cdot \circ \bullet$
$(1s_1 - 1s_2)$	σ_u	$\circ \cdot \bullet$
$(1s_1 + 1s_2)$	σ_g	$\circ \cdot \circ$

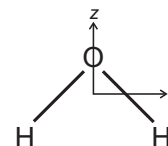
Expect:



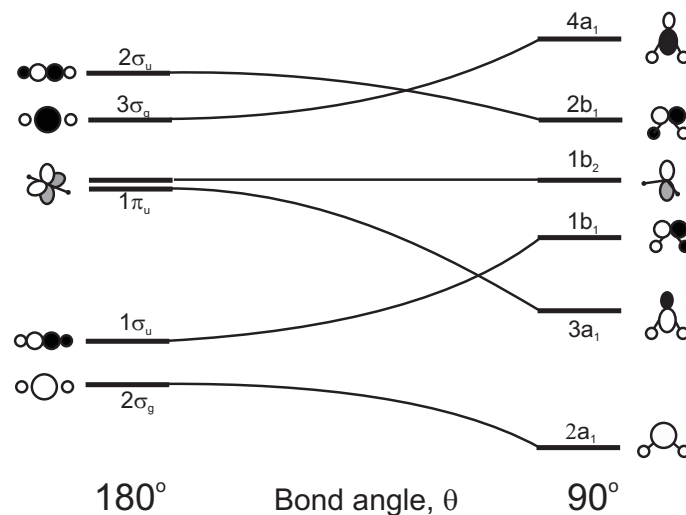
Walsh diagram for AH₂ molecules

What happens to the MO diagram on bending?

Symmetry is lowered from $D_{\infty h}$ to C_{2v} .



Descent in symmetry tables can be used to work out how the orbital symmetries in C_{2v} .



- $2a_1$ Stabilized because of weak bonding H—H interaction, and mixing with $2p_z$.
- $1b_1$ Destabilized because of reduction in overlap, and antibonding H—H interaction.
- $3a_1(p_z)$ Strongly stabilized by mixing with $4a_1$ ($3\sigma_g$) - mixing strong because close in energy.
- $1b_2(p_y)$ Remains non-bonding

Predicted bond angles for AH₂ molecules

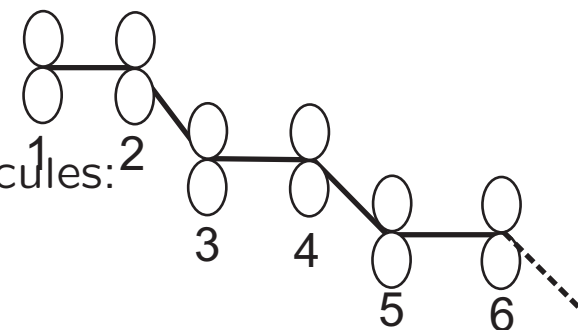
Molecule	Config.	θ	
BeH ₂	$(2a_1)^2(1b_1)^2$	180°	
BH ₂	$(2a_1)^2(1b_1)^2(3a_1)^1$	131°	
CH ₂	$(2a_1)^2(1b_1)^2(3a_1)^1(1b_2)^1$	136°	Triplet
NH ₂	$(2a_1)^2(1b_1)^2(3a_1)^2(1b_2)^1$	103°	
H ₂ O	$(2a_1)^2(1b_1)^2(3a_1)^2(1b_2)^2$	105°	

See Photochemistry lecture course next year for applications to excited electronic states of AH₂ molecules.

7: Hückel theory for polyatomic molecules

Introduction

Approximate treatment of π electron systems in organic molecules:



Approximations

1. π and σ frameworks completely separated

2. Trial wavefunctions can be used of the form:
$$\Psi = \sum_i c_i p_i^\pi$$

3. $H_{ii} = \langle p_i | \hat{H} | p_i \rangle = \alpha$ same for all atoms

4. $H_{ij} = \langle p_i | \hat{H} | p_j \rangle = \beta$ i bonded to j
 $= 0$ otherwise.

Note that β is negative.

5. $S_{ij} = \langle p_i | p_j \rangle = \delta_{ij}$,

where $\delta_{ij} = 1$ when $i = j$ and $\delta_{ij} = 0$ when $i \neq j$.

Ethene

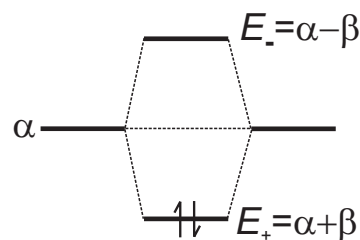
Optimize orbital coefficients as before using the variation principle.

Know already that this leads to secular equations

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

So the energies are the solutions of the secular determinant

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



Wavefunctions obtained by substituting the energies E_{\pm} back into secular equation:

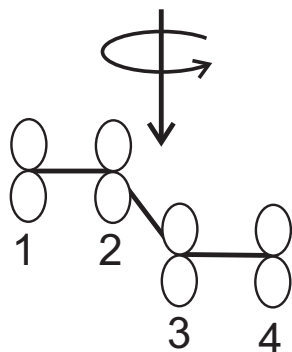
$$\Psi_{\pm} = \frac{1}{\sqrt{2}} (p_1 \pm p_2)$$

Thus, with respect to two non-bonded p^{π} electrons, ethene has a π stabilization energy of 2β (i.e., β for each electron).

See Sheet 2, question 1 for a problem involving the allyl radical.

Butadiene

There is nothing in Hückel theory that distinguishes *cis*- from *trans*-, or indeed linear, butadiene.



As before, the trial wavefunction,

$$\Psi = c_1p_1 + c_2p_2 + c_3p_3 + c_4p_4 ,$$

is optimized using the variation principle. The secular equation can be written down directly

$$\begin{pmatrix} \alpha - E & \beta & 0 & 0 \\ \beta & \alpha - E & \beta & 0 \\ 0 & \beta & \alpha - E & \beta \\ 0 & 0 & \beta & \alpha - E \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \\ c_3 \\ c_4 \end{pmatrix} = 0 .$$

Multiplying out this leads to a quartic equation. Although this can be solved, here we will use of symmetry to simplify the algebra.

cont.

Butadiene has a two-fold symmetry axis. Form symmetry adapted linear combinations (SALCs) of atomic orbitals

$$\begin{aligned}\chi_1 &= \frac{1}{\sqrt{2}}(p_1 + p_4) & \chi_2 &= \frac{1}{\sqrt{2}}(p_2 + p_3) \\ \chi_3 &= \frac{1}{\sqrt{2}}(p_2 - p_3) & \chi_4 &= \frac{1}{\sqrt{2}}(p_1 - p_4)\end{aligned}$$

χ_1 and χ_2 are symmetric (A), and χ_3 and χ_4 are antisymmetric (B) with respect to the C_2 operation.

Let

$$\Psi = c_1\chi_1 + c_2\chi_2 + c_3\chi_3 + c_4\chi_4$$

H_{ij} and S_{ij} **vanish** if i and j are of different symmetry:

$$\left(\begin{array}{cc|cc} \alpha - E & \beta & 0 & 0 \\ \beta & \alpha + \beta - E & 0 & 0 \\ \hline 0 & 0 & \alpha - \beta - E & \beta \\ 0 & 0 & \beta & \alpha - E \end{array} \right) \begin{pmatrix} c_1 \\ c_2 \\ c_3 \\ c_4 \end{pmatrix} = 0.$$

Matrix becomes block diagonal.

cont.

Look at some of the **matrix elements**

$$\begin{aligned} H_{11} &= \langle \chi_1 | \hat{H} | \chi_1 \rangle = \langle \frac{1}{\sqrt{2}}(p_1 + p_4) | \hat{H} | \frac{1}{\sqrt{2}}(p_1 + p_4) \rangle \\ &= \frac{1}{2} \left\{ \underbrace{\langle p_1 | \hat{H} | p_1 \rangle}_{\alpha} + \underbrace{\langle p_4 | \hat{H} | p_4 \rangle}_{\alpha} + \underbrace{\langle p_1 | \hat{H} | p_4 \rangle}_{0} + \underbrace{\langle p_4 | \hat{H} | p_1 \rangle}_{0} \right\} \\ &= \alpha \end{aligned}$$

$$\begin{aligned} H_{14} &= \langle \chi_1 | \hat{H} | \chi_4 \rangle = \langle \frac{1}{\sqrt{2}}(p_1 + p_4) | \hat{H} | \frac{1}{\sqrt{2}}(p_1 - p_4) \rangle \\ &= \frac{1}{2} \left\{ \underbrace{\langle p_1 | \hat{H} | p_1 \rangle}_{\alpha} - \underbrace{\langle p_4 | \hat{H} | p_4 \rangle}_{\alpha} - \underbrace{\langle p_1 | \hat{H} | p_4 \rangle}_{0} + \underbrace{\langle p_4 | \hat{H} | p_1 \rangle}_{0} \right\} \\ &= 0 \end{aligned}$$

$$\begin{aligned} H_{33} &= \langle \chi_3 | \hat{H} | \chi_3 \rangle = \langle \frac{1}{\sqrt{2}}(p_2 - p_3) | \hat{H} | \frac{1}{\sqrt{2}}(p_2 - p_3) \rangle \\ &= \frac{1}{2} \left\{ \underbrace{\langle p_2 | \hat{H} | p_2 \rangle}_{\alpha} + \underbrace{\langle p_3 | \hat{H} | p_3 \rangle}_{\alpha} - \underbrace{\langle p_2 | \hat{H} | p_3 \rangle}_{\beta} - \underbrace{\langle p_3 | \hat{H} | p_2 \rangle}_{\beta} \right\} \\ &= \alpha - \beta \end{aligned}$$

Note that, as before, the overlap integrals in the SALC basis are

$$S_{ij} = \delta_{ij}$$

cont.

Now solve the upper 2×2 determinant.

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

$$E_{\pm} = \alpha + \frac{1 \pm \sqrt{5}}{2} \beta$$

$$E_1 = \alpha + 1.62\beta \quad E_3 = \alpha - 0.62\beta$$

To get molecular orbital corresponding to E_1 substitute E_1 into secular equations

$$-1.62\beta c_1 + \beta c_2 = 0$$

$$c_1 = \frac{c_2}{1.62}$$

cont.

But wavefunction needs to be normalized

$$\psi_1 = N \left[\frac{1}{\sqrt{2}}(p_1 + p_4) + 1.62 \frac{1}{\sqrt{2}}(p_2 + p_3) \right]$$

$$\langle \psi_1 | \psi_1 \rangle = N^2 \left[\frac{1}{2} + \frac{1}{2} + \frac{1.62^2}{2} + \frac{1.62^2}{2} \right] = 1$$

So

$$\psi_1 = 0.37p_1 + 0.60p_2 + 0.60p_3 + 0.37p_4$$

Similarly, find MO ψ_3 associated with energy level E_3

$$\psi_3 = 0.60p_1 - 0.37p_2 - 0.37p_3 + 0.60p_4$$

cont.

From the lower 2×2 determinant one obtains

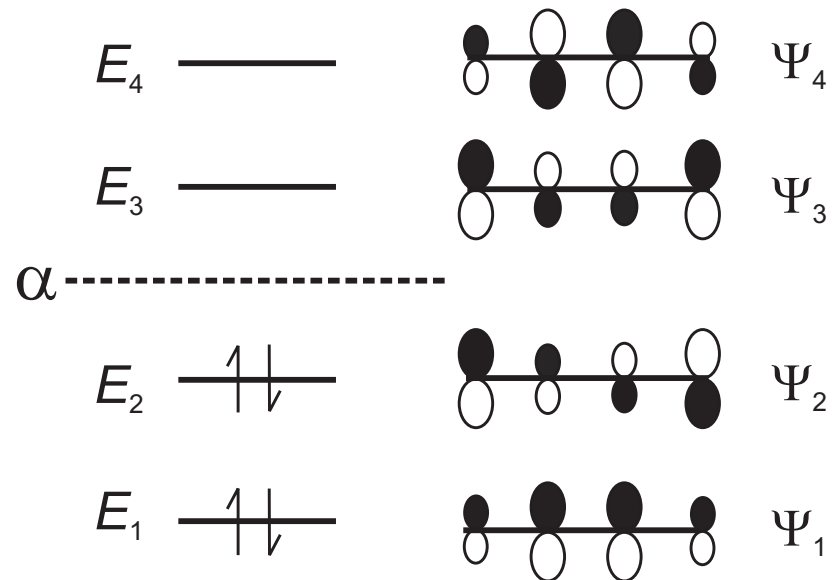
$$E_2 = \alpha + 0.62\beta \quad E_4 = \alpha - 1.62\beta$$

with the normalized wavefunctions

$$\Psi_2 = 0.60p_1 + 0.37p_2 - 0.37p_3 - 0.60p_4$$

and

$$\Psi_4 = 0.37p_1 - 0.60p_2 + 0.60p_3 - 0.37p_4$$



Charge density on atoms

Once the wavefunctions of the MOs are known the charge densities on each atom, q_i , can be obtained from

$$q_i = \sum_k n_k (c_i^k)^2,$$

where the sum over k is over all occupied molecular orbitals, and n_k is the occupation number of MO k (either 0, 1 or 2 for non-degenerate orbitals).

$(c_i^k)^2$ is the square of the coefficient in the k th orbital on the i th atom.

For butadiene, this reads (for atoms 1 and 2)

$$q_1 = 0.37^2 \times 2 + 0.60^2 \times 2 = 1$$

$$q_2 = 0.60^2 \times 2 + 0.37^2 \times 2 = 1$$

and similarly for atoms 3 and 4.

That the charge densities on all the atoms are equal is a general property of the ground states of **alternant hydrocarbons**.

These also have a **pairing of the MO energies** $E = \alpha \pm x\beta$.

See MKT for more details.

Resonance stabilization energy

In Hückel theory the resonance stabilization energy provides an indication of the increased molecular stability that arises from π bonding.

For the ground electronic state of butadiene the total electronic energy is

$$E_{\text{tot}} = 2(\alpha + 1.62\beta) + 2(\alpha + 0.62\beta) = 4\alpha + 4.48\beta$$

Thus the **resonance stabilization energy** is

$$\Delta E = E_{\text{tot}} - 4\alpha = 4.48\beta$$

This stabilization can be compared with that of 4β that would be generated from two isolated π bonds (*i.e.* in two isolated ethene molecules).

$$\Delta E_{\text{deloc}} = \Delta E - 4\beta = 0.48\beta.$$

This energy provides a measure of the **delocalization energy**, the extra stabilization that arises from delocalization of the electrons over the π system.

Bond order

Provides an indication of the strength of the π bond between adjacent atoms i and j

$$\rho_{ij} = \sum_k n_k c_i^k c_j^k.$$

The sum is over MO's k , with n_k the occupation number of those orbitals. For butadiene

$$\rho_{12} = 2(0.37 \times 0.60) + 2(0.60 \times 0.37) = 0.89$$

$$\rho_{23} = 2(0.60 \times 0.60) + 2(0.37 \times -0.37) = 0.45$$

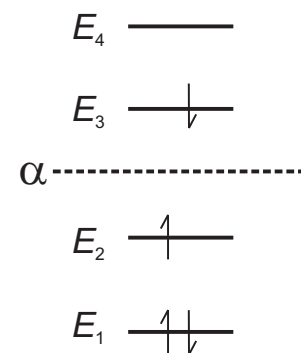
Suggests a partial π bond between the central atoms, so the terminal bonds might be shorter than the central bond.

Bond lengths in excited states

Similar treatment for excited electronic state.

$$\rho_{12} = 2(0.37 \times 0.60) + (0.60 \times 0.37) + (0.60 \times -0.37) = 0.45$$

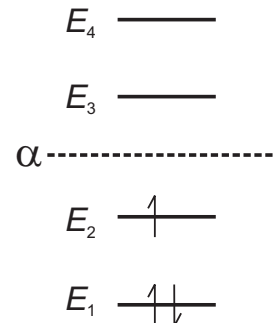
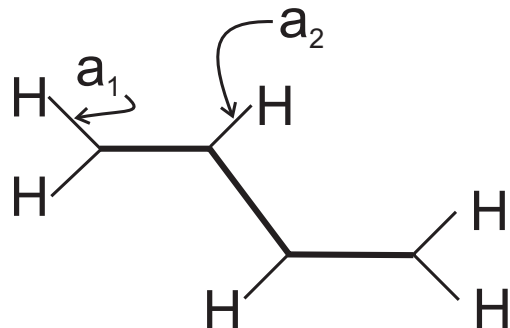
$$\rho_{23} = 2(0.60 \times 0.60) + (0.37 \times -0.37) + (-0.37 \times -0.37) = 0.72$$



Outer bonds expand, inner bond contracts on excitation to the excited electronic state.

(See Spectroscopy lectures, and the Franck-Condon principle - vibrational excitation accompanies electronic transition.)

ESR spectrum of the radical cation



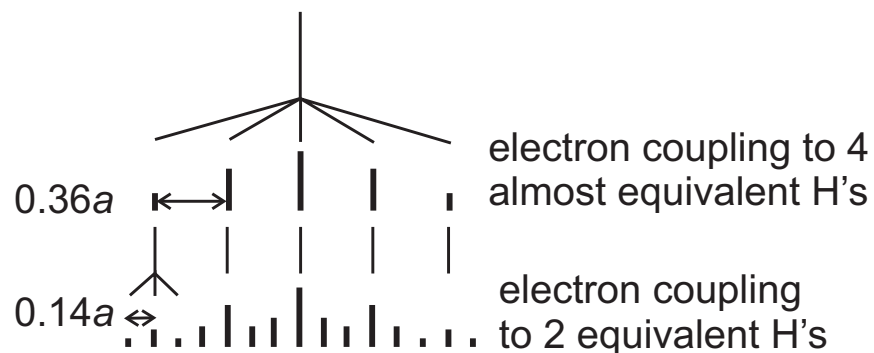
The strength of the hyperfine coupling to the protons is proportional to the unpaired electron density on the adjacent carbon atom.

For the butadiene cation, $[C_4H_6]^+$,

$$a_1 = a(c_1^2)^2 = a \times 0.60^2 = 0.36a$$

$$a_2 = a(c_2^2)^2 = a \times 0.37^2 = 0.14a$$

where a is a universal constant. The following spectrum is therefore predicted:



Susceptibility to electrophilic attack

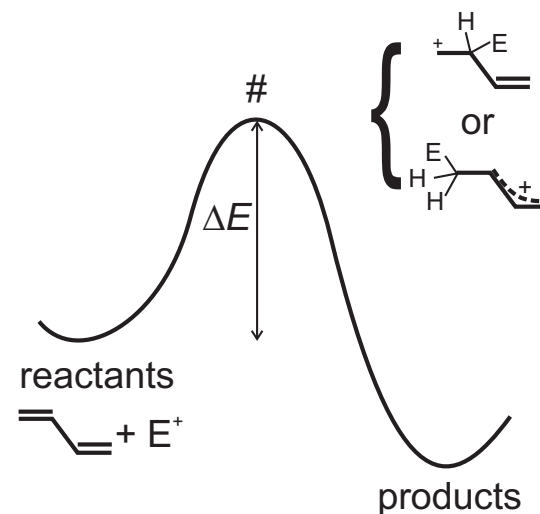
Rate of reaction is proportional to the barrier height. Estimate relative barriers for different pathways.

$$\Delta E = \Delta E_{\sigma} + \Delta E_{\pi}$$

Suppose that ΔE_{σ} is insensitive to position of attack.

$$\Delta E_{\pi} = E_{\pi}^{\ddagger} - E_{\pi}^{\text{butadiene}} = \text{change in resonance stabilization}$$

$$E_{\pi}^{\text{butadiene}} = 4\alpha + 4.48\beta$$



Attack at central carbon

$$E_{\pi}^{\ddagger}(1) \simeq 2\alpha + 2\beta \quad \# \text{ a bit like ethene}$$

$$\Delta E_{\pi}(1) = -2\alpha - 2.48\beta$$

Attack at terminal carbon

$$E_{\pi}^{\ddagger}(2) \simeq 2\alpha + 2\sqrt{2}\beta \quad \# \text{ a bit like allyl cation}$$

$$\Delta E_{\pi}(2) = -2\alpha - 1.65\beta$$

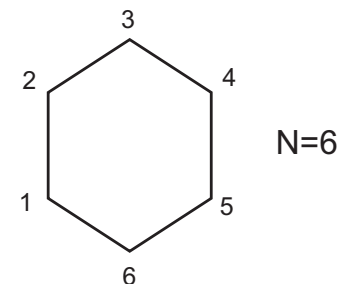
Attack at terminal atom preferred.

Many approximate methods for calculating the *localization energy* have been devised (e.g., frontier orbitals) - see recommended texts.

8: Applications of Hückel Theory

Aromaticity

π MOs of a cyclic polyene (N carbon atoms)



$$\begin{pmatrix} \alpha - E & \beta & 0 & 0 & 0 & \beta \\ \beta & \alpha - E & \beta & 0 & 0 & 0 \\ 0 & \beta & \alpha - E & \beta & 0 & 0 \\ 0 & 0 & \beta & \alpha - E & \beta & 0 \\ 0 & 0 & 0 & \beta & \alpha - E & \beta \\ \beta & 0 & 0 & 0 & \beta & \alpha - E \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \\ c_3 \\ c_4 \\ c_5 \\ c_6 \end{pmatrix} \equiv \begin{pmatrix} x & 1 & 0 & 0 & 0 & 1 \\ 1 & x & 1 & 0 & 0 & 0 \\ 0 & 1 & x & 1 & 0 & 0 \\ 0 & 0 & 1 & x & 1 & 0 \\ 0 & 0 & 0 & 1 & x & 1 \\ 1 & 0 & 0 & 0 & 1 & x \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \\ c_3 \\ c_4 \\ c_5 \\ c_6 \end{pmatrix} = 0,$$

with $x = (\alpha - E)/\beta$.

A general row of the secular equations gives

$$c_{n-1} + xc_n + c_{n+1} = 0$$

For **even membered rings** ($N = 2l$ where l is an integer)

$$c_{2l+n} = c_n$$

cont.

Hence try:

$$c_n^k = e^{i k 2\pi n / 2l} \quad \text{coefficient on } n^{\text{th}} \text{ atom for } k^{\text{th}} \text{ MO}$$

where

$$k = 0, \pm 1, \pm 2, \dots, +l$$

Substitute c_n^k back into equation for coefficients

$$e^{i k 2\pi (n-1) / 2l} + x e^{i k 2\pi n / 2l} + e^{i k 2\pi (n+1) / 2l} = 0$$

or

$$\left(e^{-i k \pi / l} + x + e^{i k \pi / l} \right) e^{i k \pi n / l} = 0$$

or

$$x = -2 \cos \frac{k\pi}{l}.$$

Therefore

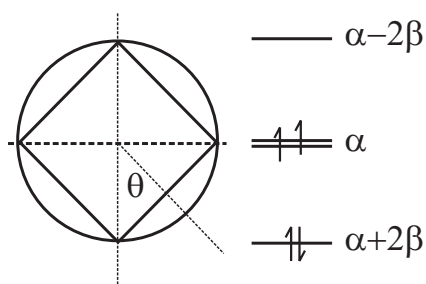
$$E_k = \alpha + 2\beta \cos \frac{k\pi}{l} \quad k = 0, \pm 1, \pm 2 \dots, +l$$

cont.

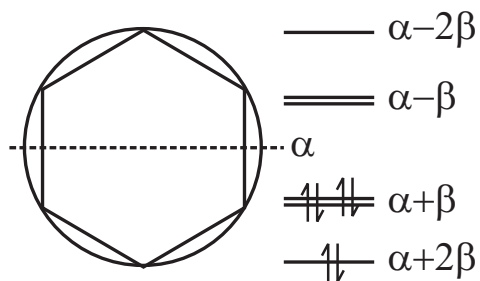
Hence, the resulting energy levels can be displayed diagrammatically

$$E_k = \alpha + 2\beta \cos \frac{k\pi}{l} \equiv \alpha + 2\beta \cos \theta \quad k = 0, \pm 1, \pm 2 \dots, +l,$$

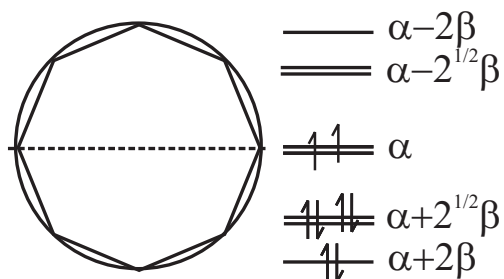
where $\theta = k\pi/l$ correspond to the angles subtended by the vertices of a regular polyhedron.



$E = 4\alpha + 4\beta \equiv$ two ethenes. No extra resonance stabilization due to delocalization. Note unpaired electrons and degenerate ground state.



$E = 6\alpha + 8\beta$, i.e. 2β lower than three ethenes - extra resonance stabilization due to delocalization.



$E = 8\alpha + 4(1 + \sqrt{2})\beta$, i.e. $4(\sqrt{2} - 1)\beta$ lower than four ethenes - extra resonance stabilization but with unpaired electrons and degenerate ground state.

cont.

For odd membered rings ($N = 2l + 1$)

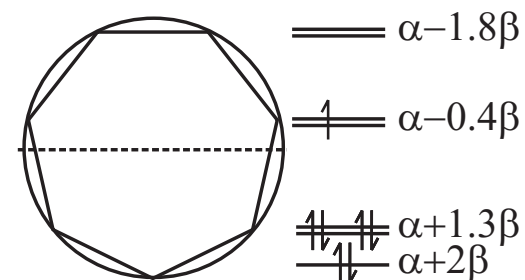
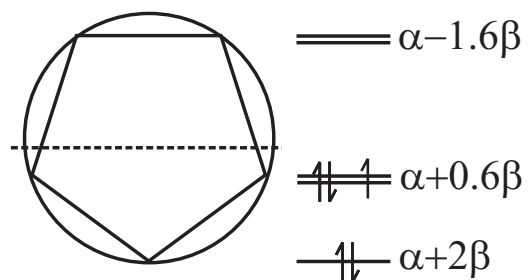
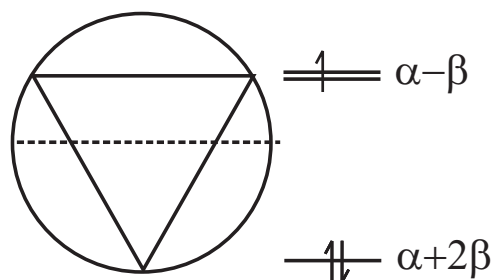
$$c_{2l+1+n} = c_n$$

Hence

$$c_n^k = e^{ik2\pi n/(2l+1)} \quad k = 0, \pm 1, \pm 2, \dots, \pm l$$

Therefore

$$E_k = \alpha + 2\beta \cos \frac{2\pi k}{2l+1} \quad k = 0, \pm 1, \pm 2, \dots, \pm l$$



Origin of the $4n + 2$ π -electron rule for stability of aromatic molecules.

Perturbation theory and steric interactions

Find approximately the properties of a system from those of a system with a slightly different (simpler) Hamiltonian.

General result - just quote

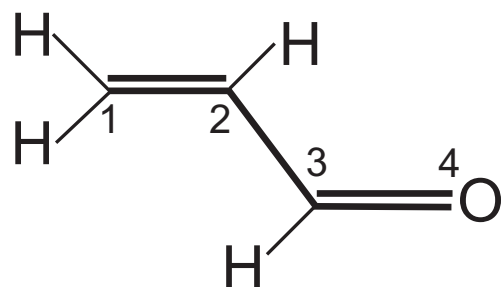
“First order energy”

$$\Delta E_k = \langle \Psi_k | \Delta \hat{H} | \Psi_k \rangle$$

- ΔE_k — change in energy of the k^{th} orbital on perturbation
- Ψ_k — orbital k of the original (unperturbed) problem
- $\Delta \hat{H}$ — difference between the original Hamiltonian and the full one (i.e. the perturbation)

Example 1

Find the π MO energies of



having solved the butadiene problem.

The only major difference is in the energy of the oxygen atom p_π orbital with respect to that of carbon, *i.e.*

$$\langle p_4 | \hat{H} | p_4 \rangle = \alpha_{\text{O}} < \alpha_{\text{C}}$$

However, we can estimate the energy lowering ($\sim 0.6\beta$) and can write

$$\alpha_{\text{O}} = \alpha_{\text{C}} + 0.6\beta$$

Now use butadiene MOs in

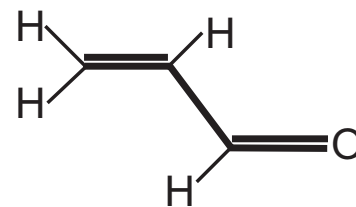
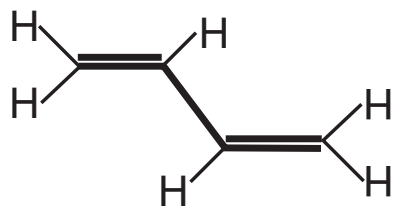
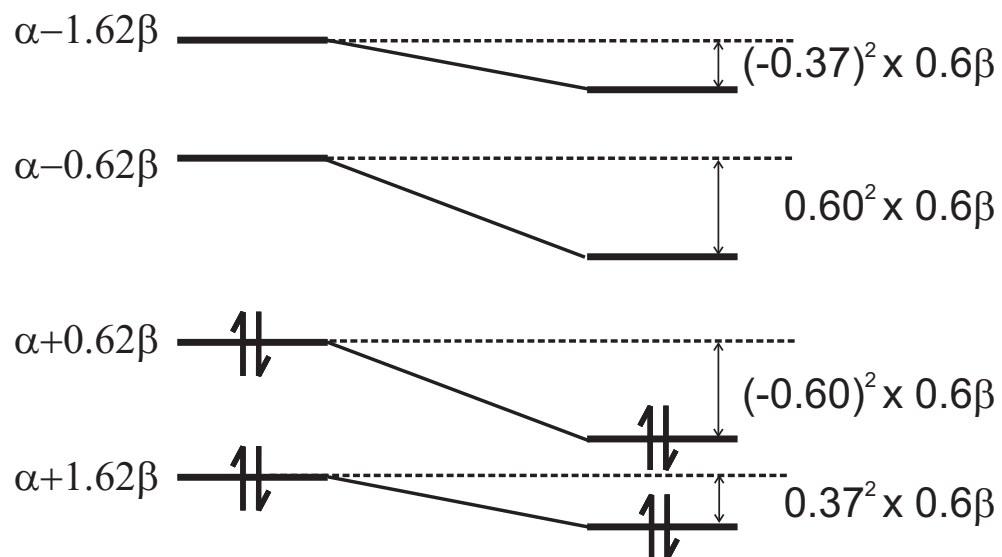
$$\begin{aligned} \Delta E_k &= \langle \Psi_k | \Delta \hat{H} | \Psi_k \rangle \\ &= \left\langle \sum_i c_i^k p_i \middle| \Delta \hat{H} \middle| \sum_j c_j^k p_j \right\rangle \\ &= \sum_{i,j} c_i^k c_j^k \langle p_i | \Delta \hat{H} | p_j \rangle \end{aligned} \tag{2}$$

cont.

But the only matrix element which is affected is $\langle p_4 | \hat{H} | p_4 \rangle$ such that

$$\Delta E_k = (c_4^k)^2 \langle p_4 | \Delta \hat{H} | p_4 \rangle = (c_4^k)^2 0.6\beta.$$

All other terms in Eqn. (2) are zero.



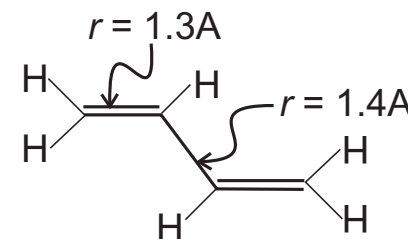
Example 2

In **butadiene** the π bond order between the central (2-3) atoms is less than the terminal (1-2, 3-4) bonds.

Matrix element H_{23} is less negative than H_{12} and H_{34} . Let

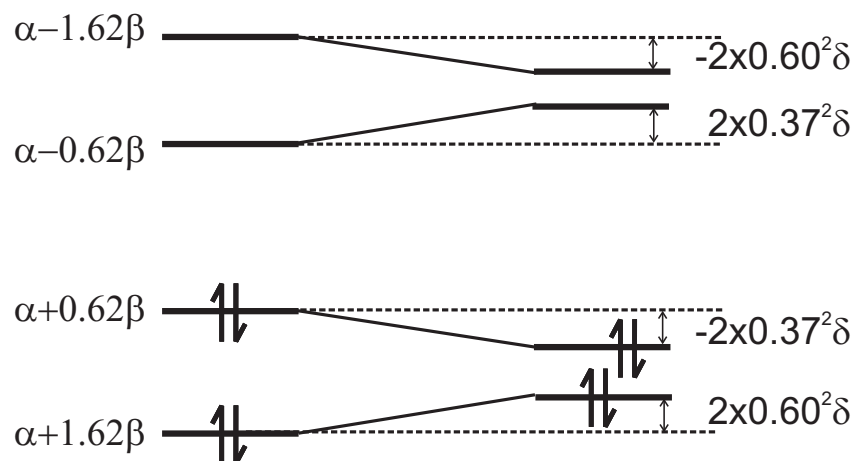
$$H_{12} = H_{34} = \beta \quad H_{23} = \beta + \delta,$$

where β is negative (as usual), but δ is positive.



Find shift in the MO energies due to this effect. Perturbation to Hamiltonian only involves $\langle p_2 | \hat{H} | p_3 \rangle$, therefore

$$\Delta E_k = (c_2^k c_3^k + c_3^k c_2^k) \langle p_2 | \Delta \hat{H} | p_3 \rangle = 2c_2^k c_3^k \delta.$$



Tending to the energy level pattern for two ethenes.

Non-crossing rule

Consider mixing of two orbitals ϕ_1 and ϕ_2

$$\Psi = c_1\phi_1 + c_2\phi_2.$$

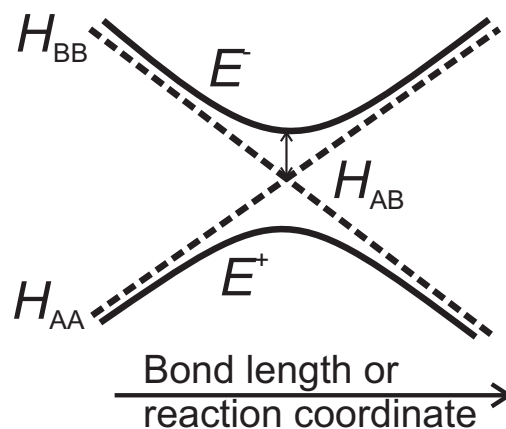
The orbitals ϕ_i could be the MOs that we have just been considering for butadiene.

We know that the energies of the mixed orbitals will be the solutions of the secular equations (see Problem sheet 1)

$$E_{\pm} = \frac{1}{2} \left\{ (H_{AA} + H_{BB}) \pm \sqrt{(H_{AA} - H_{BB})^2 + 4H_{AB}^2} \right\}.$$

So $E_+ = E_-$ only if $H_{AB} = 0$.

In general, $H_{AB} = 0$ only if the states have *different symmetry* (otherwise in region of crossing there will always be some small term in the Hamiltonian which mixes the two orbitals).



States of the same symmetry cannot cross.

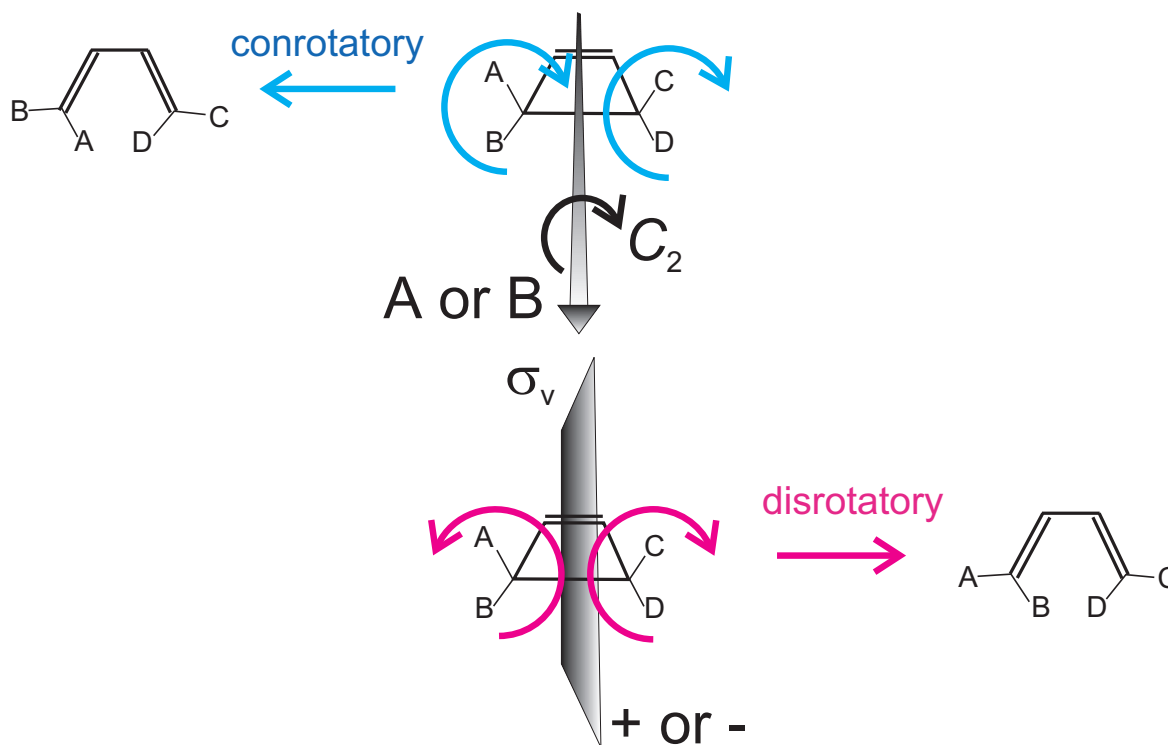
Correlation diagrams

Non-crossing rule is helpful in determining reaction pathways based on orbital symmetry arguments.

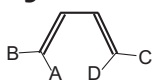
Consider the ring opening of cyclobutene.

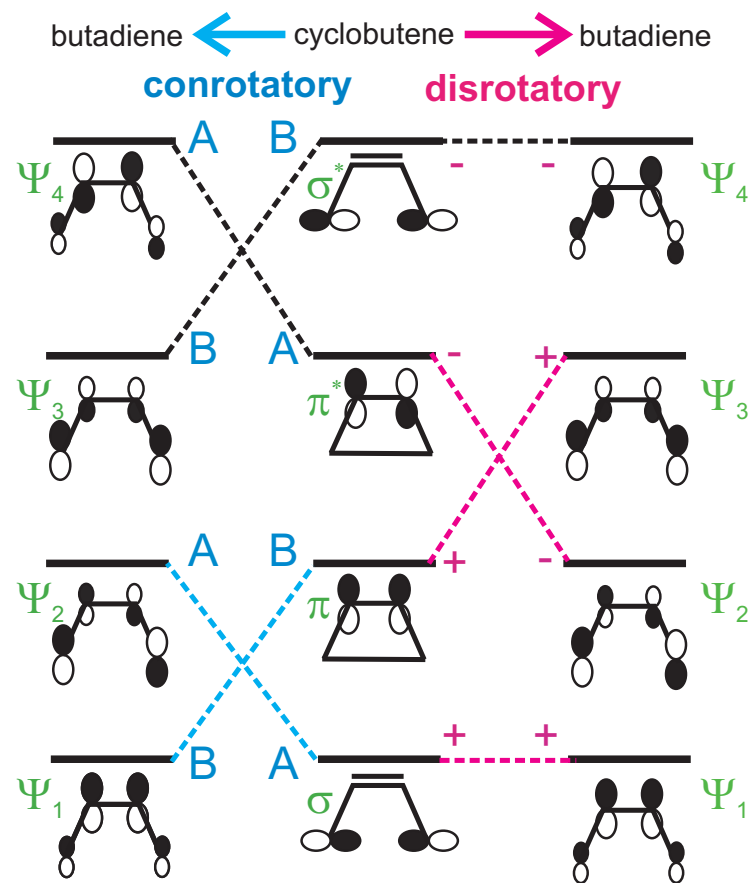


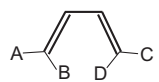
Two categories of ring-opening.



cont.

The ground electronic state of cyclobutene ($\sigma^2\pi^2$) smoothly correlates with the ground state ($\Psi_1^2\Psi_2^2$) of butadiene in the **conrotatory** mode, giving  for **thermal reaction**.



From the first excited electronic state ($\sigma^2\pi\pi^*$) of cyclobutene there is a smooth correlation with the excited state ($\Psi_1^2\Psi_2\Psi_3$) of butadiene in the **disrotatory** mode, giving  for **photon-initiated reaction**.

This is the basis of Woodward-Hoffmann rules.