<u>Orbitals</u>

Introduction

- The **chemical reactivity** of **any species** is due to its **electronic structure**.

- **Photoelectron spectroscopy** allows us to gain information about the **electronic structure** of atoms. We **bombard** the atoms with **high energy X-ray photons**, and measure the **energy** of **"knocked out" electrons**. This allows us to deduce the energy of those electrons in the atom.

- Electrons occupy different **orbitals**. Each orbital can hold **two electrons**, and is defined by the following **three quantum numbers**:

  o ***The principal quantum number, n*** – this denotes which "**shell**" the orbital is part of. $n = 1, 2, 3...$

    For a **one-electron system**, the value of n alone determines the **energy** of the electron.

  o ***The angular momentum quantum number, l*** – this denotes whether we are talking about an s, p, d or f orbital. It also determines the **orbital angular momentum** of the electron [as it spins round the nucleus]:

    $$\text{Angular momentum} = \hbar\sqrt{l(l+1)}$$

    $$l = 0\ (s),\ 1\ (p),\ 2\ (d),\ ...,\ (n-1)$$

  o ***The magnetic quantum number, m_l*** – this tell us something about the **orientation of the orbital** (specifically, it tell us about the **component** of the angular momentum on a **particular axis**).

    $$m_l = l,\ ...,\ 1,\ 0,\ -1,\ ...,\ -l$$

    [Note: the number of different possibilities is $2l + 1$ – just like spins]

  o ***The orientation of the spin angular momentum, m_s*** – this tells us about the orientation of the electron's **own** spin. The magnitude of this spin is *always* ½ for electrons, and so there are only **two** possible **orientations** of that spin. For historical reasons, we denote these by arrows. $m_s = +½\ (\uparrow),\ -½\ (\downarrow)$

Any electron in an atom has a **unique set of four quantum numbers**. This means that each orbital can only hold **two electrons**, with **opposite spins**. This is one form of the **Pauli Principle**.

- Two orbitals that have the **same energy** are said to be **degenerate**.

- Each orbital is defined by a unique **wavefunction** – in **polar coordinates**, $\psi_{n,l,m_l}(r,\theta,\phi)$. The **Born Interpretation** states that $\psi^*\psi$ gives a measure of the **probability** of **finding the electron** at a **given position**. Restriction of the wavefunction are as follows:

    o It must be **single-valued**.

    o It must not **diverge** – the area under the graph is **1**.

- Energies and wavefunctions can be found using the **Schrodinger Equation**: $\hat{H}\psi = E\psi$. It can only be solved for the **hydrogen atom**, for which it gives a **series of solutions** for the different orbitals. The **energies** are given by:

$$E_n = -\frac{R_H z^2}{n^2}$$

Where z is the **nuclear charge**, n is the **principal quantum number** and R_H is the **Rydberg Constant**. Points to notice:

    o In the hydrogen atom, all orbitals with a given principal quantum number are **degenerate**.

    o The energies are **negative** and **tend to 0** as n tends to infinity. The energy needed to promote an electron from the **lowest energy level** to **zero energy** is the **ionisation energy** of the atom.

Hydrogen Orbitals

- When expressed in **polar coordinates**, the wavefunction can be split into a **radial part** (depending on r only) and an **angular part** (depending on θ and ϕ only).

- There are several ways to represent the orbitals:

    o A graph of the **radial part** (**wavefunction** against **distance**).

    o **Contour** or **shaded** plots of the **wavefunction** (squared).

    o **Surface plots** illustrate a **volume** in which a **certain percentage** of the **electron density** is **located**.
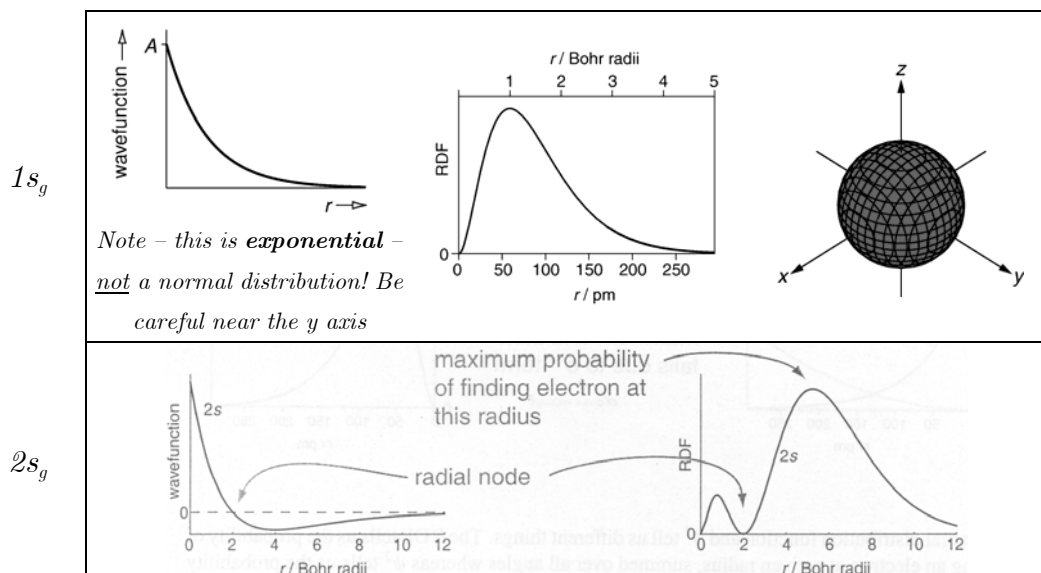
o The **radial density function** gives the probability of finding an electron at a distance r from the nucleus **summed over all angles** [in other words, of finding electrons in a **thin shell** of radius r centred on the nucleus]. Note:

  - The **wavefunction²** gives the probability of finding an electron **in a tiny volume element at a given point**. The **RDF** gives the probability of finding an electron **in a thin shell at a given radius**.

  - Their maxima and minima are therefore different.

- When the **radial part** of the **wavefunction** changes sign (**changes phase**) we have a **radial node**.

- When the **angular part** of the **wavefunction** changes sign (**changes phase**) we have an **angular node**. This could be a **nodal plane** or a **nodal cone**.

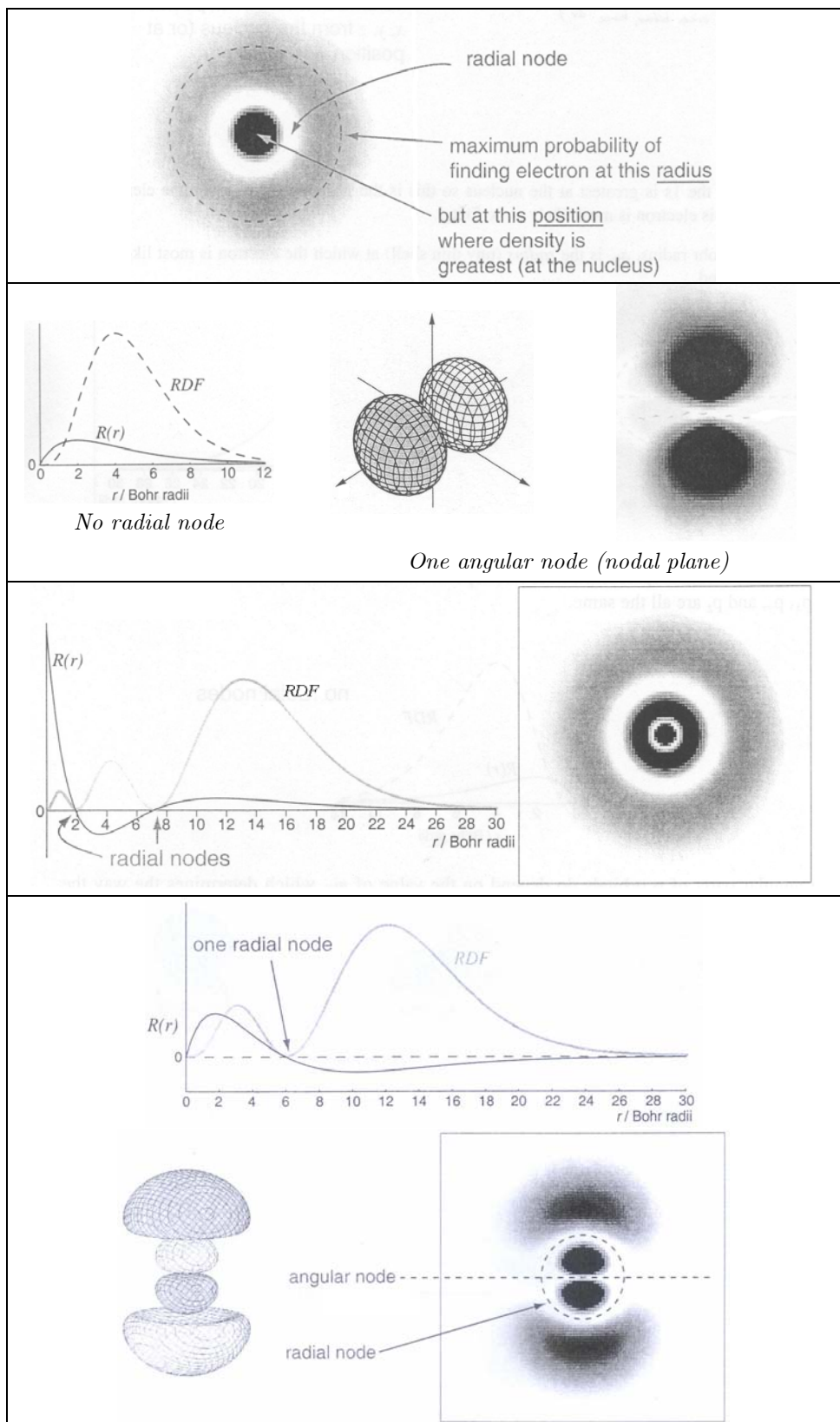- The **number of nodes** in an orbital is given as follows:

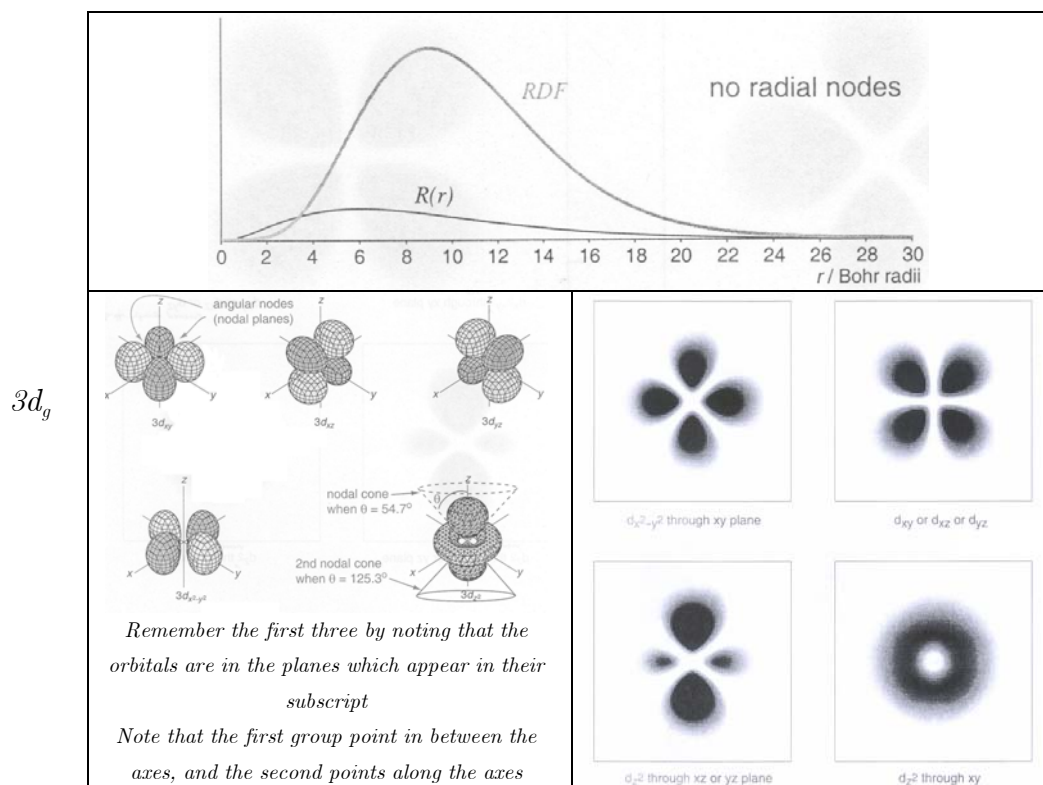$$\text{Number of angular nodes} = l$$
$$\text{Number of radial nodes} = n - 1 - l$$
$$\text{Total number of nodes} = n - 1$$

- The orbitals of the hydrogen atom are as follows:

radial node

maximum probability of
finding electron at this <u>radius</u>

but at this <u>position</u>
where density is
greatest (at the nucleus)

$2p_u$

No radial node

One angular node (nodal plane)

$3s_g$

$3p_u$

one radial node

angular node

radial node

$3d_g$

Remember the first three by noting that the orbitals are in the planes which appear in their subscript

Note that the first group point in between the axes, and the second points along the axes

- For *f* orbitals, we get 5 from modifying the *d* ones, and another with lobes pointing to the four corners of a square.

Other orbitals

- The **Schrodinger Equation** *cannot* be **solved exactly** for **multi-electron systems**, due to the **added complication** of the **repulsion between electrons**.
- However, we can obtain **orbital approximations** by saying that from the **point of view** of a **particular electron**, the effect of **all the other electrons** can be **averaged out** to give a **modified potential**, **spherically symmetric** and **centred on the nucleus**.
- This means that the **wavefunctions** of each electron takes the **same form** as those in hydrogen.
- We say that the other electrons **screen** the **effects** of the **nucleus** from the electron we're considering. How well this happens depend on the orbital. For example, *1s* electrons screen *2s* electrons rather well, but *2s* electrons nearly don't screen *1s* electrons at all.

- This means that the **nuclear charge** each electron **experiences** – the **effective nuclear charge** *(Z_{eff})* is **different** for **different electrons**. For example, in a **three-proton three-electron atom** (lithium):

  o The **1s electrons** shield each other by 30% the charge of a proton, but are not shielded by the *2s* (so $Z_{eff} = 2.7$).

  o The **1s electrons** shield the **2s** electrons **more fully**, and $Z_{eff} = {\sim}1.3$ for the **2s** electrons.

Degeneracy

- In **hydrogen**, all **orbitals** of a **given principal quantum number** have the **same energy**. This isn't obvious from the plots, but it's true!

- In **multi-electron systems**, this **degeneracy** is **lost**. We can see why this is by looking at the **RDF**s for lithium [note that the *1s* orbital is **more contracted** than the other two, because it has a **greater Z_{eff}**]:
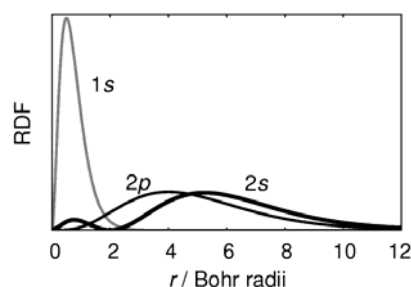
It's clear that the **2s electron** spends, on average, **more time near the nucleus** than the **1s electron**. It is said to **penetrate** the **1s** orbital to a greater extent than the *2s* orbital, which means that it has a **lower energy** [cf. $E = -R_H z^2/n^2$]. Also, *s* orbitals are the only ones with **nonzero density** at the **nucleus**.

- This can become **so significant** that it becomes **difficult to predict** the **energy order** of the orbitals in **larger atoms**.

- What happens is that **increasing nuclear charge <u>contracts</u>** the orbitals. This results in, for example, the **4s** orbital **penetrating** the **lower orbitals** *more than* the *3d* orbital.

- For example, in **lithium**, the orbitals are in their expected order:

  1s | 2s   2p | 3s   3p   3d | 4s   4p   4d   4f | 5s ...

- In **sodium**, the order is already different:

  *1s | 2s   2p | 3s   3p   **4s**   3d | 4p   **5s** ...*

The *4s* orbital is **lower** in energy than the **3d**!

- In **potassium**, the order is already completely different, with the *4s, 4p* <u>and</u> *5s* <u>all</u> lower than the *4d*!

- The **energy configuration** of a species depends on **all** the electrons in contains. Thus, even **isoelectronic species** might have **different orderings** of orbitals if the **nuclear charge** is different!

- As we go **across a period**, Z_{eff} **increases** for the **valence electrons**, because adding an extra electron **in the same shell** doesn't shield existing electrons that are in there too well! Thus, the **extra proton** is **felt fully**.

- For the same reason, **core electrons** have **very low energies** and take **little part in reactions**.

Homonuclear diatomics – principles

- As **two hydrogen atoms approach each other**, a **bond** is formed. In other words, the **H_2 molecule** is **lower in energy** than the two **H atoms**.

- We want to find **molecular orbitals** – **wavefunctions** for **molecules**. This could be done using the **Schrodinger Equation** for some simple molecules, but it's very complicated. An easier way is using the **linear combination of atomic orbitals (LCAO)**. We then say that:

$$\mathrm{MO} = c_1 \mathrm{AO}_{\text{atom 1}} + c_2 \mathrm{AO}_{\text{atom 2}}$$

Where c_1 and c_2 are **orbital coefficients**, which are provided by **quantum mechanics** and specify the proportions of the AOs in the MO.

- When orbitals are added, they always add in two ways – **in phase** and **out of phase**. For example, for two *1s* orbitals:
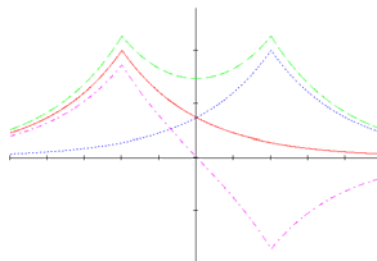
Clearly, in the **in-phase interaction**, the value of the MO **in between the two atoms** is *greater* than that in the **MO** (in fact, if we look at the **RDF**, we find that the position in between the two atoms is the point of highest

electron density). The opposite is true of the out-of-phase interaction, where we have a **node** in between the two atoms:

bonding   anti-bonding
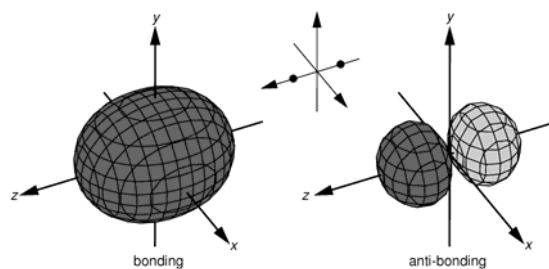
- These two new orbitals to *not* have the same energy. The **in-phase interaction** is **lower in energy** than the AOs, and the **out-of-phase intereaction** is **higher in energy** than the AOs (by more than the in-phase orbitals are lower). [It is true, in general, that more nodes means a higher energy]. This is for several reasons:

  o When the in-phase orbital is occupied, there is **increased electron density in between the nuclei**. The attraction from **both the nuclei** leads to a **lowering in the potential energy** of the electron. [The *field* from the two protons *cancels out*].

  In the **out-of-phase interaction**, there is much more electron density outside the intranuclear region, and these electrons exert a **force** on the **nuclei** which moves the **apart** from one another. Eventually, they would be **completely separate**. Thus, the **PE** in the **MO** is higher than in the separate species.

  o The **repulsion** between the two protons is **shielded** by the electron in between them in the **bonding MO**.

  o Electrons in the in-phase orbital are **more delocalised** than they were in the **AO**, and this leads in a **decrease** in the **kinetic energy** of the electron (cf. particle in a box – the larger the box, the longer the wavelength).

  The orbital contains a **node**, and its **KE** is therefore **greater** than in the **AO**s. [Alternatively, think of the Schrodinger Equation – the del squared operator describes the kinetic energy, and if there's a node, the gradient near that node is high – therefore, the KE is high].

  o The antibonding MO is more contracted and so the repulsion between electrons in there is greater.

Combinations in the **in-phase orbital** leads species to "stick together" because they cause a **lowering in energy** when they approach each other. These known as **bonding MOs**. Similarly, the **out-of-phase orbital** is known as an **antibonding MO**.

- This interaction can be summarised in an **energy level diagram**, which charts the energy of each orbital at **equilibrium separation**. This is in fact only a **slice** through the following graph:
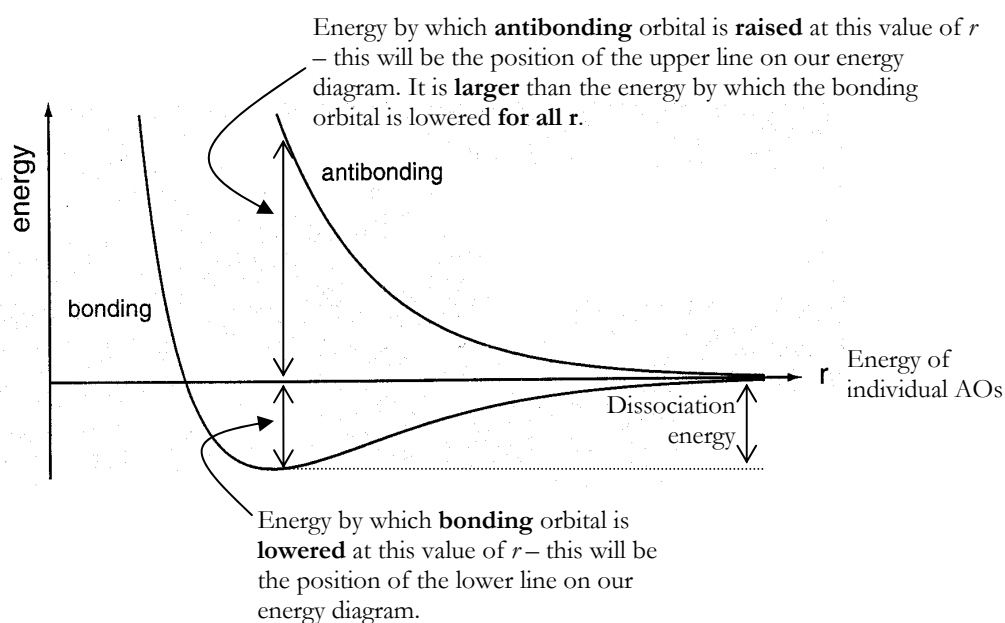
Notes:
- o It is the **lowering** of the **energy** at the **equilibrium bond length** that causes the bond to form.
- o The **further apart** the atoms are, the smaller the energy difference, because the **AOs interact less**.
- o Given the presence of electrons in these orbitals, we can then make an **overall graph of energy**. We find that:
  - ▪ If there are **more bonding AOs**, there will be a **minimum** in the graph. Thus, a **bond** is favourable, because **at that position**, it is **unfavourable** for the molecule to **fall apart**. The **more antibonding MOs** are present, the **less pronounced the minimum**.
  - ▪ If there are **more antibonding MOs**, there will be **no minimum** in the graph. There might be a **point of inflection**, but the

gradient will be **negative everywhere** – so, at **any point**, the **energy can decrease** by the atoms **moving apart**. There is therefore **no bond**.

We therefore define the **bond order** as:

$$\text{Bond order} = \tfrac{1}{2}\left(\text{electrons in bonding MOs} - \text{electrons in antibonding MOs}\right)$$

(This is very crude! Don't worry about how strong or weak the orbitals are! Also, it's a fair indication of bond strengths in exam papers – don't go into the actual levels too much).

- The interaction between *2s* orbitals will the **same**, except that:

  o   The lines will be **higher up** (because the AOs are higher up!)

  o   The two orbitals will be **more similar in energy** (because larger orbitals don't interact as well).

  o   The **equilibrium separation** will be **further apart** (because the orbitals are larger).

- $2p_z$ orbitals overlap **end-on,** whereas $2p_x$ and $2p_y$ orbitals overlap **side-on**:


2p σ$_g$ bonding MO   2p σ$_u$ anti-bonding MO   2p π$_u$ bonding MO   2p π$_g$ anti-bonding MO
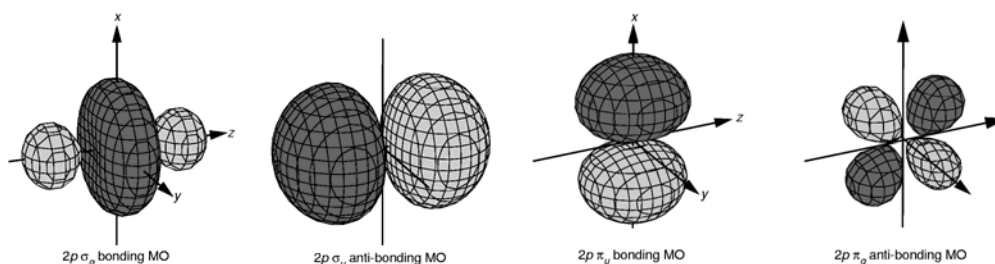
When drawing diagrams of the 2p σ MO, make sure you emphasise
the node, so it doesn't look like to s orbitals

At **equilibrium separation**, the **overlap** between the ***p*** orbitals is **better head-on** than it is **side on**. Therefore, **σ orbitals** are usually *lower* in energy than **π orbitals**. [Note, however, that if the end-on orbitals are pushed together ***much closer*** than their equilibrium separation, the interaction becomes **antibonding**, because the lobe of one orbital starts going into the opposite lob of the other. There is also a point where there is *no* bonding interaction].

Labelling Orbitals

- The labels reflect the **underlying symmetry** of the orbitals.

- σ or π label
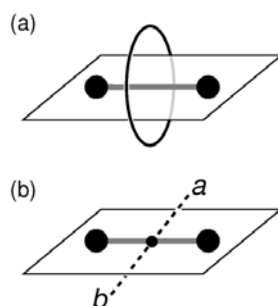
  o An **MO** is given the **σ label** if it is **symmetrical** about the **internuclear axis** – it does **not** change phase when **traversing** a **path** in a **plane perpendicular** to the **internuclear axis** (for example, path in (a) above).

  o If the **internuclear axis** contains a **nodal plane**, it is given the label **π**.

- *u* or *g* label

  o An object is said to posses a **centre of inversion** if one is able to start at **any point**, move to the **centre of inversion**, and then **carry on** exactly the **same distance** in the **opposite direction** and get to a point **equivalent to the start point**. [For example, in (b) above].

  o If the wavefunction **does not change sign** on passing through the centre of inversion, it is given the label *g* (from the German **gerade** – even).

  o If there *is* a change in sign, it is given the label *u* (from the German **ungerade**).

  o Note that this label **only applies to molecules that posses a centre of inversion**.

- **Antibonding** orbitals are sometimes labelled with a [*].

Homonuclear diatomics – practical guide

- There are several factors which determine **how well AO**s combine:

  o *Whether the orbitals have suitable symmetry to interact* – for example, if an *s* orbital and a *p* orbital interact in the wrong direction, there is **no interaction**.
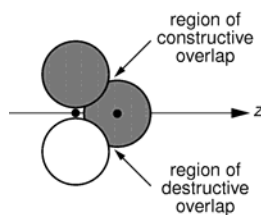
- o **_Energy match_** – the **constituted AOs** must be **close in energy** for significant interaction to occur. The **worse** the energy match, the **less perturbation** of the **MOs** compared to the **AOs**:
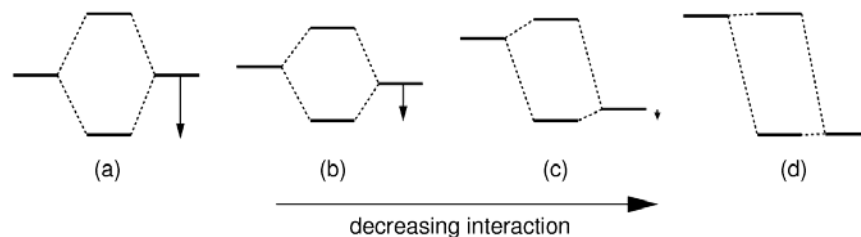

- o **_The size of the orbital_** – the interaction between two **large** orbitals is **less** than the interaction between **two small** orbitals.

- In general, n AOs interacting give n MOs.

- In general, in molecules, **only** the **valence orbitals interact**. This is because even though **lower orbitals** are **occupied**, they are **far too contracted** to **interact significantly** at the **equilibrium bond separation**. [There will be a tiny amount of interaction, but it'll only appear in the second or third decimal place].

- Molecules with **any orbitals** [one or more] in which there are **unpaired electrons** are **paramagnetic**.

- In general, if we have several **degenerate orbitals**, the most energetically favourable way to fill then is to but **one** electron in each with **spins parallel**. This is because of the **repulsion** of two electrons in an orbital.

- In **diatomics** like H_2, **HF**, O_2 and F_2, the *2s* orbitals on one species do *not* interact with the *2p* orbitals on the other. In other diatomics, however (eg, the rest of the Period I diatomics – Li_2, Be_2, B_2, C_2, N_2) *sp* mixing occurs.
    - o We could consider how this happens from the original AOs (accurate way!)
    - o However, an **easier way** is to allow the MOs **initially formed** from **just two AOs** to **further combine**, to get an **improved set of AOs**.
    - o Only orbitals of **similar symmetry** can interact. In this case, candidates are:
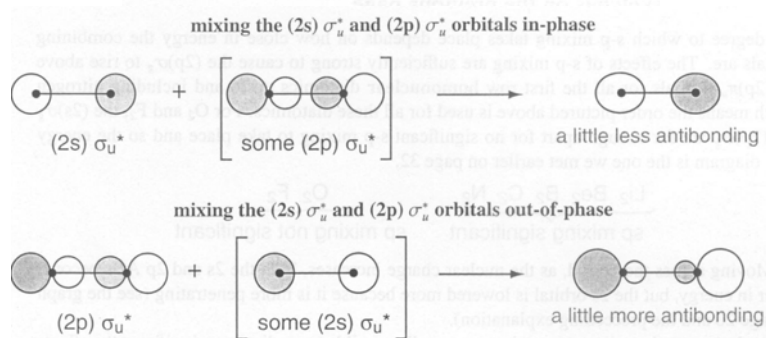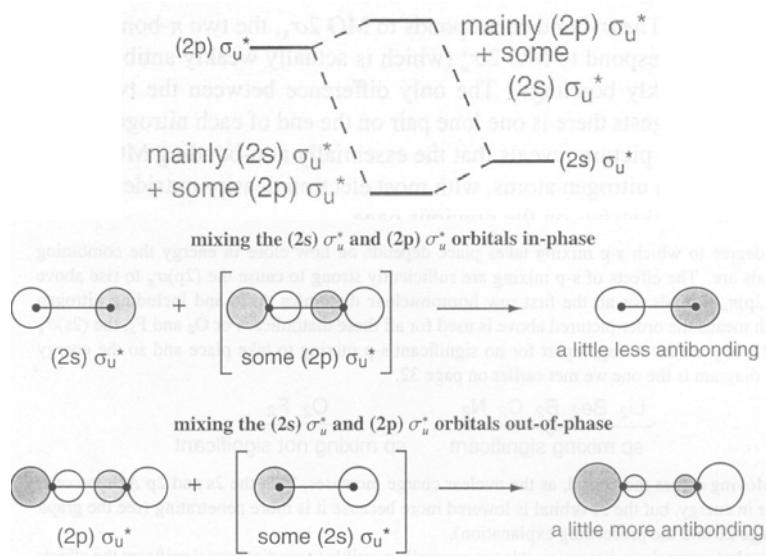
- **(2s) σ_g** and the **(2p) σ_g** – these are **fairly close in energy** and so have the **greatest interaction**:
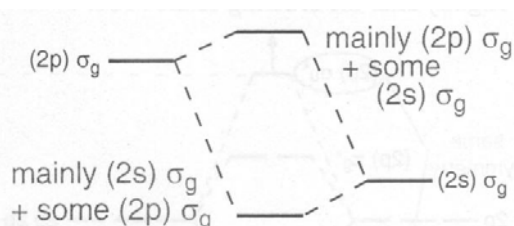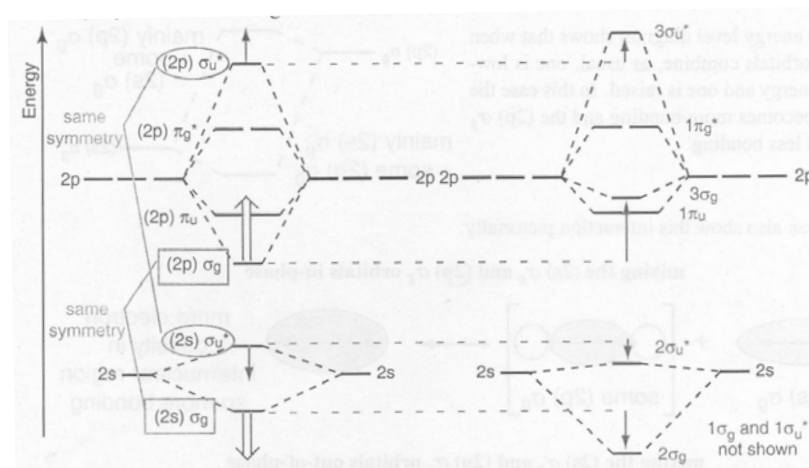

[The **(2s) σ** becomes *more bonding*, and the **(2p) σ** becomes *more antibonding*]
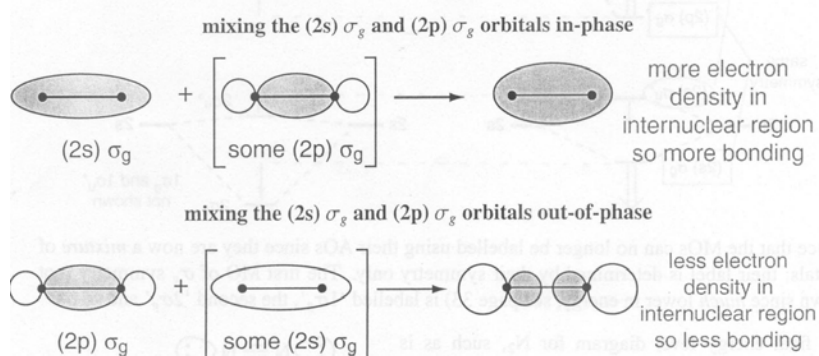
- The corresponding **antibonding MOs**. These are **further apart in energy**, so there is **less interaction**:

o This results in a slight **re-ordering of the MOs**:

o Whether the *sp* mixing that happens is enough for this **reordering** to **take place** depends on how **close in energy** these orbitals are. In the **first period**, this occurs in **Li** to N_2, but not in O_2 or F_2. As we move across the period, both the *2s* and *2p* orbitals are lowered in energy, but the *2s* orbitals are **lowered more** because they are **more penetrating** [see above]. This makes the resulting AOs orbitals **worse matched**.

o This fits in nicely with our understanding of N_2 as having a **triple bond** and **two lone pairs**, except that the lone pairs are **delocalised** over the **whole molecule**.

o **Evidence** of ***sp* mixing** includes the fact that B_2 is unexpectedly **paramagnetic**, and C_2 is unexpectedly **diamagnetic**.

o It is usually difficult to predict whether this will happen in **heteronuclear diatomics**. Even if *sp* mixing occurs in both constituent species, it won't necessarily occur in the compound (for example, CN^- does *not* display *sp* mixing).

o Note that there is never any significant *s–s* mixing – the *1s* and *2s* orbitals are too far apart.

Heteronuclear diatomics

• In general, when two **AOs** of **different energies combine**, the interaction is **not as strong** as when the two AOs have the **same energy**. Furthermore,

the two **AOs** no longer contribute **equally** to the **MO**s. There are three levels:

- o ***The AOs have identical energies*** – in such a case, the two atoms contribute **equally** in forming the **MO** in which the electrons end up. The electrons are **shared** between the two atoms and the bond is **covalent**.

- o ***The AOs have slightly different energies*** – in such a case, the interaction between the MOs will not be so good, and the bonding MO will not be lowered as much [this alone would make the bond weaker]:
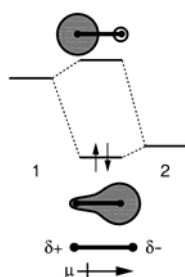
However, the **distribution** of electrons in the MOs is **unequal** – the atom with the **lowest AOs** contributes **more to the bonding MO** and less to the **antibonding MO**. Consequently, the bond is polarised is has some **ionic character**, which **strengthens** the bond.

- o ***The AOs have vastly different energies*** (eg: LiF) – in such a case, the orbitals are **so far apart** that they **hardly interact**. The resulting MOs are effectively identical to the AOs, and the electron in eventually held in what effectively is an F orbital. The two species are then held together by **attraction** between the two **ions**, and not by electrons being shared. This is an **ionic bond**.

- The **more electronegative** an element is, the **lower energy** its orbitals. [Note, however, that it's really the **other way round** – the low energy orbital *cause* the elements to be **electronegative**...]

- Note that in C–Li, the HOMO is the C–Li σ, but the **LUMO** is the **C–Li σ***! The C–C overlapping is so strong, and the C–Li overlapping is so weak, that even though the Li AOs are *higher* in energy, the C–Li σ* is lower than the C–C σ* AO.

Larger molecules

- In **larger molecules**, all the rules above are still the same:
    - n **AOs** combine to make n **MOs**.
    - The **resulting MOs** are **delocalised** over the **whole molecule**.
    - Each orbital can **still** just hold **two electrons**.
- In **even larger molecules**, we could consider all the many **AOs** interacting to give **MOs** *smeared* over the entire structure.
- However, most of the time, this is inconvenient. Instead, we think of atoms being bonded together by a **pair of electrons**.
- A convenient way to do this is to **construct approximate MOs** between **any two atoms** which are **bonded** [one bonding AO and one antibonding AO].
- Sadly, however, the **AOs** under consideration might not point in the **right** directions to **overlap efficiently** and for us to be able to do this.
- One way around this is using a procedure called **hybridisation**.

Hybridization

- **Hybridization** allows us to **mix a number of atomic orbitals *on the same atom***, to create **hybrid atomic orbitals** pointing towards atoms we wish to construct bonds with.
- This is just a **mathematical tool**; usually, we **deduce the hybridisation** *from* the **shape** which we **know** the molecules adopt.
- **Non-integer ratios** are therefore possible.
    - An **exact** 1:3 ratio of s to p orbitals gives **hybrids** that point at **109.5°** to each other. This happens to be the shape of **methane**, and so sp^3 hybrids are a plausible guess.
    - Some molecules have **smaller** bond angles (like H_2O – **104°** and PH_3 – **94°**). In such a case, we must use orbitals that have a slightly **higher p ratio**. The **more p character** HAOs have, the **closer** they point to **90°**.
- Only orbitals with the **correct symmetry** will form **HAOs**. For example, in (planar) H–Be–H, the $2p_x$ and $2p_y$ orbitals have the *completely* wrong

symmetry to be involved in bonding, so they are not involved. It is an *sp* hybrid that is used.

- **Lone pairs** must also be in an **MO** – either an **HAO** or one of the original **AO**s.

- **VSEPRT** and common works in *most* cases, and the need to be translated to hybridisation:

  o **CH₃⁻** and **NH₃** will *not* be planar. According to **VSEPRT**, this is because the **lone pair** "**squashes**" the other bonds together.

    According to our theory, it's because an sp^3 hybrid is **lower in energy** than a pure p orbital, and so it's **more advantageous** for the **lone pair** to be in an **HAO** than in an **AO**.

  o The bond angles in **NH₃** and **PH₃** are not exactly **109.5°**, but **smaller**. According to **VSEPRT**, this is because the lone pair "**repels the other bonds**" **more strongly** than they repel each other.

    According to our theory, it's because the sp^3 **hybrids** don't have an exactly **1:3** ratio of s:p – the **lone pair HAO** has **more s character** [presumably because since the bonding HAOs will combine with those on the other atom and lower their energy anyway, it's advantageous to keep the lone pair HAO as low in energy as possible by giving it lots of s character], and so the **bonding HAOs** have **more p character** and therefore **smaller bond angles**.

  o As we go down **group 5**, we find that the **bond angles** in the **hydrides** get **closer and closer to 90°**. According to **VSEPRT**, this is because the **more electronegative** the central atom, the **denser** the **electron density near the atom** of **bonds** (because of **polarisation** and **shorter bond lengths**). Electronically **denser** bonds lead to **more repulsion** compared to the repulsion of the **lone pair** (the density of which says roughly constant), and so the **bond angle** is **bigger**. [The 90° is not explained].

    According to our theory, the orbital in which the **lone pair resides** gets **more and more s character** as the atoms get **less and less**

electronegative. Eventually, the bonds are effectively **p orbitals** (at 90°) and the **lone pair** is effectively in an **s orbital**.

- Here is a summary of possible hybridisation states:

Hybridization states

| Geometry	Possible hybridization of central atom	Example
Linear	sp	BeF_2
trigonal planar	sp^2	BF_3
tetrahedral	sp^3	CF_4
square planar	sp^2d *or* p^2d^2 (Depends if s is too low to interact)	$Pt(Cl_2)(NH_3)_2$
trigonal bipyramidal (triangle based pyramid)	sp^3d *or* spd^3	PF_5 ??
Octahedral (square based pyramid)	sp^3d^2	SF_6 ??

When **different schemes** are **possible**, the **most appropriate** depends on the **energy match** between the **central atom AO** and the **ligand AOs**.

- **Note** – for the hybrids involving d orbitals, not all d orbitals can be used:
  - o In the **square planar** octahedral, we need orbitals that point along the x and y axes. The obvious one is $d_{x^2-y^2}$. However, in p^2d^2 hybrids, the d_{z^2} orbital can **also work** thanks to the **ring** which has electron density along these axes (the other orbitals point in between the axes).
  - o In the **octahedral** hybrids, we again need orbitals with density along the axes. Again, therefore, the $d_{x^2-y^2}$ and d_{z^2} are the ones we want.
- **Advantages** of hybridization is that it (a) **simplifies** the bonding scheme (b) gives more directional HAOs (c) gives MOs in which the electron aren't delocalised over many atoms (d) easier when drawing mechanisms.
- **Disadvantages** are (a) it doesn't give the best picture of the different energy levels in the molecule (b) encourages a localised view of electrons whereas they're really spread out all over the molecule.

Conjugation

- For certain molecules, the **localised valence bond scheme** may be **inadequate**. This is the case, for example, in **benzene**.

- The **σ framework** is still best considered using **HAO**s. This leaves *p* **orbitals** pointing **out of the plane**, free to form **π MOs**.

- Combining *n* orbitals gives *n* MOs. Since **successively higher energy MOs** have **more nodes**, we can **predict** the **form** of the **MOs** produced by combining the **out-of-plane *p* orbitals** using a rule based on **sine waves**. For example, with **four *p* orbitals**:
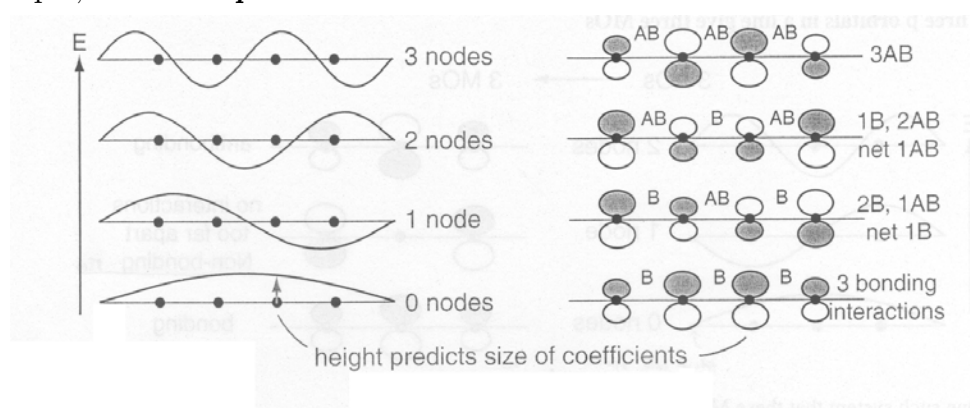
Notes:

- o The sine wave starts **one space outside** the atoms.

- o The "**coefficients**" mentioned above are the coefficients of how much each *p* AO will contribute to the MOs.

- o Note that negative values of the sine wave predict the *p* AOs contributing **out of phase**.

- o If the diagram above represents **butadiene**, there are **four** electrons available to put into the π system, and we therefore have a **filled 1π** and a **filled 2π** MO.

- o In the diagram above, the **antibonding interaction** in the 2π MO *partly* cancels out the **bonding** intereaction in the 1π MO. We therefore end up with *most* bonding between the end-two carbons, but <u>some</u> in the middle carbons.

- o Note that when considering **three *p* orbitals** in a row, we sometimes get atoms on which there is **no contribution** from the original *p* orbitals (corresponding to a node in the sine wave). In such a case,

the two contributions either side of this node are **too far apart to interact**, and the orbital is **non-bonding**.

- o The more time an **AO** shows up in the **MO**s, the **smaller** its contribution will be.

• When working out the number of electrons that will be in the π system, it's best to start from scratch, as follows:

- o Take the number of valence electrons in each atom.
- o Subtract any being used for σ bonds [including bonds to other atoms outside the system we're considering! For example, in R–COO⁻, the carbon is using a total of **three** electrons for σ bonding, not **two**].
- o Subtract any in lone pairs.
- o Add/remove any extra electrons, if the system is charged.

Then, to double check, we can think about it in terms "which orbitals stick out next to each other", and how many electrons are in each of these [but when doing this, ensure all of the above are taken into account!].

• This can explain, for example, why the **allyl anion** ($CH_2=CH–CH_2^-$) is **planar** even though one of the carbons has a **lone pair**. It turns out that this **lone pair** is **delocalised into the π system**.

• The combining p orbitals do <u>not</u> need to be from the **same element**. The only difference is that the p orbitals will have **different energies** and so the resulting MOs will not be symmetrical, and the electrons will not be shared evenly over all atoms.

• This explains why the **amide C=O bond** is *weaker* than the **ketone C=O** bond. In the amide, there is conjugation across the O=C–N bonds, and the **bonding orbital** ends up being over **three atoms** instead of **two**. This means that we have 2e⁻ shared over 3 atoms, as opposed to over 2 atoms.

Predicting Structures

• So far, we have assumed given structures and *then* worked out the molecular orbitals.

• It is also possible to go **the other way round**, but this requires **considerable computational power**.

- It involves starting with a given configuration, and **slightly altering it** to try and **lower the energy**.

- Note that it is only the energy of **electron-containing orbitals** that matters. If other orbitals are raised in energy, this is of little consequence!

Reactions

- **Curly arrow *start*** at the source of electrons and ***end*** at the place where electrons **end up**.

- The **MOs** of a **product** maybe be considered as arising from **interactions** between the **MOs** of **reactants**.

- Many remain **virtually unchanged**.

- The **most important interaction** is between the **HOMO** of one reactant and the **LUMO** of the other. This will lead to a **net lowering in energy** of the **most energetic electrons** (this is what makes a reaction **exothermic**).

- There are, however, **two possible HOMO–LUMO interactions** in each reaction (depending which MOs and AOs we use). The <u>**best**</u> interaction will be between orbitals which are <u>**closest**</u> in energy, and this will usually be between the **highest HOMO** and the **LUMO** from the other reactant.

- In general, energies are as follows (in decreasing order):
  o σ^* antibonding
  o π^* antibonding
  o Non-bonding (could be non-bonding MOs or AOs – lone pairs, for example).
  o π bonding
  o σ bonding

- Orbitals also help us get an idea of the **geometry of the attack**. For example, when the H$^-$ *1s* attacks the CO π^* in a carbonyl compound, the attack cannot be from above or from the side, because this leads to no net interaction. The best possible interaction is at $107°$, where it gets *just* the top lobe of the π^* orbital.

- There are three reasons why C=C bonds aren't attacked as easily as C=O bonds:
  o C=C bonds have no dipole moment.

- o The C=C π^* orbital is *higher in energy* than the C=O π^* orbital. [Note: it is difficult to tell whether the C=O π orbital is lower than the C=C π orbital, because even though the O orbitals are lower than C orbitals, the match is poorer and the lowering of the MO isn't as much as in C=C. Wothers drew it lowers. Here, however, we don't really care].

  o A –ve charge would end up on carbon – nowhere near as favourable as negative charge ending on electronegative oxygen.

- Finally we consider **nucleophilic substitution** at a **saturated carbon**. There, we have two candidate LUMOs – the C–H σ^* and the C–Cl σ^*. Clearly, the C–Cl σ^* is lower (because of the poorer match). Furthermore, there is a poor *size match* between C and Cl MOs (the Cl AOs are *3p*, whereas the carbon ones are *2p*). Thus, the LUMO we use is the C–Cl σ^* one.

- Again, we have an **optimal orientation** – the Nu⁻ must approach the carbon from the *back* to get the meat of the σ^* AO.

- Halfway through the reaction, the central carbon is *sp^2 hybridised*. This is obvious from the fact that there is **inversion** at the carbon centre.

- When H⁺ attacks **alkene**, it will bond to *one* of the carbons and make the **other** positive. This is because it draws electrons towards it for the bond, and takes them from the other carbon.