

Bonding and molecules 1

Bonding in Molecules

Lecture 1. Introduction, types of bonding, electrons in molecules. Crystal field theory.

Lecture 2. Molecular orbital theory. Simple diatomics.

Lecture 3. More complex examples of molecular orbital theory.

Bibliography

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BONDING BETWEEN ATOMS

There are essentially three types of bonding between atoms;

- Metallic bonding – positively charged ions in a "sea" of electrons. Usually occurs in solid metals and alloys (e.g. Fe).
- Ionic bonding – "classical" electrostatic interaction between positive ions and negative ions. Usually occurs in solid, crystalline compounds (e.g. NaCl).
- Covalent bonding – attraction between two or more uncharged atoms. Usually found in discrete molecules in the solid, liquid and gas phase (e.g. O₂).

In practice, very few compounds show one of these limiting forms of bonding but rather a mixture (e.g. HCl shows a mixture of covalent and ionic bonding).

IONIC BONDING

Ionic bonding is a simple electrostatic interaction between positive and negative charged species.

$$E = \sum_{j>i} \frac{1}{4\pi\epsilon_0\epsilon} \frac{q_i q_j}{r_{ij}}$$

ELECTRONS IN MOLECULES

As we have seen, the shapes of electron orbitals in atoms are determined by the allowed waves in a sphere and their energies are determined by electrostatic interactions with the other charged species in the atom. If we introduce more charged species, such as other atoms made of electrons and nuclei, then we might:

- alter the region of space that an electron is localised to, and hence change the shape of the orbital;
- alter the electrostatic interactions experienced by an electron, and hence change its energy.

What effects we get will depend on how large the interaction of these new charges with the electron is.

Effect is negligible compared to interactions within the atom \Rightarrow Does not change the energies or shapes of the orbitals

The electron is still localised around one atom and is indistinguishable from an atomic electron. This is the situation for electrons close to the nucleus (n-2 etc. shells -- core electrons).

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Effect is small compared to interactions within the atom \Rightarrow Changes the energies of the orbitals, but not their shape

The electron is still localised around one atom but its energy is perturbed by the extra electrostatic interactions. The electron orbital is "atomic like". This is the situation for electrons close to the nucleus (n-1 shell).

Effect is large compared to interactions within the atom \Rightarrow Changes both the shape and energies of the orbitals (no longer atomic like)

The electron is no longer localised around one atom but interacts with other atoms just as strongly. The electron orbital is no longer "atomic like". This is the situation for electrons far from the nucleus (n shell -- valence electrons).

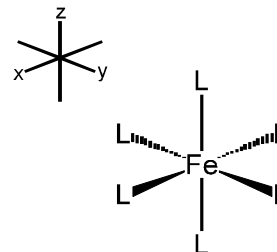
CRYSTAL FIELD THEORY

Transition metals have ns electrons and (n-1)d electrons (e.g. iron, Fe^{2+} , has an outer electron configuration $3d^6$). When we introduce a transition metal into a molecule, we would expect the ns electrons to be significantly perturbed and we would no longer be able to describe them as occupying atomic orbitals. The (n-1)d electrons, however, will only be slightly perturbed. All we will need to do is to take account of the extra electrostatic interactions between an electron and the ligands when determining its energy. This approach is called Crystal Field Theory (CFT).

[Note -- this theory is an approximation which produces qualitative results, full Molecular Orbital theory is necessary for greater accuracy].

D-ORBITALS IN AN OCTAHEDRAL COMPLEX

Consider the effect of putting six ligands around a transition metal in an octahedral (Oh) geometry. There will be an extra repulsion term between the metal electrons and the ligand electrons leading to a destabilisation of the metal electrons (increase in orbital energy). The size of this effect will depend on how close to the electrons are to the ligands.



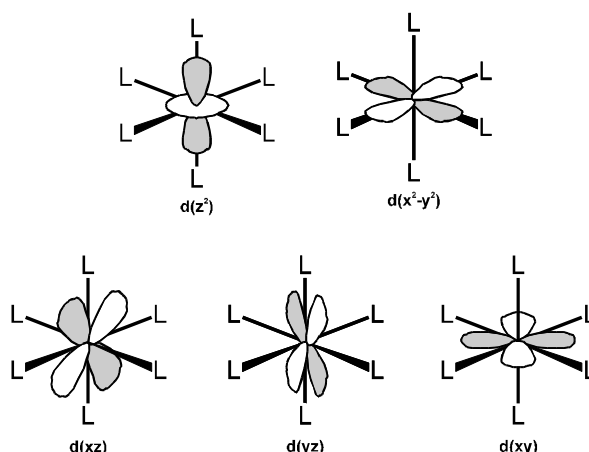
Orbital points towards ligands \Rightarrow Electron will be destabilised relative to other orbitals

Orbital points away from the ligands \Rightarrow Electron will be stabilised relative to other orbitals

Thus, different d-orbitals will experience different effects depending on their spatial orientation.

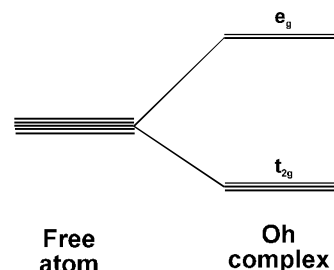
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SHAPES OF THE D-ORBITALS



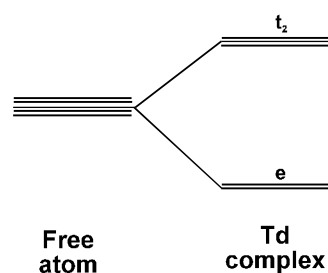
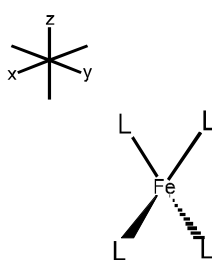
D-ORBITAL SPLITTING IN AN OCTAHEDRAL COMPLEX

In an octahedral complex, two of the d-orbitals (termed the e_g) point towards the ligands and so will be destabilised relative to all the other orbitals. Three point between the ligands (termed the t_{2g}) and so will be stabilised relative to all the other orbitals. Thus, the d-orbitals are split into three lower and two upper orbitals.



D-ORBITALS IN A TETRAHEDRAL COMPLEX

In a tetrahedral (T_d) complex, the situation is reversed compared to an O_h complex. The $d(z^2)$ and $d(x^2-y^2)$ orbitals (in this case termed the e orbitals) now point between the ligands whereas the $d(xz)$, $d(yz)$ and $d(xy)$ orbitals point at the ligands (termed the t_2 orbitals). Thus, the orbital splitting pattern is also reversed.



D-ELECTRON CONFIGURATION

The energy gap between the split d-orbitals is called the Crystal Field Splitting (Δ). Consider an O_h complex. When we put electrons into the d-orbitals, the first three electrons go unpaired into the t_{2g} orbitals. When we put the fourth electron in, we have a choice between putting it in a t_{2g} orbital or an e_g orbital.



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$t_{2g}^3 e_g^1$	high spin	minimise repulsion	electron-electronfavoured by small Δ
t_{2g}^4	low spin	minimise orbital energy	favoured by large Δ

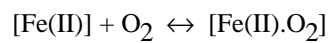
In general, Δ goes up if;

- there are more ligands
- the ligands have a higher charge density (smaller and/or higher charge)
- the ligands are closer to the metal

The *spectrochemical series* gives ligands in the order of increasing Δ .

The crystal field splitting is always smaller for a Td complex than an Oh one, because there are fewer ligands. Td complexes are always high spin.

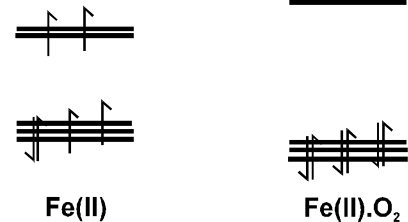
BASIS OF ALLOSTERY IN HAEMOGLOBIN



Binding of oxygen increases the number of ligands around the Fe(II) from five to six.

This increases the crystal field splitting, Δ .

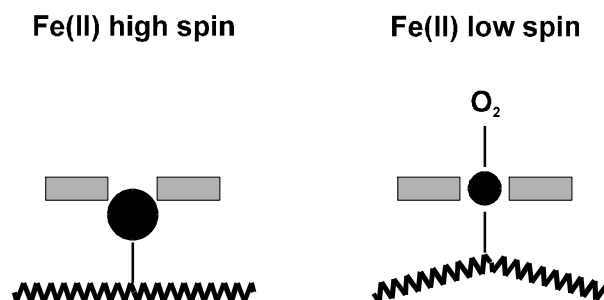
Deoxy- form	5 ligands	Small Δ	High spin
Oxy- form	6 ligands	Large Δ	Low spin



The e_g orbitals are larger than the t_{2g} orbitals (higher in energy \Rightarrow further from the nucleus).

Fe(II) high spin	Radius = 0.78 Å	Does not fit in the porphyrin ring
Fe(II) low spin	Radius = 0.61 Å	Fits in the porphyrin ring

The movement of the Fe ion into the ring causes a conformational change in the protein structure which can be relayed to the other sub-units.



Bonding in molecules 2

Summary so far ...

- Atomic orbitals are perturbed by the presence of other atoms (i.e. charged species such as nuclei and electrons).
- For a small perturbation, this can be considered as an extra energy term for the atomic orbital but will not effect the orbital shape.
- This approach (called crystal field theory) can be used to explain the behaviour of d-electrons in transition metal complexes.
- For a large perturbation, both the energy and shape of the atomic orbitals will be perturbed.

VB AND VSEPR

The “classical”, or valence bond (VB), picture of bonding :

- For molecules to be stable, bonds must exist between the atoms.
- A bond consists of one or more pairs of electrons localised between two atoms.
- The force holding the two atoms together is the attraction of the two nuclei for the electron pair.

The shapes of covalent molecules can be determined using the Valence Shell Electron Pair Repulsion theory (VSEPR).

1. Determine the number of bonding pairs and lone pairs of electrons.
2. Choose a geometry that maximises the distance between electron pairs (and hence minimises the repulsion between them).
3. Adjust the geometry to take account of the fact that repulsion involving lone pairs is greater than the repulsion involving bonding pairs.

VSEPR theory completely ignores the shapes of atomic orbitals. It is also qualitative, it cannot be used to calculate bond angles or bond energies.

To try to link the geometry of the molecule to the shapes of atomic orbitals and make the theory quantitative, the concept of hybridisation is introduced.

- Atomic orbitals on a given atom are “mixed” together to give hybrid atomic orbitals of the right shape (as determined by VSEPR).
- A hybrid orbital on each atom is shared by an electron pair to form a bond.

As with many classical theories, these theories are at best misleading or, more accurately, just wrong.

- For O_2 – VB approach says all the electrons are paired, BUT experiment shows that O_2 is paramagnetic.
- For H_2S – VSEPR says that the geometry should be based on a tetrahedron, BUT the experimental bond angle is 90° .

VB and VSEPR are useful qualitative tools for that work in for most organic compounds. They don't work for the following:

- Quantitative prediction of bond lengths, angles or energies.
- Prediction of magnetic behaviour.
- Prediction of spectroscopic behaviour.

i.e. anything where the properties of individual electrons are important.

MOLECULAR ORBITAL THEORY

The wave theory of bonding :

- For any arbitrary arrangement of nuclei there will be allowed orbitals over all the nuclei that the electrons can occupy.
- The energies of these orbitals are determined by the electrostatic interactions of the electrons with the nuclei and the other electrons.
- The most stable arrangement of nuclei (i.e. positions of the atoms) will be that with the lowest total energy (obtained by adding up the energies of all the electrons).

Bonding in molecules 2

Molecules only exist if the total energy is **lower** when the atoms are **closer together** than when they are far apart.

Core electrons experience a small perturbation – still atomic like (localised around one atom).

Valence electrons experience a large perturbation – no longer atomic like orbitals, but molecular orbitals (electrons are not localised to one atom but are spread over several atoms in the molecule).

We can treat valence electrons in molecules in exactly the same way as we obtained atomic orbitals, i.e. find out the allowed wavefunctions given the boundary conditions. However, the boundary conditions are now very complex because we have to consider a wave-function over several atoms, not just one.

LCAO APPROXIMATION

Molecular orbitals are built up by adding atomic orbitals together in appropriate ways. Take two (or more) atomic orbitals and allow them to interact. [This is the same as allowing two waves to interfere]. This can lead to constructive or destructive interference between the two orbitals, depending on the relative phases of the orbitals.

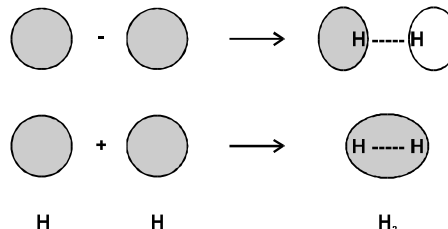
Increasing the electron density between the nuclei gives overall bonding.

- Constructive interference is favourable and leads to bonding.
- Destructive interference is unfavourable and leads to anti-bonding.

The bond order is given by the net number of bonding electrons divided by two (not equivalent to bond energy). The bond energy is given by the sum of the occupied orbital energies for the molecule minus the sum of the occupied orbital energies for the separate atoms.

EXAMPLES – HYDROGEN AND HELIUM

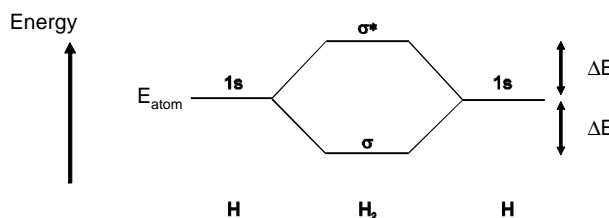
Each hydrogen atom has one electron in a valence orbital (1s). If we bring two hydrogen atoms together, there are two ways in which we could combine these orbitals.



$1s - 1s$	\Rightarrow	Reduced electron density between atoms	Anti-bonding molecular orbital
$1s + 1s$	\Rightarrow	Increased electron density between atoms	Bonding molecular orbital

The two electrons in H_2 both go into the bonding orbital and so the molecule is stable with a bond order of one.

Electron configuration -- $1s\sigma^2$



Two hydrogen atoms	Each electron is in a 1s orbital	Energy = $2 \times E_{\text{atom}}$
Hydrogen molecule	Both electrons are in the σ orbital	Energy = $2 \times (E_{\text{atom}} - \Delta E)$

$$\text{Bond energy} = 2\Delta E$$

Bonding in molecules 2

Helium (He_2) \Rightarrow same MO scheme as H_2 (uses the same orbitals)

Electron configuration -- $1s\sigma^2 1s\sigma^{*2}$

Thus the molecule has no net bonding and so **does not** exist. Helium exists as free atoms.

Helium⁺ (He_2^+) \Rightarrow same MO scheme as He_2

Electron configuration -- $1s\sigma^2 1s\sigma^*$

Thus the molecule has one net bonding electron and so **does** exist, although the bond is weak.

Bonding in molecules 3

Summary so far ...

- Valence bond/VSEPR theory is basically wrong, although it can be a very useful simplifying tool (if used carefully).
- MO theory treats electron orbitals as being spread over two or more atoms.
- Molecular orbitals are made by adding or subtracting atomic orbitals on the different atoms (the LCAO approach).
- Constructive interference between atomic orbitals gives a bonding molecular orbital, destructive interference gives an anti-bonding molecular orbital.

LCAO FOR LARGER ATOMS

For atoms other than hydrogen and helium, we have several orbitals on each atom which could be used to form molecular orbitals, e.g. for oxygen the 1s, 2s and 2p orbitals are occupied. We therefore need some rules for which atomic orbitals to use to make molecular orbitals.

- We can add or subtract two or more atomic orbitals to make a molecular orbital.
- The atomic orbitals must be large enough to overlap.
- The atomic orbitals must be of approximately the same energy (the interaction gets less as the difference in energy becomes greater).
- The atomic orbitals must be of the same symmetry.
- If we start with n atomic orbitals we must make n molecular orbitals.

Recipe for using LCAO:

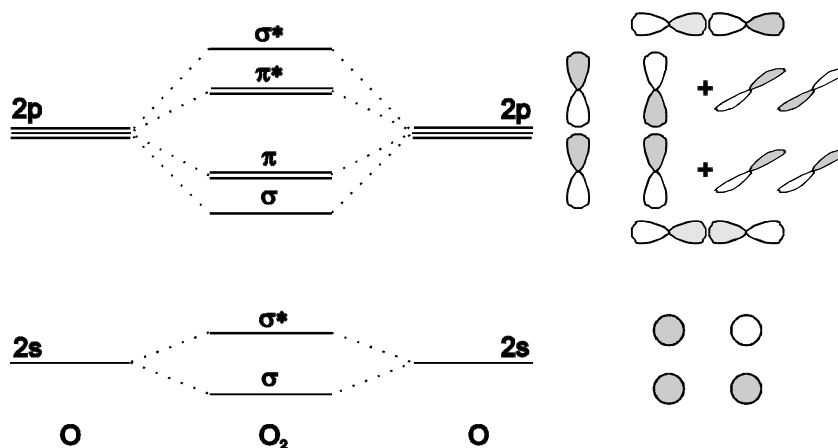
1. Write down the atomic orbitals for the atoms in the correct energy order.
2. Determine which atomic orbitals are too small to form molecular orbitals.
3. Add symmetry labels to the atomic orbitals.
4. Determine which atomic orbitals can interact based on symmetry and relative energies.
5. Put in the non-bonding orbitals (those atomic orbitals that don't interact from 2 and 4).
6. Put in the bonding and anti-bonding orbitals (with separation based on spatial overlap and energy separation of the atomic orbitals).
7. Fill up the molecular orbitals with the appropriate number of electrons.

SIMPLE DIATOMIC MOLECULES

Oxygen (O_2) :-

1. In oxygen, the 1s, 2s and 2p atomic orbitals are occupied.
2. The 1s orbitals are too small to interact with the other atom. However, the 2s and 2p orbitals can interact with the other atom.
3. The 2s and $2p_z$ have s symmetry and the $2p_x$ and $2p_y$ have p symmetry.
4. The 2s – 2p energy separation is too large for interaction, so the interactions that can occur are 2s-2s, $2p_z$ - $2p_z$, $2p_x/y$ - $2p_x/y$.
5. The only non-bonding orbitals are the 1s.
6. The 2s-2s interaction will be small because the orbitals are small. The $2p_z$ - $2p_z$ interaction will be larger because the orbitals are large and point towards each other. The $2p_x/y$ - $2p_x/y$ interaction will be smaller because although the orbitals are larger they point away from each other.
7. Each oxygen has eight electrons, so need to feed sixteen electrons into the molecular orbital diagram.

Bonding in molecules 3



- There are six valence electrons per oxygen, thus;
Electron configuration -- $2s\sigma^2 2s\sigma^{*2} 2p\sigma^2 2p\pi^4 2p\pi^{*2}$
- There are 4 net bonding electrons (bond order of 2).
- There are two unpaired electrons in the $2p\pi^*$ orbitals, thus O_2 is paramagnetic.

Oxygen⁺ (O_2^+) \Rightarrow same MO scheme as O_2

Electron configuration -- $2s\sigma^2 2s\sigma^{*2} 2p\sigma^2 2p\pi^4 2p\pi^{*1}$

There are 5 net bonding electrons (bond order of 2.5). Thus, the bond is stronger and shorter than in O_2 .

Nitrogen (N_2) \Rightarrow same MO scheme as O_2

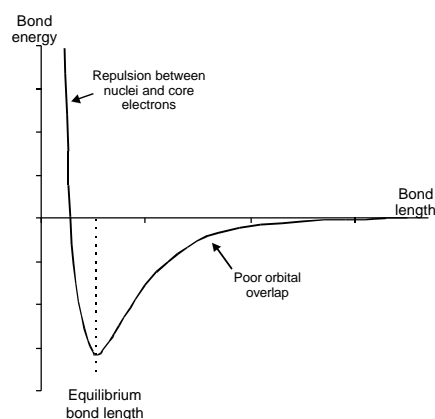
Electron configuration -- $2s\sigma^2 2s\sigma^{*2} 2p\sigma^2 2p\pi^4$

There are 6 net bonding electrons (bond order of 3). Thus the bond is stronger and than O_2 . There are no unpaired electrons, so N_2 is diamagnetic. Both N_2^+ and N_2^- have 5 net bonding electrons and so both have weaker bonds than N_2 .

DETERMINING STRUCTURES BY ENERGY MINIMISATION

We can use molecular orbital theory to calculate the energies of the bonding electrons for any given arrangement of nuclei. For a diatomic molecule, this means varying the bond length.

The same procedure can be carried out on more complex molecules to determine bond lengths and angles and thus calculate the three-dimensional structures of small molecules.

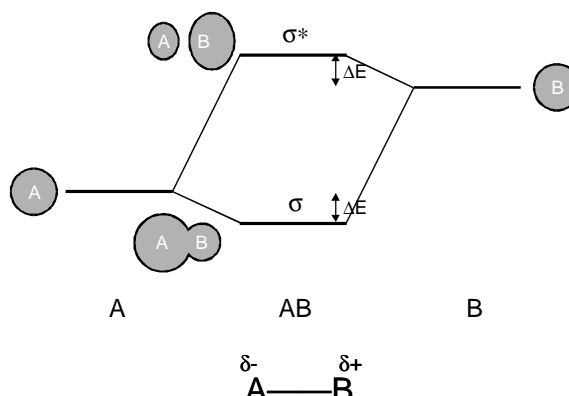


Bonding in molecules 3

HETERONUCLEAR DIATOMICS

Two orbitals of different energy will still give bonding and anti-bonding orbitals. The degree of bonding and anti-bonding (ΔE) decreases as the energy separation between the orbitals increases.

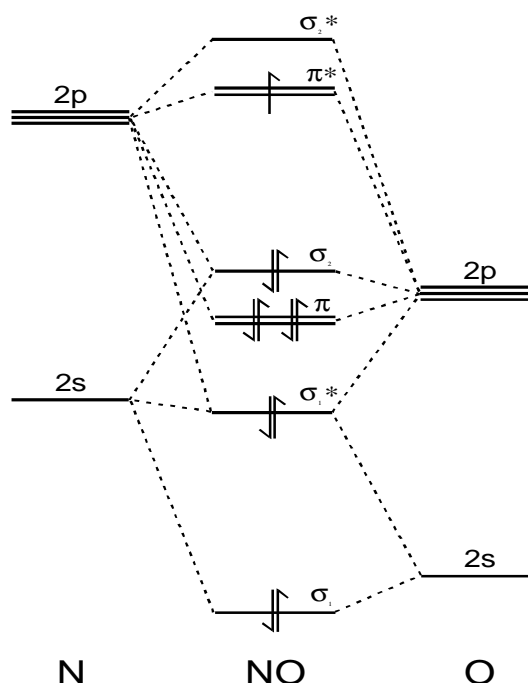
The electron density is not evenly spread over both atoms. The bonding orbital has more electron density on the atom with the lower energy atomic orbital (A) while the anti-bonding orbital has more electron density on the atom with the higher energy atomic orbital (B). This uneven electron distribution leads to a polar bond.



NITRIC OXIDE

Nitric oxide (NO) is a very short-lived radical that is generated and used as a signalling molecule in biological systems. NO is much more reactive than either O_2 or N_2 . It binds to metal ions, such as Fe, via the N at higher affinity than either O_2 or N_2 .

- NO has a dipole moment (a polar bond).
- The non-bonding σ_2 and the anti-bonding σ_1^* and π^* orbitals have more density on the N than the O. The bonding σ and π orbitals have more density on the O. The nitrogen has a partial negative charge and the oxygen has a partial positive charge, mostly due to the distribution of the non-bonding σ orbital electrons.
- The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) are the π^* .



Ionic interactions with metal ions will involve the negatively charged N end of the molecule.

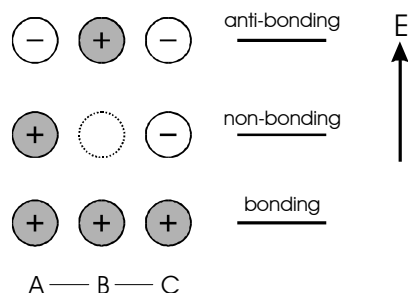
Covalent interactions with other atoms are likely to involve the highest energy electrons. As these are in the σ_2 and π^* orbitals, the N end of the molecule is the more reactive.

Both N_2 and O_2 have a symmetrical distribution of electron density and no dipole moment. The highest energy electrons occupy orbitals spread equally over both atoms instead of being concentrated in one place. Thus, both N_2 and O_2 are less reactive.

MULTINUCLEAR MOLECULES

The same approach can be used for multi-nuclear atoms, we just have more atomic orbital to mix together. We must make the same number of molecular orbitals as the number of atomic orbitals that we start with.

Bonding in molecules 3

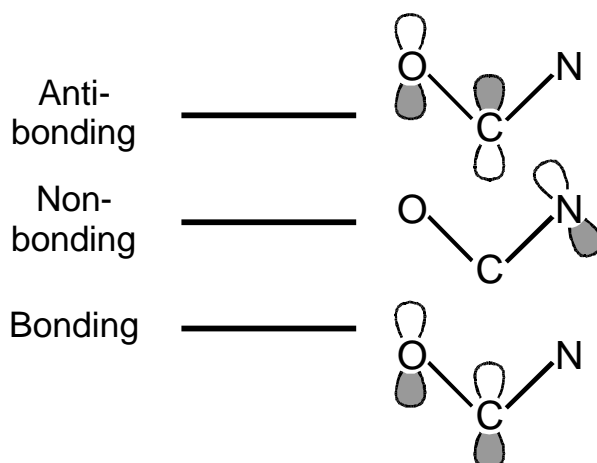


PEPTIDE LINKAGE

With a double bond between the C and O and a single bond between the C and N, there is free rotation around the C-N single bond.

A simplified molecular orbital scheme, considering only the π -electrons and the lone pair, gives bonding and anti-bonding p orbitals on the CO with a non-bonding p-orbital on the N.

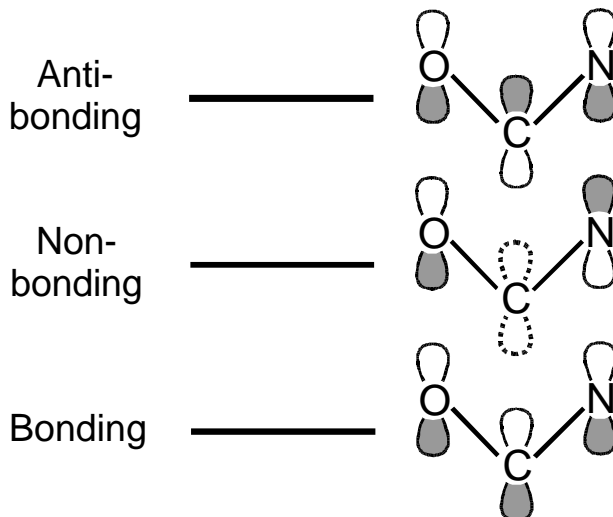
There are four electrons, which will fill the CO π -bonding and the N lone-pair non-bonding orbitals. This gives the CO bond a bond order of 2 and the CN bond a bond order of one.



The N lone pair is in a p-orbital, so it can overlap with the 2p π -orbitals on the C and O to form π molecular orbitals over the three atoms.

There are four electrons that will fill the bonding and non-bonding orbitals, giving a π -bond order of one over the three atoms.

This interaction can only happen if the peptide linkage is planar and rigid. Rotation about the C-N bond would take the nitrogen p-orbital out of alignment.



Comparing the two bonding schemes;

- Both give an overall π -bond order of one (one bonding orbital occupied).
- The delocalised system has more bonding interactions in the bonding orbital and more anti-bonding interactions in the anti-bonding orbital.
- The total energy of the delocalised system is lower and thus it is the more stable.

Implications : Peptide bonds are always planar because the N 2p orbital has to stay in alignment with the C and O 2p orbitals. The N is not basic (compared to an amine N, $-\text{CH}_2\text{-NH}_2$) because the non-bonding electron pair not localised on the N.