Topic 4: Molecular Orbitals and Bonding

We have examined atomic orbitals and how to understand their shapes and relative energies in terms of quantum theory and how spectroscopy provides us an experimental technique to determine energies. Here we examine atoms forming molecules and putting atomic orbitals together to form molecular orbitals.

Molecular Orbitals of H₂

As two H atoms come together their orbitals will overlap, allowing the electrons to move from one atom to the other and *vice versa*. The electrons no longer belong to just one atom, but to the molecule. They are now delocalized over the whole molecule, *i.e.* shared by the atoms.





As two hydrogen atoms approach each other, the overlap of their 1*s* atomic orbitals increases. The wave amplitudes add to generate a new orbital with high electron density between the nuclei.

In general, as

Atoms \rightarrow Molecule Atomic orbitals (AO) \rightarrow Molecular Orbitals (MO)

MO's are formed by combining (overlapping) AO's.

Bonding occurs if it's energetically more favourable for the electrons to be in MO's (*i.e.* in a molecule) rather than in AO's (*i.e.* in individual atoms).

Bonding and Antibonding MO's



In fact, one electron in the (bonding) MO is sufficient for bonding to occur, *i.e.* H_2^+ is predicted to be stable! (It has been verified by experiments.) Atoms will be bonded (in a molecule) provided there is an excess of bonding electrons.

 H_2 , in addition to the lowest σ and σ^* MO's, has other higher energy MO's with corresponding allowed energies, formed from the 2*s*, 2*p*,...AO's. All these MO's have lobe structures and nodes reminiscent of atomic orbitals.

The energy of the H_2 molecule is *lower than* the energy of two isolated H atoms. That is, the energy change associated with bond formation is negative.

We call this molecular orbital a *bonding orbital* for this very reason. It is symmetric to rotation about the interatomic axis, hence it's called a σ MO.

The other orbitals have higher energies than the atomic orbitals of H. Electrons in these orbitals would not contribute to the stability of the molecule; in fact they would result in destabilization. H_2 contains the simplest kind of bond, provided by a pair of shared electrons delocalised around <u>two</u> nuclei in a σ MO. The bond is therefore known as a sigma (σ) bond.

The next-lowest energy orbital is unoccupied. It lies above the energy of the 1*s* atomic orbitals (from which it's built), hence we refer to it as an *anti-bonding orbital*.

Look also at the shape of the lobes: the *anti-bonding orbital* has a node between the two nuclei.

Where the bonding orbital has an electron density <u>build-up</u> between the nuclei, the antibonding orbital would have a <u>reduced</u> electron density (Ψ^2) .

The solution to the Wave Equation for molecules leads to quantum states with <u>discrete</u> <u>energy levels</u> and well-defined shapes of electron waves (<u>molecular orbitals</u>), *just like atoms*.

Each orbital contains a maximum of two (spin-paired) electrons, just like atoms.

"Bonds" form because the energy of the electrons is lower in the molecules than it is in isolated atoms. Stability is conferred by electron *delocalization* in the molecule. This is a quantum effect: the more room an electron has, the lower its (kinetic) energy. Therefore the existence of molecules is a direct consequence of the quantum nature of electrons. This gives us a convenient picture of a bond in terms of a pair of shared (delocalized) electrons. It also suggests simple (and commonly-used) ways of representing simple sigma bonds as:

1. A shared pair of electrons (in a bonding MC	D) H : H
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2. A <u>line</u> between nuclei H–H

Bonding of Multi-Electron Atoms

What kinds of orbitals and bonds form when an atom has more than one electron to share?

We will step up the complexity gradually, first considering other diatomic molecules. These fall into two classes

1. Homonuclear Diatomics. These are formed when two *identical* atoms combine to form a bond. E.g. H_2 , F_2 , Cl_2 , O_2 ...

2. *Heteronuclear Diatomics*. These are formed when two *different* atoms combine to form a bond. E.g. HF, NO, CO, ClBr

A general and systematic approach to the construction of MO's of a homonuclear diatomic molecule is to consider pair-wise interactions between atomic orbitals of the *same energy* and *symmetry*.

Given the $1s_a$, $2s_a$ and $2p_a$ AO's on atom *a* and $1s_b$, $2s_b$ and $2p_b$ AO's on atom *b*, we can form the following *bonding* and *antibonding* MO's of σ and π symmetry:



Head to head combination of p type AO's also results in σ and σ^* MO's



Sideways (parallel) combination of p type AO's results in π and π^* MO's.

As there are two equivalent parallel sets of p type AO's (p_x , p_y), as two atoms come together, there will be two equivalent sets of π MO's (πx and πy), lying in the xz and yz planes respectively (if z corresponds to the interatomic axis).

The following generic energy level diagram applies to all homonuclear diatomic molecules (with *s* and *p* valence AO's)



Next, to determine the ground state electronic configuration of the molecule, assign the electrons to the available molecular orbitals, as dictated by

- The Aufbau Rule (fill MO's in order of increasing energy)
- Pauli Exclusion Principle (a maximum of two electrons per MO with opposite spins)
- Hund's Rule (Maximize total spin when filling degenerate MO's)

As an example, consider Li₂



Three simple kinds of molecular orbitals

1. Sigma (bonding) orbitals.

Electrons delocalized around the two two nuclei. These may be represented as shared electrons, e.g. H:H or Li:Li

2. Non-bonding orbitals

Orbitals that are essentially unchanged from atomic orbitals, and remain *localized* on a single atom (unshared). These may be represented as a pair of electrons on one atom.

3. Sigma star (anti-bonding) orbitals Orbitals with a node or nodes perpendicular to the axis between two nuclei. If occupied, these make a negative bonding contribution, i.e. cancel the contributions of occupied bonding orbitals.



 σ_{1s}

Bond Order

Simple models of bonding include the concepts of *single*, *double*, and *triple bonds*.

Molecular orbital theory provides us with a natural and general definition of <u>bond order</u> that includes all of these and also intermediate bonds as follows:

Bond Order = $\frac{1}{2}$ (No. of bonding electrons - No. of anti-bonding electrons)

E.g. H_2 bond order = 1 (2 electrons in a σ MO)

Li₂ bond order = 1 (2 electrons in a σ MO and 4 electrons in non-bonding core orbitals)

 H_2^+ bond order = 0.5 (1 electron in a σ MO)

 H_2^- and He_2^+ bond order = 0.5 (2 electrons in a σ MO and 1 electron in a σ * MO)

He₂ bond order = 0 (2 electrons in a σ MO and 2 electrons in a σ * MO)

Homonuclear diatomics: The electronic structure of N₂

Using an MO energy level diagram that focuses just on the valence electrons, allocate the 10 valence electrons of N_2

Bond order = $\frac{1}{2}(8 - 2) = 3$ There is an excess of 6 bonding electrons, corresponding to a triple bond: N=N

The 10 valence electrons of N_2 occupy bonding σ and π MO's and an antibonding σ^* MO.

The HOMO is actually a σ MO (lying slightly higher in energy than the π MO's.)

The π^* orbitals are empty - they are the (degenerate pair of) LUMO's.



Homonuclear diatomics: The electronic structure of O₂

 O_2 follows on from N_2 , the extra two electrons are placed in the degenerate pair of π^* MO's (as required by Hund's Rule).

Bond order = $\frac{1}{2}(8 - 4) = 2$. This implies a double bond: O=O

MO theory also predicts that the O_2 molecule would be paramagnetic, due to the non-zero net electron spin, i.e. non-zero magnetic moment.

Oxygen is indeed paramagnetic!

In the next couple of examples, I have used the full MO diagram that includes the core electrons as well as valence electrons. In all cases the same bond order is obtained irrespectice of whether the core electrons are included or not.



Homonuclear diatomics: The electronic structure of F₂

In F₂, the 18 electrons fill up all the MO's, up to and including the π^* MO's.

Bond order = $\frac{1}{2}(8 - 6) = 1$. This implies a single bond: F–F

To obtain Ne₂ the extra two electrons are placed in the σ^* MO. This results in a bond order of zero, i.e. no bond and no Ne₂ molecule!



Heteronuclear diatomics: The electronic structure of NO

The energies of the AO's of N and O are very similar - those on O are slightly lower. The MO's of NO therefore can be constructed the same way as for N_2 or O_2 .

Bond order = $\frac{1}{2}(8 - 3) = \frac{21}{2}$. Strength of bond is between double and triple bonds. Molecule has an unpaired spin - therefore it is paramagnetic.



Heteronuclear diatomics: The electronic structure of HF

In hydrides, such as HF, the MO's need to be constructed from a single 1s AO of H and the 1s,2s,2p AO's of F. The 1s AO of H is closest in energy to the 2p AO's of F, but can only interact with the 2pz AO of F (because of symmetry). As a result, all doubly occupied AO's of F remain largely unchanged, as non-bonding orbitals.



MO's from interaction of s and p orbitals



When forming MO's the parent AO's must have compatible symmetry!

Supplementary information; you don't need to learn this, I will always provide you with the appropriate energy level diagram.



Electron Densities in H₂, F₂, and HF

The square of a wavefunction (corresponding to an occupied orbital) tells us the charge density distribution of the electron(s) in the orbital. If we add up the charge densities from all the occupied molecular orbitals, we obtain the overall charge density distribution in the molecule.



The overall distribution of electron density in heteronuclear diatomic molecules is uneven due to the difference in nuclear charges and the different degree of attraction exerted on the electrons.

In NO the distribution of charge slightly favours O.

In HF it strongly favours F.

Similarly in HCl it favours Cl

Review Types of Orbitals and Bonds in Diatomics

We now know of <u>five</u> kinds of molecular orbitals formed by valence electrons.

1. σ (bonding) orbitals. Electrons in these bonds lower the energy of the molecule (relative to its atomic orbitals). These are shared between two nuclei and delocalised *along the axis between two nuclei*.

2. σ^* (antibonding) orbitals. Electrons in these bonds raise the energy of the molecule (oppose bonding). These orbitals have a node or nodes along the axis between two adjacent nuclei.

3. Non-bonding (nb) orbitals are localised on only one atom and do not affect bonding.

4. π (bonding) orbitals. Electrons in these orbitals lower the energy of the molecule, and are delocalised between two nuclei in two lobes on opposite sides of the internuclear axis.

5. π^* (antibonding) orbitals. These orbitals have lobes on opposite sides of the internuclear axis, and a node between adjacent atoms.



Bonding in Solids

a) Network Covalent, eg Diamond

The structure of diamond is known to be a tetrahedral arrangement of carbon atoms organised in a three-dimensional, crystalline array. This can be measured by e.g. x-ray diffraction, and the internuclear distances are known very precisely.

In our simple bonding model, every carbon atom in diamond is bonded to four carbon neighbours by a simple σ bond. The electrons are not delocalised further.

This model is a typical description of many materials we refer to as *network solids*. They are effectively large molecules with neighbouring atoms connected by a covalent σ bond.

C and Si are two elements that form covalent network crystals. Compounds that form covalent network solids include SiO_2 , SiC, BN, and Si_3N_4 .

Network solids like diamond can be treated as one large molecule, which means that the entire material has a set of quantum states (allowed energies), and that only two electrons can be in each orbital (allowed energy).

We can see the general effect of increasing molecular size by calculating the allowed energies in fragments of a 3-dimensional diamond network of increasing size. The allowed states fall into two groups, bonding and antibonding, as we would expect. As the number of atoms in the network structure increases, so does the number of allowed states and the *density of states* (how close together in energy they are).

The ground state electronic configuration of network solids has all the σ energy levels filled, and all of the σ^* energy levels empty.

The lowest energy (HOMO \rightarrow LUMO) electronic transition is given by the *band gap*, the energy difference between the top of the (filled) band of allowed σ energies and the (empty) band of allowed σ * energies.

In network solids and insulators, this band-gap energy is very large.

These materials are colourless and transparent because the longest wavelength that can be absorbed is shorter than the shortest wavelength in the visible spectrum (approx. 400 nm)

That is,
$$E_{band-gap} > \frac{hc}{\lambda_{\min}} = \frac{6.626 \times 10^{-34} \times 3.00 \times 10^8}{4.0 \times 10^{-7}}$$

 $E_{band-gap} > 5.0 \ge 10^{-19} \text{J or } 3.1 \text{eV}$

b) Metallic Bonding

Metals are also crystals in which the atoms are bonded to one another and can be treated as a single, large molecule. However in metals the bands of allowed energy levels are remarkably different from insulators.

If we take the same approach with, say sodium, as for diamond, we find that increasing the size of the fragment gives two bands of energy levels with <u>no band gap</u>. Energy levels in metals behave as a single, *partially-filled* band.

This means that there are many energy levels close together, and that the longest wavelength transition is much longer than 400nm, so the materials are <u>opaque</u>.

Natural Semiconductors are network solids with band gap energies that lie in the visible or UV range. They may thus be transparent (UV absorbing) or coloured (visible absorbing). Absorption of a photon promotes an electron from the lower, filled band into the unfilled upper band. Once in this band (the conduction band), the electron has enough thermal energy to *move* and hence to conduct electricity.

Promotion of an electron leaves a *vacancy* or hole in the lower (valence) band, so electrons there <u>also become mobile</u>, and have enough thermal energy to move between states within that band.

Conduction can be regarded as taking place through both electrons in the conduction band and holes in the valence band.

Electrons can be promoted into conduction band states by light, or by thermal excitation (heat).

Conduction band			
Valence band			
	Insulator	Semi-conductor	Metal

In natural semiconductors with small band gaps, some electrons are thermally excited into the conduction band. The fraction of excited electrons increases with temperature, *and so does the conductivity*.

Materials that are insulators at low temperatures become increasingly good semiconductors with increasing temperature.

Doped Semiconductors

Semiconductors can be synthesised by introducing foreign atoms into an insulator to modify its electronic structure. There are two types of doped semiconductors.

N-type semiconductors are prepared by introducing atoms with occupied quantum states *just below the bottom of the conduction band*.

Some electrons from these *localised* electronic states are thermally excited into the conduction band, where they become mobile and act as (negative) charge carriers.

Typical n-type semiconductors are prepared by substituting group 15 elements (P, As, Sb) into the crystal lattice of Si or Ge (group 14). Group 16 elements can act as double donors into these lattices.

P-type semiconductors are prepared by introducing atoms with vacant quantum states *just* above the top of the valence band.

Some electrons from the filled valence band are thermally excited into these localised orbitals. This leaves vacancies or holes in the valence band that are mobile and act as (positive - "p-type") charge carriers.

Typical p-type semiconductors are prepared by substituting group 13 (B, Al, Ga) or group 2 or 12 (Be or Zn) elements into the crystal lattice of an insulator.

Substitution into compound semiconductors - e.g. GaAs rather than Si or Ge - are a little more complex. For example, Group14 additives can act as donors or acceptors, depending on which element they substitute.



c) Ionic "Bonding"

Molecular Orbitals come about when the energy of delocalised valence electrons (bonding MO's) are lower than those localised on individual atoms.

In extreme cases where the allowed energies of electrons in two different atoms are very different, the lowest energy state of the two atoms together is not a bond but the transfer of one or more electrons from one atom to an atomic orbital of another.

E.g. $\text{Li}(1s^2 2s^1) + F(1s^2 2s^2 2p^5) \rightarrow \text{Li}^+(1s^2) + F^-(1s^2 2s^2 2p^6)$

This kind of electron transfer leads to the formation of two ions.

In order for this to be favourable (even more favourable than delocalisation into a MO), the available atomic orbital of the acceptor atom must be much lower in energy than the highest filled atomic orbital of the donor atom. This usually means few outer shell electrons for the donor (big atom) and an almost filled outer shell for the acceptor (small atom with tightly bound electrons)

Electronegativity again proves to be a useful concept in dealing with ionic bonds. From the periodic table we can see that the least electronegative atoms are good electron donors (cation formers), and the most electronegative atoms are good electron acceptors (anion formers).

We can use the electronegativity difference between two atoms (Δ_{EN}) to empirically define the *partial ionic character* of a bond as a fraction of the maximum possible difference, 4.0.

E.g. for HF, $\Delta_{EN} = 4.0 - 2.1 = 1.9$ Partial Ionic Character = 1.9/4.0 = 0.495

HCl: (3.0 - 2.1)/4.0 = 0.23NO: (3.5 - 3.0)/4.0 = 0.13

LiF: (4.0 - 1.0)/4.0 = 0.75 MgCl₂: (3.0 - 1.2)/4.0 = 0.45

Electronegativity differences >2 generally give ionic bonds, whereas $\Delta_{EN} <1$ are covalent (delocalised MO's). This gives a good guide to the *character* of a bond.

What we call an ionic bond is simply the long-range electrostatic attraction between cation(+) and anion(-), together with the short-range repulsion between electrons in adjacent ions. The equilibrium distance between cation and anion nearest-neighbours occurs when the <u>potential</u> energy is a minimum. That is, when the attractive and repulsive forces are exactly equal and opposite.