The Wave Equation for Molecules
Recall that the wavefunctions of atomic orbitals and allowed energy levels (eigenfunctions and eigenvalues) are obtained by solving the wave equation for electrons bound by an electrostatic potential to a single nucleus.

\[ \frac{-\hbar^2}{2m} \nabla^2 \psi + V\psi = E\psi \]

- Molecular wavefunctions and their energy levels are simply the solution to the wave equation for electrons bound by more than one nucleus.
- E.g. In diatomic molecules, the potential energy function \( V \) describes the attraction of the electrons to two nuclei.
- Computational techniques allow us to numerically solve the wave equation for an arbitrary set of nuclei, and directly obtain electronic structure.

Why Do Atoms Form Molecules?
The Aufbau principle tells us to put electrons into the lowest energy configuration in atoms. Similarly, molecules form when the total energy of the electrons is lower in the molecule than in individual atoms.

1. Molecular Orbitals
   - What are the shapes of the waves?
   - Where are the lobes and nodes?
   - What is the electron density distribution?

2. Allowed Energies
   - How do the allowed energies change when bonds form?

We will use the results of these calculations to make some simple models of bond formation, and relate these to pre-quantum descriptions of bonding. These will build a "toolkit" for describing bonds, compounds and materials.
Wavefunctions and Energies: Bonding in $\text{H}_2$

If we calculate the wavefunctions and allowed energies of a two proton, two electron system as a function of separation between the nuclei (the bond length), then we see how two atoms are transformed into a molecule.

This calculation tells us:
- Whether a bond forms - Is the energy of the molecule lower than the two atoms?
- The equilibrium bond length - What distance between the nuclei corresponds to the minimum in the energy?
- The structure of the bond - What is the electron density (charge) distribution (y)?
- Electronic properties of the molecules - Bond strength, spectroscopic transitions (colour...), dipole moment, polarizability, magnetic character...

The lowest energy state of two isolated hydrogen atoms is two 1s orbitals each with one electron. As the nuclei approach each other, the lowest energy state becomes a molecular orbital containing two paired electrons.

This lobe represents the orbital or wavefunction of the electrons delocalised around the two protons. This is a bond.

Molecular Orbital of $\text{H}_2$

The lowest energy state of two isolated hydrogen atoms is two 1s orbitals each with one electron. As the nuclei approach each other, the lowest energy state becomes a molecular orbital containing two paired electrons.

Quantum States in $\text{H}_2$ (as computed)

$\text{H}_2$ also has other electronic quantum states with corresponding allowed energies. These molecular orbitals have lobe structures and nodes just like atomic orbitals.

This diagram shows some allowed energy levels for atomic H (There are two of them) and molecular $\text{H}_2$.

$\text{R} = \infty$ denotes the two atoms at "infinite separation" – no bond.

$\text{R} = 5.735 \text{Å}$

The orbitals are filled with electrons starting with the lowest energy just like atoms.
Quantum States in H\textsubscript{2}: Allowed Energies

First let's ignore the wavefunctions (orbitals), and consider only the allowed energies, just as we did with atoms. What do we observe?

\[ R = \sqrt{\frac{\hbar^2}{2mV}} \]

\[ R = \sqrt{\frac{\hbar^2}{2mV}} \]

\[ 1s \]

\[ 2s \]

\[ 0.735 \text{ Å (H)} \]

\[ 0.735 \text{ Å (H\textsubscript{2})} \]

Quantum States in H\textsubscript{2}

The energy of the H\textsubscript{2} molecule is lower than the energy of two isolated H atoms. That is, the energy change of forming the bond is negative.

\[ R = \sqrt{\frac{\hbar^2}{2mV}} \]

\[ 0.735 \text{ Å (H)} \]

\[ 0.735 \text{ Å (H\textsubscript{2})} \]

\[ 1s \]

\[ 2s \]

We call this molecular orbital a bonding orbital for this very reason.

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.

H\textsubscript{2} contains the simplest kind of bond, a pair of electrons delocalised between two nuclei, symmetric to rotation about the interatomic axis.

This is known as a \textit{sigma (s)} bond.

Molecular Orbitals in H\textsubscript{2}

The next-lowest energy orbital is unoccupied. As it lies above the highest atomic orbital, we refer to it as an anti-bonding orbital.

\[ R = \sqrt{\frac{\hbar^2}{2mV}} \]

\[ 0.735 \text{ Å (H)} \]

\[ 0.735 \text{ Å (H\textsubscript{2})} \]

\[ 1s \]

\[ 2s \]

\[ 5 \]

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 build-up between the nuclei, the anti-bonding orbital would have a reduced electron density (\(y^2\)).

This orbital is called the \textit{Lowest Unoccupied Molecular Orbital (LUMO)}

This orbital is called the \textit{Highest Occupied Molecular Orbital (HOMO)}
Molecular Orbital Theory

The solution to the Wave Equation for molecules leads to quantum states with discrete energy levels and well-defined shapes of electron waves (molecular orbitals), 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 delocalisation in the molecule as they are bound by more than one nucleus (longer de Broglie wavelength).

This gives us a convenient picture of a bond as a pair of shared (delocalised) electrons. It also suggests some simple (and commonly-used) ways of representing simple sigma bonds as:

1. A shared pair of electrons (dots) H : H
2. A line 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. H₂, F₂, Cl₂, O₂...

   Bond lengths in homonuclear diatomic molecules are used to define the covalent radius of the atom [Lecture 5].

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

Energy Levels in F₂

This diagram shows the allowed energy levels of two isolated F atoms (1s²2s²2p³) and, between them, the F₂ molecule.

Notice that the (filled) 1s energy levels are at much lower energy than the 2s and 2p orbitals. Their energy is virtually unchanged when the bond forms.

Such electrons, below the outermost electron shell (n) are commonly referred to as core electrons, and are ignored in simple models of bonds.
Energy Levels in $F_2$

This diagram shows the outer, unfilled, valence energy levels of

Two $F$ atoms and $F_2$.

$F$ has 9 electrons, hence 7 outer shell electrons in the configuration shown. i.e. One unpaired electron each.

The electronic configuration of the 14 valence electrons of $F_2$ is shown in blue.

Each molecular orbital contains two, spin-paired electrons.

The total energy of the electrons is lower in the molecule than in the atoms.

Valence Molecular Orbitals in $F_2$

The two lowest-energy molecular orbitals are similar to the orbitals of $H_2$.

The lowest is a sigma bonding orbital, with a pair of delocalized electrons between the nuclei.

The second-lowest is a sigma-star ($\sigma^*$) anti-bonding orbital.

In $F_2$, the $2\sigma$ bonding and $\sigma^*$ anti-bonding orbitals both contain a pair of electrons.

The sum of these is no net bond.

(We’ll see where the bond comes from later.)

Bonding of Multi-Electron Atoms

Before considering the other molecular orbitals of $F_2$, we will look at a simple heteronuclear diatomic molecule, $HF$.

Here the atomic energy levels are different, so this will give us an idea about what constitutes a bond between unlike atoms.

However, $HF$ is in some ways simpler to deal with as it has fewer electrons - both valence electrons and total electrons.
Energy Levels in HF
This diagram shows the allowed energy levels of isolated H (1s) and F (1s^2/2s^2/2p^5) atoms and, between them, the HF molecule.

Note:
1. F 1s is at much lower energy than H 1s (because of the higher nuclear charge)
2. F 1s^2 electrons are core electrons. Their energy does not change when HF is formed.
3. H 1s and F 2p valence electrons go into molecular orbitals with new energies.

Bonding in HF
This diagram shows the outer, valence energy levels of H, F and HF.

The electronic configuration of the 8 valence electrons of HF is shown in blue.

There are four orbitals, each containing a pair of electrons. How do we represent these?

Molecular Orbitals in HF
This non-bonding molecular orbital (n) has an almost spherical lobe showing only slight delocalisation between the two nuclei. Non-bonding orbitals look only slightly different to atomic orbitals, and have almost the same energy.

This core orbital is almost unchanged from the F 1s orbital. The electrons are bound tightly to the F nucleus.
Molecular Orbitals in HF

These two degenerate (filled) HOMO’s are centred on the F atom, like 2pₓ and 2pᵧ orbitals. Electrons in these two orbitals are not shared (much) by the fluorine nucleus. They behave like the 2p orbitals and are also non-bonding (n).

This MO, which is like a 2pₓ orbital, is lower in energy in the molecule (a bonding orbital), and one lobe is delocalised around the H atom.

This (empty) LUMO is an antibonding orbital with a node on the interatomic axis between H and F.

Electrons in these two orbitals are not shared (much) by the fluorine nucleus. They behave like the 2p orbitals and are also non-bonding (n).

What do we take from all this?

Three simple kinds of molecular orbitals

1. Sigma (bonding) orbitals (s).
   - Electrons delocalised along the axis between two nuclei. These may be represented as shared electrons, e.g. H:H or H:F, H-H or H:F

2. Non-bonding orbitals (n)
   - Orbitals that are essentially unchanged from atomic orbitals, and remain localised on a single atom (unshared).
   - These may be represented as a pair of electrons on one atom.

3. Sigma star (anti-bonding) orbitals (s*)
   - Orbitals with a node or nodes along the axis between two nuclei. These do not contribute to bonding, they “undo” bonding.

Summary

You should now be able to
- Explain the reason for bond formation being due to energy lowering of delocalised electrons in molecular orbitals.
- Describe a molecular orbital.
- Recognise (some) sigma bonding, sigma antibonding and non-bonding orbitals.
- Be able to assign the (ground) electron configuration of a diatomic molecule.
- Define HOMO and LUMO, and homonuclear and heteronuclear diatomic molecules.

Next Lecture
- Molecular Orbitals and Multiple Bond Formation
- Bond Order