Last lecture...

- You should have a rough idea of organic nomenclature
- You know how to draw organic molecules
- But what do the lines actually mean?
- And why do we represent them in a 'zig-zag' form?

Organic drawings try to give a simple but realistic representation of a molecule's 3D structure. The shape arises from the bonding in the molecule. Here we present a simplified model of the bonding. More detailed explanations can be found in other courses.
Atomic orbitals I

- There are 3 quantum numbers that express the SIZE, SHAPE and DIRECTION of each orbital
- An orbital describes the energy and probability of finding an electron
- We are only interested in what they look like...

**Size** - simply how big each orbital is \((n=1, 2, 3 \text{ etc})\)

**Shape** - organic chemists normally interested in s & p

- Each orbital represents a 90% chance of finding an electron
- A node = 0% chance of finding an electron
- Do not confuse phase and charge!
Atomic orbitals II

Direction - p (d&f) orbitals also have a direction
Spin - Each electron can have a spin of +½ or -½
An orbital can only contain electrons of different spin (so 2 maximum)
Atomic orbitals III

- Number of electrons per atom given by atomic number
- Add electrons to lowest energy orbital first
- If orbitals have the same energy electrons will not pair up
**Linear combination of AO (LCAO)**

- Electrons shared in a covalent bond result from the overlap of two atomic orbitals (AO) to give two molecular orbitals (MO).
- Conservation of orbitals: $j$ AO $\Rightarrow$ $j$ MO

**Bonding**

\[ \bullet + \bullet \rightleftharpoons \bullet \bullet \]

**Antibonding**

\[ \bullet - \bullet \rightleftharpoons \bullet + \bullet \]

- If bonding MO is symmetrical about axis - $\sigma$ (sigma)
- If antibonding MO is symmetrical about axis - $\sigma^*$
- All s orbitals (1s, 2s, etc) combine this way

\[ \sigma^* \]

\[ \sigma \]
σ Bonds

Bonding MO σ

Antibonding MO σ∗
Combination of p orbitals

- What happens if 2 atoms with p orbitals combine?
- Only 2 of 6 AO can overlap head on
- Resultant 2 new MOs are symmetrical about axis so $\sigma$ & $\sigma^*$
- What happens to the other 4 orbitals?

\[ 2p\text{ AO} + 2p\text{ AO} \]

\[ \text{out-of-phase combination} \]

\[ 2p\sigma^* \text{ MO} \]

\[ \text{nodal plane} \]

\[ \text{rotational axis} \]

\[ 2p\sigma \text{ MO} \]

\[ \text{in-phase combination} \]
Side-on combination of p orbitals

- New bonding MO does not have a rotational axis and is a $\pi$ bond
- New antibonding MO is not symmetric about axis - $\pi^*$ bond
- Remember 2p$\pi$ MO is ONE orbital so a maximum of 2 electrons
- Remember 2p$\pi^*$ MO is ONE orbital so can only contain 2 electrons
p orbitals

Bonding MO $\pi$

Antibonding MO $\pi^*$
Why is methane tetrahedral with all bonds the same?
Why not just two bonds at 90° due to the $2p_x$ & $2p_y$ orbitals?
LCAO works for all molecules so we combine:

$$4 \times 1s \text{ AO (H)} \text{ with } 1 \times 2s \text{ AO (C)} \text{ & } 3 \times 2p \text{ AO (C)}$$
The problem with MO theory?

- MO theory is a good model that explains shape etc.
- It says electrons shared over whole molecule.
- Not very useful to organic chemists. We prefer localised bonds...

\[\text{1s} + \text{2s} + \text{2p}_x + \text{2p}_y\]

\(4\)xhydrogen \(1\)xcarbon

anti-bonding

bonding