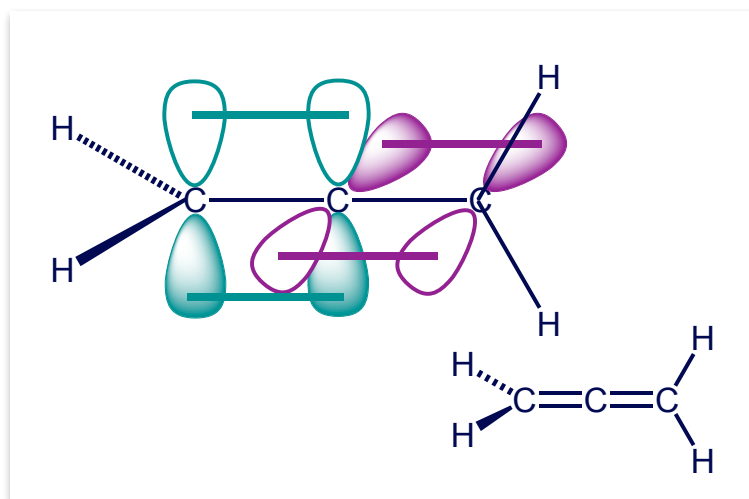


# Introduction to Organic Chemistry

## 2018 – 7 lectures

### Handout 1 - Bonding

Dr Jonathan Burton



<http://burton.chem.ox.ac.uk/teaching.html>

- *Organic Chemistry* J. Clayden, N. Greeves, S. Warren
- *Stereochemistry at a Glance* J. Eames & J. M. Peach
- *The majority of organic chemistry text books have good chapters on the topics covered by these lectures*
- *Elieil Stereochemistry of Organic Compounds* (advanced reference text)

## Course Outline

These seven lectures will focus on bonding, stereochemistry, and an introduction to mechanism (curly arrows). All of these areas are crucial to being able to rationalise, and more importantly predict, what will happen when organic molecules are treated with any of a plethora of reagents used by organic chemists and chemists in general. Aspects of bonding will receive much more in-depth treatments in both the 'inorganic' and 'physical and theoretical' lecture courses throughout the degree and here we will meet simple, but useful views of bonding, that are fit for our purposes. 'Curly arrow' mechanisms will be met in virtually all of the organic chemistry lecture courses and this course will introduce the key basic principles for drawing reasonable curly arrow mechanisms. Uniquely, this course will provide virtually all of the content you require regarding stereochemistry. Stereochemistry is chemistry in three-dimensions and developing skills to be able to manipulate molecules in 3-D in one's own head will prove important. Practising organic chemists frequently build 'ball-and-stick' models of molecules to better aid visualisation and a cheap, plastic molecular model kit can be very useful when working through stereochemical problems and will be useful throughout your degree – a decent one can be purchased here:

[https://www.cochranes.co.uk/show\\_product.asp?id=399&catid=44](https://www.cochranes.co.uk/show_product.asp?id=399&catid=44)

## Synopsis

Bonding – Lewis structures and bonding, formal charge, basic VSEPR, hybridisation, molecular orbitals, structures of some functional groups, drawing organic molecules, skeletal representations

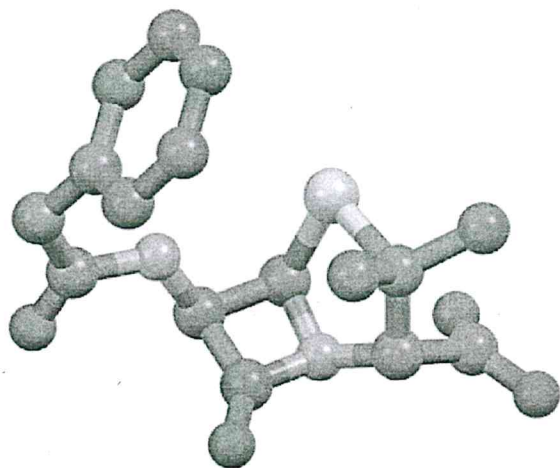
Stereochemistry – conformation, stereochemical definitions, optical activity, configuration, chirality, enantiomers and diastereomers, CIP rules, compounds with more than one stereocentre, meso compounds, racemisation, planar and helical chirality, resolution, relative and absolute configuration

Mechanism – acid base reactions, curly arrows, delocalisation

## Two of Oxford's Nobel Laureates

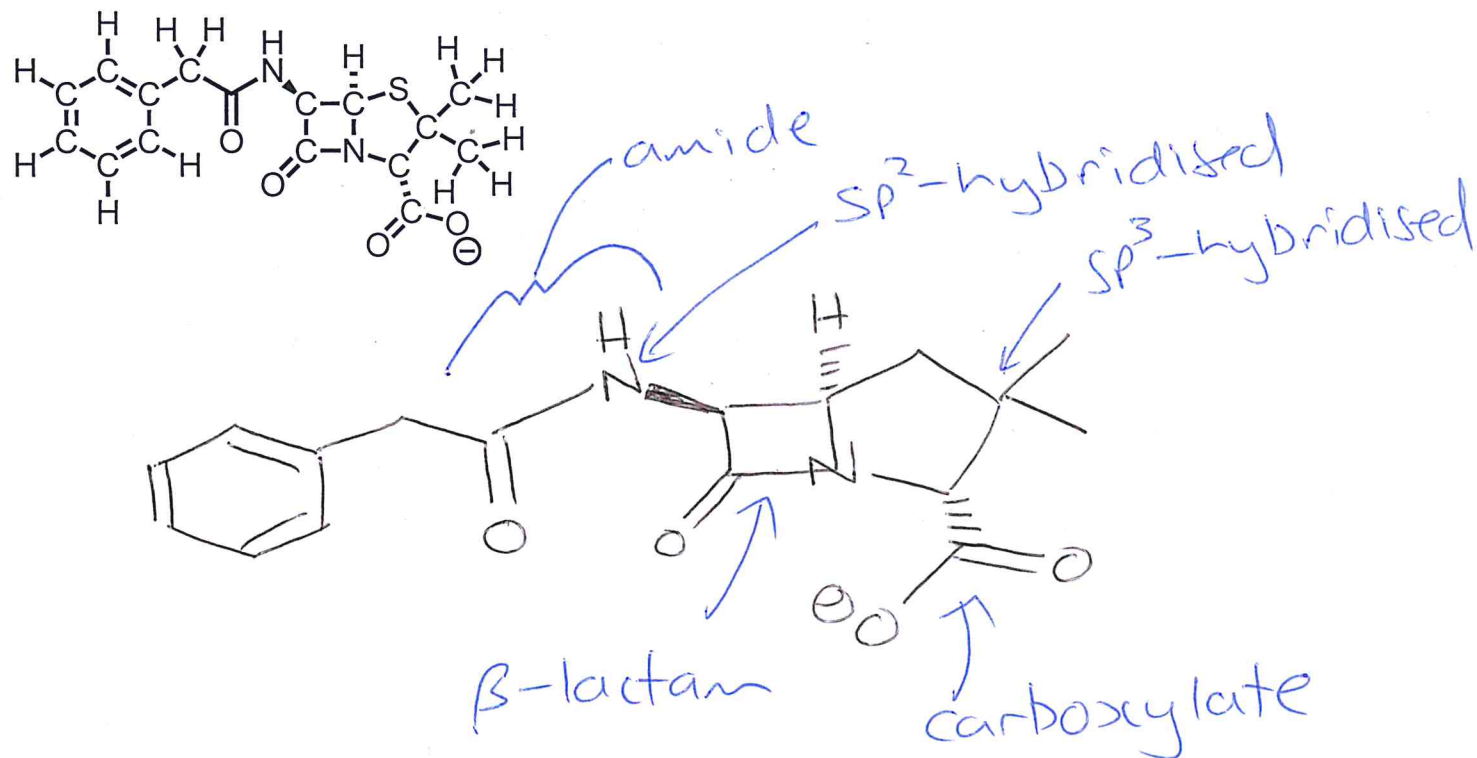
### Dorothy Hodgkin

- Dorothy Crowfoot Hodgkin (1910-1994)
- Read Chemistry at Oxford (Somerville College)
- Chemistry Tutor Somerville College
- Nobel Prize 1964 for "her determinations by X-ray techniques of the structures of important biochemical substances"
- 1945 – determined the structure of penicillin



hydrogen atoms omitted for clarity

penicillin G



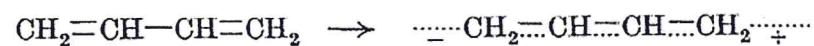
## Two of Oxford's Nobel Laureates

### Robert Robinson

- Sir Robert Robinson (1886-1975)
- Waynflete Professor of Organic Chemistry 1930-1954
- Nobel Prize 1947 for "investigations on plant products of biological importance, especially the alkaloids"
- Inventor of the 'curly arrow'



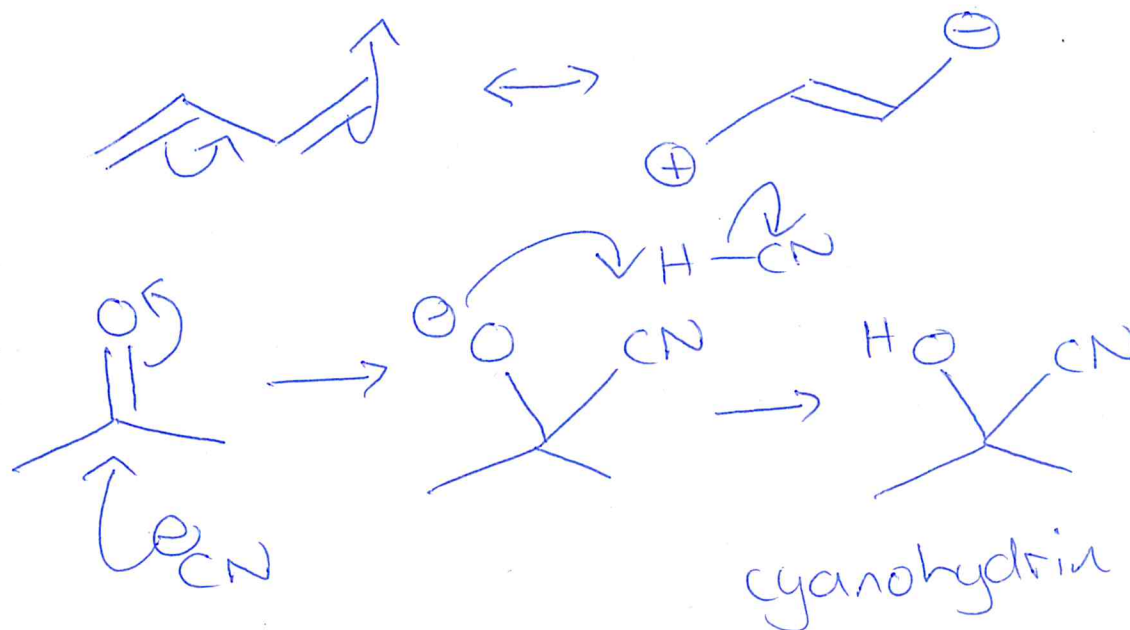
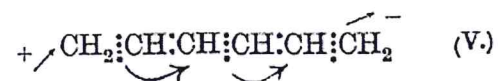
(a) *Conjugation of Ethylene Linkings.*—The representation of the active phase and conjugation of butadiene on the partial valency theory is



and on the Thomson and Lewis-Langmuir theory as now interpreted



Similarly, the conjugation of three double bonds, supposing such to occur, would be represented thus:—



## Atoms

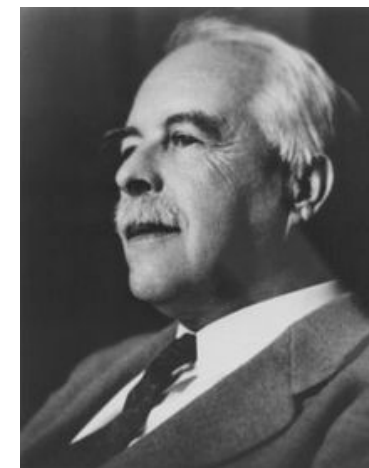
- **Bohr atomic model** - electrons moving in specific orbits, s, p, d, f.

atomic number = number of protons

Quantum number	max. no. of electrons in shell									
1	2e	${}^1\text{H}\cdot$ $1s^1$								${}^2\text{He}:$ $1s^2$
2	8e	${}^3\text{Li}\cdot$ $2s^1$	${}^4\text{Be}:$ $2s^2$	${}^5\text{B}:$ $2s^2, 2p^1$	${}^6\text{C}:$ $2s^2, 2p^2$	${}^7\text{N}:$ $2s^2, 2p^3$	${}^8\text{O}:$ $2s^2, 2p^4$	${}^9\text{F}:$ $2s^2, 2p^5$	${}^{10}\text{Ne}:$ $2s^2, 2p^6$	
3	8e	${}^{11}\text{Na}$	${}^{12}\text{Mg}$	${}^{13}\text{Al}$	${}^{14}\text{Si}$	${}^{15}\text{P}$	${}^{16}\text{S}$	${}^{17}\text{Cl}$	${}^{18}\text{Ar}$	

electrons in outer shell (valence shell)

- **Lewis Bonding Theory** (1916) – historic and useful
- Bonding = achievement of completely filled (or empty) valence shells by sharing (covalent bonds) or transfer of electrons (ionic bonds) between atoms
- **Lewis** bonding forms a simple basis for the qualitative understand of the structures and properties of organic molecules
- you will meet more sophisticated theories of bonding – particularly molecular orbital theory – as the course progresses

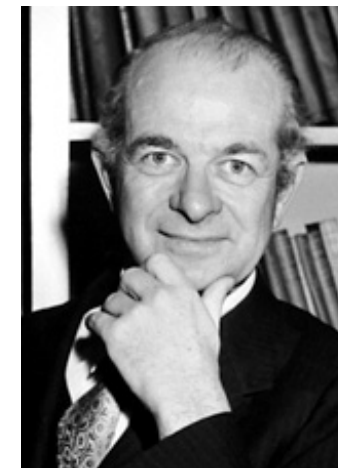


Gilbert. N. Lewis

## Atoms

■ **Electronegativity** ( $\chi$  chi) – measure of the relative ability of an atom to attract valence electrons to itself (Pauling Scale 1932, empirical)

<i>increasing electronegativity</i> →						
H 2.2						
Li 1.0	Be 1.6	B 2.0	C 2.6	N 3.0	O 3.4	F 4.0
Na 0.9	Mg 1.3	Al 1.6	Si 1.9	P 2.2	S 2.6	Cl 3.2
						Br 2.9
						I 2.6
						<i>↑ increasing electronegativity</i>



Linus Pauling

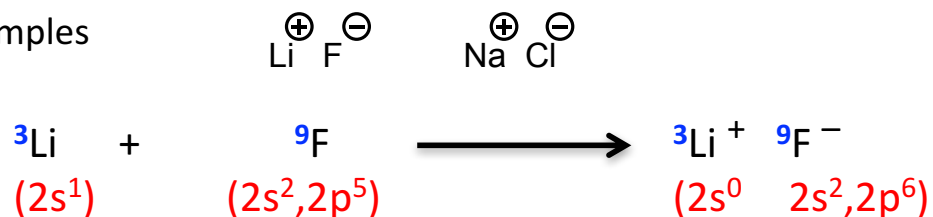
■ the following order of electronegativities can be useful to remember:  $F > O > Cl > N$

### ■ Ionic Bonds

■ usually occur between atoms at opposite ends of the periodic table i.e. between atoms that have very different electronegativities

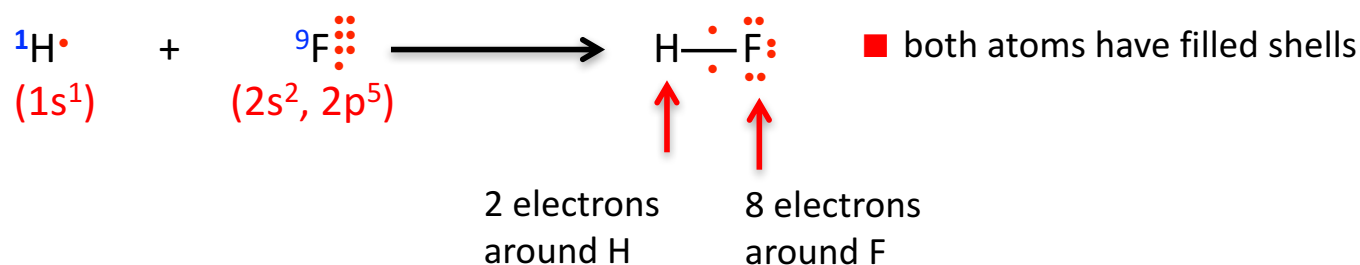
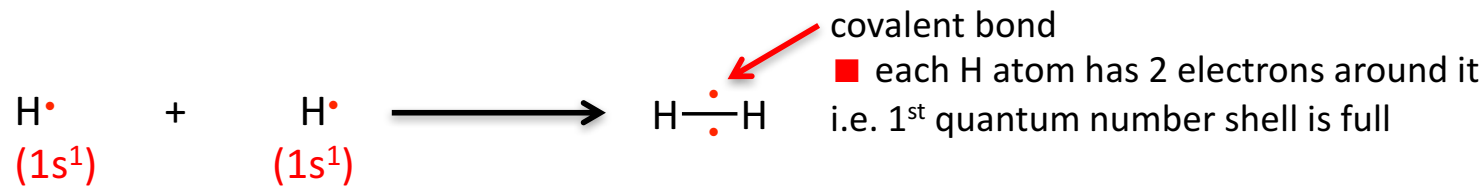
■ the atoms involved in ionic bonding achieve filled shells by the transfer of electrons (usually 1 or 2 electrons)

■ examples

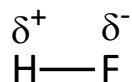


## Covalent bonds

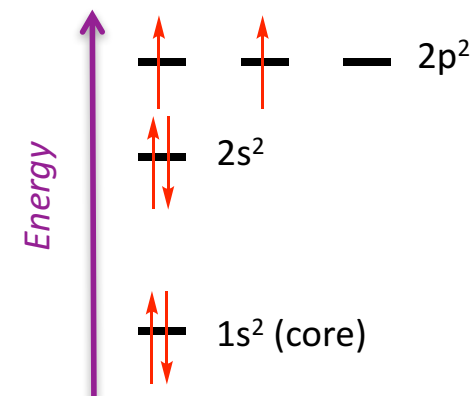
- generally between atoms of similar electronegativity – sharing of electrons



- in H—F the atoms have a large difference in nuclear charge and hence electronegativity
- the shared pair is therefore not equally distributed but displaced towards F – this is bond polarisation by the inductive effect leading to a permanent dipole

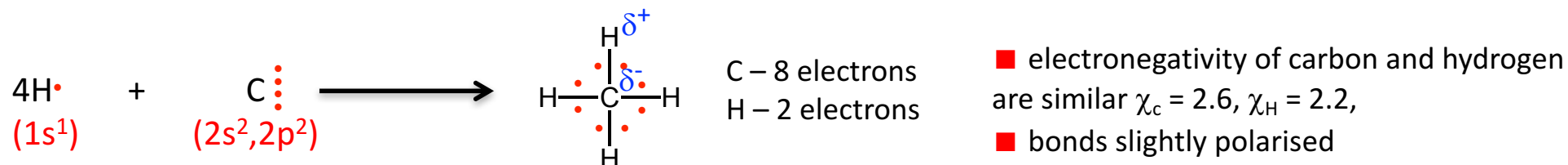


- the Greek letter  $\delta$  (delta) is used to indicate a partial charge
- organic molecules are held together by covalent bonds
- carbon is in the middle of the period, with no great difference in electronegativity with other elements
- very difficult to form stable closed shell by ionisation i.e.  $\text{C}^{4+}$  and  $\text{C}^{4-}$

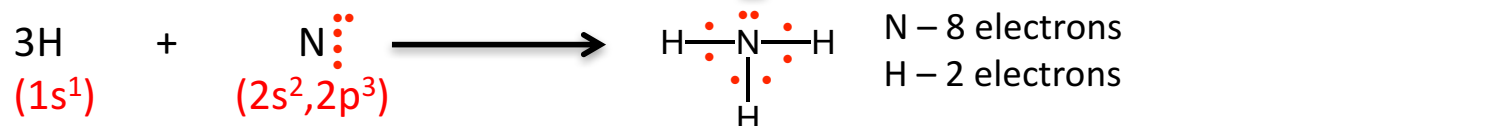


■ CH<sub>4</sub> - methane

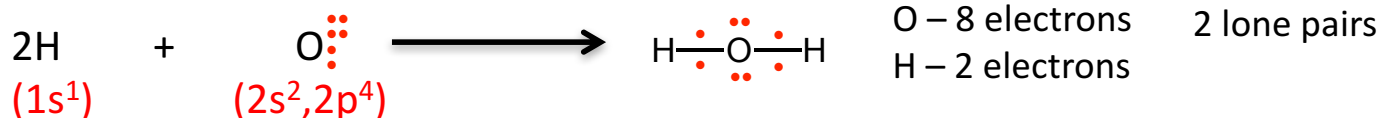
■ bonds formed by the combination of 4 H atoms (1s<sup>1</sup>) and 1 C atom (2s<sup>2</sup>, 2p<sup>2</sup>)



■ NH<sub>3</sub> - ammonia



■ H<sub>2</sub>O - water



### Rules for Lewis structures

■ line — = shared pair = covalent bond – **no more drawing dots for electrons in bonds**

■  $\cdot\cdot$  = unshared pair or lone pair

■ formal charge on atom = number of valence electrons – (number of lone pair electrons +  $\frac{1}{2}$  bonding pair electrons)

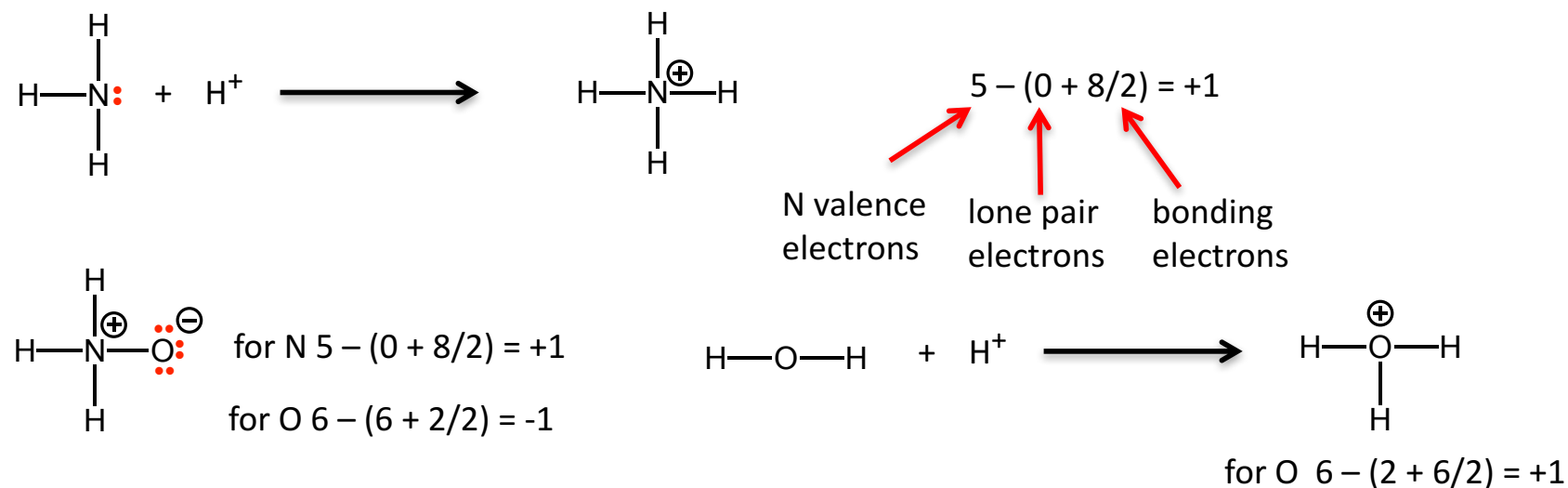
■ for 2<sup>nd</sup> row elements Li → F the sum of the number of bonds plus the number of lone pairs cannot exceed 4

i.e. **no more than 8 electrons around the atom – Lewis octet rule**

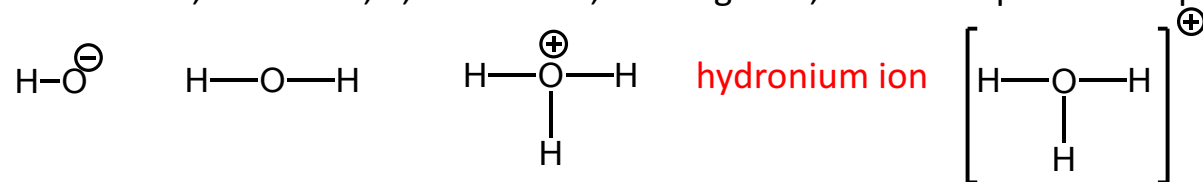


■ formal charge – charge assigned to each atom in a molecule assuming the electrons in the bonds are shared equally between atoms regardless of electronegativity – bookkeeping tool to denote relationship between the bonding electrons and those ‘formally’ belonging to each atom – a useful formalism but must be interpreted with care

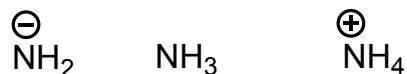
■ formal charge on atom = number of valence electrons – (number of lone pair electrons + number of bonds)



■ (organic) chemists do not work out the formal charge on atoms, they just remember that whenever oxygen has 8 electrons around it, and has 1, 2, or 3 bonds, it is negative, neutral or positive respectively



■ more generally, whenever an atom has 8 electrons around it, and has one more bond than its neutral state, it will be positively charged, and one fewer bonds it will be negative



■ in the hydronium ion the formal positive charge is drawn on oxygen

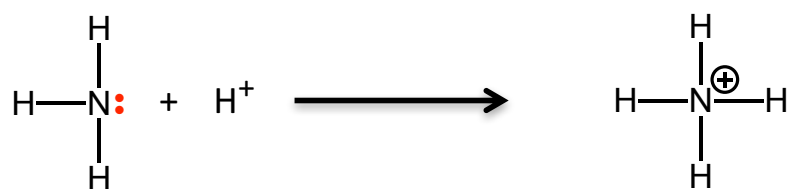
■ in reality the oxygen, being more electronegative than hydrogen, does not have a positive charge and the positive charge is spread out over the 3 hydrogen atoms

■ physical origin of bonding forces (simplified) – if two atoms form a bond, the bonded state must be more stable than the separated atoms

■ in covalent bonds the repulsion between the electrons and between the nuclei is balanced by the attraction of the electrons to the positive nuclei at the stable internuclear distance – the bond length

■ lone pairs, a.k.a. non-bonded pairs, formally interact with only one positive nucleus, hence their interelectron repulsion is greater than for a bond pair – they are higher in energy and more available for bonding

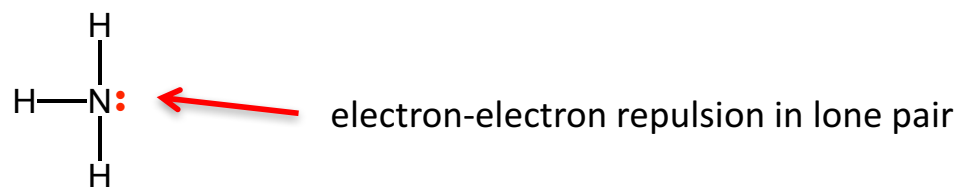
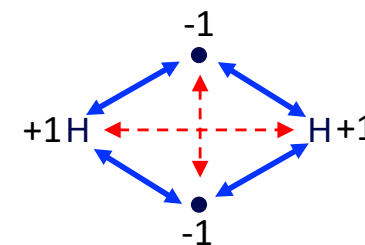
■ reactions which reduce this electron-electron repulsion are favoured



■  $\text{H}_2$

■ attraction – each electron sees 2 positive nuclei ( $\longleftrightarrow$ )

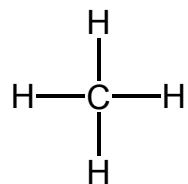
■ repulsion – electron-electron and nucleus-nucleus ( $\longleftrightarrow$ )



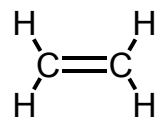
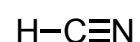
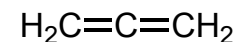
■ in the product the lone pair electrons are now a bond pair and see 2 positive nuclei

■ this is the Lewis basicity of lone pairs - frequently the reactive site of a molecule towards electrophiles

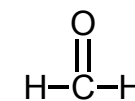
■ Lewis structures are useful in predicting the bonding in molecules but they tell us nothing of the shape of the molecules



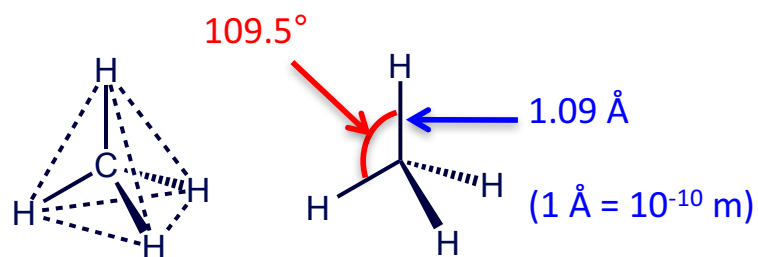
methane

ethene  
(ethylene)ethyne  
(acetylene)hydrogen  
cyanide

allene

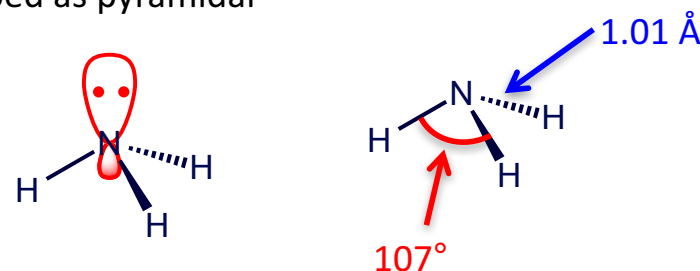
formaldehyde  
(methanal)

- the shapes of the vast majority of organic compounds are determined by repulsion between electrons in the valence shell (VSEPR - valence shell electron pair repulsion)
- i.e. bond pair – bond pair repulsions    bond pair – lone pair repulsions    lone pair – lone pair repulsions
- geometry of molecules is determined by minimising the above interactions
- for methane,  $\text{CH}_4$ , there are 4 bonding pairs of electrons and they repel each other to be as far apart as possible leading to the tetrahedral structure of methane



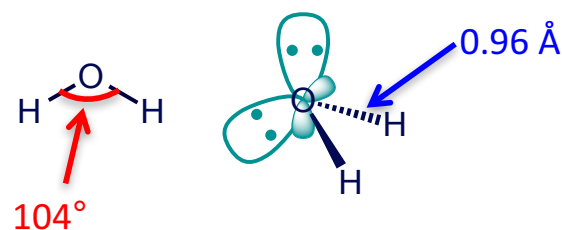
- tetrahedral geometry,  $109.5^\circ$  H-C-H bond angle

- with ammonia there are still four 'groups' to place around the central nitrogen atom – 3 bond pairs and 1 lone pair.  $\text{NH}_3$  is therefore based on a tetrahedron – its shape is described as pyramidal



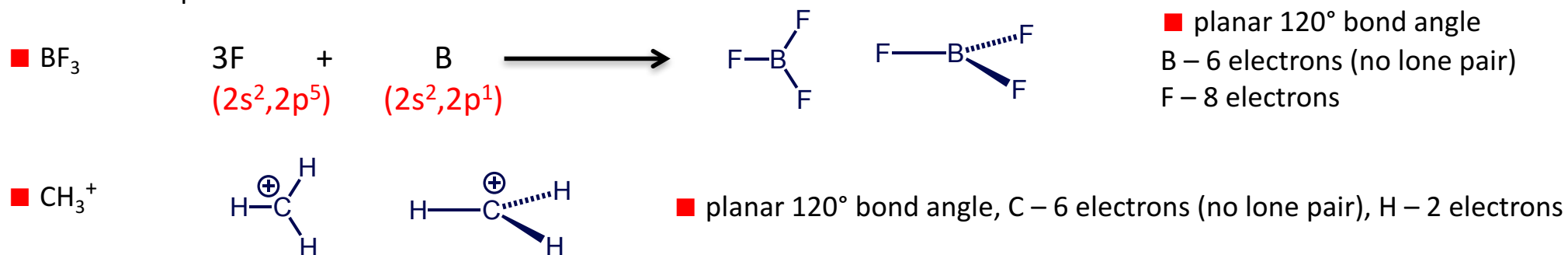
- $107^\circ$  H-C-H bond angle N-H bond length =  $1.01 \text{ \AA}$

- similarly with water there are still four 'groups' to place around the central oxygen atom – 2 bond pairs and 2 lone pairs – water  $\text{H}_2\text{O}$  is therefore also based on a tetrahedron – its shape is described as bent



- bond angles decrease in the order  $\text{CH}_4$ ,  $\text{NH}_3$ ,  $\text{H}_2\text{O}$  because: lone pair / lone pair repulsions are greater than lone pair / bond pair repulsions which are greater than bond pair / bond pair repulsions

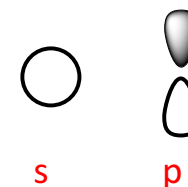
- some examples



- Quantum Numbers and Atomic Orbitals

- atomic orbitals – mathematical functions (wavefunctions) related to the probability of finding an electron in a particular region of space – for organic chemistry we will generally be concerned with s and p-orbitals

- atomic orbitals come in sets associated with the principal quantum number  $n = 1, 2, 3, \dots$



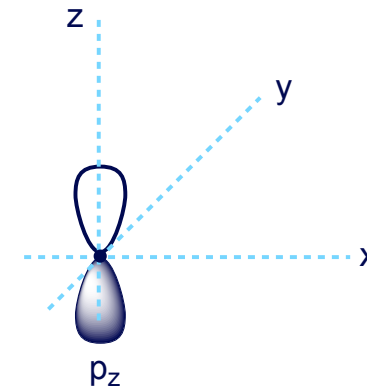
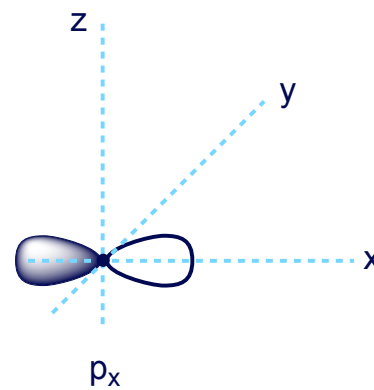
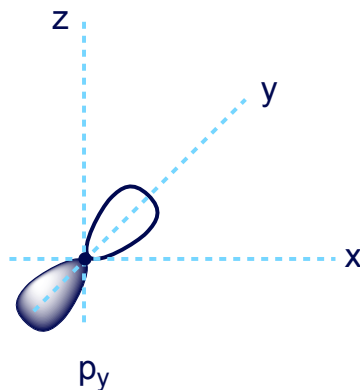
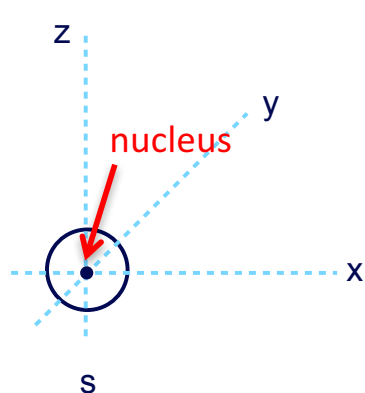
- an atom's highest principal quantum number determines the valence shell of the atom - only these orbitals are generally involved in bonding

- each row of the periodic table indicates a different principal quantum number

- for hydrogen the principal quantum number is 1 giving rise to the familiar 1s orbital

- for carbon the principal quantum number is 2 giving rise to the familiar 2s and three 2p orbitals

■ 's' and 'p' orbitals

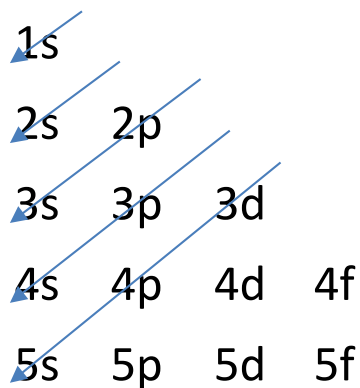


■ s-orbitals - spherical  
electron density decreases  
in moving away from the nucleus

■ there are three p-orbitals,  $p_x$ ,  $p_y$  and  $p_z$ , orthogonal to each other

■ p-orbitals have phase (sign) and a node at the nucleus (where the wavefunction changes sign) – the electron density is zero at a node

■ the order of occupancy of atomic orbitals for a ground state configuration follows the Aufbau principle



■ ground state electronic configuration

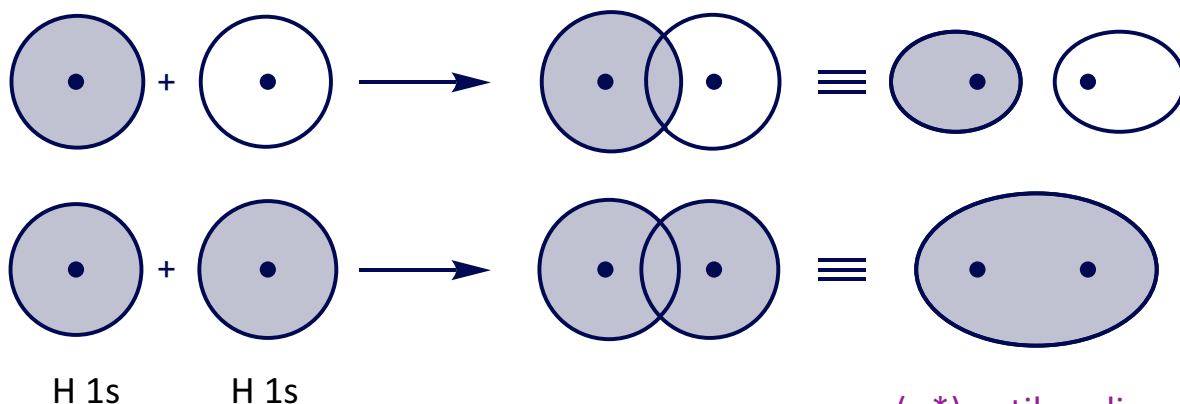
- i) orbitals filled lowest energy to highest energy following the arrows from top to bottom i.e. 1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, etc.
- ii) maximum two electrons in each orbital which must have opposite spins (Pauli exclusion principle)
- iii) empty orbitals of equal energy (e.g. 3 x 2p orbitals) take one electron each before pairing occurs (Hund's rule of maximum multiplicity)

■ **Molecular Orbitals** (simplified – an organic chemistry view)

■ molecular orbitals are formed from combining atomic orbitals – we will look at H<sub>2</sub>

■ overlap of two hydrogen 1s atomic orbitals leads to two molecular orbitals, one lower in energy, and one higher in energy, than the original atomic orbitals

■ electrons are fed into the lowest energy molecular orbital first



■ destructive overlap of atomic orbitals leads to *anti-bonding* molecular orbital (internuclear node)

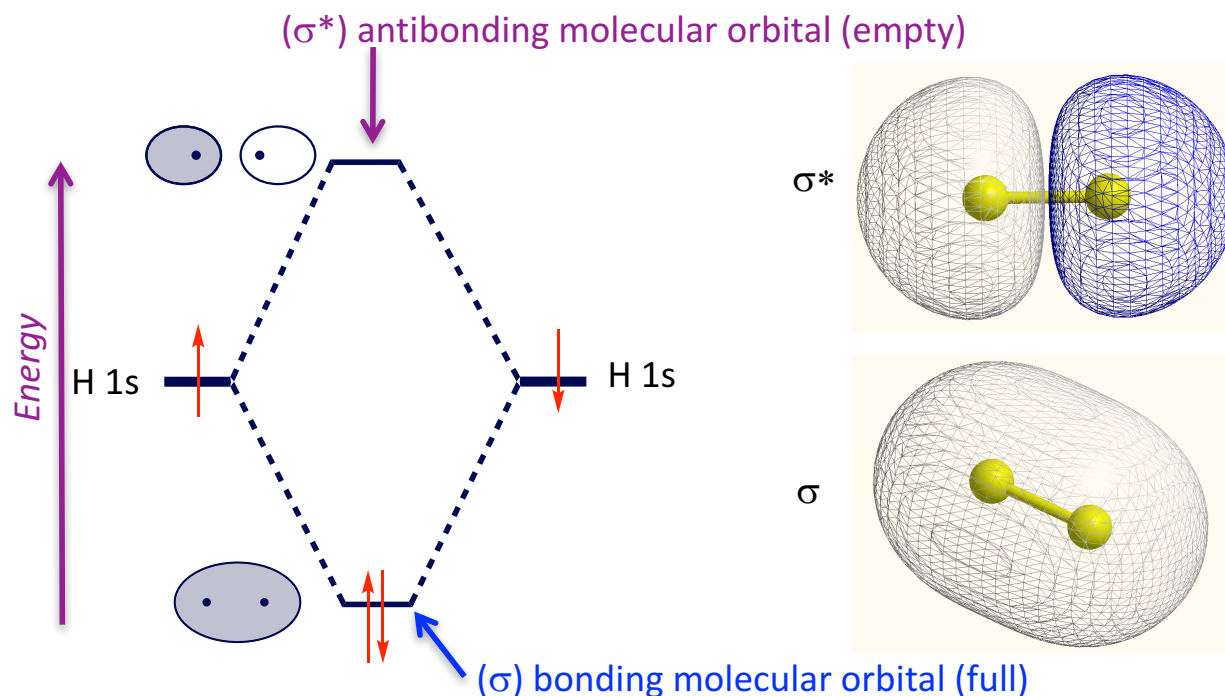
■ constructive overlap of atomic orbitals leads to *bonding* molecular orbital

■ molecular orbital diagram for H<sub>2</sub>

■ energy released in combining two hydrogen atoms to give H<sub>2</sub> is the bond strength = 432 kJmol<sup>-1</sup>

■ bonding molecular orbital in H<sub>2</sub> has cylindrical symmetry and is termed a  $\sigma$ -orbital (sigma orbital) – c.f. – s-atomic orbital

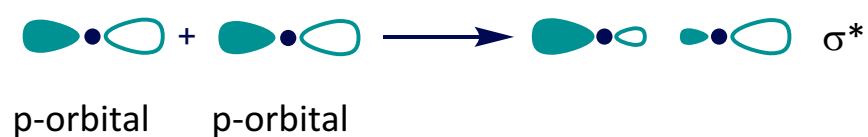
■ in H<sub>2</sub> this orbital can be viewed as the (Lewis) bond and is called a  $\sigma$ -bond although the electron density is distributed over the whole molecule



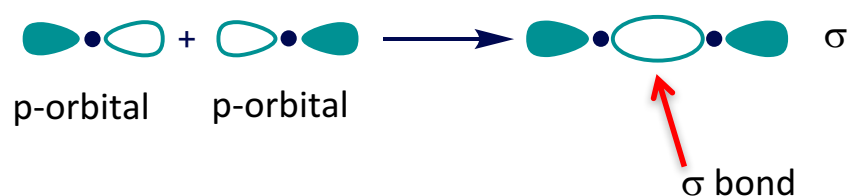
■ combinations of p-orbitals


(with all orbitals, the strongest bonding occurs when maximum overlap of (atomic) orbitals occurs)

■ in a similar manner we can combine p-orbitals to make bonding and antibonding  $\sigma$ -molecular orbitals

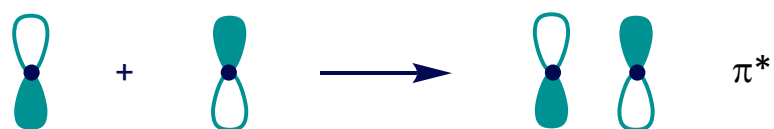


■ destructive overlap of atomic orbitals leads to *anti-bonding*  $\sigma^*$  molecular orbital – internuclear node

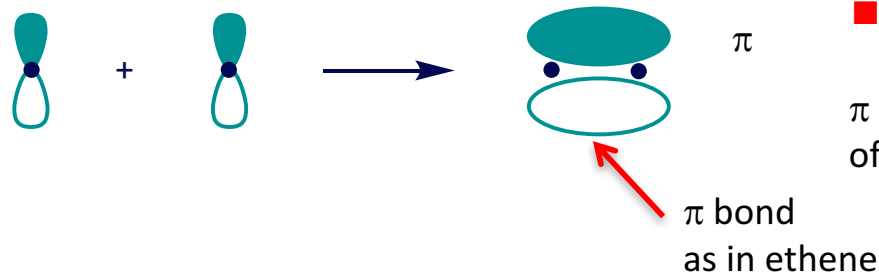


■ constructive overlap of atomic orbitals leads to a *bonding*  $\sigma$  molecular orbital - often drawn as  so the provenance of the molecular orbital is clear


■  $\pi$ -bonding – p-orbitals can also overlap edge on which leads to  $\pi$ -bonds – weaker than the corresponding  $\sigma$ -bonds as the orbital overlap is not as good



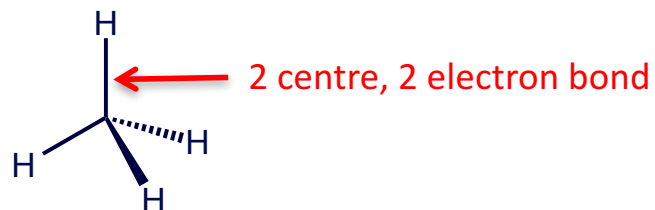
■ destructive overlap of atomic orbitals leads to an *anti-bonding*  $\pi^*$  molecular orbital – internuclear node



■ constructive overlap of atomic orbitals leads to a *bonding*

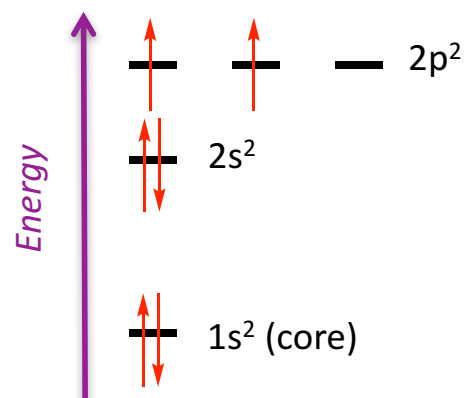
$\pi$  molecular orbital - often drawn as  so the provenance of the molecular orbital is clear

■ returning to CH<sub>4</sub> (methane)



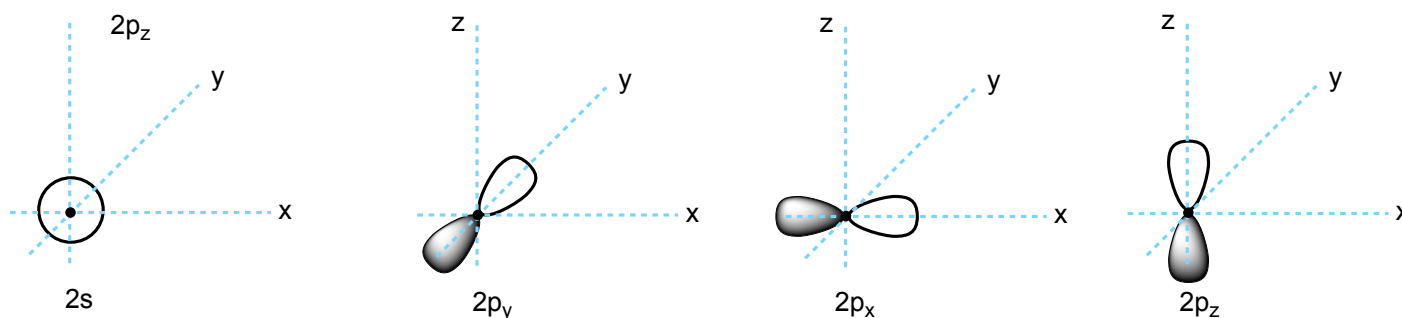
■ organic chemists generally draw Lewis structures where the line connecting the atoms represents a localised 2 centre, 2-electron bond. How can we rationalise this with a molecular orbital view of bonding involving overlap of orbitals?

■ methane – CH<sub>4</sub>



■ carbon ground state 1s<sup>2</sup>, 2s<sup>2</sup>, 2p<sup>2</sup> – the 1s electrons are core leaving the 2s and 2p valence electrons for bonding

■ the 2s orbital is spherical (non-directional) and the three 2p orbitals point along their respective axes (i.e. at 90° to one another)



■ how can s and p atomic orbitals accommodate the tetrahedral structure of methane (and the structures of many organic molecules)?

■ one approach, initially proposed by Pauling, is the idea of hybridisation – a method of creating orbitals that reproduces the observed shapes of molecules

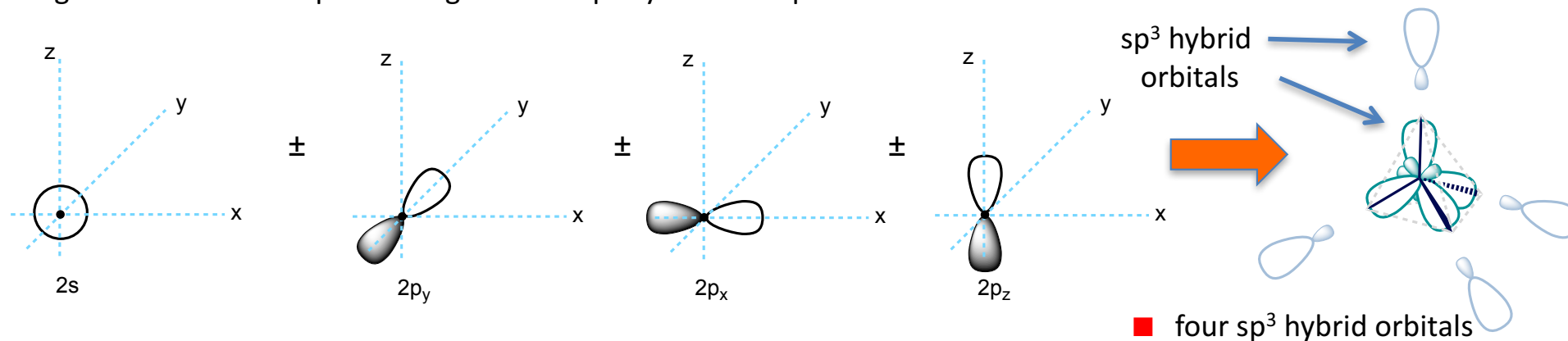
■ atomic orbitals are just mathematical functions, so we can add and subtract them (as we have done to form simple molecular orbitals)

■ full molecular orbital analysis (2<sup>nd</sup> year lecture course) is another approach

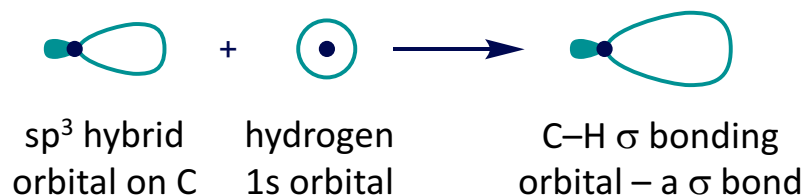


■ hybridisation

■ mixing the 2s and three 2p orbitals gives four  $sp^3$  hybrids that point towards the corners of a tetrahedron



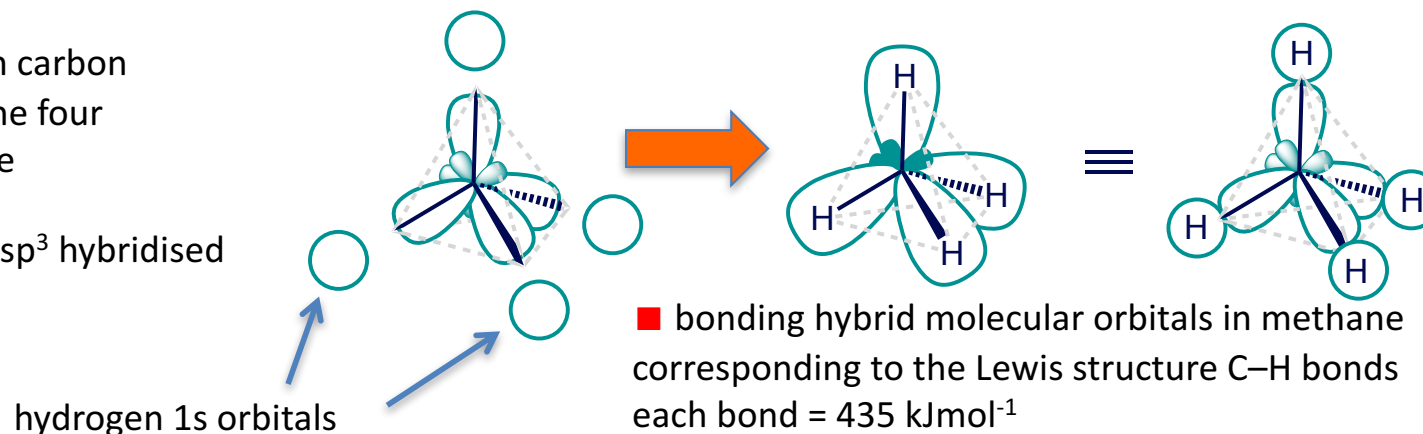
■ these hybrid orbitals can overlap with the hydrogen 1s orbitals to form C–H  $\sigma$ -bonding orbitals (and the corresponding  $\sigma^*$  antibonding orbitals)



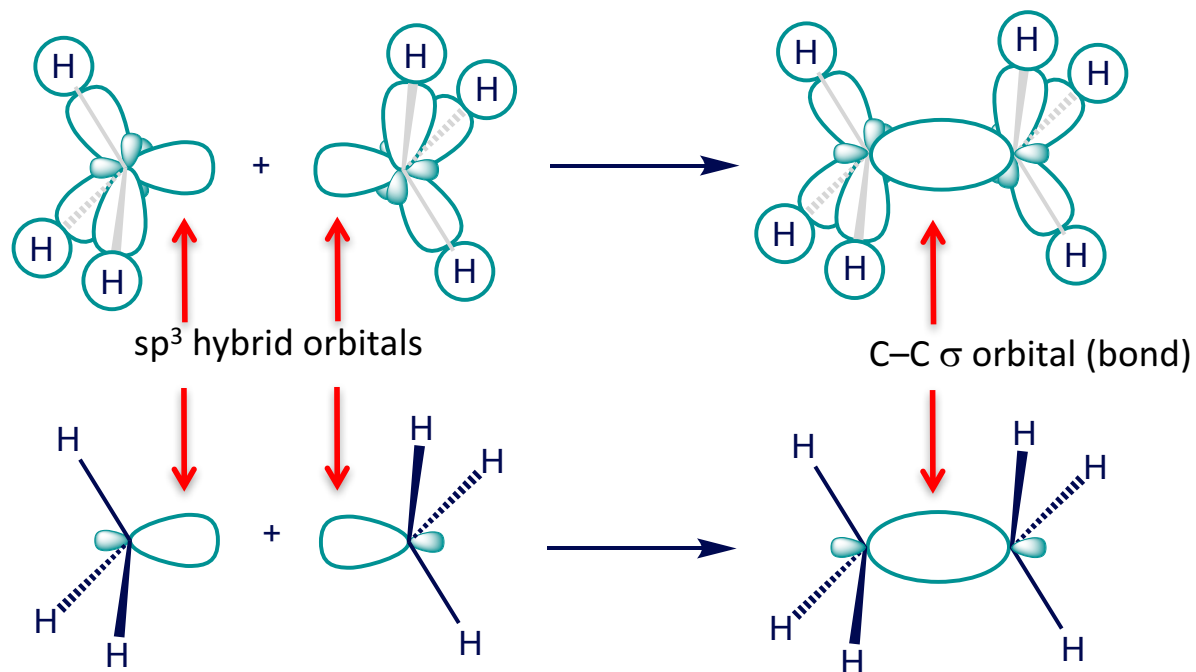
■ constructive overlap of hybrid orbital with 1s atomic orbital leads to a *bonding*  $\sigma$  molecular orbital ( $\sigma$  bond) - often drawn as so the provenance of the molecular orbital is clear

■ the four  $sp^3$  hybrid orbitals on carbon overlap with the 1s orbitals of the four hydrogen atoms to give methane

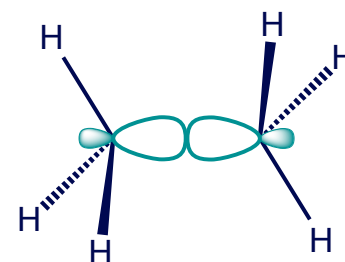
■ the carbon atom is said to be  $sp^3$  hybridised



- as hybrid orbitals are directional they provide much better overlap with the 1s orbitals of the hydrogen atoms
- ethane –  $C_2H_6$  –  $sp^3$  hybrid orbitals can overlap with each other as in the C–C bond in ethane to give a bonding  $\sigma$  molecular orbital

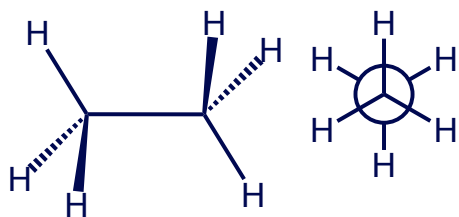


- constructive overlap of hybrid orbitals leads to *bonding*  $\sigma$  molecular orbital - often drawn as below so the provenance of the molecular orbital is clear

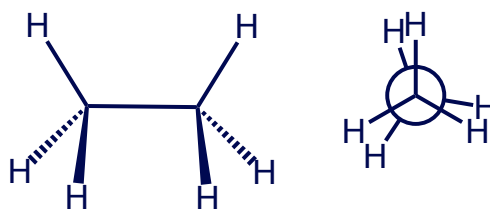


- rotation around the C–C axis does not alter the overlap of the  $sp^3$  orbitals (the C–C  $\sigma$  orbital) and occurs readily to give a variety of *conformers* of ethane – more of this later

- staggered conformation



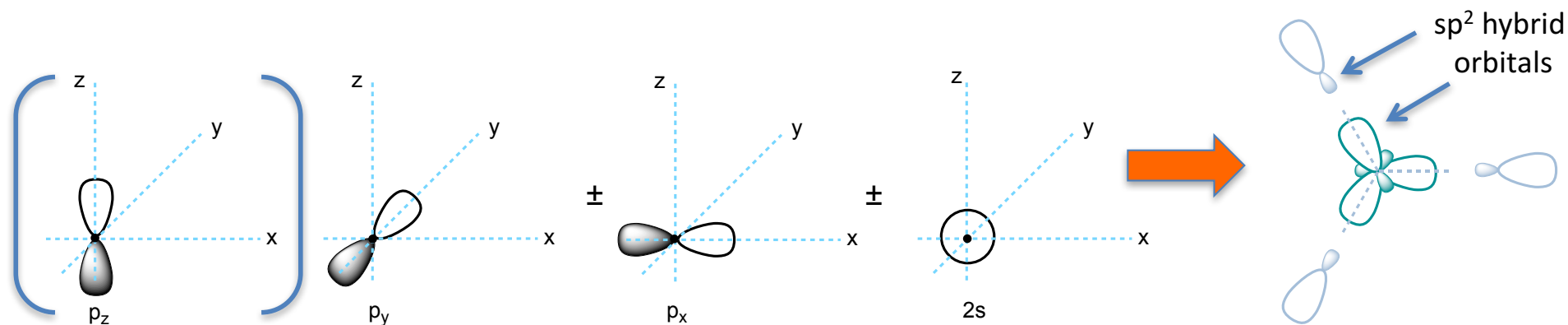
- eclipsed conformation



- the “end-on” views are termed Newman projections

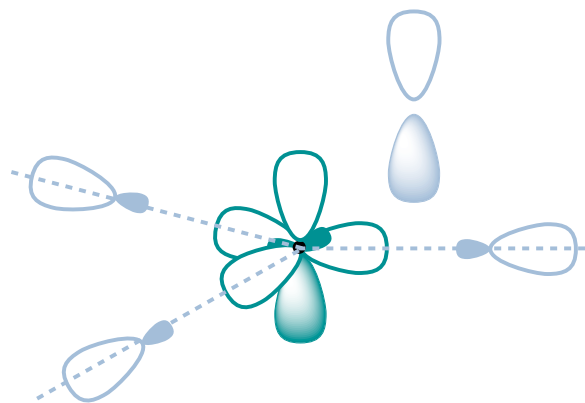
■ hybridisation –  $sp^2$

■ mixing the 2s and **two** 2p orbitals gives **three**  $sp^2$  hybrids that lead to trigonal geometry ( $120^\circ$  bond angles)



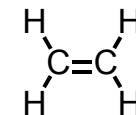
■ forming three  $sp^2$  hybrids leaves one p-orbital perpendicular to the plane containing the hybrid orbitals

■ three  $sp^2$  hybrid orbitals (drawn in xy plane)

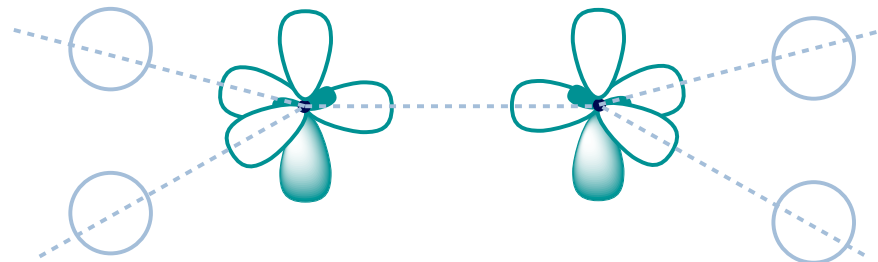


■ three  $sp^2$  hybrid orbitals and perpendicular p-orbital around central (carbon) atom

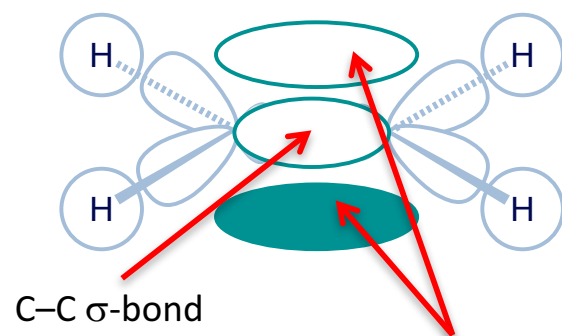
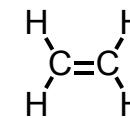
■ the bonding in ethene/ethylene ( $C_2H_4$ ) is a result of overlap of  $sp^2$  hybridised carbon atoms with each other to form the C–C  $\sigma$ -bond, and with four hydrogen 1s orbitals to form the four C–H  $\sigma$ -bonds



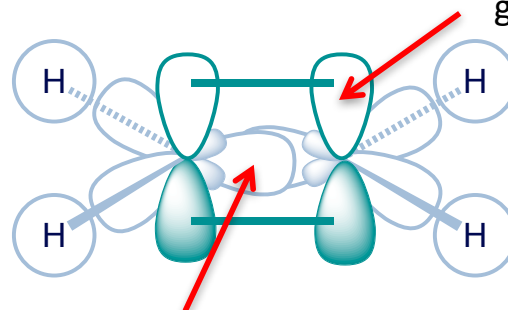
■ the remaining two p-orbitals overlap to form a  $\pi$ -bond



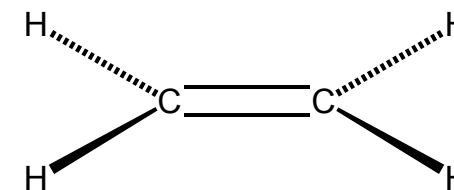
- overlap of the  $sp^2$  hybrid orbitals leads to three  $\sigma$ -bonds – two C–H bonds and one C–C bond
- overlap of the remaining perpendicular 'p'-orbitals gives a  $\pi$ -bond



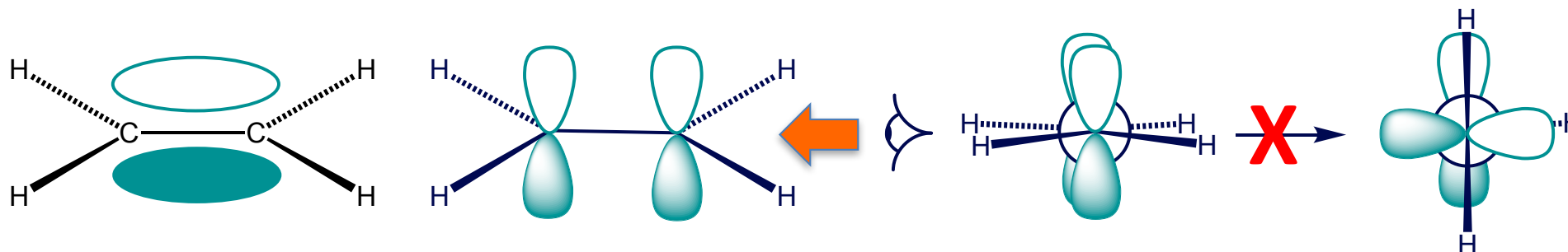
the two lobes of  
the C–C  $\pi$ -bond



overlap of  $sp^3$  hybrid  
orbitals gives C–C  $\sigma$ -bond



- the  $\pi$ -bond leads to electron density above and below the molecular plane
- rotation about the C–C axis is impossible as this would reduce overlap of the p-orbitals and would break the  $\pi$ -bond

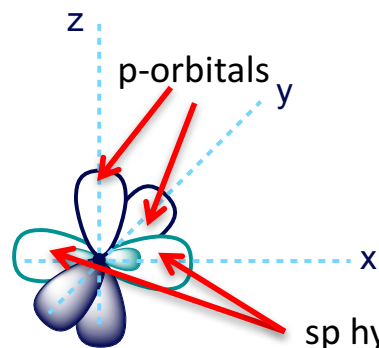
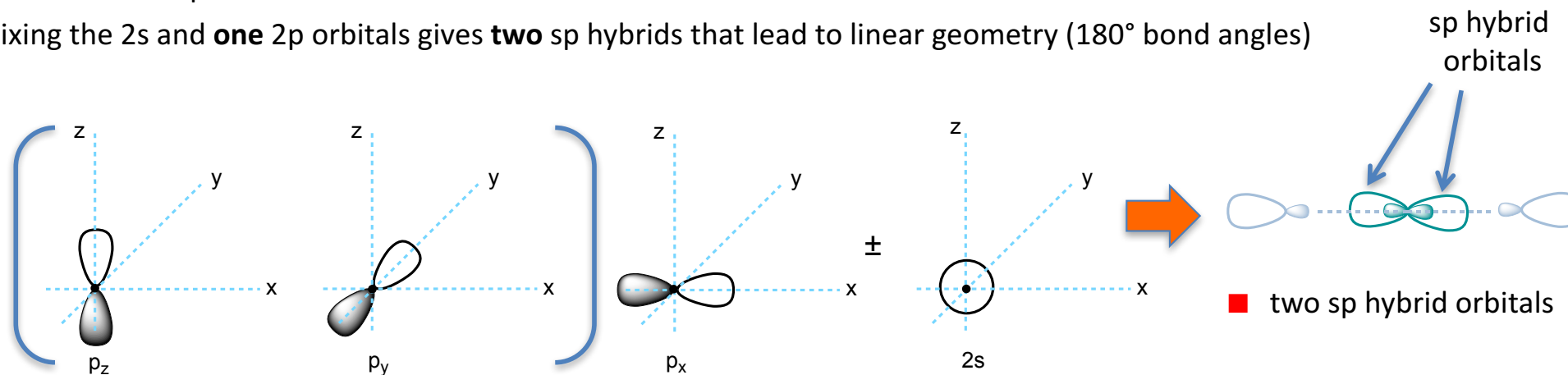


- as before the  $\pi$ -molecular orbital ( $\pi$ -bond) is generally drawn as two separate p-atomic orbitals for clarity

- rotation about C–C axis would break the  $\pi$ -bond and does not occur
- hence alkenes are configurationally stable (i.e. *cis* and *trans*)

■ hybridisation – sp

■ mixing the 2s and **one** 2p orbitals gives **two** sp hybrids that lead to linear geometry (180° bond angles)



■ forming two sp hybrids leaves two p-orbitals which can form  $\pi$ -bonds



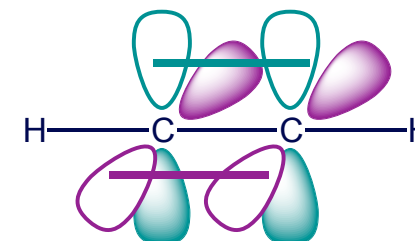
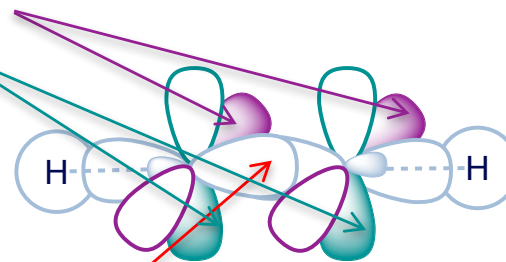
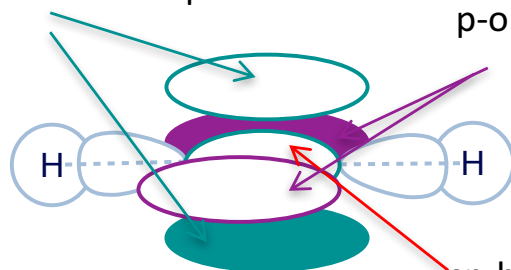
■ the two sp hybrid orbitals are arranged 180° apart

■ this is the bonding arrangement found in ethyne (acetylene) with the sp hybrids overlapping with the hydrogen 1s orbitals (not shown) the remaining p orbitals overlapping to form the two  $\pi$ -bonds

■ the triple bond in acetylene is made up from one  $\sigma$ -bond and two orthogonal  $\pi$ -bonds, the carbons are said to be sp hybridised

$\pi$ -bond formed by p-orbital overlap

$\pi$ -bond formed by p-orbital overlap



■ view without  $\sigma$ -orbitals

■ a quick method to work out the hybridisation of an atom is to count the number of substituents on that atom (including lone pairs of electrons), remembering that in the bonded environment first row elements have 8 electrons around them (there are exceptions to this method which we will meet later)

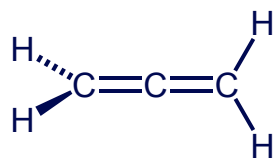
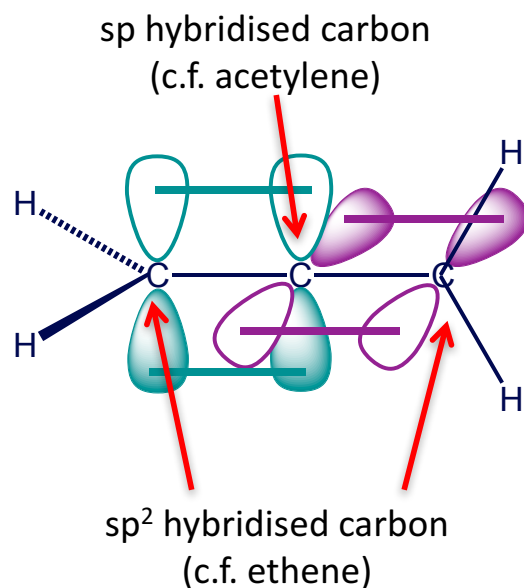
4 substituents =  $sp^3$  hybridised, 3 substituents =  $sp^2$  hybridised, 2 substituents =  $sp$  hybridised

■ allene  $CH_2=C=CH_2$  – what is its molecular shape?

■ terminal carbons bonded to 2 hydrogen atoms ( $\sigma$ -bonds) and double bonded to central carbon ( $\sigma$ -bond and  $\pi$ -bond) –  $\therefore$  terminal carbon atoms are  $sp^2$  hybridised

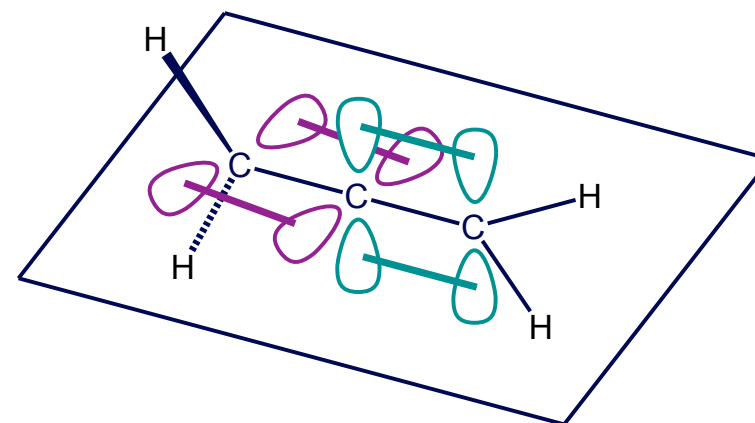
■ central carbon bonded to 2 substituents  $\therefore$  has linear geometry  $\therefore$   $sp$  hybridised

■ central carbon forms a single  $\sigma$ -bond with each terminal carbon ( $sp$ - $sp^2$  hybrid orbital overlap)



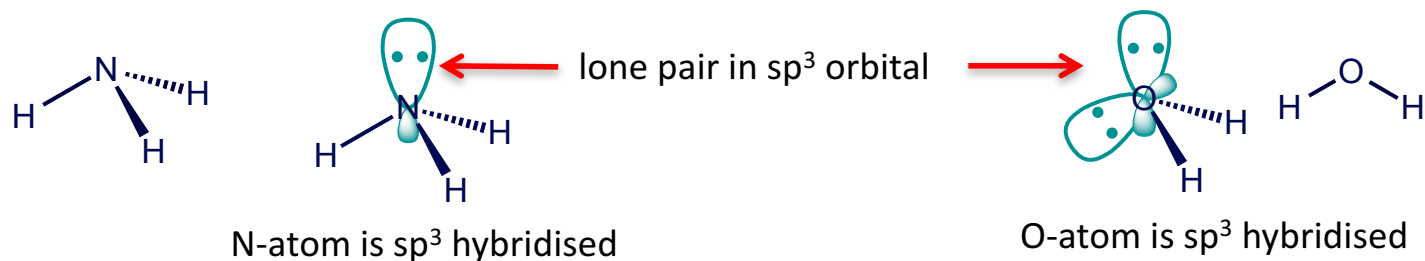
■ no free rotation

■  $CH_2$  groups are perpendicular

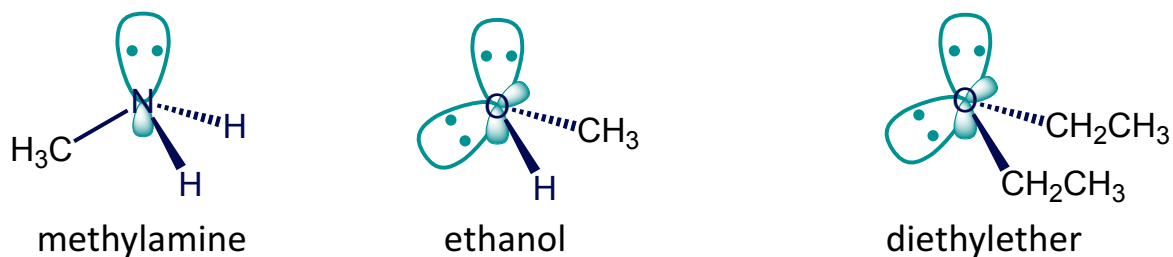


■ alternative perspective

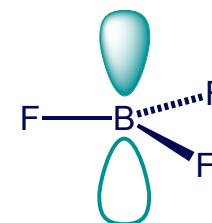
- hybridisation can be used with atoms other than carbon
- the nitrogen atom in ammonia can be viewed as  $sp^3$  hybridised as can the oxygen atom in water although the H-X-H bond angle is slightly less than  $109^\circ$  due to lone pair–bond pair repulsion



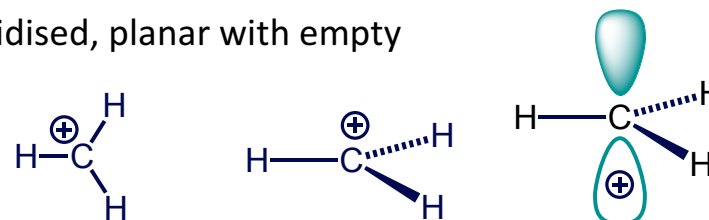
- similarly for amines, alcohols, ethers etc.



- $BF_3$  – three substituents around boron – no lone pair  $\therefore$  planar,  $sp^2$  hybridised, planar with empty p-orbital on boron

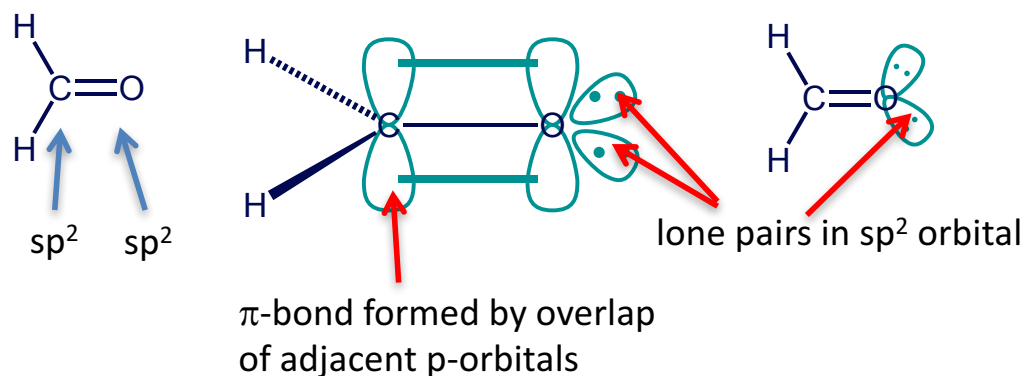


- $CH_3^+$  – three substituents around carbon – no lone pair  $\therefore$  planar,  $sp^2$  hybridised, planar with empty p-orbital on carbon – other carbocations have similar planar structure

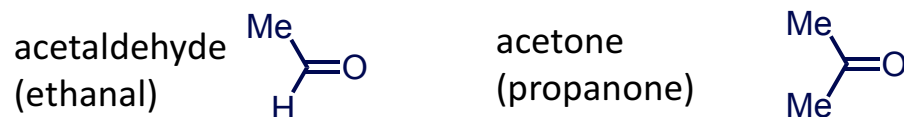


- hybridisation in functional groups (sites of chemical reactivity)

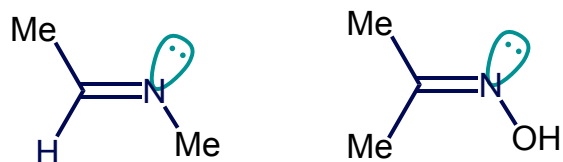
- formaldehyde (c.f. bonding in ethene)



- bonding and reactivity is similar in aldehydes and ketones



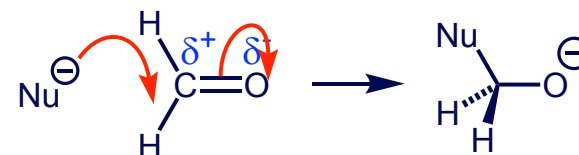
- imines – planar, lone pair in  $sp^2$  orbital



- oximes – planar, lone pair in  $sp^2$  orbital

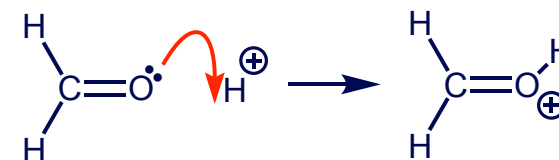
- electronegativity difference results in polarisation of C–O bond

- nucleophiles  $\therefore$  react on carbon and break the weaker  $\pi$ -bond

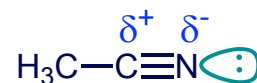


- conversely, lone pairs are sites of electron density

- electrophiles  $\therefore$  react on oxygen



- nitriles – e.g. CH3CN (c.f. bonding in acetylene)



lone pair in  $sp$ -orbital

