Chemistry I (Organic)

Stereochemistry
LECTURE 1
Hybridisation & shape

Alan C. Spivey
a.c.spivey@imperial.ac.uk

Imperial College London

Oct 2011

Format & scope of lecture

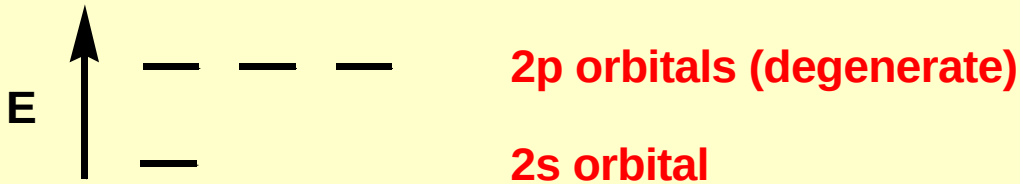
- ***Atomic orbitals – the carbon atom***
  - energies
  - shapes

- ***Hybridised atomic orbitals - carbon in molecules***
  - shapes of hybrid orbitals
  - sp^3 hybrid systems
  - sp^2 hybrid systems
  - sp hybrid systems

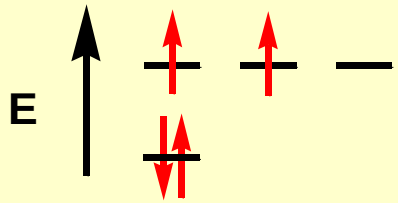
NB. For 3D Jmol models of molecules **A-C** see link @ http://www.ch.ic.ac.uk/spivey/?q=firstyear

Atomic orbitals – *the carbon atom*

- ***CARBON is in group 4 of the periodic table → 4 valence electrons***
- ***Atomic structure: $1s^2$ $2s^2$ $2p^2$***
- ***There are 1 × 2s and 3 × 2p (i.e. $2p_x$, $2p_y$ & $2p_z$) energetically available valence atomic <u>orbitals</u> with the following relative energies:***



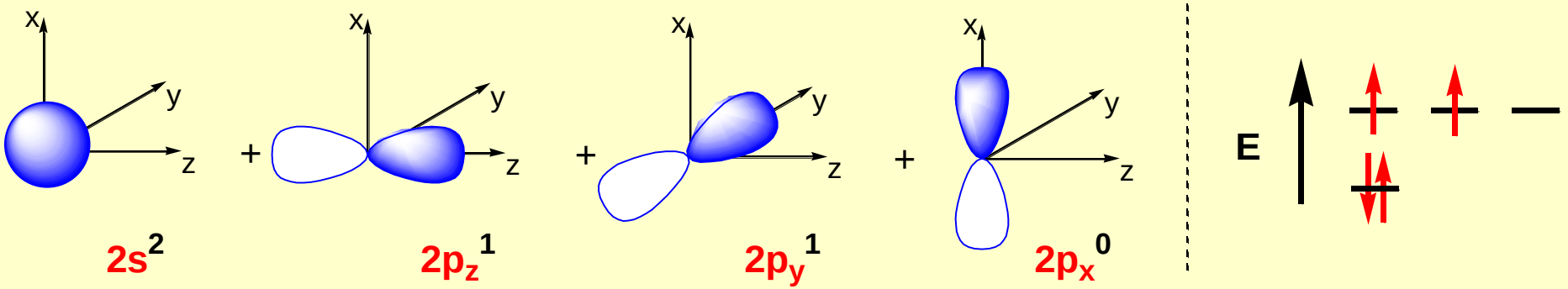
- ***In the GROUND STATE, according to the aufbau principle & Hund's rule these are occupied as follows:***



- ***i.e. $2s^2$ $2p_x^1 2p_y^1 2p_z^0$***

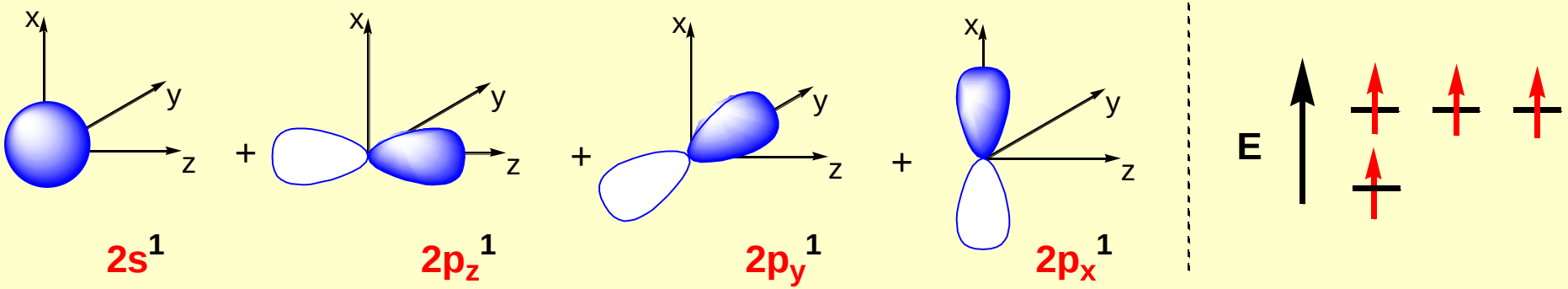
Atomic orbitals – *the carbon atom*

- ***The 2s orbital is SPHERICAL and the 2p orbitals are 'DUMBELL' shaped***
- ***So, in the GROUND STATE we have:***



$2s^2$ $2p_z^1$ $2p_y^1$ $2p_x^0$

- ***Clearly, if we want to form a molecule e.g. methane with 4 bonds to carbon we need to promote an electron 2s → $2p_z$:***

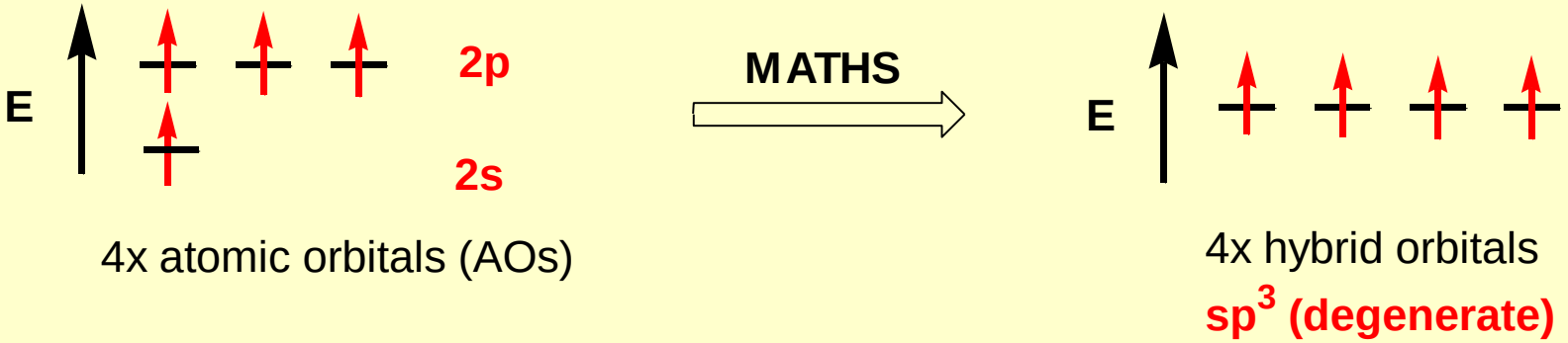


$2s^1$ $2p_z^1$ $2p_y^1$ $2p_x^1$

- ***BUT, methane is TETRAHEDRAL with all bonds equivalent (recall VSEPR theory)...***

Hybridised atomic orbitals - *sp³ carbon*

- ***This is because mathmatically [1x 2s + 3x 2p] atomic orbitals are equivalent to [4 x sp³] degenerate hybrid orbitals:***

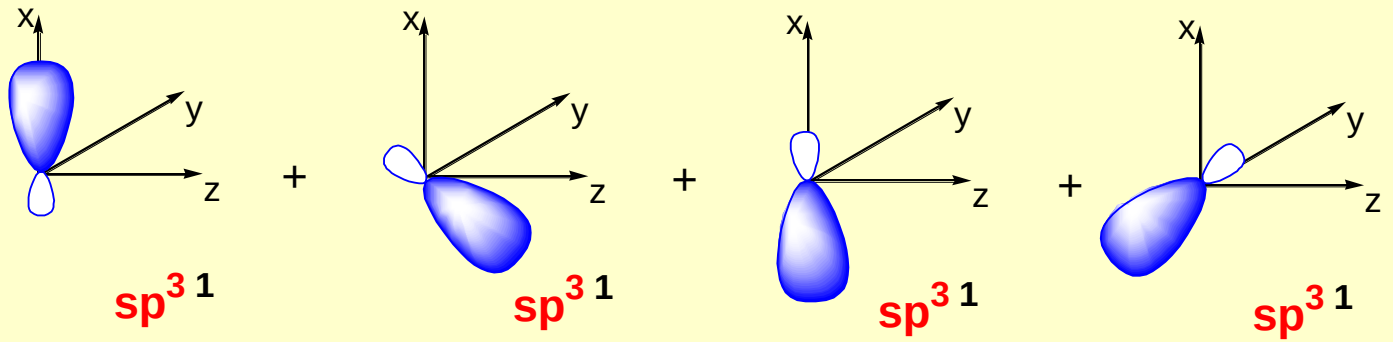


4x atomic orbitals (AOs)

4x hybrid orbitals

sp³ (degenerate)

- ***The shapes of the new orbitals are distorted dumbells pointing towards the vertices of a <u>tetrahedron</u>:***

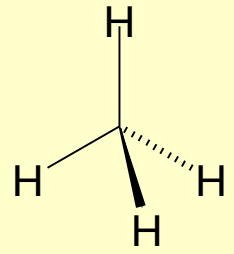


sp³ 1 **sp³ 1** **sp³ 1** **sp³ 1**

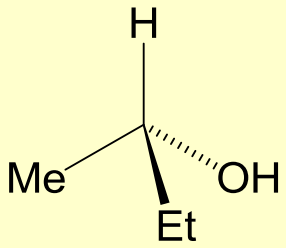
- ***i.e. sp³ hybridised: <u>tetrahedral</u> (4 × hybrid orbitals)***

Hybridised atomic orbitals - *sp*^{3} *carbon*

- ***Consequently, in molecules which have FOUR atoms/groups bonded to carbon, the carbon atom has a TETRAHEDRAL shape***
- ***e.g. methane***

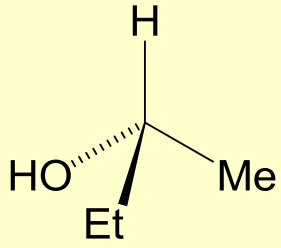


- ***This has important consequences in terms of stereochemistry when all the groups bonded to carbon are different because two stereoisomers are possible (more later...)***



A

&

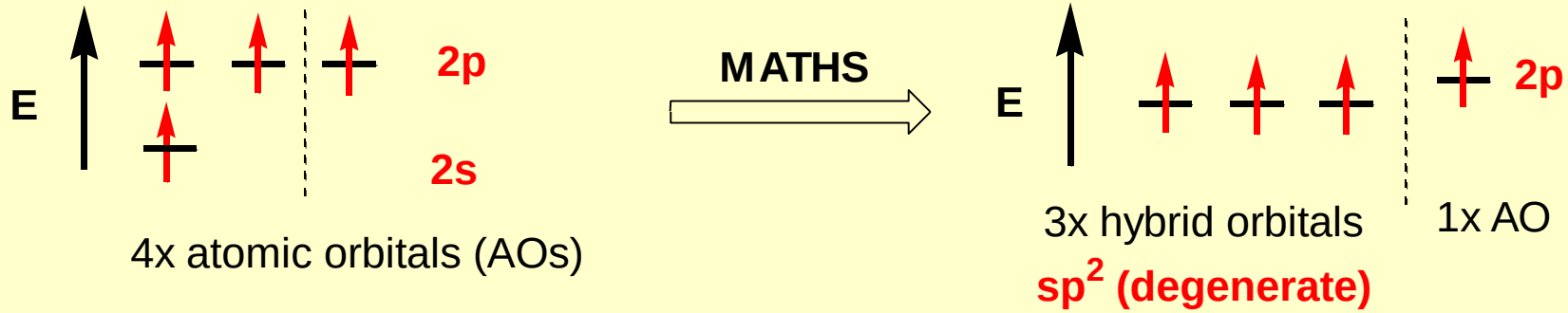


ent-A

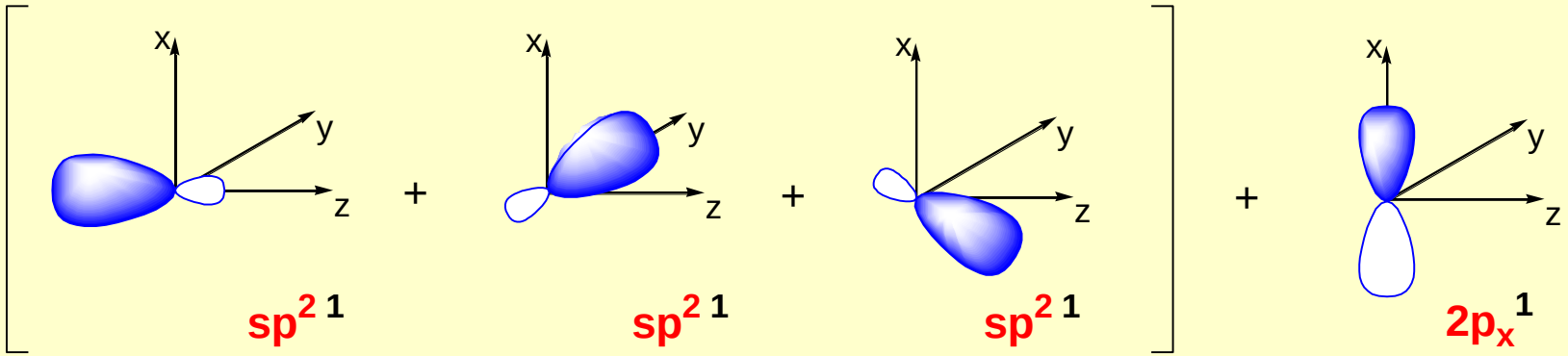
non-identical

Hybridised atomic orbitals – *sp² carbon*

- ***Similarly, [1x 2s + 2x 2p] atomic orbitals are mathmatically equivalent to [3 x sp²] degenerate hybrid orbitals:***



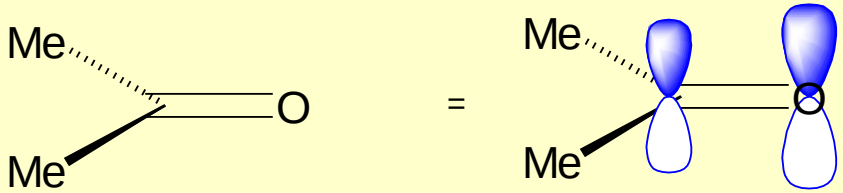
- ***The shapes of the new orbitals are distorted dumbells having a <u>trigonal planar</u> arrangement, all perpendicular to the unhybridised remaining atomic 2p orbital:***



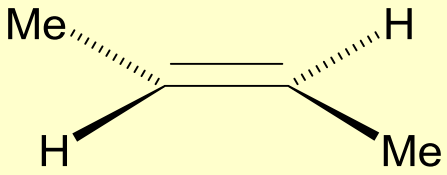
- ***i.e. sp² hybridised: trigonal planar (1× p + 3× hybrid orbitals)***

Hybridised atomic orbitals – *sp*^{2} *carbon*

- ***Consequently, in molecules which have THREE atoms/groups bonded to carbon, the carbon atom has a TRIGONAL PLANAR shape***
- ***e.g. acetone***

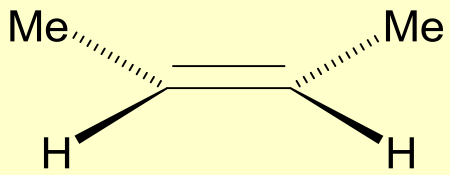


- ***This also has important consequences in terms of stereochemistry (more later...):***



***trans*-B**

&

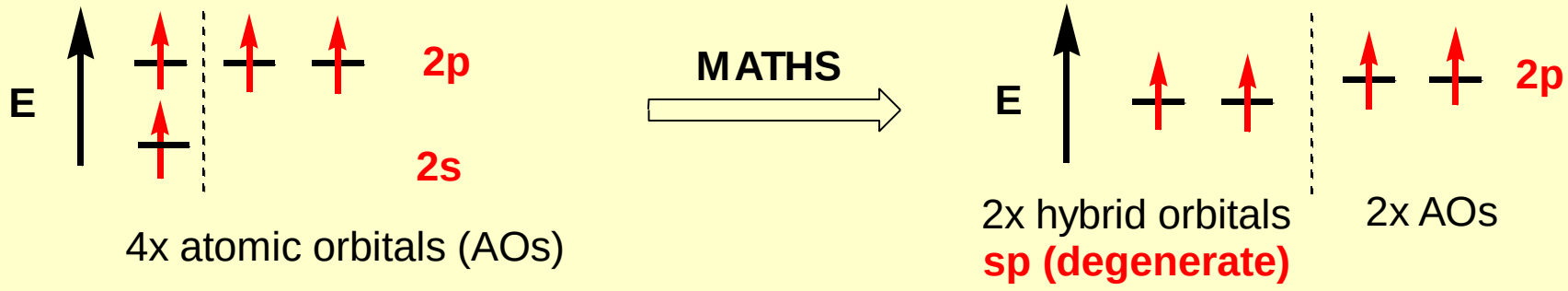


***cis*-B**

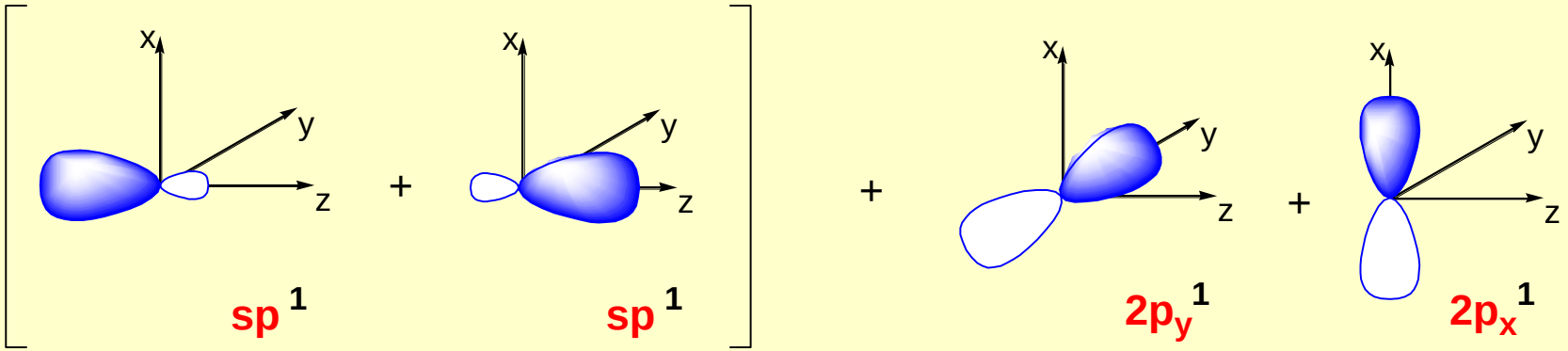
non-identical

Hybridised atomic orbitals - *sp carbon*

- ***Similarly, [1x 2s + 1x 2p] atomic orbitals are mathmatically equivalent to [2 x sp] degenerate hybrid orbitals:***



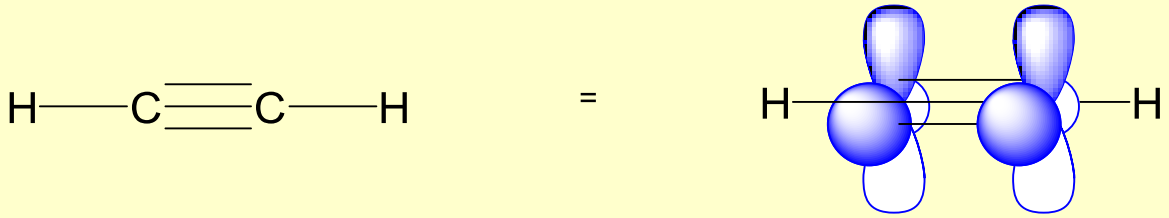
- ***The shapes of the new orbitals are distorted dumbells in a linear arrangement along an axis perpendicular to both the unhybridised remaining atomic 2p orbitals:***



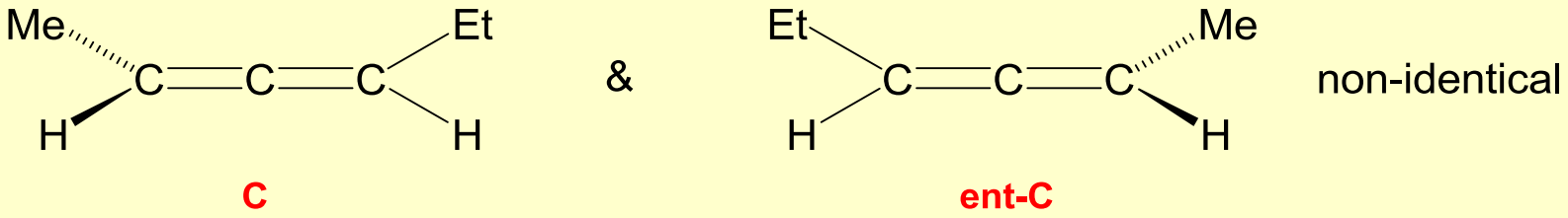
- ***i.e. sp hybridised: linear (2× p + 2× hybrid orbitals)***

Hybridised atomic orbitals - *sp carbon*

- ***Consequently, in molecules which have TWO atoms/groups bonded to carbon, the carbon atom has a LINEAR shape***
- ***e.g. ethyne***



- ***this also has important consequences in terms of stereochemistry (more later...):***



C **ent-C**