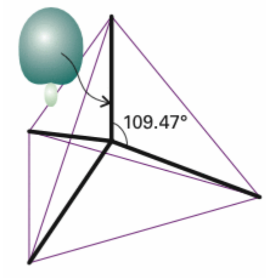
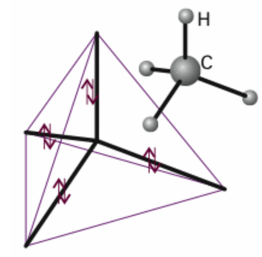
Hybridization and bond types

1. methane CH4   sp3

$$h_1 = s + p_x + p_y + p_z \qquad h_2 = s - p_x - p_y + p_z$$

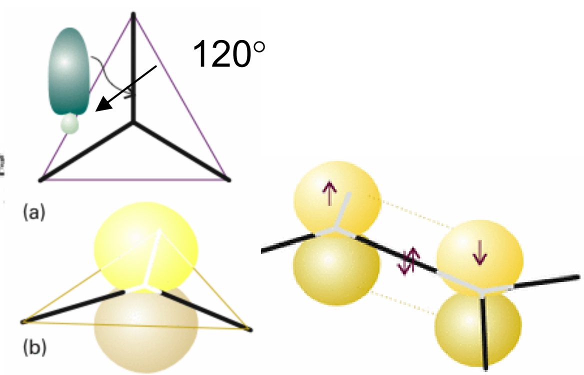
$$h_3 = s - p_x + p_y - p_z \qquad h_4 = s + p_x - p_y - p_z$$





2. ethene   H2C=CH2   sp2

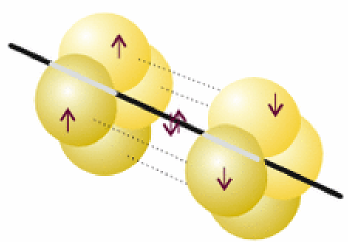
$$h_1 = s + 2^{1/2} p_y \qquad h_2 = s + \left(\tfrac{3}{2}\right)^{1/2} p_x - \left(\tfrac{1}{2}\right)^{1/2} p_y \qquad h_3 = s - \left(\tfrac{3}{2}\right)^{1/2} p_x - \left(\tfrac{1}{2}\right)^{1/2}$$



Double bond = σ(sp2-sp2) + π(p)

3. ethyne   HC≡CH   sp

$$h_1 = s + p_z \qquad h_2 = s - p_z$$



Triple bond = σ(sp-sp) + 2 x π(p)

2-electron model (e.g. p-orbitals of 2 atoms)

Write wf as a linear combination of atomic orbitals

$$\psi = c_A A + c_B B$$

Energy = expectation value of Hamiltonian

$$E = \frac{\int \psi^* \hat{H} \psi \, d\tau}{\int \psi^* \psi \, d\tau}$$

variational principle →

$$\frac{\partial E}{\partial c_A} = 0 \qquad \frac{\partial E}{\partial c_B} = 0$$

$$\int \psi^2 \, d\tau = \int (c_A A + c_B B)^2 \, d\tau$$
$$= c_A^2 \int A^2 \, d\tau + c_B^2 \int B^2 \, d\tau + 2c_A c_B \int AB \, d\tau$$
$$= c_A^2 + c_B^2 + 2c_A c_B S$$

$$\int \psi \hat{H} \psi \, d\tau = \int (c_A A + c_B B) \hat{H} (c_A A + c_B B) \, d\tau$$
$$= c_A^2 \int A\hat{H}A \, d\tau + c_B^2 \int B\hat{H}B \, d\tau + c_A c_B \int A\hat{H}B \, d\tau + c_A c_B \int B\hat{H}A \, d\tau$$

$$\alpha_A = \int A\hat{H}A \, d\tau \qquad \alpha_B = \int B\hat{H}B \, d\tau$$

$$\beta = \int A\hat{H}B \, d\tau = \int B\hat{H}A \, d\tau \text{ (by the hermiticity of } \hat{H}\text{)}$$

$$\int \psi\hat{H}\psi \, d\tau = c_A^2\alpha_A + c_B^2\alpha_B + 2c_Ac_B\beta$$

$$E = \frac{c_A^2\alpha_A + c_B^2\alpha_B + 2c_Ac_B\beta}{c_A^2 + c_B^2 + 2c_Ac_BS}$$

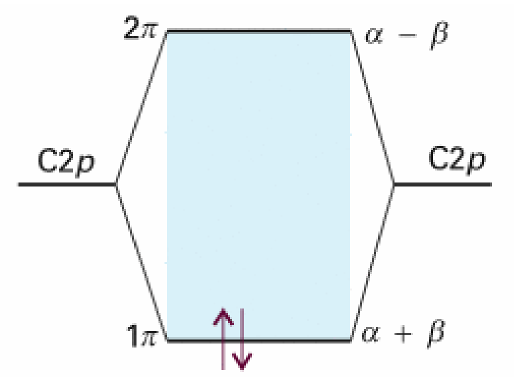
$$\frac{\partial E}{\partial c_A} = \frac{2 \times (c_A\alpha_A - c_AE + c_B\beta - c_BSE)}{c_A^2 + c_B^2 + 2c_Ac_BS} = 0$$

$$\frac{\partial E}{\partial c_B} = \frac{2 \times (c_B\alpha_B - c_BE + c_A\beta - c_ASE)}{c_A^2 + c_B^2 + 2c_Ac_BS} = 0$$

$$c_A\alpha_A - c_A E + c_B\beta - c_B SE = (\alpha_A - E)c_A + (\beta - ES)c_B = 0$$
$$c_A\beta - c_A SE + c_B\alpha_B - c_B E = (\beta - ES)c_A + (\alpha_B - E)c_B = 0$$

Solution exists if

$$\begin{vmatrix} \alpha_A - E & \beta - ES \\ \beta - ES & \alpha_B - E \end{vmatrix} = 0$$



For a homonuclear dimer

$$\begin{vmatrix} \alpha - E & \beta - ES \\ \beta - ES & \alpha - E \end{vmatrix} = (\alpha - E)^2 - (\beta - ES)^2 = 0$$

$$E_\pm = \frac{\alpha \pm \beta}{1 \pm S}$$

(overlap S=0)

Huckel approximation:
-Set S = 0
- β non-zero only between nearest neighbours

Butadieeni H2C=CHHC=CH2

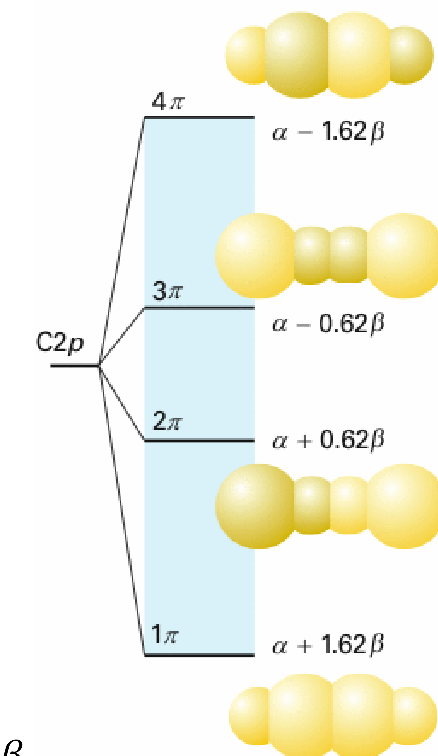
3

$$\boldsymbol{H} = \begin{pmatrix} H_{11} & H_{12} & H_{13} & H_{14} \\ H_{21} & H_{22} & H_{23} & H_{24} \\ H_{31} & H_{32} & H_{33} & H_{34} \\ H_{41} & H_{42} & H_{43} & H_{44} \end{pmatrix} = \begin{pmatrix} \alpha & \beta & 0 & 0 \\ \beta & \alpha & \beta & 0 \\ 0 & \beta & \alpha & \beta \\ 0 & 0 & \beta & \alpha \end{pmatrix}$$

$$\boldsymbol{E} = \begin{pmatrix} \alpha + 1.62\beta & 0 & 0 & 0 \\ 0 & \alpha + 0.62\beta & 0 & 0 \\ 0 & 0 & \alpha - 0.62\beta & 0 \\ 0 & 0 & 0 & \alpha - 1.62\beta \end{pmatrix}$$

$$\boldsymbol{C} = \begin{pmatrix} 0.372 & 0.602 & 0.602 & -0.372 \\ 0.602 & 0.372 & -0.372 & 0.602 \\ 0.602 & -0.372 & -0.372 & -0.602 \\ 0.372 & -0.602 & 0.602 & 0.372 \end{pmatrix}$$

$$\begin{aligned} E_1 &= \alpha + 1.62\beta & \psi_1 &= 0.372\chi_A + 0.602\chi_B + 0.602\chi_C + 0.372\chi_D \\ E_2 &= \alpha + 0.62\beta & \psi_2 &= 0.602\chi_A + 0.372\chi_B - 0.372\chi_C - 0.602\chi_D \\ E_3 &= \alpha - 0.62\beta & \psi_3 &= 0.602\chi_A - 0.372\chi_B - 0.372\chi_C + 0.602\chi_D \\ E_4 &= \alpha - 1.62\beta & \psi_4 &= -0.372\chi_A + 0.602\chi_B - 0.602\chi_C - 0.372\chi_D \end{aligned}$$

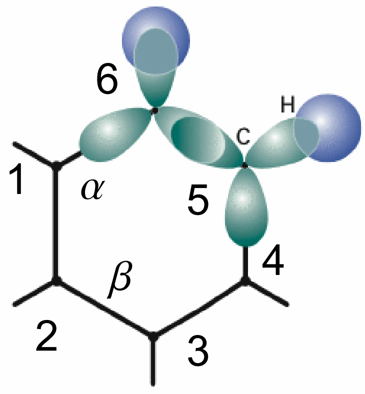


Total energy of p electrons $2(\alpha+1.62\beta) + 2(\alpha+0.62\beta) = 4\alpha+4.48\beta$

Energy of 2 double bonds = $2 \times (2\alpha+2\beta) = 4\alpha+4\beta$

→ delocalization energy 0.48β

Hückel model for benzene π-electrons



$$
\boldsymbol{H} = \begin{pmatrix} \alpha & \beta & 0 & 0 & 0 & \beta \\ \beta & \alpha & \beta & 0 & 0 & 0 \\ 0 & \beta & \alpha & \beta & 0 & 0 \\ 0 & 0 & \beta & \alpha & \beta & 0 \\ 0 & 0 & 0 & \beta & \alpha & \beta \\ \beta & 0 & 0 & 0 & \beta & \alpha \end{pmatrix}
$$

Total energy:

$$E_\pi = 2(\alpha + 2\beta) + 4(\alpha + \beta) = 6\alpha + 8\beta$$

Compare to energy of 3 double bonds:
E = $3(2\alpha+2\beta) = 6\alpha+6\beta$

→ DELOCALIZATION energy 2β (< 0)

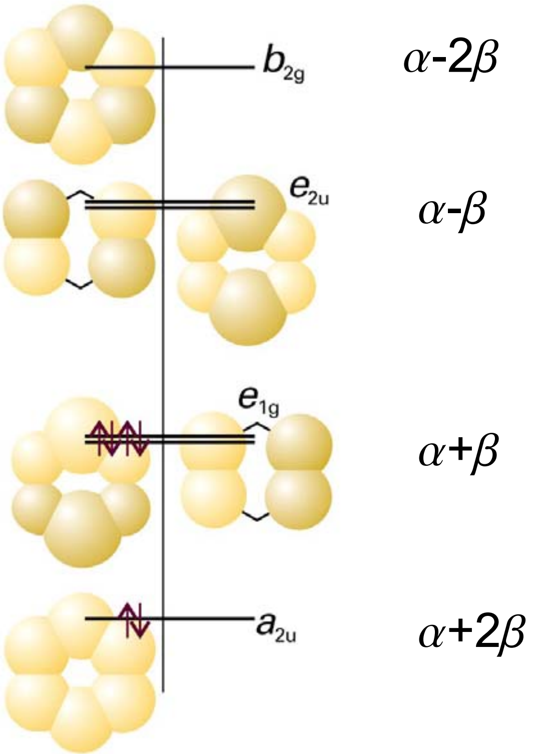
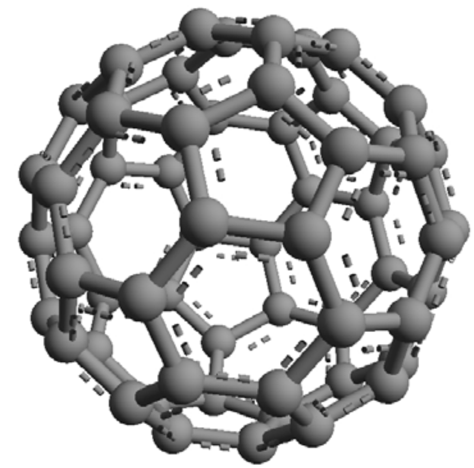


Figure 11-41
Atkins Physical Chemistry, Eighth Edition

Fullerenes

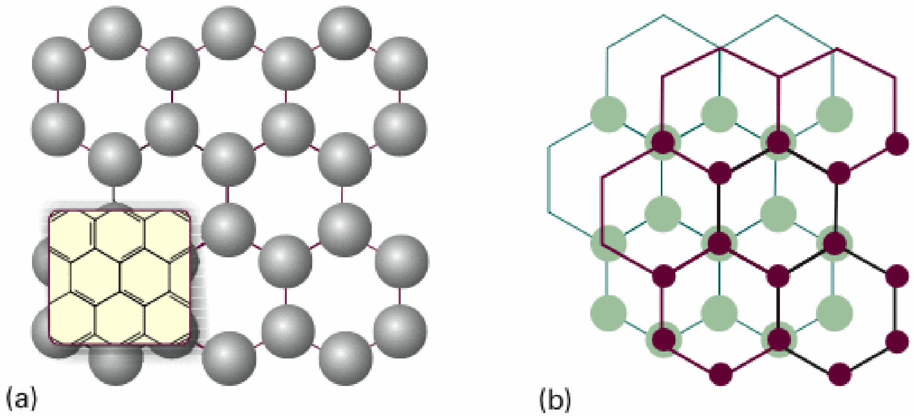
- Discovery around 1985
- Nobel Prize in chemistry 1996 Curl, Kroto, Smalley
- Closed cages of 5-fold and ~aromatic 6-fold rings
- Icosahedral symmetry (12 5-fold rings)
- Series of sizes
- Chemical stability but high electron affinity
  (reduction to -6 state observed)
- Fullerides – metal-doped fullerene solid –
  superconductors with relatively high Tc!

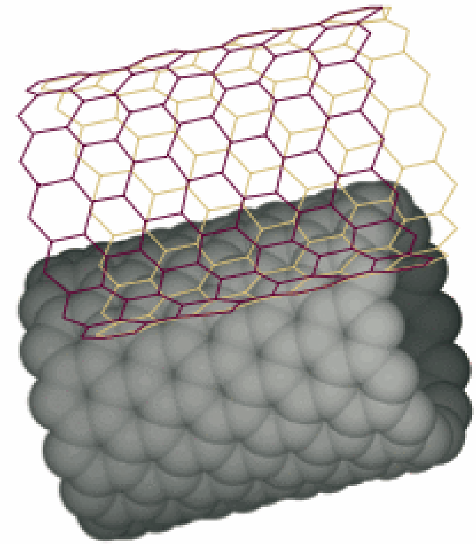


C60

http://www.chm.bris.ac.uk/motm/buckyball/c60a.htm

Graphene / graphite and nanotubes





2 –dimensional conductors:

• Graphene – one hexagonal layer of joined 6-fold rings, sp2 hybridization, 120 deg angle, π-electron delocalized ”cloud” top and below the sheet

• Graphite – material made by packing graphene layers in ABABAB… fashion

• interesting linear behaviour of dispersion near Fermi energy → ”massless electrons”!!

1 –dimensional conductor:

• Carbon nanotube – roll one (or a few) sheet(s) of graphene

• Discovered by S. Iijima 1991, for a story see

http://www.labs.nec.co.jp/Eng/innovative/E1/top.html