

# Molecular structure

## Summary of chapter 14

- previous concepts are extended to description of electronic states of molecules
  - valence bond theory uses as starting point shared  $e^-$  pairs resulting in  $\sigma$  and  $\pi$  bonds, promotion, hybridization
  - MO theory extends concept of AO's to MO's; wavefunctions spreading over all atoms in a molecule
- chapter deals with strengths, numbers, 3D arrangement of chemical bonds

the covalent bond (Lewis 1916) used concept of shared electron pairs

## Born-Oppenheimer - Approximation

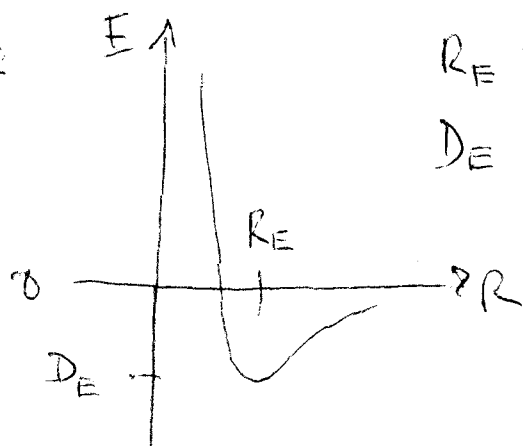
- Schrödinger eq. for atoms can be solved exactly
- not possible for molecules (3 particles at least; 2 nuclei + electron)
- nuclei: heavy compared to electrons, move slowly, treated as stationary
- appropriate for ground state molecules; calculations give 1000-fold higher speed for electrons compared to nuclei,  $\Rightarrow$  small error
- exceptions: excited polyatomic molecules, ground states of cations

## procedure (BO-approx.)

-2-

- > Selection of a fixed internuclear separation
- > change the separation
- > exploration how energy changes dependent on separation length

Result:



$R_E$  : equilibrium bond length

$D_E$  : dissociation energy

## Valence-bond theory

- First ~~the~~ quantum mechanical theory of bonding
- introduced language especially used in chemistry of organic compounds!

-> The hydrogen molecule,  $H_2$

- simplest molecule with an electron pair bond

Spatial wavefunction of 2 separated H atoms

$$\Psi = \Psi_{H1s_A}(\vec{r}_1) \Psi_{H1s_B}(\vec{r}_2)$$

here: electron 1 is on atom A, electron 2 on atom B

More simple written:  $\Psi = A(1)B(2)$

close atoms: not possible to distinguish between states where 1 is on A or B

equally described with  $\Psi = A(2)B(1)$

q.m. principle: two equally probable outcomes

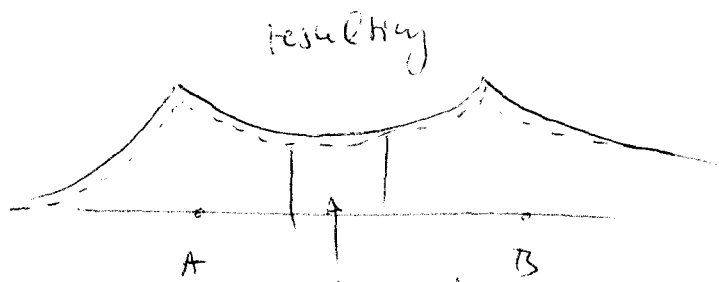
⇒ true state of the system is described as a superposition of the wave functions for each possibility

$$\Psi = A(1)B(2) \pm A(2)B(1)$$

+ sign: combination with lower energy

⇒ valence bond wave function of  $H_2$

$$\Psi = A(1)B(2) + A(2)B(1) \quad (= \Psi_{H_2})$$



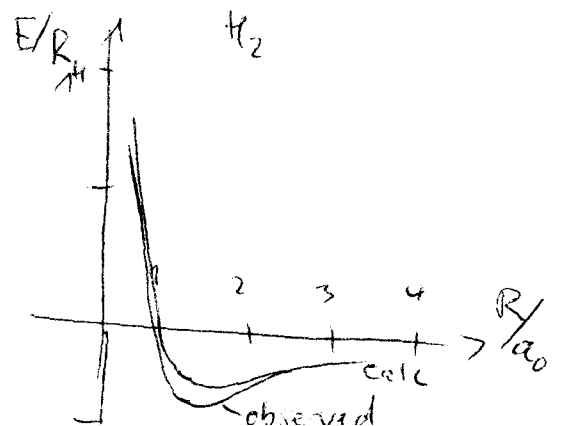
description of  $\sigma$  bond

$\sigma$  bond: High probability that the electrons are between the nuclei → bond them together  
constructive interference of wave packets

$\sigma$  bond: cylindrical symmetry around the internuclear axis, resembles s when viewed along this axis

Molecular potential energy for  $H_2$

- changing internuclear distance  $R$
- evaluating the expectation value
- small separations: repulsion of nuclei



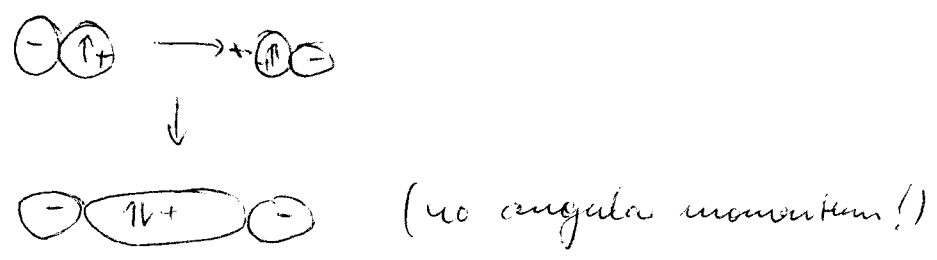
→ role of electron spin

- spins pair as atomic orbitals overlap (since they now occupy the same orbital)
- $\Psi_{H_2}$  can only be formed if electrons have opposed spins, achieving a wave function corresponding to low energy
- Pauli principle (wave functions of two electrons change sign when labels of electrons are interchanged)

Homonuclear diatomic molecules (general case)

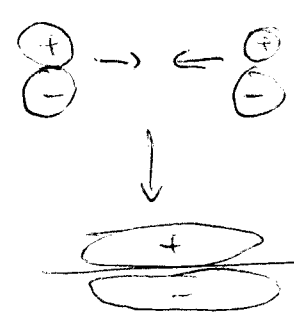
example:  $N_2$ , nitrogen

- electron configuration  $2s^2 2p_x^1 2p_z^1 2p_y^1$  (Hund's rule)
- $\sigma$  bond: spin pairing of  $2 \times 2p_z^1$



- remaining p orbitals → can not merge to  $\sigma$  bonds

$\pi$  - bond formation



$\pi$  bond resembles a pair of electrons in a p orbital  
 1  $\sigma$   
 $N_2$ : 2  $\pi$  bonds! (consistent with Lewis  $N \equiv N$ )  
 (one angular momentum, one angular node)

# Polyatomic molecules

- $\sigma$  bonds: spin pairing of electrons with cylindrical symmetry along the relevant nuclear axis
- $\pi$  bonds: pairing of electrons which occupy AO of the appropriate symmetry

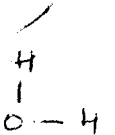
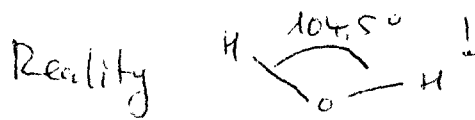
## discrepancies

example  $H_2O$ : O configuration of the valence electrons  
 $2s^2 2p_x^2 2p_y^1 2p_z^1$

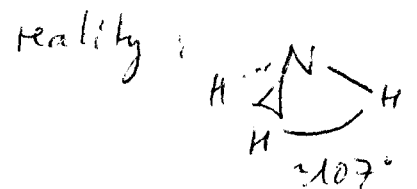
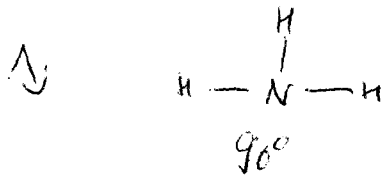
→ two unpaired 2p electrons → pair with a H1s each

$p_y$  and  $p_z$ : oriented to each other with  $90^\circ$

→  $H_2O$ : angular molecule

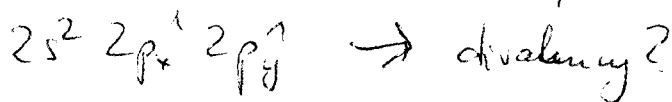


→  $NH_3$ : N configuration  $2s^2 2p_x^1 2p_y^1 2p_z^1$



## Promotion

VB theory can not account for tetravalence of C:



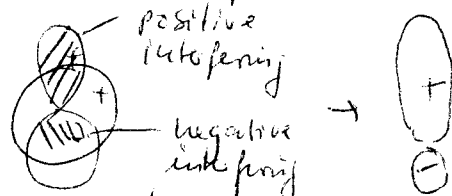
Solution: promotion to  $2s^1 2p_x^1 2p_y^1 2p_z^1$

- promotion is no real process; however energy contribution to bonding!

- C can now form 4  $\sigma$  bonds  $\rightarrow$   $\text{CH}_4$  -6-  
 - energy of promotion recovered by bond formation (+2  $\sigma$ !)

## b) Hybridization

- description of  $\text{CH}_4$  bonding (also  $\text{NH}_3$ ,  $\text{H}_2\text{O}$ , see above)  
 still incomplete, bond angles need to be explained
- problem: unequal  $\sigma$  bonds? (not observed in  $\text{CH}_4$ )  
 due to  $1s^2 + 3 \times 2p^1$  (1) which form 5 bonds
- Overcome: each electron of C occupies a hybrid orbital formed by interference of 2s and 2p orbitals  
 4 AO  $\rightarrow$  four new shapes



Linear combination leading to 4 equivalent hybrid orbitals

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

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

result: large lobe pointing into the corner of a regular tetrahedron

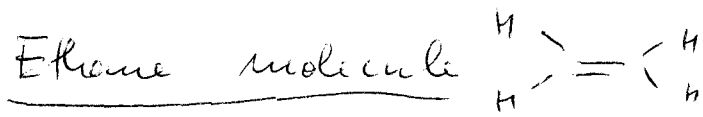
$1s + 3p \rightarrow sp^3$  hybrid orbital

wavefunction in analogy to  $\text{H}_2 \sigma$  ( $h_1$  and  $1s$ )

$$\Psi = h_1(1)A(2) + h_1(2)A(1)$$

each  $sp^3$ : same composition, all four  $\sigma$  in  $\text{CH}_4$  identical! (apart orientation)

- properties of hybrid orbitals - pronounced directional character  
 - increased bond strength  $\rightarrow$   
 - helps to repay promotion energy



- planar, HCH angles:  $120^\circ$   
 - promotion:  $\rightarrow 2s^1 2p^3$   
 - now using 3  $\times$   $sp^2$  hybrid orbitals

$$h_1 = s + 2^{1/2} p_y \quad h_2 = s + \left(\frac{3}{2}\right)^{1/2} p_x + \left(\frac{1}{2}\right)^{1/2} p_y$$

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

$\rightarrow$  lie in plane, point to triangle corners

Superpositions in general: proportion in the mixture is given by the square of the corresponding coefficient

$$h_1 : s \text{ to } p \pm 1:2$$

$$h_2 + h_3 : \text{total } p \text{ contribution also } 2 \left( \pm \frac{3}{2} + \frac{1}{2} \right)$$

different signs  $\rightarrow$  result in different regions where constructive interference takes place

Structure of  $H_2C=CH_2$ :

- 3  $sp^2$  form  $\sigma$  bonds;  $CH_2$  are in the same plane  
 to allow unhybridized  $p_z$ -Orbitals to form a  $\pi$ -bond  
 $\rightarrow$   $\pi$ -bond & no rotation possible

Ethyne  $\text{HC}\equiv\text{CH}$

-8-

$sp$  hybridized,

$\sigma$  bonds from  $h_1 = s + p_z$ ,  $h_2 = s - p_z$

along the C-C axis

4 electrons in  $2p$  orbitals  $\rightarrow$  2  $\pi$  bonds,  
perpendicular

General: hybridization of NAO  $\rightarrow$  formation  
of  $N$  hybrid orbitals

more examples of hybridization schemes

Coordination number	arrangement	composition
2	linear, Angular	$sp, pd, sd$ $sd$
3	trigonal planar " pyramidal	$sp^2, p^2d$ $pd^2$
6	octahedral	$sp^3d^2$