

CHAPTER 10

BONDING THEORY AND MOLECULAR STRUCTURE

THE VALENCE SHELL ELECTRON PAIR REPULSION METHOD (VSEPR) IS BASED ON THE IDEA THAT PAIRS OF ELECTRONS IN BONDED ATOMS REPEL EACH OTHER.

A MOLECULE IS IN ITS MOST STABLE GEOMETRY WHEN ITS ELECTRON PAIRS ARE AS FAR APART AS POSSIBLE

ELECTRON GROUPS THAT EXERT REPULSION UPON ONE ANOTHER INCLUDE:

- SINGLE UNPAIRED ELECTRONS $C\cdot$
- LONE PAIRS $H-\overset{\cdot\cdot}{O}-H$
- ONE BONDED PAIR $C-C$
- TWO BONDED PAIRS $C=C$
- THREE BONDED PAIRS $C\equiv C$

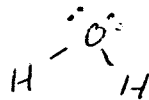
ONCE ELECTRON GROUPS MAXIMIZE DISTANCE FROM ONE ANOTHER, SIMPLE LOGIC DICTATES THE MOLECULAR GEOMETRY

- 2 GROUPS \rightarrow LINEAR
- 3 GROUPS \rightarrow TRIGONAL PLANAR
- 4 GROUPS \rightarrow TETRAHEDRAL
- 5 GROUPS \rightarrow TRIGONAL BIPYRAMIDAL
- 6 GROUPS \rightarrow OCTAHEDRAL

IN THE VSEPR NOTATION, A STANDS FOR THE CENTRAL ATOM
X STANDS FOR TERMINAL ATOMS
E STANDS FOR LONE PAIRS

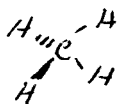
NUMERICAL SUBSCRIPTS INDICATE HOW MANY OF EACH

EXAMPLE H_2O



AX_2E_2 4 GROUPS \rightarrow TETRAHEDRAL

CH_4



AX_4 4 GROUPS \rightarrow TETRAHEDRAL

VSEPR METHOD

- 1) DRAW A LEWIS STRUCTURE
- 2) COUNT THE ELECTRON GROUPS (EITHER BONDS OR LONE PAIRS)
- 3) ESTABLISH ELECTRON GROUP GEOMETRY
- 4) ESTABLISH MOLECULAR GEOMETRY (NEGLECT LONE PAIRS)

EXAMPLES

NITRATE ION



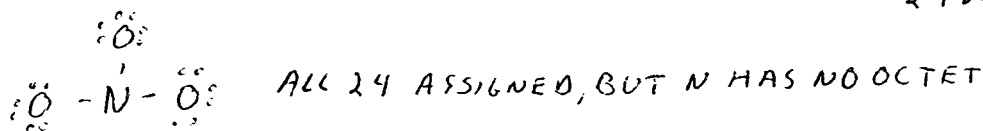
O HAS 6 e⁻ 3 x 6 = 18

N HAS 5 e⁻ 1 x 5 = 5

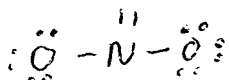
ONE MINUS CHARGE = 1

24 VALENCE e⁻

1) LEWIS STRUCTURE



SO, MOVE ONE PAIR TO BONDING PAIR



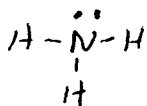
2) COUNT ELECTROW GROUPS → 3 OR AX₃

3) ELECTROW GROUP GEOMETRY → 3 GROUPS → TRIGONAL PLANAR

4) MOLECULAR GEOMETRY → 3 GROUPS → TRIGONAL PLANAR

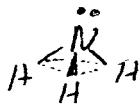
STRUCTURES WITH LONE PAIRS

NH₃ AMMONIA TOTAL 5 + 3 → 8 ELECTRONS AX₃E

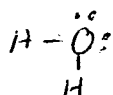


4 GROUPS → TETRAHEDRAL

MOLECULAR GEOMETRY IS TRIGONAL PYRAMIDAL

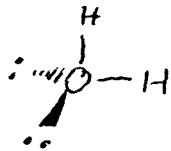


H₂O TOTAL 6 + 2 = 8 ELECTRONS AX₂E₂

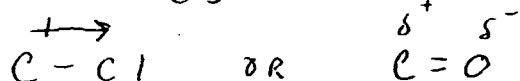


4 GROUPS → TETRAHEDRAL

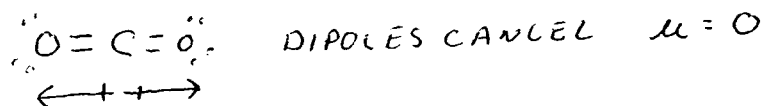
MOLECULAR GEOMETRY IS ANGULAR



NOW THAT WE CAN USE MOLECULAR GEOMETRY, WE CAN SHOW THE DIFFERENCE BETWEEN POLAR BONDS AND POLAR MOLECULES
RECALL THAT A POLAR BOND IS ONE BETWEEN ATOMS OF DIFFERENT ELECTRO NEGATIVITIES



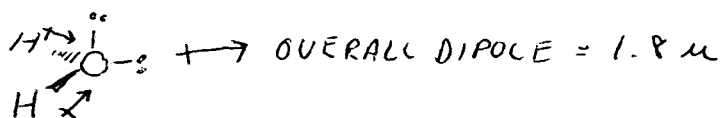
IF A MOLECULE IS HIGHLY SYMMETRICAL, IT WILL BE NONPOLAR EVEN IF IT CONTAINS POLAR BONDS



THE CLASSIC EXAMPLE IS CARBON TETRACHLORIDE CCl_4



THE CLASSIC EXAMPLE OF AN ASYMMETRIC, POLAR MOLECULE IS H_2O



VALENCE BOND THEORY

A COVALENT BOND IS FORMED BY THE PAIRING OF 2 ELECTRONS WITH OPPOSING SPINS IN THE REGION OF OVERLAP OF ATOMIC ORBITALS BETWEEN 2 ATOMS. THE OVERLAP OF 2 ATOMIC ORBITALS RESULTS IN A MOLECULAR ORBITAL, WHICH IS A REGION OF HIGH ELECTRON DENSITY BETWEEN 2 NUCLEI

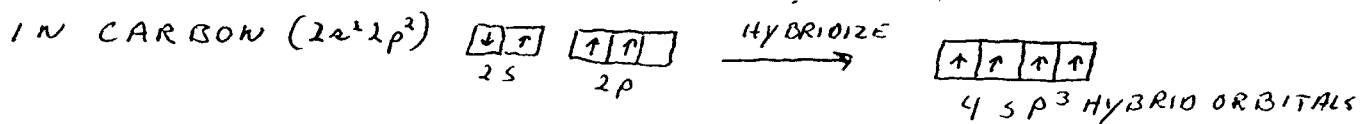
SOME HIGHLIGHTS

- IN A COMPOUND, MOST ELECTRONS REMAIN IN THE SAME ORBITAL LOCATIONS THEY OCCUPIED IN THE UNBONDED ATOMS
- BONDING ELECTRONS ARE "LOCALIZED" IN THE REGION OF ATOMIC ORBITAL OVERLAP

HYBRID ORBITALS

TO ACCOUNT FOR THE OBSERVED STRUCTURES AND GEOMETRIES OF MOST MOLECULES, WE INTRODUCE HYBRID ORBITALS. HYBRID ORBITALS ARE THEORETICALLY MADE BY "BLENDING" ATOMIC ORBITALS TOGETHER

AN sp^3 HYBRID ORBITAL BLENDS 1 s PLUS 3 p TO MAKE 4 sp^3 HYBRID.



HYBRID ORBITALS

- OFTEN USED FOR ONLY THE CENTRAL ATOM
- THE NUMBER OF HYBRID ORBITALS FORMED IS EQUAL TO THE NUMBER OF ATOMIC ORBITALS COMBINED
- FOR BONDING, HYBRID ORBITALS MAY OVERLAP WITH OTHER HYBRID ORBITALS OR WITH ATOMIC ORBITALS
- MOLECULAR GEOMETRY IS DETERMINED BY THE SHAPES AND ORIENTATIONS OF THE HYBRID ORBITALS

$sp \rightarrow$ LINEAR

$sp^2 \rightarrow$ TRIGONAL PLANAR

$sp^3 \rightarrow$ TETRAHEDRAL

$sp^3d \rightarrow$ TRIGONAL BIPYRAMIDAL

$sp^3d^2 \rightarrow$ OCTAHEDRAL

THE sp^3 HYBRID

- 4 EQUAL ORBITALS \rightarrow TETRAHEDRAL
- ALMOST ALL OF CARBON CHEMISTRY IS sp^3 (SMALLER AMOUNTS OF sp^2 , sp)
- ALSO SEEN IN AX_3E (NH_3) AX_2E_2 (H_2O)

THE sp^2 HYBRID

- MOST USEFUL IN DOUBLE BONDS $C=C$, $C=O$, ETC

THE sp HYBRID

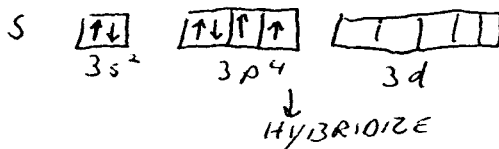
- TRIPLE BONDS $C\equiv C$, $C\equiv N$, ETC

HYBRID ORBITALS WITH D SHELLS

sp^3d - TRIGONAL BIPYRAMIDAL

sp^3d^2 - OCTAHEDRAL

AS IN SF_6



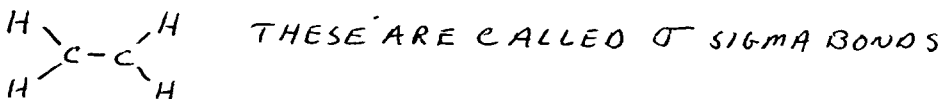
$\begin{array}{|c|c|c|c|c|c|} \hline \uparrow & \uparrow & \uparrow & \uparrow & \uparrow & \uparrow \\ \hline \end{array} \rightarrow$ SIX EQUAL ORBITALS

$\begin{array}{|c|c|} \hline & \\ \hline \end{array} \rightarrow$ REMAINING D ORBITALS

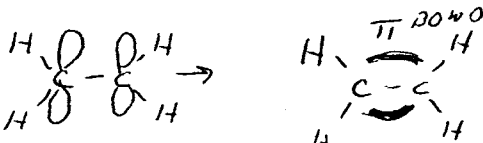
HYBRID ORBITALS AND DOUBLE BONDS

ESPECIALLY IN CARBON, DOUBLE BONDS ARE FORMED FROM sp^2 HYBRIDS

$\begin{array}{|c|c|c|} \hline \uparrow & \uparrow & \uparrow \\ \hline \end{array}$ $\begin{array}{|c|} \hline \uparrow \\ \hline \end{array}$ \leftarrow A CARBON WITH THIS HYBRIDIZATION CAN FORM 3 SINGLE BONDS AND HAVE 1 ELECTRON IN A P ORBITAL

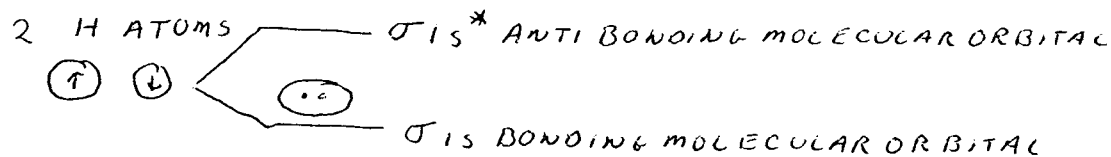


EACH CARBON HAS A P ORBITAL OVERLAP OF P ORBITALS MAKES A π BOND



THE FINAL PIECE OF THE PUZZLE IS MOLECULAR ORBITALS

FORMED BY A LINEAR COMBINATION OF ATOMIC ORBITALS (LCAO)
THE NUMBER OF MOLECULAR ORBITALS IS THE SUM OF THE NUMBER
OF ATOMIC ORBITALS COMBINED



- ELECTRONS SEEK THE LOWEST MO AVAILABLE
- A MAXIMUM OF 2 ELECTRONS IN EACH MO (PAULI EXCLUSION)
- ELECTRONS ENTER MOLECULAR ORBITALS OF IDENTICAL ENERGIES SINGLY WITH PARALLEL SPINS BEFORE THEY PAIR UP (HUND'S RULE)

2nd PERIOD ELEMENTS

4 ATOMIC ORBITALS (1s, 3p) \rightarrow 8 MOLECULAR ORBITALS

SEE FIGURE 10.27 p 447

4 BONDING, 4 ANTI BONDING

FOR THESE ORBITALS AND THE DIATOMIC MOLECULES OF THE 2nd PERIOD
IT PREDICTS THE NET TRIPLE BOND AND UNPAIRED ELECTRONS IN O_2

SKILLS

USE THE VSEPR METHOD

PROBLEMS

EX 10.1, 10.2, 31, 37

UNDERSTAND MOLECULAR DIPOLE MOMENTS

EX 10.4, 10.5, 43

USE VALENCE BOND THEORY FOR HYBRID ORBITALS

EX 10.6, 49, 51

BE ABLE TO USE MOLECULAR ORBITAL THEORY

EX 10.7, 10.7A

SPECIALLY FOR DIATOMICS OF 2nd PERIOD

EX 10.9 EXERCISE 10.9

67, 69

NOT COVERED

GEOMETRIC ISOMERISM p 440-442

BONDING IN BENZENE p 448-451