BOND THEORIES

VALENCE BOND THEORY

- Electron-dot structures and the VSEPR model allow us to predict molecular shape and electron distribution
- But what about the electronic nature of a bond?
- A quantum mechanical model called valence bond theory can be used to describe and visualize bonds using orbital pictures
    - Uses spatial overlap of orbitals to explain bond formation
- Covalent bonds are formed by overlap of atomic orbitals, each of which contains one electron of opposite spin
    - To get a bonding interaction in the valence bond model, the overlapping orbitals must be of the same phase
    - Important for p and higher orbitals
- The greater the overlap, the stronger the bond
- Bond formation by head-on overlap of orbitals gives sigma bonds
- How can valence bond theory explain molecular shapes?
    - How can the bonding in CH4 be explained
        - Carbon ground state configuration: 2s^2 2p^2
        - Carbon excited state configuration: 2s^1 2p^3
- Linus Pauling showed that QM wave functions for s and p orbitals can be mathematically combined to form a new set of equivalent wave functions called hybrid atomic orbitals
- spy hybridization is also possible when lone pairs are involved
    - Some of the sp3 orbitals simply don't overlap with another bonding partner
- Molecules with 5 or 6 charge clouds obviously must involve other orbitals, but recent QM studies have shown that bonding is much more complex than originally assumed
- Orbital names reflect number of orbitals used: sp, sp2, sp3

CONTINUED HYBRID ORBITALS

- Atoms with three charge clouds form sp2 hybrid orbitals from one s and two p orbitals (120 degrees apart)
- One p orbital stays unchanged and oriented at 90 degrees to hybrid orbitals
- For sp2 hybridized atoms, the unhybridized p orbitals can also form a bond in a sideways fashion
- Electrons are shared in areas above and below the line connecting the nuclei
- A pi bond is the sideways overlap of p orbitals

- Atoms with 2 charge clouds form sp hybrid orbitals from one s and one p orbitals (180 degrees apart)
- Two p orbitals stay unchanged and oriented at 90 degrees to each other and the sp hybrid orbitals
- For sp hybridized atoms, the two unhybridized p orbitals can form two pi bonds
    - Either one triple or two double bonds

MOLECULAR ORBITAL THEORY

- The concepts introduced so far are easy to visualize and can explain most molecules
- However, some properties of molecules cannot be satisfactorily explained with valence bond theory
    - We need a better description in such cases
- Molecular orbital theory is more complex and less visual but can give a better description of certain molecules than valence bond theory
    - This includes "simple" molecules like O2 as we will see later
- MO theory extends the QM concepts introduced for atoms
    - Atomic orbital: A wave function whose square gives the probability of finding an electron in a given region of space in an atom
    - Molecular orbital: A wave function whose square gives the probability of finding an electron in a given region of space in a molecule.
- MO has many similarities to atomic orbitals
    - Specific energy levels
    - Can be occupied by a maximum of two electrons with opposite spins
- Molecular orbitals form through additive or subtractive combination of atomic orbital wave functions
- Molecular orbitals can be represented with energy diagrams similar to what we used for atomic orbitals

BOND ORDER = (# bonding electrons - # antibonding electrons) / 2

- MOs are to molecules what atomic orbitals are to atoms
- MOs are formed by combining atomic orbitals on different atoms
    - The number of MOs is the same as the starting number of AOs
- MOs that are lower in E than the starting AOs are called bonding, MOs that are higher in E are called anti bonding
- Electrons occupy MOs beginning with the lowest E
    - Two electrons per orbital, which are spin paired
- Bond orders are calculated by subtracting the number of electrons in anti bonding MOs from the number in bonding MOs and dividing by 2

- Equal orbitals interact (e.g. 2s/2s; 2p/2p)