

Ch 1 Structure and Bonding

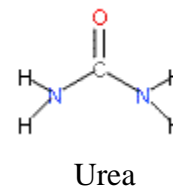
Organic Chemistry is the science of carbon compounds.

Prior to the 19th century, the term referred only to compounds in living tissue.

This changed when it was shown that organic compounds could be prepared in a lab.

Chevreul prepared glycerin and fatty acids from animal fat in 1816.

Wöhler prepared urea (H_2NCONH_2) from ammonium cyanate in 1828.



Carbon forms many compounds because it has 4 valence e^{-1} and forms 4 covalent bonds.

C nucleus has 6 protons ($Z = 6$) with 6 or 7 neutrons, so $A = 12$ or 13 amu.

(Carbon 14 has 8 neutrons, but is radioactive and has a very low abundance.)

The atomic mass of carbon on the periodic table is 12.011 amu.

This mass is an average wt which incorporates the natural abundance of the two isotopes.

98.9% of natural C is ^{12}C and 1.1% is ^{13}C , which gives us: $(12 \times 0.989) + (13 \times 0.011) = 12.011$.

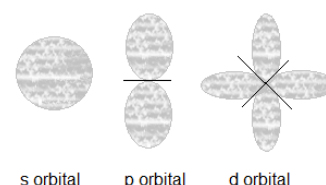
The e^{-1} 's are arranged in orbitals or wave functions (Ψ or psi), which are the solutions to the quantum wave equations (Schrödinger's equation).

Probabilities for an e^{-1} 's location can be found using Ψ^2 , which is a probability density function.

Orbitals do not have sharp boundaries, and are often set arbitrarily where the probability of finding the e^{-1} within a given volume is 90 to 95%.

The subshell types s, p, d, and f, have 1, 3, 5, and 7 total orbitals, respectively.

Orbital shape is determined by the number of nodes, which are planes where the e^{-1} cannot be. The **s** orb has no nodes and is **spherical**, **p** has one node, which results in **two lobes**, and **d** has two nodes, which results in **four lobes**.



The orbitals are arranged in shells, where the principle quantum # is the shell #.

Shell 1 has only an s subshell, containing one s orb only ($1s^2$).

Shell 2 has s and p subshells, where the p subshell consists of three p orbs ($2s^2 2p^6$).

Shell 3 has s, p and d subshells, where the d subshell consists of five p orbs ($3s^2 3p^6 3d^{10}$).

The lowest energy arrangement, or ground state, for the e^{-1} 's is found using a set of rules.

Aufbau principle is that subshells are filled by lowest E first: 1s, 2s, 2p, 3s, 3p, 4s, 3d, etc.

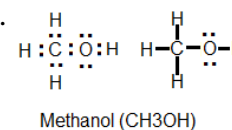
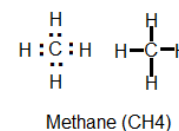
Pauli Exclusion Principle is that only two e^{-1} 's can fit in an orb, and they have opposing spins.

Hund's rule is that e^{-1} half-fill all orbs in a subshell before they spin-pair with two e^{-1} 's in an orb.

C has four valence units and forms four covalent bonds.

The bonding e^{-1} 's are shared in a covalent bond, rather than transferred as in an ionic bond.

There are eight shared e^{-1} 's in shell 2 from the four bonds, which fulfills the octet rule, as can be seen in the Lewis (dot) and Kekulé (line bond) structures of CH_4 and CH_3OH .



Valence Bond Theory

- Covalent bonds are described by two theories: Valence Bond and Molecular Orbital.
- Valence bond theory basically describes bonding as overlap of two atomic orbitals (Fig 1.7).
- The H_2 molecule's two spherical 1s orbs overlap to create a cylindrically symmetrical bond.
- A bond like this, which is created by head-on overlap, is called a σ (sigma) bond.
- The e^{-1} density for a σ bond is primarily located directly between the two nuclei.



Bond Stability

- A chemical bond creates stability, and the bond strength is equivalent to the energy released when the bond is formed. For H_2 , the bond strength is 436 kJ.
- Although bonds constantly vibrate like springs, the distance between nuclei with the lowest E is the bond length. For H_2 , the bond length is 74 pm (7.4×10^{-11} m).

Hybrid Orbitals

- Hybrid orbitals are combinations of atomic orbitals from *more than one subshell*.
- Hybridization of different types of orbitals creates a set of composite orbitals which all have the same shape, size, and energy.
- The hybrid orbitals' features are essentially averages of the component orbitals' features.
- The total number of orbitals does not change.
- Hund's rule predicts that an orbital with two e^{-1} 's will donate one e^{-1} to an empty orbital if it has the same energy.
- As a result, hybridization maximizes the number of half-filled orbitals which are available to form covalent bonds
- The name of the hybrid orbital type uses the component orbitals, along with superscripts denoting the number of orbitals from that subshell. For instance, one s orbital and three p orbitals will form four identical (averaged) sp^3 orbitals.
- Carbon has four valence orbitals in two subshells. They contain four valence e^{-1} 's, and their unhybridized configuration is $2s^2 2p^2$. This configuration has only two unpaired e^{-1} 's, which could only form two normal covalent bonds.

But, carbon can actually form four.

- The s orbital can hybridize with up to three p orbitals. The s orbital, along with three p orbitals, will form four sp^3 orbitals, and each hybridized orbital will have one unpaired e^{-1} . This configuration forms four identical normal covalent bonds in compounds such as CH_4 .
- These bonds are also equally spaced apart, so that the geometry is tetrahedral, and the bond angles are all 109.5° .
- All four bonds with the sp^3 orbitals are σ , that is, they have head-on overlap.
- Because the orbital shape is averaged from its components, an sp^3 orbital is 25% s shaped and 75% p shaped. This shape is similar to a p orb, but is unsymmetrical.

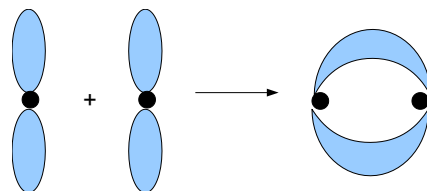
Multiple Bonds

- To form a multiple bond, more than one orbital from each atom has to overlap.
- The 2nd and 3rd e⁻¹ pairs of double and triple bonds use unhybridized p orbitals only.
- Only the remaining p orbitals can now hybridize with the s orbital.
- One of those hybridized orbitals is then used for the 1st e⁻¹ pair of the multiple bond.
The remaining hybridized orbitals will bond with the remaining atoms.

Double Bonds

- In H₂C::CH₂, the 2nd e⁻¹ pair of the double bond uses unhybridized p orbitals from each C.
- The 2nd bond overlaps at each of the two lobes of the p orbitals to create a Π (pi) bond.

The Π bond has two lobes, one above the plane, and the other below. The e⁻¹ density is primarily in the two lobes, and not directly between the two nuclei.



- This leaves two 2p orbitals and one 2s orbital to hybridize as three sp² orbitals.
- The three sp² orbitals create three σ (sigma) bonds to the other C and the two H's.
These bonds have trigonal planar geometry, and are 120° apart.

Triple Bonds

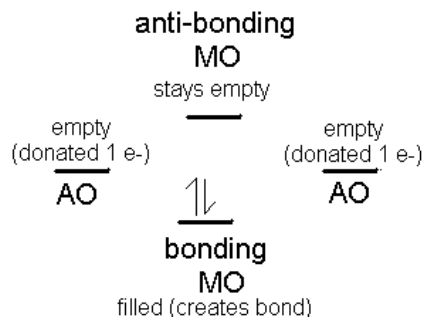
- In HC:::CH, the 2nd and 3rd e⁻¹ pairs of the triple bond use unhybridized p orbitals from each C.
- The 2nd and 3rd e⁻¹ pairs create two Π bonds.
- This leaves one 2p orbital and one 2s orbital to hybridize as two sp orbitals.
The two sp orbitals create two σ (sigma) bonds to the other C and the H.
These bonds have linear geometry, and are 180° apart.

Hybrid Orbitals for N and O

- O and N atoms typically have both bonding and nonbonding (lone) e⁻¹ pairs.
- In NH₃, the N has four sp³ orbitals, where three are used for σ bonds, and the fourth is a nonbonding (lone) pair.
- The e⁻¹ pair arrangement includes all four orbs and is tetrahedral.
- Bond angle is 107.3°, deviating slightly from tetrahedral because the lone pair requires more space.
- In H₂O, the O has four sp³ orbitals as well. Two are used for σ bonds, and the other two are lone pairs. Bond angle is 104.5° as a result of the two lone pairs.
- Formaldimine, H₂C::NH, has a carbon-nitrogen double bond, where both N and C are sp² with one σ bond and one Π bond between them.

Molecular Orbital Theory

- Covalent bonds can be described as a combination of two atomic orbitals (AO's) to form two molecular orbitals (MO's) that are shared by all nuclei of the molecule.
- That is, e^{-1} 's no longer belong completely to specific atoms, but are part of the molecule as a whole.
- An MO describes a region of space in a molecule (not atom) where the e^{-1} 's can be located. The AO's can be added together to create a **bonding MO** (covalent bond) or subtracted to partially cancel each other to create an **anti-bonding MO** (detracts from bond strength).
- So, two AO's will form two MO's. One will be bonding and the other will be anti-bonding.
- A chemical bond exists if there are more bonding e^{-1} 's than anti-bonding e^{-1} 's.
- The e^{-1} 's in bonding MO's are at lower E than the corresponding AO's, which stabilizes the bonding.
- The e^{-1} 's in anti-bonding MO's are at higher E than the corresponding AO's, which destabilizes the bonding.
- Bonding MO's are cylindrical and connect the two atoms.
- Anti-bonding MO's contain a node and separate the two atoms.

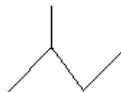


Condensed Structures

- Created by eliminating line bonds in a Kekulé structure and grouping like-atoms together.
- The result contains only the atomic symbols with their number subscripts.
- Lines are sometimes shown for clarity where necessary, but are otherwise eliminated.
- The structures are generally written a single line, if possible.
- For instance, 2-methylbutane becomes $(\text{CH}_3)_2\text{CHCH}_2\text{CH}_3$.

Skeletal Structures

- Created by keeping line bonds between carbon atoms and eliminating C's and H's.
- The number of H's present is understood because an uncharged C always has 4 bonds.
- C's are at the intersections and ends of the lines, and are only shown if needed for clarity.
- Atoms other than C and H are always shown.
- Ethane (H_3CCH_3) is simply — , which represents one carbon-carbon single bond.
- Ethene (H_2CCH_2) is = , which represents one carbon-carbon double bond.
- Ethyne (HCCH) is ≡ , which represents one carbon-carbon triple bond.
- 2-methylbutane, or $(\text{CH}_3)_2\text{CHCH}_2\text{CH}_3$, is shown as:



Molecular Models

- [Space-filling models](#) use atoms that are semi-spherical and attached directly to each other.
- [Ball-and-stick models](#) use balls for atoms and sticks or springs to connect them.