Chapter 1: The Basics - Bonding and Molecular Structure

1.1 - We Are Stardust
- Organic chemistry is simply the study of carbon-based compounds, hydrocarbons, and their derivatives, which all originally came from exploding star supernovae.

1.2 - Atomic Structure
- In atoms, the electrons are what create most of the volume.
- The symbol, Z, is used to denote the atomic number of an element.

1.3 - The Structural Theory of Organic Chemistry
- **Constitutional Isomers**: Different compounds that have the same molecular formula but differ in the sequence in which their atoms are bonded, that is, their connectivity but not number of bonds (older term: structural isomers).

1.4-1.6 - Chemical Bonds: The Octet Rule, How To Write Lewis Structures, Exceptions to the Octet Rule
- **Electronegativity**: The ability of an atom to attract electrons.
- Elements of the third period and beyond have d orbitals that can be used for bonding and thus can exceed the octet rule.
- Elements such as boron and beryllium can have fewer than eight electrons (e.g., BF₃).
- Oxygens are very rarely bonded to other oxygens in stable molecules because these peroxo groups are very unstable and reactive.

1.7 - Formal Charges
\[ F = Z - \left(\frac{1}{2}\right)S - U, \]
where \( F \) is the formal charge, \( Z \) is the group number, \( S \) is the number of shared electrons, and \( U \) is the number of unshared electrons.
- An easier way to think about formal charges is to just take the group number and subtract the number of free electrons as well as the number of bonds connected to that atom.

1.8 - Resonance Theory
- In resonant structures, one structure can be converted to another via the movement of electrons (and therefore changing bonds) with the atoms still in the same arrangement in 3-space and obeying conservation of charge.
- To show the movement of electrons, a curved arrow, \( \rightarrow \), is drawn with the tail of the arrow beginning at the current position of the electron pair and the head of the arrow pointed to where the electron pair will be in the next structure.
- Resonant structures are not real representations of the actual molecule (not in equilibrium). The actual molecule is a hybrid of all resonance contributors.
- A double-headed arrow, \( \leftrightarrow \), is used to equate resonance structures.
- To depict what a hybrid structure may be both solid lines and dashed lines are used for bonds where the dashed lines indicate the superimposed bonds of the resonance contributors. Partial charges, \( \delta \), are also used.
- The energy of the resonance hybrid is lower than the energy of any contributing structure.
- Resonance structures stabilize a molecule or ion, especially when the resonance structures are equivalent and is known as **resonance stabilization**.
- The more stable an individual resonance contributor is on its own, the greater its contribution to the overall hybrid structure.

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Footnote for myself: Don’t be disruptin’ them hydrogen atoms, foo!  
\(^1\)Constitutional isomers can’t be the same if rotated (e.g., not tetrahedral geometries)  
\(^2\)Footnote for myself: Don’t be disruptin’ them hydrogen atoms, foo!
Determination of Stability for Resonance Structures, in order of decreasing significance:
- The more covalent bonds a structure has, the more stable it is
- Charge separation (formal charges) decreases stability
- Negative charges on the more electronegative elements and positive charge on the more electropositive elements is more favorable

1.9 - Quantum Mechanics and Atomic Structure
- Each wave function, \( \psi \), corresponds to a different energy state for an electron
- Each energy state is a sublevel where one or two electrons can reside
- The relative probability of finding an electron in a given region of space can be found with \( \psi^2 \) and is known as the electron probability density
- A solution to a wave function can be positive, negative, or zero (the graph of \( \psi \) has nodes)
- The phase sign of a wave equation indicates whether the solution is positive or negative when calculated for a given point in space relative to the nucleus
- Constructive interference occurs when wave functions with the same phase sign interact and reinforce the amplitude of the resultant wave
- Destructive interference occurs when wave functions with opposite phase signs interact and subtract the amplitude of the resultant wave

1.10 - Atomic Orbitals and Electron Configuration
- An orbital is a region of space where the probability of finding an electron is high
- Atomic orbitals are plots of \( \psi^2 \) in three dimensions
- All s orbitals are spheres with higher levels having an inner nodal surface where \( \psi^2 = 0 \) (eg: 2s is a large sphere with a smaller sphere inside separated by a node)
- In order to have a node where \( \psi^2 = 0 \), there must be a phase sign difference (from + to − or vice versa) between the different quantum number levels
- All p orbitals are shaped like dumbbells with a nodal plane separating the two lobes of a p-orbital, and the three p orbitals of a given energy level are arranged along the \( x \), \( y \), and \( z \) axes

Configurations:
- Electrons of lower quantum numbers have lower energy since they are closest to the nucleus
- For orbitals of the same quantum number, the higher \( l \) quantum number (shape of the atomic orbital) has more energy (eg: a 2p orbital has more energy than a 2s orbital)
- Orbitals of equal energy (such as the three 2p orbitals) are called degenerate orbitals

Rules of configuration:
- The Aufbau Principle states that orbitals are filled so that those of lowest energy are filled first
- The Pauli Exclusion Principles states that a maximum of two electrons may be placed in each orbital but only when the spins of the electrons are paired (\( \uparrow \) and \( \downarrow \) can be paired but never \( \uparrow \) or \( \downarrow \))
- Hund’s Rule states that, when degenerate orbitals are considered, we add one electron to each with their spins unpaired until each degenerate orbital contains one electron. Afterward, the second set of electrons are aided to pair the spins

3For the purposes of drawing all resonance structures, it is not considered a violation of the octet rule if a second-row element, like carbon, has fewer than an octet. It is simply less likely but still imperative to draw.
1.11 - Molecular Orbitals
- The ideal internuclear distance between two atoms is known as the bond length
- The Heisenberg Uncertainty Principle states that we cannot simultaneously known the position and momentum of an electron
- A Molecular Orbital (MO) represents the region of space where one or two electrons of a molecule are likely to be found (remember that atomic orbitals represent an analogous probability but for isolated atoms)
- When atomic orbitals combine to form molecular orbitals, the number of molecular orbitals that result always equal the number of atomic orbitals that combine
- A bonding molecular orbital ($\psi_{\text{molecular}}$) results when two orbitals of the same phase overlap
- An antibonding molecular orbital ($\psi_{\text{molecular}}^*$) results when two orbitals of opposite phase overlap
- In the Linear Combination of Atomic Orbitals (LCAO) Method, wave functions for atomic orbitals are combined in a linear fashion in order to obtain new wave function for MOs
- The energy of a bonding molecular orbital is less than the energy for the corresponding atomic orbital while the energy of an antibonding molecular orbital is higher than the energy for the corresponding atomic orbital (refer to your typical MO diagram for a simple visualization of this fact)

1.12 - The Structure of Methane and Ethane: $sp^3$ hybridization
- Orbital Hybridization combines individual wave functions for $s$ and $p$ orbitals to form new orbitals known as hybrid atomic orbitals
- The type of hybridization directly correlates to the molecular geometry for the structure: $sp$ is linear, $sp^2$ is trigonal planar, $sp^3$ is tetrahedral, etc.
- A bond formed from the overlap of an $sp^3$ orbital and a $1s$ orbital is an example of sigma (\(\sigma\)) bond
- A sigma bond has a circularly symmetrical orbital cross section, and all single bonds are sigma bonds
- Rotation of groups joined by a single bond do not require a lot of energy input
- More $s$ (less $p$) character means bonds are shorter
- The contributing structure with the largest bond angle will determine the overall geometry as well as level of hybridization for molecules with a lone pair that participates in resonance since the geometry of an atom must be representative of all possible resonance forms$^4$
- Each $\pi$ bond is a degree of saturation, and a ring is an example of a degree of unsaturation that can be used to eliminate hydrogen atoms from a molecular formula

1.13 - The Structure of Ethene: $sp^2$ hybridization
- The common name for ethene is ethylene and propylene for propene
- Hydrocarbons whose molecules contain a carbon-carbon double bond are known as alkenes
- Sideways overlap of $p$ orbitals and sharing of the two electrons between atoms leads to a pi (\(\pi\)) bond
- $\pi$-bonds, and thus overlapping $p$ orbitals, overlap above and below the plane of the $\sigma$-bond framework
- When two $p$ atomic orbitals combine to form a $\pi$-bond, two molecular orbitals form: one is a bonding MO, and one is an antibonding MO
- Bonding $\pi$ MOs form when $p$ orbitals of like signs overlap and vice versa
- The energy diagram for a standard MO set of bonds is, in order of increasing energy, $\sigma, \pi, \pi^*, \sigma^*$
- There is a large energy barrier to rotation associated with a group that has a $\pi$-bond because rotating one carbon of a double bond breaks the $\pi$ bond
- Since $-\text{cis}$ and $-\text{trans}$ isomers have identical connectivity (just on different sides), they are not constitutional isomers but are rather stereoisomers

$^4$Important: All carboxylic amides have the functional group's nitrogen as $sp^2$ regardless of geometry!
1.14-1.15 - The Structure of Ethyne (Acetylene): $sp$ hybridization, A Summary of Important Concepts That Come from Quantum Mechanics
- The common name of ethyne is acetylene
- Hydrocarbons composed of triple bonds are known as alkynes
- The greater the $s$ orbital character and lesser the $p$ orbital character the shorter the bond length
- Bonds involving $sp$ hybrids are shorter than $sp^2$ hybrids, which are shorter than $sp^3$ hybrids, etc.

Techniques for Drawing Resonance Structures Systematically
First Step: Always draw out the electron pairs!

Factor 1: A lone pair next to a $\pi$ bond
1) Move the two electrons that compose the lone pair and turn them into a bond to make a new $\pi$ bond
2) Turn the $\pi$ bond that was originally next to the lone pair into a $\sigma$ bond and add an electron pair to the atom attached to the new $\sigma$ bond atom as compensation for the loss of 2 electrons. Check to see if this option can be performed again.

Factor 2: A lone pair next to a positive charge
- Simply “slide” the lone electron pair to the nearby bond of the positively charged atom to make all formal charges zero and a new $\pi$ bond

Factor 3: A $\pi$ bond next to a positive charge
- Simply shift the $\pi$ bond to the $\sigma$ bond of the positively charged atom. If there is conjugation of double bonds, shift them all for another structure. This will make the positive formal charge move to the opposite end of the molecule

Factor 4: A $\pi$ bond between two atoms where one is electronegative
- Turn the $\pi$ bond into a $\sigma$ bond, and give the pair of electrons lost from this to the electronegative atom

Factor 5: $\pi$ bonds going all the way around a ring
- Simply change the $\pi$ bonds to $\sigma$ bonds and vice versa

Important Note: Do not draw a resonance structure where two carbon atoms bear opposite charges (insignificant)

1.17, 1.18 - How to Interpret and Write Structural Formulas, Applications of Basic Principles
- The dot structure includes all the valence electrons
- Atoms joined by single bonds can rotate relatively freely with respect to one another
- Dash structural formulas are used to indicate the way in which atoms are attached, also known as the connectivity, to distinguish constitutional isomers
- Condensed structural formulas have the hydrogen atoms written immediately after the carbon. Also, in fully condensed formulas all of the atoms that are attached to the carbon are written immediately after the carbon, listing hydrogens first
- A bond-line formula have no carbons or hydrogens written (on occasion hydrogens may be added to indicate the geometry). Lines represent bonds, and carbon atoms are inferred at each bend. The number of hydrogen atoms is also inferred based on the octet rule

$^5$Some factors become more apparent after drawing out one of the resonance structures and looking at that new drawing
$^6$"Next to" means that the lone pair is separated from the double bond by exactly one single bond
**1.16 - Molecular Geometry: The Valence Shell Electron Pair Repulsion (VSEPR) Model**

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<th>Number of Electron Domains</th>
<th>Electron-Domain Geometry</th>
<th>Bonding Domains</th>
<th>Non-bonding Domains</th>
<th>Molecular Geometry</th>
<th>Example</th>
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