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Molecular Literacy for All

making sense of the “monstrous and boundless thicket” of everyday chemistry

The model of covalency leads to predictable patterns of molecular geometry and bonding in molecules

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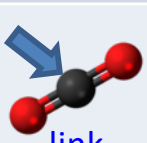
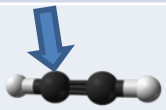
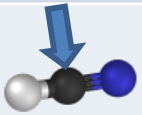
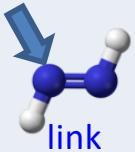
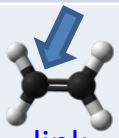
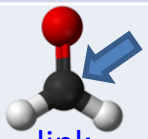
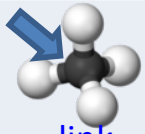
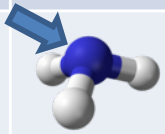
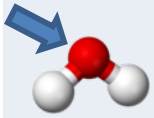
number of nonbonding electron pairs	number of electron-pair domains		
	four	three	two
0			
1			
2			
3			
4			

The table of octet electron configurations

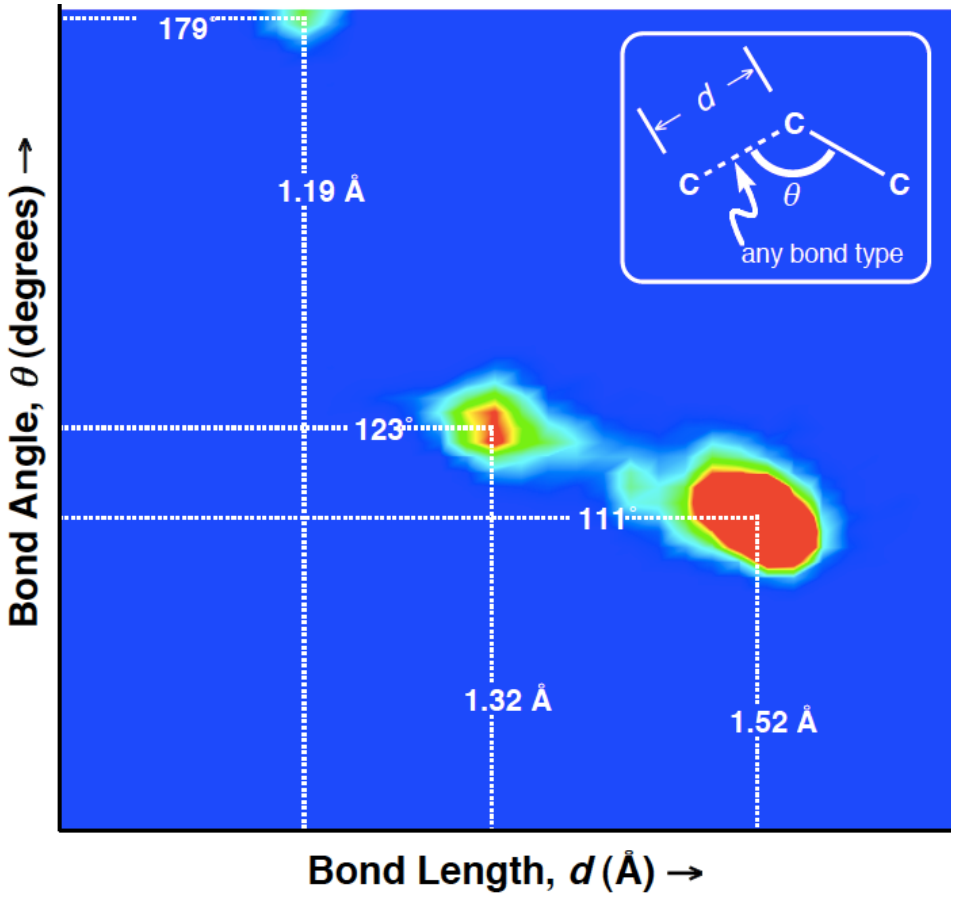
Just as written language has a limited number of syllables, there are only a limited number of ways to satisfy the octet electron rule. This table shows all of them. The letter "A" represents an atom (it may be C, N, O, or F). Complete the table by drawing bonds and lone pairs that satisfy the octet rule for each atom indicated. Three are done for you as examples. Note that there are two ways to satisfy the octet rule for an atom with two electron-pair domains and having zero nonbonding electron pairs. Some regions in the table are impossible and these are left blank. Shade in these regions and explain why they are inconsistent with octet configurations. Similarly, why did we consider atoms having four electron-pair domains, but not five?

The table reveals the eleven ways to satisfy the octet rule. That's it – there are no more.

Molecular geometry and the number of EPDs*

No of EPDs	2			3			4		
examples	CO_2	C_2H_4	HCN	H_2N_2	C_2H_4	CH_2O	CH_4	NH_3	H_2O
models (hyper-linked)	 link	 link	 link	 link	 link	 link	 link	 link	 link
structure									
bond angle									
geometry									

*The relationship between EPDs and geometry is known as the Valence Shell Electron Pair Repulsion or VSEPR model



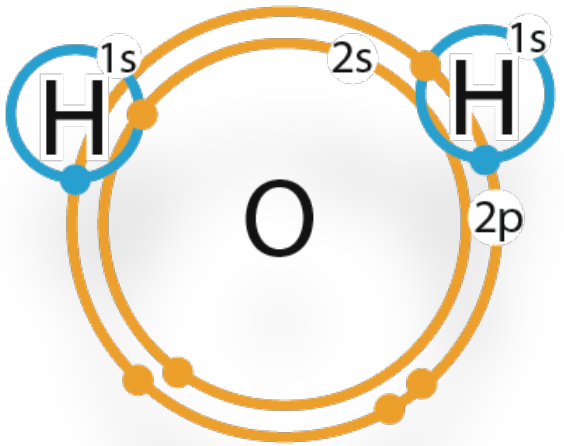
The geometry of atoms in molecules comes in only 3 flavors: linear, planar, tetrahedral

Validation of VSEPR as an approximate model for carbon-containing structural fragments. The data comes from a large collection of structural data that's available in the Cambridge Structural Database. This plot is based on more than 46,000 structural fragments whose geometry has been experimentally determined by X-ray diffraction. Think of this plot like a histogram, whereby each structural fragment is grouped according to its bond length and bond angle (see the inset for the definition of these parameters). The frequency of occurrence at a particular bond-length and bond-angle is color-coded, red being most frequent, blue being the least. The plot shows that nearly all of the 46,000 fragments fall within one of three regions. These regions correspond to linear geometry (bond angle ca. 180°), trigonal planar geometry (bond angle ca. 120°) and tetrahedral geometry (bond angle ca. 110°). The data show a strong correlation between bond length and bond angle. The bond angles are seen to deviate slightly from the ideal angles predicted by the VSEPR model.

Deviations from ideal bond angles results in strain, which makes the molecule more reactive. Consider penicillin.

Tracking Charge

Charge is an important part of molecular structure. Charge is a marker that provides important information about a molecule's physical and chemical properties. We previously saw how to determine the charge of an entire molecule. Here we show how to assign charge to each atom in a molecule.



Assigning charge to an atom requires a new electron counting technique. So that we don't get confused, let's first remind ourselves of the octet rule for covalent bonding. Each atom is trying to fill its valence shell with electrons. Bonds are shared electron pairs. Each atom that shares the pair counts those electrons as contributing to its valence shell. In essence, the shared electrons in bonds are double counted, since each atom of the bond counts those electrons to complete its shell.

But when we consider an atom's charge, the shared electrons are equally split between the bonded atoms. There's no double counting of electrons here.

			Charge due to			
subshell	no. e^-	filled	proton	core electrons	valence electrons	net charge
1s	2	T	+1	0	-1	0
2s	2	T	+8	-2	-6	0
2p	6	T				

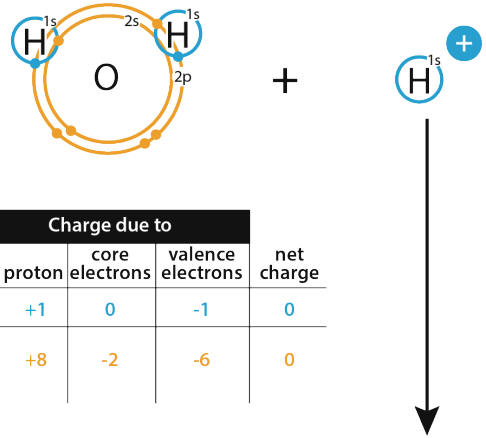
Assigning charge to atoms is helpful to track charge in chemical reactions. Next, we show examples of charge tracking. An important rule is that charge is conserved. The total charge on the left-hand side of a chemical equation must balance the charge on the right-hand side.

Water reacts with a proton yielding hydronium ion

Chemical equation

$$H_2O + H^+ \longrightarrow H_3O^+$$

Electron counting analysis

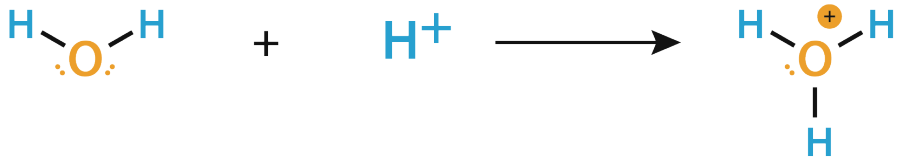


subshell	no. e⁻	filled	Charge due to: proton	core electrons	valence electrons	net charge
1s	2	T	+1	0	-1	0
2s	2	T	+8	-2	-6	0
2p	6	T				

subshell	no. e⁻	filled	Charge due to: proton	core electrons	valence electrons	net charge
1s	2	T	+1	0	-1	0
2s	2	T	+8	-2	-5	+1
2p	6	T				

subshell	no. e⁻	filled	Charge due to: proton	core electrons	valence electrons	net charge
1s	2	T	+1	0	0	+1

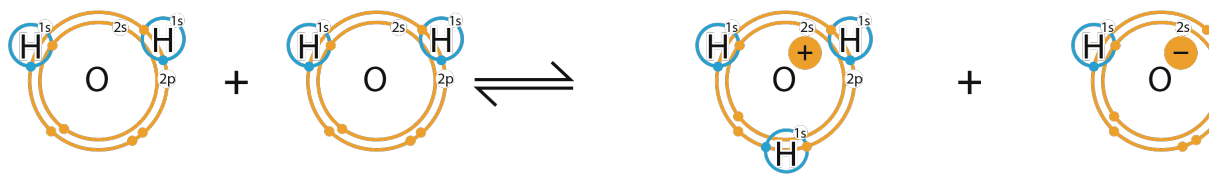
Molecular structure analysis



Charge is balanced in a chemical reaction

Chemical equation

Electron counting analysis

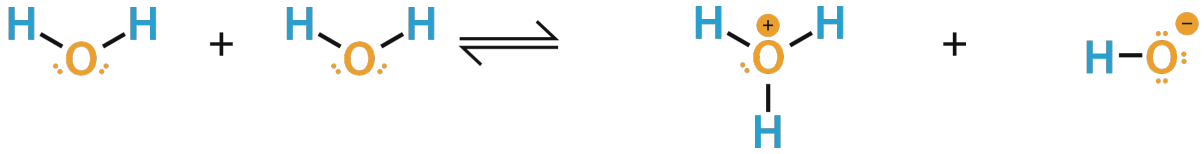


subshell	no. e⁻	filled	Charge due to: proton	core electrons	valence electrons	net charge
1s	2	T	+1	0	-1	0
2s	2	T	+8	-2	-6	0
2p	6	T				

subshell	no. e⁻	filled	Charge due to: proton	core electrons	valence electrons	net charge
1s	2	T	+1	0	-1	0
2s	2	T	+8	-2	-5	+1
2p	6	T				

subshell	no. e⁻	filled	Charge due to: proton	core electrons	valence electrons	net charge
1s	2	T	+1	0	-1	0
2s	2	T	+8	-2	-7	-1
2p	6	T				

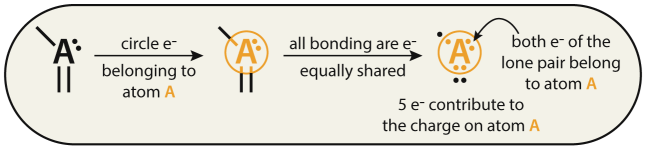
Molecular structure analysis



Calculating charge on atoms in molecules

Determine charge on atom **A**
in a molecule

Determine electron count on **A** in bonded molecule



Determine electron count on atom **A** in isolation (valence e⁻ count)

Does **A** in the molecule have a **surplus** or **shortage** of electrons compared to the isolated atom?

e⁻ surplus

In the molecule, **A** carries a **negative** charge **(-)**

e⁻ shortage

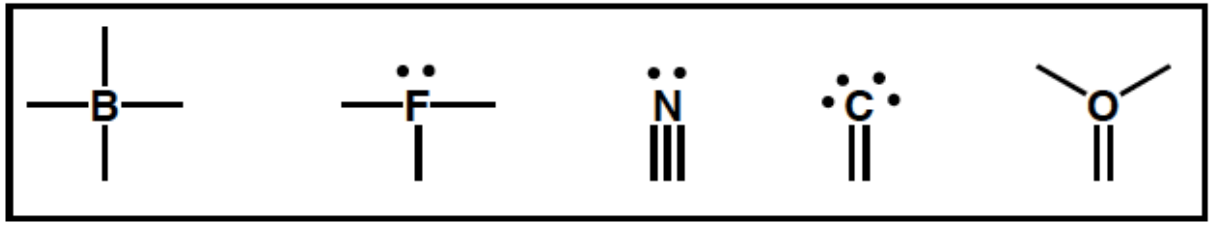
In the molecule, **A** carries a **positive** charge **(+)**

The difference in e⁻ count gives the charge on **A** in the molecule

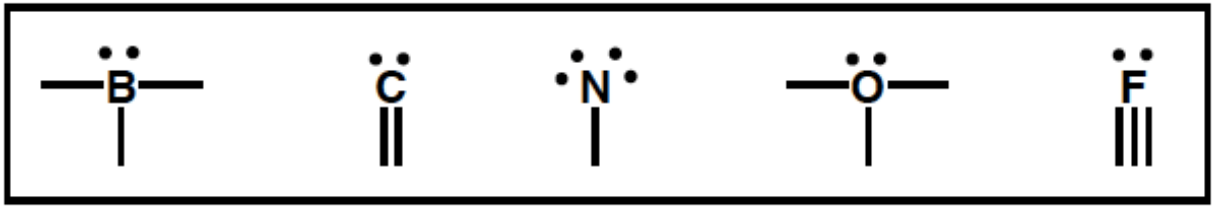
(free atom) - (bonded atom) = charge

Charges on atoms in molecules fall in the the range of –1 to +1

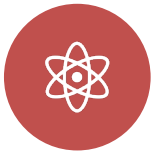
Each bonded atom satisfies the octet rule. Assign charges. Strike through any that are outside the normal range.



Some of these building blocks are not reasonable, either because they have a charge outside the normal range or because they have an incomplete octet. Strike through the outliers and state the reason.



The descriptive language of molecules



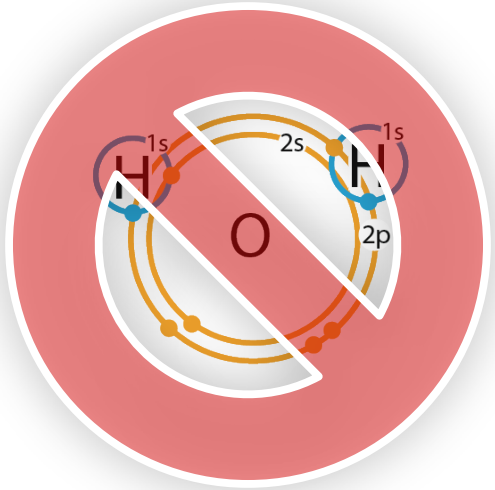
As we develop the language of molecules, **patterns of bonding** for various atoms will become evident. When we spot deviations from normal patterns (e.g., an unexpected geometry), intuition will tell us to suspect special behavior or properties (e.g., high reactivity as in penicillin).

The octet rule is one way to count valence electrons around an atom. **Think of double-counting electrons at the intersections of overlapping circles.** The octet rule describes how an atom shares its electrons through covalent bonding in order to fill its valence shell (the second shell is filled when it has eight electrons).

Formal charge is a way to count electrons that describes where charge is located within the molecule. S**hared electrons between bonded atoms are divided equally between these two atoms.** Regions of positive or negative charge bring special behavior or special properties to these locations.

Charge on!

Shell representations of molecules are clumsy and inefficient ways to represent complicated molecular structure. We need a language that efficiently communicates all the principles of molecular structure without the burden and awkwardness of the shell representation. Let's get after it!



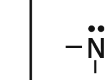
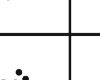
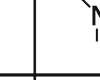
Building blocks of the language of molecules

Number of Domains	the neutral building blocks formal charge = 0				
	hydrogen	carbon	nitrogen	oxygen	fluorine
four 		C	N	O	F
three 		C	N	O	
two 		C C	N		
one	H				
zero 					

the negatively charged building blocks formal charge = -1				
hydrogen	carbon	nitrogen	oxygen	fluorine
	C	N	O	F
	C	N		
	C			
H				

the positively charged building blocks formal charge = +1				
hydrogen	carbon	nitrogen	oxygen	fluorine
		N	O	F
	C	N	O	F
	C	N N	O	
H				

Building blocks of the language of molecules

Number of Domains	the neutral building blocks formal charge = 0				
	hydrogen	carbon	nitrogen	oxygen	fluorine
four					
three					
two					
one					
zero					

the negatively charged building blocks formal charge = -1				
hydrogen	carbon	nitrogen	oxygen	fluorine

the positively charged building blocks formal charge = +1				
hydrogen	carbon	nitrogen	oxygen	fluorine