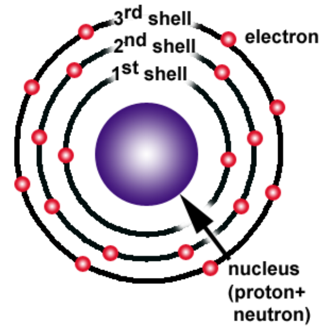
Supplement 2 – Ions, Chemical Bonds, and Hybrid Orbitals

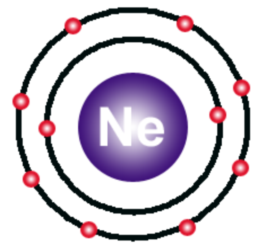


A simpler representation of the orbitals considers that all of the orbits of the same level exist as a shell, or single orbit, around the atom. For the case of the atoms in the first two rows of the periodic table:

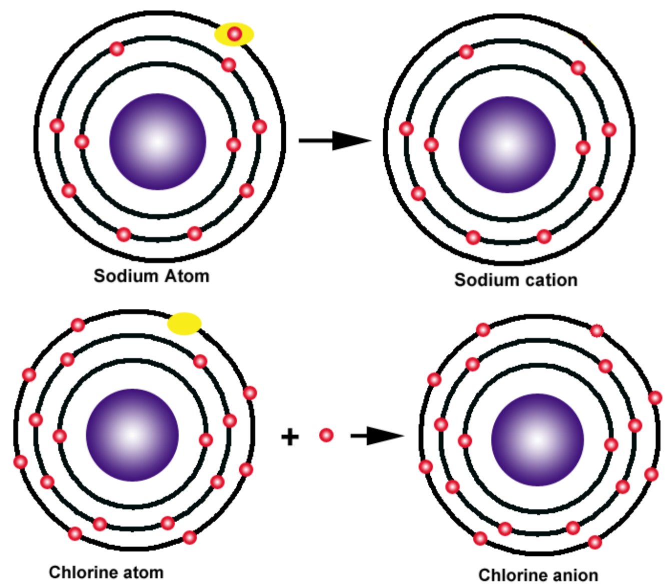
1st shell contains the 1s orbital and can hold at most 2 electrons.

2nd shell contains the 2s and the three 2p orbitals, so it can hold 8 electrons.

3rd shell - for atoms in the third row, the 3s and 3p orbitals are filled, and the 3rd shell contains 8 electrons. The 3d orbitals are ignored in this representation since they are filled after the 4s orbitals.



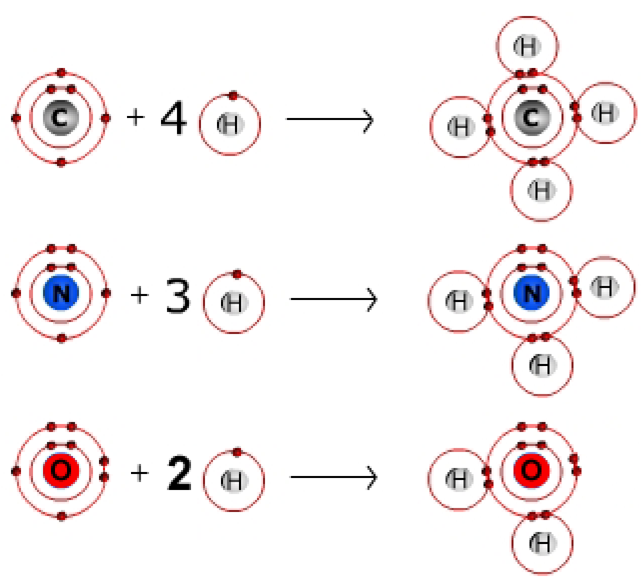
Atoms are most stable when the outer, or highest energy shell, is full. This is the case of the elements in the right most column of the periodic table, hence these atoms are unreactive (inert) and exist as monoatomic gases. The electrons in the 1st and 2nd electron shells of Ne are shown on the right, both the 1st and 2nd shell are full. Helium has a completely full first shell with two electrons, and argon would have all three shells full, with a total of 18 electrons.



Atomic Ions: Atoms that do not have a full shell can form ions by losing or gaining electrons to complete their shell. For example, Li and sodium will lose an electron such that their shells contain the same number of electrons as He and Ne, respectively. Since they lost one electron these ions are positively charged, which are called **cations**.

Similarly, fluorine and chlorine can gain an electron to fill their outer shells. Since they gained an electron their charge is -1 and they are called **anions**. The generation of Na and chloride ions are illustrated on the right.

Mg will also lose electrons to complete its shell. The remaining elements in the 2nd and 3rd row will not ionize because they would have to lose or gain too many electrons to complete their shells. This is not stable due to the large positive or negative charge on the ion. In the 3rd row most of the elements can form ions.

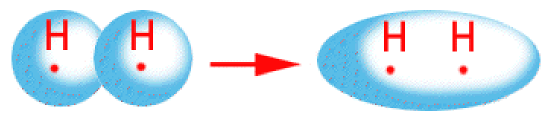


Covalent Bonds: In addition to ionizing, atoms can complete their outer shell by the formation of covalent bonds. Covalent bonds occur when atoms share the electrons in their outer shell, with each atom contributing to the formation of the bond. The electrons in the outer shell are called **valence or bonding electrons.**

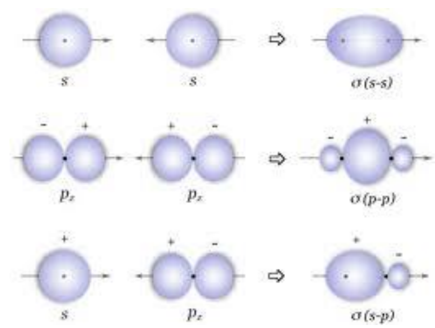
The number of missing electrons in the outer shell indicates the number of bonds that the atom can form.

Hydrogen forms one bond because its 1st shell contains one electron and forming one bond with another atom will complete its shell.

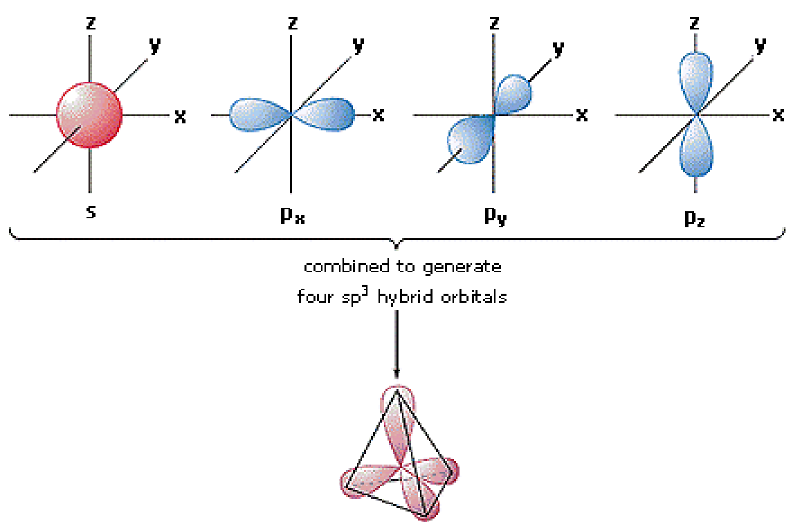
Carbon forms four bound because its 2nd shell only contains four electrons, and forming four bonds will complete its shell.
Nitrogen forms three bonds because it has five electrons in its 2nd shell and needs three more to complete its shell.
Oxygen forms two bonds because it has 6 electrons in its outer shell.
Sulfur and phosphorous can form variable numbers of bonds because they can use the 3d orbital to generate ½ filled orbitals for bond formation. Sulfur can form two or more bonds and phosphorous typically forms five.



When bonds are formed the orbitals on each atom that are used for bonding are combined to make a molecular orbital. For example, in H_2, the 1s orbital on hydrogen would combine with the 1s orbital on hydrogen to form a single bonding orbital, as illustrated on the right. A 1s orbital can also combine with a p orbital and two p orbitals that are directed at each other can also combine to make a bond. In all cases the new bonding orbital is between the two bonded atoms. Bonding orbitals of this type are called sigma (σ) bonds.



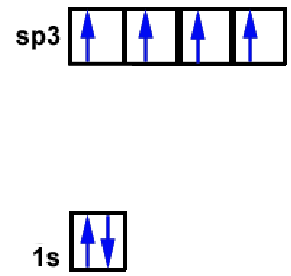
Hybrid orbitals: The electronic orbitals for isolated atoms are the s and p orbitals. However, when atoms form molecules they may modify their orbitals to produce a geometry that will reduce the energy of the molecule more so than if the s and p orbitals were used for bonding. A good example of this is carbon. The outer shell of carbon has four electrons, you could imagine that these electrons are distributed such that one is in the 2s orbital and the remaining three are in each 2p orbital. Carbon forms 4 bonds, such as in methane, CH_4. If the s and p orbitals were used for bonding, three of the hydrogens would form bonds utilizing the p-orbitals of carbon and the fourth hydrogen would form a bond using the s-orbital of carbon. This arrangement would crowd the hydrogen atoms, which would be unfavorable. In addition, the C-H bonds would be of two types, one utilizing the 2s orbital of carbon and the other three utilizing the 2p orbitals of carbon. Experimentally, it has been observed that all four bond are identical in methane, therefore carbon cannot be using its 2s and 2p orbitals to form bonds, it uses hybrid orbitals.



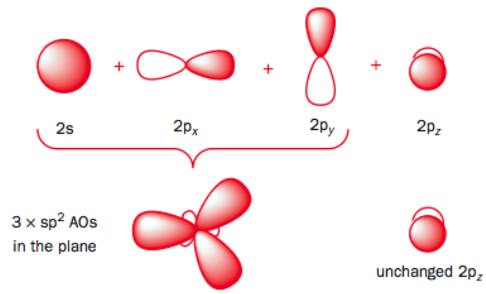
sp^3 Hybrid Orbitals: The four original orbitals (2s, 2p) are rearranged to make four new hybrid orbitals, call sp^3 hybrid orbitals. These orbitals are linear combinations of the original 2s and 2 p orbitals. All four sp^3 orbitals are identical and they form a tetrahydral shape, with an angle of 109 degrees between each orbital. Each sp^3 orbital can contain up to two electros. In carbon, each will contain one electron, thus carbon will form four bonds using each of its sp^3 orbitals. This arrangement is lower in energy; the hydrogen atoms are further apart from each other, and each carbon-hydrogen bond is equal, in agreement with experiment.

Nitrogen and oxygen can also form sp^3 hybrid orbitals and will do so if the tetrahydral geometry will result in a lower energy for the molecule.

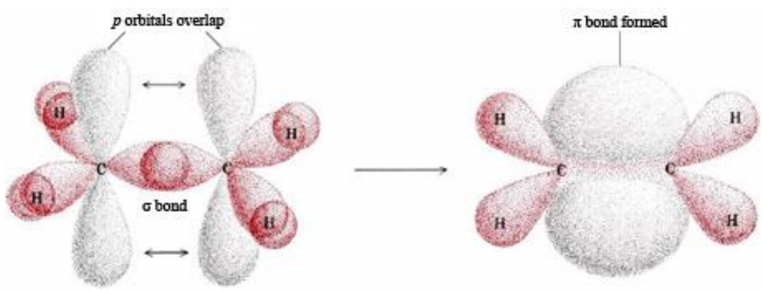
Hybridization of the orbitals changes the energy levels, with the sp^3 orbitals becoming equal in energy. The rules for filling the orbitals are the same, lowest energy first, with the largest number of unpaired electrons for orbitals of the same energy. The electron configuration of sp^3 hybridized carbon is shown on the right. Note that there are still four half-filled orbitals, so carbon forms four bonds. Nitrogen forms three bonds and oxygen two when sp^3 hybridized. Typically the sp^3 orbitals would be involved in σ bonds. For example, in H_2O a σ bond is formed between the 1s orbital of hydrogen and one of the ½ full sp^3 orbitals on oxygen.



sp^2 Hybrid Orbitals: Carbon, oxygen, and nitrogen can also form sp^2 hybrid orbitals, which are generated from the 2s, $2p_x$, and $2p_y$ orbitals. The three resultant sp^2 orbitals lie in the same plane and are 120 degrees apart. Typically the sp^2 orbitals are involved in σ bonds. For example, in formaldehyde (H_2CO) a σ bond is formed between the 1s orbital of hydrogen and one of the ½ full sp^2 orbitals on carbon.



The remaining, unhybridized $2p_z$ orbital, is still present. Atoms usually form sp^2 hybridized orbitals if they are participating in double bonds. The unhybridized $2p_z$ orbitals are ideally positioned to form the "second' bond because they are aligned with each other, allowing overlap of the p_z orbitals to create a bond. This type of bond is called a π-bond. .



The rules for filling the sp^2 orbitals are the same. The unhybridized $2p_z$ orbital is slightly higher in energy than the sp^2. The electronic configuration for carbon is shown on the right. Although the $2p_z$ is slightly higher in energy, the overall energy of the system is lower if the electrons in the sp^2 orbitals remain unpaired, "forcing" an electron into the $2p_z$ orbital. Once again, carbon has four ½ filled orbitals and can form 4 bonds, three with its sp^2 hybridized orbitals and one with its $2p_z$ orbital.