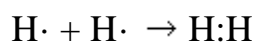
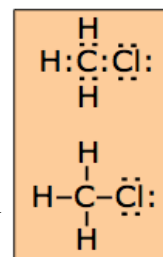


LEWIS ELECTRON-DOT FORMULAS

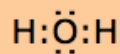
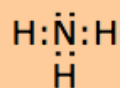
The shared electron-pair is such a fundamental concept of chemical bonding that it is important to have a simple way of writing out a formula that explicitly shows the disposition of the shared pairs between the different atoms. This is commonly accomplished by depicting the valence (outermost) electrons of each bonded atom as dots that are written around the atom symbols. For example, the formation of H₂ can be depicted as



The Lewis theory makes no prediction about molecular shapes, so it is permissible to arrange the dot pairs and other atoms around the central atom in an arbitrary way that is usually governed more by esthetics than reality. It is sometimes preferable to represent an electron pair by a line: H—H which of course is the traditional way of representing a chemical bond.



Bonding and nonbonding electrons: lone pairs

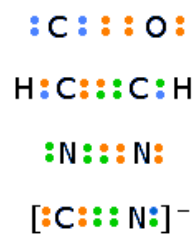


In many molecules, not all of the electron pairs comprising the octet are shared between atoms. The unshared electron pairs are often called lone pairs.

Although lone pairs are not directly involved in bond formation, they should always be shown in Lewis formulas; we will see later that they have an important role to play in determining the shape of the molecule.

Multiple bonds

If one pair of electrons shared between two atoms constitutes a chemical bond, it seems logical that two or three pairs could be shared to produce double and triple bonds. Such formulations appear quite naturally when the octet rule is applied to elements such as C, O, S, and N.



The colors of the electron-dots in this illustration are intended only to help you keep track of the number of electrons contributed by each atom. Because electrons are indistinguishable, it makes no sense to identify a given electron-dot with a given atom.

Since multiple bonds place more electron density between the two nuclei, the latter are held toward each other more closely and tightly; multiple bonds are therefore shorter and stronger than single bonds.

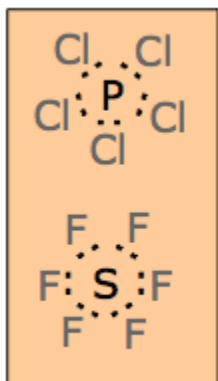
Can there be bonds of higher order than three? No one thought so for a long time, but beginning in the 1960s, experiments and theoretical computations began to reveal that this just might be possible; some molecules just don't follow the rules!

bond type	bonded atoms	molecules	when/who
quadruple	Re:::Re	[Re ₂ Cl ₈] ²⁻	1964 F. Albert Cotton, Texas A&M University
quintuple	Cr:::::Cr	RCrCrR (R=large organic group)	2005 Philip Power, U of California, Davis
sextuple	W:::::W	W ₂	2006 (Roos, Gagliardi, Borin, U of São Paulo)

Adding to the fun, a 2006 article presented evidence that the carbon atom in C(PPh₃)₂ (where Ph stands for a benzene ring) has two lone pair electrons, but no electrons connected to the bonded groups— thus introducing the concept of a "zero-uple" bond.

Expanded octets

As mentioned previously, the octet rule works best for the elements in the second period (Li through F) of the periodic table. The reason for this is that electrons, whether shared or not, must be contained in orbitals, and the energies of electrons



in such orbitals must be relatively low; otherwise, there would be no energetic advantage in forming a bond in the first place— the atoms would be better off by themselves.

For the second- and third-period elements, the $n=2$ and $n=3$ s^2p^6 sets comprise the octet. Some of the third-period elements (Si, P, S, and Cl)

can bond to more than four atoms, and thus need to involve more than the four pairs of electrons available in an s^2p^6 octet. This is possible because at $n=3$, an additional set of d orbitals can exist. Although their energies are higher (ordinarily higher than the $4s$ orbitals), they can participate in the valence shells of these atoms.

Examples of molecules in which the $n=3$ central atom contains an expanded octet are the phosphorus pentahalides and sulfur hexafluoride.

Similarly, for atoms in the fourth period and beyond, higher d orbitals can sometimes be used to accommodate additional shared pairs beyond the octet. If you review a diagram showing the relative energies of the different kinds of atomic orbitals you will notice that all the energy gaps become smaller as the principal quantum number increases, so the energetic cost of using these higher orbitals becomes smaller.

Source: <http://www.chem1.com/acad/webtext/chembond/cb03.html>