TETRAHEDRAL COORDINATION WITH LONE PAIRS

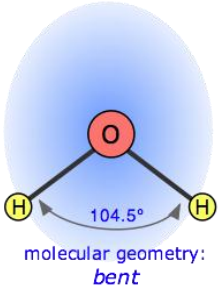
In the examples we have discussed so far, the shape of the molecule is defined by the coordination geometry; thus the carbon in methane is tetrahedrally coordinated, and there is a hydrogen at each corner of the tetrahedron, so the molecular shape is also tetrahedral.

It is common practice to represent bonding patterns by "generic" formulas such as AX4, AX2E2, etc., in which "X" stands for bonding pairs and "E" denotes lone pairs. (This convention is known as the "AXE method")

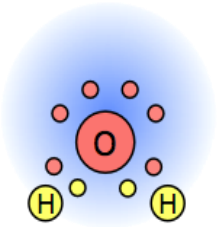
The bonding geometry will not be tetrahedral when the valence shell of the central atom contains nonbonding electrons, however. The reason is that the **nonbonding electrons** are also in orbitals that occupy space and repel the other orbitals. This means that in figuring the coordination number around the central atom, we must count both the bonded atoms and the nonbonding pairs.

The water molecule: AX2E2

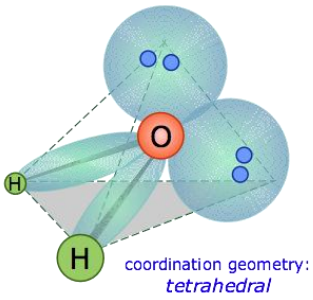
In the water molecule, the central atom is O, and the Lewis electron dot formula predicts that there will be two pairs of nonbonding electrons.



The oxygen atom will therefore be tetrahedrally coordinated, meaning that it sits at the center of the tetrahedron as shown below. Two of the coordination positions are occupied by the shared electron-pairs that constitute the O–H bonds, and the other two by the non-bonding pairs. Thus although the oxygen atom is tetrahedrally coordinated, the bonding geometry (shape) of the H2O molecule is described as **bent**.

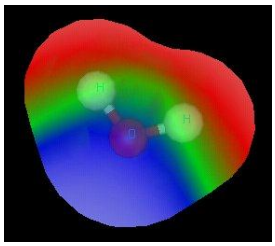


There is an important difference between bonding and non-bonding electron orbitals. Because a nonbonding orbital has no atomic nucleus at its far end to draw the electron cloud toward it, the charge in such an orbital will be concentrated closer to the central atom. As a consequence, nonbonding orbitals exert more repulsion on other orbitals than do bonding orbitals. Thus in H2O, the two nonbonding orbitals push the bonding orbitals closer together, making the H–O–H angle 104.5° instead of the tetrahedral angle of 109.5°.



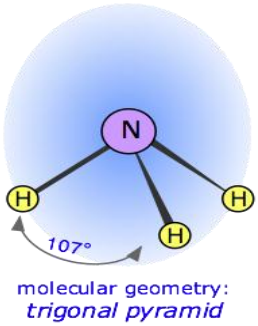
Although the water molecule is electrically neutral, it is not electrically uniform; the non-bonding electrons create a higher concentration of negative charge (blue color) at the oxygen end, making the hydrogen side relatively positive (red).

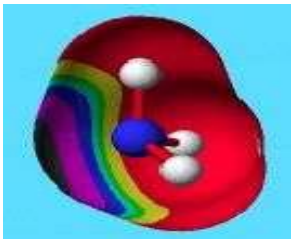
This charge unbalance gives rise to many of the so-called anomalous properties of water.



This image was produced by a computer simulation based on the more complete molecular orbital model.

Ammonia: AX_3E





Computer-generated image of NH3 molecule showing electrostatic potential (red=+, blue=–.)

The electron-dot structure of NH3 places one pair of nonbonding electrons in the valence shell of the nitrogen atom. This means that there are three bonded atoms and one lone pair, for a coordination number of four around the nitrogen, the same as occurs in H2O. We can therefore predict that the three hydrogen atom will lie at the corners of a tetrahedron centered on the nitrogen atom. The lone pair orbital will point toward the fourth corner of the tetrahedron, but since that position will be vacant, the NH3molecule itself cannot be tetrahedral. Instead, it assumes a **pyramidal** shape. More precisely, the shape is that of a **trigonal pyramid** (i.e., a pyramid having a triangular base).

The hydrogen atoms are all in the same plane, with the nitrogen above (or below, or to the side; molecules of course don't know anything about "above" or "below"!) The fatter orbital containing the non-bonding electrons pushes the bonding orbitals together slightly, making the H–N–H bond angles about 107°.

Source: http://www.chem1.com/acad/webtext/chembond/cb05.html