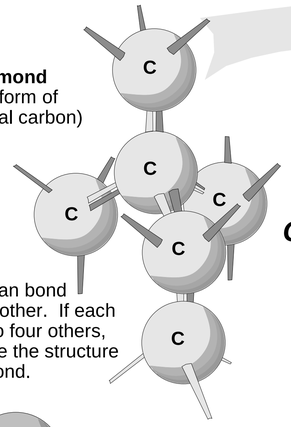
OF IONS AND ORBITALS

Some sketches and comparisons across part of the periodic table

Carbon

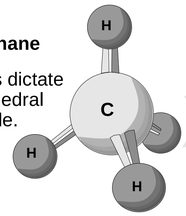
Diamond (one form of elemental carbon)

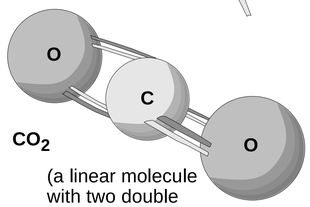


Carbon atoms can bond to each other. If each bonds to four others, they give the structure of diamond.

Methane

Orbitals dictate a tetrahedral molecule.



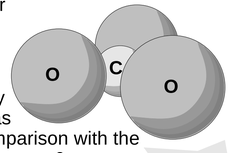


CO_2

(a linear molecule with two double bonds around C^{4+})

Carbonate $[CO_3]^{2-}$

A triangular structural group

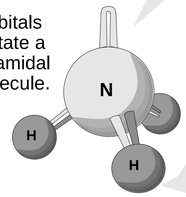


The model provided by methane, as well as comparison with the SiO_4^{2-} and GeO_4^{2-} oxyanions formed Si and Ge, which have the same number of valence electrons, would suggest that carbonate would be a CO_4^{2-} anion with each oxygen forming a covelent bond with C. However, the small size of C^{4+} dictates threefold coordination. Chemists explain that the four already-hybridized sp^3 orbitals now hybridize to three orbitals, two with a single bond and one with a double bond, but the double bond is not localized to one particular oxygen.

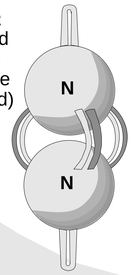
Nitrogen

Ammonia

Orbitals dictate a pyramidal molecule.

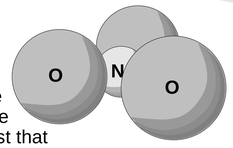


N_2 (and its triple bond)



Nitrate $[NO_3]^-$

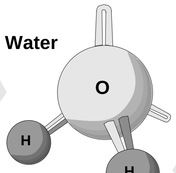
A triangular structural group



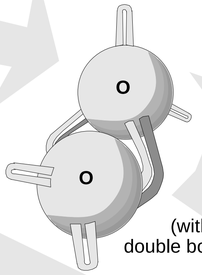
Comparison with methane and phosphite would suggest that N would bond wtih thee Os in a pyramidal structure. Instead, relative sizes, Pauling's Rules, and O-O repulsions dictate that the tiny N^{5+} form a planar nitrate anion.

Oxygen

Water



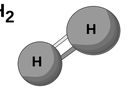
Orbitals dictate a non-linear molecule.



O_2 (with its double bond)

Hydrogen

H_2

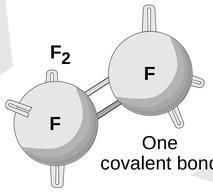


One covalent bond

Helium

Fluorine

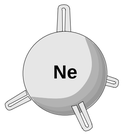
F_2



One covalent bond

In elemental form, fluorine and chlorine bond covalently, sharing electrons. With the gain of an electron, they become anions that form ionic bonds with cations to make minerals like halite and fluorite.

Neon

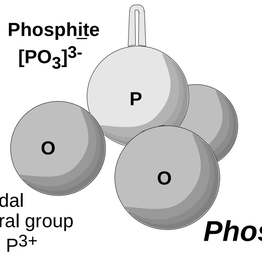


or

Happiness in solitude

Phosphorus

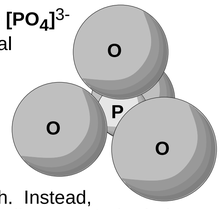
Phosphite $[PO_3]^{3-}$



A pyramidal structural group around P^{3+}

Phosphate $[PO_4]^{3-}$

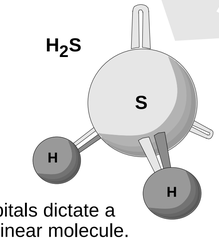
A tetrahedral structural group



For P^{5+}, orbitals no longer matter much. Instead, relative size dictates tetrahedral coordination according to Pauling's Rules.

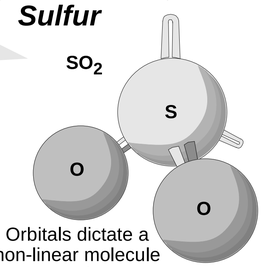
Sulfur

H_2S



Orbitals dictate a non-linear molecule.

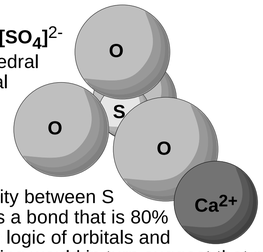
SO_2



Orbitals dictate a non-linear molecule around S^{4+} here.

Sulfate $[SO_4]^{2-}$

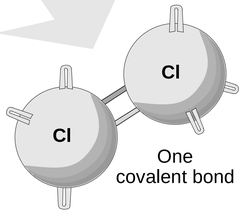
A tetrahedral structural group



The difference in electronegativity between S and O predicts a bond that is 80% covalent. The logic of orbitals and covalent bonding would in turn suggest that no more than two oxygens could bond to a sulfur atom. However, S^{6+} enters into tetrahedral (four-fold) coordination because relative size of S^{6+} and O^{2-} dictates tetrahedral coordination according to Pauling's Rules.

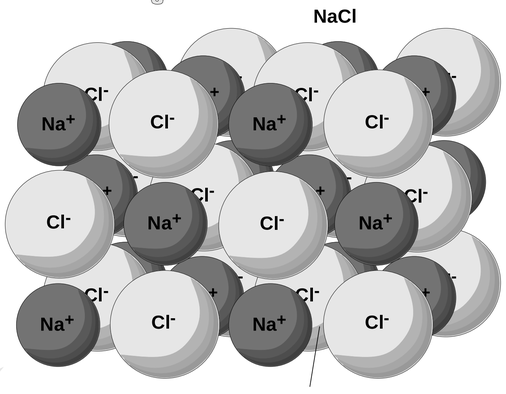
Chlorine

Cl_2



One covalent bond

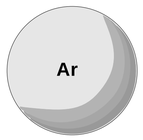
NaCl



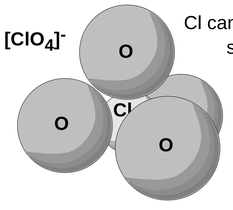
No sharing of electons

Argon

or



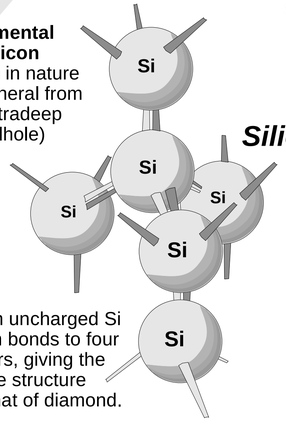
Perchlorate $[ClO_4]^-$



Cl can also lose all seven sp^3 electrons shown above in Cl_2 and coordinate with four O^{2-} as perchlorate.

Silicon

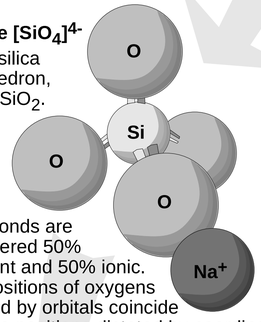
Elemental silicon (known in nature as a mineral from an ultradeep drillhole)



Each uncharged Si atom bonds to four others, giving the same structure as that of diamond.

Silicate $[SiO_4]^{4-}$

The silica tetrahedron, as in SiO_2.

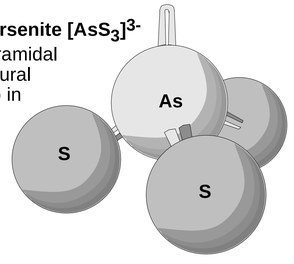


Si-O bonds are considered 50% covalent and 50% ionic. The positions of oxygens dictated by orbitals coincide with the positions dictated by coordination around Si^{4+}. Note that O's bonds to other ions are essentially ionic and O's other orbitals have little influence on bonding or structure, as suggested here by its ionic bond to Na^+.

Arsenic

Sulfarsenite $[AsS_3]^{3-}$

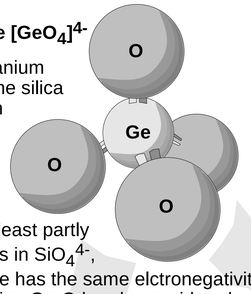
(a pyramidal structural group in sulfo-salts)



Germanium

Germanate $[GeO_4]^{4-}$

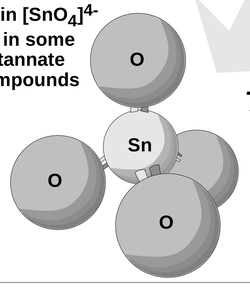
The germanium analog of the silica tetrahedron



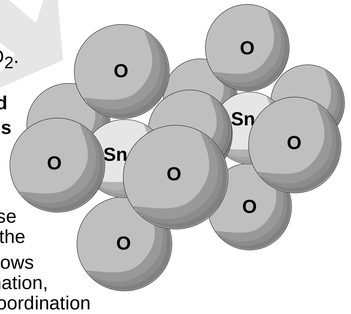
Ge-O bonds are shown here as at least partly covalent, as in SiO_4^{4-}, because Ge has the same elctronegativity as Si. yielding Ge-O bonds considered 50% covalent and 50% ionic. This tetrahedron is the structural group of GeO_2, just as the silica tetrahedron is the structural group of SiO_2.

Tin

$^{[4]}Sn$ in $[SnO_4]^{4-}$ as in some stannate compounds



$^{[6]}Sn$ in SnO_2 and other compounds

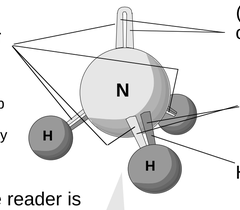


Sn has the same electronegativity as Si and Ge, so Sn-O bonds should be as covalent as those in GeO_2 and SiO_2. However, the larger size of the Sn^{4+} cation allows either four-fold or six-fold coordination, rather than strictly the four-fold coordination suggested by the four unpaired sp^3 electrons.

This document is intended to address the shizophrenia in chemistry, or at least in the author's mind, about the relative importance of orbitals and covalent bonding on the one hand and ionic behavior on the other. As an example of that schizophrenia, consider an oxygen atom in a sulfate tetrahedron bonded to a calcium atom, as in anhydrite. The S-O bond is considered 80% covalent, and the Na-O bond is considered 80% ionic. How does an oxygen atom remain, to 80% of its character, in its un-ionized elemental form with six valence electrons, while simultaneously, again to 80% of its character, gaining two more electrons to be the O^{2-} anion?

From a structural standpoint, we're faced with the question "Do sizes of atoms, radius ratios, and Pauling's Rules dictate coordination and positions of atoms (the ionic view), or do numbers and positions of orbitals control these things (the covalent view)?". Clearly numbers and positions of orbitals dictate the shape of ammonia, water, H_2S, and SO_2 molecules (where the coordinating H atoms are small, and an isolated molecule is formed). On the other hand, sizes of atoms and Pauling's Rules dictate the coordination in structures like carbonate groups (where the coordinated central atom is small). Sizes of atoms and Pauling's Rules also dictate the coordination in continuous (non-molecular) structures like SnO_2 (where the coordinated central atom is large, and it must be surrounded by coordinating atoms to shield its charge from the next central atom). The answer thus seems to be "sizes of atoms and Pauling's rules establish a maximum coordination number of a particular atom, and positions and number of orbitals can dictate the positions of atoms so long as those orbitals do not require coordination in a continuous lattice made impossible by Pauling's Rules and the need for shielding.

Legend:



Electrons in four sp^3 orbitals ("s-p-three", not "s-p-cubed": one s orbital and three p orbitals symmetrical around the atom, thereby minimizing repulsion between electrons.

(One atom's) pair of electrons filling one orbital

One covalent bond (two atoms sharing two electrons, one from each atom)

Hydrogen's electron

Pathways that the reader is encouraged to follow (i.e., through elemental forms like N_2 and O_2; through H-bearing forms like methane, ammonia, & water; and through radicals formed by Group IV elements (C, Si, Ge, Sn, etc.)

LBR Crystal&Covalent22 4/2006