Chemical Bonding

A Chem1 Reference Text

Stephen K. Lower • Simon Fraser University
quantumdot@shaw.ca

Why you need to know this stuff

The uniqueness of a particular chemical substance must ultimately lie in the number and geometrical arrangement of the atoms of which it is composed. The lower the potential energy of a particular aggregation of atoms, the more stable the chemical substance. C***hemical bonding*** refers to the set of principles and theories that govern the structure and stability of chemical substances, and thus of the rearrangements that occur during ***chemical reactions*** in which one substance is transformed into another. The study of chemical bonding is thus one of the fundamental pillars of modern chemical science.

Dept of Chemistry - Simon Fraser University - Burnaby BC V5A 1S6 Canada

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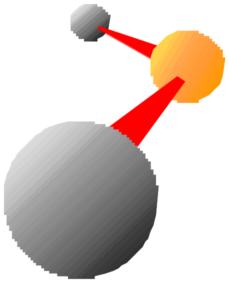
1. Bonds and molecules

What is a chemical bond?



A chemical bond is so often represented as a line drawn between atom symbols or a stick connecting two balls in a plastic molecular model that we sometimes tend to think of chemical bonds as "things". It is more useful, however, to regard a chemical bond as an ***effect*** that causes the energy of two atoms close together to be markedly lower (by about 100 kJ per mole or more) than when they are far apart.

The forces that hold bonded atoms together are basically just the same kinds electrostatic attractions that bind the electrons of an atom to its positively-charged nucleus; a chemical bond occurs when these same forces are able to act on electrons subject to the simultaneous influence of ***two*** nuclei.

When two atoms combine to form a molecule, they do so because the presence of two nearby positive centers (the nuclei) allows the electrons to rearrange themselves into locations (orbitals) in which *more electrons are closer to more nuclei.*

This is the most important fact about chemical bonding that you should know, but it is not of itself a workable theory of the chemical bond because it does not describe the conditions under which bonding occurs, nor does it make useful predictions about the properties of the bond.

What is a molecule?

All atoms attract one another at small distances; the universal attractive interactions known as ***van der Waals forces*** exist between all matter, and play an important part in determining the properties of liquids and solids. These attractions are extremely weak, however, and they lack specificity: they do not lead to aggregates having any special structure or composition.

A molecule is an aggregate of atoms that possesses distinctive and distinguishing properties.

Chemical bonding connotes the existence of an aggregate of atoms that is sufficiently stable to possess a characteristic structure and composition. The important thing to understand about the definition written at the left is that it is essentially an ***operational*** one; as our ability to observe the characteristic properties of loosely-bound aggregates of atoms increases, our ideas of what constitutes a molecule will change. This was illustrated quite vividly in the early 1980's, when ***metal clusters—*** stable arrangements of 5-20 metallic atoms— were first characterized. These had not previously been recognized as molecules because no one know how to observe them. More recently, advances in technology that allow chemists to observe chemical species that can only exist for tiny fractions of a second have greatly extended the range of what we can call "molecules".

Stability and reactivity

The fall in energy when atoms join together is a measure of the stability of the new aggregate. In order to be regarded as a ***molecule***, the aggregate must be sufficiently ***stable*** to resist disruption by thermal motions long enough to enable the observation of whatever distinctive properties and composition it might have.

Some molecules are stable or observable only under certain conditions: many, such as KrF_2, are so weakly bound that they decompose at all but the lowest temperatures. Others, such as gaseous LiF, can be observed only at temperatures around 1000 °C.

There are many molecules that are energetically stable, but are so ***reactive*** that their lifetimes are too brief to make their observation possible. The molecule CH_3, methyl, is a good example: it can be formed by electrical discharge in gaseous CH_4, but it is so reactive that it reacts with almost any molecule it strikes within a few collisions. It was not until the development of spectroscopic methods (in which a molecule is characterized by the wavelengths of light that it absorbs) that methyl was recognized as a stable molecule that is an important intermediate in many chemical processes ranging from flames to atmospheric chemistry.

Potential energy curves

In an earlier unit of this course, you were introduced to plots in which the energy possessed by a system of two atoms is shown as a function of the distance between them. These ***Morse curves***, as they are sometimes called, are quite useful in defining certain properties of a chemical bond.

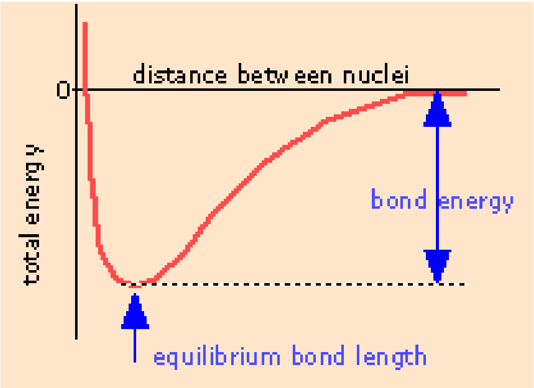


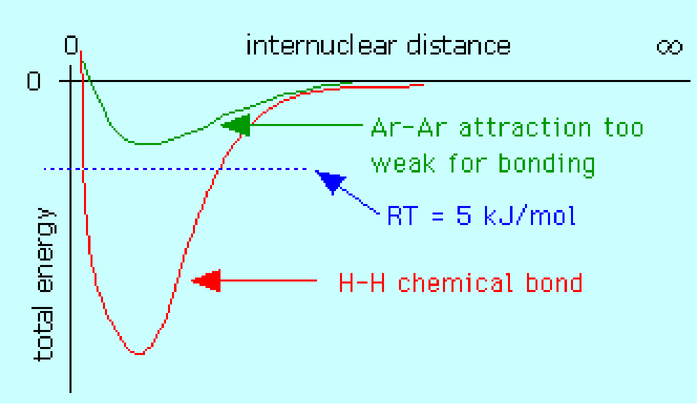
Fig. 1: Bond energy and the Morse curve.

The energy of a system of two atoms depends on the distance between them. At large distances the energy is zero, meaning “no interaction”. At distances of several atomic diameters attractive forces dominate, whereas at very close approaches the force is repulsive, causing the energy to rise. The attractive and repulsive effects are balanced at the minimum point in the curve. If the energy minimum is at least of the order of *RT*, the two atoms will be able to withstand the disruptive influence of thermal energy., and a chemical bond can be said to exist between them.

The internuclear distance at which the energy minimum occurs defines the ***bond length***. This is more correctly known as the ***equilibrium*** bond length, because thermal motion causes the two atoms to vibrate about this distance. In general, the stronger the bond, the smaller will be the bond length.

Fig. 2: When does attraction result in bonding?

Attractive forces operate between all atoms, but unless the potential energy minimum is at least of the order of RT, the two atoms will not be able to withstand the disruptive influence of thermal energy long enough to result in an identifiable molecule. Thus we can say that a chemical bond exists between the two atoms in H2. The weak attraction between argon atoms does not allow Ar2 to exist as a molecule, but it does correspond to the *van Der Waals force* that holds argon atoms together in the liquid and solid.



Potential energy and kinetic energy. Quantum theory tells us that an electron in an atom possesses kinetic energy ***K*** as well as potential energy ***P***, so the total energy ***E*** is always the sum of the two: ***E*** = ***P*** + ***K***. The relation between them is surprisingly simple: ***K*** = –0.5 ***P***. This means that when a chemical bond forms (an exothermic process with ΔE < 0), the decrease in potential energy is accompanied by an increase in the kinetic energy (embodied in the momentum of the bonding electrons), but the magnitude of the latter change is only half as much, so the change in potential energy always dominates. The bond energy –ΔE has half the magnitude of the fall in potential energy.

2. Observable properties of chemical bonds

Chemical bonds, of course, cannot be observed directly; the best we can do is to carry out experiments on substances containing the appropriate pair of atoms, and then try to make inferences about the nature of the bonding force between them.

It is important to bear in mind that the exact properties of a specific kind of bond will be determined in part by the nature of the other bonds in the molecule; thus the energy and length of the C–H bond will be somewhat dependent on what other atoms are connected to the carbon atom. Similarly, the C-H bond length can vary by as much a 4 percent between different molecules. For this reason, the values listed in tables of bond energy and bond length are usually ***averages*** taken over a variety of environments for a specific atom pair.

In some cases, such as C—O and C—C, the variations can be much greater, approaching 20 percent. In these cases, the values fall into groups which we interpret as representative of ***single-*** and ***multiple*** bonds: double, and triple.

2.1 Bond energies

The bond energy is the amount of work that must be done to pull two atoms completely apart; in other words, it is the same as the depth of the "well" in the potential energy curve in Fig. 1. This is almost, but not quite the same as the ***bond dissociation energy*** actually required to break the chemical bond; the difference is the very small ***zero-point energy*** as explained inFig. 3.

Bond energies are usually determined indirectly from thermodynamic data, but there are two main experimental ways of measuring them directly:

1. The direct ***thermochemical*** method involves separating the two atoms by an electrical discharge or some other means, and then measuring the heat given off when they recombine. Thus the energy of the C—C single bond can be estimated from the heat of the recombination reaction between methyl radicals, yielding ethane:

   $$CH_3 + CH_3 \rightarrow H_3CCH_3$$

   Although this method is simple in principle, it is not easy to carry out experimentally. The highly reactive components must be prepared in high purity and in a stream of moving gas.

2. The ***spectroscopic*** method is based on the principle that absorption of light whose wavelength corresponds to the bond energy will often lead to the breaking of the bond and dissociation of the molecule. For some bonds, this light falls into the green and blue regions of the spectrum, but for most bonds ultraviolet light is required. The experiment is carried out by observing the absorption of light by the substance being studied as the wavelength is decreased. When the wavelength is sufficiently small to break the bond, a characteristic change in the absorption pattern is observed.

   Spectroscopy is quite easily carried out and can yield highly precise results, but this method is only applicable to a relatively small number of simple molecules. The major problem is that the light must first be ***absorbed*** by the molecule, and relatively few molecules happen to absorb light of a wavelength that corresponds energetically to a bond energy.

Experiments carried out on diatomic molecules such as O_2 and CS yield unambiguous values of bond energy, but for more complex molecules there are complications. For example, the heat given off in the CH_3 combination reaction written above will also include a small component that represents the differences in the energies of the C-H bonds in methyl and in ethane. These can be corrected for by experimental data on reactions such as

$$CH_3 + H \rightarrow CH_4$$

$$CH_2 + H \rightarrow CH_3$$

By assembling a large amount of experimental information of this kind, a consistent set of average bond energies can be obtained. The energies of double bonds are greater than those of single bonds, and those of triple bonds are higher still.

	H	C	N	O	F	Cl	Br	I	Si
H	436	415	390	464	569	432	370	295	395
C		345	290	350	439	330	275	240	360
N			160	200	270	200	245		
O				140	185	205	220	200	370
F					160	255	235	280	540
Cl						243	220	210	359
Br							190	180	290
I								150	210
Si									230

Table 1: Average energies of some single bonds (kJ/mol)

Use of bond energies in estimating heats of reaction

One can often get a very good idea of how much heat will be absorbed or given off in a reaction by simply finding the difference in the total bond energies contained in the reactants and products.

As an example, consider the reaction of chlorine with methane to produce dichloromethane and hydrogen chloride:

$$CH_4(g) + 2Cl_2(g) \rightarrow CHCl_2(g) + 2HCl(g)$$

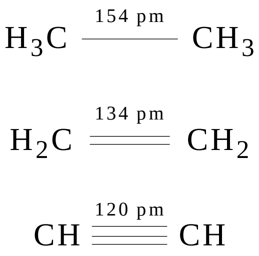
In this reaction, two C–H bonds and two Cl–Cl bonds are broken, and two new C–H and H–Cl bonds are formed. The net change is

$$2(C–H) + 2(Cl–Cl) – 2(C–Cl) –2\ (H–Cl) = (830 + 486 -660 - 864)\ kJ$$

which comes to –208 kJ per mole of methane; this agrees quite well with the observed heat of reaction, which is –202 kJ/mol.

2.2 Bond lengths

The bond length is the internuclear distance: the distance between the centers of the two bonded atoms. Bond distances are customarily expressed in Angstrom units (1Å = 10^{-8} cm = 100 pm) and are mostly in the range 1-2 Å. Even though the bond is vibrating, equilibrium bond lengths can be determined to within 0.01Å.



$$H_3C \overset{154\text{ pm}}{\text{—}} CH_3$$

$$H_2C \overset{134\text{ pm}}{=} CH_2$$

$$CH \overset{120\text{ pm}}{\equiv} CH$$

Bond lengths reflect the sizes of the atoms; thus those involving hydrogen can be quite short. The shortest, H–H, is only 0.74Å. Multiply-bonded atoms are closer together than singly-bonded ones; this is a major criterion for experimentally determining the multiplicity of a bond.

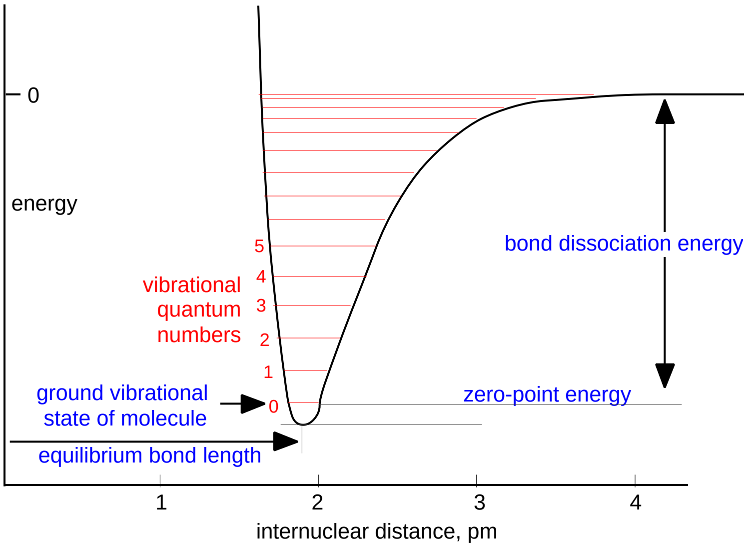
The most common method of measuring bond lengths in solids is by analysis of the diffraction or scattering of X-rays when they pass through the regularly-spaced atoms in the crystal. For gaseous molecules, neutron- or electron-diffraction can also be used.

2.3 Stretching frequency and infrared absorption

When an atom is displaced from its equilibrium position in a molecule, it is subject to a restoring force which increases with the displacement. A spring follows the same law (Hooke's law); a chemical bond is therefore formally similar to a spring that has weights (atoms) attached to its two ends. A mechanical system of this kind possesses a natural vibrational frequency which depends on the masses of the weights and the stiffness of the spring.

Fig. 3: A close-up view of the bottom of the potential energy curve.

A chemical bond is something like a vibrating spring, except that the vibrational motions are *quantized*: only vibrations having certain discrete energies are possible. The Uncertainty Principle does not allow us to simultaneously observe energy and position, so the minimum potential energy lies somewhat above the minimum of the potential energy curve. For this reason, the bonded atoms are never at rest and always possess at least a zero-point energy. For this reason, the bond dissociation energy is slightly smaller than the energy corresponding to the bottom of the curve.



On the atomic scale in which all motions are quantized, a vibrating system can possess only certain allowed vibrational frequencies, or ***states***. These are depicted by the horizontal lines in the potential energy curve shown here. Notice that the very bottom of the curve does not correspond to an allowed state, as this allows for no change in the position of the atoms at all, and would therefore violate the uncertainty principle.

> The lowest-allowed, or ground vibrational state is the one denoted by 0, and it is normally the only state that is significantly populated in most molecules at room temperature. In order to jump to a higher state, the molecule must absorb a photon whose energy is equal to the distance between the two states. For chemical bonds, these energies correspond to light that falls in the infrared region of the spectrum.

For ordinary chemical bonds, these natural frequencies correspond to those of infrared light. Each wavelength of infrared light that excites the vibrational motion of a particular bond will be absorbed by the molecule. In general, the stronger the bond and the lighter the atoms it connects, the higher will be its natural stretching frequency and the shorter the wavelength of light absorbed by it. Thus the C–H bond absorbs at a shorter wavelength than does the C–C bond, and C–C bonds are easily distinguished from C=C double bonds. Studies on a wide variety of molecules have made it possible to determine the wavelengths absorbed by each kind of bond. By plotting the degree of absorption as a function of wavelength, one obtains the ***infrared spectrum*** of the molecule which allows one to "see" what kinds of bonds are present.

Actual infrared spectra are complicated by the presence of more complex motions (stretches involving more than two atoms, wagging, etc.), and absorption to higher quantum states (overtones), so infrared spectra can become quite complex. This is not necessarily a disadvantage, however, because such spectra can serve as a "fingerprint" that is unique to a particular molecule and can be helpful in identifying it. Largely for this reason, infrared spectrometers are standard equipment in most chemistry laboratories.

Infrared absorption and global warming

The aspect of bond stretching and bending frequencies that impacts our lives most directly is the way that some of the gases of the atmosphere absorb infrared light and thus affect the heat balance of the Earth. Owing to their symmetrical shapes, the principal atmospheric components N_2 and O_2 do not absorb infrared light, but the minor components water vapor and carbon dioxide are strong absorbers, especially in the long-wavelength region of the infrared. Absorption of infrared light by a gas causes its temperature to rise, so any source of infrared light will tend to warm the atmosphere; this phenomenon is known as the ***greenhouse effect***.

The incoming radiation from the Sun (which contains relatively little long-wave infrared light) passes freely through the atmosphere and is absorbed by the Earth's surface, warming it up and causing it to re-emit some of this energy as long-wavelength infrared. Most of the latter is absorbed by the H_2O and CO_2 in the atmosphere, effectively trapping the radiation as heat. Thus the atmosphere is heated by the Earth, rather than by direct sunlight. Without the "greenhouse gases" in the atmosphere, the Earth's heat would be radiated away into space, and our planet would be too cold for life.

Since the beginning of the Industrial Revolution in the 19th century, huge quantities of additional greenhouse gases have been accumulating in the atmosphere. Carbon dioxide from fossil fuel combustion has been the principal source, but intensive agriculture also contributes significant quantities of methane (CH_4) and nitrous oxide (N_2O) which are also efficient far-infrared absorbers. The measurable increase in these gases is believed by many to be responsible for the increase in the average temperature of the Earth that has been noted over the past 50 years— a trend that could initiate widespread flooding and other disasters if it continues.

3. Why do chemical bonds form?

The answer to this question would ideally be a simple, easily understood theory that would not only explain why atoms bind together to form molecules, but would also predict the three-dimensional structures of the resulting compounds as well as the energies and other properties of the bonds themselves. Unfortunately, no one theory exists that accomplishes these goals in a satisfactory way for all of the many categories of compounds that are known. Moreover, it seems likely that if such a theory does ever come into being, it will be far from simple.

When we are faced with a scientific problem of this complexity, experience has shown that it is often more useful to concentrate instead on developing ***models***. A scientific model is something like a theory in that it should be able to explain observed phenomena and to make useful predictions. But whereas a theory can be discredited by a single contradictory case, a model can be useful even if it does not encompass all instances of the phenomena it attempts to explain. We do not even require that a model be a credible representation of reality; all we ask is that it be able to explain the behavior of those cases to which it is applicable in terms that are consistent with the model itself. An example of a model that you may already know about is the ***kinetic molecular theory*** of gases. Despite its name, this is really a model (at least at the level that beginning students use it) because it does not even try to explain the observed behavior of real gases. Nevertheless, it serves as a tool for developing our understanding of gases, and as a starting point for more elaborate treatments.

Given the extraordinary variety of ways in which atoms combine into aggregates, it should come as no surprise that a number of useful bonding models have been developed. Most of them apply only to certain classes of compounds, or attempt to explain only a restricted range of phenomena. In this section we will provide brief descriptions of some of the bonding models; the more important of these will be treated in much more detail in later parts of this chapter.

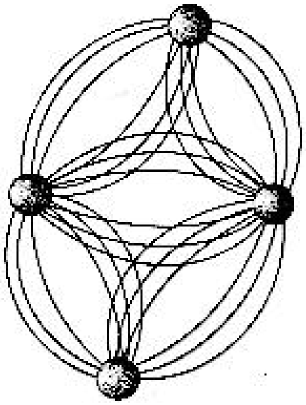
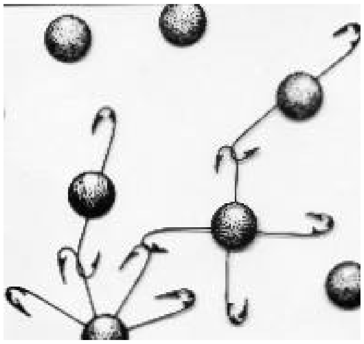


Fig. 4: Some early views of chemical bonding

Intense speculation about “chemical affinity” began in the 18th century. Some likened the tendency of one atom to “close” with another as an expression of a human-like kind of affection. Others attributed bonding to magnetic-like forces (left) or to varying numbers of “hooks” on different kinds of atoms (right). The latter constituted a primitive (and extremely limited) model of combining power or *valence*.



3.1 Classical models

By ***classical***, we mean models that do not take into account the quantum behavior of small particles, notably the electron. These models generally assume that electrons and ions behave as point charges which attract and repel according to the laws of electrostatics. Although this completely ignores what has been learned about the nature of the electron since the development of quantum theory in the 1920's, these classical models have not only proven extremely useful, but the major ones also serve as the basis for the chemist's general classification of compounds into "covalent" and "ionic" categories.

The ionic model

Ever since the discovery early in the 19th century that solutions of salts and other electrolytes conduct electric current, there has been general agreement that the forces that hold atoms together must be electrical in nature. Electrolytic solutions contain ions having opposite electrical charges, opposite charges attract, so perhaps the substances from which these ions come consist of positive and negatively charged atoms held together by electrostatic attraction.

It turns out that this is not true generally, but a model built on this assumption does a fairly good job of explaining a rather small but important class of compounds that are called ***ionic solids***. The most well known example of such a compound is sodium chloride, which consists of two interpenetrating lattices of Na^+ and Cl^- ions arranged in such as way that every ion of one type is surrounded (in three dimensional space) by six ions of opposite charge.

One can envision the formation of a solid NaCl unit by a sequence of events in which electrons are removed from one mole of Na atoms and given to Cl atoms, followed by condensation of the resulting ions into a crystal lattice:

$Na(g) \rightarrow Na^+(g) + e^-$ +494 kJ(***ionization energy***)

$Cl(g) + e^- \rightarrow Cl^-(g)$ –368 kJ(***electron affinity***)

$Na^+(g) + Cl^-(g) \rightarrow NaCl(s)$ –498 kJ(***lattice energy***)

Since the first two energies are known experimentally, as is the energy of the sum of the three processes, the lattice energy can be found by difference. It can also be calculated by averaging the electrostatic forces exerted on each ion over the various directions in the solid, and this calculation is generally in good agreement with observation, thus lending credence to the model. The sum of the three energy terms is clearly negative, and corresponds to the liberation of heat in the net reaction $Na(g) + Cl(g) \rightarrow NaCl(s)$, which defines the Na–Cl "bond" energy. The ionic solid is more stable than the equivalent number of gaseous atoms simply because the three-dimensional NaCl structure allows more electrons to be closer to more nuclei. This is the criterion for the stability of ***any*** kind of molecule; all that is special about the "ionic" bond is that we can employ a conceptually simple electrostatic model to predict the bond strength.

The main limitation of this model is that it applies really well only to the small class of solids composed of Group 1 and 2 elements with highly electronegative elements such as the halogens. Although compounds such as $CuCl_2$ dissociate into ions when they dissolve in water, the fundamental units making up the solid are more like polymeric chains of covalently-bound $CuCl_2$ molecules that have little ionic character.

Shared-electron (covalent) model

This model originated with the theory developed by G.N. Lewis in 1916, and it remains the most widely-used model of chemical bonding. The essential elements of this model can best be understood by examining the simplest possible molecule. This is the ***hydro-***

gen molecule ion H_2^+, which consists of two nuclei and one electron.

First, however, think what would happen if we tried to make the even simpler molecule H_2^+. Since this would consist only of two protons whose electrostatic charges would repel each other at all distances, it is clear that such a molecule cannot exist; something more than two nuclei are required for bonding to occur.

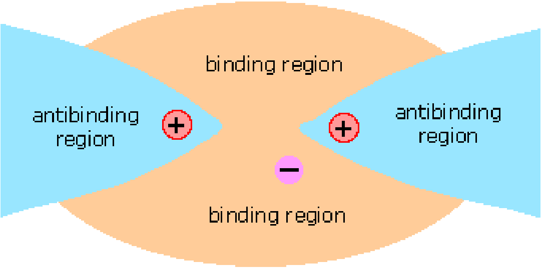


Fig. 5: Locations at which an electron will bind two nuclei

In the ***hydrogen molecule ion*** H_2^+ we have a third particle, an electron. The effect of this electron will depend on its location with respect to the two nuclei. If the electron is in the space between the two nuclei, it will attract both protons toward itself, and thus toward each other. If the total attraction energy exceeds the internuclear repulsion, there will be a net bonding effect and the molecule will be stable. If, on the other hand, the electron is off to one side, it will attract both nuclei, but it will attract the closer one much more strongly, owing to the inverse-square nature of Coulomb's law. As a consequence, the electron will now help the electrostatic repulsion to push the two nuclei apart.

We see, then, that the electron is an essential component of a chemical bond, but that it must be in the right place: between the two nuclei. Coulomb's law can be used to calculate the forces experienced by the two nuclei for various positions of the electron. This allows us to define two regions of space about the nuclei, as shown in the figure. One region, the ***binding region***, depicts locations at which the electron exerts a net binding effect on the new nuclei. Outside of this, in the antibinding region, the electron will actually work against binding.

This simple picture illustrates the number one rule of chemical bonding: *chemical bonds form when electrons can be simultaneously close to two or more nuclei.* It should be pointed out that this principle applies also to the ionic model; as will be explained later in this chapter, the electron that is "lost" by a positive ion ends up being closer to more nuclei (including the one from whose electron cloud it came) in the compound.

The polar covalent model

A purely covalent bond can only be guaranteed when the electronegativities (electron-attracting powers) of the two atoms are identical. When atoms having different electronegativities are joined, the electrons shared between them will be displaced toward the more electronegative atom, conferring a polarity on the bond which can be described in terms of percent ionic character. The polar covalent model is thus an generalization of covalent bonding to include a very wide range of behavior; it is discussed in greater detail beginning on Page 23.

The Coulombic model

This is an extension of the ionic model to compounds that are ordinarily considered to be non-ionic. Combined hydrogen is always considered to exist as the hydride ion H^-, so that methane can be treated as if it were C^{4+} H^-_4. This is not as bizarre as it might seem at first if you recall that the proton has almost no significant size, so that it is essentially embedded in an electron pair when it is joined to another atom in a covalent bond. This model, which is not as well known as it deserves to be[1], has considerable predictive power, both as to bond energies and structures.

VSEPR model

The ***valence shell electron repulsion*** model is not so much a model of chemical bonding as a scheme for explaining the ***shapes*** of molecules. It is based on the quantum mechanical view that bonds represent ***electron clouds***— physical regions of negative electric charge that repel each other and thus try to stay as far apart as possible. We will explore this concept in much greater detail beginning on Page 30.

3.2 Quantum mechanical models of the chemical bond

These models of bonding take into account the fact that a particle as light as the electron cannot really be said to be in ***any*** single location. The best we can do is define a region of space in which the probability of finding the electron has some arbitrary value which will always be less than unity. The shape of this volume of space is called an ***orbital*** and is defined by a mathematical function that relates the probability to the (***x,y,z***) coordinates of the molecule.

Like other models of bonding, the quantum models attempt to show how more electrons can be simultaneously close to more nuclei. Instead of doing so through purely geometrical arguments, they attempt this by predicting the nature of the orbitals which the valence electrons occupy in joined atoms.

The hybrid orbital model

This was developed by Linus Pauling in 1931 and was the first quantum-based model of bonding. It is based on the premise that if the atomic ***s, p***, and ***d*** orbitals occupied by the valence electrons of adjacent atoms are combined in a suitable way, the hybrid orbitals that result will have the character and directional properties that are consistent with the bonding pattern in the molecule. The rules for bringing about these combinations turn out to be remarkably simple, so once they were worked out it became possible to use this model to predict the bonding behavior in a wide variety of molecules. The hybrid orbital model is most usefully applied to the ***p***-block elements the first two rows of the periodic table, and is especially important in organic chemistry; see Page 37.

The molecular orbital model

This model takes a more fundamental approach by regarding a molecule as a collection of valence electrons and positive cores. Just as the nature of atomic orbitals derives from the spherical symmetry of the atom, so will the properties of these new ***molecular*** orbitals be controlled by the interaction of the valence electrons with the multiple positive centers of these atomic cores. These new orbitals, unlike those of the hybrid model, are ***delocalized***; that is, they do not “belong” to any one atom but extend over the entire region of space that encompasses the bonded atoms. The available (valence) electrons then fill these orbitals from the lowest to the highest, very much as in the Aufbau principle that you learned for working out atomic electron configurations. For small mole-

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[1] For more information on the coulombic model, see the articles by Lawrence J. Sacks in ***J. Chemical Education***, 1986: 288-297, and 373-378.

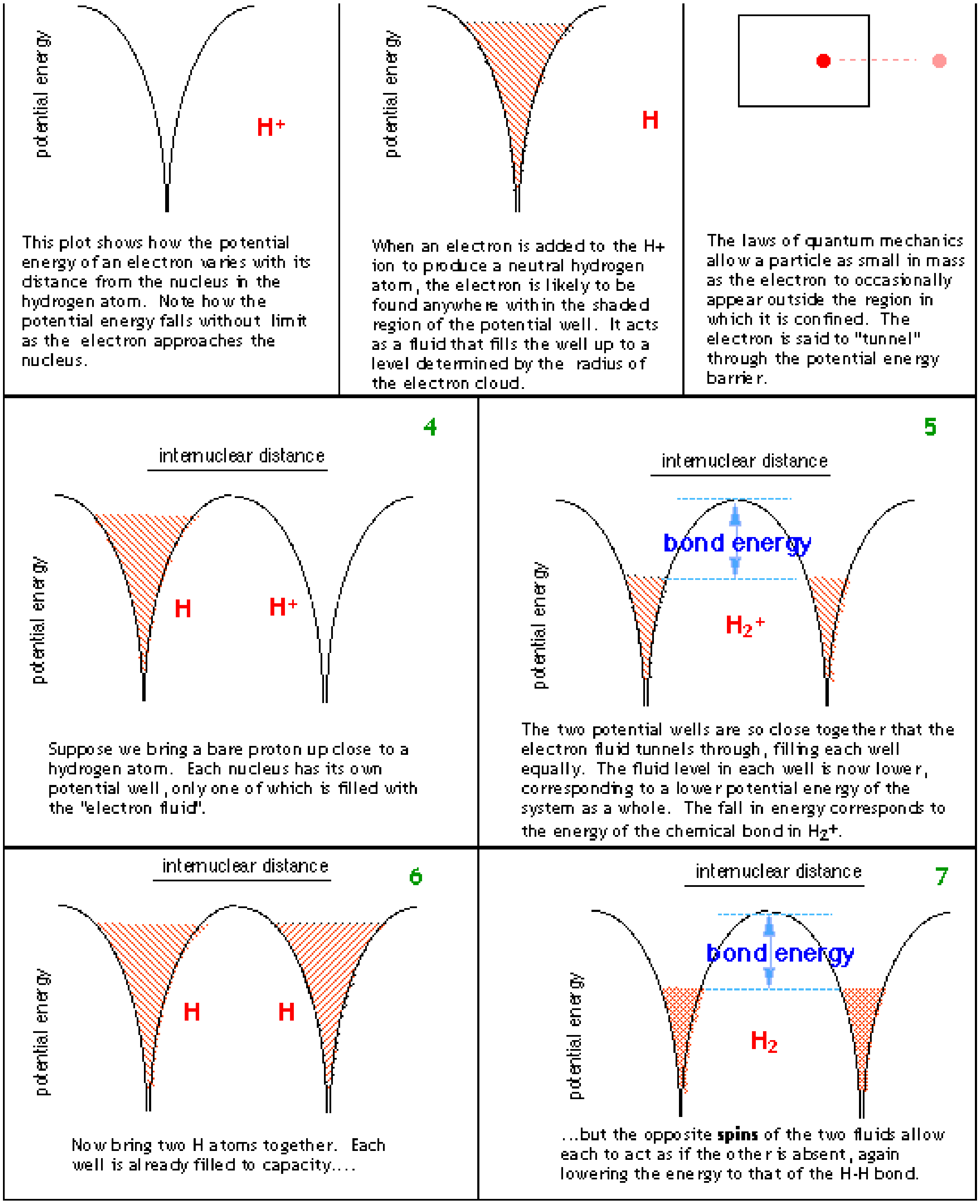
cules (which are the only ones we will consider here), there are simple rules that govern the way that atomic orbitals transform themselves into molecular orbitals as the separate atoms are brought together. The real power of molecular orbital theory, however, comes from its mathematical formulation which lends itself to detailed predictions of bond energies and other properties. This model is developed (and extended to metals) beginning on Page 54.

The electron-tunneling model

A common theme uniting all of the models we have discussed is that bonding depends on the fall in potential energy that occurs when opposite charges are brought together. In the case of covalent bonds, the shared electron pair acts as a kind of “electron glue” between the joined nuclei. In 1962, however, it was shown that this assumption is not strictly correct, and that instead of being concentrated in the space between the nuclei, the electron orbitals become even more concentrated around the bonded nuclei. At the same time however, they are free to “move” between the two nuclei by a process known as ***tunneling***. This refers to a well-known quantum mechanical effect that allows electrons (or other particles small enough to exhibit wavelike properties) to pass (“tunnel”) through a barrier separating two closely adjacent regions of low potential energy. One result of this is that the effective volume of space available to the electron is increased, and according to the uncertainty principle this will reduce the kinetic energy of the electron.

According to this model, the bonding electrons act as a kind of fluid that concentrates in the region of each nucleus (lowering the potential energy) and at the same time is able to freely flow between them (reducing the kinetic energy). A summary of the concept, illustrating its application to a simple molecule, is shown on the next page. Despite its conceptual simplicity and full acknowledgment of the laws of quantum mechanics, this model is less known than it deserves to be and is unfortunately absent from most textbooks.

A more detailed summary of this model and examples of its application is shown on the next page.



This plot shows how the potential energy of an electron varies with its distance from the nucleus in the hydrogen atom. Note how the potential energy falls without limit as the electron approaches the nucleus.

When an electron is added to the H+ ion to produce a neutral hydrogen atom, the electron is likely to be found anywhere within the shaded region of the potential well. It acts as a fluid that fills the well up to a level determined by the radius of the electron cloud.

The laws of quantum mechanics allow a particle as small in mass as the electron to occasionally appear outside the region in which it is confined. The electron is said to "tunnel" through the potential energy barrier.

Suppose we bring a bare proton up close to a hydrogen atom. Each nucleus has its own potential well, only one of which is filled with the "electron fluid".

The two potential wells are so close together that the electron fluid tunnels through, filling each well equally. The fluid level in each well is now lower, corresponding to a lower potential energy of the system as a whole. The fall in energy corresponds to the energy of the chemical bond in H_2^+.

Now bring two H atoms together. Each well is already filled to capacity....

...but the opposite **spins** of the two fluids allow each to act as if the other is absent, again lowering the energy to that of the H-H bond.

Fig. 6: Electron-tunneling model of chemical bonding

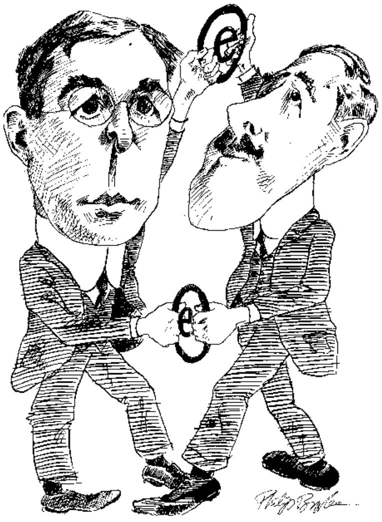
These diagrams are adapted from those in the article by Sture Nordholm: *Delocalization– the key concept of covalent bonding.* 1986: J. Chem. Education 581-584.

4. The shared-electron model of chemical bonding

Prior to the discovery of nuclei and electrons around 1900, theories of chemical bonding were based mainly on the rather vague concept of "chemical affinities" between different kinds of atoms. Beyond this, the primary need was to explain the different combining capacities, or "valences", of the different elements. These valences tended to vary with the periodic group of the element, and were therefore thought to encompass a range of from zero to eight; once the electron shell arrangement of atoms was worked out, the connection between outer-shell electron occupancy and bonding became apparent.

4.1 The Octet Rule

The first successful theory of chemical bonding was formulated by G.N.Lewis in 1916.



Philip Burke

G.N. Lewis (1875-1946; right) created the Chemistry Department at the University of California, Berkeley, and made it into one of the world's best. His other notable work included the first isolation of heavy water (D_2O), the thermodynamics of solutions, and the phosphorescence and magnetic properties of molecules.

Although Lewis originated the idea of the electron-pair bond, much of the credit for its early acceptance must go to Irving Langmuir, who extended it somewhat and enthusiastically popularized it to the extent that it began to be known as the Lewis-Langmuir theory, and even as the "Langmuir theory" (much to Lewis' annoyance!)

Irving Langmuir (1881-1967, Nobel Prize 1932) was an industrial scientist employed by the General Electric Co. His most notable work was on the chemistry of surfaces and monomolecular layers. Lewis and Langmuir were probably the two greatest American chemists of the first half of the twentieth century.

At the time Lewis began developing his ideas in 1902, it was widely believed that chemical bonding involved electrostatic attraction between ion-like entities. This seemed satisfactory for compounds such as NaCl that were known to dissociate into ions when dissolved in water, but it failed to explain the bonding in non-electrolytes such as CH_4. Atomic orbitals had not yet been thought of, but the concept of "valence" electrons was known, and the location of the noble gases in the periodic table suggested that all except helium possess eight valence electrons. It was also realized that elements known to form simple ions such as Ca^{2+} or Cl^- do so by losing or gaining whatever number of electrons is needed to leave eight in the valence shell of each. Lewis sought a way of achieving this ***octet*** in a way that did not involve ion formation, and he found it in his ***shared electron-pair theory*** published in 1916.

Present-day shared electron-pair theory is based on the premise that the s^2p^6 ***octet*** in the outermost shells of the noble gas elements above helium represents a particularly favorable configuration. This is not because of any mysterious properties of octets (or of noble gas elements); by allowing each nucleus to claim half-ownership of a shared electron, more electrons are effectively "seeing" more nuclei, leading to increased electrostatic attractions and a lowering of the potential energy.

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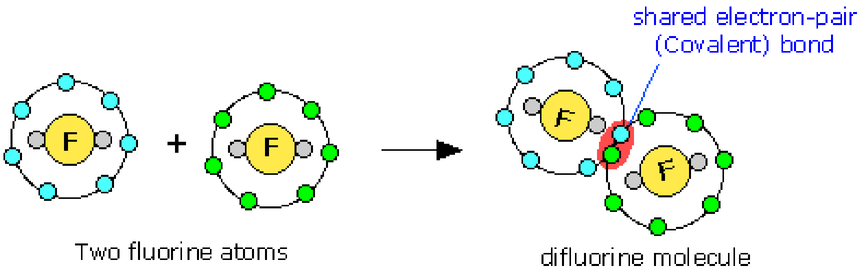
Fig. 7: shared electron-pair bond

Sharing of one or more valence electrons between two atoms allows each to possess a noble gas (s^2p^6) valence shell configuration. Each atom can claim half-ownership of each shared electron.



Lewis' idea that the electrons are shared in ***pairs*** stemmed from his observation that most molecules possess an even number of electrons. This paired sharing also allows the formulas of a large number of compounds to be rationalized and predicted— a fact that led to the widespread acceptance of the Lewis model by the early 1920s.

For the lightest atoms the octet rule must be modified, since the noble-gas configuration will be that of helium, which is simply $\boldsymbol{s^2}$ rather than $s^2\boldsymbol{p}^6$. Thus we write LiH as Li:H, where the electrons represented by the two dots come from the ***s*** orbitals of the separate atoms.

The octet rule applies quite well to the first full row of the periodic table (Li through F), but beyond this it is generally applicable only to the non-transition elements, and even in many of these it cannot explain many of the bonding patterns that are observed. The principal difficulty is that a central atom that is bonded to more than four peripheral atoms must have more than eight electrons around it if each bond is assumed to consist of an electron pair. In these cases, we hedge the rule a bit, and euphemistically refer to the larger number of electrons as an "expanded octet".

In spite of the octet rule's many exceptions and limitations, the shared electron-pair model is the one that chemists most frequently employ in their day-to-day thinking about molecules. It continues to serve as a very useful guiding principle and can be a good starting point for more sophisticated theories.

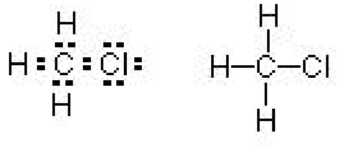
4.2 Lewis electron-dot formulas

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 shows the disposition of the shared pairs between the different atoms. This is commonly accomplished by depicting the valence (outermost) electrons of an atom as dots that are written around the atom symbols. Sometimes it is convenient to represent the electrons that are contributed by different atoms by different symbols. For example, the formation of H_2 can be depicted as

$$H\cdot + H\circ \rightarrow H \overset{\circ}{\bullet} H$$

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. Usually, a more or less symmetrical arrangement is written.

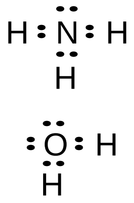
It is sometimes preferable to represent an electron pair by a line; this is most commonly done with shared electron pairs, which correspond to chemical bonds which have traditionally been represented in this way.



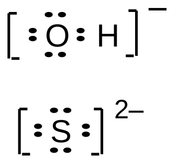
The Lewis theory makes no prediction about molecular shapes, so it is permissible to arrange the dot pairs and other atoms around the central atom in an arbitrary way. Usually, a more or less symmetrical arrangement is written.

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.



Lewis formulas of ions



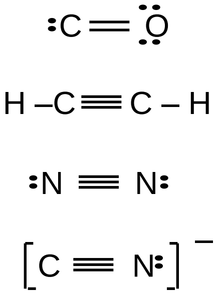
The Lewis formulas of charged molecules are no different from those of neutral molecules. It is customary to enclose the formulas in brackets so that the charge can be depicted as belonging to the molecule as a whole, rather than being localized on a particular atom.

Notice that the Lewis formulas of monatomic cations such as H+ and Ca^{2+} contain no dots at all, since these ions have no valence electrons.

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.

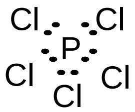
Since multiple bonds place more electron density between the two nuclei, the latter are held toward each other more closely and tightly; multiple bonds are therefore shorter and stronger than single bonds.

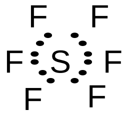


Expanded octets

As mentioned previously, the octet rule works best for the elements in the first 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 first-period elements, the only available orbitals are the $s^2\boldsymbol{p}^6$ set that, when filled, comprise the octet. In order to place more than four other atoms around any one of these elements, the additional shared electrons would have to go into the much-higher-energy $3s^2 3p^6$ set.





With elements in the fourth period (K through Cl) and beyond, these higher empty 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. Also, the gap between the higher ***s***- and ***p***- orbitals is bridged by the ***d*** orbitals that begin at ***n=3***.

For these reasons, it is common for elements such as S, Cl, P, and Si to form compounds in which five or six electron pairs surround the central atom. These pairs may all be shared with other atoms, or some of them may remain as lone pairs.

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

Electron structures without molecules

Although there are many violations of the octet rule, most electron dot structures that one can write down in accordance with this rule and its general scope of validity correspond to molecules that actually exist. Sometimes, however, we are surprised to find that the molecules corresponding to an apparently reasonable Lewis formula are not known.

In some cases, this has been shown to be a consequence of the very high chemical reactivity of the molecules. Thus hypofluorous acid, HOF, has never been isolated. It was not until 1967 that its short-lived presence was detected spectroscopically. It is now believed that the molecule is stable, but that the products obtained when it reacts with itself are so much more stable that it decomposes almost as fast as it is formed:

$$2HOF(g) \rightarrow 2HF(g) + O_2(g)$$

Other molecules having proper Lewis structures but no apparent existence may be stable only at very low temperatures; examples are O_4 and H_2O_4.

The fluorate ion, FO_3^-, has also never been detected, even though analogs containing the other halogen elements are well known. The problem here may well lie with the very small fluorine atom, which would allow the oxygens to approach so closely that they would repel each other.

Small size is also suggested as the reason for the non-existence of the nitrogen analogs of the sulfate and sulfite ions. These would have the formulas NO_4^{3-} and NO_3^{3-}. Here, the problem is believed to be the high charge density: it costs a lot of energy to squeeze this much electric charge in such a small volume. Sulfur, having a larger radius, forms larger ions having lower charge densities, and the total charge would also be only –2 instead of –3.

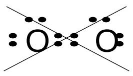
Molecules without electron structures

There are also examples of molecules whose existence is beyond question, but for which no satisfactory Lewis structures can be written. Two examples are the triiodide ion I_3^-, and the bifluoride ion HF_2^-. The triiodide ion is a well known species found in aqueous solutions containing iodine and iodide ions:

The bifluoride ion is formed in a rather similar way in hydrofluoric acid solutions containing fluoride ion:

Try writing electron-dot structures for these two species, and you will see the problem!

Paramagnetic molecules



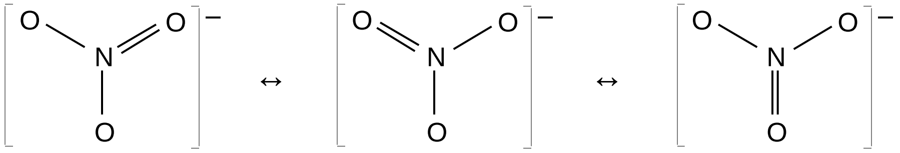
A somewhat different situation is exemplified by the common oxygen molecule. It is easy to write a proper Lewis structure for O_2 that places an octet around each oxygen atom and a double bond between them. However, it takes only a simple experiment to show that the electrons in dioxygen cannot all be arranged in pairs: if you place a magnet near some liquid oxygen, the liquid will be drawn to the magnet. This can only mean one thing: there are at least two unpaired electrons in the O_2 molecule. A more exact experiment shows that this number is exactly two. Are they in the bond or are they non-bonding electrons? You can decide this by sketching out a few possible structures.

The paramagnetism of oxygen is an anomaly in terms of the Lewis theory, although it is predicted by a more comprehensive theory that we will look at later. There are, however, a few other molecules that we would expect to be paramagnetic simply because they contain an odd number of valence electrons. The most well known example is nitric oxide, NO. Since oxygen has four and nitrogen has five outer electrons, the total number of valence electrons is nine, and magnetic measurements show that one of these is unpaired.

4.3 Too many structures: resonance hybrids

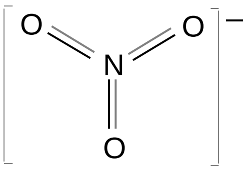
There is a rather large class of molecules for which one has no difficulty writing Lewis structures; in fact, we can write more than one valid structure for a given molecule. This raises a new problem: how do we decide which one to use?

The answer is simple: if the structures are all equivalent, we use them all. As an example, consider the nitrate ion NO_3^-, for which three Lewis structures can be written:



These structures differ only in which oxygen atom is attached by the double bond. Since there is no reason to prefer one over another, the NO_3^- ion is regarded as a superposition, or ***hybrid*** of these three structures.

The term ***resonance*** has been used to describe this phenomenon, which is indicated in the above structures by the double-ended arrows. The choice of this word was unfortunate, because it connotes the existence of some kind of dynamic effect that has led to the mistaken idea that the structure is continually alternating between the three possibilities. The correct interpretation is simply that none of the hybrid structures completely represents the molecule; the “real” structure is a superposition of the individual contributing structures.



bond order 4/3

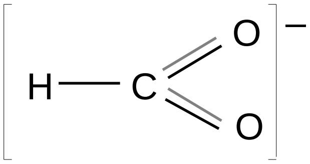
Thus there is no true double bond in NO_3^-; what we have instead are three “4/3 bonds”. A more realistic way of representing the structure might be to show the fractional bonds as dotted lines:

This interpretation is supported by structural studies on crystalline nitrate compounds; all the N-O bond distances are the same, and they are intermediate in length between the values expected for single and double bonds.

Since electrons in molecules tend to arrange themselves into configurations that give the lowest possible energy, it is not surprising that the resonance hybrid represents a more stable (i.e., strongly bound) molecule than does any one of the contributing structures.

There is a good quantum-mechanical reason for this; according to the Heisenberg uncertainty principle, the energy of the electron will be more uncertain as its position is more exactly specified. Since energies cannot be negative, the more “uncertain” the energy can be, the higher it can be. If an electron is spread out over three bonds as in the NO_3^- hybrid instead of being confined to the space between only two atoms, its exact location is much less exactly known, and so its energy will be less uncertain, and therefore lower.

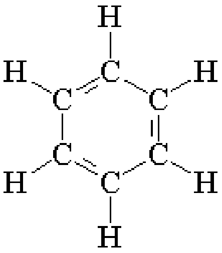
This is all that is meant by the statement you will often see, particularly in the older literature, that a given structure “is stabilized by resonance”. This jargon is used, for example, to explain the acidity of the -COOH group found in organic acids. The idea is that resonance is only possible when the proton has been lost, and that the lower energy of the “resonating” structure provides the driving force for the loss of the proton, and thus is the source of the acidity carboxylic group.



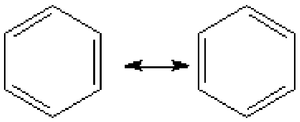
The Benzene ring

Perhaps the most well known molecule whose structure must be represented as a resonance hybrid is benzene, C_6H_6. The structure of this molecule had long been something of a mystery, in that it was difficult to understand how this formula could be consistent with the well-established tetravalence of carbon in organic compounds. The breakthrough came when the German chemist August Kekulé proposed that the molecule is based on a hexagonal ring of carbon atoms as shown at the left below.

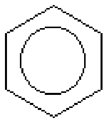
However, this structure is not consistent with the chemistry of benzene, which does not undergo the reactions that would be expected of a molecule containing carbon-carbon double bonds. Such compounds are normally quite reactive, while benzene, in contrast, tends to be rather inert to all but the most powerful reagents.



Kekulé structure



renonance structure



resonance hybrid

This apparent discrepancy disappeared after the resonance hybrid theory was developed; benzene is regarded as a hybrid of the two structures shown above. The structure of benzene is often represented by either of the figures shown at the left, in which the dashed or solid circle represents a “half bond”, so that the bond order of each C–C bond is 1.5. Bond length measurements are entirely consistent with this interpretation; they are almost exactly halfway between the values found in compounds known to contain single and double bonds.

In writing out resonance structures, it is important to bear in mind that only the electron pairs can be moved around; the atoms must all be kept in the same place. In some cases it is necessary to move electrons to locations that would produce a positive charge on one atom and a negative charge on the other. Since the separation of electric charge always costs energy, such resonance forms will tend to be less stabilizing and will not be as important contributors to the overall structure as those in where there is no charge separation.

5. Polar and nonpolar bonds

5.1 Electronegativity

The electrons constituting a chemical bond are simultaneously attracted by the electrostatic fields of the nuclei of the two bonded atoms. In a homonuclear molecule such as O_2 the bonding electrons will be shared equally by the two atoms. In general, however, differences in the sizes and nuclear charges of the atoms will cause one of them to exert a greater attraction on the bonding pair, causing the electron cloud to be displaced toward the more strongly-attracting atom.

The electronegativity of an atom denotes its relative electron-attracting power *in a chemical bond*.

> It is important to understand that electronegativity is ***not*** a measurable property of an atom in the sense that ionization energies and electron affinities are, although it can be correlated with both of these properties. The actual electron-attracting power of an atom depends in part on its chemical environment (that is, on what other atoms are bonded to it), so tabulated electronegativities should be regarded as high-precision predictors of the behavior of electrons in more complicated molecules.

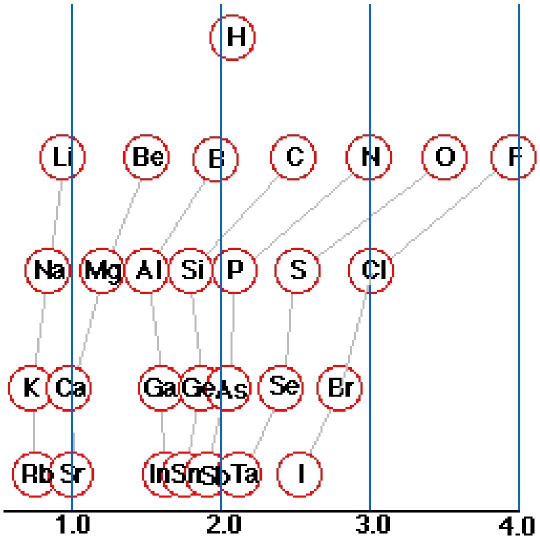
There are several ways of computing electronegativities, which are expressed on an arbitrary scale. The concept of electronegativity was introduced by Linus Pauling and his 0-4 scale continues to be the one most widely used.

.

Fig. 8: Electronegativities

The 0-4 electronegativity scale of Pauling is the best known of several arbitrary scales of this kind. Electronegativity values are not directly observable, but are derived from measurable atomic properties properties such as ionization energy and electron affinity. The place of any atom on this scale provides a good indication of its ability to compete with another atom in attracting a shared electron pair to it, but the presence of bonds to other atoms, and of multiple- or nonbonding electron pairs may make predictions about the nature a given bond less reliable.

An atom that has a small electronegativity is said to be *electropositive*. As the diagram shows, the metallic elements are generally electropositive. The position of **hydrogen** in this regard is worth noting; although physically a nonmetal, much of its chemisry is metal-like.



5.2 Dipole moments

When non-identical atoms are joined in a covalent bond, the electron pair will be attracted more strongly to the atom that has the higher electronegativity. As a consequence, the electrons will not be shared equally; the center of the negative charges in the molecule will be displaced from the center of positive charge. Such bonds are said to be ***polar*** and to possess ***partial ionic character***, and they may confer a polar nature on the molecule as a whole.

A **polar molecule** acts as an electric dipole which can interact with electric fields that are created artificially or that arise from nearby ions or polar molecules. Dipoles are conventionally represented as arrows pointing in the direction of the negative end. The magnitude of interaction with the electric field is given by the ***permanent electric dipole moment*** of the molecule. The dipole moment corresponding to an individual bond (or to a diatomic molecule) is given by the product of the quantity of charge displaced $q \equiv \delta^{\pm}$ and the bond length r:

$$\mu = q \times r$$

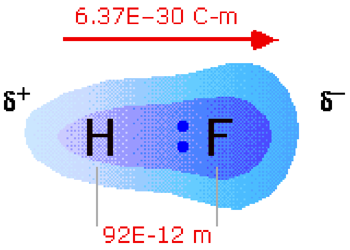
In SI units, q is expressed in coulombs and r in meters, so m has the dimensions of C-m. If one entire electron charge is displaced by 100 pm (a typical bond length), then

$$m = (1.6022 \times 10^{-19}\ \text{C}) \times (10^{-10}\ \text{m}) = 1.6 \times 10^{-29}\ \text{C-m} = 4.8\ \text{D}$$

The quantity at the right, the ***Debye*** unit, is still commonly used to express dipole moments. It was named after PETER DEBYE (1884-1966), the Dutch physicist who pioneered the study of dipole moments and of electrical interactions between particles, and won the Nobel Prize for Chemistry in 1934.

Measurement of dipole moments. When a solution of polar molecules is placed between two oppositely-charged plates, they will tend to align themselves along the direction of the field. This process consumes energy which is returned to the electrical circuit when the field is switched off, an effect known as ***electrical capacitance.*** Measurement of the capacitance of a gas or solution is easy to carry out and serves as a means of determining the magnitude of the dipole moment of a substance.

Problem Example: Estimate the percent ionic character of the bond in hydrogen fluoride from the experimental data shown at the right.



Solution:

$$\frac{6.37\text{E}{-30}\ \text{C-m}}{92\text{E}{-12}\ \text{m}} = 6.92\ \text{E}{-20}\ \text{C} \quad \text{(charge displaced)}$$

$$\frac{6.92\ \text{E}{-20}\ \text{C}}{1.60\text{E}{-19}\ \text{C/electron}} = 0.43 \quad \text{(ionic character of bond)}$$

Dipole moments of more complicated molecules.

In molecules containing more than one polar bond, the molecular dipole moment is just the vector combination of the individual bond dipoles. In some cases this can result in a molecule containing polar bonds to be nonpolar, as in the example of carbon dioxide shown in Fig. 9. In molecules containing nonbonding electrons or multiple bonds, the elecronegativity difference may not correctly predict the bond polarity. A good example of this is carbon monoxide, in which the partial negative charge resides on the carbon (Fig. 11), as predicted by its negative formal charge (see next page.)

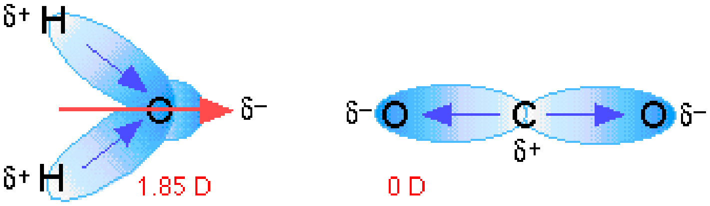


Fig. 9: Dipole moments of H_2O and CO_2

5.3 Formal charge and oxidation number

Although the total number of valence electrons in a molecule is easily calculated, there is sometimes no simple and unambiguous way of determining how many reside in a particular bond or as non-bonding pair on a particular atom. For example, one can write valid Lewis octet structures for carbon monoxide showing either a double or triple bond between the two atoms, depending on how many nonbonding pairs are placed on each:

::C::O: and **C:::O::** . The choice between structures such as these is usually easy to make on the principle that the more electronegative atom tends to surround itself with the greater number of electrons. In cases where the distinction between competing stsructures is not all that clear, an arbitrarily-calculated quantity known as the ***formal charge*** can often serve as a guide. ***The formal charge on an atom is the electric charge it would have if all bonding electrons were shared*** *equally* ***with its bonded neighbors.***

The formal charge on an atom is calculated by the following algorithm:

FC = core charge – number of unshared electrons – number of bonding pairs

in which the ***core charge*** is the electric charge the atom would have if all its valence electrons were removed.

In simple cases, the formal charge can be worked out visually directly from the Lewis structure, as is illustrated farther on.

> **Problem Example:** Lewis structures for carbon monoxide can be written in which the C–O bond is either double or triple. Calculate the formal charges on carbon and oxygen in the two alternative structures.
>
> Solution: For **::C::O:** :
>
> **C**: 4 – 4 – 2 = **–2**　　**O**: 6 – 2 – 2 = **+2**
>
> For **C:::O::**:
>
> **C**: 4 – 0 – 3 = **+1**　　6 – 4 – 3 = **+1**

The general rule for choosing between alternative structures is that the one involving the smallest formal charges is most favored, so we would assign carbon monoxide the triple-bonded structure. In a species such as the thiocyanate ion (below) in which two structures having the same minimal formal charges can be written, we would expect the one in which the negative charge is on the more electronegative atom to predominate.

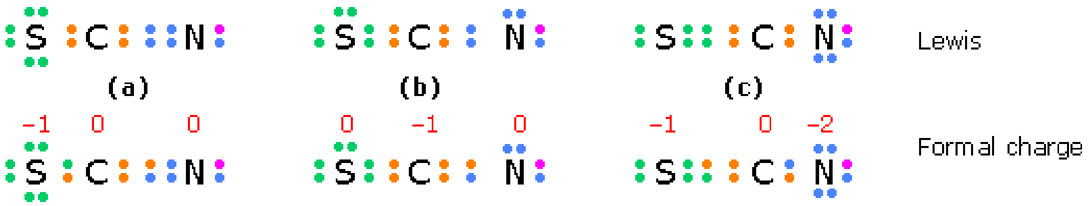


Fig. 10: Alternative Lewis structures for the thiocyanate ion SCN^-

The electrons in the structures of the top row are the valence electrons for each atom; an additional electron (purple) completes the nitrogen octet in this negative ion. The electrons in the bottom row are divided equally between the bonded atoms; the difference between these numbers and those above gives the formal charges.

Formal charge can also help answer the question “where is the charge located?” that is frequently asked about polyatomic ions. Thus by writing out the Lewis structure for the ammonium ion NH_4^+, you should be able to convince yourself that the nitrogen atom has a formal charge of +1 and each of the hydrogens has 0, so we can say that the positive charge is localized on the central atom.

Oxidation number is another arbitrary way of characterizing atoms in molecules. In contrast to formal charge, in which the electrons in a bond are assumed to be shared equally, ***oxidation number is the electric charge an atom would have if the bonding electrons were assigned exclusively to the more electronegative atom.*** Oxidation number serves mainly as a tool for keeping track of electrons in reaction in which they are exhanged between reactants, and for characterizing the “combining power” of an atom in a molecule or ion.

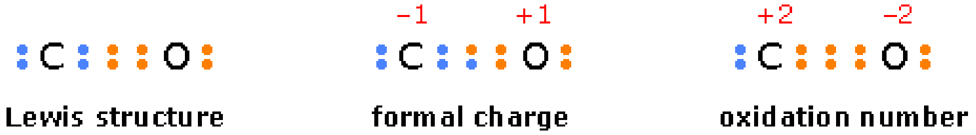


Fig. 11: Comparison of electron assignments for formal charge and oxidation number.

5.4 Ionic compounds

The shared-electron pair model introduced by G.N. Lewis showed how chemical bonds could form in the absence of electrostatic attraction between oppositely-charged ions. As such, it has become the most popular and generally useful model of bonding in all substances other than metals. A chemical bond forms when electrons are simultaneously attracted to two nuclei, thus acting to bind them together in an energetically-stable arrangement. The ***covalent bond*** is formed when two atoms are able to share a pair of electrons:

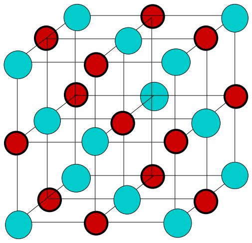
$$A\cdot \quad + \quad B\cdot \quad \rightarrow \quad A:B$$

In general, however, different kinds of atoms exert different degrees of attraction on their electrons, so in most cases the sharing will not be equal. One can even imagine an extreme case in which the sharing is so unequal that the resulting “molecule” is simply a pair of ions:

$$A\cdot \quad + \quad B\cdot \quad \rightarrow \quad A^{+} \; :B^{-}$$

The resulting substance is sometimes said to contain an ***ionic bond***. Indeed, the properties of a number of compounds can be adequately explained using the ionic model. But does this mean that there are really two kinds of chemical bonds, ionic and covalent?

Bonding in ionic solids



According to the ionic electrostatic model, solids such as NaCl consist of positive and negative ions arranged in a crystal lattice. Each ion is attracted to neighboring ions of opposite charge, and is repelled by ions of like charge; this combination of attractions and repulsions, acting in all directions, causes the ion to be tightly fixed in its own location in the crystal lattice.

Since electrostatic forces are nondirectional, the structure of an ionic solid is determined purely by geometry: two kinds of ions, each with its own radius, will fall into whatever repeating pattern will achieve the lowest possible potential energy. Surprisingly, there are only a small number of possible structures; the very common ***simple cubic*** lattice of NaCl is illustrated here.

Is there such as thing as an ionic bond?

When two elements form an ionic compound, is an electron really lost by one atom and transferred to the other one? In order to deal with this question, consider the data on the ionic solid LiF. The average radius of the neutral Li atom is about 2.52Å. Now if this Li atom reacts with an atom of F to form LiF, what is the average distance between the Li nucleus and the electron it has “lost” to the fluorine atom? The answer is 1.56Å; the electron is now closer to the lithium nucleus than it was in neutral lithium. So the answer to the above question is both yes and no: yes, the electron that was now in the ***2s*** orbital of Li is now within the grasp of a fluorine ***2p*** orbital, but no, the electron is now even closer to the Li nucleus than before, so how can it be “lost”? The one thing that is inarguably true about LiF is that there are more electrons closer to positive nuclei than there are in the separated Li and F atoms. But this is just the rule we stated at the beginning of this unit: ***chemical bonds form when electrons can be simultaneously near two or more nuclei***.

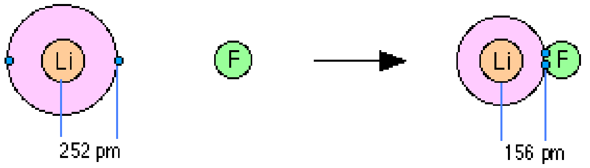


Fig. 12: Polar covalence in an "ionic" solid
After the 2s electron has been "lost" by lithium, it is even closer to the Li nucleus than before!

It is obvious that the electron-pair bond brings about this situation, and this is the reason for the stability of the covalent bond. What is not so obvious (until you look at the numbers such as were quoted for LiF above) is that the "ionic" bond results in the same condition; even in the most highly ionic compounds, both electrons are close to both nuclei, and the resulting mutual attractions bind the nuclei together. This being the case, is there really any fundamental difference between the ionic and covalent bond?

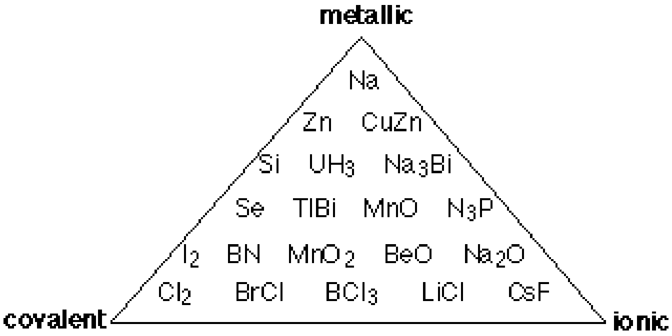
The answer, according to modern chemical thinking[1] is probably "no"; in fact, there is some question as to whether it is realistic to consider that these solids consist of "ions" in the usual sense. The preferred picture that seems to be emerging is one in which the electron orbitals of adjacent atom pairs are simply skewed so as to place more electron density around the "negative" element than around the "positive" one.

This being said, it must be reiterated that the ionic model of bonding is a useful one for many purposes, and there is nothing wrong with using the term "ionic bond" to describe the interactions between the atoms in "ionic solids" such as LiF and NaCl.

Polar covalence

If there is no such thing as a "completely ionic" bond, can we have one that is completely covalent? The answer is yes, if the two nuclei have equal electron attracting powers. This situation is guaranteed to be the case with ***homonuclear diatomic molecules--*** molecules consisting of two identical atoms. Thus in Cl_2, O_2, and H_2, electron sharing between the two identical atoms must be exactly even; in such molecules, the center of positive charge corresponds exactly to the center of negative charge: halfway between the two nuclei.

Fig. 13: Mixed bond types
Categorizing all chemical bonds as either ionic, covalent, or metallic is a gross oversimplification; as the diagram shows, there are examples of compounds that exhibit varying degrees of all three bonding characteristics.



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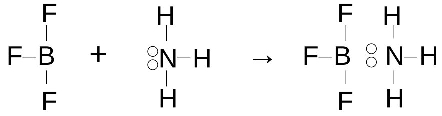
[1] See R.T. Sanderson: ***Chemical bonds and bond energy***, Chapter 9 (Academic Press)

5.5 Electron donor-acceptor bonds

In most covalent bonds, we think of the electron pair as having a dual parentage, one electron being contributed by each atom. There are, however, many cases in which both electrons come from only one atom. This can happen if the donor atom has a non-bonding pair of electrons and the acceptor atom has a completely empty orbital that can accommodate them.

This is the case, for example, with boron trifluoride and ammonia:



In BF_3, one the ***2p*** orbitals is unoccupied and can accommodate the lone pair on the nitrogen atom of ammonia. The electron acceptor, BF_3, acts as a Lewis acid here, and NH_3 is the Lewis base.

Bonds of this type (sometimes known as ***coordinate covalent*** or ***dative*** bonds) tend to be rather weak (usually 50-200kJ/mol); in many cases the two joined units retain sufficient individuality to justify writing the formula as a ***molecular complex*** or ***adduct***.

6. The Shapes of Molecules: the VSEPR model

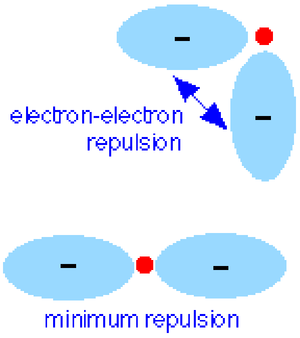
Molecules are three-dimensional objects that occupy a three-dimensional world; it is easy to forget this after seeing so many depictions of molecular structures on a two-dimensional page. In general, only the smallest molecules can be said to have a fixed geometrical shape; the icosahedral C_{60} "soccer ball" is a rare exception. In most molecules, those parts joined by single bonds can rotate with respect to each other, giving rise to many different geometric forms. However, the local geometry surrounding a given atom that is covalently bound to its neighbors is constant. Being able to understand and predict these bond angles is an important part of chemistry and is the subject of this section.

> The Lewis electron-dot structures you have learned to draw have no geometrical significance other than depicting the order in which the various atoms are connected to one another. Nevertheless, a slight extension of the simple shared-electron pair concept is capable of rationalizing and predicting the geometry of the bonds around a given atom in a wide variety of situations.

6.1 Electron pair repulsion

The ***valence shell electron pair repulsion*** (VSEPR) model focuses on the bonding and nonbonding electron pairs present in the outermost ("valence") shell of an atom to which are connected two or more other atoms. Like all electrons, these occupy orbitals whose precise character can be left to more detailed theories. All you have to remember at this stage is that these orbitals represent regions of negative electric charge, and because like charges repel, these valence-shell orbitals will be energetically most stable when they are as far from each other as possible.

The covalent model of chemical bonding assumes that the electron pairs responsible for bonding are concentrated into the region of apace between the bonded atoms. The fundamental idea of VSEPR theory is that these regions of negative electric charge will repel each other, causing them (and thus the chemical bonds) to stay as far apart as possible. If the central atom also contains one or more pairs of nonbonding electrons, these additional regions of negative charge will behave very much like those associated with the bonded atoms. The orbitals associated with the various bonding and nonbonding pairs in the valence shell will extend out from the central atom in directions that minimize their mutual repulsions.



If the central atom possesses partially occupied ***d*** -orbitals, it may be able to accommodate five or six electron pairs, forming what is sometimes called an "expanded octet".

6.2 Coordination geometry and molecular geometry

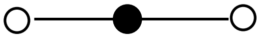
Coordination number refers to the number of electron pairs that surround a given atom; we often refer to the atom of interest as the ***central atom*** even if this atom is not really located at the center of the molecule. If all of the electron pairs surrounding the central atom are shared with neighboring atoms, then the ***coordination geometry*** is the same as the ***molecular geometry***. The application of VSEPR theory then reduces to the simple problem of naming (and visualizing) the geometric shapes associated with various numbers of points surrounding a central point (the central atom) at the greatest possible angles. Both classes of geometry are named after the shapes of the imaginary geometric figures (mostly regular solid polygons) that would be centered on the central atom and would have an electron pair at each vertex.

If one of more of the electron pairs surrounding the central atom is not shared with a neighboring atom (that is, if it is a ***lone pair)***, then the molecular geometry is simpler than the coordination geometry, and it can be worked out by inspecting a sketch of the coordination geometry figure.

6.3 Digonal and trigonal coordination

Linear molecules

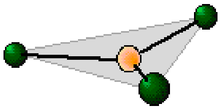
The simplest possible case will be a triatomic molecule of the type AX_2 in which the ***coordination number*** (number of bonded atoms X) around the central atom A is 2. What angle between the two A-B bonds will give the greatest possible separation between them, thus minimizing the repulsion between the associated electron clouds? It is not very difficult to see that the answer is 180°; the two bonds must extend out from the A atom in opposite directions.

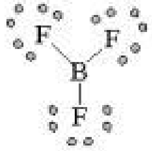


Examples of triatomic molecules for which VSEPR theory predicts a linear shape are $BeCl_2$ (which, you will notice, does not conform to the octet rule) and CO_2. If you write out the electron dot formula for carbon dioxide, you will see that the C-O bonds are double bonds. This makes no difference to VSEPR theory; the central carbon atom is still joined to two other atom, and the coordination number is still only 2.

Plane-trigonal molecules

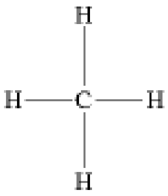
In the molecule BF_3, there are three regions of electron density extending out from the central boron atom. The repulsion between these will be at a minimum when the angle between any two is 120°. This requires that all four atoms be in the same plane; the resulting shape is called trigonal planar, or simply ***trigonal***.

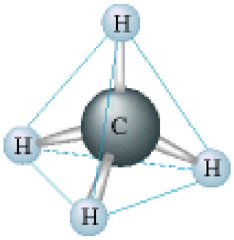


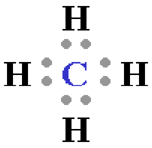


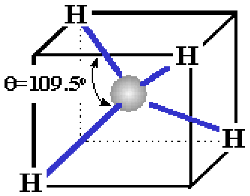
6.4 Tetrahedral coordination

Methane, CH_4, contains a carbon atom to which are connected four hydrogens. What bond angle would lead to the greatest possible separation between the electron clouds associated with these bonds? In analogy with the preceding two cases, where the bond angles were 360°/2=180° and 360°/3=120°, you might guess 360°/4=90°; if so, you would be wrong. The latter calculation would be correct if all the atoms were constrained to be in the same plane (we will see cases where this happens later), but here there is no such restriction. Consequently, the four equivalent bonds will point in four equivalent directions in three dimensions. The angle between any two bonds will be 109.5°.

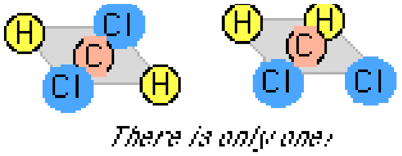








This is called ***tetrahedral*** coordination; the four hydrogen atoms will be located at the corners of a tetrahedron that has the carbon at its center. ***This is the most important coordination geometry in Chemistry: it is imperative that you be able to sketch at least a crude perspective view of a tetrahedral molecule.***

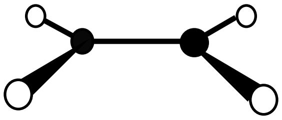


It is interesting to note that the tetrahedral coordination of carbon in most of its organic compounds was worked out in the nineteenth century on purely geometrical grounds and chemical evidence. For example, it was noted that there is only one dichloromethane, CH_2Cl_2. If the coordination around the carbon were square, then there would have to be ***two*** isomers of CH_2Cl_2, as shown in the pair of structures above. The distances between the two chlorine atoms would be different, giving rise to differences in physical properties would allow the two isomers to be distinguished and separated.

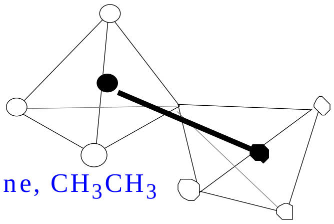
The existence of only one kind of CH_2Cl_2 molecule means that all four positions surrounding the carbon atom are geometrically equivalent, which requires a tetrahedral coordination geometry. Unfortunately, this fact can only really be made convincing by inspecting a three-dimensional mechanical model of the molecule.

Tetrahedrally-coordinated carbon chains

Carbon atoms are well known for their tendency to link together to form the millions of organic molecules that are known. We can work out the simpler hydrocarbon chains by looking at each central atom separately. Thus ethene consists of two plane-trigonal CH_2 units joined together, whereas ethane is essentially two CH_3 tetrahedra joined end-to-end.



Ethene, CH_2CH_2



Ethane, CH_3CH_3

Both of these structures can be extended indefinitely into very long hydrocarbon chains.

6.5 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.

This will ***not*** be the case when the valence shell of the central atom contains nonbonding electrons. 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

You will recall that CO_2, lacking any lone pair electrons on the central atom, is a linear molecule; there two bonded atoms and the coordination number around the carbon is also two.

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, even though the number of atoms bound to it is only two. The two nonbonding orbitals are very much like the bonding ones, except that there are no other atoms at their far ends.

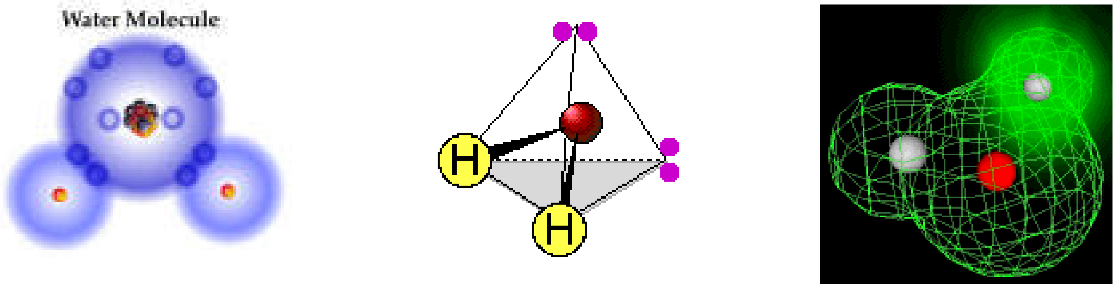


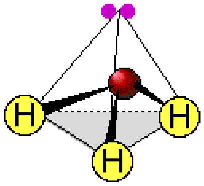
Fig. 14: three views of the H_2O molecule

Notice the two non-bonding electron pairs in the schematic diagrams at right and center. The computer-generated picture on the right shows the higher electron density around the oxygen atom.

The O-H bond angle in water is 104.5°. This is somewhat less than the tetrahedral angle of 109.5°, and it means that the four orbitals are not entirely equivalent. This is not at all surprising, considering that two of them are nonbonding. Because a nonbonding orbital has no atom at its far end to draw the electron cloud to 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 H_2O, the two nonbonding orbitals push the bonding orbitals closer together, closing the angle somewhat.

> The bent shape of the water molecule can be a source of confusion if you are not careful: the oxygen atom in water is ***tetrahedrally*** coordinated, but the molecule itself has a shape defined by its ***atoms*** rather than its orbitals. The two hydrogen atoms are situated near the corners of a tetrahedron that is centered on the oxygen atom, but these three points define only a bent shape, not a complete tetrahedron.

Ammonia



The electron-dot structure of NH_3 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. 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 NH_3 molecule 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"!)

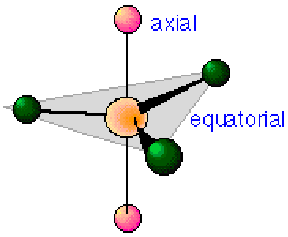
6.6 Atoms bonded to five atoms

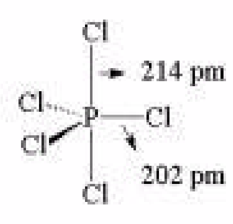
Compounds of the type AB_5 are formed by some of the elements in Group 15 of the periodic table; PCl_5 and AsF_5 are examples.

In what directions can five electron pairs arrange themselves in space so as to minimize their mutual repulsions? In the cases of coordination numbers 2, 3, 4, and 6, we could imagine that the electron pairs distributed themselves as far apart as possible on the surface of a sphere the resulting shapes correspond to the regular polyhedron whose number of vertices is equal to the coordination number.

The problem with coordination number 5 is that there is no such thing as a regular polyhedron with five vertices

> In 1758, the great mathematician EULER proved that there are only five regular convex polyhedra: tetrahedron (4 triangular faces), octahedron (6 triangular faces), icosahedron (20 triangular faces), cube (6 square faces), and dodecahedron (12 pentagonal faces). Chemical examples of all are known; the first icosahedral molecule, LaC_{60} (in which the La atom has 20 nearest C neighbors) was prepared in 1986.
>
> Besides the five regular solids, there can be 15 semi-regular isogonal solids in which the faces have different shapes, but the vertex angles are all the same. These geometrical principles are quite important in modern structural chemistry.



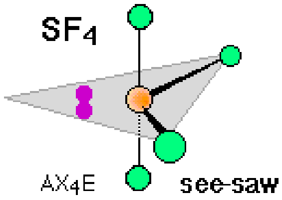


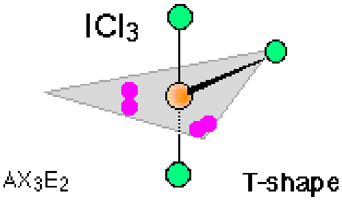
The shape of PCl_5 and similar molecules is a ***trigonal bipyramid.*** This consists simply of two triangular-base pyramids joined base-to-base. Three of the chlorine atoms are in the plane of the central phosphorus atom, while the other two atoms are above and below this plane.

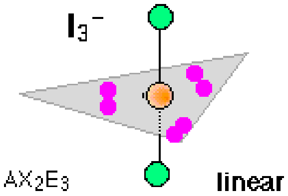
Since the trigonal bipyramid is not a regular Eulerian polyhedron, the atoms in the ***axial*** positions above and below the plane are not equivalent to those in the ***equatorial*** positions in the plane. Thus in PCl_5, there are two sets of Cl-P-Cl bond angles ***(what are their values?)***, and the axial and equatorial chlorine atoms will behave differently in chemical reactions.

The non-equivalence of the axial and equatorial positions also affects the disposition of any lone pair electrons. Because the nonbonding orbitals tend to concentrate electron density closer to the central atom, they exert more repulsive force on other orbitals. This repulsion (and the energy it costs) will be smaller when the nonbonding orbitals occupy equatorial positions; this can be seen by comparing the numbers neighboring orbitals at 90° and 120° to an axial and an equatorial location.

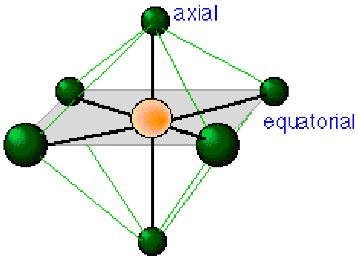
Using this reasoning, we can predict that an AX_4E molecule (that is, a molecule in which the central atom A is coordinated to four other atoms "X" and to one nonbonding electron pair) such as SF_4 will have a "see-saw" shape; substitution of more nonbonding pairs for bonded atoms reduces the triangular bipyramid coordination to even simpler molecular shapes, as shown below. (See the examples on the next page.)







6.7 Octahedral coordination

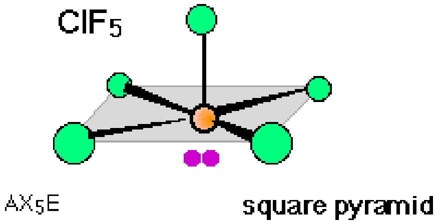


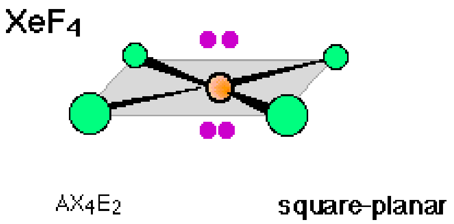
Just as four electron pairs experience the minimum repulsion when they are directed toward the corners of a tetrahedron, six electron pairs will try to point toward the corners of an ***octahedron***. An octahedron is not as complex a shape as its name might imply; it is simply two square-based pyramids joined base to base. You should be able to sketch this shape as well as that of the tetrahedron.

At first, you might think that a coordination number of six is highly unusual; it certainly violates the octet rule, and there are only a few molecules (SF_6 is one) where the central atom is hexavalent. It turns out, however, that this is one of the most commonly encountered coordination numbers in inorganic chemistry. There are two main reasons for this:

- Many ***transition metal ions*** form coordinate covalent bonds with lone-pair electron donor atoms such as N (in NH_3) and O (in H_2O). Since transition elements can have an outer configuration of $\boldsymbol{d}^{10}\boldsymbol{s}^2$, up to six electron pairs can be accommodated around the central atom. A coordination number of 6 is therefore quite common in transition metal hydrates, such as $Fe(H_2O)_6^{3+}$.
- Although the central atom of most molecules is bonded to fewer than six other atoms, there is often a sufficient number of ***lone pair*** electrons to bring the total number of electron pairs to six.

There are well known examples of 6-coordinate central atoms with 1, 2, and 4 lone pairs. Since the corners of an octahedron are geometrically equivalent, the distinction between axial and equatorial atoms that we had to consider in the 5-coordinate case no longer exists; thus the horizontal rectangles you see in the sketches below have no special significance and could just as well be placed in either of the two possible vertical planes.





6.8 Summary of VSEPR theory

The VSEPR model is an extraordinarily powerful one, considering its great simplicity. Its application to predicting molecular structures can be summarized as follows:

1. Electron pairs surrounding a central atom repel each other; this repulsion will be minimized if the orbitals containing these electron pairs point as far away from each other as possible.
2. The coordination geometry around the central atom corresponds to the polyhedron whose number of vertices is equal to the number of surrounding electron pairs (coordination number). Except for the special case of 5, and the trivial cases of 2 and 3, the shape will be one of the regular polyhedra.
3. If some of the electron pairs are nonbonding, the shape of the molecule will be simpler than that of the coordination polyhedron.
4. Orbitals that contain nonbonding electrons are more concentrated near the central atom, and therefore offer more repulsion than bonding pairs to other orbitals.

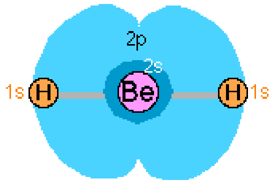
While VSEPR theory is quite good at predicting the general shapes of most molecules, it cannot yield exact details. For example, it does not explain why the bond angle in H_2O is 104.5°, but that in H_2S is about 90°. This is not surprising, considering that the emphasis is on electronic repulsions, without regard to the detailed nature of the orbitals containing the electrons, and thus of the bonds themselves.

7. Hybrid orbitals: the valence bond model

As useful and appealing as the concept of the shared-electron bond is, it raises a somewhat troubling question that we must sooner or later face: what is the nature of the ***orbitals*** in which the shared electrons are contained? Up until now, we have been tacitly assuming that each valence electron occupies the same kind of atomic orbital as it did in the isolated atom. As we shall see below, his assumption very quickly leads us into difficulties.

Bonding in beryllium hydride

Consider how we might explain the bonding in a compound of divalent beryllium, such as beryllium hydride, BeH_2. The beryllium atom, with only four electrons, has a configuration of $1s^2 2s$. This means that there are only ***two*** electrons in the outer shell of beryllium; these electrons are paired up together in the ***2s*** orbital.



Now according to covalent bond theory, each beryllium-hydrogen bond must consist of two electrons, shared between the two different atoms. One of these electrons is contributed by the hydrogen, while the other comes from the beryllium atom.

The question then arises: how can the two outer-shell electrons of beryllium interact with the hydrogen electrons? Two electrons in the same orbital have opposite spins, and constitute a stable pair that has no tendency to interact with unpaired electrons on other atoms. Electron sharing, as we have seen so far, can only take place when UNpaired electrons on adjacent atoms interact.

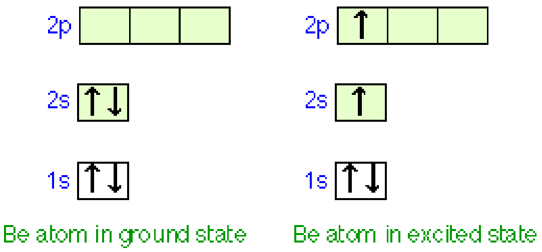


Fig. 15: Electron configurations of Be in its ground- and excited states

The ground state of an atom is its normal, lowest-energy state. The excited state shown accounts for the bivalency of Be, but not for the equivalence of the two bonded atoms.

The only way that we can obtain two unpaired electrons for bonding in beryllium is to promote one of the ***2s*** electrons to the ***2p*** level. However, the energy required to carry out this promotion would be sufficiently great to discourage bond formation. It is observed that Be does form reasonably stable bonds with other atoms. Moreover, the two bonds in BeH_2 and similar molecules are completely equivalent; this would not be the case if the electrons in the two bonds shared Be orbitals of different types.

In fact, there is little reason to believe that ***s***, ***p***, and ***d*** orbitals really do exist in the outer shells of many bonded atoms. Remember that these different orbitals arise in the first place from the interaction of the electron with the central electrostatic force field associated with the positive nucleus. An outer-shell electron in a bonded atom will be under the influence of a force field, emanating from ***two*** positive nuclei rather than one, so we would expect the orbitals in the bonded atoms to have a somewhat different character from those in free atoms. We can, in fact, throw out the concept of atomic orbital altogether and reassign the electrons to a new set of ***molecular orbitals*** that are characteristic of each molecular configuration. This approach is indeed valid, but we will defer a discussion of it until later. For now, we will look at a less-radical model that starts out with the familiar valence-shell atomic orbitals, and allows them to combine to form ***hybrid orbitals*** whose shapes conform quite well to the bonding geometry that we observe in a wide variety of molecules.

7.1 What are hybrid orbitals?

Orbitals of all types are simply mathematical functions that describe particular standing-wave patterns that can be plotted on a graph but have no physical reality of their own. Because of their wavelike nature, two or more orbitals (i.e., two or more functions ψ) can be combined both in-phase and out-of-phase to yield a pair of resultant orbitals which, to be useful, must have squares that describe actual electron distributions in the atom or molecule.

The ***s,p,d*** and ***f*** orbitals that you are familiar with are the most convenient ones for describing the electron distribution in isolated atoms because assignment of electrons to them according to the usual rules always yields an overall function ψ^2 that predicts a spherically symmetric electron distribution, consistent with all physical evidence that atoms are in fact spherical. For atoms having more than one electron, however, the ***s,p,d, f*** basis set is only one of many possible ways of arriving at the same observed electron distribution. Because it happens to be the simplest description of the atom we use it, but it is not unique.

In the case of a molecule such as BeH_2, we know from experimental evidence that the molecule is linear and therefore the electron density surrounding the central atom is no longer spherical, but must be concentrated along two directions 180° apart, and we need to construct a function ψ^2 having these geometrical properties. There are any number of ways of doing this, but the simplest is to use a new set of functions ψ (which we call hybrid orbitals) that are constructed by combining the atomic ***s,p,d, f*** functions that are already familiar to us.

> You should understand that ***hybridization is not a physical phenomenon;*** it is merely a mathematical operation that allows us to describe the electron distribution about a bonded atom in terms of one particular set of functions that we prefer to use because it is convenient to do so.

This approach, which assumes that the orbitals remain more or less localized on one central atom, is the basis of the valence-bond theory which was developed in the early 1930s, mainly by LINUS PAULING[1]. Although it has proven very powerful (especially in organic chemistry), it does have its limitations. For example, it predicts that both H_2O and H_2S will be tetrahedrally coordinated bent molecules with bond angles slightly smaller than the tetrahedral angle of 109.5° owing to greater repulsion by the non-bonding pair. This description fits water (104.5°) quite well, but the bond angle in hydrogen sulfide is only 92°, suggesting that atomic p orbitals (which are 90° apart) provide a better description of the electron distribution about the sulfur atom than do

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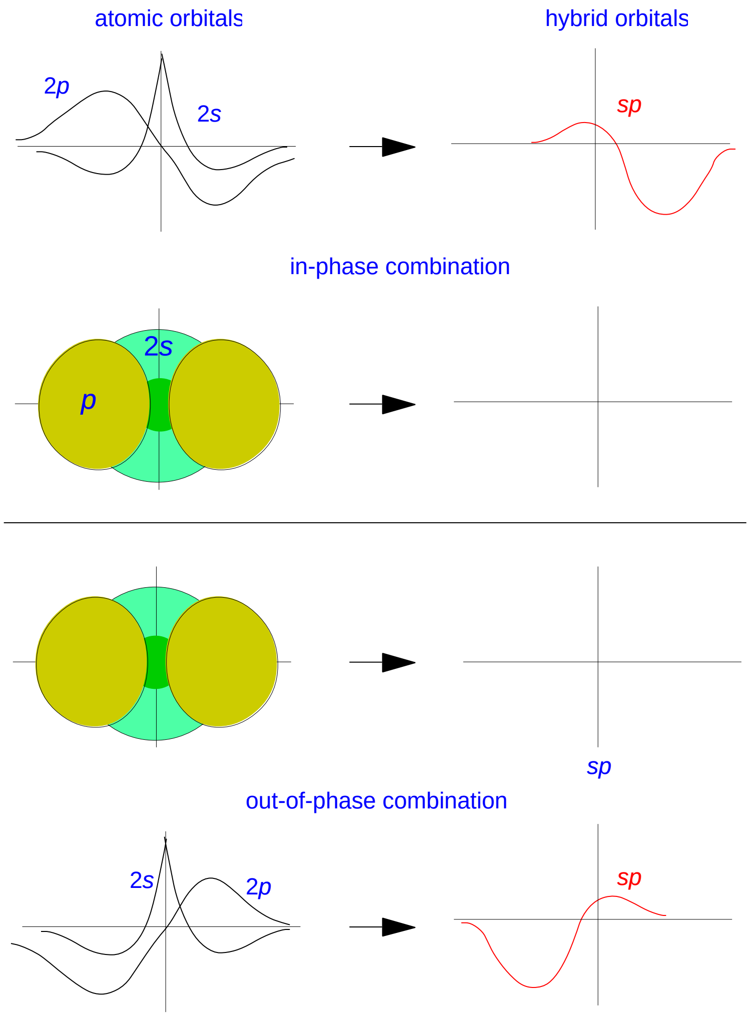
[1] Linus Pauling (1901-1994) was the most famous American chemists of the 20th century and the author of the classic ***The nature of the chemical bond***. His early work pioneered the application of X-ray diffraction to determine the structure of complex molecules; he then went on to apply quantum theory to explain these observations and predict the bonding patterns and energies of new molecules. Pauling, who spent most of his career at Cal Tech, won the Nobel Prize for Chemistry in 1954 and the Peace Prize in 1962.

sp^3 hybrid orbitals.

The valence bond approach tends to be much better at explaining or rationalizing the structure of a known molecule, than it is at ***predicting*** a structure or shape. In other words, it works for some molecules, but not for others. This model is fairly simple to apply and understand, but it is best regarded as one special way of looking at a molecule that can often be misleading. Another viewpoint, called the ***molecular orbital*** theory, offers us a complementary perspective that it is important to have if we wish to develop a really thorough understanding of chemical bonding in a wider range of molecules.

Understanding hybrid orbitals

Hybrid orbitals are formed from “constructive” and “destructive” combinations of 2p and 2s atomic wave functions, as illustrated by the line plots below. The solid figures depict the corresponding probability functions ψ^2 which describe the electron density in the various directions around the bonded atm.



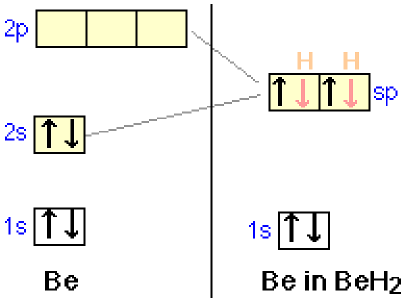
First, recall that the electron, being a quantum particle, cannot have a distinct location; the most we can do is define the region of space around the nucleus in which the probability of finding the electron exceeds some arbitrary value, such as 90% or 99%. This region of space is the *orbital*. Because of the wavelike character of matter, the orbital corresponds to a standing wave pattern in 3-dimensional space which we can often represent more clearly in 2-dimensional cross section. The quantity that is varying (“waveing”) is a number denoted by ψ whose value varies from point to point according to the wave function for that particular orbital.

Hybrid orbitals are constructed by combining the ψ functions for atomic orbitals. Because wave patterns can combine both constructively and destructively, a pair of atomic wave functions such as the *s*- and *p*- orbitals shown at the left can combine in two ways, yielding the *sp* hybrids shown.

The probability of finding the electron at any location is given not by ψ, but by ψ^2, whose form is roughly conveyed by the solid figures in this illustration.

7.2 Digonal bonding: *sp*-hybrid orbitals

To see how the concept of hybrid orbitals helps us understand bonding, let’s go back to the example of BeH_2 that we mentioned on Page 37. Instead of assuming that the two bonding electrons occupy ***s***- and ***p***- orbitals characteristic of the isolated atoms, we place them in ***sp hybrid*** orbitals of ***identical*** character which arise from in- and out-of-phase combinations of the atomic orbitals as described above.



Each of the two ***sp***-hybrid orbitals contains a single unpaired electron which is readily shared with a similar electron on another atom such as hydrogen. Notice how the ***sp*** hybrid orbital is intermediate in energy between the ***2s*** and ***2p*** orbitals of atomic beryllium. This means that it doesn’t cost the beryllium atom much in energy to get its two outer electrons into the ***sp*** hybrid- what the beryllium atom must “pay” in order to promote its ***2s*** electron up to the level of the ***sp*** hybrid, the atom more than gains in the energy ***lost*** when the previously promoted ***2p*** electron now drops down to the ***sp***-hybrid level.

Shape of the sp hybrid orbital

What is the shape of the electron cloud corresponding to the sp hybrid orbital? As we might expect, the characteristics of the parents can be seen in the progeny: the ***p***-orbital is elongated, and so is the hybrid, but since the ***s***-orbital is spherical, the hybrid is not as drawn out as a pure ***p*** orbital. Notice that whereas a single ***p***-orbital has lobes on both sides of the atom, a single ***sp***-hybrid has most of its electron density on ***one*** side.The two ***sp*** hybrid orbitals in the bonded beryllium atom point away from the central atom in opposite directions. We can expect any central atom that uses ***sp***-hybridization in bonding to exhibit linear geometry when incorporated into a molecule.

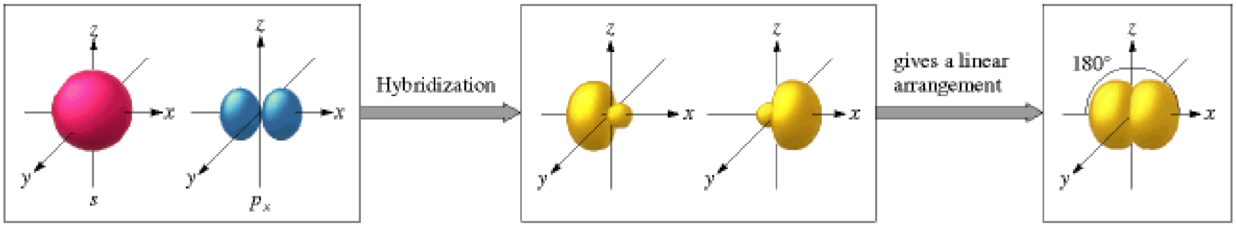
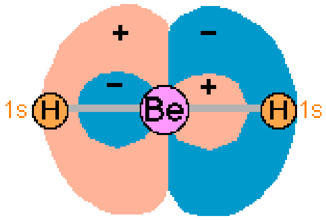


Fig. 16: Formation of a *sp*-hybrid orbital

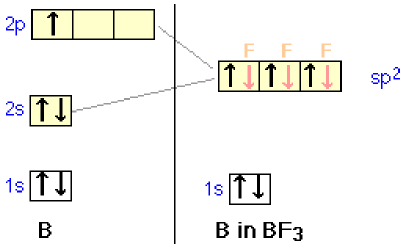
Mixing of an *s*- and a *p*-orbital yields the two *sp*-hybrid orbitals shown in the middle picture. At the far right the two hybrid orbitals are centered on the same atom, giving rise to the linear geometry.
[From www.wellesley.edu/Chemistry/chem120/hybrids.html]

Sigma bonds



The figure depicts the electron clouds in a complete beryllium hydride molecule. Notice that the hydrogen 1***s*** orbitals are ***not*** hybridized here; they are still spherical. The two "bonds" in beryllium hydride are the regions of overlap between the hydrogen ***1s*** and beryllium ***sp***-hybrid orbitals. Since this bonding region is symmetrical about the line of centers joining the three atoms, the resulting bond is said to be of the σ (sigma) type. A σ bond is one whose electron density is concentrated around the line-of-centers between two or more atoms.

7.3 Trigonal (sp^2) hybridization



We can now go on to apply the same ideas to some other simple molecules. In boron trifluoride, for example, we start with the boron atom, which has three outer-shell electrons in its normal or ground state, and three fluorine atoms, each with seven outer electrons. As shown in the upper diagram, one of the three boron electrons is unpaired in the ground state. In order to explain the trivalent bonding of boron, we postulate that the atomic ***s***- and ***p***- orbitals in the outer shell of boron mix to form three equivalent hybrid orbitals. These particular orbitals are called ***sp***^{2} hybrids, meaning that this set of orbitals is derived from one ***s***-orbital and two ***p***-orbitals of the free atom.

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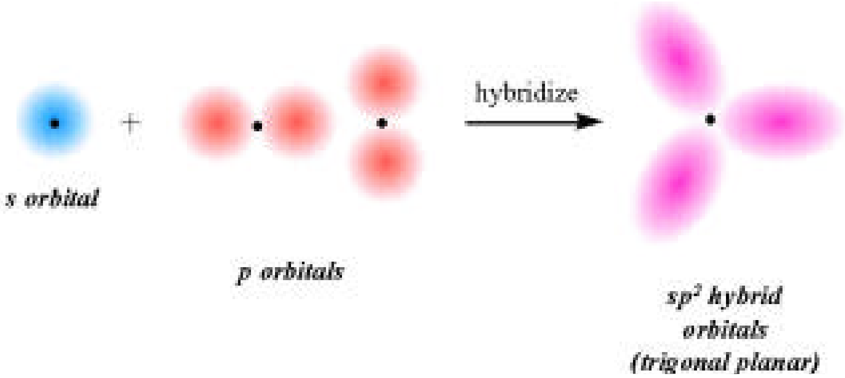
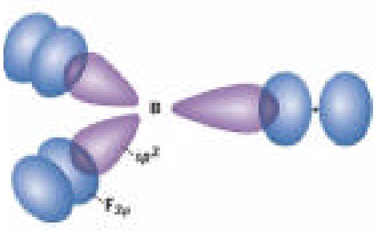
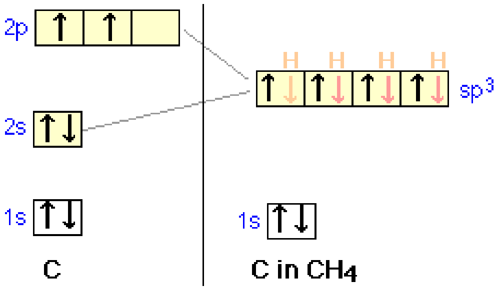


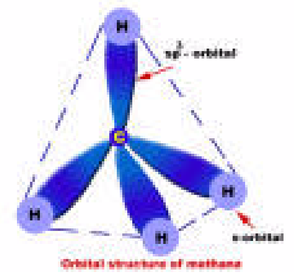


Boron trifluoride has a plane trigonal shape; a 2***p*** orbital on each fluorine atom overlaps with a boron ***sp***^{2} hybrid. In general, we can expect that all molecules in which a central atom uses three equivalent ***sp***^{2} hybrid orbitals will exhibit plane trigonal geometry, since this represents the most symmetrical, and hence "equivalent", arrangement of the three bonds.

7.4 Tetrahedral (*sp*^{3}) hybridization

Let us now look at several tetravalent molecules, and see what kind of hybridization might be involved when four outer atoms are bonded to a central atom. Perhaps the commonest and most important example of this bond type is methane, CH_4.

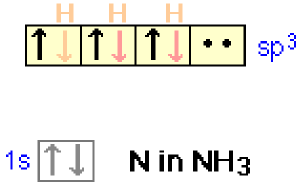


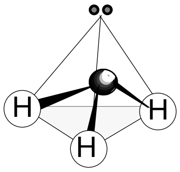


In the ground state of the free carbon atom, there are two unpaired electrons in separate ***2p*** orbitals. In order to form four bonds (tetravalence), need four unpaired electrons in four separate but equivalent orbitals. We assume that the single ***2s***, and the three ***2p*** orbitals of carbon mix into ***four sp***^{3} hybrid orbitals which are chemically and geometrically identical; the latter condition implies that the four hybrid orbitals extend toward the corners of a tetrahedron centered on the carbon atom.

Lone pair electrons

If lone pair electrons are present on the central atom, these can occupy one or more of the ***sp***^{3} orbitals. This causes the molecular geometry to be different from the coordination geometry, which remains tetrahedral.

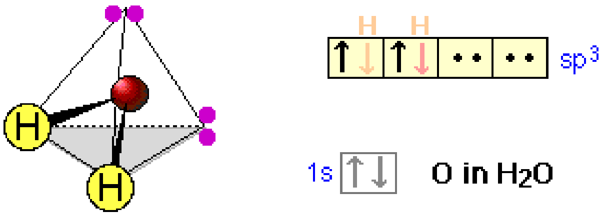




In the **ammonia** molecule, for example, the nitrogen atom normally has three unpaired ***p*** electrons, but by mixing the ***2s*** and ***3p*** orbitals, we can create four ***sp***^{3}-hybrid orbitals just as in carbon. Three of these can form shared-electron bonds with hydrogen, resulting in ammonia, NH_3. The fourth of the ***sp***^{3} hybrid orbitals contains the two remaining outer-shell electrons of nitrogen which form a non-bonding lone pair. In acidic solutions these can coordinate with a hydrogen ion, forming the ammonium ion NH_4^+.

Although no bonds are formed by the lone pair in NH_3, these electrons do give rise to a charge cloud that takes up space just like any other orbital, and thus the nonbonding electrons occupy one of the four tetrahedral regions. The other three corners of the tetrahedron are occupied by hydrogen atoms, and these three points define the base of the pyramid that describes the shape of molecules containing three bonding pairs and one lone pair of electrons around the central atom.

In the **water** molecule, the oxygen atom can form four ***sp***^{3} orbitals. Two of these are occupied by the two lone pairs on the oxygen atom, while the other two are used for bonding. The observed H-O-H bond angle in water (104.5°) is less than the tetrahedral angle (109.5°); one explanation for this is that the non-bonding electrons tend to remain closer to the central atom and thus exert greater repulsion on the other orbitals, thus pushing the two bonding orbitals closer together.



Hybridization can also help explain the existence and structure of many **inorganic molecular ions**. Consider, for example, the zinc compounds shown here. At the top is shown the electron configuration of atomic zinc, and just below it, of the divalent zinc ion. Notice that this ion has no electrons at all in its 4-shell. In zinc chloride, shown in the third row, there are two equivalent chlorine atoms bonded to the zinc. The bonding orbitals are of ***sp*** character; that is, they are hybrids of the ***4s*** and one ***4p*** orbital of the zinc atom. Since these orbitals are empty in the isolated zinc ion, the bonding electrons themselves are all contributed by the chlorine atoms, or rather, the chlor***ide ions***, for it is these that are the bonded species here. Each chloride ion possesses a complete octet of electrons, and two of these electrons occupy each ***sp*** bond orbital in the zinc chloride complex ion. This is an example of a ***coordinate covalent bond***, in which the bonded atom contributes both of the electrons that make up the shared pair.

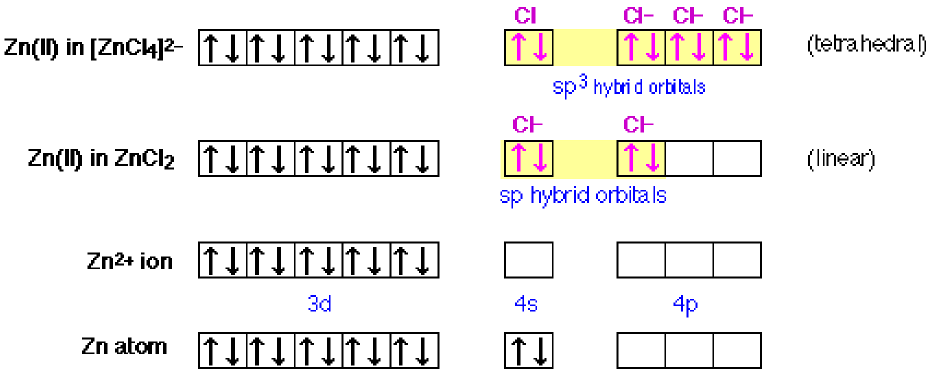


Fig. 17: Multiple hybridization schemes in zinc compounds

The empty 4*s* and 4*p* orbitals of Zn^{2+} allow it to accept electron pairs from two chlorine atoms in solid $ZnCl_2$, or from four in the complex ion tetrachlorozinc(II).

The ***tetrachloro zinc ion*** is another structure derived from zinc and chlorine. As we might expect, this ion is tetrahedral; there are four chloride ions surrounding the central zinc ion. The zinc ion has a charge of ***+2***, and each chloride ion is -1, so the net charge of the complex ion is ***-2***.

7.5 Hybrid types and multiple bonds

Up to now we have dealt with molecules in which the orbitals on a single central atom are considered to be hybridized. Let us now see how these various models of hybridization can help us understand bonding between pairs of such atoms. Because of its extreme importance, we will use the element carbon as an example.

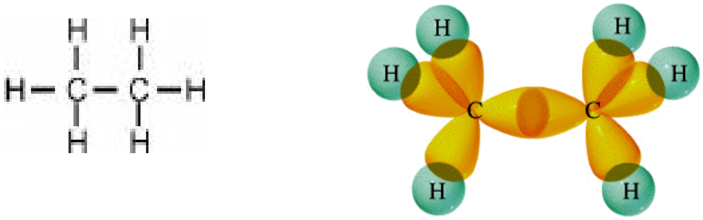
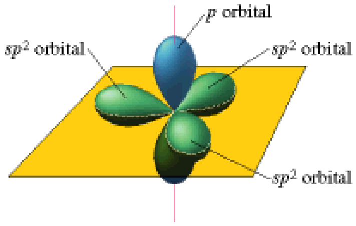


Fig. 18: Bonding in ethane

The carbon-carbon bond is formed by overlap of an sp^3 orbital from each carbon, creating a space in which two electrons can be simultaneously close to two nuclei as in any covalent bond.

We have already seen how ***sp*** hybridization in carbon leads to a combining power of four in the methane molecule. Two such tetrahedrally coordinated carbons can link up together to form the molecule ***ethane*** C_2H_6. In this molecule, each carbon is bonded in the same way as the other; each is linked to four other atoms, three hydrogens and one carbon, by means of straight-line σ bonds.The ability of carbon-to-carbon linkages to extend themselves indefinitely and through all coordination positions accounts for the millions of organic molecules that are known.

Trigonal hybridization in carbon: the double bond



But carbon and hydrogen can also form a compound, ethylene, in which each carbon atom is linked to only ***three*** other atoms. Here, we can regard carbon as being ***tri***valent. We can explain this trivalence by supposing that the orbital hybridization in carbon is in this case not ***sp***^{3}***, but is sp***^{2} instead; in other words, only two of the three ***p*** orbitals of carbon mix with the 2***s*** orbital to form hybrids; the remaining ***p***-orbital, which we will call the ***p***$_z$ orbital, does not take part in bond formation. Each carbon is bonded to three other atoms in the same kind of plane trigonal configuration that we saw in the case of boron trifluoride, where the same kind of hybridization occurs. Notice that the bond angles around each carbon are all 120°.

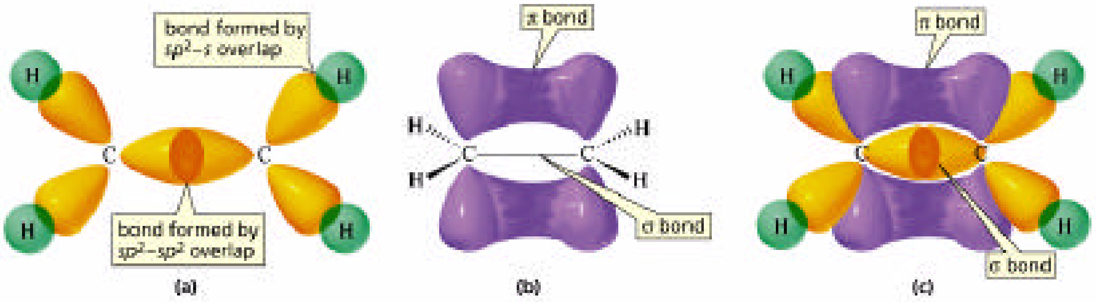


Fig. 19: bond hybridization in ethylene

These three views of the ethylene molecule emphasize different aspects of the disposition of shared electron pairs in the various bonding orbitals of ethene (ethylene). **(a)** The "backbone" structure consisting of sigma (σ) bonds formed from the three sp^2-hybridized orbitals on each carbon. **(b)** The π (pi) bonding system formed by overlap of the unhybridized pz orbital on each carbon. The pi orbital has two regions of electron density extending above and below the plane of the molecule. **(c)** A cutaway view of the combined sigma and pi system.

This alternative hybridization scheme explains how carbon can combine with four atoms in some of its compounds and with three other atoms in other compounds. You may be aware of the conventional way of depicting carbon as being tetravalent in ***all*** its compounds; it is often stated that carbon always forms four bonds, but that sometimes, as in the case of ethylene, one of these may be a ***double*** bond. This concept of the multiple bond preserves the idea of tetravalent carbon while admitting the existence of molecules in which carbon is clearly combined with fewer than four other atoms.

As shown above, ethylene can be imagined to form when two -CH2 fragments link together through overlap of the half-filled sp2 hybrid orbitals on each. Since sp2 hybrid orbitals are always in the same plane, the entire ethylene molecule is planar. However, there remains on each carbon atom an electron in an unhybridized atomic pz orbital that is perpendicular to the molecular plane. These two parallel pz orbitals will interact with each other; the two orbitals merge, forming a sausage-like charge cloud (the p bond) that extends both above and below the plane of the molecule. It is the pair of electrons that occupy this new extended orbital that constitutes the "fourth" bond to each carbon, and thus the "other half" of the double bond in the molecule.

More about sigma and pi bonds

The σ (sigma) bond has its maximum electron density along the line-of-centers joining the two atoms (below left). Viewed end-on, the σ bond is cylindrically symmetrical about the line-of-centers. It is this symmetry, rather than its parentage, that defines the sigma bond, which can be formed from the overlap of two ***s***-orbitals, from two ***p***-orbitals arranged end-to-end, or from an ***s***- and a ***p***-orbital. They can also form when

sp-hybrid orbitals on two atoms overlap end-to-end.

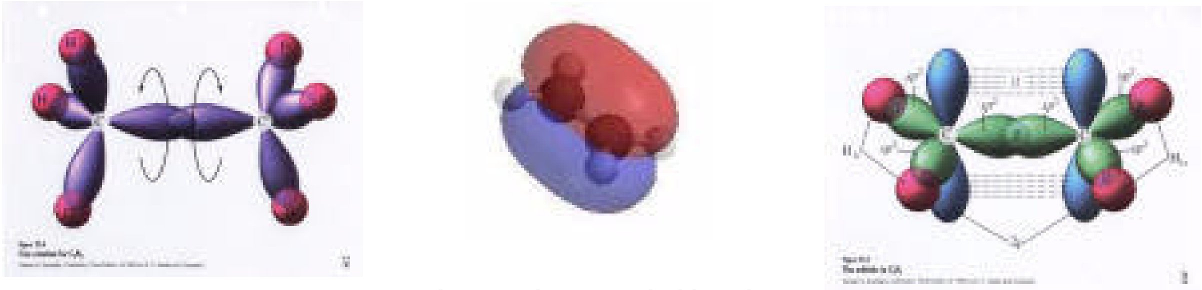


Fig. 20: Sigma- and pi bonds.

The sigma bond, being symmetric about the x-axis of the molecule, can allow free rotation of the two joined atoms. Pi bonds prevent this rotation, giving rise to the possibility of geometrical isomers in multiply-bonded compounds.

Pi orbitals, on the other hand, require the presence of two atomic ***p*** orbitals on adjacent atoms. Most important, the charge density in the π orbital is concentrated above and below the molecular plane; it is almost zero along the line-of-centers between the two atoms.It is this perpendicular orientation with respect to the molecular plane (and the consequent lack of cylindrical symmetry) that defines the π orbital. The combination of a σ bond and a π bond extending between the same pair of atoms constitutes the double bond in molecules such as ethylene.

Triple bonds

We have not yet completed our overview of multiple bonding, however. Carbon and hydrogen can form yet another compound, acetylene, in which each carbon is connected to only ***two*** other atoms: a carbon and a hydrogen. This can be regarded as an example of ***di***valent carbon, but is usually rationalized by writing a ***triple*** bond between the two carbon atoms.

We assume here that since two geometrically equivalent bonds are formed by each carbon, this atom must be ***sp***-hybridized in acetylene. On each carbon, one ***sp*** hybrid bonds to a hydrogen and the other bonds to the other carbon atom, forming the σ bond skeleton of the molecule.

In addition to the ***sp*** hybrids, each carbon atom has two half-occupied ***p*** orbitals, oriented at right angles to each other, and to the interatomic axis. These are two sets of parallel and adjacent ***p*** orbitals, and they can thus merge into two sets of π orbitals.

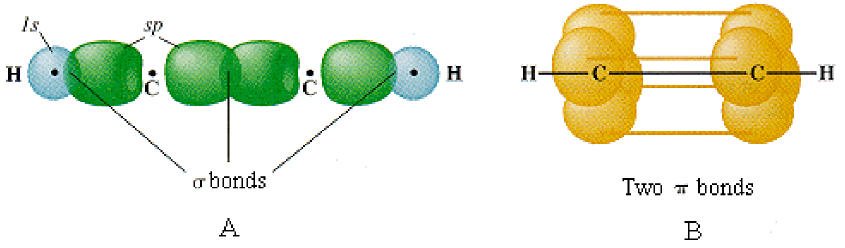


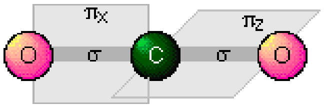
Fig. 21: Triple bond in acetylene.

The two pi bonds (occupying orthogonal planes) are depicted by the colored horizontal lines on the right.

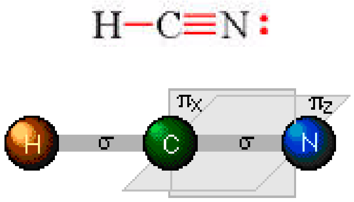
The triple bond in acetylene is seen to consist of one σ bond joining the line-of-centers between the two carbon atoms, and two π bonds whose lobes of electron density are in mutually-perpendicular planes. The acetylene molecule is of course ***linear***, since the angle between the two ***sp*** hybrid orbitals that produce the σ skeleton of the molecule is

180°.

Multiple bonds between unlike atoms



Multiple bonds can also occur between dissimilar atoms. For example, in **carbon dioxide** each carbon atom has two unhybridized atomic ***p*** orbitals, and each oxygen atom still has one p orbital available. When the two O-atoms are brought up to opposite sides of the carbon atom, one of the p orbitals on each oxygen forms a π bond with one of the carbon ***p***-orbitals. In this case, ***sp***-hybridization is seen to lead to two double bonds. Notice that the two C-O π bonds are mutually perpendicular.



Similarly, in **hydrogen cyanide**, HCN, we assume that the carbon is ***sp***-hybridized, since it is combined with only two other atoms, and is hence in a divalent state. One of the ***sp***-hybrid orbitals overlaps with the hydrogen 1***s*** orbital, while the other overlaps end-to-end with one of the three unhybridized ***p*** orbitals of the nitrogen atom. This leaves us with two nitrogen ***p***-orbitals, which form two mutually perpendicular π bonds to the two unhybridized ***p*** orbitals on the carbon. Hydrogen cyanide thus contains one single and one triple bond, the latter consisting of a σ bond from the overlap of the two ***sp*** hybrid orbitals, and two mutually perpendicular π] bonds deriving from unhybridized atomic ***p*** orbitals on the carbon and nitrogen atoms.

7.6 Conjugated double bonds

We have seen that the π bonding orbital is distinctly different in shape and symmetry from the σ bond. There is another important feature of the π bond that is of far-reaching consequence, particularly in organic and coordination chemistry.

Consider, for example, an extended hydrocarbon molecule in which alternate pairs of carbon atoms are connected by double and single bonds. Each non-terminal carbon atom forms two s bonds to two other carbons and to a hydrogen (not shown.) This molecule can be viewed as a series of ethylene molecules joined together end-to-end. Each carbon, being sp hybridized, still has a half-filled atomic p orbital. Since these p orbitals on adjacent carbons are all parallel, we can expect them to interact with each other to form p bonds between alternate pairs of carbon atoms as shown below.

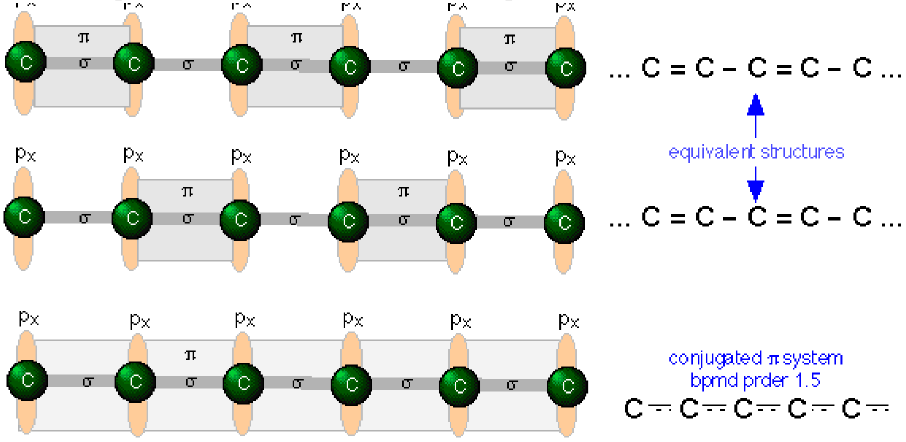
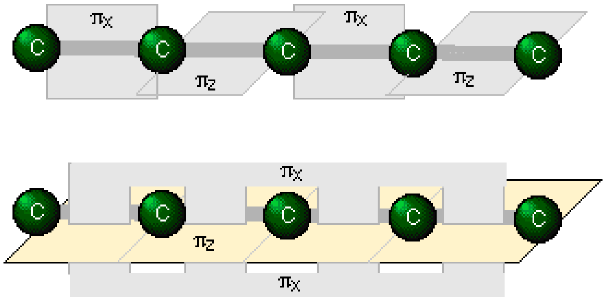


Fig. 22:
A conjugated carbon chain
When single and double bonds alternate in a chain of carbon atoms, the two π bonding arrangements shown at the top are equivalent. The resulting structure is said to be conjugated and tend to be especially stable. The C–C bond order is 1.5.

Each carbon, being ***sp*** hybridized, has a half-filled atomic ***p*** orbital that can form a p bond with either of its neighbors (but not with both at the same time.) You will recall that when there are two equivalent choices for the arrangements single and double bonds in a molecule, we generally consider the structure to be a ***resonance hybrid***. In keeping with this idea, we would expect the electron density in the π system of this kind to be extended or shared out evenly along the entire molecular framework (bottom structure above.)

A system of alternating single and double bonds, as we have here, is called a ***conjugated*** system. Chemists say that the π bonds in a conjugated system are ***delocalized***; they are, in effect, “smeared out” over the entire length of the conjugated part of the molecule.

An even higher degree of conjugation exists in compounds containing extended $(C=C)_n$ chains. These compounds, known as **cumulenes**, form polymers that exhibit interesting electrical properties and whose derivatives can act as “organic wires”.



$$\ldots C = C = C = C \ldots$$

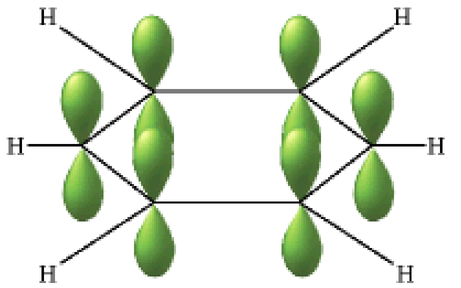
Benzene

The classic example of π bond delocalization is found in the cyclic molecule benzene (C_6H_6), which consists of six carbon atoms bound together in a hexagonal arrangement. Each carbon has a single hydrogen atom attached to it. Earlier, you learned to represent the benzene structure as a composite of two resonance forms.

Modern hybridization theory offers a somewhat less contrived view: each carbon atom is ***sp*** hybridized, producing trigonal bond geometry about each node in the hexagon. Each carbon atom also has a half-occupied unhybridized ***p*** orbital; two of these together, on adjacent carbon atoms, can form two equivalent sets of π bonds as shown in the center section. The net effect is depicted at the right. The π bonding system is drawn out into two donut shaped electron clouds, one on either side of the molecular plane. The “double bonds” in benzene are delocalized so that they extend around the entire hexagonal skeleton.

7.7 The nitrate ion

Pi **bond delocalization** furnishes a means of expressing the structures of other molecules that require more than one electron-dot or structural formula for their accurate



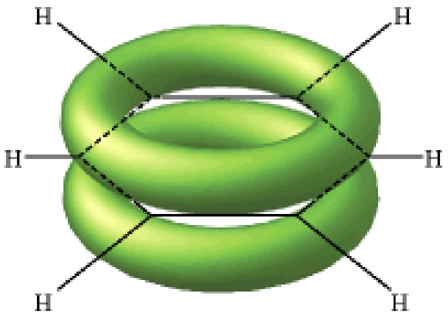
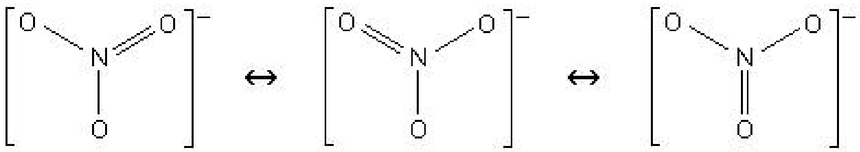
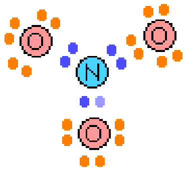


Fig. 23: Bonding in benzene

Left: the unhybridized 2*p* atomic orbitals of the carbon atoms are shown superimposed on the trigonally-hybridized *sp*^{2} *sigma* bonding system. Right: overlap of the *sp*^{2} orbitals leads to a *pi* orbital system that extends around the molecule

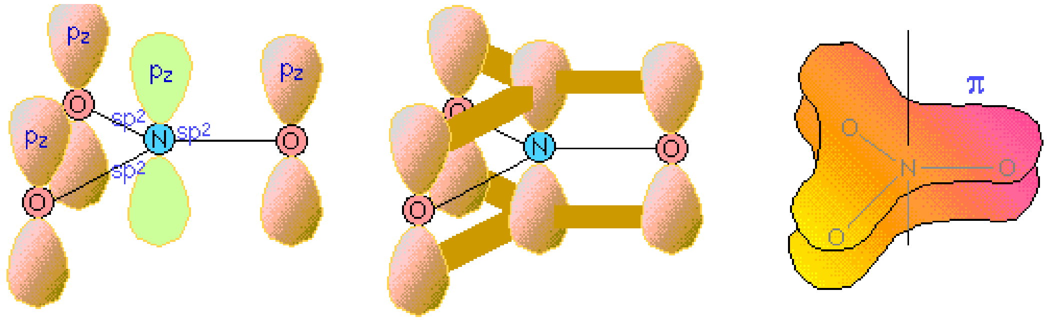
representation. A good example is the nitrate ion.





Nitrogen has three half-occupied ***p*** orbitals available for bonding, all perpendicular to one another. Since the nitrate ion is known to be planar, we are forced to assume that the nitrogen outer electrons are ***sp***^{2} hybridized. The addition of an extra electron fills all three hybrid orbitals completely. Each of these filled ***sp***^{2} orbitals forms a σ bond by overlap with an empty oxygen 2***p***$_z$ orbital; this, you will recall, is an example of ***coordinate covalent bonding***, in which one of the atoms contributes both of the bonding electrons.

The empty oxygen ***2p*** orbital is made available when the oxygen electrons themselves become ***sp*** hybridized; we get three filled ***sp*** hybrid orbitals, and an empty ***2p*** atomic orbital, just as in the case of nitrogen.



Unhybridized atomic p orbitals and σ-bonding backbone

The π bonds are formed by overlap of the p_z orbitals

A representation of the entire NO_3^- molecule

Fig. 24: *Sigma* and *pi* bonds in the nitrate ion

The π bonding system arises from the interaction of one of the occupied oxygen ***sp*** orbitals with the unoccupied ***2p***$_z$ orbital of the nitrogen. Notice that this, again, is a coordinate covalent sharing, except that in this instance, it is the ***oxygen*** atom that donates both electrons.

Pi bonds can form in this way between the nitrogen atom and any of the three oxygens; there are thus three equivalent π bonds possible, but since nitrogen can only form one complete π bond at a time, the π bonding is divided up three ways, so that each N-O bond has a bond order of 4/3.

7.8 Hybrids involving *d* orbitals

In atoms that are below those in the first complete row of the periodic table, the simple octet rule begins to break down. For example, we have seen that PCl_3 does conform to the octet rule but PCl_5 does not. We can describe the bonding in PCl_3 very much as we do NH_3: four ***sp***^{3} hybridized orbitals, three of which are shared with electrons from other atoms and the fourth containing a nonbonding pair.

In order to understand the bonding in PCl_5, we have to consider the ***d*** orbitals in addition to the ***s***- and ***p*** types. When ***d*** orbitals are energetically close to the outmost ***s***- and ***p*** orbitals, additional hybrid types can be built. In the case of PCl_5 we need five hybrid orbitals, and these can be constructed by adding two ***d***-orbital functions to the mathematical mixture of one ***s***- and two ***p***-orbitals, resulting in five ***sp***^{3}***d***^{2} hybrid orbitals directed toward the corners of a trigonal bipyramid, as is predicted by VSEPR theory.

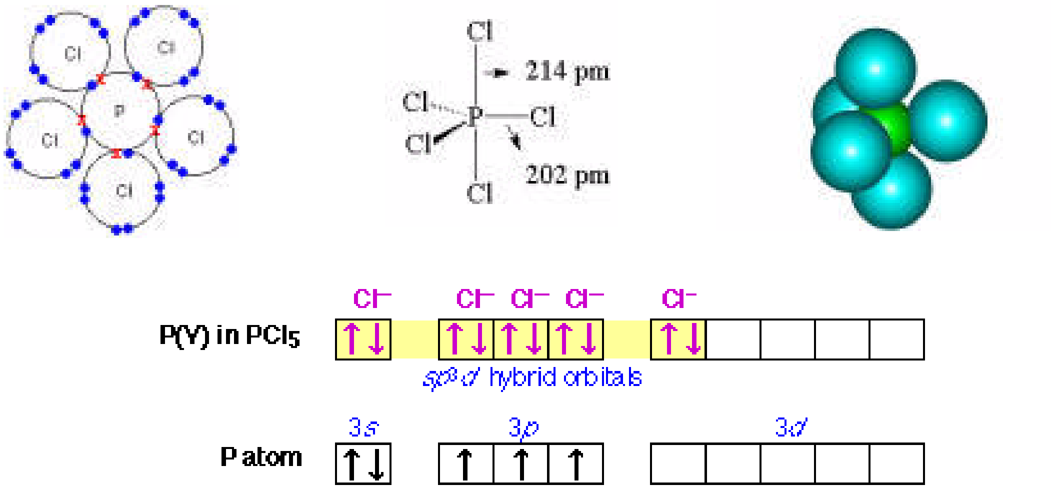


Fig. 25: Bonding in PCl_5
Notice that in the trigonal bipyramid, the axial and equatorial (in-plane) atoms are not equivalent as evidenced by the shorter lengths of the equatorial bonds.

Some of the most important and commonly encountered compounds which involve the ***d*** orbitals in bonding are the ***transition metal complex***. The term “complex” in this context means that the molecule is composed of two or more kinds of species, each of which can have an independent existence. For example, the ions Pt^{2+} and Cl^- can form the ion $[PtCl_4]^{2-}$ which is found experimentally to be square planar. To understand the hybridization scheme, it helps to start with the neutral Pt atom, then imagine it losing two electrons to become an ion, followed by grouping of the two unpaired 5***d*** electrons into a single ***d*** orbital, leaving one vacant.This vacant orbital, along with the 6***s*** and two of the 6***p*** orbitals, can then accept an electron pair from four chlorines.

Octahedral coordination

The molecule ***sulfur hexafluoride*** SF_6 exemplifies one of the most common types of ***d***-orbital hybridization. The six bonds in this octahedrally-coordinated molecule are derived from mixing six atomic orbitals into a hybrid set. The easiest way to understand how these come about is to imagine that the molecule is made by combining an imaginary S^{6+} ion (which we refer to as the S(VI) valence state) with six F^- ions to form the neutral molecule. These now-empty 3***s*** and 3***p*** orbitals then mix with two 3***d*** orbitals to form the ***sp***^{3}***d***^{2} hybrids.

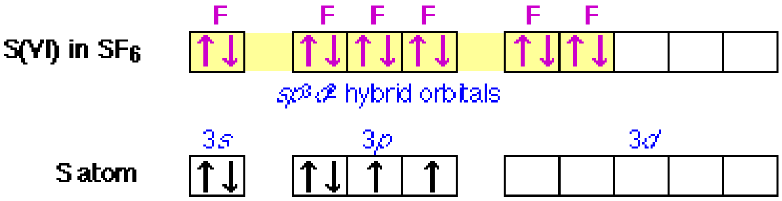


Fig. 26: Bonding in sulfur hexafluoride

"S(VI)" represents the six-coordinated *valence state* of sulfur, which is considered to have lost its 3*s* and 3*p* electrons, making six equivalent *sp*^{3}*d*^{2}-hybridized orbitals available for accepting lone pairs contributed by the fluorine atoms.

This same type of hybridization can be invoked to explain the structures of many transition metal cations; the ***hexamminezinc(II) cation*** depicted below is typical.

7.9 Transition metal complexes

Some of the most important and commonly encountered compounds which involve the d orbitals in bonding are the transition metal complexes. The term "complex" in this context means that the molecule is composed of two or more kinds of species, each of which can have an independent existence.

Square-planar molecules: *dsp*^{2} hybridization

For example, the ions Pt^{2+} and Cl^- can form the ion $[PtCl_4]^{2-}$. To understand the hybridization scheme, it helps to start with the neutral Pt atom, then imagine it losing two electrons to become an ion, followed by grouping of the two unpaired 5***d*** electrons into a single ***d*** orbital, leaving one vacant.This vacant orbital, along with the 6s and two of the 6***p*** orbitals, can then accept an electron pair from four chlorines.

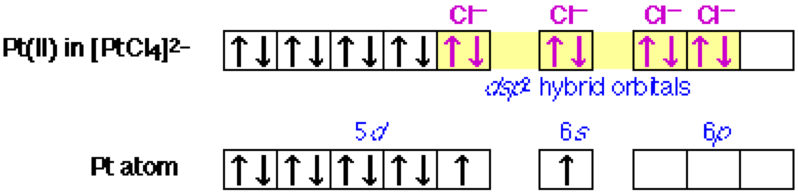


Fig. 27: bonding in $[PtCl_4]^{2-}$

All four Pt-Cl bonds are equivalent and point to the corners of a square centered on the Pt

All of the four-coordinated molecules we have discussed so far have tetrahedral geometry around the central atom. Methane, CH_4, is the most well known example. It may come as something as a surprise, then, to discover that the **tetrachlorplatinum (II) ion $[PtCl_4]^{2-}$** has an essentially two-dimensional square-planar configuration. This type of bonding pattern is quite common when the parent central ion (Pt^{2+} in this case) contains only eight electrons in its outmost d-subshell.

Octahedral complexes: *sp^3d^2* and *d^2sp^3*

Many of the most commonly encountered transition metal ions accept electron pairs from donors such as CN^- and NH_3 (or lacking these, even from H_2O) to form octahedral coordination complexes. The **hexamminezinc(II)** cation depicted below is typical.

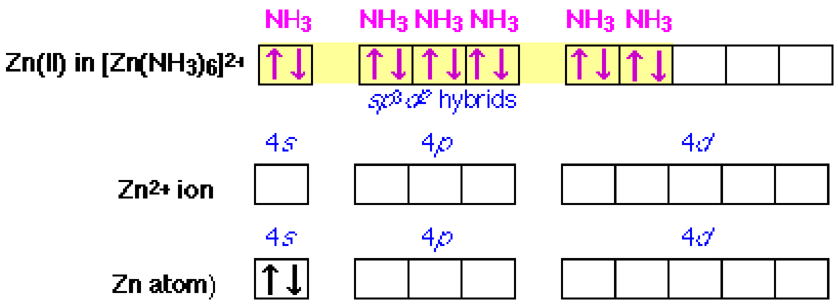


Fig. 28: bonding in $Zn(NH_3)_6^{2+}$
Again, the bonding electron pairs are contributed by the ligands, in this case ammonia, and they fill hybrids made by mixing the lowest-energy unoccupied orbitals of the central atom.

In ***sp^3d^2*** hybridization the bonding orbitals are derived by mixing atomic orbitals having the same principal quantum number (***n*** = 4 in the preceding example). A slightly different arrangement, known as ***d^2sp^3*** hybridization, involves ***d*** orbitals of lower principal quantum number. This is possible because of the rather small energy differences between the ***d*** orbitals in one “shell” with the ***s*** and ***p*** orbitals of the next higher one—hence the term “inner orbital” complex which is sometimes used to describe ions such as **hexaminecobalt(III)**, shown below. Both arrangements produce octahedral coordination geometries.

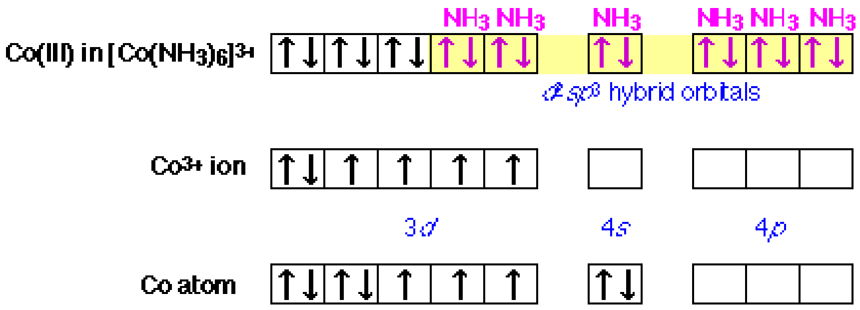


Fig. 29: bonding in $Co(NH_3)_6^{2+}$
Here the two *d* orbitals needed for mixing are made available by consolidating the 3*d* electrons of Co.

In some cases, the same central atom can form either inner or outer complexes depending on the particular ligand and the manner in which its electrostatic field affects the relative energies of the different orbitals.Thus the hexacyanoiron(II) ion utilizes the iron 3d orbitals, whereas hexaaquoiron(II) achieves a lower energy by accepting two H2O molecules in its 4d orbitals.

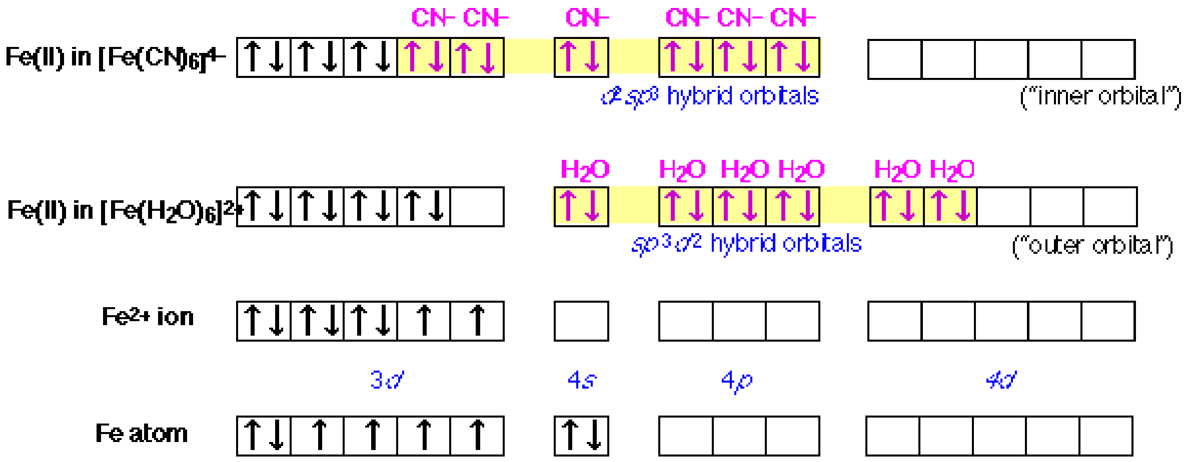


Fig. 30: “Inner” and “outer” orbital octahedral coordination

Although this “inner-outer” hybrid model was a instrumental in explaining the properties of transition metal complexes in the first half of the 20th century, it has now been replaced with a more comprehensive model known as ***ligand field theory*** which is introduced

7.10 Limitations of the hybrid model

As is the case with any scientific model, the hybridization model of bonding is useful only to the degree to which it can predict phenomena that are actually observed. Most models contain weaknesses that place limits on their general applicability. The need for caution in accepting this particular model is made more apparent when we examine the shapes of the molecules below the first row of the periodic table. For example, we would expect the bonding in **hydrogen sulfide** to be similar to that in water, with tetrahedral geometry around the sulfur atom. Experiments, however, reveal that the bond H-S-H bond angle is only 92°. Hydrogen sulfide thus deviates much more from tetrahedral geometry than does water, and there is no apparent and clear reason why it should. It is certainly difficult to argue that electron-repulsion between the two nonbonding orbitals is pushing the H-S bonds closer together (as is supposed to happen to the H-O bonds in water); many would argue that this repulsion would be less in hydrogen sulfide than in water, since sulfur is a larger atom and is hence less electronegative.

It might be, then, that our model of orbital hybridization into four equivalent ***sp***^{3} orbitals does not apply to H_2S. It looks like the “simple” explanation that bonding occurs through two half occupied atomic-***p*** orbitals 90° apart comes closer to the mark. Perhaps hybridization is not an all-or-nothing phenomenon; perhaps the two ***3p*** orbitals are substantially intact in hydrogen sulfide, or are only hybridized very slightly. In general, the hybridization model does not work very well with nonmetallic elements below the first row of the periodic table, and there is as yet no clear explanation why. We must simply admit that we have reached one of the many points in chemistry where our theory is not sufficiently developed to give a clear and unequivocal answer. This does not detract, however, from the wide usefulness of the hybridization model in elucidating the bond character and bond shapes in the millions of molecules based on first-row elements, particularly of carbon.

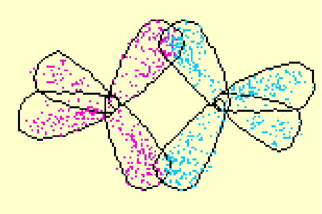
Are hybrid orbitals real?

The justification we gave for invoking hybridization in molecules such as BeH_2, BF_3 and CH_4 was that the bonds in each are geometrically and chemically equivalent, whereas the atomic ***s***- and ***p***-orbitals on the central atoms are not. By combining these into new orbitals of ***sp***, ***sp***^{2} and ***sp***^{3} types we obtain the required number of completely equivalent orbitals. This seemed easy enough to do on paper; we just drew little boxes and wrote "***sp***^{2}" or whatever below them. But what is really going on here?

The full answer is beyond the scope of this course, so we can only offer the following very general explanation. First, recall what we mean by "orbital": a mathematical function ψ having the character of a standing wave whose square ψ^2 is proportional to the probability of finding the electron at any particular location in space. The latter, the electron density distribution, can be observed (by X-ray scattering, for example), and in this sense is the only thing that is "real".

A given standing wave (ψ function) can be synthesized by combining all kinds of fundamental wave patterns (that is, atomic orbitals) in much the same way that a color we observe can be reproduced by combining different sets of primary colors in various proportions. In neither case does it follow that these original orbitals or colors are actually present in the final product.

An alternative to hybrids: the Bent-Bond model.



It turns out, in fact, that the electron distribution and bonding in ethylene can be equally well described by assuming no hybridization at all. The ***"bent bond"*** model depicted at the right requires only that the directions of some of the atomic-p orbitals be distorted sufficiently to provide the overlap needed for bonding. So one could well argue that hybrid orbitals are ***not*** "real"; they do turn out to be convenient for understanding the bonding of simple molecules at the elementary level, and this is why we use them.

8. The molecular orbital Model

In the models of chemical bonding we have discussed up to now, we have assumed that the electrons that interpose themselves between adjacent nuclei (the "bonding electrons") are in orbitals associated with one or the other of the parent atoms. In the simple Lewis and VSEPR models, these were just the ordinary ***s***, ***p***, and ***d*** orbitals. The more sophisticated hybridization model recognized that these orbitals will be modified by the interaction with other atoms, and the concept of mixed (hybrid) orbitals was introduced.

These models in which the bonding electrons are regarded as occupying atomic-type orbitals are known generally as valence-***bond*** models. Although they are quite useful for understanding many of the features of chemical bonding (such as molecular shapes), valence-bond models are generally unable to predict more detailed characteristics such as the numerical values of bond energies.

The main difficulty with the valence-bond approach is that the atomic orbitals, whether hybridized or not, result from the interaction of electrons with a single central force field-- that of the atomic nucleus. An electron that spends most of its time between two nuclei will find itself in a very different, two-center force field, and this will give rise to new types of orbitals that are better characterized as molecular, rather than as atomic orbitals.

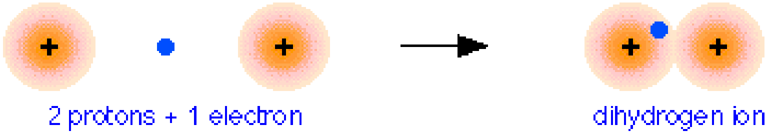
8.1 Molecular orbitals

OnPage 12 it was pointed out that an electron that occupies the region of space between two nuclei exerts a mutual attraction on the two positive centers, leading to a net binding effect. Conversely, if the electron is off to one side, in an anti-binding region, it actually adds to the repulsion between the two nuclei.

The easiest way of visualizing a molecular orbital is to start by picturing two isolated atoms and the electron orbitals that each would have separately. These are just the orbitals of the separate atoms, by themselves, which we already understand. We will then try to predict the manner in which these atomic orbitals interact as we gradually move the two atoms closer together. Finally, we will reach some point where the internuclear distance corresponds to that of the molecule we are studying. The corresponding orbitals will then be the molecular orbitals of our new molecule.

8.2 The hydrogen molecule ion

To see how this works, we will consider the simplest possible molecule, H_2^+. This is the ***hydrogen molecule ion***, which consists of two nuclei of charge +1, and a single electron shared between them.



As two H nuclei move toward each other, the 1***s*** atomic orbitals of the isolated atoms gradually merge into a new molecular orbital in which the greatest electron density falls between the two nuclei. Since this is just the location in which electrons can exert the most attractive force on the two nuclei simultaneously, this arrangement constitutes a ***bonding*** molecular orbital. Regarding it as a three- dimensional region of space, we see that it is symmetrical about the line of centers between the nuclei; in accord with our usual nomenclature, we refer to this as a σ (***sigma***) orbital.

8.3 Bonding and antibonding molecular orbitals

Conserving orbitals

There is one minor difficulty: we started with two orbitals (the 1***s*** atomic orbitals), and ended up with only one orbital. Now according to the rules of quantum mechanics, orbitals cannot simply appear and disappear at our convenience. For one thing, this would raise the question of at just what internuclear distance do we suddenly change from having two orbitals, to having only one? It turns out that when orbitals interact, they are free to change their forms, but there must always be the same number. This is the same as saying that there must always be the same number of possible allowed sets of electron quantum numbers.

In-phase and out-of-phase wave combinations

How can we find the missing orbital? To answer this question, we must go back to the wave-like character of orbitals that we developed in our earlier treatment of the hydrogen atom. You are probably aware that wave phenomena such as sound waves, light waves, or even ocean waves can combine or interact with one another in two ways: they can either reinforce each other, resulting in a stronger wave, or they can interfere with and partially destroy each other. A roughly similar thing occurs when the “matter waves” corresponding to the two separate hydrogen 1***s*** orbitals interact; both in-phase and out-of-phase combinations are possible, and both occur. One of the resultants is the bonding orbital that we just considered. The other, corresponding to out-of-phase combination of the two orbitals, gives rise to a molecular orbital that has its greatest electron probability in what is clearly the antibonding region of space. This second orbital is therefore called an ***antibonding*** orbital.

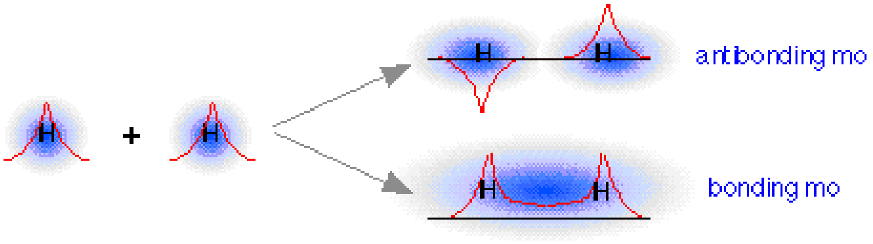


Fig. 31: Bonding and antibonding molecular orbitals formed by in- and out-of-phase combinations of atomic orbitals

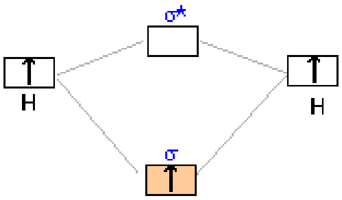
When the two 1s wave functions combine out-of-phase, the regions of high electron probability do not merge. In fact, the orbitals act as if they actually repel each other. Notice particularly that there is a region of space exactly equidistant between the nuclei at which the probability of finding the electron is zero. This region is called a ***nodal surface***, and is characteristic of antibonding orbitals. It should be clear that any electrons that find themselves in an antibonding orbital cannot possibly contribute to bond formation; in fact, they will actively oppose it.

We see, then, that whenever two orbitals, originally on separate atoms, begin to interact as we push the two nuclei toward each other, these two atomic orbitals will gradually merge into a pair of molecular orbitals, one of which will have bonding character, while the other will be antibonding. In a more advanced treatment, it would be fairly easy to show that this result follows quite naturally from the wave-like nature of the combining orbitals.

What is the difference between these two kinds of orbitals, as far as their potential energies are concerned? More precisely, which kind of orbital would enable an electron to be at a lower potential energy? Clearly, the potential energy decreases as the electron moves into a region that enables it to “see” the maximum amount of positive charge. In a simple diatomic molecule, this will be in the internuclear region-- where the electron can be simultaneously close to two nuclei. The bonding orbital will therefore have the lower potential energy.

8.4 Molecular orbital diagrams

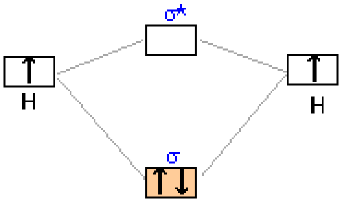
This scheme of bonding and antibonding orbitals is usually depicted by a molecular orbital diagram such as those shown below.



dihydrogen ion H_2^+
H-H+ bond energy 270 kJ

Electrons fill the lower-energy molecular orbitals before the higher ones, just as is the case for atomic orbitals. Thus in H_2^+, the single electron goes into the bonding orbital, leaving the antibonding orbital empty. Since any orbital can hold a maximum of two electrons, the bonding orbital in H_2^+ is only half-full. This single electron is nevertheless enough to lower the potential energy of one mole of hydrogen nuclei pairs by 270 kJ-- quite enough to make them stick together and behave like a distinct molecular species. Although H_2^+ is ***stable in this energetic sense, it happens to be an extremely reactive*** molecule-- so much so that it even reacts with itself, so these ions are not commonly encountered in everyday chemistry.

Dihydrogen

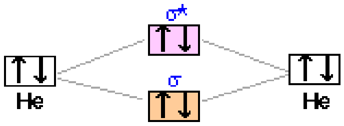


dihydrogen H_2
H-H bond energy 452 kJ

If one electron in the bonding orbital is conducive to bond formation, might two electrons be even better? We can arrange this by combining two hydrogen atoms-- two nuclei, and two electrons. Both electrons will enter the bonding orbital, as depicted in the Figure. We recall that one electron lowered the potential energy of the two nuclei by 270 kJ/mole, so we might expect two electrons to produce twice this much stabilization, or 540 kJ/mole.

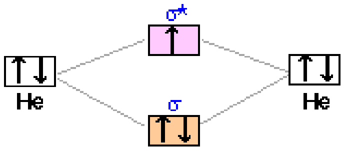
Experimentally, one finds that it takes only 452 kJ to break apart a mole of hydrogen molecules. The reason the potential energy was not lowered by the full amount is that the presence of two electrons in the same orbital gives rise to a repulsion that acts against the stabilization. This is exactly the same effect we saw in comparing the ionization energies of the hydrogen and helium atoms.

Dihelium



dihelium He_2

He-He bond energy 0.054 kJ



dihelium ion He_2^+

He-He+ bond energy 301 kJ

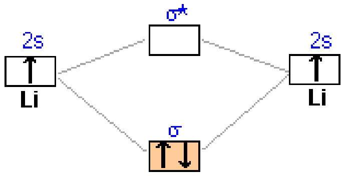
With two electrons we are still ahead, anyway, so let's try for three. The dihelium positive ion is a three-electron molecule. We can think of it as being from two helium nuclei and three electrons. This molecule is stable, but not as stable as dihydrogen; the energy required to break He_2^+ is 301 kJ/mole. The reason for this should be obvious; two electrons were accommodated in the bonding orbital, but the third electron must go into the next higher slot-- which turns out to be the ***sigma antibonding*** orbital. The presence of an electron in this orbital, as we have seen, gives rise to a repulsive component which acts against, and partially cancels out, the attractive effect of the filled bonding orbital.

Taking our building-up process one step further, we can look at the possibilities of combining to helium atoms to form dihelium. You should now be able to predict that He_2 cannot be a stable molecule; the reason, of course, is that we now have four electrons-- two in the bonding orbital, and two in the antibonding orbital. The one orbital almost exactly cancels out the effect of the other. Experimentally, the bond energy of dihelium is only.084 kJ/mol; this is not enough to hold the molecule together in the presence of random thermal motion at ordinary temperatures, so the molecule is unstable.

8.5 Diatomic molecules containing second-row atoms

The four simplest molecules we have examined so far involve molecular orbitals that derived from two 1s atomic orbitals. If we wish to extend our model to larger atoms, we will have to contend with higher atomic orbitals as well. One greatly simplifying principle here is that only the valence-shell orbitals need to be considered. Inner atomic orbitals such as 1s are deep within the atom and well-shielded from the electric field of a neighboring nucleus, so that these orbitals largely retain their atomic character when bonds are formed.

Dilithium



dilithium Li_2

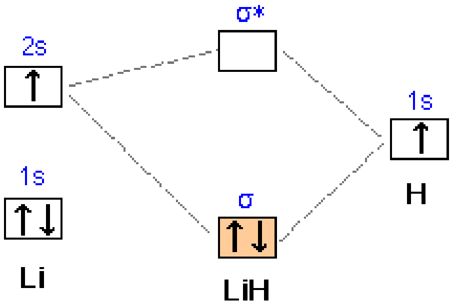
Li-Li bond energy 452 kJ

For example, when lithium, whose configuration is $1s^22s^1$,bonds with itself to form Li_2, we can forget about the 1**s** atomic orbitals and consider only the σ bonding and antibonding orbitals shown at the right. Since there are not enough electrons to populate the antibonding orbital, the attractive forces win out and we have a stable molecule. The bond energy of dilithium is 104.6 kJ/mole; notice that this value is far less than the 270 kJ bond energy in dihydrogen, which also has two electrons in a bonding orbital.

The reason, of course, is that the 2**s** orbital of Li is much farther from its nucleus than is the 1s orbital of H, and this is equally true for the corresponding molecular orbitals. It is a general rule, then, that the larger the parent atom, the less stable will be the corresponding diatomic molecule.

Lithium hydride

All the molecules we have considered thus far are ***homonuclear***; they are made up of one kind of atom. As an example of a heteronuclear molecule, let's take a look at a very simple example-- lithium hydride. Lithium hydride is a stable, though highly reactive molecule. The diagram below shows how the molecular orbitals in lithium hydride can be related to the atomic orbitals of the parent atoms. One thing that makes this diagram look different from the ones we have seen previously is that the parent atomic orbitals have widely differing energies; the ***s*** orbital of lithium has a much lower energy than the 1***s*** hydrogen orbital, owing to the greater nuclear charge of lithium. On this diagram, the ***2p*** orbitals of both parent atoms, and the 2***s*** orbital of hydrogen, are shown. These orbitals are not occupied in the ground states of the parent atoms, so we need not concern ourselves with them, although in a more thorough treatment their existence would need to be taken into account.



There are two occupied atomic orbitals on the lithium atom, and only one on the hydrogen. With which of the lithium orbitals does the hydrogen 1s orbital interact? The lithium 1***s*** orbital is the lowest-energy atomic orbital on the diagram. Because this orbital is so small and retains its electrons so tightly, we can forget about it as far as bonding goes; we need consider only 2***s*** orbital of lithium which combines with the 1***s*** orbital of hydrogen to form the usual pair of sigma bonding and antibonding orbitals. Of the four electrons in lithium and hydrogen, two are retained in the lithium 1s orbital, and the two remaining ones go into the 2s bonding orbital.

> The resulting molecule is 243 kJ/mole more stable than the parent atoms. As we might expect, the bond energy of the heteronuclear molecule is very close to the average of the energies of the corresponding homonuclear molecules. Actually, it turns out that the correct way to make this comparison is to take the geometric mean, rather than the arithmetic mean, of the two bond energies. The geometric mean is simply the square root of the product of the two energies.
>
> The geometric mean of the H_2 and Li_2 bond energies is 213 kJ/mole, so it appears that the lithium hydride molecule is 30 kJ/mole more stable than it "is supposed" to be. This is attributed to the fact that the electrons in the ***2***σ bonding orbital are not equally shared between the two nuclei; the orbital is skewed slightly so that the electrons are attracted somewhat more to the hydrogen atom. This bond polarity, which we considered in some detail near the beginning of our study of covalent bonding, arises from the greater electron-attracting power of hydrogen-- a consequence of the very small size of this atom. The electrons can be at a lower potential energy if they are slightly closer to the hydrogen end of the lithium hydride molecule. It is worth pointing out, however, that the electrons are, on the average, also closer to the lithium nucleus, compared to where they would be in the 2***s*** orbital of the isolated lithium atom. So it appears that everyone gains and no one loses here!

8.6 Sigma and pi orbitals

The molecules we have considered thus far are composed of atoms that have no more than four electrons each; our molecular orbitals have therefore been derived from ***s***-type atomic orbitals only. If we wish to apply our model to molecules involving larger atoms, we must take a close look at the way in which ***p***-type orbitals interact as well. Although two atomic ***p*** orbitals will be expected to split into bonding and antibonding orbitals just as before, it turns out that the extent of this splitting, and thus the relative energies of the resulting molecular orbitals, depend very much on the nature of the particular p orbital that is involved.

The importance of direction

You will recall that there are three possible p orbitals for any value of the principal quantum number. You should also recall that ***p*** orbitals are not spherical, like ***s*** orbitals, but are elongated, and thus possess definite directional properties. The three ***p*** orbitals correspond to the three directions of Cartesian space, and are frequently designated p_x, p_y, and p_z, to indicate the axis along which the orbital is aligned. Of course, in the free atom, where no coordinate system is defined, all direction are equivalent, and so are the ***p*** orbitals. But when the atom is near another atom, the electric field due to that other atom acts as a point of reference that defines a set of directions. The line of centers between the two nuclei is conventionally taken as the ***x*** axis. If this direction is represented horizontally on a sheet of paper, then the ***y*** axis is in the vertical direction and the ***z*** axis would be normal to the page.

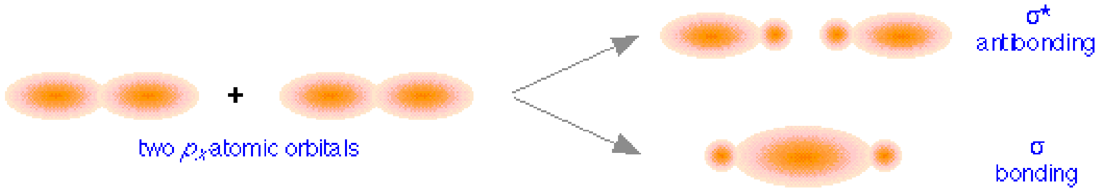


Fig. 32: Formation of *sigma* bonding- and antibonding molecular orbitals from end-to-end atomic *p* orbitals.

These directional differences lead to the formation of two different classes of molecular orbitals. The above figure shows how two p_x atomic orbitals interact. In many ways the resulting molecular orbitals are similar to what we got when ***s*** atomic orbitals combined; the bonding orbital has a large electron density in the region between the two nuclei, and thus corresponds to the lower potential energy. In the out-of-phase combination, most of the electron density is away from the internuclear region, and as before, there is a surface exactly halfway between the nuclei that corresponds to zero electron density. This is clearly an antibonding orbital-- again, in general shape, very much like the kind we saw in hydrogen and similar molecules. Like the ones derived from s-atomic orbitals, these molecular orbitals are σ orbitals.

Sigma orbitals are ***cylindrically symmetric*** with respect to the line of centers of the nuclei; this means that if you could look down this line of centers, the electron density would be the same in all directions.

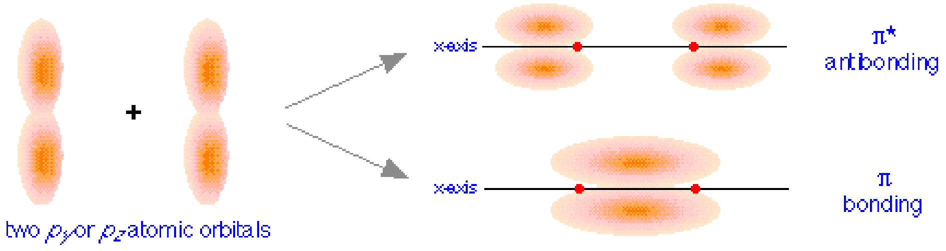


Fig. 33: Formation of *pi* bonding and antibonding orbitals from two parallel atomic-*p* orbitals.

When we examine the results of the in- and out-of-phase combination of ***p_y* and *p_z*** orbitals, we get the bonding and antibonding pairs that we would expect, but the resulting molecular orbitals have a different symmetry: rather than being rotationally symmetric about the line of centers, these orbitals extend in both perpendicular directions from this line of centers.Orbitals having this more complicated symmetry are called π ***(pi)*** orbitals. There are two of them, ***p_y*** and ***p_z*** differing only in orientation, but otherwise completely equivalent.

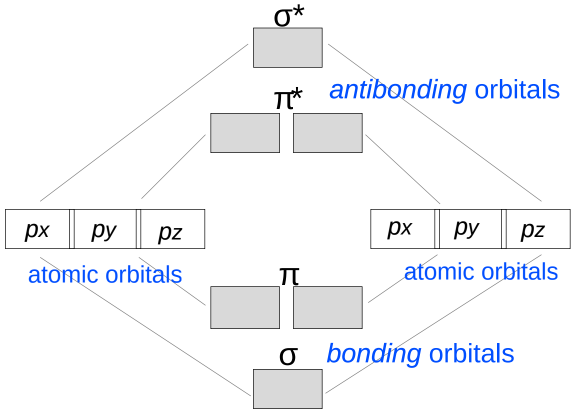
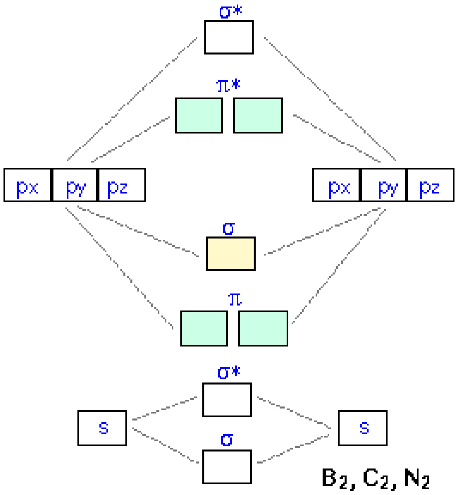


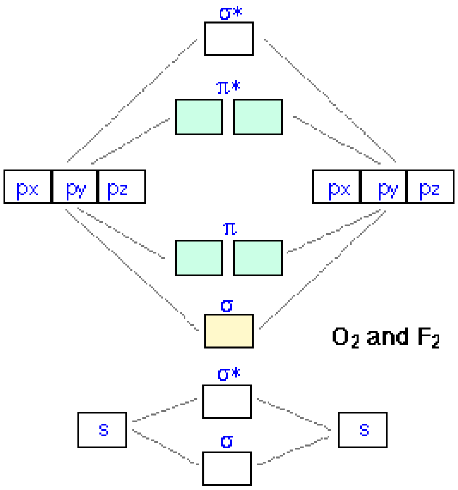
Fig. 34: Splitting scheme for *p* orbitals

The different geometric properties of the π and σ orbitals causes the sigma orbitals to split more than the pi orbitals, so that the sigma antibonding orbital always has the highest energy. The sigma bonding orbital can be either higher or lower than the pi bonding orbitals, depending on the particular atom.

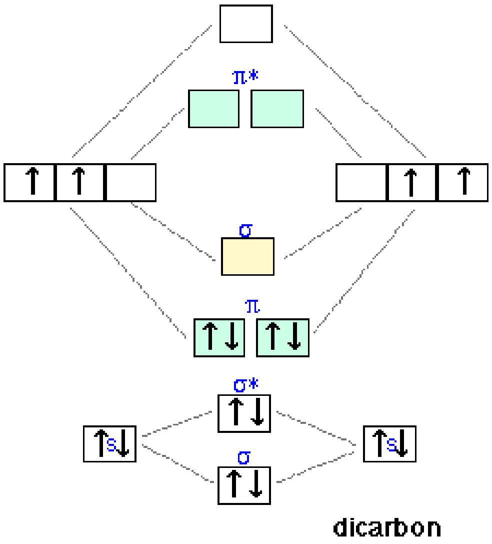
If we combine the splitting schemes for the 2s and 2p orbitals, we can predict bond order in all of the diatomic molecules and ions composed of elements in the first complete row of the periodic table. Remember that only the valence orbitals of the atoms need be considered; as we saw in the cases of lithium hydride and dilithium, the inner orbitals remain tightly bound and retain their localized atomic character.



One minor complication that you should be aware of is that the relative energies of the σ and π bonding molecular orbitals are reversed in some of the second-row diatomics. However, the order in which these two orbitals are filled has no effect on the predicted bond orders, so there is ordinarily no need to know which molecules follow which scheme.



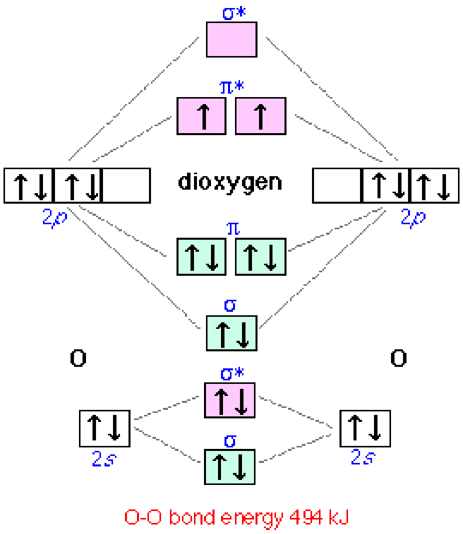
Dicarbon



Carbon has four outer-shell electrons, two 2***s*** and two ***2p***. For two carbon atoms, we therefore have a total of eight electrons, which can be accommodated in the first four molecular orbitals. The lowest two are the 2***s*** -derived bonding and antibonding pair, so the “first” four electrons make no net contribution to bonding. The other four electrons go into the pair of ***pi*** bonding orbitals, and there are no more electrons for the antibonding orbitals— so we would expect the dicarbon molecule to be stable, and it is.

You will recall that one pair of electrons shared between two atoms constitutes a “single” chemical bond; this is Lewis’ original definition of the covalent bond. In C_2 there are two paris of electron in the pi bonding orbitals, so we have what amounts to a double bond here. Actually, the preferred nomenclature is “bond order”; the bond order in dicarbon is two.

Dioxygen



The electron configuration of oxygen is $1s^2 2s^2 2p^4$. In O_2, therefore, we need to accommodate twelve valance electrons in molecular orbitals. As you can see from the diagram, this places two electrons in antibonding orbitals. Each of these electrons occupies a separate π* orbital because this leads to less electron-electron repulsion. Owing to these two unpaired electrons, O_2 is ***paramagnetic***. The paramagnetism of oxygen can readily be demonstrated by pouring liquid O_2 past a pole of a strong permanent magnet; the liquid stream will be deflected toward the magnet.

The potential energy of molecular oxygen is 494 kJ/mole below that of the parent atoms. This is a lower bond energy than nitrogen has— not surprising, considering that oxygen has two electrons in an antibonding orbital, compared to nitrogen's one.

Although this ground-state form of O_2 (also known as ***triplet*** oxygen) is the energetically favored, and therefor the common form, the other variety, in which the two electrons are paired up in a single ***pi*** antibonding orbital, is also well known. This "singlet" oxygen, as it is called, has a bond energy of only 402 kJ/mole. The lower value reflects the action of electrostatic repulsion between the two electrons in the same orbital.

Although it does not exist under normal conditions, singlet oxygen can be formed by the action of light and in certain chemical reactions, and it has an interesting and unique chemistry of its own.

Since molecular oxygen contains two electrons in an antibonding orbital, it might be possible to make the molecule more stable by removing one of these electrons, thus increasing the ratio of bonding to antibonding electrons in the molecule. Just as we would expect, and in accord with our model, O_2^+ has a bond energy higher than that of neutral dioxygen; removing the one electron actually gives us a more stable molecule. This constitutes a very good test of our model of bonding and antibonding orbitals. In the same way, adding an electron to O_2 results in a weakening of the bond, as evidenced by the lower bond energy of O_2-minus. The bond energy in this ion is not known, but the length of the bond is greater, and this is indicative of a lower bond energy.

molecule	H_2	He_2^+	He_2	Li	Be_2	B_2	C_2	N_2	O_2	F_2
bond order	1	0.5	0	1	0	1	2	3	2	1
bond energy, kJ/mol	458	299	0	99	0	290	569	941	490	154
bond length, pm	74	108		267		131	131	109	121	144

Table 2: Bonding in the second-row diatomic molecules

9. Bonding in coordination complexes

What is a complex?

If you have taken a lab course in chemistry, you have very likely admired the deep blue color of copper sulfate crystals, $CuSO_4 \cdot 5H_2O$. The proper name of this substance is copper(II) sulfate pentahydrate, and it is typical of many salts that incorporate ***waters of hydration*** into their crystal structures. It is also a ***complex***, a term used by chemists to describe a substance composed of two other substances (in this case, $CuSO_4$ and H_2O) each of which is capable of an independent existence. The binding between the components of a complex is usually weaker than a regular chemical bond; thus most solid hydrates can be decomposed by heating, driving off the water and yielding the anhydrous salt:

$$CuSO_4 \cdot 5H_2O \rightarrow CuSO_4\,(s) + 5\,H_2O$$

Driving off the water in this way also destroys the color, turning it from a beautiful deep blue to a nondescript pale yellow. If the anhydrous salt is now dissolved in water, the blue color now pervades the entire solution. It is apparent that the presence of water is somehow necessary for the copper(II) ion to take on a blue color, but why should this be?

A very common lab experiment that most students carry out is to add some dilute ammonia to a copper sulfate solution. At first, the solutions turns milky as the alkaline ammonia causes the precipitation of copper hydroxide: $Cu^{2+} + 2\,OH^{-} \rightarrow Cu(OH)_2(s)$. But if more ammonia is added, the cloudiness disappears and the solution assumes an intense deep blue color that makes the original solution seem pale by comparison. The equation for this reaction is usually given as

$$Cu^{2+} + 6NH_3 \rightarrow Cu(NH_3)_6^{\,2+}$$

The new product is commonly known as the ***copper-ammonia complex ion***, or more officially, hexamminecopper(II). This equation is somewhat misleading, however, in that it implies the formation of a new complex where none existed before. In fact, since about 1895 it has been known that the ions of most transition metals dissolve in water to form complexes with water itself, so a better representation of the reaction of dissolved copper with ammonia would be

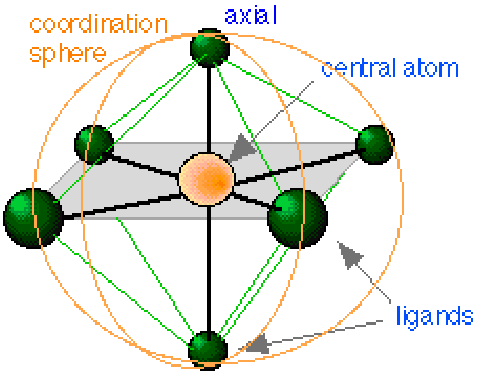
$$Cu(H_2O)_6^{\,2+} + 6\,NH_3 \rightarrow Cu(NH_3)_6^{\,2+} + 6\,H2O$$

In effect, the ammonia binds more tightly to the copper ion than does water, and it thus displaces the latter when it comes into contact with the hexaaquocopper(II) ion, as the dissolved form of Cu^{2+} is properly known.

9.1 The basics of coordination complexes

Although our primary focus in this unit is on bonding, the topic of coordination complexes is to important in chemistry and biochemistry that some of their basic features are worth knowing about, even if their detailed chemistry is beyond the scope of this course. These complexes play an especially crucial role in physiology and biochemistry. Thus heme, the oxygen-carrying component of red blood cells (and the source of the red color) is basically a complex of iron, and the part of chlorophyll that converts sunlight into chemical energy within green plants is a magnesium complex.

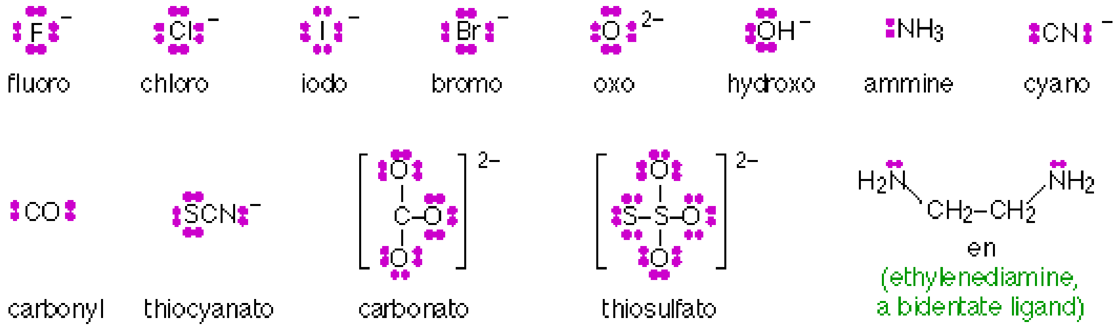
Some definitions



We have already defined a ***complex*** as a substance composed of two or more components capable of an independent existence. A ***coordination complex*** is one in which a ***central atom*** or ion is joined to one or more ligands (Latin ***ligare***, to tie) through what is formally a coordinate covalent bond in which both of the bonding electrons are supplied by the ligand. In such a complex the central atom acts as an electron-pair acceptor (Lewis base) and the ligand as an electron-pair donor (Lewis acid). The central atom and the ligands coordinated to it constitute the ***coordination sphere***. Thus the salt [Co$(NH_3)_5$CuCl_2 can be considered to be composed of the complex ion $[Co(NH_3)_5Cl]^{2+}$ and two $Cl^–$ ions; components within the square brackets are inside the coordination sphere, whereas the two chloride ions are situated outside the coordination sphere. These latter two ions could be replaced by other ions such as $NO_3^–$ without otherwise materially changing the nature of the salt.

The central atoms of coordination complexes are most often positive ions, but may in some cases be neutral atoms, as in nickel carbonyl $Ni(CO)_4$.

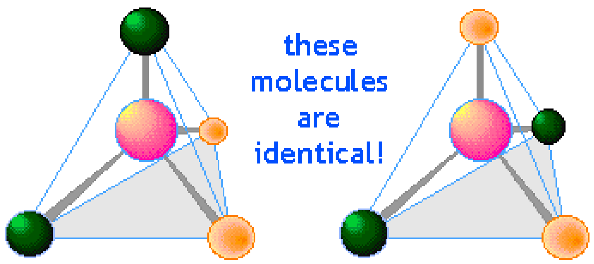
Ligands composed of ions such as $F^–$ or small molecules such as H_2O or $CN^–$ possess more than one set of lone pair electrons, but only one of these pairs can coordinate with a central ion. Such ligands are said to be ***monodentate*** ("one tooth".) Larger ligands may contain more than atom capable of coordinating with a single central ion, and are described as ***polydentate***. Thus ethylenediamine (shown below) is a bidentate ligand. Polydentate ligands whose geometry enables them to occupy more than one coordinating position of a central ion act as ***chelating agents*** (Greek χελοσ ***chelos***, claw) and tend to form extremely stable complexes known as ***chelates***.

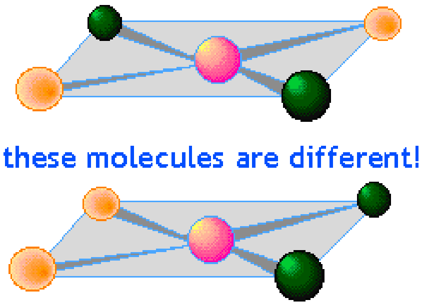


9.2 Structures and bonding in transition metal complexes

Complexes such as $Cu(NH_3)_6^{2+}$ have been known and studied since the mid-nineteenth century. Why they should form, or what their structures might be, were complete mysteries. At that time all inorganic compounds were thought to be held together by ionic charges, but ammonia, of course, is electrically neutral. A variety of theories such as the existence of “secondary valences” were concocted, and various chain-like structures such as $CuNH_3$-NH_3-NH_3-NH_3-NH_3-NH_3 were proposed. Finally, in the mid-1890s, after a series of painstaking experiments, the chemist ALFRED WERNER (Swiss, 1866-1919) presented the first workable theory of complex ion structures. (Werner claimed that his theory first came to him in a flash after a night of fitful sleep; he had written his landmark paper by the end of the next day. He was awarded the 1913 Nobel Prize in Chemistry for his work.)

Werner was able to show, in spite of considerable opposition, that transition metal complexes consist of a central ion surrounded by ligands in a square-planar, tetrahedral, or octahedral arrangement. This an especially impressive accomplishment at a time long before X-ray diffraction and other methods had become available to observe structures directly. His basic method was to make inferences of the structures from a careful examination of the chemistry of these complexes and particularly the existence of structural isomers. For example, the existence of two different compounds AX_4 having the same composition shows that its structure must be square-planar rather than tetrahedral.





What holds them together?

An understanding of the nature of the bond between the central ion and its ligands would have to await the development of Lewis’ shared-electron pair theory. and Pauling’s valence-bond picture. We have already shown (Page 50) how hybridization of the ***d*** orbitals of the central ion creates vacancies able to accommodate one or more pairs of unshared electrons on the ligands. Although these models correctly predict the structures of transition metals, they are by themselves unable to account for several of their special properties:

- The metal-to-ligand bonds are generally much ***weaker*** than ordinary covalent bonds;
- Some complexes utilize “inner” ***d*** orbitals of the central ion, while others are “outer-orbital” complexes;
- Transition metal ions tend to be intensely ***colored***.

Paramagnetism of coordination complexes

Unpaired electrons act as tiny magnets; if a substance that contains unpaired electrons is placed near an external magnet, it will undergo an attraction that tends to draw it into the field. Such substances are said to be ***paramagnetic***, and the degree of paramagnetism is directly proportional to the number of unpaired electrons in the molecule. Magnetic studies have played an especially prominent role in determining how electrons are distributed among the various orbitals in transition metal complexes.

> Studies of this kind are carried out by placing a sample consisting of a solution of the complex between the poles of an electromagnet. The sample is suspended from the arm of a sensitive balance, and the change in weight is measured with the magnet on and off. An increase in the weight when the magnet is turned on indicates that the sample is attracted to the magnet (paramagnetism) and must therefore possess one or more unpaired electrons. The precise number can be determined by calibrating the system with a substance whose electron configuration is known.

9.3 Ligand field theory

The current model of bonding in coordination complexes developed gradually between 1930-1950, and has largely superseded the hybridization model discussed previously. It is essentially a simplified adaptation of molecular orbital theory which focuses on the manner in which the electric field due to the unpaired electrons on the ligands interact with the five different ***d*** orbitals of the central ion.

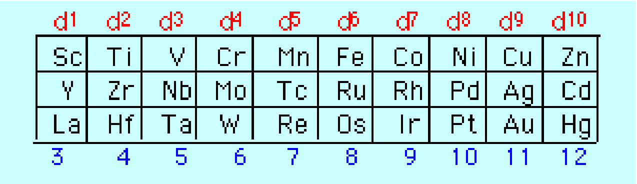
In an isolated transition metal atom the five outermost ***d*** orbitals all have the same energy which depends solely on the spherically symmetric electric field due to the nuclear charge and the other electrons of the atom. Suppose now that this atom is made into a cation and is placed in solution, where it forms a hydrated species in which six H_2O molecules are coordinated to the central ion in an octahedral arrangement. An example of such an ion might be hexaaquotitanium(III), $Ti(H_2O)_6^{3+}$.

The ligands (H_2O in this example) are bound to the central ion by electron pairs contributed by each ligand. Because the six ligands are located at the corners of an octahedron centered around the metal ion, these electron pairs are equivalent to clouds of negative charge that are directed from near the central ion out toward the corners of the octahedron. We will call this an octahedral electric field, or the ***ligand field***.

d-orbital splitting

Although the five ***d*** orbitals of the central atom all have the same energy in a spherically symmetric field, their energies will ***not*** all be the same in the octahedral field imposed by the presence of the ligands. The reason for this is apparent when we consider the different geometrical properties of the five ***d*** orbitals. Two of the ***d*** orbitals, designated d_{x^2} and $d_{x^2-y^2}$, have their electron clouds pointing directly toward ligand atoms. We would expect that any electrons that occupy these orbitals would be subject to repulsion by the electron pairs that bind the ligands that are situated at corresponding corners of the octahedron. As a consequence, the energies of these two ***d*** orbitals will be raised in relation to the three other ***d*** orbitals whose lobes are not directed toward the octahedral positions.

The number of electrons in the ***d*** orbital of the central atom is easily determined from the location of the element in the periodic table, taking in account, of course, of the number of electrons removed in order to form the positive ion.



d1	d2	d3	d4	d5	d6	d7	d8	d9	d10
Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg
3	4	5	6	7	8	9	10	11	12

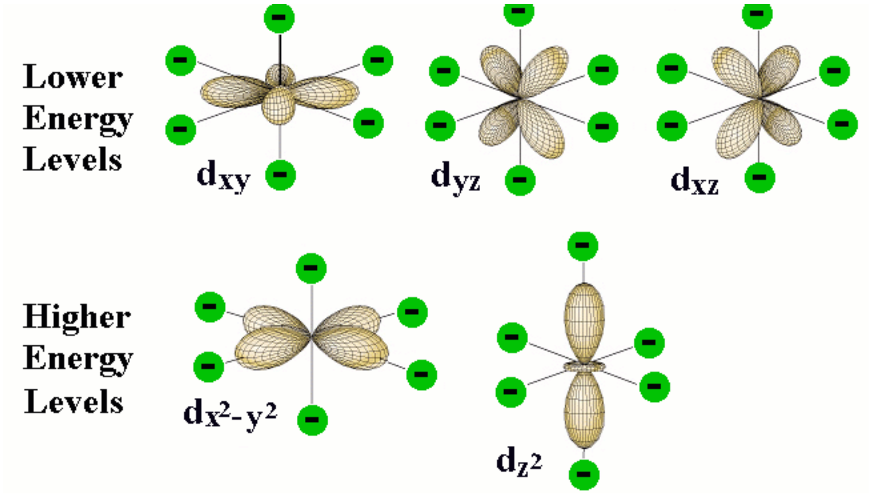


Fig. 35: *d* orbitals in an octahedral field
The green circles represent the coordinating electron-pairs of the ligands located at the six corners of the octahedron around the central atom. The two *d* orbitals at the bottom have regions of high electron density pointing directly toward the ligand orbitals; the resulting electron-electron repulsion raises the energy of these *d* orbitals. (Diagram from a Perdue U. chemistry site.]

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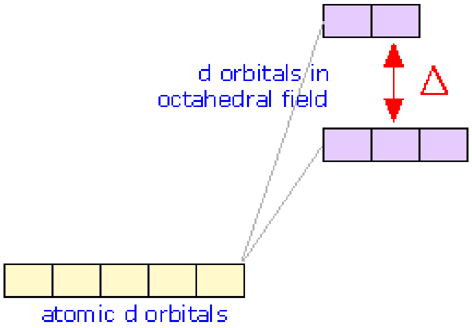
The effect of the octahedral ligand field due to the ligand electron pairs is to split the ***d*** orbitals into two sets whose energies differ by a quantity denoted by Δ which is known as the ***d* orbital splitting.** Note that ***both*** sets of central-ion ***d*** orbitals are repelled by the ligands and are both raised in energy; the upper set is simply raised by a greater amount. Both the total energy shift and Δ are strongly dependent on the particular ligands.



Why are transition metal complexes often highly colored?

Returning to our example of $Ti(H_2O)_6^{3+}$, we note that Ti has an outer configuration of $4s^2 3d^2$, so that Ti^{3+} will be a d^1 ion. This means that in its ground state, one electron will occupy the lower group of d orbitals, and the upper group will be empty. The ***d***-orbital splitting in this case is 240 kJ per mole which corresponds to light of blue-green color; absorption of this light promotes the electron to the upper set of ***d*** orbitals, which represents the exited state of the complex. If we illuminate a solution of $Ti(H_2O)_6^{3+}$ with white light, the blue-green light is absorbed and the solution appears violet in color.

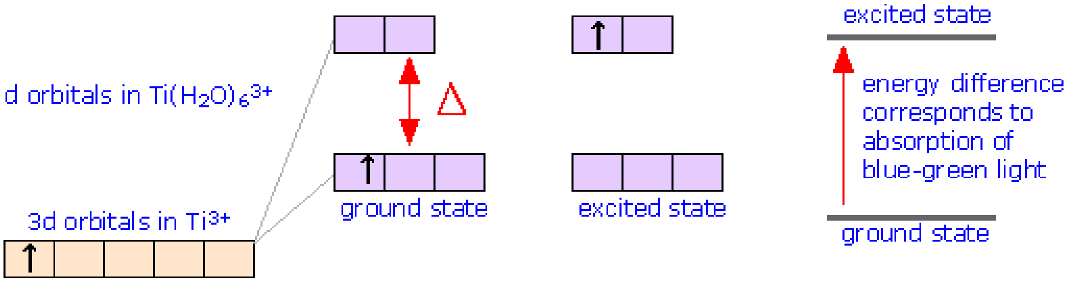


Fig. 36: Origin of color in a coordination complex
Absorption of light which is energetically equal to Δ promotes the electron to the upper d-orbital level, producing an excited state atom. Removal of this color from white life causes Ti^{3+} solutions to appear purple in color.

High- and low spin complexes

The magnitude of the ***d*** orbital splitting depends strongly on the nature of the ligand and in particular on how strong an electrostatic field is produced by its electron pair bond to the central ion. If Δ is not too large then the electrons that occupy the d orbitals do so with their spins unpaired until a d^5 configuration is reached, just as occurs in the normal Aufbau sequence for atomic electron configurations. Thus a weak-field ligand such as H_2O leads to a “high spin” complex with Fe(II).

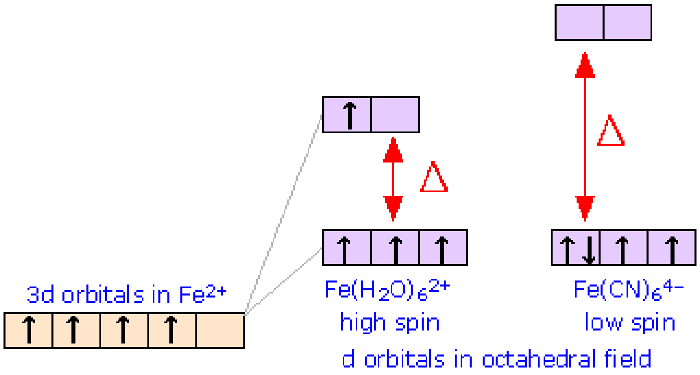


Fig. 37: Effect of ligand type on magnetic moment of complex

In contrast to this, the cyanide ion acts as a strong-field ligand; the ***d*** orbital splitting is so great that it is energetically more favorable for the electrons to pair up in the lower group of ***d*** orbitals rather than to enter the upper group with unpaired spins. Thus hexacyanoiron(II) is a “low spin” complex— actually zero spin, in this particular case.

Different ***d*** orbital splitting occur in square planar and tetrahedral coordination geometries, so a very large number of arrangements are possible. In most complexes the value of Δ corresponds to the absorption of visible light, accounting for the colored nature of many such compounds in solution and in solids such as $CuSO_4 \cdot 5H_2O$.

9.4 Coordination complexes in biochemistry

Approximately one-third of the chemical elements are present in living organisms.

Many of these are metallic ions whose passage through cell walls and function within the cell depends on the formation of coordination complexes. The ions Na^+, K^+, Ca^{2+} and Mg^{2+} are particularly important and serve a wide range of functions. These ions, being in the s-block of the periodic table, bind to suitable polydentate ligands through ordinary polarization forces rather then through ***d***-orbital complexing. Many of the micronutrient metals such as Fe, Cu, Mo, Zn and Mn are essential components of enzymes in which the metal ion is bound through ***d***-orbitals.

Chlorophyll

Chlorophyll is the light-harvesting pigment present in green plants. Its name comes from the Greek word ***chloros***, meaning “green”— the same root from which chlorine gets its name. Chlorophyll consists of a ring-shaped tetradentate ligand known as a ***porphin*** coordinated to a central magnesium ion. A histidine residue from one of several types of associated proteins forms a fifth coordinate bond to the Mg atom.

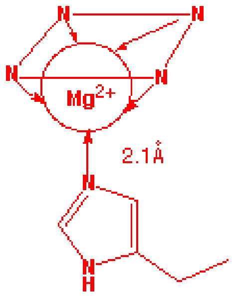
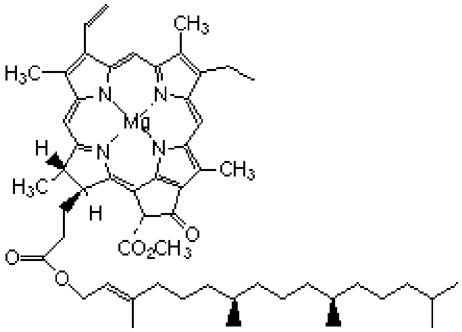


Fig. 38: Chlorophyll
Left: detail of Mg coordination; notice that the metal is slightly out of the plane of the porphin ring. Right: plan view of Mg within the porphin ligand. A histidine residue from an associated protein forms the fifth coordination point to the Mg atom.



Chlorophyll *a*

The light energy trapped by chlorophyll is utilized to drive a sequence of reactions whose net effect is to bring about the reduction of CO_2 to glucose ($C_6H_{12}O_6$) which serves as the fuel for all life processes in both plants and animals.

Hemoglobin

Hemoglobin performs the essential task of transporting dioxygen molecules from the lungs to the tissues in which it is used to oxidize glucose, this oxidation serving as the source of free energy required for cellular metabolic processes. Like chlorophyll, hemoglobin consists of a tetradentate ligand, ***heme***, combined with a polypeptide (mini-protein) chain which together coordinate with an iron atom in five positions. The sixth position in the octahedrally-coordinated iron is taken up either by an oxygen molecule or by a water molecule, depending on whether the hemoglobin is in its oxygenated state (in arteries) or deoxygenated state (in veins.)

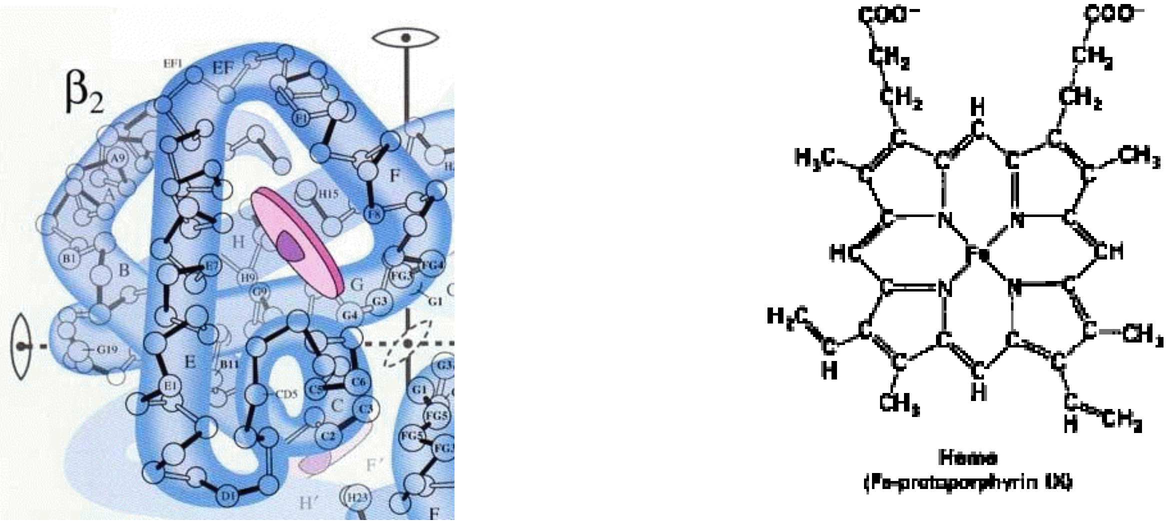


Fig. 39: Hemoglobin

Left: The heme molecules (purple) are enfolded within a peptide chain. There are for of these subunits in each hemoglobin molecule.
Right: the heme molecule.

Other ligands, notably cyanide ion and carbon monoxide, are able to bind to hemoglobin much more strongly than does iron, thereby displacing it and rendering hemoglobin unable to transport oxygen. Air containing as little as 1 percent CO will convert hemoglobin to carboxyhemoglobin in a few hours, leading to loss of consciousness and death. Even small amounts of carbon monoxide can lead to substantial reductions in the availability of oxygen. The 400-ppm concentration of CO in cigarette smoke will tie up about 6% of the hemoglobin in heavy smokers; the increased stress this places on the heart as it works harder to compensate for the oxygen deficit is believed to be one reason why smokers are at higher risk for heart attacks.

10. Bonding in metals and semiconductors

Most of the known chemical elements are metals, and many of these combine with each other to form a large number of intermetallic compounds. The special properties of metals-- their bright, lustrous appearance, their high electrical and thermal conductivities, and their malleability-- suggest that these substances are bound together in a very special way.

The fact that the metallic elements are found on the left side of the periodic table gives us two important preliminary clues to the nature of their bonding.

- These elements all possess ***low electronegativities***, and readily form positive ions M^{n+}. They show no tendency to form negative ions, so the kind of bonding present in ionic solids can immediately be ruled out.

- The metallic elements have empty or nearly-empty outer ***p*** orbitals, so there are never enough outer-shell electrons to place a complete octet around an atom.

These points lead us to the simplest picture of metals, which regards them as a lattice of positive ions immersed in a “sea of electrons” which can freely migrate throughout the solid. In effect the electropositive nature of the metallic atoms allows their valence electrons to exist as a mobile fluid which can be displaced by an applied electric field, hence giving rise to their high electrical conductivities. Because each ion is surrounded by the electron fluid in all directions, the bonding has no directional properties; this accounts for the high malleability and ductility of metals.

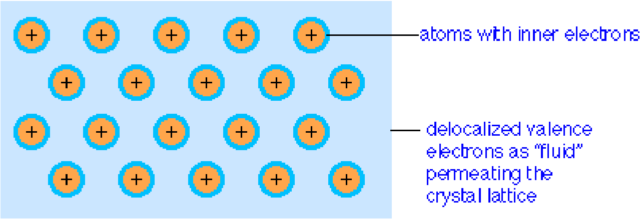


Fig. 40: Electron-fluid model of metallic bonding

This view is really an oversimplification that fails to explain metals in a quantitative way, nor can it account for the differences in the properties of individual metals. A more detailed treatment, known as the ***bond theory of metals***, applies the idea of resonance hybrids to metallic lattices. In the case of an alkali metal, for example, this would involve a large number of hybrid structures in which a given Na atom shares its electron with its various neighbors.

10.1 Molecular orbitals in metals

The most useful treatment of metallic solids is based on the molecular orbital approach. It is best understood by considering first a succession of molecules based on lithium (or any other alkali metal having a single s electron in its valence shell). The figure on the next page shows how the m.o. wave functions for Li_2, Li_3 and Li_4 will look. These are all constructed by combining the individual atom ***s*** functions just as is done in simple m.o. theory. The only thing new here is that the new molecular orbitals extend over all the atoms involved, and that the orbitals of intermediate energy have both bonding and antibonding character in different regions. Every time we add another atom, we get two new m.o.’s, but since each atom contributes only a single valence electron, the m.o.’s are never more than half filled. If we extrapolate this to a giant “molecule” Li_N containing a very large number of atoms, we get 2***N*** m.o.’s that are so closely spaced in energy that they form what is known as a ***band*** of allowed energies. In metallic lithium only the lower half of this band is occupied.

Take two atoms, add a third, then a fourth, and keep on going until you have about a mole! Here we start with two Li atoms, each of which has a single valence electron in its 2s orbital. (The purple dots indicate locations of the Li nuclei.) In Li_2 we get the usual pair of bonding and antibonding MOs, but only the former are occupied, so this is a stable molecule. In Li_3 and beyond, only the highest- and lowest-energy MOs are “pure” bonding and antibonding in character.

In Li4 we begin to see a trend in which the lower (mostly bonding) MO’s are filled and the upper (mostly antibonding) ones are empty.

Now jump to a one-mole chunk of Li. The 10^{23} MO’s now coalesce into a **band** of closely-spaced levels, with only the bottom half occupied, implying strong bonding.

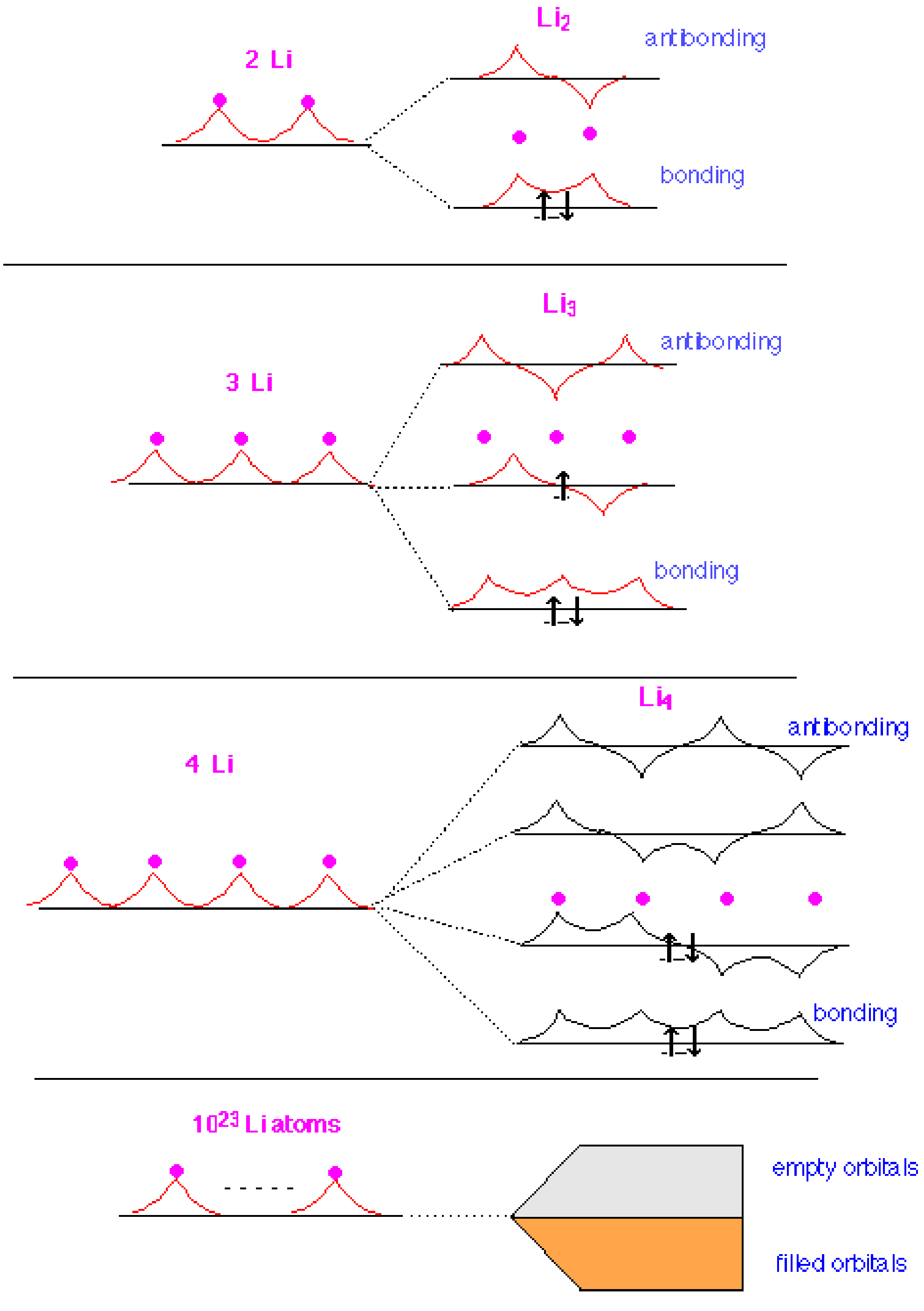
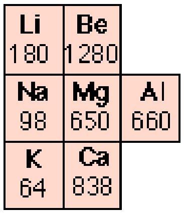


Fig. 41: Recipe for a metal

10.2 Why metals are different

Metallic solids possess special properties that set them apart from other classes of solids and make them easy to identify and familiar to everyone. All of these properties derive from the liberation of the valence electrons from the control of individual atoms, allowing them to behave as a highly mobile fluid that fills the entire crystal lattice. What were previously valence-shell orbitals of individual atoms become split into huge numbers of closely-spaced levels known as ***bands*** that extend throughout the crystal.



Li 180	Be 1280	
Na 98	Mg 650	Al 660
K 64	Ca 838	

Fig. 42: Melting points of some metals (temperatures are in °C.)

Melting point and strength The strength of a metal derives from the electrostatic attraction between the lattice of positive ions and the fluid of valence electrons in which they are immersed. The larger the nuclear charge (atomic number) of the atomic kernel and the smaller its size, the greater this attraction. As with many other periodic properties, these work in opposite ways, as is seen by comparing the melting points of some of the Group 1-3 metals (right). Other factors, particularly the lattice geometry are also important, so exceptions such as is seen in Mg are not surprising. In general, the transition metals with their valence-level d electrons are stronger and have higher melting points: Fe, 1535°C; Os 3700°C; W 3370°C (this is tungsten, the highest-melting of all the metals; do you know what principal use of tungsten derives from this very high melting point?)

Malleability and ductility These terms refer respectively to how readily a solid can be shaped by pressure (forging, hammering, rolling into a sheet) and by being drawn out into a wire. Metallic solids are known and valued for these qualities, which derive from the non-directional nature of the attractions between the kernel atoms and the electron fluid. The bonding within ionic or covalent solids may be stronger, but it is also directional, making these solids subject to fracture (brittle) when struck with a hammer, for example. A metal, by contrast, is more likely to be simply deformed or dented.

Electrical conductivity In order for a substance to conduct electricity, it must contain charged particles (***charge carriers***) that are sufficiently mobile to move in response to an applied electric field. In the case of ionic solutions and melts, the ions themselves serve this function. (Ionic solids contain the same charge carriers, but because they are fixed in place, these solids are insulators.) In metals the charge carriers are the electrons, and because they move freely through the lattice, metals are highly conductive. The very low mass and inertia of the electrons allows them to conduct high-frequency alternating currents, something that electrolytic solutions are incapable of. In terms of the band structure, application of an external field simply raises some of the electrons to previously unoccupied levels which possess greater momentum.

> The conductivity of an electrolytic solution decreases as the temperature falls due to the decrease in viscosity which inhibits ionic mobility. The mobility of the electron fluid in metals is practically unaffected by temperature, but metals do suffer a slight conductivity decrease (opposite to ionic solutions) as the temperature rises; this happens because the more vigorous thermal motions of the kernel ions disrupts the uniform lattice structure that is required for free motion of the electrons within the crystal. Silver is the most conductive metal, followed by copper, gold, and aluminum.

Thermal conductivity Everyone knows that touching a metallic surface at room temperature produces a colder sensation than touching a piece of wood or plastic at the same temperature. The very high thermal conductivity of metals allows them to draw heat out of our bodies very efficiently if they are below body temperature. In the same way, a metallic surface that is above body temperature will feel much warmer than one made of some other material. The high thermal conductivity of metals is attributed to vibrational excitations of the fluid-like electrons; this excitation spreads through the crystal far more rapidly than it does in non-metallic solids which depend on vibrational motions of atoms which are much heavier and possess greater inertia.

Appearance We usually recognize a metal by its “metallic lustre”, which refers to its ability of reflect light. When light falls on a metal, its rapidly changing electromagnetic field induces similar motions in the more loosely-bound electrons near the surface. A vibrating charge is itself an emitter of electromagnetic radiation, so the effect is to cause the metal to re-emit, or reflect, the incident light, producing the shiny appearance. What ***color*** is a metal? With the two exceptions of copper and gold, the closely-spaced levels in the bands allow metals to absorb all wavelengths equally well, so most metals are basically black, but this is ordinarily evident only when the metallic particles are so small that the band structure is not established.

Thermionic effect The electrons within the electron fluid have a distribution of velocities very much like that of molecules in a gas. When a metal is heated sufficiently, a fraction of these electrons will acquire sufficient kinetic energy to escape the metal altogether; some of the electrons are essentially “boiled out” of the metal. This ***thermionic effect***, which was first observed by Thomas Edison, was utilized in ***vacuum tubes*** which served as the basis of electronics from its beginning around 1910 until semiconductors became dominant in the 1960’s.

10.3 Band structure in metals

Most metals are made of atoms that have an outer configuration of s^2, which we would expect to completely fill the band of m.o.’s we have described. With the band completely filled and no empty levels above, we would not expect elements such as beryllium to be metallic. What happens is that the empty ***p*** orbitals also split into a band. Although the energy of the 2p orbital of an isolated Be atom is about 160 kJ greater than that of the 2s orbital, the bottom part of the 2p band overlaps the upper part of the 2s band, yielding a continuous ***conduction band*** that has plenty of unoccupied orbitals. It is only when these bands become filled with 2p electrons that the elements lose their metallic character.

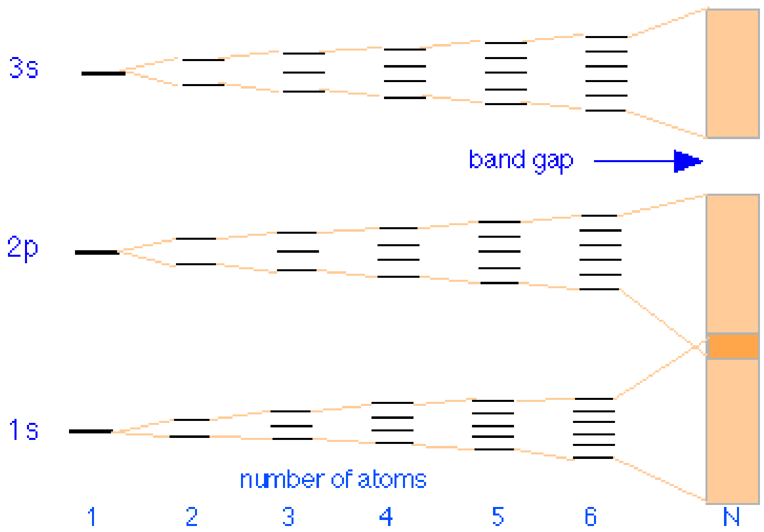


Fig. 43: Band structure in 3rd-row metals

This diagram illustrates the band structure in a 3rd-row metal such as Na or Mg, and how it arises from MO splitting in very small aggregates M_2 - M_6. The conduction bands for the "infinite" molecule M_N are shaded.

In most metals there will be bands derived from the outermost ***s***-, ***p***-, and ***d*** atomic levels, leading to a system of bands, some of which will overlap as described above. Where overlap does not occur, the almost continuous energy levels of the bands are separated by a forbidden zone, or ***band gap***. Only the outermost atomic orbitals form bands; the inner orbitals remain localized on the individual atoms and are not involved in bonding.

10.4 Metals, insulators and semiconductors

The band theory of solids provides a clear set of criteria for distinguishing between conductors (metals), insulators and semiconductors. As we have seen, a **conductor** must posses an upper range of allowed levels that are only partially filled with valence electrons. These levels can be within a single band, or they can be the combination of two overlapping bands. A band structure of this type is known as a ***conduction band***.

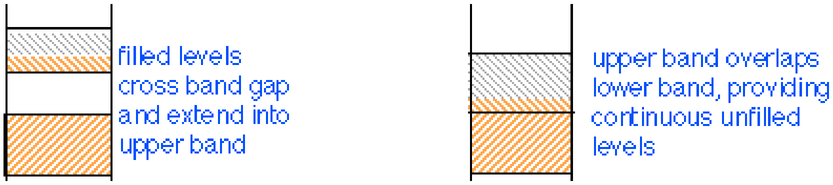


Fig. 44: Possible band organizations in conducting solids

An **insulator** is characterized by a large band gap between the highest filled band and an even higher empty band. The band gap is sufficiently great to prevent any significant population of the upper band by thermal excitation of electrons from the lower one. The presence of a very intense electric field may be able to supply the required energy, in which case the insulator undergoes ***dielectric breakdown***. Most molecular crystals are insulators, as are covalent crystals such as diamond.

If the band gap is sufficiently small to allow electrons in the filled band below it to jump

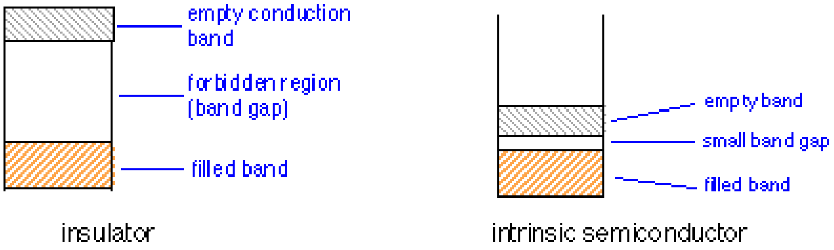


Fig. 45: Band organizations in insulators and intrinsic semiconductors

into the upper empty band by thermal excitation, the solid is known as a **semiconductor**. In contrast to metals, whose electrical conductivity decreases with temperature (the more intense lattice vibrations interfere with the transfer of momentum by the electron fluid), the conductivity of semiconductors increases with temperature. In many cases the excitation energy can be provided by absorption of light, so most semiconductors are also photoconductors. Examples of semiconducting elements are Se, Te, Bi, Ge, Si, and graphite.

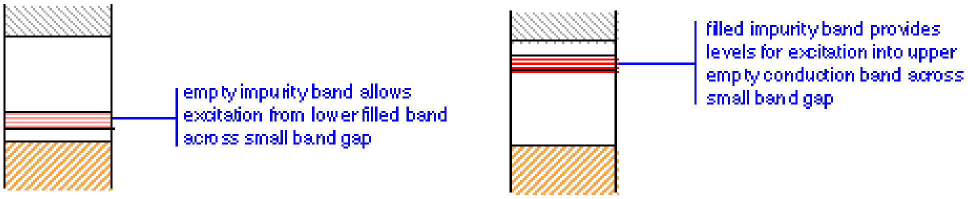


Fig. 46: Doped semiconductors

The presence of an impurity in a semiconductor can introduce a new band into the system. If this new band is situated within the forbidden region, it creates a new and smaller band gap that will increase the conductivity. The huge semiconductor industry is based on the ability to tailor the band gap to fit the desired application by introducing an appropriate impurity atom (***dopant***) into the semiconductor lattice. The dopant elements are normally atoms whose valance shells contain one electron more or less than the atoms of the host crystal. For example, a phosphorus atom introduced as an impurity into a silicon lattice possesses one more valence electron than Si. This electron is delocalized within the impurity band and serves as the charge carrier in what is known as an ***N-type semiconductor***. In a semiconductor of the ***P-type***, the dopant might be arsenic, which has only three valence electrons. This creates what amounts to an electron deficiency, or ***hole*** in the electron fabric of the crystal, although the solid remains electrically neutral overall. As this vacancy is filled by the electrons from silicon atoms the vacancy hops to another location, so the charge carrier is effectively a positively charged hole, hence the P-type designation.