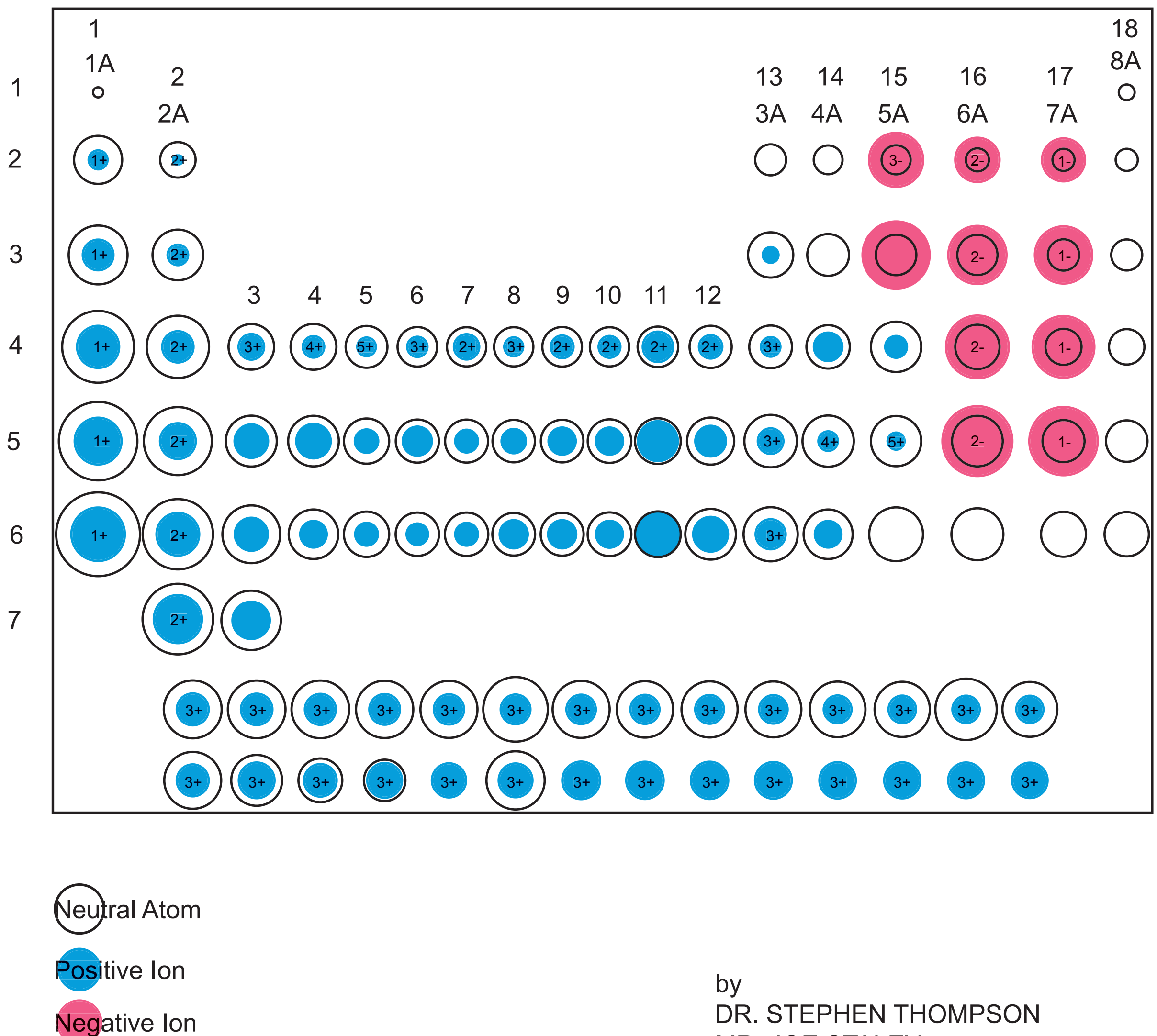
CHEMICAL BONDING



by
DR. STEPHEN THOMPSON
MR. JOE STALEY

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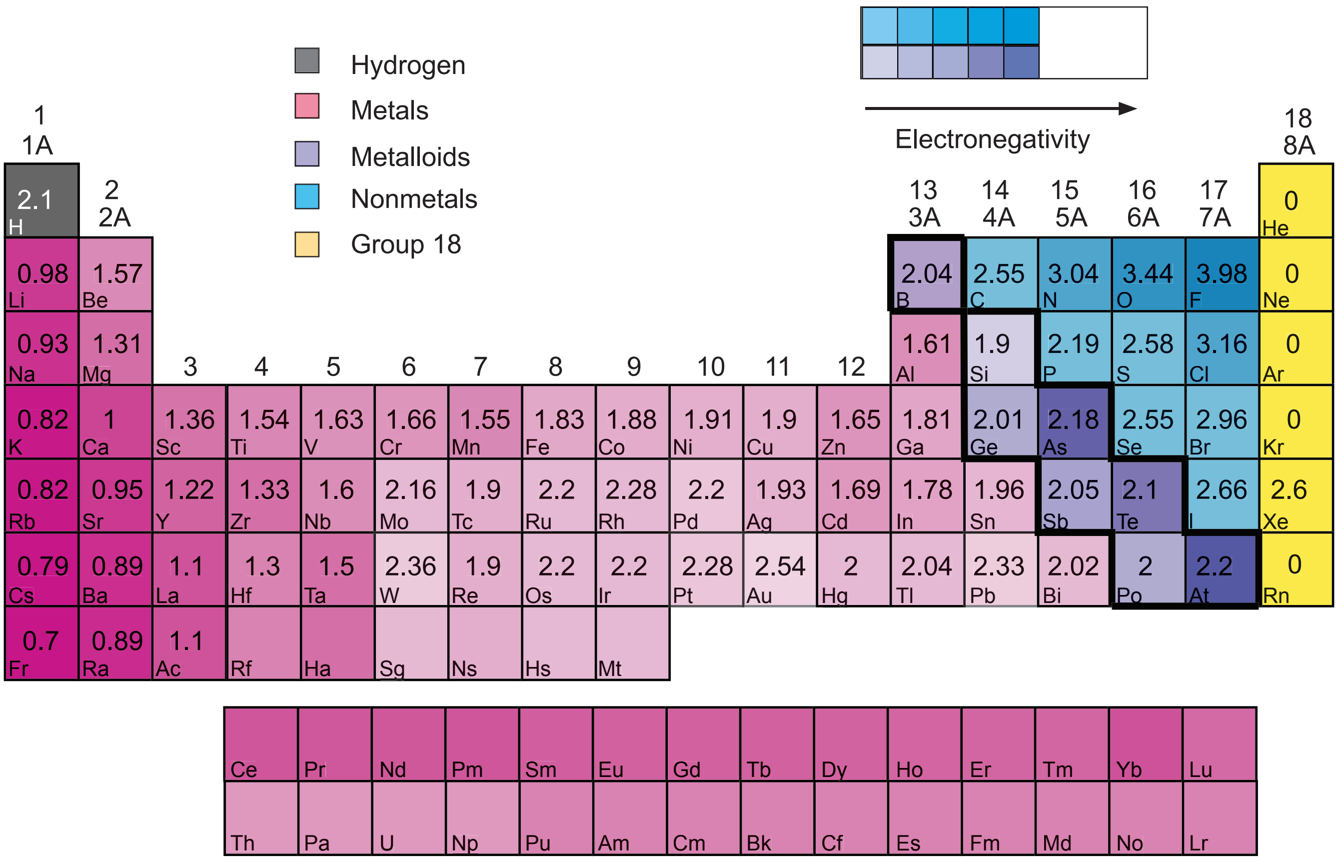
CHEMICAL BONDING
CONTENTS

ELECTRONEGATIVITY



Electronegativity is the ability of an atom to attract shared electrons to itself.
It is largely the difference between the electronegativities of two atoms which determines what kind of bond is formed between them.

What is the most electronegative element?

What is the least electronegative element (aside from the noble gases)?

What is the range of electronegativity for the metals? Metalloids? Nonmetals?

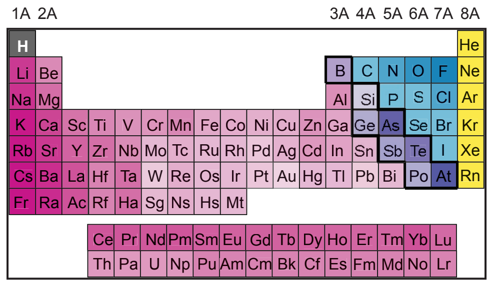
Why is the electronegativity of the noble gases listed as zero?

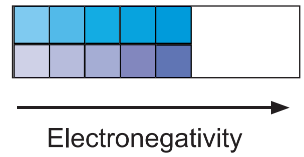
For an electron shared between hydrogen and chlorine, would you expect the electron to be closer to the hydrogen or the chlorine?

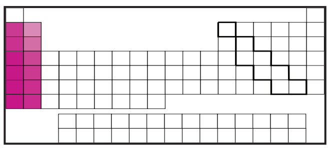
CHEMICAL BONDING

ROAD MAP

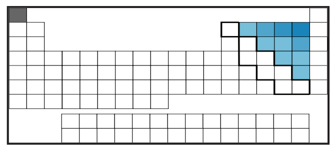
- Hydrogen
- Metals
- Metalloids
- Nonmetals
- Group 18



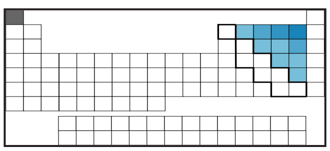



Groups 1 and 2 Metals

+


NonMetals and H

→ **Ionic Bonding**


NonMetals and H

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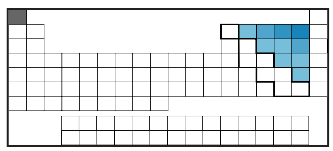
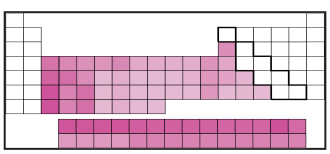
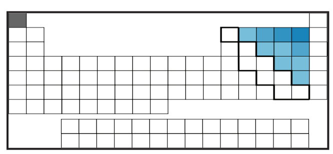

NonMetals and H

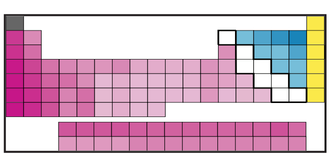
→ **Covalent Bonding**


Other Metals

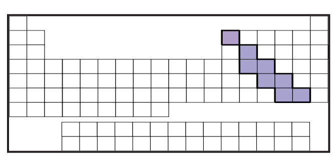
+


NonMetals and H

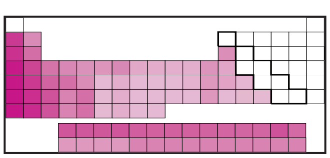
→ **Polar Bonding**


Non Metalloids

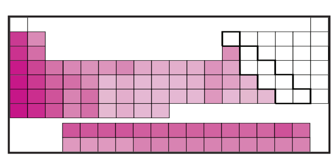
+


Metalloids

→ **Polar Bonding**


Metals

+

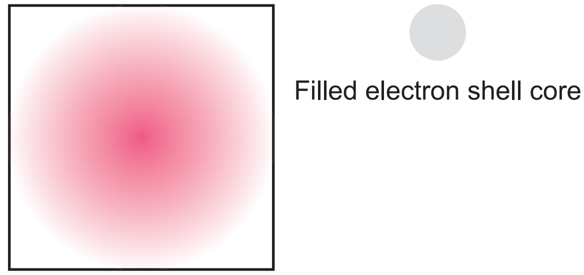

Metals

→ **Metallic Bonding**

CHEMICAL BONDING

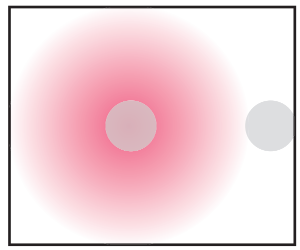
TYPES OF BONDING

The different types of chemical bonding are determined by how the valence electrons are shared among the bonded atoms.



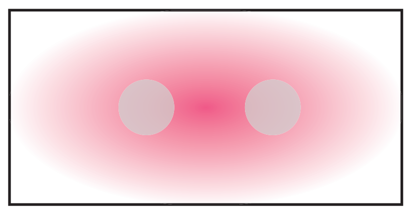
Valence Electron Cloud

In **IONIC BONDING** the valence electrons are completely transferred from one atom to the other atom. Ionic bonds occur between metals and nonmetals when there is a large difference in electronegativity.



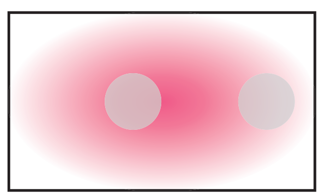
Ionic Bonding

In **COVALENT BONDING** the valence electrons are shared as pairs between the bonded atoms.
Pure covalent bonding only occurs when two nonmetal atoms of the same kind bind to each other. When two different nonmetal atoms are bonded or a nonmetal and a metal are bonded, then the bond is a mixture of covalent and ionic bonding called polar covalent bonding.



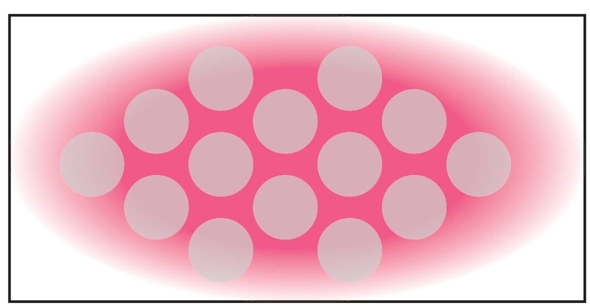
Covalent Bonding

In **POLAR BONDING** the electrons are shared but NOT equally. Many compounds have the characteristics of BOTH ionic and covalent bonding. Electronegativity differences determine the balance of character.



Polar Bonding

In **METALLIC BONDING** the valence electrons are shared among all of the atoms of the substance. Metallic bonding occurs when metals bond to either themselves or mixed with other metals in alloys.



Metallic Bonding

Using the periodic table of electronegativities from the last page, write down examples of atom pairs which you would expect to form covalent bonds, polar covalent bonds and ionic bonds.

CHEMICAL BONDING

PROPERTIES CONTROLLED BY CHEMICAL BOND

Chemical bonding determines the physical properties of substances. These properties are listed below for covalent, ionic and metallic bonding.

Covalent

Gas, liquid, or a soft solid.

Low melting point and low boiling point.

Insoluble in H_2O
Soluble in nonpolar solvents.

Nonconductor of heat and electricity.

Nonlustrous

Using the list of properties on the left, try to assign as many of the common substances in your environment to one of the types of bonding.

List and describe some substances which do not seem to fit into any of the three types of bonding.

Ionic

Crystalline solid.

Very high melting point.

Soluble in H_2O.
Insoluble in nonpolar solvents.

Nonconductor of heat and electricity.
Conducts electricity in aqueous solutions.

Examples: NaCl, $CaCO_3$

Metallic

Malleable solid.

High melting point and boiling point.

Insoluble in H_2O.
Insoluble in nonpolar solvents.

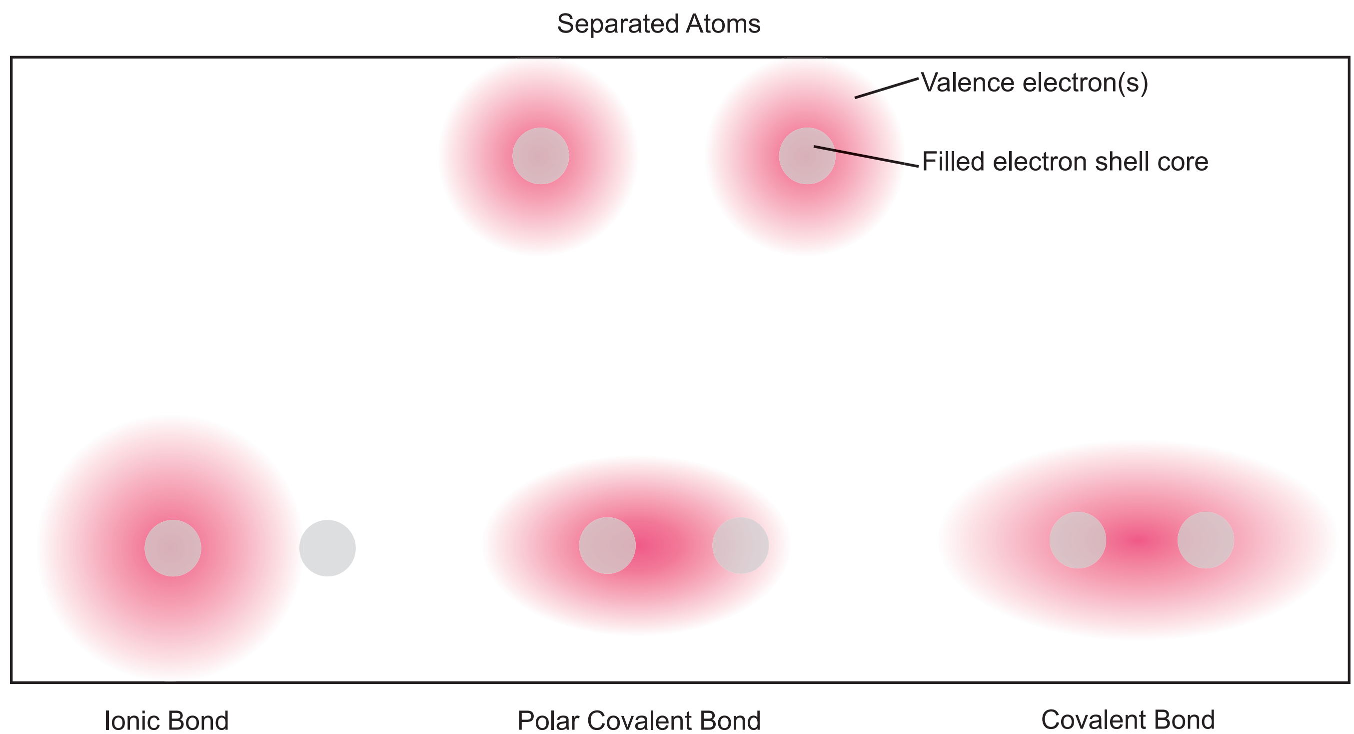
Conducts heat and electricity.
Lustrous

Examples: gold, copper

CHEMICAL BONDING

POLAR BONDS

Ionic and covalent bonds are two ideal types.
Many bonds share characteristics of both ionic and covalent bonding. They are called polar covalent bonds and they tend to occur between atoms of moderately different electronegativities.
In polar covalent bonds the electrons belong predominantly to one type of atom while they are still partially shared by the other type, as illustrated in the following pictures of the valence electron densities.



In the picture above, the separated atoms look alike. If, in fact, they are the same kind of atom, which of the three bonds shown is possible?
Why only that one?
What other type of bonding is possible between identical atoms?

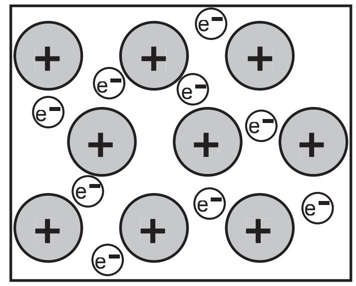
Using the chart of electronegativities, arrange the following compounds in an order from most ionic to most covalent:
Al_2O_3 , $CaCl_2$, NaF , O_2, NaCl,

CHEMICAL BONDING

METALLIC BONDING

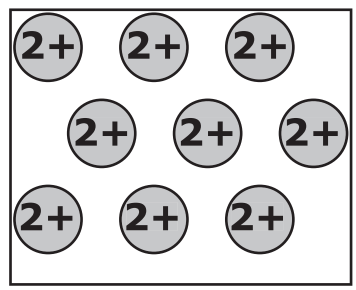
'ELECTRON SEA' MODEL FOR METALS

Metals are formed from elements on the left hand side of the periodic table. Having generally low electronegativity they tend to lose their valence electrons easily. When we have a macroscopic collection of the same or similar type of metallic atoms, the valence electrons are detached from the atoms but not held by any of the other atoms. In other words, these valence electrons are free from any particular atom and are only held collectively by the entire assemblage of atoms. In a metal the ion cores are held more or less at fixed places in an ordered, or crystal, lattice. The valence electrons are free to move about under applied stimulation, such as electric fields or heat.



1

Picture 1 presents a regular arrangement of the ion cores for a metal with a single valence electron per atom as well as a snapshot of the location of the freely moving valence electrons.



2

Picture 2 shows a collection of ion cores for a metal with two valence electrons. Draw in the valence electrons. (Little circles are good enough.)
HINT: Metals are neutral in charge.

What is the origin of electrical and thermal conductivity in sodium metal?

Why do metals exhibit a wide range of melting points and hardness?

CHEMICAL BONDING

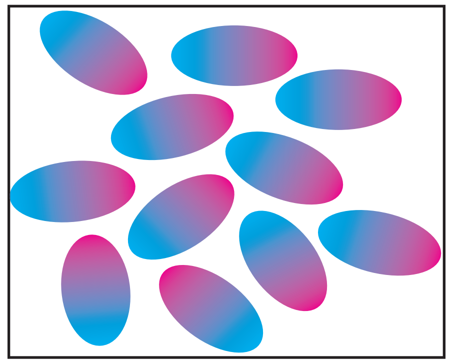
INTERMOLECULAR FORCES

In addition to covalent, polar, ionic and metallic bonding there are intermolecular forces which contribute to the stability of things. These include dipole-dipole forces, hydrogen bonding and London dispersion forces.

DIPOLE-DIPOLE FORCES

Many molecules are electric dipoles, that is, they have net positive charge on one part of the molecule and net negative charge on another part. Since opposite charges attract and like charges repel, these molecules will tend to orient themselves so that there is the most attraction and the least repulsion.

Why is dipole-dipole interaction more important in liquids than in solids?
Why is it more important in liquids than in gases?
Can homonuclear diatomic molecules such as H_2, O_2 and N_2 have dipole-dipole forces?

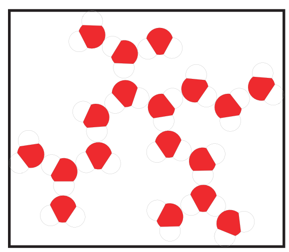


DIPOLE-DIPOLE INTERACTION

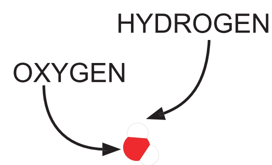
HYDROGEN BONDING

A particularly strong and important variety of dipole-dipole interaction is called hydrogen bonding. A hydrogen atom on one molecule is attracted to a highly electronegative atom in another molecule. Hydrogen bonding is strong both because of the high polarity involved and because the small size of the hydrogen atom permits a close approach between it and the electronegative atom

Hydrogen bonding is particularly noted between water molecules, but from the description given above you should be able to deduce other substances in which hydrogen bonding occurs.



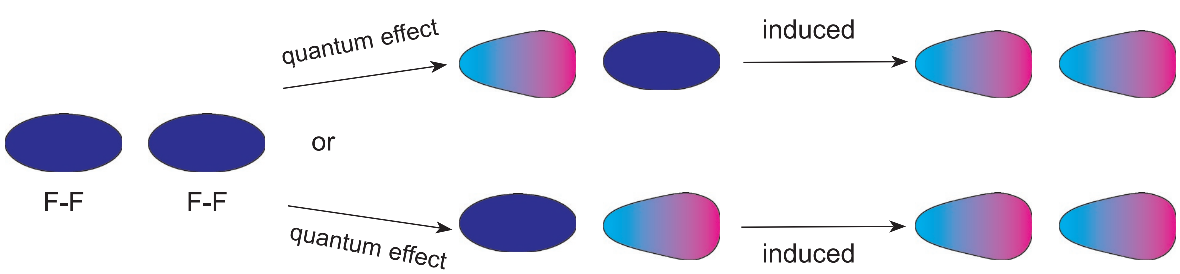
HYDROGEN BONDING



WATER MOLECULE

LONDON DISPERSION FORCES

Even nonpolar molecules have a random fluctuation of charge making the molecule temporarily polar. This then induces an opposite fluctuation in a neighboring molecules so that the two molecules have opposite charges on their near sides and attract each other.

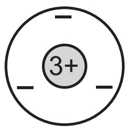


CHEMICAL BONDING

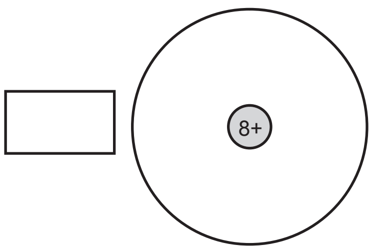
IONS: COUNTING ELECTRONS AND PROTONS

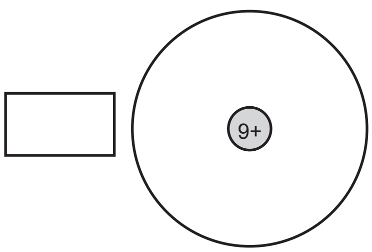
NEUTRAL ATOMS

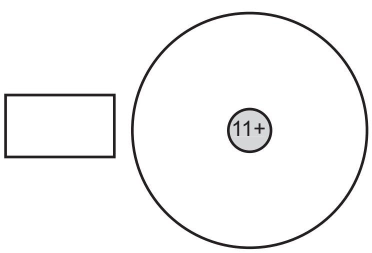
Neutral atoms have the same number of electrons as protons. In the picture below, the nuclear charge is represented by the gray circle marked 3+, for the 3 protons in the nucleus of lithium. Electrons are marked as horizontal dashes, one for each electron.

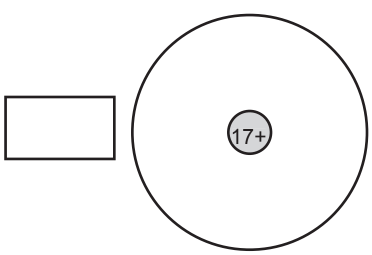
Li 

In the pictures below, draw in the number of electrons required to make the atom neutral and write the element symbol in the box to the left of the atom.



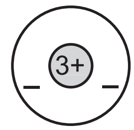




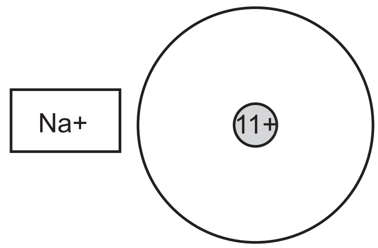


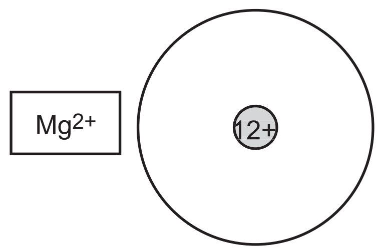
POSITIVE IONS

Positive ions have more protons than electrons. Since the number of protons an atom has is fixed in ordinary chemical reactions, positive ions are produced by removing electrons from the atoms.

Li+ 

In the pictures below draw in the number of electrons needed to make the ion named in the box.

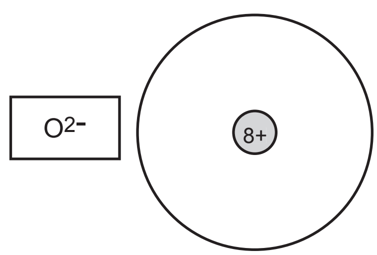


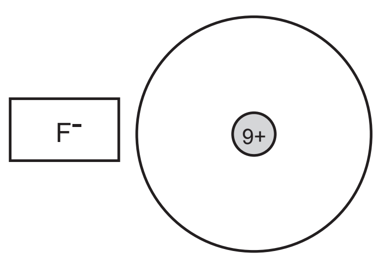


NEGATIVE IONS

Negative ions have more electrons than protons. Since the number of protons is unchanged from the neutral atom, negative ions are formed by the addition of electrons.

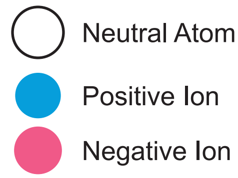
In the pictures below draw in the number of electrons needed to make the ion named in the box.

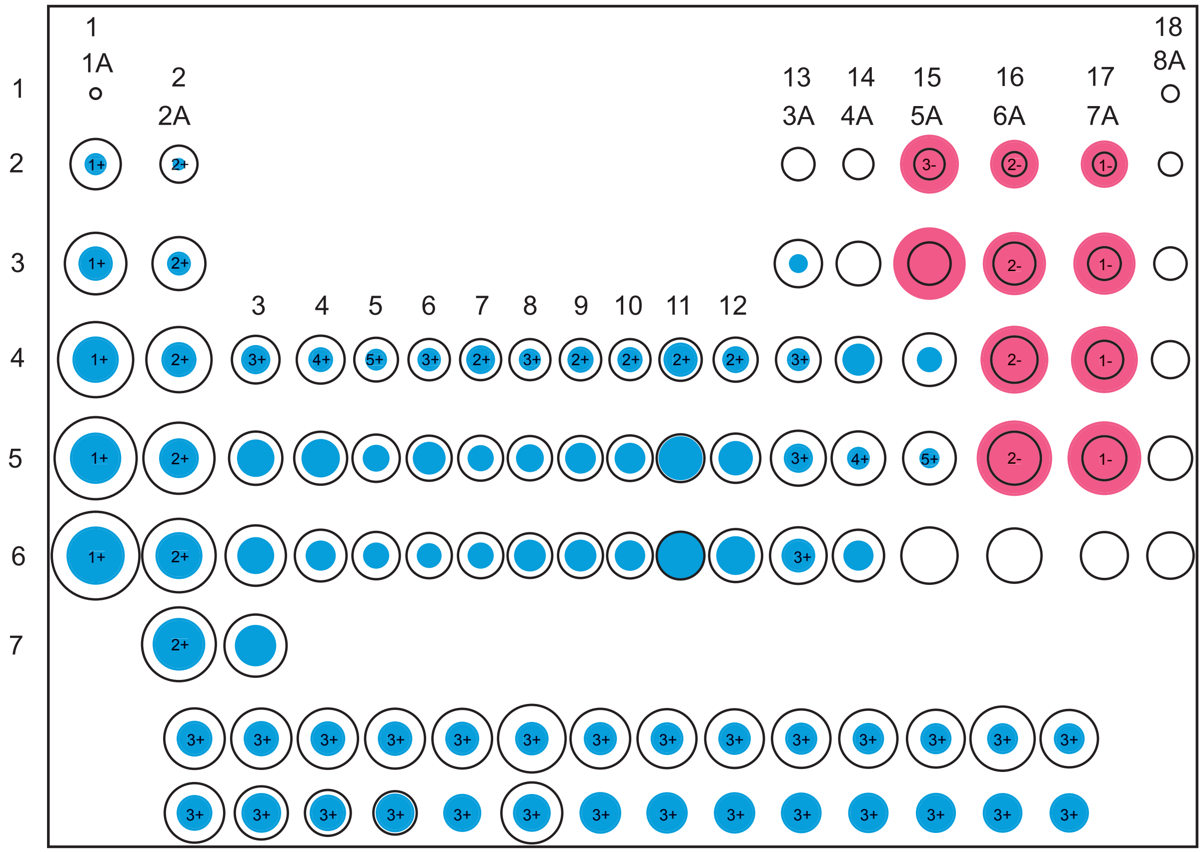




CHEMICAL BONDING

ATOMIC AND IONIC RADII





In this version of the periodic table the relative sizes of both neutral atoms and of their most common ions are shown, as well as the charges on their ions. The atoms are shown as black outline circles and the ionic diameters are colored blue for positive ions and red for negative ions.

Why are the positive ions smaller than their neutral atoms while the negative ions are larger than the neutral atoms?

Why do both ions and atoms tend to grow larger as we go down the periodic table?

What is the smallest atom? What atom has the smallest ion (too small to show on the table)? Find the largest atom and identify it on a standard periodic table.

What kind of ions do atoms with large electronegativities tend to form?

What makes the atoms and ions in the middle of periods 4, 5 and 6 so small? What makes the samarium atom so large?

Identify the two kinds of atom which appear about the same size as their ion and explain why this is so.

Why are the antimony and beryllium ions so small? Differentiate between the causes.

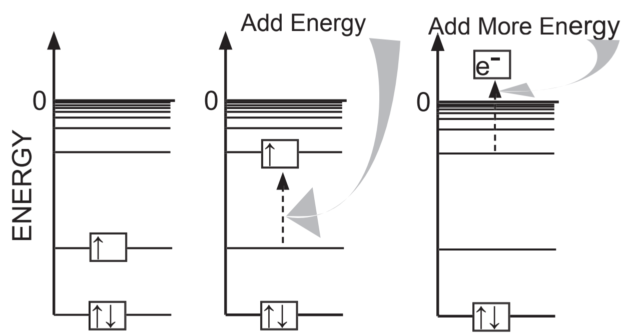
Why are the Lanthanide ions of such similar size?

How might you use the chart of atomic and ionic radii to explain the strengths of ionic bonding between various ions?

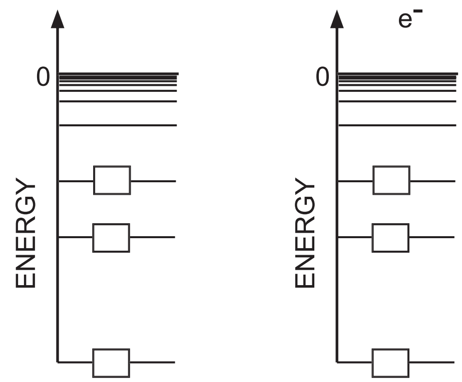
Compare the ionic and atomic radii table above with the chart of electronegativities and attempt to explain as many aspects of the sizes of atoms and ions in terms of electronegativity as possible.

CHEMICAL BONDING

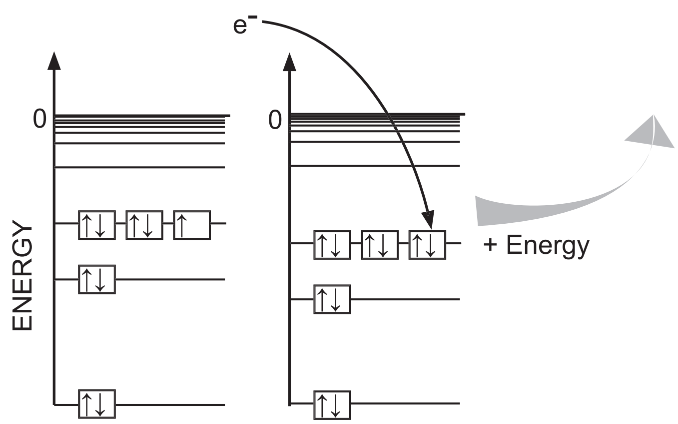
IONS AND ENERGY



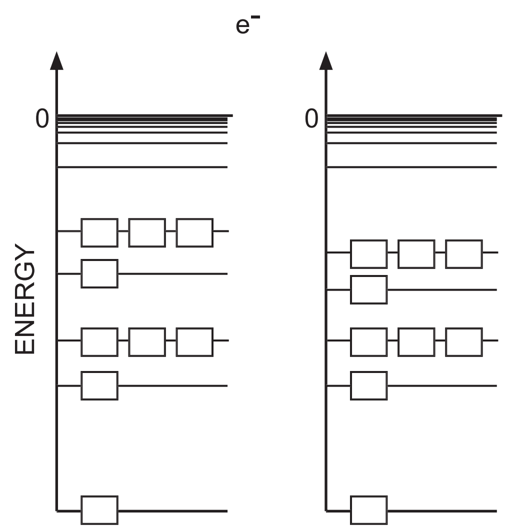
The diagrams above show the ground state of the lithium atom, followed by an excited state, followed by the lithium ion with the free electron. What is the charge of the lithium ion in the right hand drawing?



In the diagrams above, draw in the electrons as arrows which occupy the ground state orbitals of the sodium atom in the left hand picture. In the right hand picture draw in the orbitals and electrons of the sodium ion.



The diagrams above show the ionization of fluorine. What is the charge of the fluoride ion?



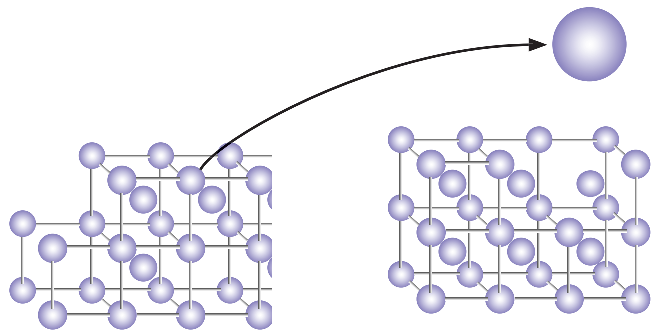
In the diagrams above, draw in the electrons (arrows) for the chlorine atom on the left and for the chloride ion on the right. What is the charge of the chloride ion?

CHEMICAL BONDING

LITHIUM FLUORIDE

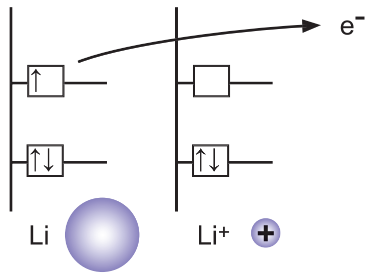
$2Li_{(s)} \rightarrow 2Li_{(g)}$

It requires 155 kJ/mol to separate lithium atoms from their body centered cubic crystal structure.



$2Li_{(g)} \rightarrow 2Li^{+}_{(g)} + 2e^{-}_{(g)}$

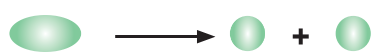
It requires 520 kJ/mol to ionize lithium atoms.



Add the energies which are associated with the process a making lithium fluoride crystal lithium crystal and difluoride molecules. Is the net reaction endothermic or exothermic?

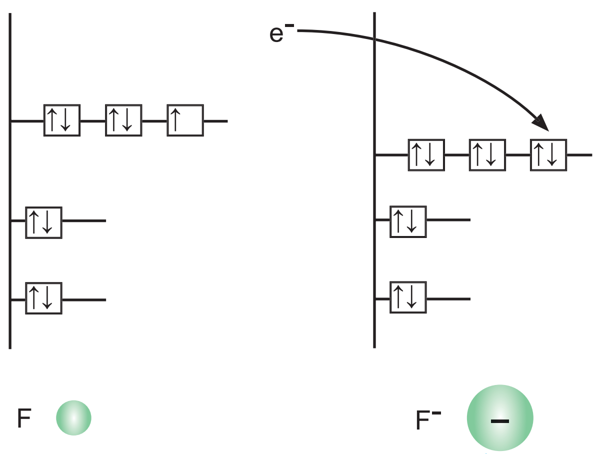
$F_{2(g)} \rightarrow 2F_{(g)}$

It requires 80 kJ/mol to dissociate the difluoride molecule.



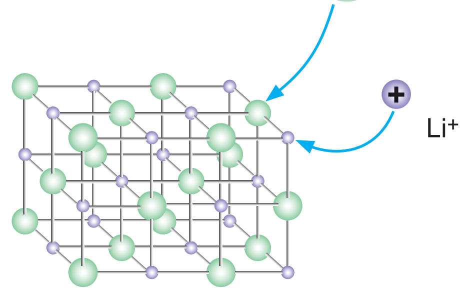
$2F_{(g)} + 2e^{-}_{(g)} \rightarrow 2F^{-}_{(g)}$

Ionization of the fluorine atom gives off 328 kJ/mol of energy.

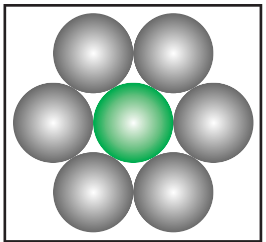


$2Li^{+}_{(g)} + 2F^{-}_{(g)} \rightarrow 2Li^{+}F^{-}_{(s)}$

Combining the lithium and fluoride ions into their crystal gives off 1030 kJ/mol of energy.

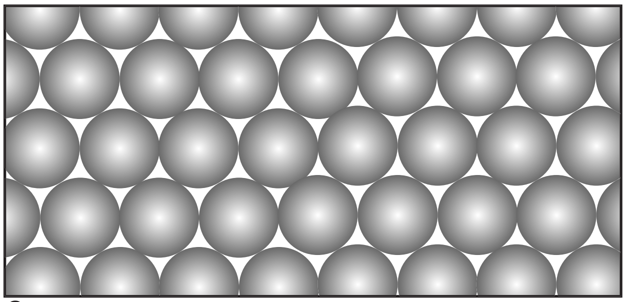


CRYSTAL PACKING

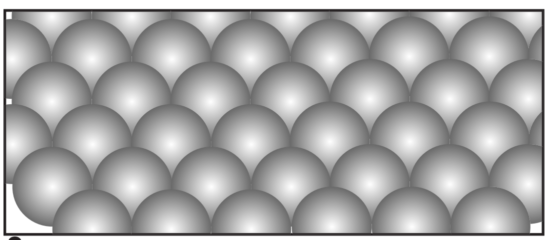

1

The picture at left shows seven spheres packed as close together as possible in the plane. This is called close packing. How many gray spheres touch the green sphere?

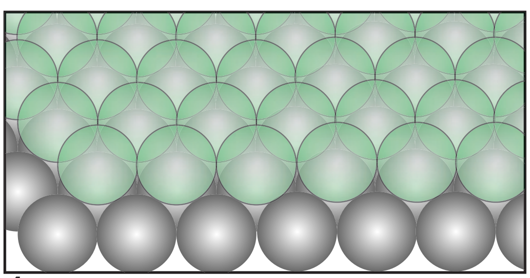
Using circles, sketch in the box above another way to tile the plane.


2

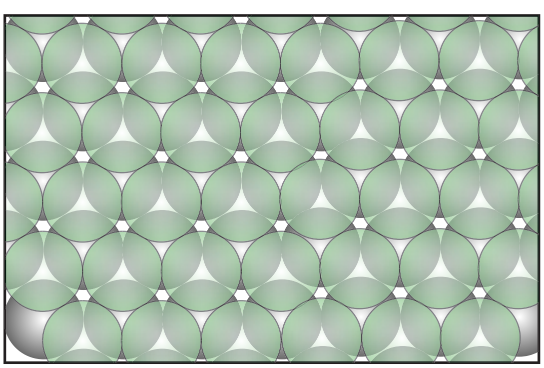
The picture above shows how close packing can fill, or *tile*, the plane. Notice the little triangles (with curved sides) that lie in between the spheres. Some of them point up and some of them point down. Compare the number of each kind of triangle.


3

Picture 3 is simply picture 2 looked at through an angle.


4

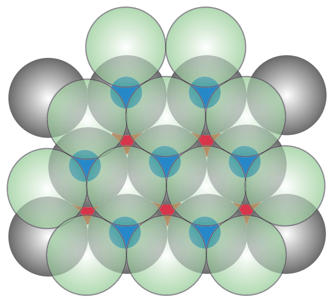
Picture 4 shows the spheres of picture 3 topped by another plane of spheres set to fit as closely as possible into the lower plane. For clarity, the second plane is semitransparent green with a black outline.


5

Picture 5 shows the same planes of atoms as in picture 4 but viewed from above. What proportion of the triangular spaces between the spheres of the lower (grey) plane are occupied by the second (green) plane of spheres?

CRYSTAL PACKING

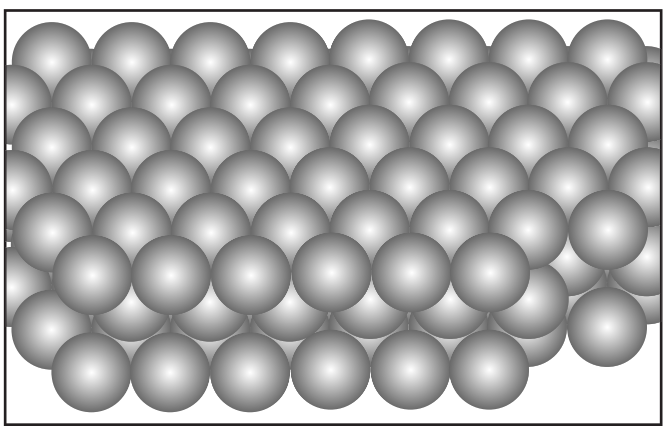
Picture 6 shows the same two layers as picture 5 but two different sets of spaces between the green spheres of layer 2 are marked either red or blue. We can construct a third layer by placing spheres either in the blue spaces or the red spaces.



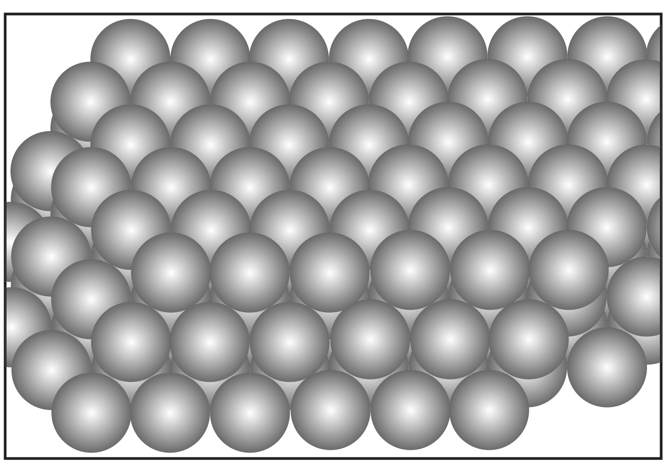
6

Notice that the blue spaces lie directly above the grey spheres of layer 1. If we use these spaces for layer 3 then we get a two level repeating structure. If we name layer 1 A and Name layer 2 B then we can describe the structure as ABABAB....
This is called hexagonal close packing or hcp for short.

Alternatively we can place the third layer of spheres in the red spaces. Then the third layer is differently located than either of the first two and is named C. We can describe this structure as ABCABC....
It is called cubic close packing or ccp.



7 hcp



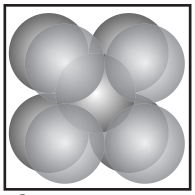
8 ccp

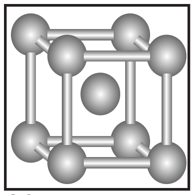
Why can we not use both the red and the blue spaces for placing the layer 3 spheres?

Using colored pencils, pens or crayons, draw circles representing the hcp structure in the box above.

Using colored pencils, pens or crayons, draw circles representing the ccp structure in the box above.

CRYSTAL PACKING


9

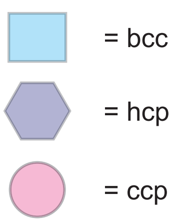

10

Here you see another packing structure in which eight atoms are located at the corners of a cube and a ninth atom is at the center of the cube. This is called body centered cubic, or bcc. Picture 9 shows a space filling model and picture 10 shows a ball and stick model.

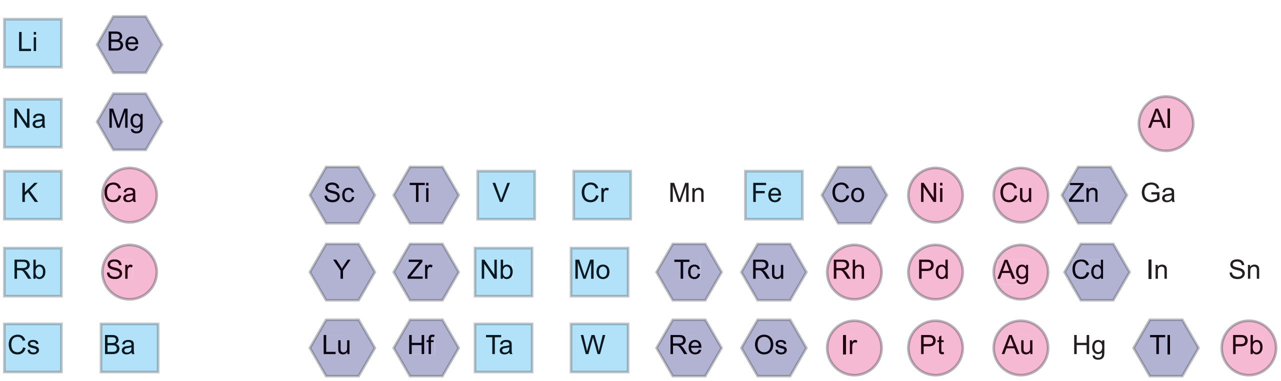
In the box below, you draw a bcc structure for 13 atoms.

Using spheres, such as marbles, bbs, ping pong balls, etc. experiment with hcp, ccp and bcc packing in order to determine which is the most efficient packing, i.e., which can get the most spheres into the same space.

As you can see in the table below, the metals have packing structures which are related to their places in the periodic table.

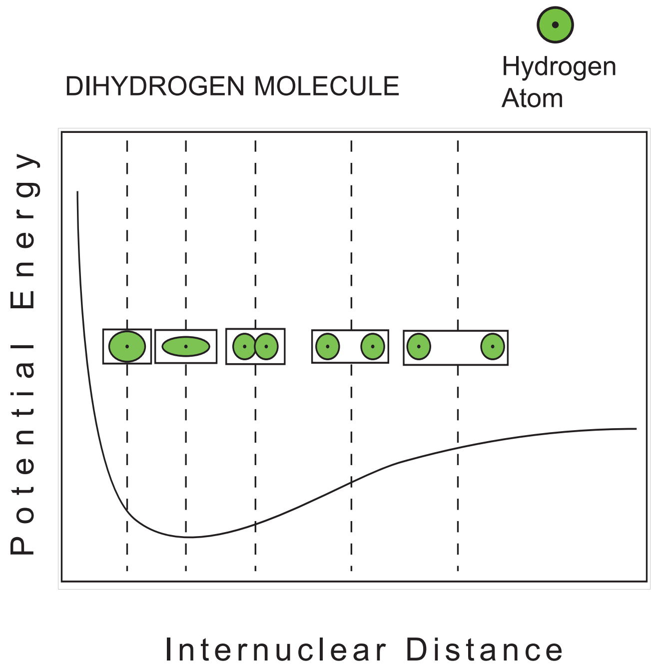


Comparing the packing structures of the metals to their electronegativity, do you find any relationship?



CHEMICAL BONDING

COVALENT H_2

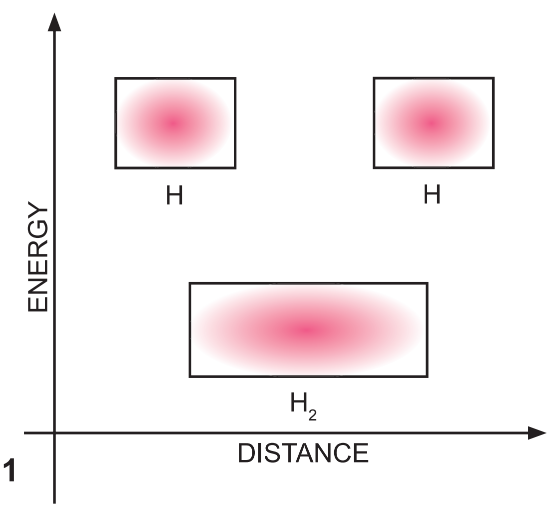


Confining electrons makes them ‘dance’. This is part of quantum theory. The tighter electrons are squeezed the harder they dance. Dancing electrons have kinetic energy. But electrons will slow down if they can. When they have more room they can slow down, which means they have less kinetic energy.
In a hydrogen molecule the electrons can move through the space of two atoms instead of one, which means that they have more room and thus can dance slower and have less kinetic energy. (Picture 1)
There are also electric attractions and repulsions between the particles in the molecule. Picture 2 shows the repulsions of like charges as colored arrows and the attractions of opposite charges as black arrows.
The additive combination of the electric and kinetic energy effects gives the covalent bond for hydrogen.

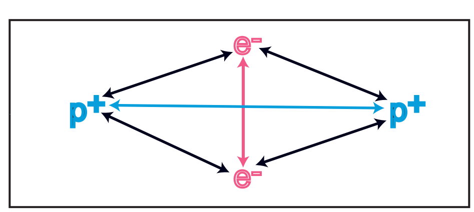
Suppose you have two well separated hydrogen atoms and begin moving them closer together. From the picture aboveyou can see that the energy of the system will decline as they are being moved together until at some distance the system will have a minimum energy.

What causes to energy to rise as the atoms are moved closer than the minimum energy?

A dihydrogen molecule consists of two hydrogen nuclei (protons) held a fixed distance apart and surrounded by a probability density cloud of two electrons.
As you can see from the picture above, the separation is that at which the system is in the state of lowest energy. But what are the factors which cause this to be a low energy state?
There are primarily two factors. They are quantum and electrostatic effects.
Quantum theory produces two effects, lowered energy and discrete energy levels.



1



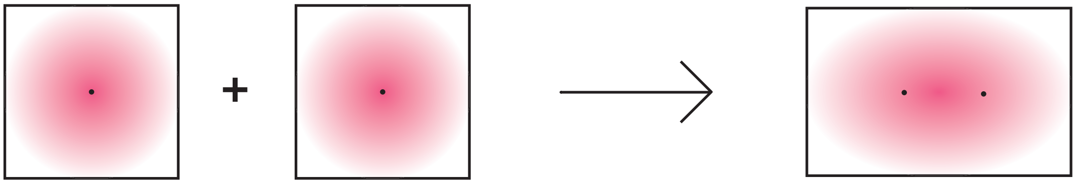
2

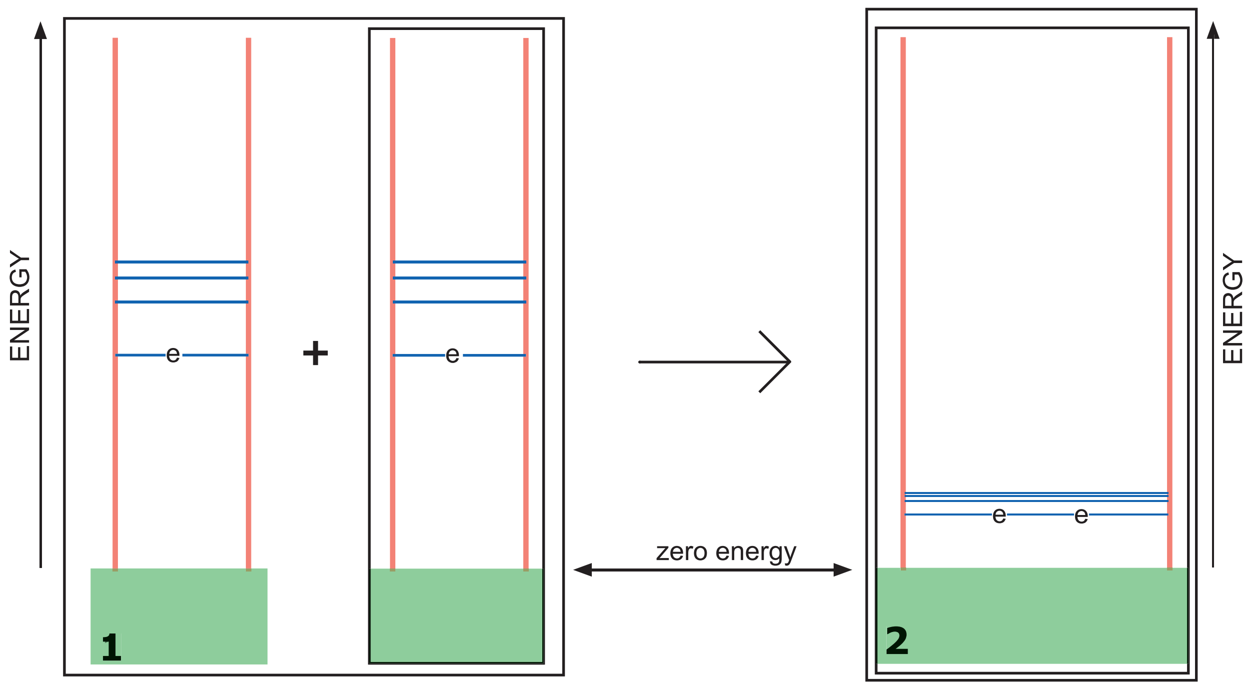
CHEMICAL BONDING

QUANTIZATION

Just below we show two hydrogen atoms and their combination as H_2 on the right.

The red electron cloud represents the probable location of the electrons. Notice that the space for electrons is larger in the H_2 molecule than it is in the separated hydrogen atoms.





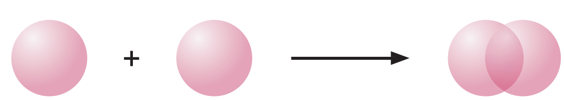
One of the basic principles of quantum mechanics is that whenever anything is confined in a finite space, it can only occupy one of a discrete set of energy levels. It is also the case that when the space is made larger the energy states are lower.
In picture 1 the blue lines represent the energy states available for a particle confined between the orange walls.
In picture 2 the blue lines show how the energy states are lower when the particles are given more space.

Which picture, number 1 or number 2, has the lowest total energy?

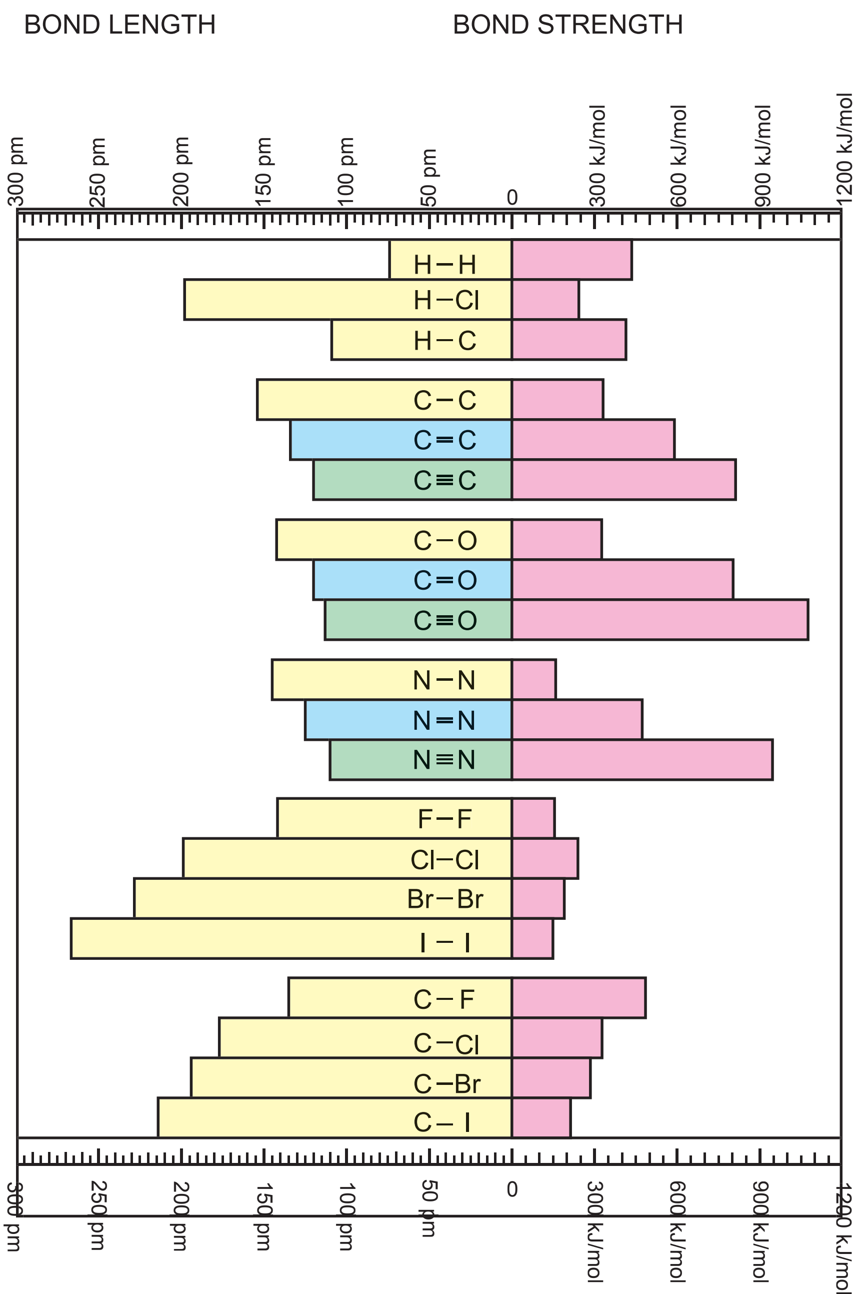
If picture 1 represents the energy states of two separate hydrogen atoms, then what could picture 2 represent?

These pictures do not necessarily show that if you move two hydrogen atoms close together they will bond to form a hydrogen molecule but they do show that the hydrogen molecule will be at a lower energy state than the combined energies of the separate atoms and that you would need to add energy to the molecule to get the atoms separated and that therefore the molecule will hold together until you add that energy.

Now that we know why covalent bonding occurs we will use simplified pictures known as overlapping orbitals to describe more complicated molecules. Just to the right we show this model for hydrogen.



BOND LENGTH AND STRENGTH

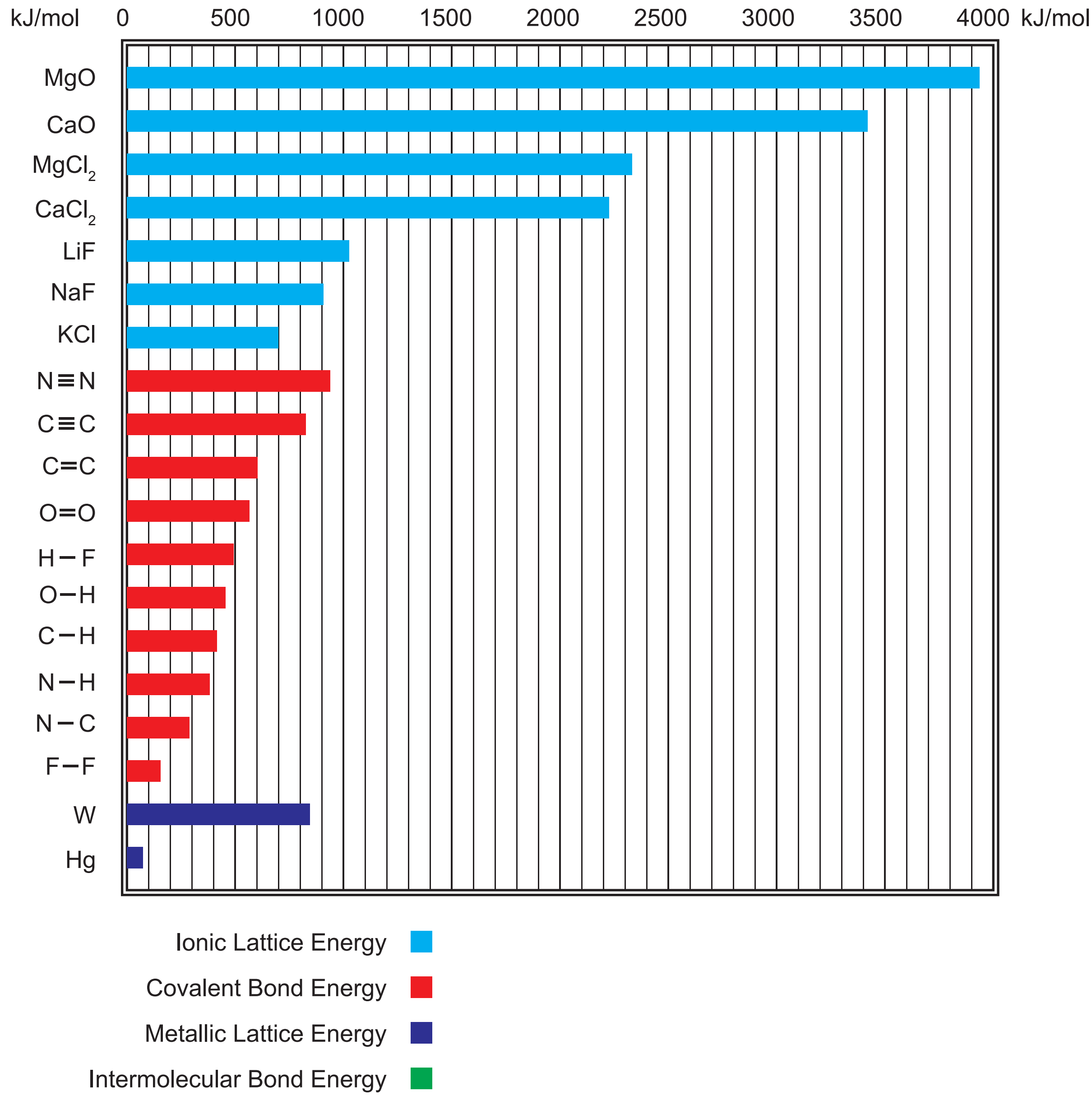


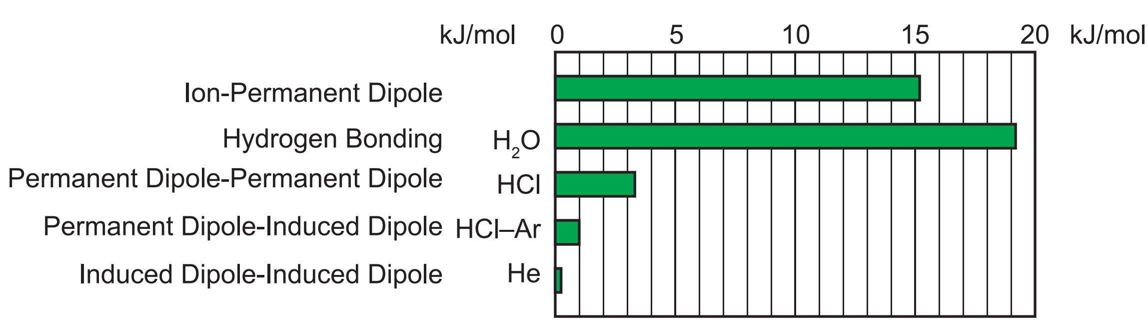
Which are the longest and shortest bonds shown?
Which are the strongest and weakest bonds shown?

In each group of related compounds, what correlation do you observe between bond length and bond strength?
What are some exceptions?

CHEMICAL BONDING

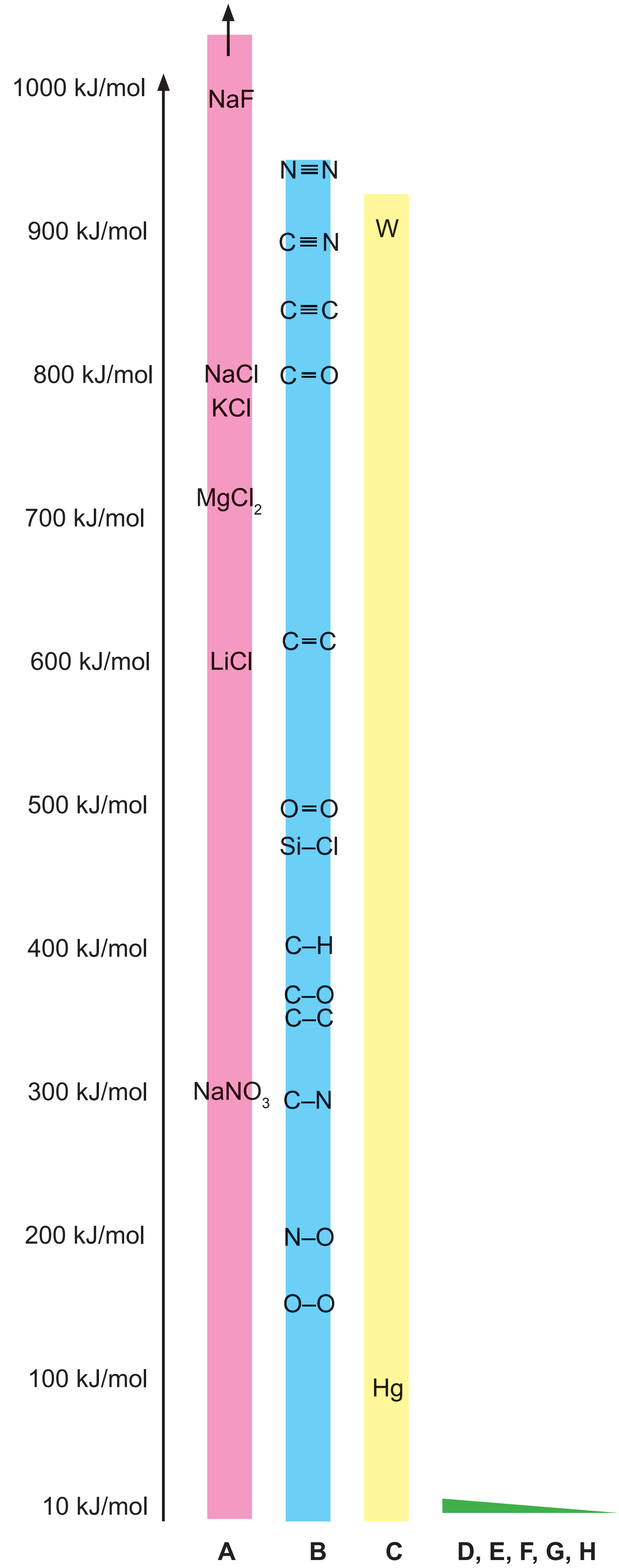
STRONG AND WEAK BONDS





CHEMICAL BONDING

STRONG AND WEAK BONDS



STRONG BONDS

A. Ionic
Much of the strength of ionic bonding comes about when the ions are packed together in crystal lattices, so that each ion is held in an attractive field with several neighbors of the opposite charge. These binding energies can range up to several thousand kilojoules per mole.

B. Covalent
Covalent bonds are also strong, ranging up to 940 kilojoules per mole for triple bound N_2.

C. Metallic
Metals are also strongly bonded, as you can deduce from their strength and hardness, although the liquid metal mercury is an exception.

WEAK BONDS

Weak bonds, often called intermolecular forces, are several orders of magnitude weaker that strong bonds described above. One of the relatively stronger of the weak bonds is hydrogen bonding with energies ranging from two to ten kilojoules per mole.

D. Ion-Permanent Dipole
These would include salts dissolved in a polar substance, e.g., NaCl dissolved in water.

E. Permanent Dipole - Permanent Dipole
This class of bond includes hydrogen bonding.

F. Ion - Induced Dipole

G. Permanent Dipole - Induced Dipole

H. Induced Dipole - Induced Dipole
These are also known as van der Waals forces or as London dispersion forces. They are quite weak but they always exist between nearby molecules and they are always attractive.

CHEMICAL BONDING

COVALENT TO METALLIC

While we have a simple gradation between ionic and covalent compounds, we are also able to find a path of bonding types which goes from covalent to metallic bonding. This is not a simple gradation but rather detours through the network covalent bonds, some of which are semiconductors.

Our essential procedure in tracing the connections between these types of bonding is to follow the valence electrons.
In covalent bonding the bonding pairs of electrons are held in distinct orbitals, even though their physical location is, as always, given by a continuous probability density.
Several atoms, both like and unlike, can be connected pair-wise together by covalent bonds and large molecules, particularly organic, can be constructed this way. However, we also begin to see phenomena other than pair wise bonding between definite atoms appearing. An example is ozone, O_3 , a linear molecule in which each of the outer atoms is bonded to the central atom equally, but with both of them sharing three bonds between them. In this case the individual electrons cannot be assigned to a definite bond and are said to be delocalized.
There are some types of atoms, such as carbon and silicon, where covalent bonds form between unlimited numbers of the atoms. In the graphite form of carbon three of the bonding electrons of each carbon atom form covalent bonds between neighboring atoms to form a hexagonal planar structure, but the fourth bonding electron sticks out between planes. These bonds overlap and connect the planes together and they are also delocalized, which means that these electrons are free to move around under, say the pressure of an electric field and thus graphite is an electrical conductor.
Finally, in metals, all of the valence electrons are held communally by the whole substance and are thus free to conduct electricity or heat.
There are also more extreme cases of delocalization than metals. These include superconductors and the new Bose-Einstein condensates.

Electrons can only be located in space with a probability density, but we can also locate electrons with regard to their situation with respect to other entities.

For example, there are free electrons which are not bound to any atom or molecule but are pushed about by electric and magnetic fields. On earth, they usually do not remain free very long but end up (at least for a while) in one of the following situations.

Describe the location , stability and energy level of an electron in each of the situations listed below.

An electron in an **atomic orbital.**

An electron in a **subshell.**

An electron in a **shell.**

A **valence** electron.

An electron in a filled **shell.**

An electron in an **atom.**

An electron in an **excited state.**

An electron in a **negative ion.**

An electron in a **positive ion.**

An electron in a **molecular orbital.**

A valence electron in a **metal.**

A valence electron in a **superconductor.**

An electron in a **Bose-Einstein condensate.**

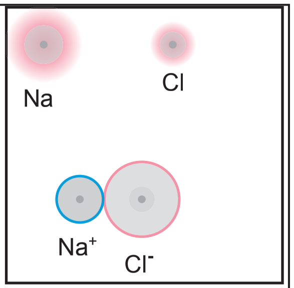
CHEMICAL BONDING — ELECTRON DELOCALIZATION

Localized ⟵⟶ Delocalized

1	2	3	4	5	6	7	8	9
Ionic	Polar Covalent	Covalent	Molecular Orbitals	Semiconductors	Semi-metallic	Metals	Superconductors	Bose-Einstein
CsF NaCl	H_2O CO_2 CO	O_2	O_3 C_6H_6	Si	Graphite	Gold	K_3C_{60} at 19K	Rb at 10^{-8}K
Electrons are held by each atom in completed shells.	Bonding electron pairs cluster around the most electronegative atom(s).	Bonding electron pairs are shared equally by both atoms.	Some bonding electrons are held collectively inside the molecule.	A small proportion of the electrons are free to move about the lattice.	In graphite, valence electrons are free to move in two dimensions.	All valence electrons are free to move throughout the lattice.	All the valence electrons are free to move without resistance.	In a Bose-Einstein condensate all of the electrons become part of a single 'atom'.

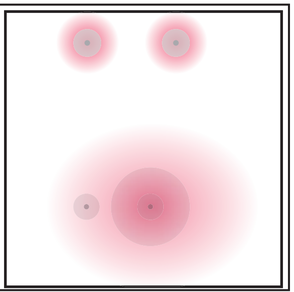
1

Filled shells are shown in grey.
Valence electron clouds are in red.
Negative ions are outlined in red.
Positive ions are outlined in blue.



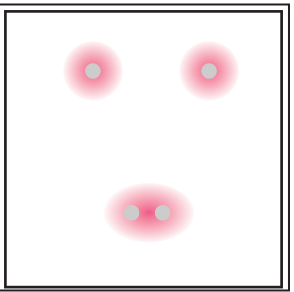
2

When two atoms of moderately different electronegativity are bound, the binding electrons are shared unevenly, tending toward the more electronegative atom.



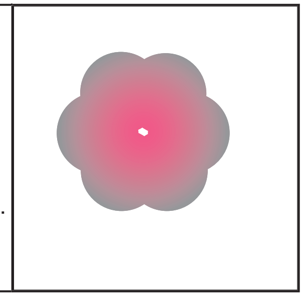
3

In a homonuclear diatomic molecule the binding electron pairs are shared evenly and symmetrically by both atoms.



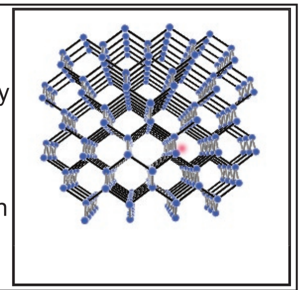
4

In Benzene six of the bonding electrons are held collectively by the molecule as a whole. In the picture these are represented by the red cloud.



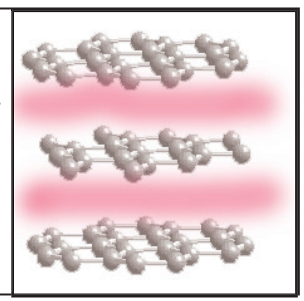
5

In a semiconductor, such as Silicon, a small minority of valence electrons are free to move about the lattice.
The free electron is shown as the small red blur at right.



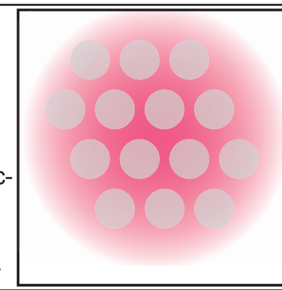
6

In graphite the carbon atoms are bound in hexagons that are arranged in sheets. The sheets are loosely bound to each other and the electrons between the sheets are free to move.



7

In the picture at right, the gray circles represent the core of filled shells while the red cloud is the set of valence or conducting electrons held in common by the metal. Compare and contrast with number nine.



8

9

In the picture at right, the small grey dots represent the separate nuclei. The red cloud represents all (not just the valence) electrons held in common by the substance, as if it were one atom.