ELECTRON AFFINITY:

In chemistry and atomic physics, the **electron affinity** of an atom or molecule is defined as the energy *change* when an electron is added to a neutral atom or molecule to form a negative ion.

$$X + e^{-} \rightarrow X^{-} + \text{energy}$$

When an electron is added to a neutral atom, i.e. first electron affinity, energy is released; thus, the first electron affinities are negative. However, when an electron is added to a negative ion, i.e. second electron affinity, more energy is required. Thus, more energy is released to add the electron into an ion because the negative ion has to force the electron to go into its electron orbital; thus, the second electron affinities are positive.

First Electron Affinity (negative energy because energy released):

$$X(g)+e^{-}\rightarrow X^{-}(g)$$

Second Electron Affinity (positive energy because energy needed is more than gained):

$$X^{-}(g)+e^{-}\rightarrow X^{2-}(g)$$

For example,

$O_{(g)} + e^{-} \longrightarrow O^{-}_{(g)}$ 1st EA = -142 kJ mol^{-1}

$O^{-}_{(g)} + e^{-} \longrightarrow O^{2-}_{(g)}$ 2nd EA = $+844$ kJ mol^{-1}

The positive sign shows that you have to put in energy to perform this change. The second electron affinity of oxygen is particularly high because the electron is being forced into a small, very electron-dense space.

From table (5) these data are listed along with the electron configurations of these elements, however, they make sense. These data can be explained by noting that electron affinities are much smaller than ionization energies. As a result, elements such as helium, beryllium, nitrogen, and neon, which have unusually stable electron configurations, have such small affinities for extra electrons that no energy is given off when a neutral atom of these elements picks up an electron. These configurations are so stable that it actually takes energy to force one of these elements to pick up an extra electron to form a negative ion.

Table (5) Electron Affinities and Electron Configurations for the First 10 Elements in the Periodic

Element	*Electron Affinity (kJ/mol)*	*Electron Configuration*
H	72.8	$1s^1$
He	<0	$1s^2$
Li	59.8	[He] $2s^1$
Be	<0	[He] $2s^2$
B	27	[He] $2s^2\,2p^1$
C	122.3	[He] $2s^2\,2p^2$
N	<0	[He] $2s^2\,2p^3$
O	141.1	[He] $2s^2\,2p^4$
F	328.0	[He] $2s^2\,2p^5$
Ne	<0	[He] $2s^2\,2p^6$

Factors Affecting Electron Affinity

1. **Size of Atom (n):** Smaller the size of the atom, stronger is the attraction of its nucleus for the electron to be added. Thus, the smaller the size of an atom, greater is the electron affinity (E.A.).

2. **Magnitude of Nuclear Charge (z):** Greater the magnitude of the nuclear charge of an element, stronger is the attraction for the electrons to be added. Thus, greater the nuclear charge, greater is the electron affinity.
3. **Electronic Configuration:** An atom with stable configuration has no tendency to gain an electron. Such an atom has zero or positive electron affinity. An atom has stable configuration which has

- Fully-filled orbitals
- Half-filled orbitals of the same sub-shell.
- Inert gas configuration.

Electron affinities of Be, Mg and N are almost zero:

- Be (Z = 4; $1s^2\ 2s^2$) and Mg (Z =12; $1s^2\ 2s^2\ 2p^2\ 3s^2$) have available, fully filled s-orbitals in their valence shell. Fully-filled orbitals are the most stable due to symmetry. Thus, these elements have least tendency to accept an electron. Hence, Be and Mg have almost zero electron affinity.
- N (Z = 7; $1s^2\ 2s^2\ 2p_x^1 2p_y^1 2p_z^1$) has half-filled 2p-sub-shell. Half-filled sub-shells are most stable due to symmetry (Hund's rule). Thus, nitrogen has least tendency to accept electron.

Noble Gases have Zero Electron Affinity:

All noble gases (2He=$1s^2$; $_{10}$Ne=$1s^2\ 2s^2\ 2p^6$) have fully-filled valence shells. Fully-filled orbitals are most stable due to symmetry (octet rule). Thus, these elements have no tendency to accept electron.

MOLECULAR ORBITALS:

Covalent bonding in molecules other than H_2, diatomic as well as polyatomic, is usually a more complicated story. It would be yet more complicated but for the fact that any alteration in the electronic structure of an atom due to the proximity of another atom is confined to its outermost (or valence) electron shell.

There are two reasons for this:

<u>First</u>, the inner electrons are much more tightly bound and hence less responsive to external influences, partly because they are closer to their parent nucleus and partly because they are shielded from the nuclear charge by fewer intervening electrons.

<u>Second</u>, the repulsive interatomic forces in a molecule become predominant while the inner shells of its atoms are still relatively far apart. Direct evidence in support of the idea that only the valence electrons are involved in chemical bonding is available from the X-ray spectra that arise from transitions to inner-shell electron states; it is found that these spectra are virtually independent of how the atoms are combined in molecules or solids.

When two atoms come together, their orbitals overlap and the result will he either an increased electron probability density between them that signifies a bonding molecular orbital or a decreased concentration that signifies an antibonding molecular orbital. We saw how the 1s orbitals of two hydrogen atoms could combine to form either the bonding orbital Ψ_s or the antibonding orbital Ψ_A . In the terminology of molecular physics, Ψ_s is referred to as a 1sσ orbital and Ψ_A as a l$s\sigma^*$ orbital. The "1s" identifies the atomic orbitals that are imagined to combine to form the molecular orbital. The Creek letter σ signifies that the molecular state has no angular momentum about the bond axis (which is taken to be the z axis).

This component of the angular momentum of a molecule is quantized, and is restricted to the values $\lambda\hbar$, where $\lambda = 0, 1,2$ …..Molecular states for which $\lambda = 0$ are denoted by σ, those for which $\lambda = 1$ by π, those for which $\lambda = 2$ by δ, and so on in alphabetical order. Finally, an antibonding orbital is labeled with an asterisk, as in lsσ* for the antibonding H_2, orbital Ψ_A.

Figure (2) contains boundary-surface diagrams that show the formation of σ and π molecular orbitals from s and p atomic orbitals in homonuclear diatomic molecules. Evidently σ orbitals show rotational symmetry about the bond axis, while π orbitals change sign upon a 180° rotation about the bond axis. Since the lobes of p_z orbitals are on the bond axis, these atomic orbitals form σ molecular orbitals. The p_x and p_y orbitals both form π molecular orbitals.

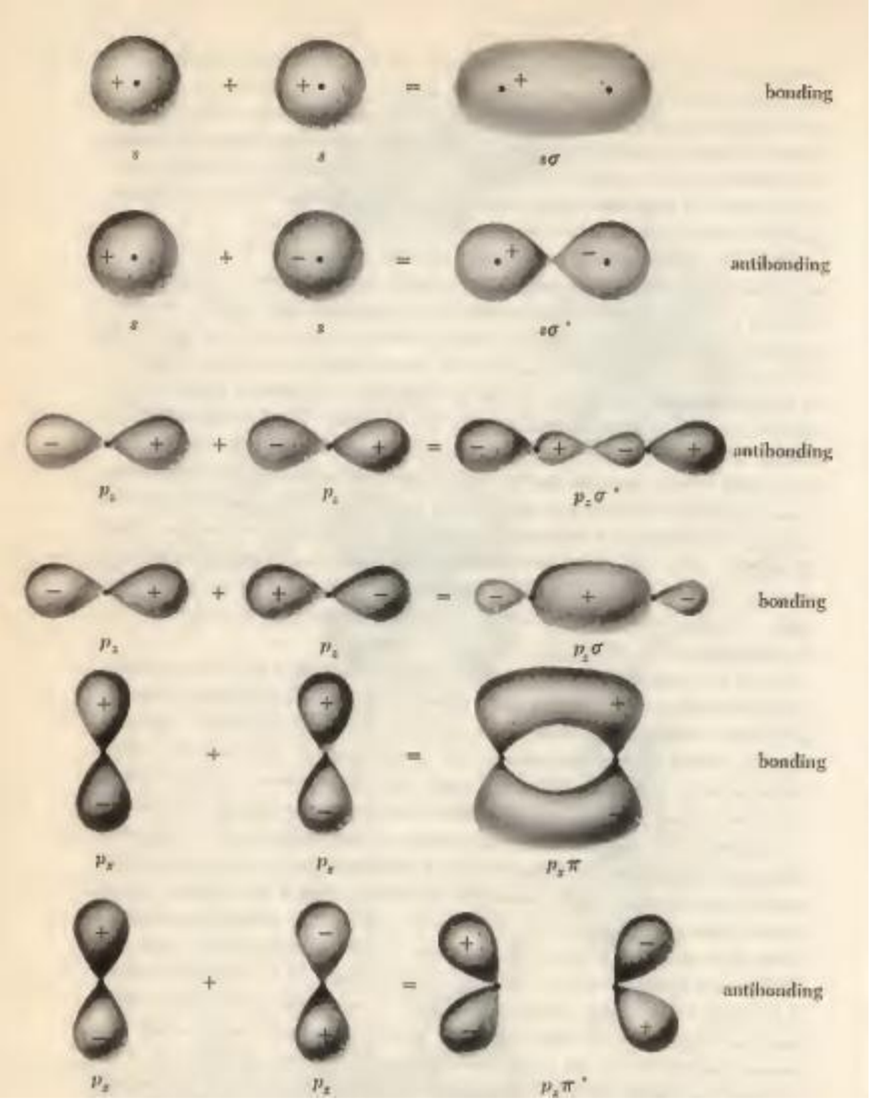

FIG.(2) Boundary surface diagrams showing the formation of molecular orbitals from *s* and *p* atomic orbitals in homonuclear diatomic molecules. The *z* axis is along the internuelear axis of the molecule in each case, and the plane of the paper is the *xy* plane. The $p_y\pi$ and $p_y\pi^*$ orbitals are the same as the $p_z\pi$ and $p_z\pi^*$ orbital except that they are rotated through 90^0.

A heteronuclear diatomic molecule consists of two unlike atoms. In general, the atomic orbitals are not the same in such molecules, so that the bonding electrons in them are not equally shared by both atoms. LiH is the simplest heteronuclear molecule and is a good example of this effect. The normal configuration of the H atom is Is and that of the Li atom is ls^{2}2s which means in each case that there is a single valence electron. The Is orbital of H and the 2s orbital of Li form a σ bonding orbital in LiH that is occupied by the two valence electrons (Fig. 3). In both atoms the effective nuclear charge acting on a valence electron is +e (in Li the core of two Is electrons shields + 2e of the total nuclear charge of + 3e), but in Li a valence electron is on the average several times farther from the nucleus than in H. (The respective ionization energies reflect this difference, with the ionization energy of H being 13.6 eV while it is 5,4 eV in Li.)

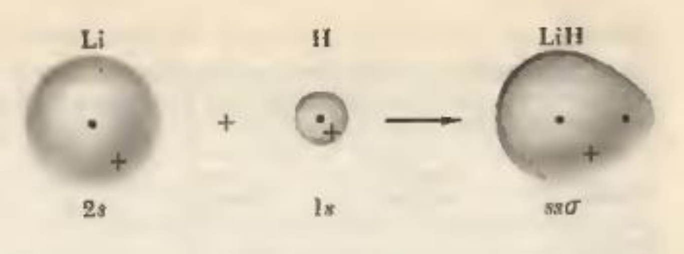

FIG (3) the bonding electrons in LiH occupy a σ molecular orbital formed from 1*s* orbital of the H atom and the 2*s* orbital of the Li atom.

Hence the electrons in the a bonding orbital of LiH favor the H nucleus, and there is a partial separation of charge in the molecule. If there were a complete separation of charge in LiH, as there is in NaCl, the molecule would consist of an Li$^+$ ion and a H$^-$ ion, and the bond would be purely ionic. Instead the bond is only partially ionic, with the two bonding electrons spending perhaps 80% of the time in the neighborhood of the H nucleus and 20% in the neighborhood of the Li nucleus. In contrast, the bonding electrons in a homonuclear molecule such as H_2 or O_2 spend 50% of the time near each nucleus. Molecules whose bonds are neither purely covalent nor purely ionic are sometimes called polar covalent, since they possess electric dipole moments. The relative tendency of an atom to attract shared electrons when it is part of an atom is called its electronegativity. In the LiH molecule, for instance, H is more electronegative than Li.

In a heteronuclear molecule the atomic orbitals that are imagined to combine to form a molecular orbital may be of different character in each atom. An example is HF, where the 1*s* atomic orbital of H joins with the 2p_z orbital of F.

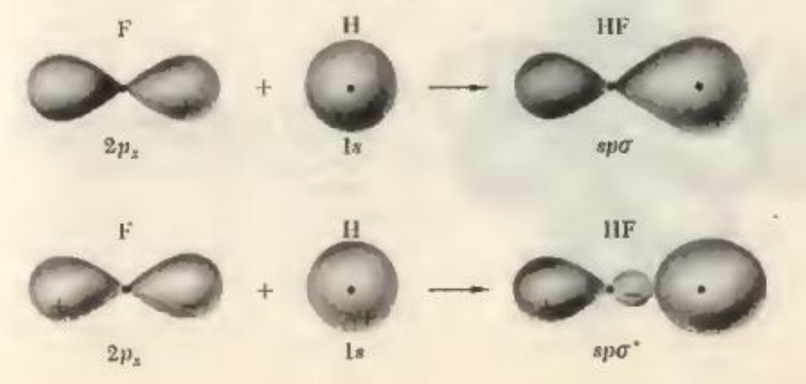

Fig (4). Bonding and antibonding of molecular orbitals in HF.

There are two possibilities, as in Fig. (4) , a bonding *spσ* molecular orbital and an antibonding *spσ** orbital. Since the Is orbital of H and the $2p_z$ orbital of F each contain one electron, the *spσ* orbital in HF is occupied by two electrons, and we may regard HF as being held together by a single covalent bond. The electron structure of the HF molecule is shown in Fig. (5).

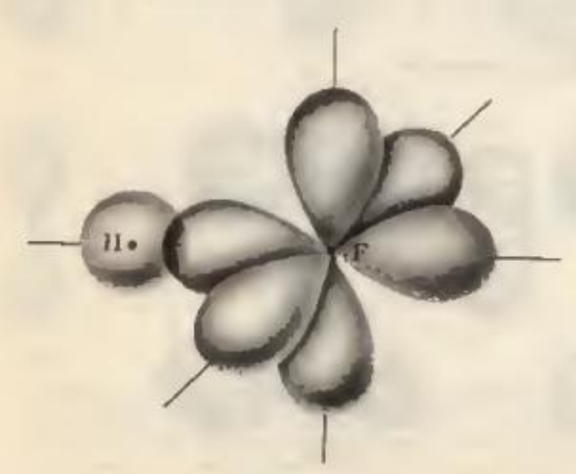

FIG (5) Valence atomic orbital in HF. the atomic orbitals shown as overlapping form a σ bonding molecule