Inorganic Pharmaceutical Chemistry: Atomic and Molecular Structure/Complexation Part I

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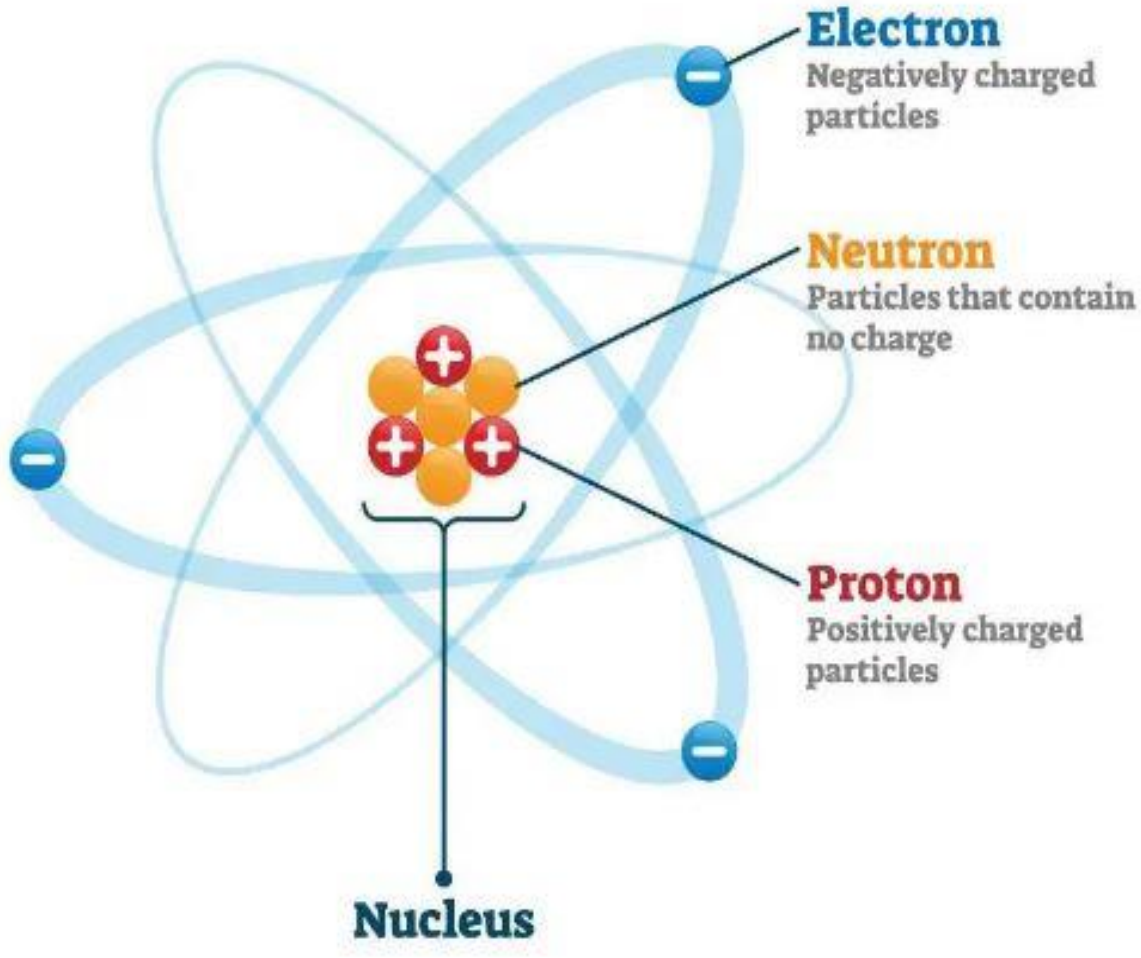
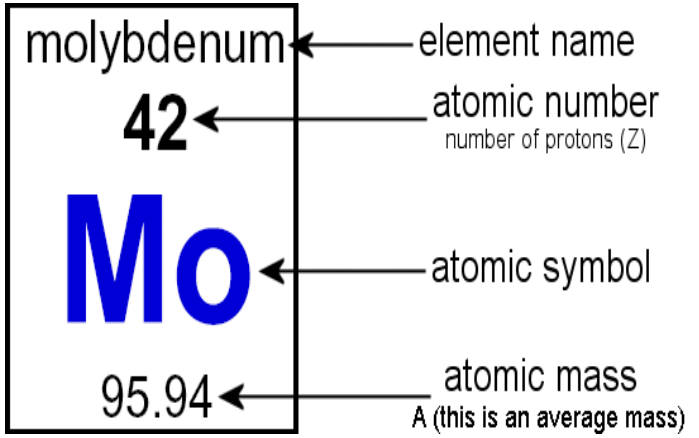
Electronic Structure of Atoms

- The fundamental unit of all matter is the **atom**.
- The various **chemical** and **physical** properties of matter are determined by its **elemental composition**.
- Elements are composed of **atoms** and their **isotopes**.
- In order to be able to predict the properties of matter, molecules, or elements, it is important to understand the **structure of atoms**.



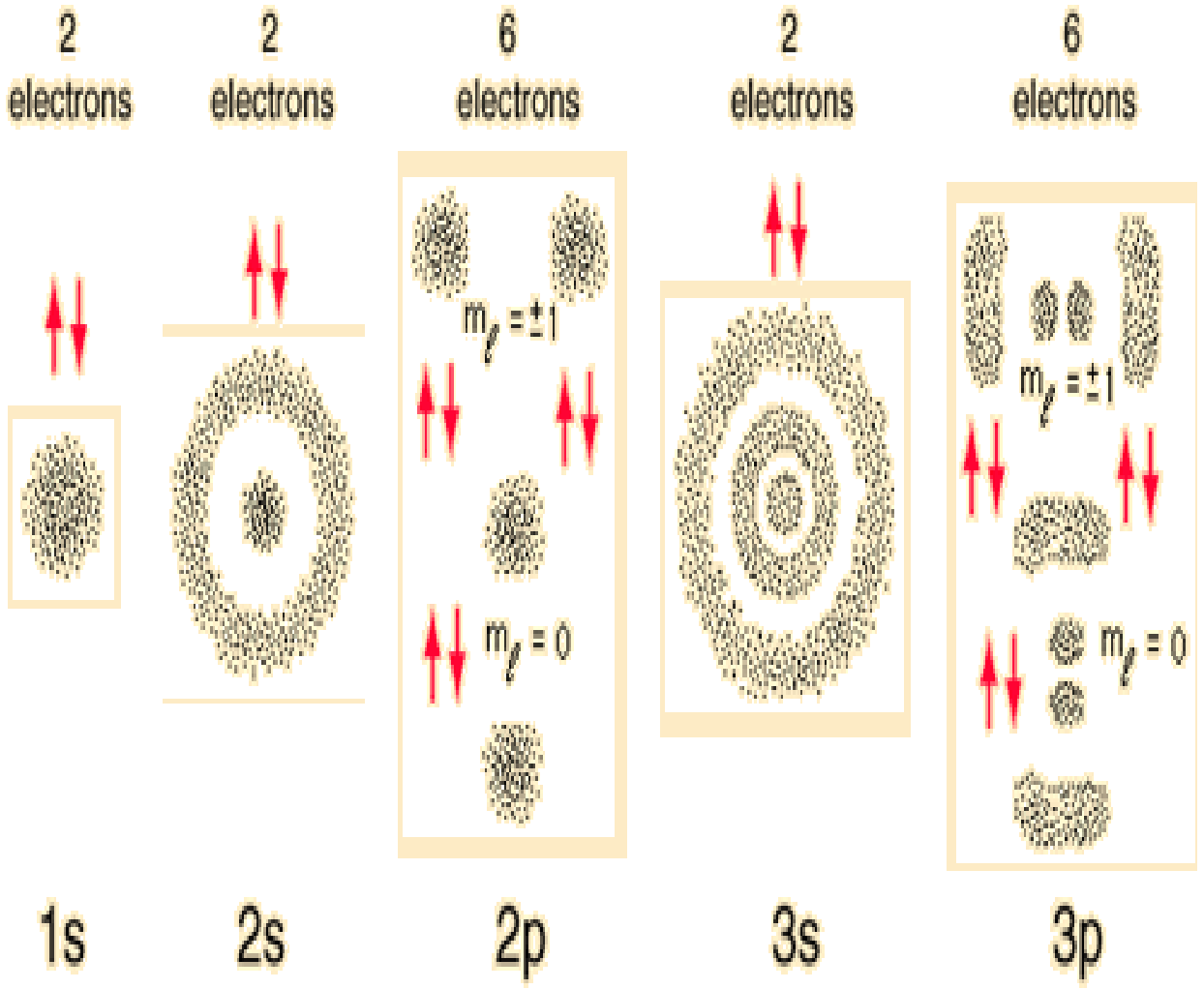
Subatomic Particles

- Atoms are composed of a central nucleus surrounded by electrons which occupy discrete regions of space.
- Every stable nucleus contains a certain number of protons (equal to the number of electrons in the neutral atom) and a particular number of neutrons.
- The sum of the masses of the protons and neutrons accounts for most of the **atomic mass** (or weight) of the element, and the number of protons is equal to the **atomic number**.
- **Isotopic** forms of a particular element differ in the number of neutrons, and therefore, in the atomic mass. For example, there are three kinds of carbon atoms ^{12}C, ^{13}C, and ^{14}C. They all have the same number of protons, but the number of neutrons varies
- The **positron** might be thought of as the direct counterpart of the electron in that it is similar in mass and opposite in charge.
- The betatron (negatron) or beta particle is an electron emitted from the nucleus.
- Its site of origin is the major factor distinguishing it from the electron. There are some indications that the positron and beta particle are components of the neutron.



Atomic Orbitals

- The early quantitative description of electronic structure came from Niels Bohr in 1913 and involved a planetary picture of the atom.
- Electrons were considered as particles that revolved around the nucleus in stationary planar orbits and which had definite energies.
- Electrons are placed in discrete volumes of space about the nucleus. These volumes of space are referred to by the term atomic orbitals, and the electrons contained within their boundaries are described by a set of four numbers called quantum numbers.
- The uncertainty principle of Heisenberg states that it is not possible to fix simultaneously the momentum and the position of an electron.



Quantum Numbers

- The four quantum numbers set the probability limits within which an electron can be found.

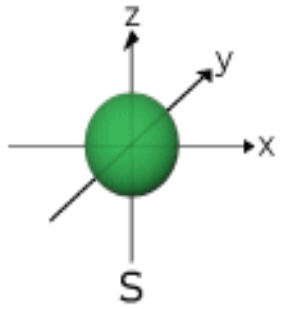
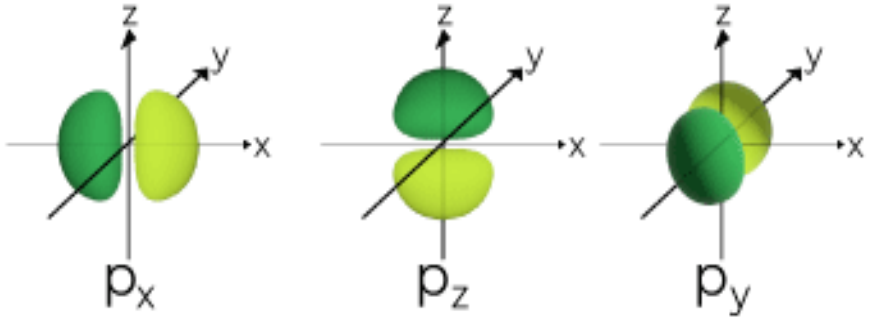
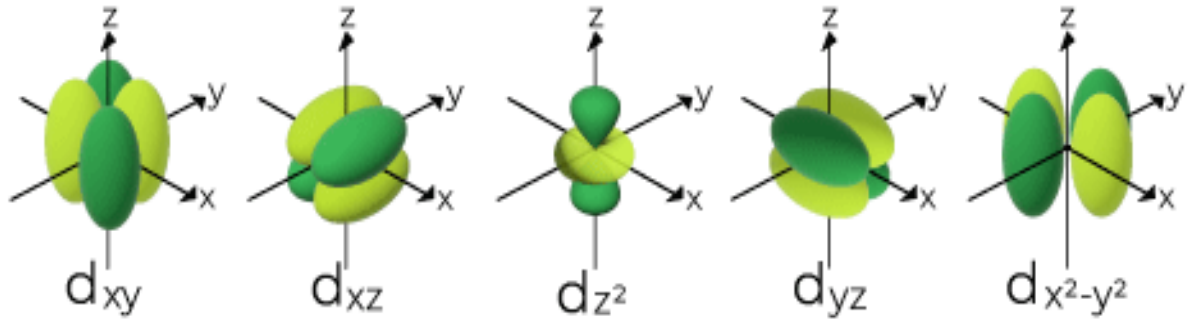
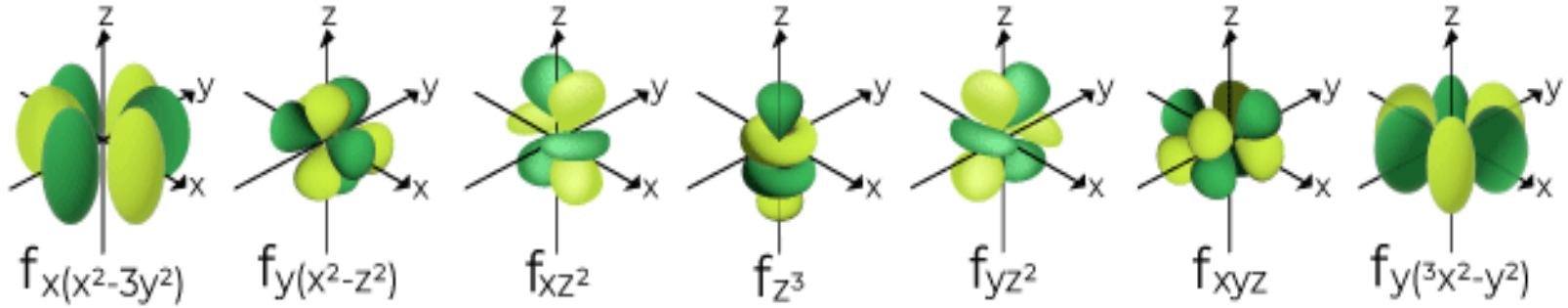
1. The Principal Quantum Number (n): The principal quantum number describes the relative position of the energy levels of the electrons and their distance from the nucleus. The values this number can assume are integers from n = 1, 2, 3, ….., ∞. When n = 1the electron is found in the energy level closest to the nucleus. In older literature, the shells referred to as K, L, M, etc., correspond to n = 1, 2, 3, etc.
2. The Suborbital Quantum Number (l): The suborbital quantum number describes the shape of the orbital or the " electron cloud". This number can assume integer values limited by the corresponding value of n such that l = 0, 1, 2, … (n -1). Thus, when n = 1, the only permissible value is l = 0. When n = 2, l can take two values, l = 0 and l = 1.

The value of l is generally designated by the letters s, p, d, and f for the orbitals.

The s orbitals are spherical, with the nucleus at the center of the sphere. The other orbitals have points with zero probability of finding an electron. These are called nodes, and the nodal plane passes through the nucleus of the atom.

3. The Magnetic Quantum Number (ml). This number tells which particular orbital the electron occupies within an energy suborbital. Also, it determines the specific orientation in space of the orbital relative to the nucleus. For any value of l, there are (2l + 1) allowed values of ml. The allowed values are restricted by the value of l and can be positive or negative integer values according to: ml = -1, …., 0, …., +1. Obviously, when l = 0 the orbital is a (spherical) and can only have one orientation, ml= 0. When l = 1, there are three possible orientations of the associated p orbital, ml = -1,0,+1. These correspond to the three p orbitals along the x, y, and z axes. Likewise, when l = 2 there are five possible orientations for the d orbital, ml = -2, -1, 0, +1, +2.

4. The Spin Quantum Number (ms). This number describes the two ways in which an electron may be aligned in a magnetic field, parallel to or opposed to the magnetic field. The electron can be thought of as rotating in either a clockwise or a counterclockwise direction. The spin quantum number, ms, can have only two values, +½ or -½. The significance of this is that for two electrons to occupy the same orbital they must have opposing spin. If one has ms = + ½, the other must-have ms = -½.

s orbital		n = 1, 2, 3, … 7 l = 0 m = 0
p orbital		n = 2, 3, … 6 l = 1 m = 0, ±1
d orbital		n = 3, 4,and 5 l = 2 m = 0, ±1, ±2
f orbital		n = 4 l = 3 m = 0, ±1, ±2, ±3

❖Aufbau Principle: an electron occupied the lowest energy orbital that can receive it.

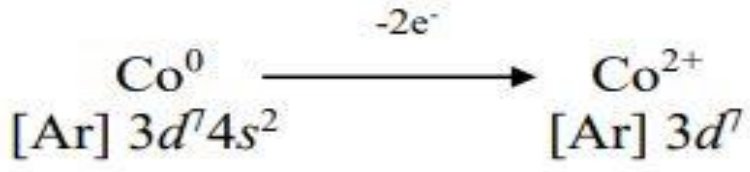
❖Pauli exclusion principle: only two electrons per orbital, and they must have opposite spin.

❖Hund's Rule: orbitals of equal energy are each occupied by one election before any orbital is occupied by a second election

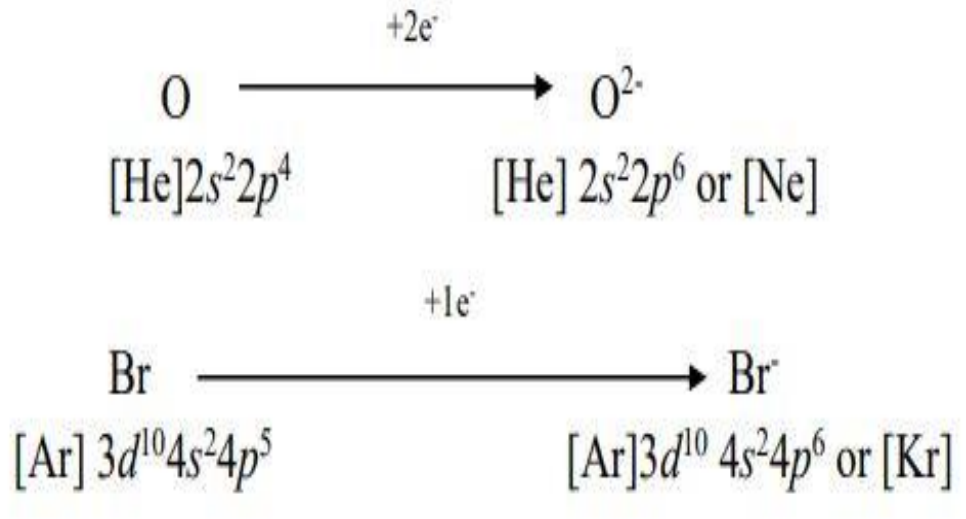
Element	Total electrons	Orbital diagram									Electron configuration
		1s		2s		2p			3s		
Li	3	↑↓		1							$1s^2 2s^1$
Be	4	↑↓		↑↓							$1s^2 2s^2$
B	5	↑↓		↑↓		1					$1s^2 2s^2 2p^1$
C	6	↑↓		↑↓		1	1				$1s^2 2s^2 2p^2$
N	7	↑↓		↑↓		1	1	1			$1s^2 2s^2 2p^3$
Ne	10	↑↓		↑↓		↑↓	↑↓	↑↓			$1s^2 2s^2 2p^6$
Na	11	↑↓		↑↓		↑↓	↑↓	↑↓	1		$1s^2 2s^2 2p^6 3s^1$

Ionization

- The process of losing one or more electrons by chemical or physical means is known as ionization, and the positive ion produced is termed a cation.
- Usually, atoms in the transition series with incompletely filled d orbitals will ionize to leave d ions, that is, ions in which the outer "shells" are d orbitals which may contain from one to ten electrons, depending upon the atom in question. For example, cobalt (At. No. 27) would ionize:

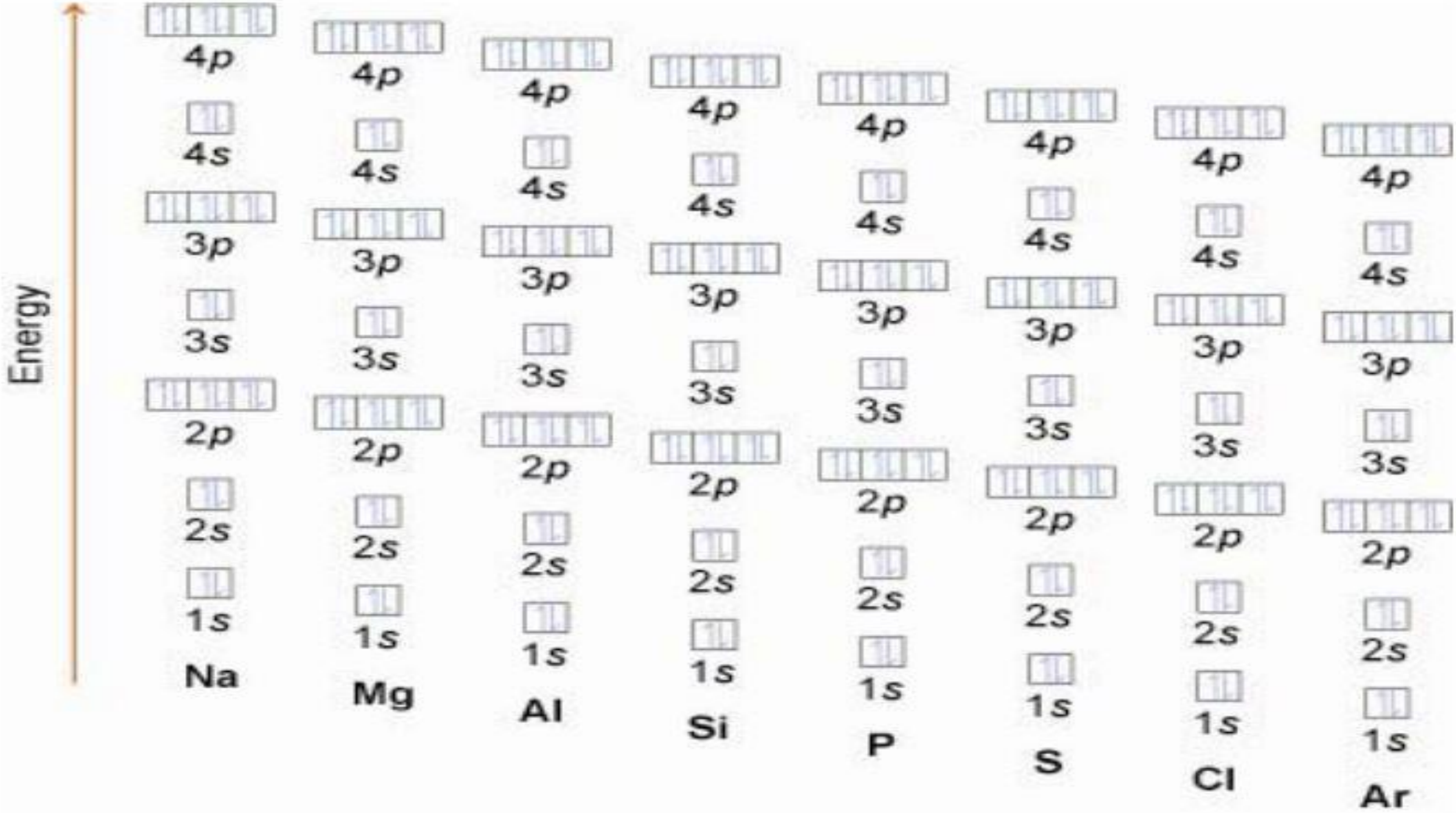


- Elements in Group VIA and VIIA which have larger numbers of electrons in their p orbitals tend to ionize by accepting electrons to form anions. These ions have completely filled p orbitals so that the valence shell structure is the same as the inert gas in the same period as the neutral element. An example of this can be seen in oxygen (At. No. 8) and bromine (At. No. 35):



Electronic Structure of Molecules

- Most of the electrons are in atomic orbitals surrounding the individual nuclei, and the remainder (valence electrons) are in more generalized multinuclear **molecular orbitals**.
- When atoms are incorporated into molecules, there are three major forces that are involved in the overall combination. Coulombic attraction occurs between the negatively charged electrons in the valence orbitals on one atom and the positively charged nucleus of another atom.
- **A stable molecule is possible when the proper balance between these forces exists, and the energy of the resulting system of atoms is less than the sum of the energies of the "isolated" atoms**.
- As the atoms approach each other, there are two repulsive forces that tend to "push" the atoms away:
- 1) electron-electron repulsion between valence electrons on neighbor atoms and (2) nuclear repulsion between neighboring nuclei.
- Depending upon the type of bonding interaction which is likely to occur (eg., ionic, covalent, etc.), there are other criteria based on the differences in electronegativity, availability of electrons, and the nature of the valence state atomic orbitals.


Energy
4p
4s
3p
3s
2p
2s
1s
Na
Mg
Al
Si
P
S
Cl
Ar

Types of Bonding Interactions

1. Ionic Bonding: It is the electrostatic force that exists between two chemical atoms of opposite charge. The species bearing the positive charge is known as the cation, and the negative species is the anion. When the two reacting entities are sufficiently far apart in their respective electronegativities (or far apart in the periodic table), the least electronegative entity loses one or more of its valence electrons to the more electronegative entity (or entities) to produce the respective cation and anion.

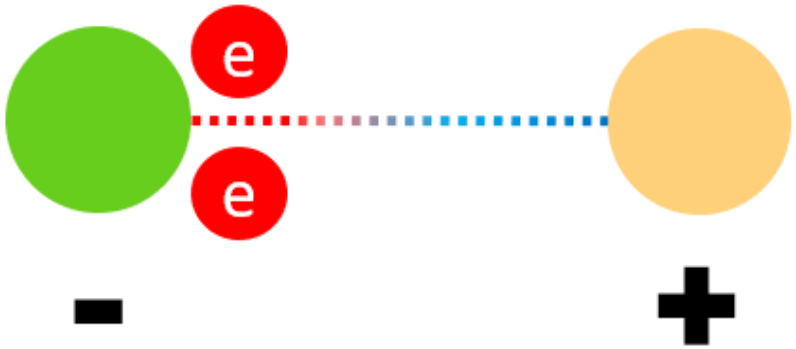
2. Covalent Bonding: the attractive force that exists between two chemical entities due to their "sharing" a pair of electrons. This type of bonding prevails when the electronegativity difference between the atoms is not sufficient to produce ions. Although quite common in inorganic compounds, covalent bonding is most prevalent in organic chemistry.

Covalent Bonds: Molecules

Nonpolar

Polar

Ionic Bonds: Ionic Compounds



3. Coordinate Covalent Bonding: This type of bonding is still a covalent interaction but, in this case, both electrons in the bond arise from a single orbital on one of the atoms forming the bond.

This type of bonding is found most frequently between complexes.

The atom providing the pair of electrons is generally referred to as the donor species.

The acceptor species is electron-deficient and has an empty orbital that can overlap with the orbital from the donor.

The representation of the bond, in order to distinguish it from covalent bonds, is an arrow drawn so that it points from the donor atom to the acceptor atom.