Study material for first semester NEP (Major) Department of Chemistry Government General Degree College, Chapra

Topic- Periodic properties

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Periodic properties

Introduction

The periodic table, also known as the periodic table of the elements, is an ordered arrangement of the chemical elements into rows ("periods") and columns ("groups"). It is an icon of chemistry and is widely used in physics and other sciences. It is a depiction of the periodic law, which states that when the elements are arranged in order of their atomic numbers an approximate recurrence of their properties is evident. The table is divided into four roughly rectangular areas called blocks. Elements in the same group tend to show similar chemical characteristics. Vertical, horizontal and diagonal trends characterize the periodic table. Metallic character increases going down a group and from right to left across a period. Nonmetallic character increases going from the bottom left of the periodic table to the top right. The first periodic table to become generally accepted was that of the Russian chemist Dmitri Mendeleev in 1869; he formulated the periodic law as a dependence of chemical properties on atomic mass. As not all elements were then known, there were gaps in his periodic table, and Mendeleev successfully used the periodic law to predict some properties of some of the missing elements. The periodic law was recognized as a fundamental discovery in the late 19th century. It was explained early in the 20th century, with the discovery of atomic numbers and associated pioneering work in quantum mechanics, both ideas serving to illuminate the internal structure of the atom. A recognizably modern form of the table was reached in 1945 with Glenn T. Seaborg's discovery that the actinides were in fact f-block rather than d-block elements. The periodic table and law are now a central and indispensable part of modern chemistry. The periodic table continues to evolve with the progress of science. In nature, only elements up to atomic number 94 exist to go further, it was necessary to synthesize new elements in the laboratory. By 2010, the first 118 elements were known, thereby completing the first seven rows of the table however, chemical characterization is still needed for the heaviest elements to confirm that their properties match their positions. New discoveries will extend the table beyond these seven rows, though it is not yet known how many more elements are possible; moreover, theoretical calculations suggest that this unknown region will not follow the patterns of the known part of the table. Some scientific discussion also continues regarding whether some elements are correctly positioned in today's table. Many alternative representations of the periodic law exist, and there is some discussion as to whether there is an optimal form of the periodic table.

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|---|--------------------------|-------------------|---------------------|-----------------------------|------------|------------|-------------------|----------------------------|------------------|----------------|------------------------------------|-----------|---------------------|-----------|-------------------|--------------------|---------------------|----------------|
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| | Li | BERMLULAN | - | YMBOL | BORON | | | Lanthanide Actinide | STAN Ne Ga | - gas | Fe - sold | (Pa) | B | C | N NITROGEN | O CATYGEN | F FLUORINE | NEO NEO |
| | Na | Mg | 3 1118 | 4 IVB | 5 VB | 6 VIB | 7 VIIB | 8 | - VIIIB - | 10 | 11 IB | 12 118 | | Si | Р | S | Cl | ANGO |
| | 19 39.096 | 20 40.078 | 21 44.956 | 22 47.867 | 23 50.942 | 24 51.996 | 25 54.938 | 26 55.845 | 27 58.933 | 28 58.693 | 29 63.546 | 30 65.39 | 31 69.723 | 32 72.64 | 33 74.922 | 34 78.96 | 35 79.904 | 36 8 |
| I | K | Ca | Sc | Ti | V | Cr | Mn | Fe | Co | Ni | Cu | Zn | Ga | Ge | As | Se | Br | K |
| 4 | POTASSIUM | CALCIUM | SCANDIUM | TITANUM | VANADIUM | CHROMIUM | MANGANESE | IRON | COBALT | NICKEL | COPPER | ZINC | GALLIUM | GERMANNUM | ARSENIC. | SELENUM | BROMINE | KRYP |
| | DL | 38 87.62 | 39 88.906 | 40 91.224 | 41 92.906 | 42 95.94 | 4.3 (96) PTT%_ | H 101.07 | 45 102.91 | 46 106.42 | 47 107.87 | 48 112.41 | 49 114.82 | 50 118.71 | 51 121.76 | 52 127.60 | 53 126.90 T | 54 13 |
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| ł | 55 132.91 | 56 137.33 | 57.71 | 72 178.49 | 73 180.95 | 74 183.84 | 75 186.21 | 76 190.23 | 77 192.22 | 78 195.08 | 79 196.97 | 80 200.59 | 81 204.38 | 82 207.2 | 83 208.96 | 84 (209) | 85 (210) | 86 (|
| | CS | Ва | La-Lu Lanthanide | H | Ta | W | Re | OSMUM | Ir | Pt PLATINUM | Au | Hg | TI | Pb | Bi | POLONIUM | At | RAD |
| | 87 (223) | 88 (226) | 89-103 | 104 (261) | 105 (262) | 106 (266) | 107 (264) | 108 (277) | 109 (268) | 110 (281) | 111 (272) | 112 (205) | | 114 (289) | 1 | | 1 | |
| | Fr | Ra | Ac-Lr | IRf | IDb | Sg | IBh | IHIS | MIt | Uum | Uuu | Uub | | Uwq | | | | |
| 2 | FRANCIUM | RADIUM | Actinide | LANTHAN | DUBNUM | SEABOROIUM | DOHRIUM | HASSIUM | MEITNERIUM | UNUNNER | UNUNUNIUM | UNUNBIUM | | unnanan | | Copyright C 19 | 06-2003 EniG (| (oni@41 |
| | | | | 57 138.91 | 58 140.12 | 59 140.91 | 60 144.24 | 61 (145) | 62 150.36 | 63 151.96 | 64 157.25 | 65 158.93 | 66 162.50 | 67 164.93 | 68 167.26 | 69 168.93 | 70 173.04 | 71 17 |
| | | | | La | Ce | Pr | Nd | Pm | Sm | Eu | Gd | ID | Dy | Ho | Er | Im | YD | |

АСТІМІДЕ 89 (227) 90 232.94 91 231.04 92 238.03 93 (237) 94 (244) 95 (243) 96 (247) 97 (247) 98 (251) 99 (252) 100 (257) 101 (256) 102 (259) 103 (262) AC Th Pa U Np Pu Aim Cim Bik Cif Es Fin Mid No Lip АСТИМИМ ТНОРЦИИ РИПОЛСТИКИ ИНАНИМ НЕРТИНИМ РИТОНИМ АМЕРСИМ СИГИМ СИГОРИИМЕНЯТЕНИИМ ГЕРМИИМ ИНСЕЦИИМ ИНФЕСНИИ ИНФЕСНИИ ИНФЕСНИИ ИНФЕСНИИ

Periodic Properties of the Elements

The elements in the periodic table are arranged in order of increasing atomic number. All of these elements display several other trends and we can use the periodic law and table formation to predict their chemical, physical, and atomic properties. Understanding these trends is done by analyzing the elements electron configuration; all elements prefer an octet formation and will gain or lose electrons to form that stable configuration.

Atomic Radius

We can never determine the atomic radius of an atom because there is never a zero probability of finding an electron, and thus never a distinct boundary to the atom. All that we can measure is the distance between two nuclei (internuclear distance). A covalent radius is one-half the distance between the nuclei of two identical atoms. An ionic radius is one-half the distance between the nuclei of two identical atoms. An ionic radius is one-half the distance between the nuclei of two adjacent atoms in a crystalline structure. The noble gases are left out of the trends in atomic radii because there is great debate over the experimental values of their atomic radii. The SI units for measuring atomic radii are the nanometer (nm) and the picometer (pm). 1 $nm = 1 \times 10^{-9} m$ and 1 $pm = 1 \times 10^{-12} m$.



Figure 1: (left) Covalent Radii, (middle) Ionic Radii, (right) Metallic Radii. Provided courtesy of Jessica Thornton (UCD)

To explain this trend, the concept of screening and penetration must be understood. Penetration is commonly known as the distance that an electron is from the nucleus. Screening is defined as the concept of the inner electrons blocking the outer electrons from the nuclear charge. Within this concept we assume that there is no screening between the outer electrons and that the inner electrons shield the outer electrons from the total positive charge of the nucleus. In order to comprehend the extent of screening and penetration within an atom, scientists came up with the **effective nuclear charge**, Z_{eff} . The equation for calculating the effective nuclear charge is shown below.

$$Z_{eff} = Z - S$$

In the equation S represents the number of inner electrons that screen the outer electrons. Students can easily find S by using the atomic number of the noble gas that is one period above the element. For example, the S we would use for Chlorine would be 10 (the atomic number of Neon). Z is the total number of electrons in the atom. Since we know that a neutral atom has an identical number of protons and electrons, we can use the atomic number to define Z. For example, Chlorine would have a Z value of 17 (the atomic number of Chlorine). Continuing to use Chlorine as an example, the 10 inner electrons (S) would screen out the positive charge of ten protons. Therefore there would be and effective nuclear charge of 17-10 or +7. The effective nuclear charge shows that the nucleus is pulling the outer electrons with a +7 charge and therefore the outer electrons are pulled closer to the nucleus and the atomic radii is smaller. In summary, the greater the nuclear charge, the greater pull the nucleus has on the outer electrons and the smaller the atomic radii. In contrast, the smaller nuclear charge, the lesser pull the nucleus has on the outer electrons, and the larger atomic radii. Additionally, as the atomic number increases, the effective nuclear charge also increases. Figure 3 depicts the effect that the effective nuclear charge has on atomic radii.



Figure 2: Courtesy of Jessica Thornton (UCD)

Now we are ready to describe the atomic radius trend in the periodic table. The atomic number increases moving left to right across a period and subsequently so does the effective nuclear charge. Therefore, moving left to right across a period the nucleus has a greater pull on the outer electrons and the atomic radii decreases. Moving down a group in the periodic table, the number of filled electron shells increases. In a group, the valence electrons keep the same effective nuclear charge, but now the orbitals are farther from the nucleus. Therefore, the nucleus has less of a pull on the outer electrons and the atomic radii are larger.



Figure 3: Courtesy of Jessica Thornton (UCD)

We can now use these concept to explain the atomic radius differences of cations and anions. A cation is an atom that has lost one of its outer electrons. Cations have a smaller radius than the atom that they were formed from. With the loss of an electron, the positive nuclear charge out powers the negative charge that the electrons exert. Therefore, the positive nucleus pulls the electrons tighter and the radius is smaller. An anion is an atom that has gained an outer electron. Anions have a greater radius than the atom that they were formed from. The gain of an electron does not alter the nuclear charge, but the addition of an electron causes a decrease in the effective nuclear charge. Therefore, the electrons are held more loosely and the atomic radius is increased.



Ionization Energy (ionization potential)

Expelling an electron from an atom requires enough energy to overcome the magnetic pull of the positive charge of the nucleus. Therefore, ionization energy (I.E. or I) is the energy required to completely remove an electron from a gaseous atom or ion. The Ionization Energy is always positive.



Figure 5: Courtesy of Jessica Thornton (UCD)

The energy required to remove one valence electron is the first ionization energy, the second ionization energy is the energy required to remove a second valence electron, and so on.

1st ionization energy

$$Na(g) \longrightarrow Na^+(g) + e^-(g)$$

2nd ionization energy

$$Na^+(g) \longrightarrow Na^{2+}(g) + e^{-}$$

Ionization energies increase relative to high effective charge. The highest ionization energies are the noble gases because they all have high effective charge due to their octet formation and require a high amount of energy to destroy that stable configuration. The highest amount of energy required occurs with the elements in the upper right hand corner. Additionally, elements in the left corner have a low ionization energy because losing an electron allows them to have the noble gas configuration. Therefore, it requires less energy to remove one of their valence electrons

Table 1: Ionization Energies of certain elements (1st IE, 2nd IE, etc)

| Element | 1st | 2nd | 3rd | 4th | 5th | 6th | 7th |
|---------|-------|------|------|-------|-------|-------|--------------------|
| Na | 496 | 4562 | | | | | |
| Mg | 738 | 1451 | 7733 | | | | |
| Al | 577 | 1817 | 2745 | 11580 | | | |
| Si | 786 | 1577 | 3232 | 4356 | 16090 | | |
| Р | 1060 | 1903 | 2912 | 4957 | 6274 | 21270 | |
| S | 999.6 | 2251 | 3361 | 4564 | 7013 | 8496 | 27110 |
| CI | 1256 | 2297 | 3822 | 5158 | 6542 | 9362 | <mark>11020</mark> |
| Ar | 1520 | 2666 | 3931 | 5771 | 7238 | 8781 | 12000 |

These are the ionization energies for the period three elements. Notice how Na after in the second I.E., Mg in the third I.E., Al in the fourth I.E., and so on, all have a huge increase in energy compared to the proceeding one. This occurs because the proceeding configuration was in a stable octet formation; therefore it requires a much larger amount of energy to ionize.

Ionization Energies increase going left to right across a period and increase going up a group. As you go up a group, the ionization energy increases, because there are less electron shielding the outer electrons from the pull of the nucleus. Therefore, it requires more energy to out power the nucleus and remove an electron. As we move across the periodic table from left to right, the ionization energy increases , due to the effective nuclear charge increasing. This is because the larger the effective nuclear charge, the stronger the nucleus is holding onto the electron and the more energy it takes to release an electron.



Figure 6: Courtesy of Jessica Thornton (UCD)

The ionization energy is only a general rule. There are some instances when this trend does not prove to be correct. These can typically be explained by their electron configuration. For example, Magnesium has a higher ionization energy than Aluminum. Magnesium has an electron configuration of [Ne]3s2. Magnesium has a high ionization energy because it has a filled 3s orbital and it requires a higher amount of energy to take an electron from the filled orbital.

Factors affecting Ionisation Energy

The size of the ionisation energy is determined by the strength of the attraction between the outer shell electrons and the central nucleus. The stronger the attraction, the harder it is to remove the electron and the higher the ionisation energy. The following factors determine the strength of the attraction between the nucleus and outer electrons:

Atomic Radius:

The higher the atomic radius, the lower the ionisation energy. This is because a higher atomic radius means that the outer electrons are further from the nucleus, and hence the attractive pull from the nucleus is lower.

Nuclear Charge:

The higher the nuclear charge, the higher the ionisation energy. This is because the greater the positive charge of the nucleus, the stronger the attraction for the outer electrons.

Number of Inner Shells:

The more inner shells present, the lower the ionisation energy. Inner shells refers the shells between the outer shell and the nucleus. For example, if the outer electron is in shell 4, then there are 3 inner shells to inner shells repel the outer electrons, lessening the pull towards the nucleus. This effect is called shielding.

Electron Affinity

Electron affinity (E.A.) is the energy change that occurs when an electron is added to a gaseous atom. Electron affinity can further be defined as the enthalpy change that results from the addition of an electron to a gaseous atom. It can be either positive or negative value. The greater the negative value, the more stable the anion is.

· (Exothermic) The electron affinity is positive

$$X(g) + e^- \longrightarrow X^- + Energy$$

· (Endothermic) The electron affinity is negative

$$X(g) + e^- + Energy \longrightarrow X^-$$

It is more difficult to come up with trends that describe the electron affinity. Generally, the elements on the right side of the periodic table will have large negative electron affinity. The electron affinities will become less negative as you go from the top to the bottom of the periodic table. However, Nitrogen, Oxygen, and Fluorine do not follow this trend. The noble gas electron configuration will be close to zero because they will not easily gain electrons.

Factors Affecting Electron Affinity

Electron Affinity is affected by three main factors. These factors are generally related to the structure and configuration of the molecule in question. The three factors affecting the electron affinity of a molecule are Nuclear Charge, Atomic Size, and Electronic Configuration.

Nuclear Charge: The greater the nuclear charge, the greater will be the attraction of the incoming electron. This will result in a larger value of electron affinity. To explain it in simpler terms, the nuclear charge can be understood as the pull that is exerted by the nucleus on the electrons. Therefore, the greater the pull of the nucleus, the greater the chance of electrons attaching to the atom.

Atomic Size: The larger the size of an atom, the larger will be the distance between the nucleus and electron. This will result in a smaller force of attraction by electrons. Therefore, the value of electron affinity will be small. In general, too, the electronic affinity increases by going down the group and decreases from left to right across the periods.

Electronic Configuration:

Stable the configuration of an atom, its tendency will be less to accept the electron. Therefore, it will face a lower value of its electron affinity. Electron affinity is almost zero or low in elements having a stable electronic configuration. This is due to the small tendency to accept another electron. Electron affinities of inert gases are zero. This is due to their atoms having stable ns²np⁶ configuration in their shell. Electron affinity of Beryllium, and calcium is practically zero. If the atom has fully or half-filled orbits, its electron affinity will be less.



Electronegativity

Electronegativity is the measurement of an atom to compete for electrons in a bond. The higher the electronegativity, the greater its ability to gain electrons in a bond. Electronegativity will be important when we later determine <u>polar and nonpolar</u> molecules. Electronegativity is related with ionization energy and electron affinity. Electrons with low ionization energies have low electronegativities because their nuclei do not exert a strong attractive force on electrons. Elements with high ionization energies have high electronegativities due to the strong pull exerted by the positive nucleus on the negative electrons. Therefore the electronegativity increases from bottom to top and from left to right.



Figure 8: Courtesy of Jesscia Thornton (UCD)

The concept of electronegativity was first introduced by Linus Pauling (1930s) to describe the ability of an atom to attract electrons to itself in a chemical bond with another element. Relative elements were compiled by Pauling from available bond energies (see later). Subsequently, a number of other approaches have been made to describe the same property of an element, giving rise to different "electronegativity scales".

The electronegativity values of elements in the same scale show periodic variation. However, electronegativity differs from other periodic properties described before (e.g., ionization energy, electron affinity etc.) as it is not an inherent property of an isolated atom. Hence the value of electronegativity environment of the atom. The value of electronegativity in the same scale may also vary depending upon the physical data used like bond energy, electron affinity etc. Hence electronegativity values are relatively less precise. Nevertheless, electronegativity values within the same scale provide satisfactory qualitative guideline to understand the chemical behaviour of an element or its compounds. Quantitative correlations are also quite satisfactory in many cases, for example the Schoemaker-Stevenson rule for the estimation of bond length (sec. 5.3.3).

Let us first summarize the main electronegativity scales:

(i) *The Pauling scale* (1932): This is the first and by far the most widely accepted scale, based on bond energies.

If two elements A and B have electronegativities x_A and x_B respectively, then

$$|x_{\rm A} - x_{\rm B}| = 0.102\sqrt{\Delta}$$

where Δ is obtained from the bond energies (*E*, in kJ mol⁻¹; actually enthalpies) as:

$$\Delta = E_{A-B} - (E_{A-A} \cdot E_{B-B})^{1/2}$$

(ii) The Mulliken scale (1934): Average of ionization potential and electron affinity, both in electronvolts (eV) per atom, is taken as a measure of electronegativity.

$$x_{\rm M} = \frac{1}{2} ({\rm I}.{\rm E}.+{\rm E}.{\rm A}.)$$

where x_{M} is the electronegativity of an element in the Mulliken scale.

The ionization potential and electron affinity refer to the *valence state* of the element in a compound and not to the ground state of the atom (see later).

Mulliken electronegativity values (x_M) may be related to the Pauling electronegativity (x_P) through the relation

$$x_{\rm P} = 1.35 \ (x_{\rm M})^{1/2} - 1.37$$

(iii) The Allred and Rochow scale (1958): It relates electronegativity to the electric field at the surface of an atom (covalent radius = r).

$$x_{\rm AR} = 0.744 + \frac{3590Z_{eff}}{(r/pm)^2}$$

Effective Nuclear Charge

It has been observed that the radial part of the wave function changes appreciably with atomic number Z but the angular parts of the wave functions remain nearly the same as with the hydrogenic functions. So the basic shapes of s, p, ... etc. orbitals may be roughly taken to be the same for all atoms. The radial functions are expressed by modifying the actual nuclear charge (Z; in terms of e) by an effective nuclear charge Z^* or Z_{eff} which is equal to the nuclear charge Z minus a shielding (or screening) factor σ arising from the presence of other electrons in the atom.

$$Z_{eff} = Z - \sigma$$
 (in units of *e*)

where σ = sum of the shielding contributions from all *other* electrons.

The shielding factor represents the sum of all the reductions of the nuclear charge caused by electrons closer than or at about the same distance from the nucleus relative to the electron under consideration.

Let us consider the lithium atom as an example. The 2s electron will be shielded by the inner 1s electrons and hence experience a lower effective nuclear charge than the 1s electrons. Again as the radial distribution curve of the 2s orbital has some finite distribution inside the 1s shell (penetration), the 2s electron does not get complete shielding by the 1s electrons. Slater proposed (1930) a set of empirical rules for estimating the shielding contributions by electrons in different orbitals. These are known as Slater's rules.

Slater's rules for estimation of shielding contributions

- (i) The electrons of the atom are divided into groups like
 - $(1s), (2s 2p), (3s 3p), (3d), (4s 4p), (4d), (4f), (5s 5p), (5d), \dots$ etc.
 - The fraction (of e) contributed to shielding on any electron in a particular electron group by other electrons is now estimated as

(ii) electrons in groups on the right of the one under consideration: zero.

(iii) each other electron in the same group:

0.30 if the group is 1s; otherwise 0.35.

(iv) if the electron under consideration belongs to an (ns, np) group, all electrons with a principal quantum number less by one : 0.85 each.

All electrons in groups further left : 1.0 each

(v) if the electron under consideration belongs to a d or f group, all electrons in groups lying left of this group : **1.0 each**.

| | Contribution to shielding by each electron in | | | | | | |
|--------------------------------|---|---------------|---------------------------|---------------------|--|--|--|
| Electron group | all higher groups | same group | groups (<i>n</i> – 1) | groups $\leq (n-2)$ | | | |
| ·1 <i>s</i> | 0 | 0.30 | - | - | | | |
| (ns, np) | 0 | 0.35 | 0.85 | 1.00 | | | |
| (<i>nd</i>) or (<i>nf</i>) | 0 | 0.35 | 1.00* | 1.00 | | | |

*for all groups on left, including s or p electrons of the same n. See illustration.

Illustration: Let us consider an atom of iron in the ground state configuration $1s^2 2s^22p^6$ $3s^23p^63d^64s^2$ (Z = 26). The electrons are first separated into orbital groups:

$$(1s)^2 (2s2p)^8 (3s3p)^8 (3d)^6 (4s)^2.$$
The shielding contribution and Z_{eff} for an electron (in e) may now be calculated;
(i) **1s electron:** This is shielded by only one other electron in 1s.
Electrons in groups to the right of 1s = 0
The remaining electron in 1s = 0.30
Total (σ) = 0.30
Hence, $Z_{eff} = 26 - 0.30 = 25.70$.
(ii) **2s or 2p electron:**
Electrons in groups to the right = 0
7 other electrons in the 2s2p group; 0.35 each : (7 × 0.35) = 2.45

2 electrons in the (n - 1) group i.e., 1s; 0.85 each : (2×0.85) = 1.70 Total (σ) = 4.15

$$Z_{eff} = 26 - 4.15 = 21.85.$$

| (iii) 3s or 3p electron | |
|---|---------|
| Electrons in 3d and 4s | = 0 |
| 7 other electrons in $3s3p$ group, 0.35 each: 7×0.35 | = 2.45 |
| 8 electrons in $(n - 1)$ group i.e., $(2s2p)$, 0.85 each : 8×0.85 | = 6.80 |
| 2 electrons in group further left (1s), 1.0 each : 2×1.0 | = 2.00 |
| Total (σ) | = 11.25 |
| $Z_{eff} = 26 - 11.25 = 14.75.$ | |

| (iv) 3d electron | The second second |
|--|-------------------|
| Electrons in 4s | = 0 |
| 5 other electrons in the 3d group, 0.35 each : 5×0.35 | = 1.75 |
| 18 electrons in all the groups to the left of the 3d group, | |
| $1.0 \ each: 18 \times 1.0$ | = 18.0 |
| Total (σ) | = 19.75 |
| $Z_{eff} = 26 - 19.75 = 6.25.$ | |
| (v) 4s electron. | |
| One other electron in the same group | = 0.35 |
| 14 electrons in $(n-1)$ groups, $(3s \ 3p)$ and $3d$: | |
| 0.85 each : 14 × 0.85 | = 11.90 |
| 10 electrons in groups further left i.e., $\leq (n-2)$, | indiana Directory |
| 1.0 each : 10 × 1.0 | = 10.00 |
| Total (σ) | = 22.25 |
| $Z_{eff} = 26 - 22.25 = 3.75$ | |

Slater applied these values of Z_{eff} to obtain a set of *Slater orbitals* corresponding to each hydrogenlike orbital. The angular dependence of these orbitals is identical to that of the hydrogenlike orbital but the radial function is of the type

 $R(r) = N \cdot r^{n^*-1} \cdot e^{-Z_{eff}r/n^*}$ (N = normalization constant)

 n^* is called the "effective principal quantum number" (n^*) having the following values:

| | n | = | 1 | 2 | 3 | 4 | 5 | 6 | |
|------------|------------|--------|---------------|-----------|---------|----------|------|-----|--|
| | <i>n</i> * | = | 1.0 | 2.0 | 3.0 | 3.7 | 4.0 | 4.2 | |
| The differ | ence be | etween | n and n^* | is called | the qua | ntum def | ect. | | |

Inert pair effect

The inert pair effect refers to the tendency of the outermost s electrons in heavier p-block elements to remain non-bonding or inert due to poor shielding by the inner d and f orbitals. This results in a reluctance of these s electrons to participate in bonding. This effect is primarily observed in the heavier elements of the p-block of the periodic table, particularly in groups 13 and 14. As we move down these groups, the inert pair effect becomes more pronounced. Consider the group 13 elements: boron (B), aluminum (Al), gallium (Ga), indium (In), and thallium (Tl). The general electronic configuration for these elements is ns² np¹, where n represents the principal quantum number. The group 13 elements can exhibit two oxidation states: +1 and +3. For example, if an element loses one p electron, it can exist in the +1 oxidation state. If it loses both s electrons and one p electron, it can exist in the +3 oxidation state. As we move down the group from aluminum to thallium: The +3 oxidation state becomes less stable, while the +1 oxidation state becomes more stable. For thallium (Tl), it predominantly exists in the +1 state due to the inert pair effect, where the 6s electrons are reluctant to participate in bonding because they are pulled closer to the nucleus due to poor shielding from the inner d orbitals. Thus, the inert pair effect leads to the stabilization of lower oxidation states (+1 for thallium) in heavier p-block elements, while the higher oxidation states (+3) become less favored.

SUGGESTED READINGS/REFERENCES:

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2. R.P. Sarkar, General and Inorganic Chemistry