Penetration & Shielding

Penetration and shielding are two underlying principles in determining the physical and chemical properties of elements. We can predict basic properties of elements by using shielding and penetration characteristics to assess basic trends.

Introduction

Electrons are negatively charged and are pretty close to each other, which means that they can repel each other. The repulsion an electron feels is *shielding* and the attraction it feels to the nucleus is *penetration*. The specific math is Coulomb's Law (an analogy with classical physics):

$$F=kqQr2.$$

The force that an electron feels is dependent on the distance from the nearest charge (i.e., an electron, usually with bigger atoms and on the outer shells) and the amount of charge. More distance between the charges will result in less force, and more charge will have more force of attraction.

In an ideal setting (for atoms at least), every electron should feel the same amount of "pull" from the nucleus. This means that the negative to positive charge ratio should be 1:1. However, that is not the case when observing atomic behavior. When considering the core electrons (or the electrons closest to the nucleus), the ratio is 1:1, or at least close to it. As you proceed from the core electrons to the outer valence rings of electrons, the negative to positive charge ratio falls below 1:1. This is because of *shielding*, or simply the electrons repelling each other, but these same core electrons *penetrate* and feel more of the nucleus than the other electrons.

Orbital Penetration

Penetration describes the proximity of electrons in an orbital to the nucleus. Electrons which experience greater penetration experience less shielding and therefore experience a larger *Effective Nuclear Charge* (Z_{eff}) but shield other electrons more effectively. Electrons in different orbitals have different wavefunctions and therefore different distributions around the nucleus.However, contrary to what many think, penetration is not the outer electrons penetrating through the shield of the core electrons. It is actually just how well the electrons feel the nucleus. This is similar to the idea of outer electrons penetrating, but not the same. They are not the same because the core electrons have more penetration than the outer electrons since they (the core electrons) feel the strongest pull.

To relate the idea of penetration, we can use the idea of Z_{eff} or the effective nuclear charge. It is essentially the number of protons' charge minus the number of electrons shielding- basically how effective the nucleus is at attracting the electrons. Since core electrons do not shield themselves, they penetrate the most and are exposed to the most (effective) nuclear charge.

Different orbitals have greater nuclear penetration than others. Penetration refers to how effectively electrons can get close to the nucleus. The electron probability density for s-orbitals is highest in the center of the orbital, or at the nucleus. If we imagine a dartboard that represents the circular shape of the s-orbital and if the darts landed in correlation to the probability to where and electron would be found, the greatest dart density would be at the 50 points region but most of the darts would be at the 30 point region. When considering the 1s-orbital, the spherical shell of 53 pm is represented by the 30 point ring.

In a multi-electron system, the penetration of the nucleus by an electron is measured by the relative electron density near the nucleus of an atom for each shell and subshell of an electron. For example, we see that since a 2s electron has more electron density near the nucleus than a 2p electron, it is penetrating the nucleus of the atom more than the 2p electron. The penetration power of an electron, in a multi-electron atom, is dependent on the values of both the shell and subshell of an electron in an atom.

Therefore, for the same shell value (n) the penetrating power of an electron follows this trend in subshells:

$$s>p>d>f$$

And for different values of shell (n) and subshell (l), penetrating power of an electron follows this trend:

$$1s>2s>2p>3s>3p>4s>3d>4p>5s>4d>5p>6s>4f....$$

and the energy of an electron for each shell and subshell goes as follows...

$$1s<2s<2p<3s<3p<4s<3d<4p....$$

Shielding

An atom (assuming its atomic number is greater than 2) has core electrons that are extremely attracted to the nucleus in the middle of the atom. However the number of protons in the nucleus are never equal to the number of core electrons (relatively) adjacent to the nucleus. The number of protons increase by one across the periodic table, but the number of core electrons change by periods. The first period has no core electrons, the second has 2, the third has 10, and etc. This number is not equal to the number of protons. So that means that the core electrons feel a stronger pull towards the nucleus than any other electron within the system. The valence electrons are farther out from the nucleus, so they experience a smaller force of attraction.

Shielding refers to the core electrons repelling the outer rings and thus lowering the 1:1 ratio. The nucleus has "less grip" on the outer electrons and are shielded from them.

Shielding describes the amount of screening from nuclear charge that one electron can do with respect to its neighboring electrons. Electrons that have greater penetration can get closer to the nucleus and effectively block out the charge from electrons that have less proximity. For example, Z_{eff} is calculated by subtracting the magnitude of shielding from the total nuclear charge. The value of Z_{eff} will provide information on how much of a charge an electron actually experiences.

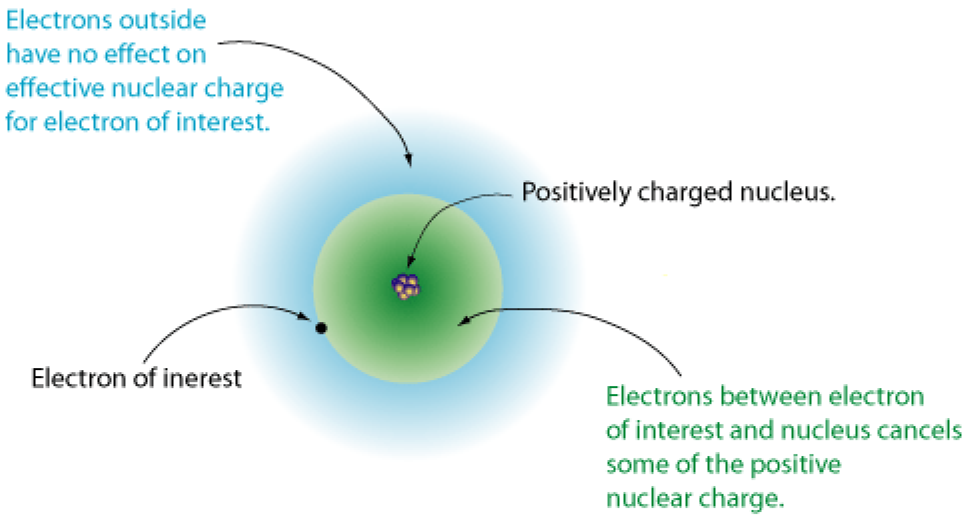

Figure 2. This image shows how inner electrons can shield outer electrons from the nuclear charge.(http://www.grandinetti.org/Teaching/...tielectron.gif

Because the order of electron penetration from greatest to least is s, p, d, f; the order of the amount of shielding done is also in the order s, p, d, f.

Since the 2s electron has more density near the nucleus of an atom than a 2p electron, it is said to shield the 2p electron from the full effective charge of the nucleus. Therefore the 2p electron feels a lesser effect of the positively charged nucleus of the atom due to the shielding ability of the electrons closer to the nucleus than itself, (i.e. 2s electron).

These electrons that are shielded from the full charge of the nucleus are said to experience an *effective nuclear charge* (*Z_{eff}*)of the nucleus, which is some degree less than the full nuclear charge an electron would feel in a hydrogen atom or hydrogenlike ions. The effective nuclear charge of an atom is given by the equation:

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

where.

- Z is the atomic number (number of protons in nucleus) and
- S is the shielding constant

We can see from this equation that the effective nuclear charge of an atom increases as the number of protons in an atom increases. Therefore as we go from left to right on the periodic table the effective nuclear charge of an atom increases in strength and holds the outer electrons closer and tighter to the nucleus. This phenomena can explain the decrease in atomic radii we see as we go across the periodic table as electrons are held closer to the nucleus due to increase in number of protons and increase in effective nuclear charge.

Radial Distribution Graphs

A radial distribution function graph describes the distribution of orbitals with the effects of shielding. The small peak of the 2s orbital shows that the electrons in the 2s orbital are closest to the nucleus. Therefore, it is the electrons in the 2p orbital of Be that are being shielded from the nucleus, by the electrons in the 2s orbital.

The following is the radial distribution of the 1s and 2s orbitals. Notice the 1s orbital is shifted to the right, while the 2s orbital has a node. The shift is due to the proximity of the electrons to the nucleus in the 1s orbital. Nodes may be determined by the formula: {(n-L-1)=nodes}, where "n" describes the "shell", or energy level the electrons reside, and "L" describes the orbital's angular momentum, or the "shape" of the orbital. Recall that L=0 corresponds to the s-orbital, L=1 to p-orbital, L=2 to d-orbital, and L=4 to f-orbital, and the s-shell consists of 1 atomic orbital, p-shell to 3 atomic orbitals, d-shell to 5, and f-shell to 7.

Periodic Trends Due to Penetration and Shielding

A) Effective Nuclear Charge (Z_{eff})

The effective nuclear charge increases from left to right and increases from top to bottom on the periodic table.

B) Atomic Radius

The atomic radius decreases from left to right, and increases from top to bottom.

C) Ionization Energies

The ionization energies increase from left to right, and decrease from top to bottom.

E) Electronegativity

The electronegativity of the elements is highest near flourine. In general, it increases from left to right and decreases from top to bottom.

Source: http://chemwiki.ucdavis.edu/?title=Physical_Chemistry/Quantum_Mechanics/Quantum_Theory/Trapped_Particles/Atoms/Multi-Electron_Atoms/Penetration_%26_Shielding