LECTURE 5. PERIODIC TRENDS EXPLAINED BY EFFECTIVE NUCLEAR CHARGE

Summary. The periodic table was created as a consequence of the boundary conditions imposed by the quantum mechanical solutions to Schrodinger's wave equations for multi-electron systems. What we will learn in this lecture is that in defining the properties of atoms and ions in the table, there will turn out to be periodic trends to those properties. Specifically, we will see that as we go across the table from left to right, or down the table from top to bottom, we will see that a systematic increase or decrease in the quantitative measure of a property is observed. This is good for two reasons. First, allows us to cement into place the important ideas that explain the properties. And second, it keeps us from having to to much memorization since we can make nice sweeping generalizations.

What are the trends that we will be able to explain? There are a lot of them. But here are six you will see over the next several lectures:

• Atomic radius size	• Electron affinity
• Ionic radius size	• Metallic character
• Ionization energy	• Electronegativity

And what are the two big ideas that explain the trends for these six properties? They are the titles of the next two lectures:

Rule 1: Effective nuclear charge (ENC) will explain the relative size and interest in electrons for atoms and ions. As will be shown, for example, as ENC⇓ Size ⇑ and as ENC⇑ Size ⇓. A similar trend can be defined for how much an ion or atom wants an electron.   ENC arguments are the most important argument in explaining the overall trends in the periodic table.

Rule 2: Filled and half filled shells have additional stability.   As mentioned when drawing the electronic configurations of atoms, whenever a filled shell or half filled shell can be created, it will have a stability out of bounds with that expected by ENC. Filled shell stability, for example, is the root of the idea of the octet rule in explaining chemical bonds. We will also see it impact the fine structure in many of our trends, for example creating exceptions to the Aufbau principle and creating fine structure exceptions to the trends for ionization energy and electron affinity.

The Multielectron Schrodinger Equation

Recall that when we had a single e⁻ and a single nucleus, +, there was a simple potential to stick in the Schrodinger Equation

1 e⁻ case   => $V(r) = \dfrac{(-e)(+e)}{4\,\Pi\,E_o\,r}$ which yields the solution $E = \dfrac{hR}{h^2}$

But what happens with more than one e⁻? Things quickly get more complicated with a repulsion term in addition to attraction.

2 e⁻ case   => $V(r) = \dfrac{-2e^2}{4\,\Pi\,E_o\,r_1}$ - $\dfrac{2e^2}{4\,\Pi\,E_o\,r_2}$ + $\dfrac{e^2}{4\,\Pi\,E_o\,r_{12}}$

⇧   ⇧   ⇧

attraction of   attraction of   repulsion of
e⁻$_1$, to nucleus   e⁻$_2$, to nucleus   e⁻$_1$ from e⁻$_2$

The key thing to note is that in addition to the simple attractions between protons in nucleus and each e⁻, there are REPULSIONS between electrons. This repulsive effect result, called electron shielding, has a profound implication in that it keeps atom sizes from getting smaller and smaller as the number of protons increases. We would live in a very different world if an atom with 100 protons was smaller than an atom with one proton just because attractive forces ruled everything.

Sheilding and Effective Nuclear Charge

The calculation of V(r) is not some thing we can do to determine the relative extent of repulsion, so we simplify and make a nice freshman chemistry definition of shielding. A singly charged electron has just as much repulsive effective as a singly charged proton. So in the drawing below, the perimeter electron has all of its attraction to the single proton completely canceled and as a result, it has no attraction. It is completely shielded and is on its own.
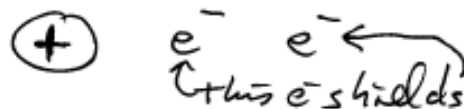
While this argument is certainly an oversimplification, it is remarkable useful in providing a semi-quantitative measure of shielding. The math equation below determines the effective (or actual) nuclear charge and as mentioned before, ENC explains all of the trends in the periodic table. So be able to do this calculation.

ENC= effective nuclear charge= (# of protons in nucleus) – (# of shielding inner shell electrons)

ENC Calculations: An analogy to getting good seats at a concert

A better understanding of ENC might come from: creating an analogy to attending a concert. The band is the protons and the people watching are the electrons. Who sees the band best (has the best effective nuclear charge?) The people in front see all of the show. And the people in back rows? They are are shielded and see less of the band (have lower effective nuclear charge.) Let's imagine a 13 person band and think about ENC for the various rows at the show.Also note in this theatre that there are only 2 seats in the front row, 8 seats in the second row, and 10 seats in the third row (I see an analogy coming.)
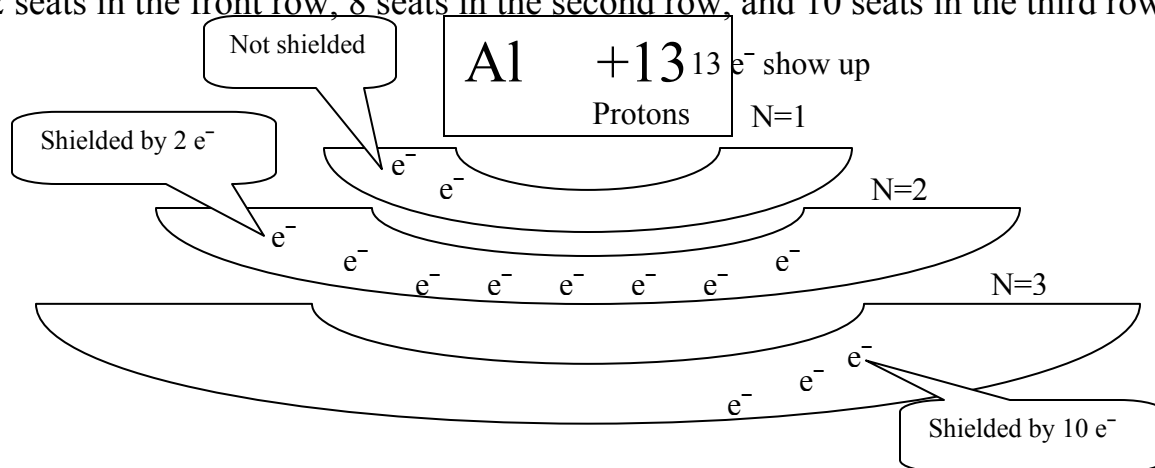
ENC Calculations when the actual nuclear charge= +13

First row, n=1 with no shielding: ENC= 13-0 =13
Second row, n = 2 with a shielding by the two electrons in the front row: ENC= 13-2 =11
Third row, n = 3 with a shielding by the ten electrons in the front two rows: ENC= 13-10 =3

Unless you haven't been paying attention, you see that I can straighten out the rows in the concert above and I am staring at the periodic table, and specifically looking what ENC is for the electrons attracted to the 13th element, Al.

for electrons in the n=3 row, ENC= 13-10=3
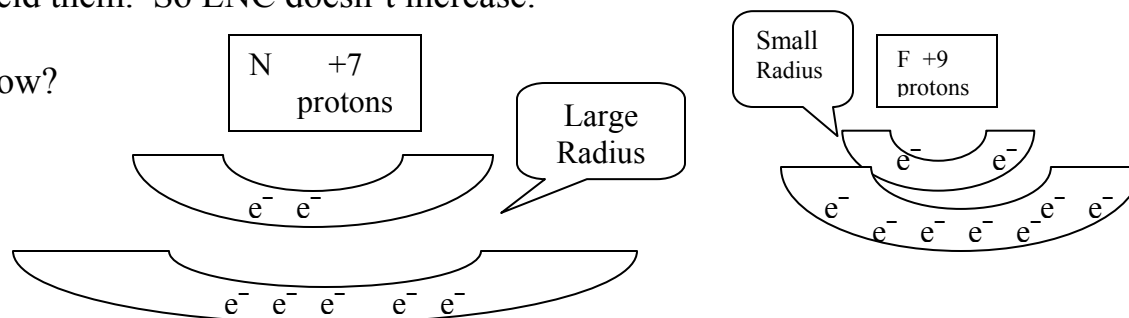
*Note as shielding increases the ENC goes down

The rows of the table are rows of seats

13 e⁻

$2e^-$ → n=1
$8e^-$ → n=2
$3e^-$ → n=3

s   d   p
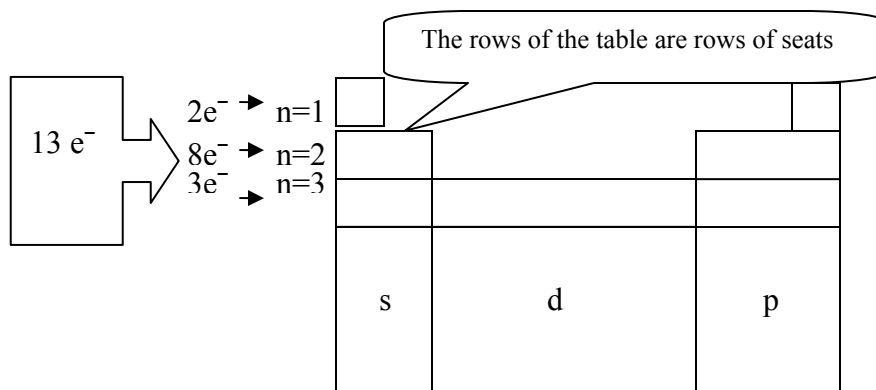
Trends in ENC down and across the table

We can see why it is that as we go down the periodic table, electrons are not getting closer. There are more protons, but there are an equivalent number of electrons to shield them. So ENC doesn't increase.

But what happens to ENC across the same row?

ENC for N= 7-2 = 5
and ENC for F = 9-2 = 7

N   +7 protons

Large Radius

Small Radius

F +9 protons

e^- e^-

e^- e^- e^- e^- e^-

e^- e^-
e^-
e^- e^- e^- e^- e^- e^-

So going across the row, ENC actually increases.

.

Note as move to the right, p+ goes up, but e⁻ doesn't shield (people in your row don't shield you) so going to the right, ENC ⇧, smaller radius

So how well do our pictures map to the actual calculation. Perfectly. Study the nice zig-zag shape.

Now what impact do these observations have on the six trends in periodicity. It follows what out trends will look like as we move across and down the periodic table. In fact, this is exactly what the atomic radius trend looks like.
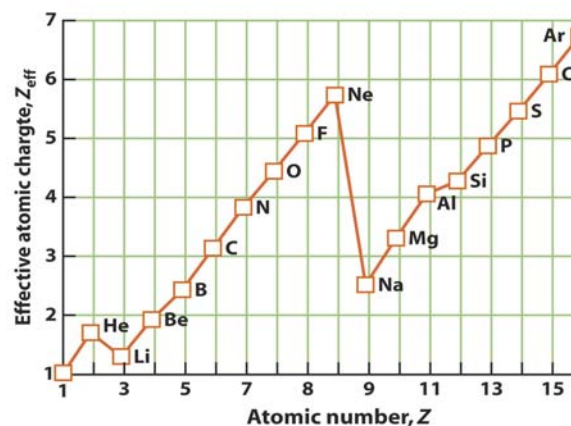
Trends in Size: Atomic and Ionic Radius

Both atomic and ionic radius follow the ENC arguments closely and without exception. The arguments are simple. The bigger the ENC, the more attraction to the nucleus and the small the atom or ion. The smaller the ENC, the smaller the attraction and the larger the atom or ion.

Atomic Radius is the easiest to understand and the simple cartoon drawing fits the actual data perfectly.

ENC ⇧, Size ⇩

ENC ⇩, Size ⇧
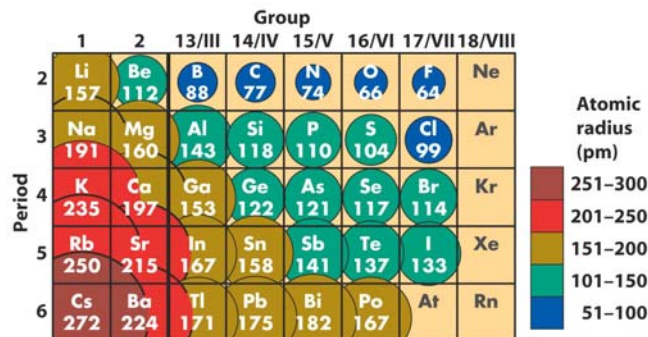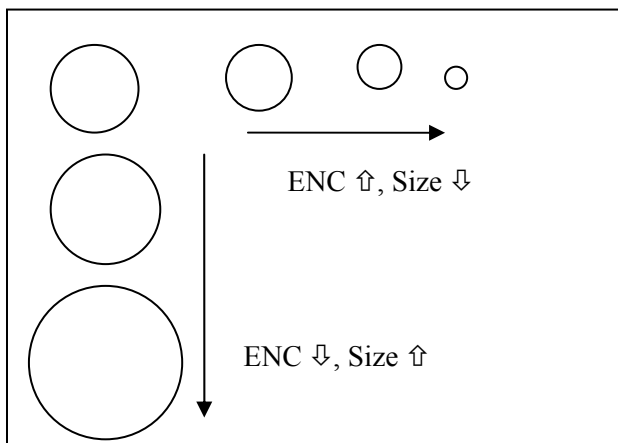
Ionic radius trends are also explained perfectly by ENC. But there is a complication because it doesn't follow the periodic table which is built on the idea of neutral atoms that have equal numbers of protons and electrons. So to see the smooth trend in ENC we need to rearrange the periodic table in terms of isoelectonic species. For example, here is the isoelectronic series around 10 electrons.

	N^{-3}	O^{-2}	F^{-1}	Ne	Na^+	Mg^{+2}	Al^{+3}
e-	10	10	10	10	10	10	10
p+	7	8	9	10	11	12	13

Smallest ENC, biggest Ion   Biggest ENC, Smallest Ion

Shown pictorially along the periodic table:

109
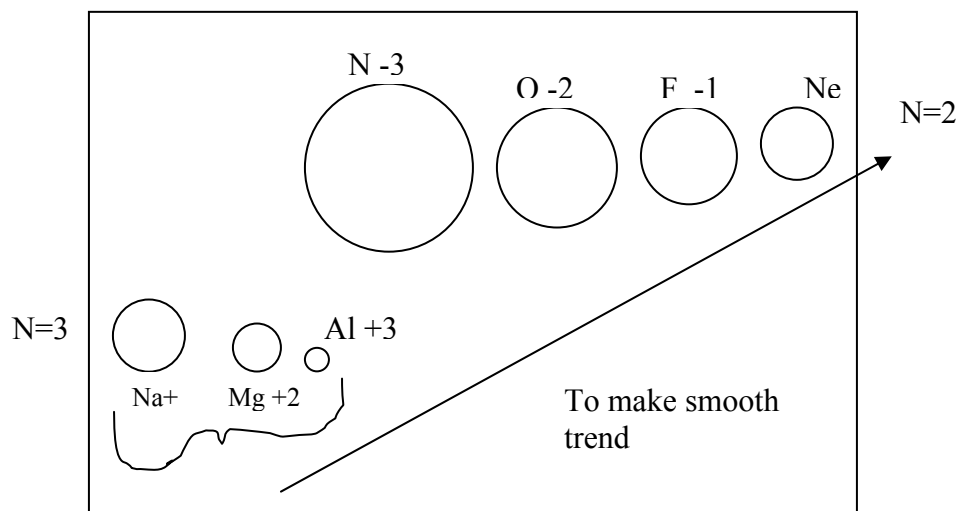
Remember that in class I argue that one easy way to create an isoelectronic table is to tear the periodic table in half and rearrange as I have so attractively done below. The n= 2 row is now isoelectronic with 10 electrons, the n = 3 row is isoelectronic with 18 electrons. Maybe not the esiest to see, but fun to show your friends.

.ve chopped up the
p......... .able and rearranged
it to show trends:
N -3 ⇨ Al +3
P -3 ⇨ Ga +3
By isoelectronic group

Trends in Electron Interest: Ionization Energy and Electron Affinity.

But what is important to see is that the trend based on ENC is the same (larger going down and smaller to the right) as happened with atomic radius. ENC arguments can also be used to explain the primary trends associated with how easily an electron is removed from an atom (ionization energy) and how easily an electron is attracted to an atom.
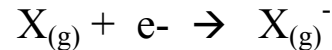
Ionization Energy:

First Ionization Energy $M \rightarrow M^+ + e\text{-}$
Second Ionization Energy $M^+ \rightarrow M^{++} + e\text{-}$

Eletron Affininty (applies to gases only):

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

So what should we expect? For ionization energy, getting rid of an electron should be easiest when ENC is least. So IE should be lowest in the lower right of the periodic table. For electron affininty, coveting an electron should be greatest when ENC is highest, which is the upper right of the periodic table.
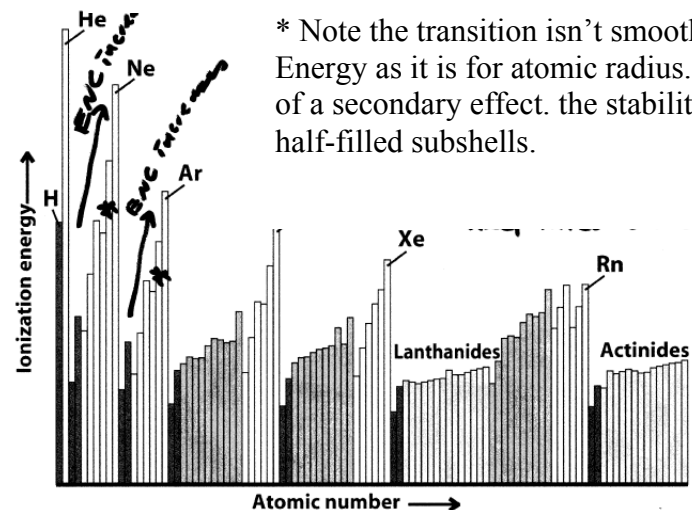
Ionization energy: ENC and removing an electron

Higher Ionization Energy →

Smaller
Ionization
Energy
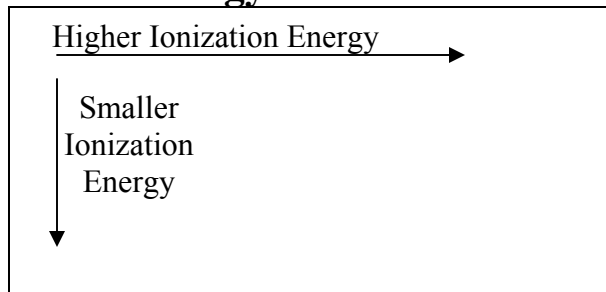
Going to the right as ENC ⇧, stronger hold
on e⁻, Ionization Energy ⇧

Going down as ENC ⇩, weaker hold on e⁻,
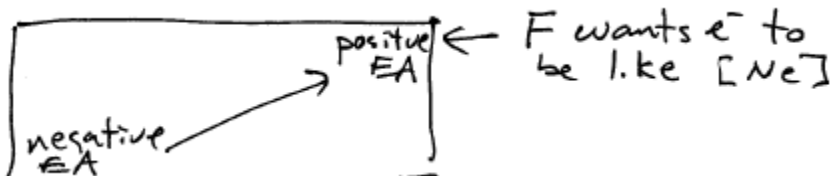Ionization Energy ⇩

Ionization Energy vs. Atomic Number

* Note the transition isn't smooth for Ionization
Energy as it is for atomic radius. This is because
of a secondary effect. the stability of filled and
half-filled subshells.

Electron Affinity: ENC and adding an electron

The trends are generally correct as predicted.

F wants e⁻ to
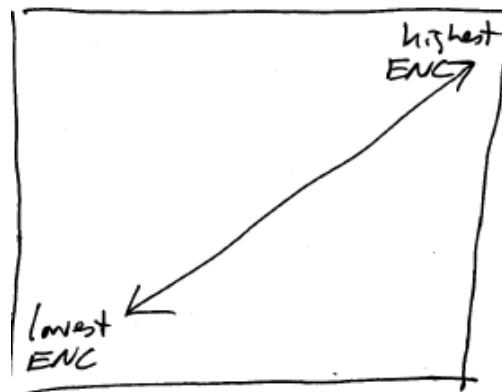be like [Ne]

To the right and up, to the right and up.

If you ever saw the movie JFK, Kevin Costner keeps saying the phrase "Back, and to the left... back, and to the left... back, and to the left" over and over as proof that there were two gunmen who shot JFK. Most of that has faded from my memory, but the cadence he used, remains, because it is the same way to remember how ENC is related to ALL six trends of interest to us. It is the creation of a diagonal that starts in the lower left hand corner and works its way to the upper right hand corner.

ENC goes down because protons increase

|
ENC goes down
as e⁻s in outer
shells are
shielded

Periodic ∨
Table
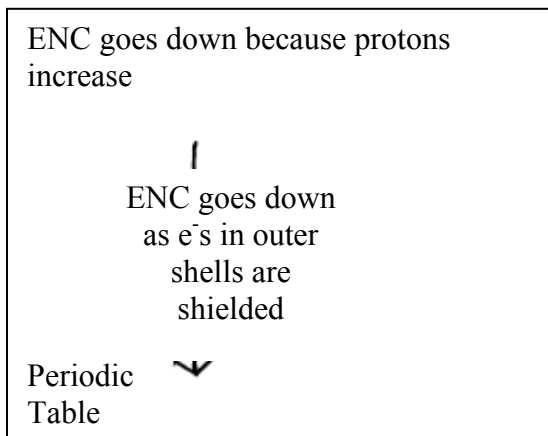
→
so all
trends
follow the
diagonal
shown
based on
ENC

And summarizing our six trends: as **ENC increases to the right and up**
- atomic radius decreases
- ionic radius decreases (isoelectronic forms)
- electron affinity increases
- ionization potential increases
- electronegativity increases
- metallic character decreases