

Slater's rules^{1,2,3,4}

Slater's rules are a guideline for determining shielding and, therefore, Z_{eff} . The rules are best used for atoms with $n > 1$. Remember, when we wish to determine or conceptualize Z_{eff} , we are considering only one of the outer most electrons. We are interested in the electron with the highest energy (n, l) as the electron that is being shielded by the other electrons in the atom. For example, a sodium atom has 11 electrons, but 10 of those electrons are shielding the outermost electron in the highest n, l . This means that all of the electrons in $n = 1$, and $n = 2$ shield the electron in $3s$ for sodium from the nucleus, with the $1s$ electrons being more effective at shielding than the $2s$ and $2p$ electrons. Electrons with the same n and l as the electron of interest are not as good at shielding that electron as inner electrons of $n-1$, or smaller n 's. Of course, electrons closest to the nucleus shield the best.

How can we use the Slater's Rules and Z_{eff} ? Slater's rules help us conceptualize trends. Consider the lithium atom. Lithium has an $IE_1 = 520 \text{ kJ/mol}$, while the IE_1 for hydrogen is 1310 kJ/mol . This means one needs more energy to remove an electron from the hydrogen atom than one needs for the same process for lithium. The average radius for lithium is larger than that of hydrogen. Therefore, the outer electron is further from the nucleus for lithium because that electron is a $2s$ orbital. Inner core electrons repel the electron of interest, the $2s^1$ electron, so it does not penetrate the nucleus effectively. Therefore, this electron is easily removed. Most of the $1s$ electrons density is very close to the nucleus. The electron of interest has a Z_{eff} of 1.3 based on Slater's Rules. This concedes with computer simulations of the radius. The radial distribution of the $2s$ orbital shows that it can penetrate to the nucleus-just not very well.

Rules to determine shielding based on Slater's values:

- Write the electron configuration for the atom based on the order of the periodic table
- Put that configuration in energy order
- Group electron configurations by n value
- $(1s)(2s,2p)(3s,3p)(3d)(4s,4p)(4d)(4f)(5s,5p)(5d)(5f)$
- For ns , or np electrons:
 - Electrons in the same group shield 0.35, Except $1s$, which shields 0.30 for H and He only.
 - When $n=2$, we use 0.35 for the $1s$ electrons
 - Electrons in the $n-1$ group shield 0.85
 - Electrons in the $n-2$ group shield 1.00
 - Electrons in nd or nf shield 0.35
- Assign any electrons to the left of the d or f electrons 1.00
- Electrons to the right of the electron of interest do not shield.

	Summary of the information above		
orbitals	Multiplier based on location of electrons in orbitals		
	(n)	($n-1$)	($n-2$), ($n-2$)
S or p orbital	0.35	0.85	1
d or f orbital	0.35	1	1

A general equation: $S = 1.00(\#e^-)_{n-2} + 0.85(\#e^-)_{n-1} + 0.35(\#e^-)_{n_0}$.⁵

- n_0 is the energy level where the electron of interest is housed.
- n_{n-1} is one shell less; n_{n-2} is any other core electrons. For example, an electron is in $n=4$ shell. n_0 refers to $n=4$, n_{n-1} refers to $n=3$, while n_{n-2} refers to $n=2$ and $n=1$ shells.

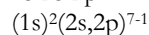
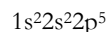
¹ A broken link that no longer exists. I don't know how to document this information. But W.B. Wells, thank you for the background information.

² Ref: <http://www.chm.davidson.edu/vce/atomicorbitals/ZeffSize.html>

³ <http://intro.chem.okstate.edu/WorkshopFolder/Slater'sRule.html>

⁴ J.C. Slater's, *phys Rev* **1930**, v36, p57

⁵ Similar calculators can be found on line. They are good for checking work, but of little use during a test. Here is one such calculator: <http://calistry.org/calculate/slaterRuleCalculator>

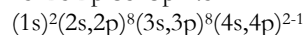
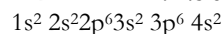
EXAMPLE 1: 2p electron in fluorine

$$S = 1.00(\#e^-)_{n-2} + 0.85(\#e^-)_{n-1} + 0.35(\#e^-)_{n_0}$$

$$S = 2 \times 1.00 + 6 \times 0.35 = 3.8; 9 - 3.8 = 5.2.$$

Explanation of values: There are 2 electrons in $n=1$. There are 7 e in $n=2$ but this includes the electron of interest so, subtract 1 leaving 6 electrons that we count in $n=2$, because an electron does not shield itself. There aren't any "n-2" electrons.

The Z_{eff} that the outer most electron of fluorine "feels" is 5.2, much lower than the +9 charge.

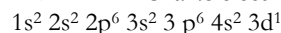
EXAMPLE 2: 4s electron in calcium

$$S = 1.00(\#e^-)_{n-2} + 0.85(\#e^-)_{n-1} + 0.35(\#e^-)_{n_0}$$

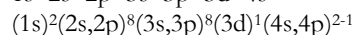
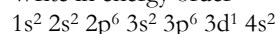
$$2 \times 1.00 + 8 \times 1.00 + 8 \times 0.85 + 1 \times 0.35 = 17.15; 20 - 17.15 = 2.85.$$

The Z_{eff} of Ca is 2.85

Explanation of values: Calcium has 10 electrons that are considered inner core, $n-2$ or lower in energy. These are the 2 electrons from $n=1$, and 8 electrons from $n=2$. There are 8 electrons from $n=3$, but these are $n-1$, so count for 0.85 shielding. 4s has two electrons (it's calcium!), but we consider only 1 of these electrons at 0.35 shielding.

EXAMPLE 3: a 4s electron in scandium

Write in energy order



$$S = 1.00(\#e^-)_{n-2} + 0.85(\#e^-)_{n-1} + 0.35(\#e^-)_{n_0}$$

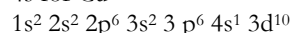
$$2 \times 1.00 + 8 \times 1.00 + 9 \times 0.85 [\text{b/c } 8 \text{ } n=3 \text{ e in } 3s \text{ and } 3p \text{ and } 1 \text{ in } 3d] + 1 \times 0.35 = 18;$$

$$21 - 18 = 3$$

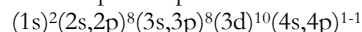
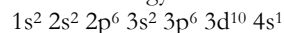
For most transition metals, $nd > ns$ or np , in the Slater's rules, and nd electrons are considered inner core electrons. Sc is the odd ball. The nuclear "pull" is about the same for 3d as for 4s

EXAMPLE 4: 4s¹ for Cu vs. 3d for Cu

4s for Cu



Write in energy order

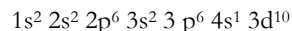


$$S = 1.00(\#e^-)_{n-2} + 0.85(\#e^-)_{n-1} + 0.35(\#e^-)_{n_0}$$

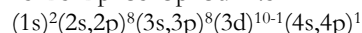
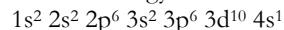
$$S = 2 \times 1.00 + 8 \times 1.00 + [8 \times 0.85 + 10 \times 0.85] + 0 \times 0.35 = 25.3$$

$$Z_{\text{eff}} = 29 - 25.3 = 3.70$$

An electron in the 3d for Cu



Write in energy order



$$S = 1.00(\#e^-)_{n-2} + 0.85(\#e^-)_{n-1} + 0.35(\#e^-)_{n_0}$$

$$S = 2 \times 1.00 + 8 \times 1.00 + 8 \times 1.00 + 9 \times 0.35 + \text{ignore } 4s = 21.15$$

$$29 - 21.15 = 7.85$$

Explanation of values: Copper has 10 electrons that are considered inner core, $n-2$ or lower in energy. These comprise the 2 electrons from $n=1$, and 8 electrons from $n=2$ and are the same for any outer electron for copper.

We find differences in values when we look at the electron shielding in different higher energy orbitals on the copper atom.

Let's look at the electron in the 4s orbital. It is shield by everything in $n=3$. The 8 electrons from 3s and 3p and the 10 electrons from 3d comprise the 18 electrons that are shielding at 0.85 because they are a complete n value. There is one electron in 4s, so it does no shielding (it can't shield itself).

Contrast this with an electron in 3d. 9 other electrons in the same sub-shell shield the 3d electron. The other electrons shield these extremely well, and are given a value of 1.00. The 4s electron does not shield the 3d electrons; it is higher in energy.

The 3 electron has a stronger attraction to the nucleus than the 4s electron. The Z_{eff} is higher; a stronger attraction means it takes more energy to remove that electron. The electron that is removed for ionization must come from 4s⁵.

Cations and anions shielding work in a similar manner!

EXAMPLE 5: 6s¹ electron in platinum

$$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 6s^1 4f^{14} 5d^9$$

$$(1s)^2 (2s, 2p)^8 (3s, 3p)^8 (3d)^{10} (4s, 4p)^8 (4d)^{10} (4f)^{14} (5s, 5p)^8 (5d)^9 (6s)^{1-1}$$

$$1.00 \times 2 + 1.00 \times 8 + 1.00 \times 8 + 1.00 \times 10 + 1.00 \times 8 + 1.00 \times 10 + 1.00 \times 14 + 0.85 \times 17 = 74.45$$

$$Z_{\text{eff}} = 78 - 74.45 = 3.55$$

Explanation of values: Platinum has a lot of electrons. Consider the outer electrons first. The electron of interest is in the 6s orbital. The energy shell below that is n=5. There are 16 electrons in n= 5; the electrons in n=4 and lower shield by 1.00.

EXAMPLE 6: 1s electron in Os

$$\text{Os: } (1s)^2 (2s, 2p)^8 (3s, 3p)^8 (3d)^{10} (4s, 4p)^8 (4d)^{10} (4f)^{14} (5s, 5p)^8 (5d)^6 (5f)^0 (6s, 6p)^2$$

For the 1s valence electron: $S = (1)(0.30) + \text{the rest don't matter since they don't shield}$ so $Z_{\text{eff}} = 76 - 0.3 = 75.7$

The 1s electrons are poorly shielded. It will be very difficult to remove an electron from the 1s orbital.

PROBLEMS

1. Write the electron configuration for the elements listed below, then group the s and p (d and f) electrons together, by n values; group the electron configurations using the Slater equation. Determine Slater's shielding value and the Z_{eff} for each of the element's outer most shell.

Element: P	Slater
Configuration	$1s^2 2s^2 2p^6 3s^2 3p^3$
n-value grouping	$(1s)^2 (2s, 2p)^8 (3s, 3p)^5$
groupings via Slater.	$(1s)^2 (2s, 2p)^8 (3s, 3p)^{5-1}$
Slater's shielding value and Z_{eff} .	$S = 2 \times 1.00 + 8 \times 0.85 + 4 \times 0.35 = 10.2; 15 - 10.2 = 4.8$

Element: N	Slater
Configuration	
n-value grouping	
groupings via Slater.	
Slater's shielding value and Z_{eff} .	

Element: C	Slater
Configuration	
n-value grouping	

groupings via Slater.	
Slater's shielding value and Z_{eff} .	

Element: Mg	Slater
Configuration	
n-value grouping	
groupings via Slater.	
Slater's shielding value and Z_{eff} .	

Element: Cl	Slater
Configuration	
n-value grouping	
groupings via Slater.	
Slater's shielding value and Z_{eff} .	

Element: Zn	Slater
Configuration	
n-value grouping	
groupings via Slater.	
Slater's shielding value and Z_{eff} .	

Element: Te	Slater
Configuration	
n-value grouping	
groupings via Slater.	
Slater's shielding value and Z_{eff} .	

2. We are interested in the behavior of outer core electrons, but we can use Slater's Rules for any electron. As seen in the rules, electrons that are in orbitals that are after the electron of interest do not contribute to the shielding of that electron. Begin by writing the electron configuration for the element. Remember that n_0 is the energy level that contains the outer most electron. Determine the S and Z_{eff} for each of the following.

Element	Configuration
A 2s electron in P	$1s^2 2s^2 \cancel{2p^6} \cancel{3s^2} \cancel{3p^3}; (1s)^2 (2s \cancel{2p})^{2-1} (\cancel{3s} \cancel{3p})^{6+1}$ $S = 1 \times 0.35 + 2 \times 0.85 = 2.05$ $15 - 2.05 = 12.95$
A 2p electron in Mg	
2s electron in Cl	

Element	Configuration
1s electron in He	(follow the steps!)
1s electron in Mg	

3. Cations and anions: follow the rules!

Element	Configuration
2s electron in Na^+	$1s^2 2s^2 2p^6 3s^1$; $(1s)^2 (2s 2p)^{8-1} (3s 3p)^0$ $S = 7 \times 0.35 + 2 \times 0.85 = 4.15$. $11 - 4.15 = 6.85$
3p electron in Cl^-	
2p electron in Mg^{2+}	
1s electron in Li^+	(follow the steps!)

4. Transition elements: reviewing the rules: electrons in the same (nd) group contribute 0.35 towards the overall shielding. Elements in all groups to the left in the Slater configuration format contribute 1.00 towards overall shielding. Electrons in all groups to the right in the Slater configuration contribute nothing towards overall shielding.

Element	Configuration
A 3d electron in Ni	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^8 4s^2$; $(1s)^2 (2s 2p)^8 (3s 3p)^8 (3d)^{8-1} (4s)^2$; $S = 18 \times 1.00 + 7 \times 0.35 = 20.45$; $28 - 20.45 = 7.55$
3d electron in Mn	
4d electron in Ru	

Using the techniques above, give a reason why the following occurs:

- The radius of Cd^{2+} is smaller than that of Sr^{2+} . Calculate the Z_{eff} for the outer most orbital for each atom and each ion. Calculate the Z_{eff} for a 3s orbital for each atom. Give a rational explanation for your findings.
- The ionization potentials increase subtly for Ru and Rh and have a large increase for Pd, but decrease in the series Fe, Co, Ni. The electron of interest is in the 5s orbital for Ru, Rh, and 4d orbital for Pd (4d because 5s is empty), and 4s for Fe, Co, and Ni. Rationalize the ionization energies for the atoms based on Slater Rule calculations, Z_{eff} and other trends; Do the same for Fe, Co, Ni. [Hint; a table will help! Example below]

element	Ionization energy	e-configuration	Slater order	Z_{eff} based on either 4s, 5s or 4d
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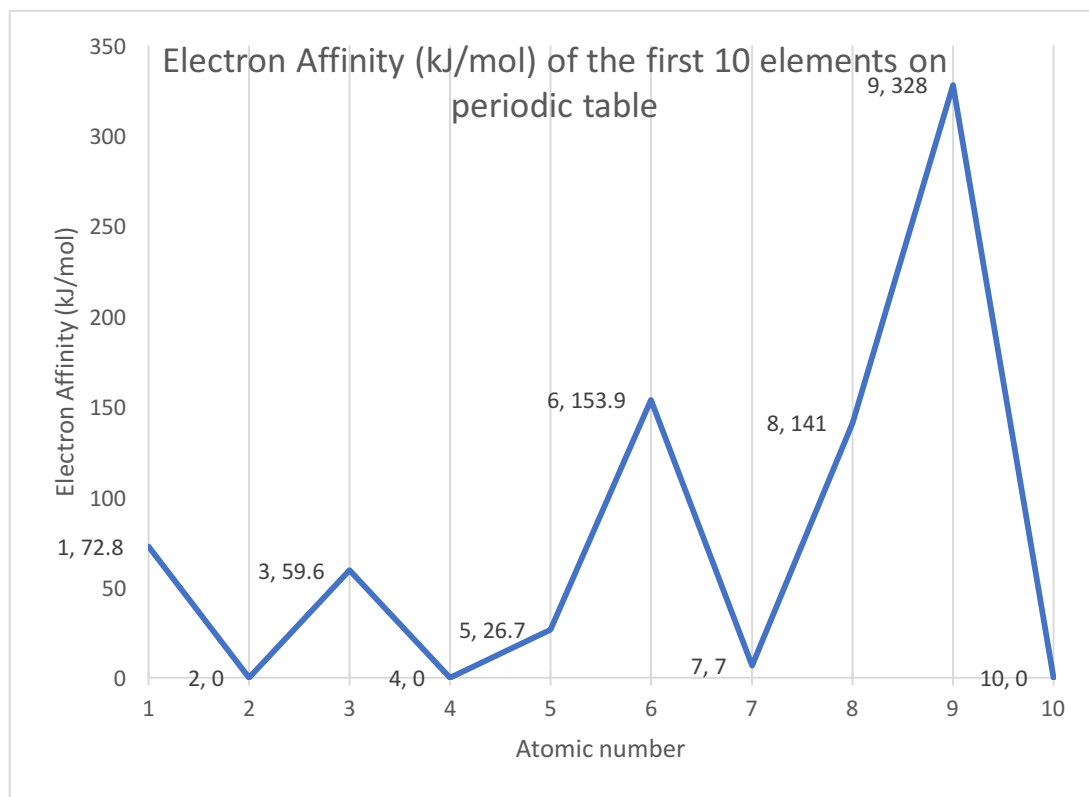
710.2 kJ x mol⁻¹ Ru
 719.7 kJ x mol⁻¹ Rh
 804.4 kJ x mol⁻¹ Pd
 762.5 kJ x mol⁻¹ Fe
 760.4 kJ x mol⁻¹ Co
 737.1 kJ x mol⁻¹ Ni

7. Consider the melting point data for the natural forms of the second row elements. Calculate Z_{eff} using Slater's rules (again: tables are helpful) for the outermost electron for each of these elements. Does Z_{eff} give a reasonable accounting of the trend in the melting point? Why or why not? Should melting point be considered a periodic property of atoms? Why or why not?

Element	Melting Point (°C)
Na	98
Mg	650
Al	660
Si	1414
P	44
S	115
Cl	-101.5
Ar	-189

8. Calculate Z_{eff} for the highest energy electron in the following ions: K⁺, Ca⁺, Sc⁺, Ti⁺, V⁺. Does Z_{eff} account for the observed values of the second ionization potential of these elements? Why or why not? Some have argued that Ca⁺ should be considered a transition metal. Give an argument to support this contention.
9. Look at a plot for the electron affinity as a function of atomic number for the atoms from H to Ne. In general, does Z_{eff} account for the variation in electron affinity? Why or why not? Are there any specific anomalies in the trend? If so, give an explanation.⁶

⁶ Physical and chemical data of elements <http://periodictable.com/Elements/001/data.html>



PS-Would I ask these questions on a test. How about an answer with no hedging, “maybe-maybe not”. You should be able to do the examples and read through the problem answers with a nod of the head and a, “hmmm, I think I get it!”. Think about how you might summarize the answer. [Oh and I have asked #1 & 5 on a test!]