Key for Madelung's and Slater's Rules

Madelung's Rule

For an atom with more than one electron, an electron's ionization energy depends on both n and on l. Explain why n affects ionization energy.

- The quantum number n is related to the average distance of an electron from the nucleus. From Coulomb's law, we know that ionization energy is inversely proportional to distance; thus, as n increases, ionization energy decreases.

Explain why l affects ioniziation energy.

- The quantum number l is related to an orbital's shape, which affects the probability of finding an electron at different distances from the nucleus. Although electrons in orbitals with the same n have the same average distance from the nucleus, if they have different values for l, then one will be more effective at screening the other electron. The more an electron is screened from the nucleus, the smaller the effective nuclear charge, Z_{eff} that it "senses." From Coulomb's law, we know that ionization energy is directly proportional to Z_{eff}; thus, an electron that "senses" a smaller Z_{eff} will have a smaller ionization energy.

The table below gives values of n and of l for elements in the first five rows of the periodic table. Note that some possible values of n and of l are not included in this table because they apply to elements that appear after the fifth row.

n	l	orbital	$n + l$	rank order
1	0	$1s$	1	1
2	0	$2s$	2	2
2	1	$2p$	3	3
3	0	$3s$	3	4
3	1	$3p$	4	5
3	2	$3d$	5	7
4	0	$4s$	4	6
4	1	$4p$	5	8
4	2	$4d$	6	10
5	0	$5s$	5	9
5	1	$5p$	6	11

Because both n and l affect an electron's ionization energy, let's assume as a first approximation that the smaller the sum or $n + l$, the more stable the electron and the greater its ionization energy. For orbitals with identical values for $n + l$, lets assume as a second approximation that the smaller the value of n, the more stable the electron and the greater its ionization energy. Using these two rules—which are known as Madelung's rules—rank the oribitals from largest ionization energy to smallest ionization energy. After you complete the table, list the orbitals below in the order in which they accept electrons.

- The completed table is shown above. The order in which the orbitals are filled is, from left-to-right

$$1s < 2s < 2p < 3s < 3p < 4s < 3d < 4p < 5s < 4d < 5p$$

Note that this order is consistent with the structure of the periodic for the first five rows.

Slater's Rule

For the first 18 elements, H $\longrightarrow$ Ar, the order in which orbitals fill is consistent with our expectations in that there is no case where an orbital with a larger n is more stable than an orbital with a smaller n. This is not the case when we get to potassium, K, where the 19th electron enters a $4s$ orbital instead of a $3d$ orbital. One possible explanation for this is that it is the result of screening.

Slater's rules are an attempt to estimate screening so that we can better estimate Z_{eff}, where
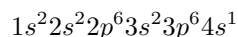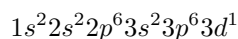
$$Z_{\text{eff}} = Z - S$$

where S is a screening constant. Slater's rules—which are empirical and, therefore, not grounded in a rigorous theory—provide a way to estimate the screening constant. Here is one form of Slater's rules that applies to elements in the first five rows.

1. write the electron configuration in groups using this order

$$(1s) \quad (2s, 2p) \quad (3s, 3p) \quad (3d) \quad (4s, 4p) \quad (4d) \quad (5s, 5p)$$

2. identify the group in which the electron of interest lies and ignore all electrons to the right of this group

3. if the electron of interest is an s or p electron, then

   - each additional electron in its group (ns, np) contributes 0.35 to S
   - each electron in the $n - 1$ shell contributes 0.85 to S
   - each electron further to the left contributes 1.00 to S

4. if the electron of interest is a d electron, then

   - each additional electron in its (nd) group contributes 0.35 to S
   - each electron further to the left contributes 1.00 to S

For example, here are two possible electron configurations, one in which the outermost electron is in a $3d$ orbital and one in which it is in a $4s$ orbital.

$$1s^2 2s^2 2p^6 3s^2 3p^6 3d^1$$

$$1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$$

Here is how we apply Slater's rules to the first possibility:

1. $(1s^2) \, (2s^2, 2p^6) \, (3s^2, 3p^6) \, (3d^1)$

2. electron of interest is in a $3d$ orbital

3. not relevant for this electron configuration

4. $Z_{\text{eff}} = Z - S = 19 - (0)(0.35) - (18)(1.00) = 19 - 18 = 1$

Apply Slater's rules to the second possibility and report a value for Z_{eff}. Explain how your results supports $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$ as the more likely electron configuration for K.

1. $(1s^2) \, (2s^2, 2p^6) \, (3s^2, 3p^6) \, (3d^0) \, (4s^1)$

2. electron of interest is in a $4s$ orbital

3. $Z_{\text{eff}} = Z - S = 19 - (0)(0.35) - (8)(0.85) - (10)(1) = 19 - 16.8 = 2.2$

4. not relevant

> The greater the value for Z_{eff} the greater the ionization energy and the more stable the electron; thus we expect the electron configuration of $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$ to be more likely than the other option of $1s^2 2s^2 2p^6 3s^2 3p^6 3d^1$.