Aufbau Principle

A. Electrons go into the orbital of lowest energy that is available.

B. Pauli Exclusion Principle: no two electrons can have the same set of quantum numbers.

C. Hund's Rule: For a degenerate set of orbitals, the energy is minimized when the electrons occupy different orbitals and have the same spin quantum number.

To guess the lowest energy orbital we make the following observations:

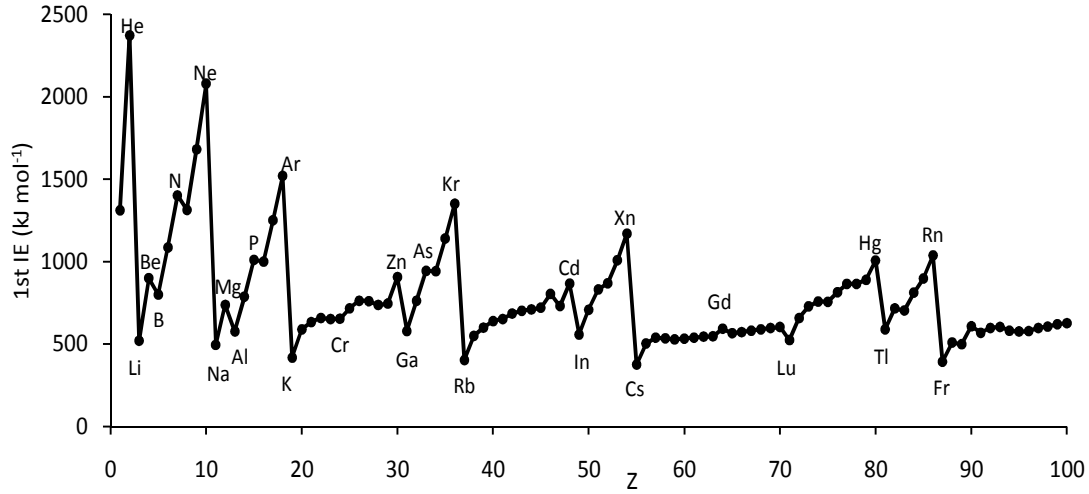
I. Each successive shell is shielded to a greater extent by previous shells. This shows that Z_{eff} does not increase as quickly as Z. Inner orbitals decrease in energy faster than outer orbitals.

II. Orbitals with low l penetrate more and then are less easily shielded by outer electrons. This shows that Z_{eff} is greater for low ℓ orbitals than high ℓ orbitals with the same principle quantum number.

III. Electrons in the same subshell don't shield each other well. This shows that Z_{eff} for electrons with the same ℓ increases with Z.

IV. Half filled or totally filled subshells have a special stability. (See Be, N, Cr and Cu for examples)

V. Half filled or totally filled subshells are efficient shielders. (See B and O for examples)



Slater-type Orbitals (STOs): $\Psi_{n\ell\, m_\ell} = N\, Y_{\ell,m_\ell}\, r^{(n_{eff}-1)}\, e^{-Z_{eff}\, r/n_{eff}\, a_o}$

n	1	2	3	4	5	6
n_{eff}	1	2	3	3.7	4.0	4.2

Slater Orbital Parameters[1], Z_{eff}.

	$_1$H							$_2$He
1s	1.0000							1.6875
	$_3$Li	$_4$Be	$_5$B	$_6$C	$_7$N	$_8$O	$_9$F	$_{10}$Ne
1s	2.6906	3.6843	4.6795	5.6727	6.6651	7.6579	8.6501	9.6421
2s	1.2792	1.9120	2.5762	3.2166	3.8474	4.4916	5.1276	5.7584
2p			2.4214	3.1358	3.8340	4.4532	5.1000	5.7584
	$_{11}$Na	$_{12}$Mg	$_{13}$Al	$_{14}$Si	$_{15}$P	$_{16}$S	$_{17}$Cl	$_{18}$Ar
1s	10.6259	11.6089	12.5910	13.5745	14.5578	15.5409	16.5239	17.5075
2s	6.5714	7.3920	8.2136	9.0200	9.8250	10.6288	11.4304	12.2304
2p	6.8018	7.8258	8.9634	9.9450	10.9612	11.9770	12.9932	14.0082
3s	2.5074	3.3075	4.1172	4.9032	5.6418	6.3669	7.0683	7.7568
3p			4.0656	4.2852	4.8864	5.4819	6.1161	6.7641

Slater's Rules: $Z_{eff} = Z - S$

1st period (first element in period Z = 1): $Z_{eff} = Z - 0.35\,(Z - 1)$

2nd period (2 next shell core electrons, first element in period Z = 3,):

$$Z_{eff} = Z - 0.85\,(2) - 0.35\,(Z - 3)$$

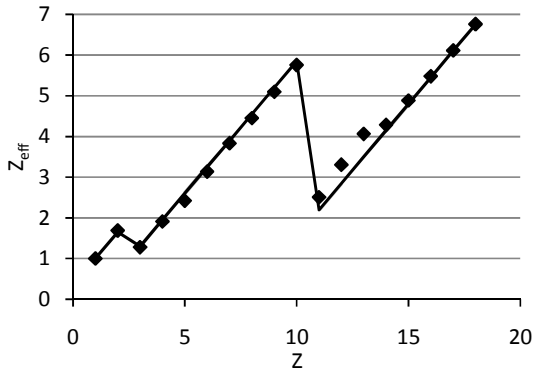
next core shell *valence shell*

3rd period (2 inner core electrons, 8 next shell core electrons, first element in period Z = 11):

$$Z_{eff} = Z - 1.00\,(2) - 0.85\,(8) - 0.35\,(Z - 11)$$

inner core *next core shell* *valence shell*

100% efficient *85% efficient* *35% efficient*



1. J. S. Winn, Physical Chemistry, Harper Collins, New York, NY, 1994, Table 13.1