

For **orbital energies**:

$$n = 4 > n = 3 > n = 2 > n = 1$$

and for **ℓ** :

$$f > d > p > s$$

In general for orbital energies:

1) Orbital energies increase with increasing $(n+\ell)$

2) For $(n+\ell)$ of equal value, that of lower n is more stable
(electron is closer on average to the positive nucleus).

Note for example the case where n only is considered:

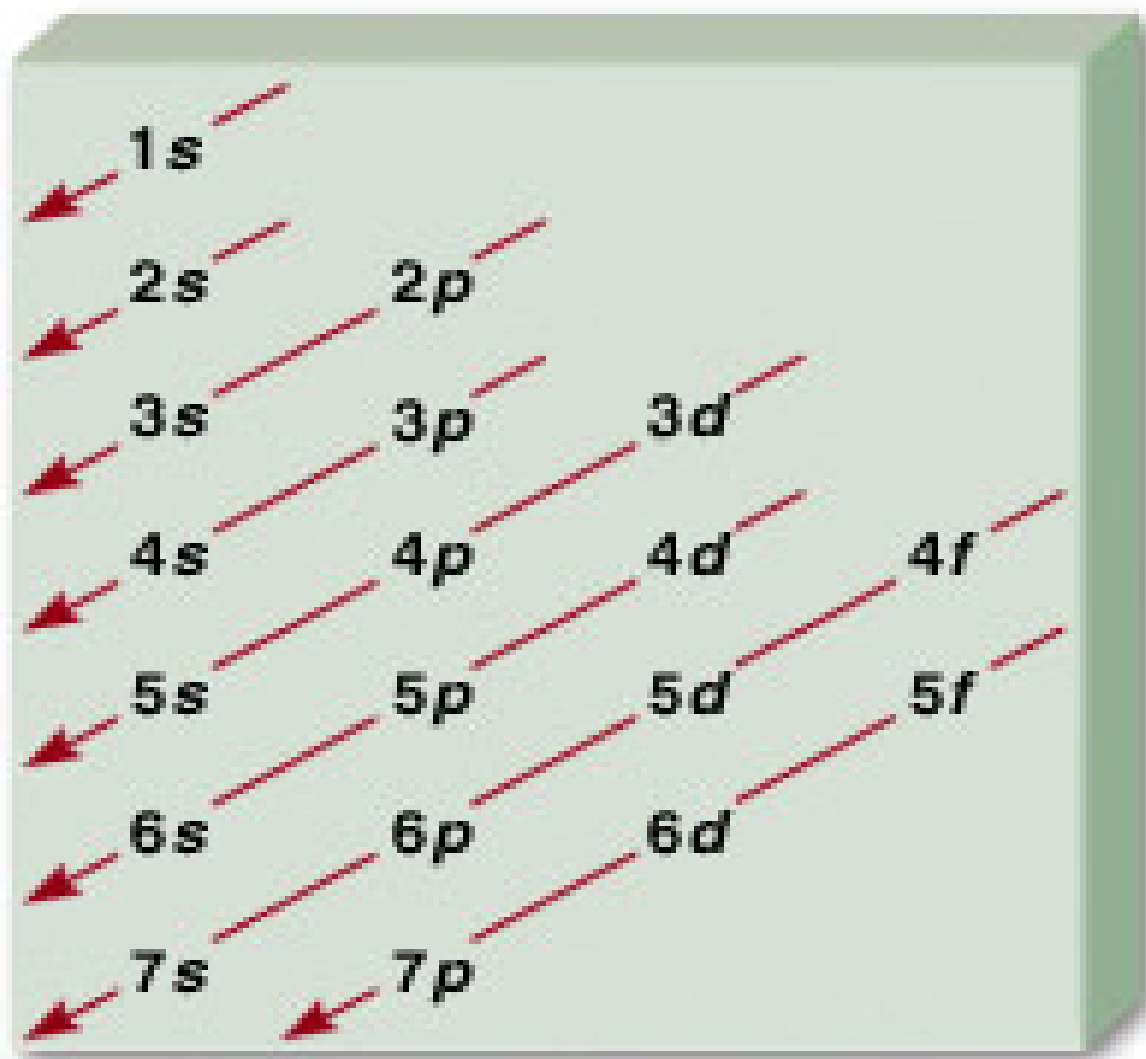
$$\mathbf{4s} \quad n = 4 \quad \ell = 0 \quad n + \ell = 4$$

$$\mathbf{3d} \quad n = 3 \quad \ell = 2 \quad n + \ell = 5$$

∴ Order of energy is $3d > 4s \equiv "(n+\ell)"$ rule

A simple guide to the order in which electrons fill orbitals is:

Order in Which Atomic Subshells are Filled



Since each orbital can hold a maximum of $2e^-$, it is possible to construct the electronic configuration of elements as follows:

Example: for $^{13}\text{Al} = 1s^2 2s^2 2p^6 3s^2 3p^1 \equiv 13 e^-$

Here again, $1s^2$ means 2 electrons in the 1s orbital; $2p^6$ means 6 electrons in the 2p orbitals, etc.

This notation is termed spectroscopic notation

The lowest energy configuration = ground state

A shorter form of the notation gives the symbol for the rare gas whose configuration is identical to that of the closed shells of an element

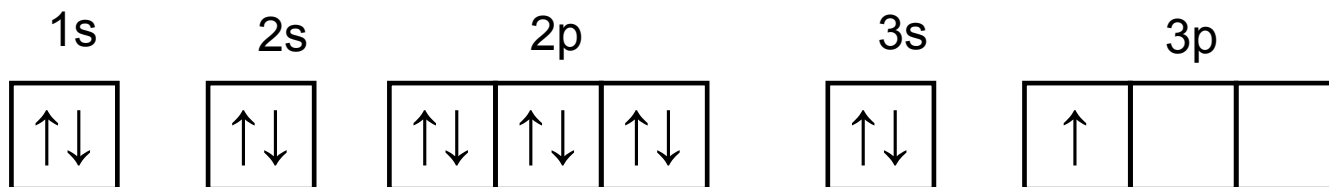
\therefore for ^{13}Al above: $1s^2 2s^2 2p^6 \equiv$ configuration for ^{10}Ne

\therefore notation becomes $^{13}\text{Al} = [\text{Ne}]3s^2 3p^1$

Note: electrons in the orbital of highest n are called **valence electrons**; the rest are **core electrons**

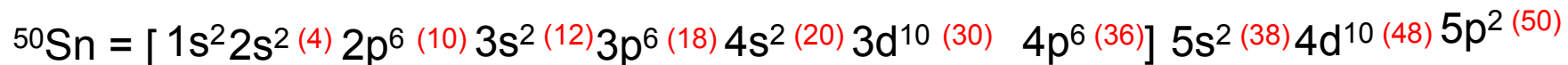
If you wish to illustrate orbitals occupied by electrons more clearly you can use an **orbital box** diagram:

Example: $^{13}\text{Al} \equiv$



Question: Use spectroscopic notation to describe the electron configuration for ^{50}Sn .

What are the quantum numbers of the highest energy electron?

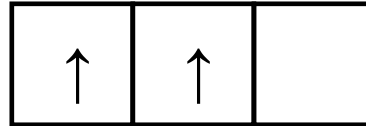


Main question is how to distribute the 2 highest energy e^- in the 3 5p-orbitals.

Filling of orbitals to give ground state configurations follows **Hund's Rule**.

Hund's rule states that electrons occupy orbitals of equal energy in such a way that the number of unpaired electrons is at a maximum, thus minimizing inter-electronic repulsion

For ^{50}Sn this means $5p^2 \equiv$



but not:



or



and clearly not:



or



- quantum numbers of the highest energy electron are: $n = 5$, $\ell = 1$,
- • $m_\ell = -1, 0, \text{ or } +1$, $m_s = +\frac{1}{2} \text{ or } -\frac{1}{2}$

Who was Hund?



- Friedrich Hund was a German scientist.
- He was born 1896 and died 1997!
- You can live a long time working in Chemistry!

Note : 3d/4s and 4d/5s orbitals are very close in energy.
Therefore, sometimes the scheme does not work for transition metals.

Consider the electronic configuration of ^{24}Cr

Might expect electronic configuration = $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^4$
= $[\text{Ar}]4s^2 3d^4$

Not the case.

Instead it is energetically favorable to have both the
3d and 4s orbitals half filled to minimize electron repulsions. = $[\text{Ar}]4s^1 3d^5$

≡ another way of stating **Hund's Rule:**

lowest energy corresponds to a configuration of **maximum number of unpaired electrons**

Similarly, **complete 3d orbitals are favorable:** eg ^{29}Cu .

The energy of 3d falls below that of 4s because of the increased nuclear charge.

Electronic configuration of ^{29}Cu = $[\text{Ar}]4s^1 3d^{10}$

Cu and Cr belong to the first series of the transition metals.
Second series metals behave similarly.

Atomic Ions

When an atom loses electrons to form a cation, the electrons are always lost from the valence shell of **highest n**

Thus, for transition metals, the electrons remaining over the noble gas core are always found in the 3d orbitals

- • Configuration of Fe = $[\text{Ar}]3d^64s^2$ but $\text{Fe}^{2+} = [\text{Ar}]3d^64s^0$ and $\text{Fe}^{3+} = [\text{Ar}]3d^54s^0$

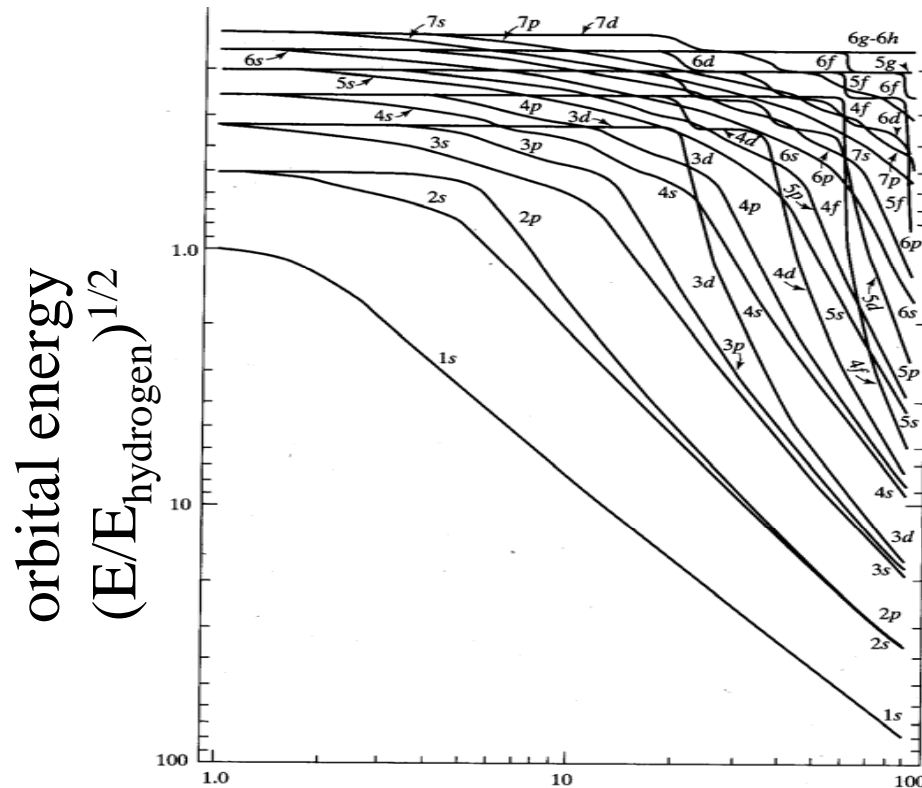
Ultimately, the reason for this is related to finding the configuration with the highest nuclear charge, and therefore the lowest energy.

- • $(\text{V}^{2+}, \text{Sc}^0)$ or $(\text{Fe}^{3+}, \text{V}^0)$ have the same number of electrons, but are **not** isoelectronic; that is, they have different electronic configurations

An aside (not responsible for this)

You may have noticed that we don't actually write down the "energy" of an orbital.

This is because an orbital energy depends on which element we are discussing, (and hence the nuclear charge and how many other electrons there are).



Atomic number, Z