

Chemistry 1000 Lecture 8: Multielectron atoms

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Spin

- **Spin** (with associated quantum number s) is a type of angular momentum attached to a particle.
- Every particle of the same kind (e.g. every electron) has the same value of s .
- Two types of particles:
 - Fermions:** s is a half integer
 - Examples:** electrons, protons, neutrons ($s = \frac{1}{2}$)
 - Bosons:** s is an integer
 - Example:** photons ($s = 1$)

Spin magnetic quantum number

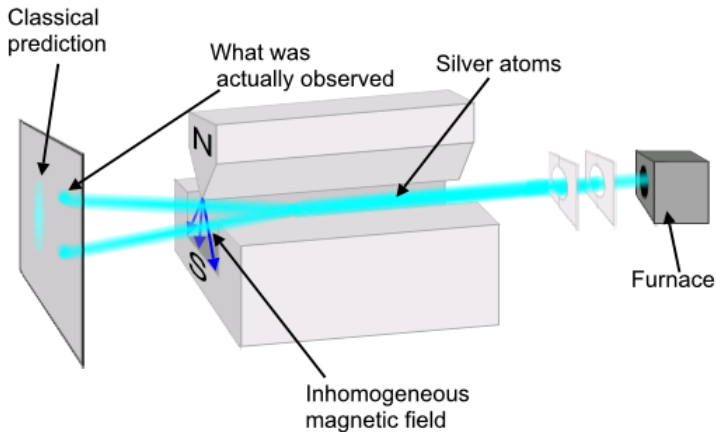
- All types of angular momentum obey similar rules.
- There is a spin magnetic quantum number m_s which gives the z component of the spin angular momentum vector:

$$S_z = m_s \hbar$$

- The value of m_s can be $-s, -s + 1, \dots, s$.
- For electrons, $s = \frac{1}{2}$ so m_s can only take the values $-\frac{1}{2}$ or $\frac{1}{2}$.

Stern-Gerlach experiment

How do we know that electrons (e.g.) have spin?



Source: Theresa Knott, Wikimedia Commons, http://en.wikipedia.org/wiki/File:Stern-Gerlach_experiment.PNG

Pauli exclusion principle

No two fermions can share a set of quantum numbers.

Multielectron atoms

- Electrons occupy orbitals similar (in shape and angular momentum) to those of hydrogen.
 - Same orbital names used, e.g. $1s$, $2p_x$, etc.
 - The number of orbitals of each type is still set by the number of possible values of m_ℓ , so e.g. there are three $2p$ orbitals.
- In multielectron atoms, the orbital energies depend on both n and ℓ . Orbitals corresponding to the same values of n and ℓ have the same energy, e.g. the five $3d$ orbitals all have the same energy.

Rule of thumb: Orbital energy increases with $n + \ell$.

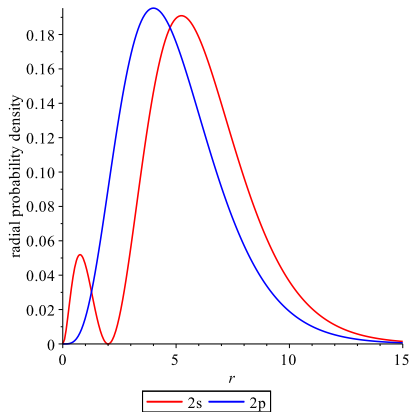
If two orbitals have the same value of $n + \ell$, the one with the smaller n is lower in energy.

Radial probability density

- The radial probability density is the probability density for finding the electron in a small interval of width dr at distance r from the nucleus.

- You can think of it as the probability density averaged over all angles.

Why do orbitals of larger ℓ have higher energy?



- Note the 2s density close to the nucleus.
- Electron density near nucleus energetically favorable for 2s orbital
- Electron density near nucleus “screens” some of the nuclear charge from the 2p electrons
 \implies less net attraction of 2p electrons raises their energy

Examples of orbital ordering

- Which is lower in energy, the 3d or 4s orbital?

For the 3d orbitals, $n + \ell = 3 + 2 = 5$, while for the 4s orbital, $n + \ell = 4 + 0 = 4$.

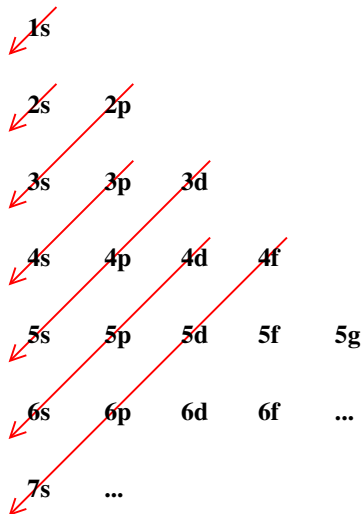
The 4s is therefore lower in energy.

- Which is lower in energy, the 2p or 3s orbital?

For the 2p orbitals, $n + \ell = 3$, while for the 3s orbital, $n + \ell = 3 + 0 = 3$. The $n + \ell$ test therefore doesn't help.

The tie-breaker is the value of n , so the 2p orbitals are lower in energy.

A simple way to remember the orbital ordering



Ground-state electron configurations of atoms

- An electron configuration is a way of arranging the electrons of an atom in its orbitals.
- Configurations are denoted by showing the number of electrons in an orbital type as a superscript, e.g. $1s^22p^1$ would denote an atom with 2 electrons in its 1s orbital, and one in the 2p orbital.
- The ground state configuration is the lowest-energy configuration.

Rules for determining the ground state configuration

(Aufbau rules)

- 1 An orbital can hold exactly one electron with each value of m_s (Pauli principle)
- 2 Electrons are added to the lowest energy orbital available.
- 3 Electrons are spread over degenerate orbitals when possible.
- 4 Maximize the number of parallel spins when possible (Hund's rule).
- 5 Exceptions:
 $(n - 1)d^5 ns^1$ configurations are generally lower in energy than $(n - 1)d^4 ns^2$ configurations.
 $(n - 1)d^{10} ns^1$ configurations are generally lower in energy than $(n - 1)d^9 ns^2$ configurations.
- 6 There are other exceptions (not to be learned), particularly in the transition metals (after the first row), lanthanides and actinides.

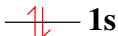
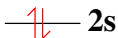
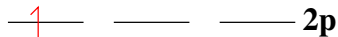
Orbital energy diagrams

- Not usually drawn to scale
- Electrons represented by up or down arrows (representing the two possible values of m_s)

Example: Ground-state electronic configuration of lithium:



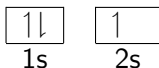
Example: Ground-state electronic configuration of boron:



Orbital box diagrams

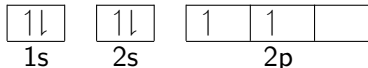
- Compact version of orbital energy diagram with each orbital represented as a box arranged along a line

Example: Ground-state electronic configuration of lithium:



Equivalent line notation: $1s^2 2s^1$

Example: Ground-state electronic configuration of carbon:



Equivalent line notation: $1s^2 2s^2 2p^2$

Valence vs core electrons

- All atoms beyond helium have a **noble gas core**, i.e. a set of electrons with the configuration of the previous noble gas.

Example: Carbon has a $1s^2$ core, equivalent to the ground-state configuration of helium.

These **core electrons** are chemically inert.

- Chemical reactivity is associated with the **valence electrons**, i.e. the electrons outside the noble gas core.
- When writing down electron configurations, it's a pain to write down the core electrons, which aren't that interesting anyway. We use the noble-gas abbreviation to represent these electrons.

Example: The electron configuration of carbon can be written $[\text{He}]2s^22p^2$.

- The noble-gas abbreviation can also be used with orbital box diagrams.

Electron configurations and the periodic table

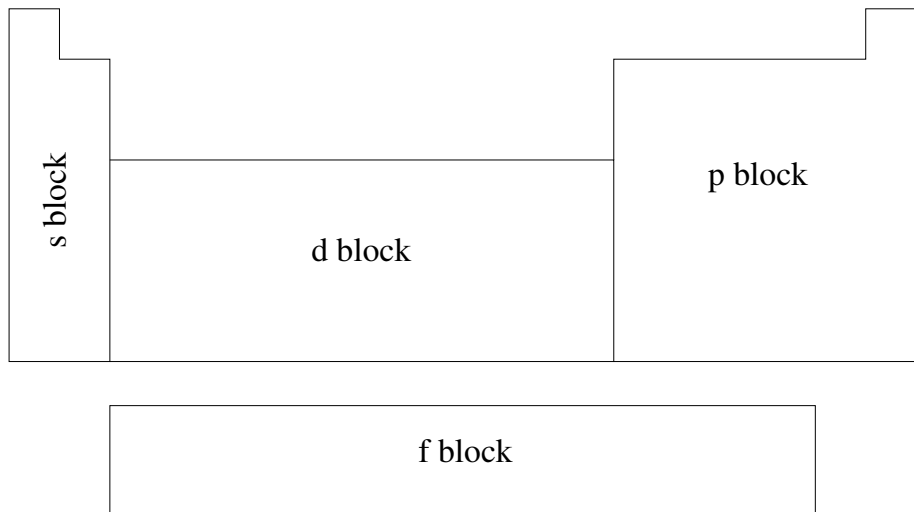
- Electron configurations can be read off the periodic table
- Examples: F, Cl, Br
- Examples: Cr, Mo, W
- How the periodic table *should* look:

	Group																															
	1	2	3		4	5	6	7	8	9	10	11	12	13	14	15	16	17	18													
1	1 H																		2 He													
2	3 Li	4 Be													5 B	6 C	7 N	8 O	9 F	10 Ne												
3	11 Na	12 Mg													13 Al	14 Si	15 P	16 S	17 Cl	18 Ar												
4	19 K	20 Ca	21 Sc																													
5	37 Rb	38 Sr	39 Y																													
6	55 Cs	56 Ba	57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
7	87 Fr	88 Ra	89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Nh	114 Fl	115 Mc	116 Lv	117 Ts	118 Og

Source:

https://commons.wikimedia.org/wiki/File:32-column_periodic_table-a.png

Periodic table blocks



Refining the concept of valence electrons

- When writing down electron configurations with the noble gas abbreviation, we have to write down all electrons outside the noble gas core.
- For chemical purposes, the valence electrons are those electrons that can be involved in chemical reactions.
- A closed (filled) d subshell is chemically inert.
- d electrons are not valence electrons for elements in the p block.

Example: For As ($[\text{Ar}]4s^23d^{10}4p^3$), the valence electrons are the 4s and 4p electrons.

Ions

- A closed (full) shell (noble gas configuration) represents a particularly unreactive electronic configuration.
- Common ions are often those which have gained or lost electrons to obtain a closed shell.

Examples:

- Na has a ground-state electronic configuration of $1s^2 2s^2 2p^6 3s^1$.
Removing the 3s electron leaves us with the noble gas configuration $1s^2 2s^2 2p^6$, so a sodium ion is Na^+ .
- Oxygen has a ground-state electronic configuration of $1s^2 2s^2 2p^4$.
Adding two p electrons would fill the outer shell so an oxygen ion is O^{2-} with electronic configuration $1s^2 2s^2 2p^6$.

Cations

Rule: Remove electrons from shell of largest n first.

If there are electrons in more than one subshell with the same n , remove electrons from the shell of largest ℓ .

- Example:**
- Pb has the ground-state electronic configuration $[\text{Xe}]6s^2 4f^{14} 5d^{10} 6p^2$.
 - Removing the $6p$ electrons gives Pb^{2+} with ground-state electronic configuration $[\text{Xe}]6s^2 4f^{14} 5d^{10}$.
 - Pb^{4+} is also known. In lead(IV) compounds, the cation has the electronic configuration $[\text{Xe}]4f^{14} 5d^{10}$.

Exceptions: Al^{3+} and Ga^{3+} are the most common ions of these metals. Al^+ is unknown, and Ga^+ is uncommon.

Cations

Example: copper

- Copper has the ground-state electronic configuration $[\text{Ar}]4s^1 3d^{10}$.
- It has two commonly observed ions, Cu^+ and Cu^{2+} .
- Cu^+ has the ground-state electronic configuration $[\text{Ar}]3d^{10}$.
- Cu^{2+} has the ground-state electronic configuration $[\text{Ar}]3d^9$.

Why Cu^{2+} and not, say, Cu^{3+} ? In this case, the existence of the former and not of the latter is an empirical observation.

Cations

Example: molybdenum

- Molybdenum has the ground-state electronic configuration $[\text{Kr}]5s^1 4d^5$.
- Mo^{2+} , Mo^{3+} , Mo^{4+} and Mo^{5+} are all known in aqueous solution.
- Why not Mo^+ ? This is an empirical observation.
It is unusual since we almost always get a common ion by removing the ns electrons from transition metals.
- Mo^{2+} has the ground-state electronic configuration $[\text{Kr}]4d^4$.
- Mo^{3+} has the ground-state electronic configuration $[\text{Kr}]4d^3$.
- ... and so on

Magnetic properties

A **diamagnetic substance** is repelled by a magnetic field.

⇒ Occurs when all the electrons are paired.

A **paramagnetic substance** is attracted by a magnetic field.

⇒ Occurs when there are unpaired electrons.

Ferromagnetism is an extreme form of paramagnetism in which the magnetic field generated by the spin in one atom tends to align the magnetic moment in its neighbors. Ferromagnetic materials can therefore acquire permanent magnetization.

Examples:

- The Cr^{3+} ion has a ground-state electronic configuration of $[\text{Ar}]3d^3$ and is **paramagnetic**.
- All noble gas atoms are **diamagnetic**.