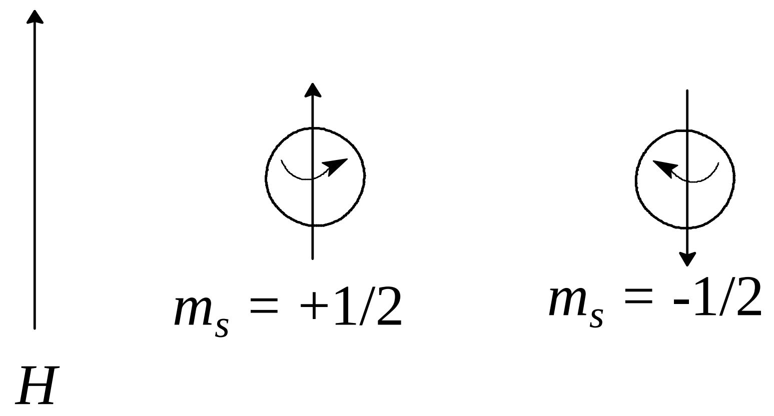
Electron Spin

- ☞ In 1921 Otto Stern and Walter Gerlach showed that a beam of neutral silver atoms ($Z = 47$) passing through a nonhomogeneous magnetic field was split into two divergent beams.
  - ✔ Atoms in each beam had different orientations of a magnetic moment from their one unpaired electron.

- ☞ In 1925 George Uhlenbek and Samuel Goudsmit interpreted the doublet line structure in the emission spectra of multielectron atoms in terms of two magnetic orientations for the electron, which they attributed to *electron spin.*
  - ✔ Electron spin is quantized according to two allowed values of a *spin quantum number,* m_s, with values of +½ or –½, corresponding to alignment of the electron's magnetic moment with or against an applied magnetic field.

Model of Quantized Electron Spin



- The electron acts as if it were spinning on its axis, where opposite spin directions would create opposite magnetic moments.
  - ✔ In light of wave-particle duality the picture of a spinning electron should not be taken too literally.

- When two electrons with different spin state occur within the same atom (spins in opposition) net cancellation of their oppositely oriented magnetic moments results.

$$M_s = \overset{\underline{\;\upharpoonleft\;\downharpoonright\;}}{+\tfrac{1}{2} - \tfrac{1}{2}} = 0$$

- In a multielecton atom, all electrons of one spin comprise a set of α electrons, and all electrons of the opposite spin comprise a set of β electrons.

Pauli Principle

- The complete wave function for a system of electrons in a multielectron atom depends upon an orbital and spin contribution; i.e., $\psi = \psi_{\mathrm{orb}}\psi_{\mathrm{spin}} = \psi(n,l,m_l)\psi(m_s)$.

- All electrons are identical and indistinguishable, so interchanging positions or spins of any two must leave the system unchanged; e.g., $P \propto \psi^2 = (\pm\psi)^2$.

☞ Pauli Principle for Electrons: When the roles of any two electrons are interchanged, the total wave function must change sign; i.e., it must be "antisymmetric".

- This requirement (which was formulated without theoretical proof) does not change the overall state of the system.

☞ Corollary — Pauli Exclusion Principle: No two electrons in the same orbital (same n, l, m_l) may have the same spin states (i.e., one must be α, and one must be β).

☞ Corollary — No two electrons with the same spin can occupy the same point in space simultaneously.

☞ Corollary —Electrons avoid occupying a space occupied by two electrons with opposite spins. ("Pauli force" — not a real force)

Symmetric and Antisymmetric Orbital and Spin Functions
Two Electrons (1 & 2), Two Orbitals (1*s* & 2*s*), Two Spin States (α & β)
$\psi = \psi_{orb}\psi_{spin}$

Orbital functions:

$\psi^{1s1s} = 1s(1)1s(2) \leftrightarrow 1s(2)1s(1)$ symm

$\psi^{2s2s} = 2s(1)2s(2) \leftrightarrow 2s(2)2s(1)$ symm

$\psi^{1s2s+} = 1s(1)2s(2) + 1s(2)2s(1) \leftrightarrow 1s(2)2s(1) + 1s(1)2s(2)$ symm

$\psi^{1s2s-} = 1s(1)2s(2) - 1s(2)2s(1) \leftrightarrow 1s(2)2s(1) - 1s(1)2s(2)$ antisymm

Spin functions:

$\psi^{\alpha\alpha} = \alpha(1)\alpha(2) \leftrightarrow \alpha(2)\alpha(1)$ symm

$\psi^{\beta\beta} = \beta(1)\beta(2) \leftrightarrow \beta(2)\beta(1)$ symm

$\psi^{\alpha\beta+} = \alpha(1)\beta(2) + \alpha(2)\beta(1) \leftrightarrow \alpha(2)\beta(1) + \alpha(1)\beta(2)$ symm

$\psi^{\alpha\beta-} = \alpha(1)\beta(2) - \alpha(2)\beta(1) \leftrightarrow \alpha(2)\beta(1) - \alpha(1)\beta(2)$ antisymm

General product results:

(symm)(symm) = symm (antisymm)(antisymm) = symm

(symm)(antisymm) = antisymm (antisymm)(symm) = antisymm

Example disallowed by Pauli Principle

$\psi^{1s1s}\,\psi^{\alpha\alpha} = [1s(1)1s(2)][\alpha(1)\alpha(2)]$ (symm)(symm) = symm

Examples allowed by Pauli Principle:

$\psi^{1s1s}\,\psi^{\alpha\beta-} = [1s(1)1s(2)][\alpha(1)\beta(2) - \alpha(2)\beta(1)]$

(symm)(antisymm) = antisymm

$\psi^{1s2s-}\psi^{\alpha\alpha} = [1s(1)2s(2) - 1s(2)2s(1)][\alpha(1)\alpha(2)]$

(antisymm)(symm) = antisymm

Pauli Principle and Coulombic Repulsions

- The Pauli Principle prohibits two electrons with the same spin from occupying the same point in space.

- Two electrons of opposite spin can occupy the same point in space, but unless compelled to do so by a force field Coulombic repulsions will generally prevent it.

- In a free atom the α set of electrons and the β set of electrons avoid interacting.

  > "There are two worlds that do not see each other in terms of the Pauli principle: the set of α electrons and the set of β electrons."[1]

- An α and β electron with the same wave function are not occupying a single orbital with a certain orientation in space.

- Each electron in each set has its own wave function (its own orbital) with its own (not necessarily coincident) orientation.

☞ In a free atom there are no "electron pairs".

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[1] Gillespie & Popelier, p.66.

Electronic Configurations of Multielectron Atoms

☞ The arrangement or **configuration** of electrons in various orbitals gives rise to a total **energy state** for the atom.

- There are many possible electronic configurations, so there are many possible corresponding energy states.

☞ The lowest possible overall energy state for an atom is its **ground state**.

- The configuration of electrons in specific orbitals that gives rise to this lowest energy state is called the **ground state configuration.**

- Any other configuration will result in a higher energy state, called an **excited state** for the atom.

The Aufbau Concept

aufbauen (Ger.) = to build up

☞ The ground state configuration of an atom can be predicted by a bookkeeping process in which electrons are added sequentially to orbitals in the order of their increasing energy.

   ☺ The predicted configurations are always correct for the main-group elements (A groups) and are usually correct (with some notable exceptions) for the first transition series elements (period 4).

   ☹ Predictions are often slightly or seriously wrong for 5th and 6th period transition elements and the elements of both the lanthanide and actinide series.

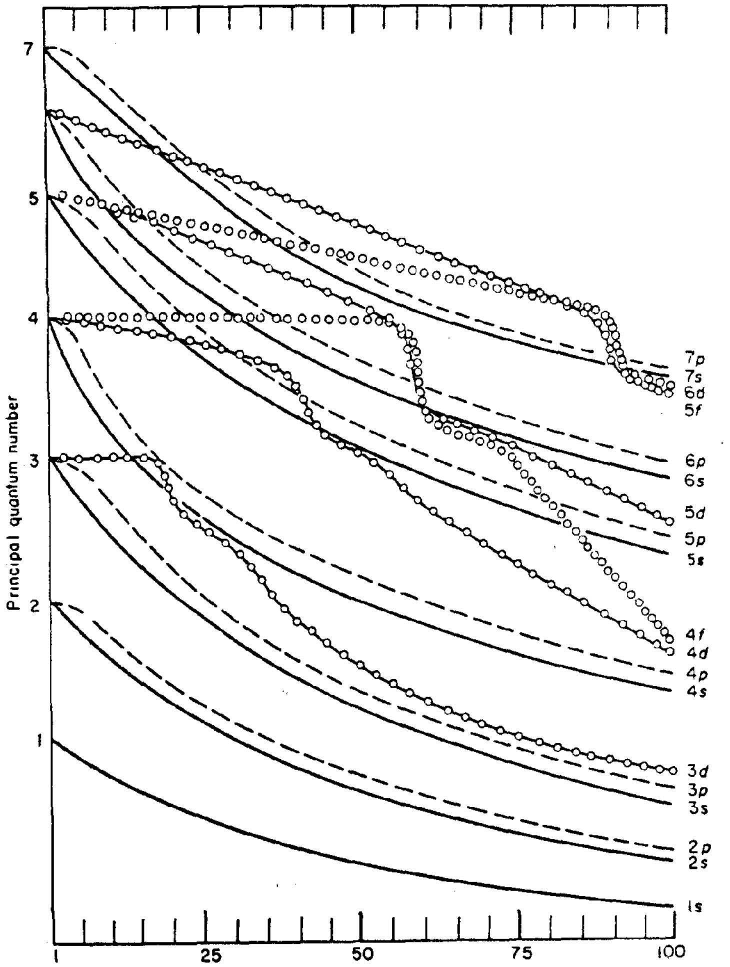
Orbital Energies in Multielectron Atoms

☞ Orbital energies depend upon both *n* and *l*, not just *n* as in the one-electron atoms.

☞ Within the same shell (same *n*), subshells vary in energy in the order

$$ns < np < nd < nf$$

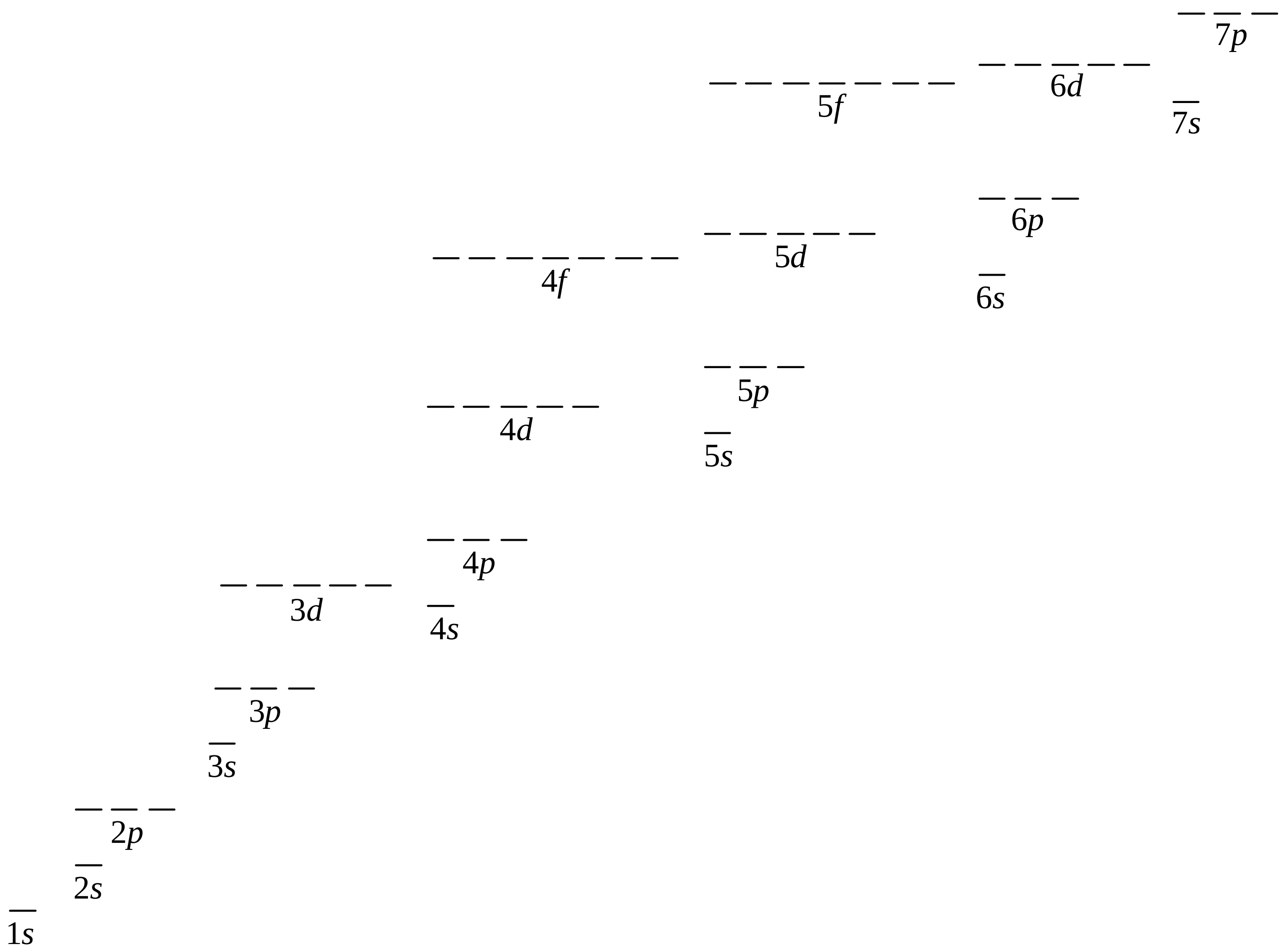
☞ The relative ordering of subshells from different shells varies in a complicated way with changing nuclear charge, *Z*.



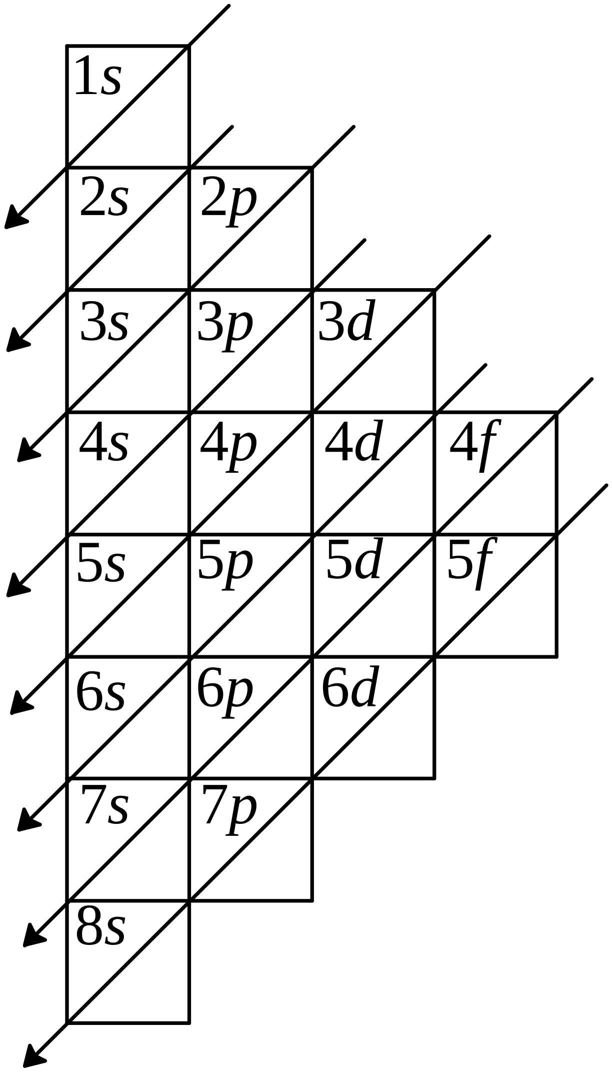
Aufbau Order of Atomic Orbitals

- ☺ For the purposes of applying aufbau principles to predict ground-state electronic configurations, we only need to know the relative energy order of the subshells when electrons occupy them in the ground-state configuration.

The Aufbau Order of Subshells



Mnemonic for the Aufbau Order



Pauli Exclusion Principle

Wolfgang Pauli - 1925

No two electrons in the same atom can have the same set of all four quantum numbers (n, l, m_l, m_s).

Consequences:

1. If n, l, and m_l are the same for two electrons, then one must have $m_s = +½$ and the other must have $m_s = -½$. The two electrons are said to be *paired* in the same orbital.

   Paired electrons: $\underline{\ \uparrow\downarrow\ }$

2. Each orbital can have only two electrons, and the capacities of subshells are thus two times the number of orbitals comprising them.

   Maximum capacities: s^2, p^6, d^{10}, f^{14}

Hund's Rule of Maximum Multiplicity

Frederic Hund - 1925

Electrons in the same subshell will tend to distribute so that they are in different degenerate (same energy) orbitals with their spins parallel (same value of m_s), so long as the Pauli Exclusion Principle allows.

Consequences:

1. Electrons occupy different degenerate orbitals when possible, because this minimizes electron-electron repulsions.

   $\underline{\;\upharpoonleft\;}\ \underline{\;\upharpoonleft\;}\ \underline{\quad}$ not $\underline{\upharpoonleft\downharpoonright}\ \underline{\quad}\ \underline{\quad}$

2. Electrons avoid pairing when possible, because it requires energy to pair (*pairing energy*).

3. Electrons must pair when a subshell is more than half filled (Pauli Exclusion Principle).

   $\underline{\upharpoonleft\downharpoonright}\ \underline{\;\upharpoonleft\;}\ \underline{\;\upharpoonleft\;}$ not $\underline{\upharpoonleft\upharpoonleft}\ \underline{\;\upharpoonleft\;}\ \underline{\;\upharpoonleft\;}$

☞ Hund's rule applies to the ground-state configuration of an atom, not to its excited states.

Exchange Energy

☞ Configurations in which a subshell is half- or fully-filled have extra stability.

↿ ↿ ↿ ↿ ↿   ↿⇂ ↿⇂ ↿⇂ ↿⇂ ↿⇂

half-filled $3d$ fully-filled $3d$

- ✓ These configurations result in a symmetrical distribution of electronic charge, which minimizes repulsions.

- ✓ The slight energy advantage of these configurations is called **exchange energy**.

- ✓ Exchange energy becomes more significant with greater orbital multiplicity (more orbitals per subshell); i.e.,

$$s < p < d < f$$

☛ Exchange energy sometimes results in ground-state configurations that deviate from the aufbau predictions.

Examples: $_{24}$Cr is $3d^54s^1$ (not $3d^44s^2$) and $_{29}$Cu is $3d^{10}4s^1$ (not $3d^94s^2$)