Beyond Bohr

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Bohr's model was only successful in describing the energy of one-electron atoms (H, He^+, Li^{2+}).

Bohr himself abandoned this model by the late 1920s.

Bohr's model was at odds with the "new physics" discovered in the 1920s.

Beyond Bohr

De Broglie (1923) had shown that electrons have wave-particle duality:

$$\lambda = h / p = h / mv$$

Heisenberg's Uncertainty Principle (1927) had shown that position and momentum cannot be known simultaneously with absolute precision:

$$\Delta x \Delta p = h / 4\pi$$

Schroedinger's Wave Equation

$$H\Psi = E\Psi$$

Electron described by a wave function, Ψ, and its associated energy, E.

Ψ is a solution to $H\Psi = E\Psi$.

$H\Psi = E\Psi$ has an infinite number of Ψs.

Copenhagen Interpretation
(Max Born - 1926)

Ψ has no physical meaning.

Value of Ψ^2 for a vanishingly small volume of space (virtually a point) gives the probability of finding the electron there: $P = N\Psi^2$

Copenhagen Interpretation and Ψ

- Ψ has a value for every point in space. Otherwise the probability would be undefined somewhere.
- Ψ can have only one value at any point. Otherwise the probability would be ambiguous at some points.

Copenhagen Interpretation and Ψ

- Ψ cannot be infinite at any point in space.

Otherwise its position would be fixed, in violation of the Heisenberg Uncertainty Principle.

Copenhagen Interpretation and Ψ

- Ψ can be zero at some points in space. Any point or series of points with $\Psi = 0$ defines a *node*, where $P = \Psi^2 = 0$.
- The sum of Ψ^2 over all space is unity. The electron must be somewhere.

Ψ and Quantum Numbers

Mathematical form of Ψ is defined in terms of three quantum numbers:

n	Principle quantum number
l	Angular momentum quantum number
m_l	Magnetic quantum number

Ψ_{nlm} defines an **orbital**.

Principle Quantum Number, *n*

Values: $n = 1, 2, 3, \ldots$

Determines energy, *E*, for one-electron atoms.

Related to concept of shells (*K*, *L*, *M*, …)

Angular Momentum Quantum Number, l

Values: $l = 0, 1, 2, \ldots, n - 1$

Related to shape of electron probability distribution (electron density) of orbital.

Related to concept of subshells.

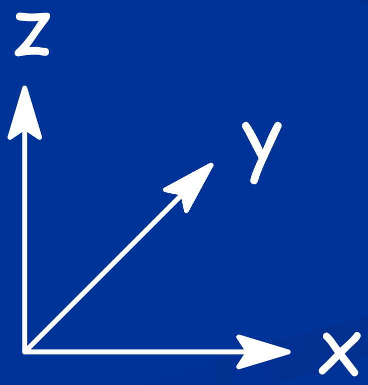
Subshell Designations

Value of *l*	0	1	2	3	4	…
Label	*s*	*p*	*d*	*f*	*g*	…

Magnetic Quantum Number, m_l

Values: $m_l = -l, (-l + 1), \ldots, 0, \ldots, (l - 1), l$

Related to orientation of orbitals relative to a Cartesian coordinate system.



The Fourth Quantum Number

Electron Spin Quantum Number, m_s

Values: $m_s = +1/2, -1/2$

Defines orientation of electron's own magnetic moment relative to an applied magnetic field.

Important for multielectron cases.

Quantum Numbers, Orbitals, and Subshells

n	l	m_l	subshell	orbitals
1	0	0	1*s*	1
2	0	0	2*s*	1
2	1	-1, 0, +1	2*p*	3

Quantum Numbers, Orbitals, and Subshells

n	l	m_l	subshell	orbitals
3	0	0	3*s*	1
3	1	-1, 0, +1	3*p*	3
3	2	-2, -1, 0, +1, +2	3*d*	5

Quantum Numbers, Orbitals, and Subshells

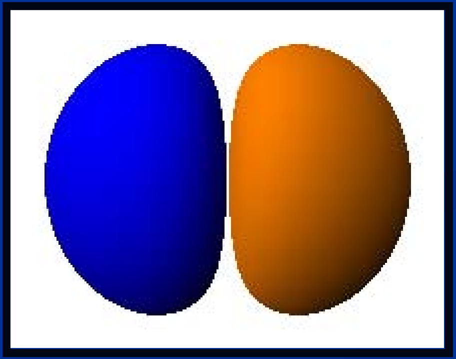
n	l	m_l	subshell	orbitals
4	0	0	4*s*	1
4	1	-1, 0, +1	4*p*	3
4	2	-2, -1, 0, +1, +2	4*d*	5
4	3	-3, -2, -1, 0, +1, +2, +3	4*f*	7

Visualizing Orbitals

Orbital Viewer

David Manthey's *free* Windows Program for generating and displaying orbitals

www.orbitals.com/orb



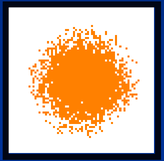
Visualizing Orbitals

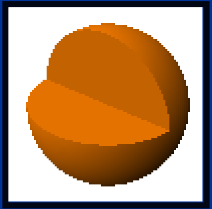
Orbitron

Mark Winter's animated plots of Ψ and Ψ^2 with 3D images of orbitals.

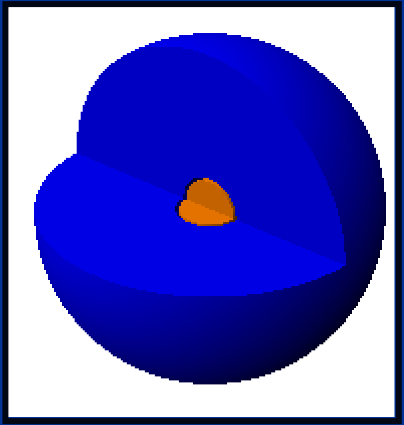
www.shef.ac.uk/chemistry/orbitron/

s Orbitals



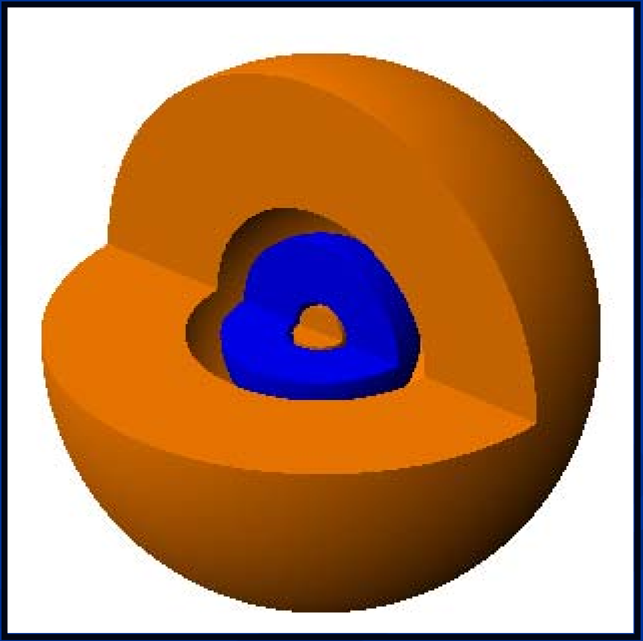


1*s*



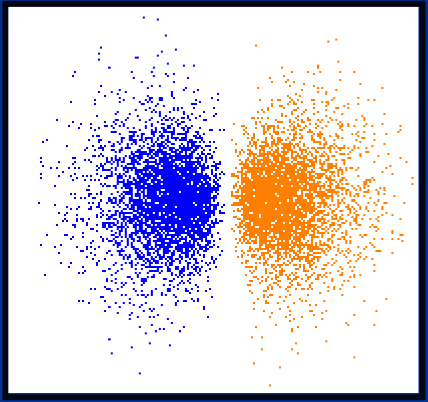
2*s*

Size and nodes increase with *n*.

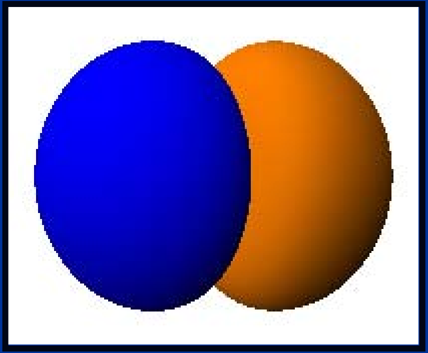


3*s*

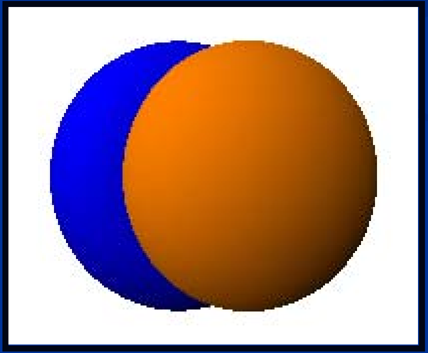
$2p$ Orbitals



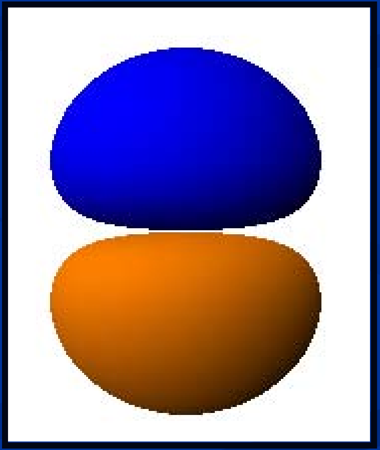
Three degenerate orbitals with lobes on *x*, *y*, and *z* axes. Nodal plane between lobes.



$2p_x$



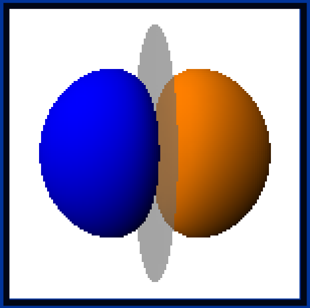
$2p_y$



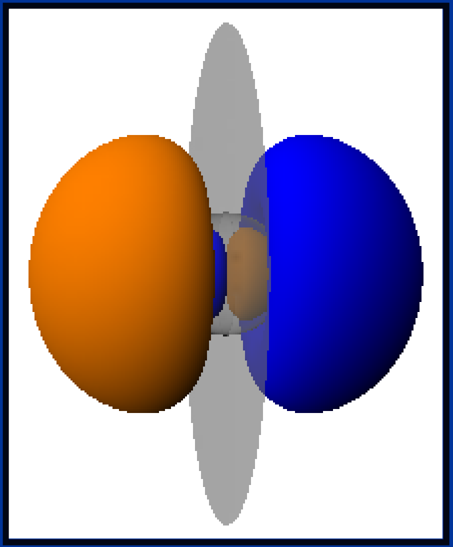
$2p_z$

np Orbitals

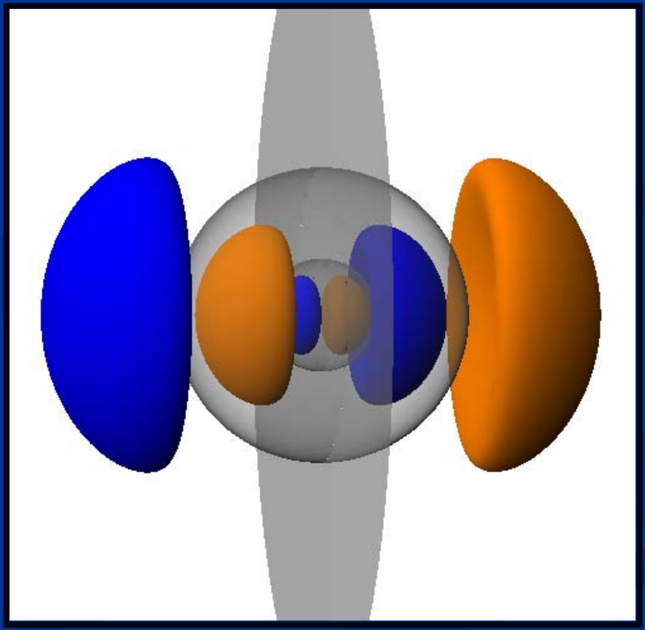
Size and nodes increase as *n* increases.



2*p*



3*p*



4*p*

All three *np* orbitals in a subshell are degenerate.

3*d* Orbitals

$3d_{xy}$, $3d_{xz}$, $3d_{yz}$, $3d_{x^2-y^2}$, $3d_{z^2}$

Cloverleaf shape, lobes between axes:

d_{xy}, d_{xz}, d_{yz}

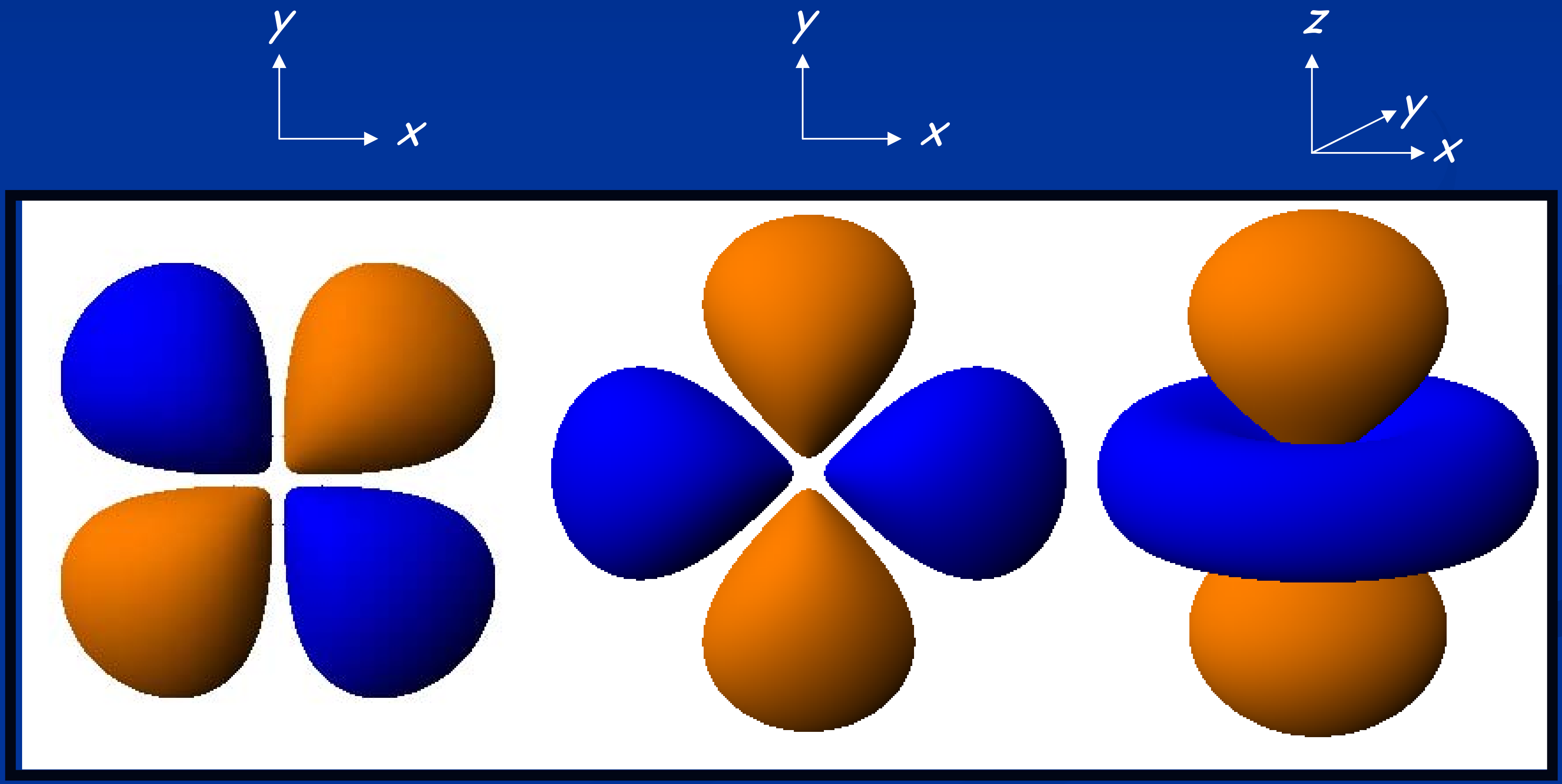
Cloverleaf shape, lobes on x and y axes:

$d_{x^2-y^2}$

Dumbbell and doughnut shape:

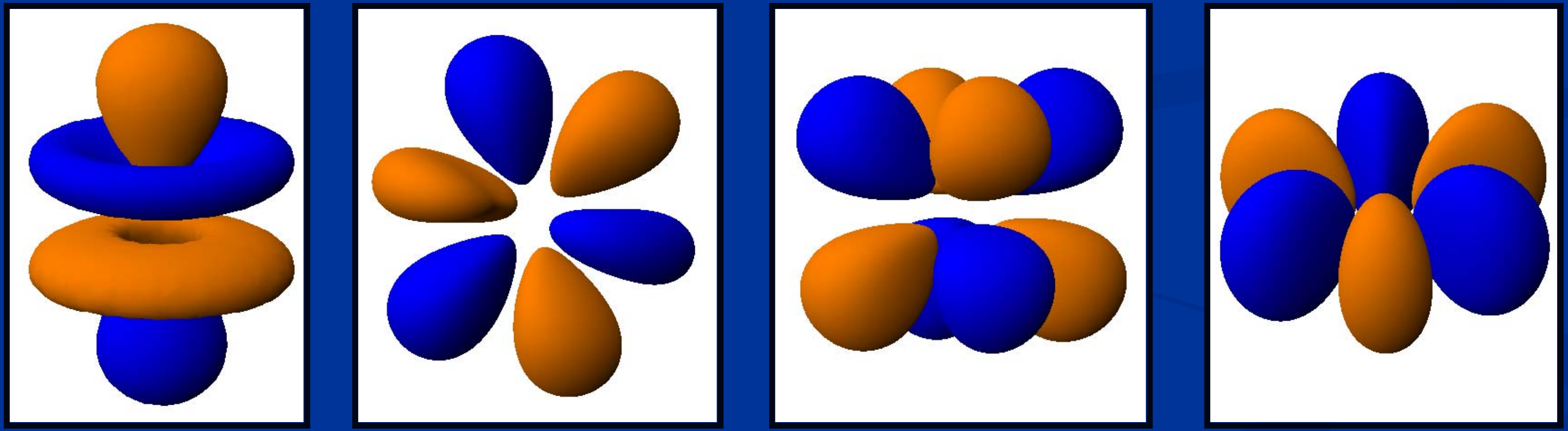
d_{z^2}

Shapes of $3d_{xy}$, $3d_{x^2-y^2}$, and $3d_{z^2}$ Orbitals



4*f* Orbitals

Seven degenerate orbitals with many lobes and nodes.



Individual *f* orbital names and shapes are not important for most chemistry.

Extending the Schroedinger Equation to Multielectron Atoms

In principle, we can write an equation of the form $H\Psi = E\Psi$ for any multielectron atom.

The equations are so complex that they cannot be solved exactly.

Empirical corrections are made to the hydrogen-like wave functions.

Electronic Configurations

Arrangement of electrons in certain orbitals

A specific configuration results in an overall energy for the atom.

The ground state configuration is the lowest energy configuration.

Any other configuration is an excited state.

Aufbau Approach

(German *aufbauen* – to build up)

The ground state configuration of an atom can be predicted by a "building up" process of adding electrons to available orbitals in order of increasing energy.

In multielectron atoms, subshell energies vary in a complicated way depending on n, l, and Z (nuclear charge).

Subshell Energies

Orbitals in the same subshell are still degenerate in multielectron atoms.

$$2p_x = 2p_y = 2p_z$$

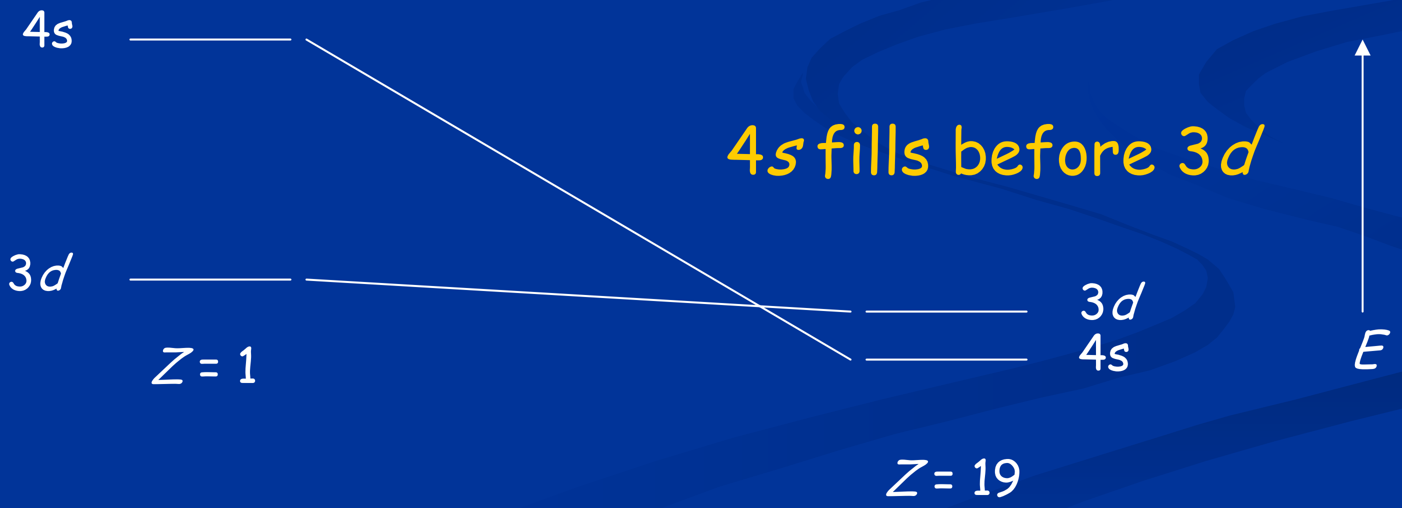
Subshells in the same shell rise in energy with l.

$$ns < np < nd < nf$$

Subshell energies go down (more favorable) as Z increases.

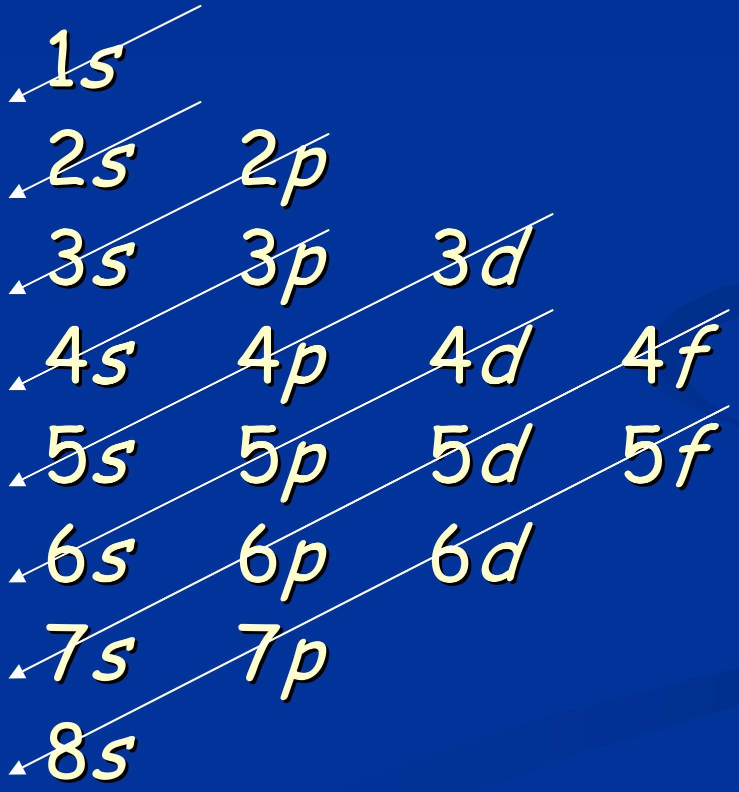
Subshell Energy Crossing

At $Z > 14$, some subshells from different shells cross energies.



4*s* fills before 3*d*

Aufbau Filling Order



1s
2s 2p
3s 3p 3d
4s 4p 4d 4f
5s 5p 5d 5f
6s 6p 6d
7s 7p
8s

Pauli Exclusion Principle

No two electrons in the same atom can have the same complete set of quantum numbers n, l, m_l, and m_s.

If two electrons occupy the same orbital, one has $m_s = +1/2$, and one has $m_s = -1/2$.

Two electrons in the same orbital are spin paired.

↑↓ not ↑↑

Pauli Exclusion Principle

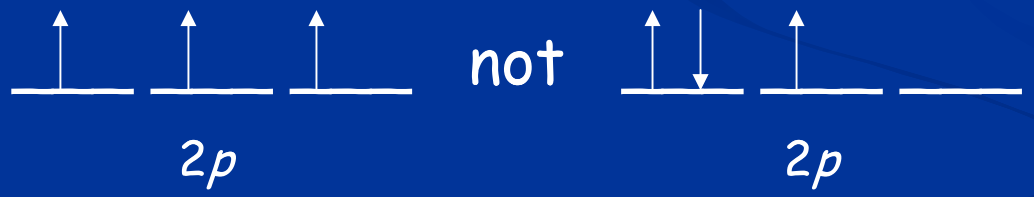
Subshell electron capacities are 2 x ($2l$ + 1)

Subshell	s	p	d	f
Capacity	2	6	10	14
Notation	s^2	p^6	d^{10}	f^{14}

Hund's Rule of Maximum Multiplicity

In the ground state, electrons in the same subshell will tend to distribute so that they are in different degenerate orbitals with their spins parallel (same m_s value), so long as the Pauli exclusion principle allows.

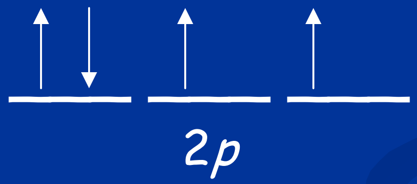
$2p^3$



Hund's Rule of Maximum Multiplicity

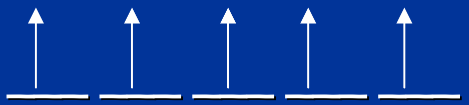
Electrons pair when a subshell is more than half filled.

$2p^4$

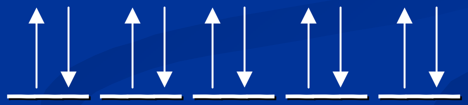


Exchange Energy

Half-filled and fully-filled subshells have extra stability (exchange energy).



half-filled *d* subshell

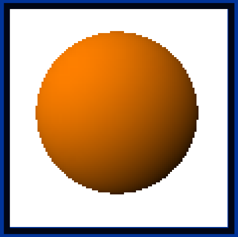


fully-filled *d* subshell

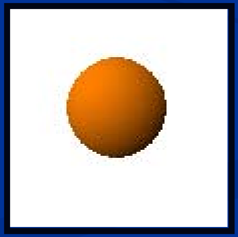
The exchange energy bonus sometimes favors configurations that differ from the usual Aufbau predictions.

Electronic Configurations of H and He

Element	**$1s$**	**Spectroscopic Notation**
H	↑	$1s^1$
He	↑ ↓	$1s^2$ (closed shell config.)



H (Z = 1) $1s^1$



He (Z = 2) $1s^2$

Valence Configuration

The valence configuration is the configuration of outermost electrons (highest energy occupied subshells), which are lost in cation formation, shared in covalent bond formation, and into whose subshells additional electrons are added in anion formation.

$_{3}\mathrm{Li}$ $1s^2\,2s^1$

[He] core

valence electron

Electronic Configurations in Period 2

Element	1*s*	2*s*	2*p*			Spectroscopic Notation
$_3$Li	↑ ↓	↑				$1s^2\,2s^1$
$_4$Be	↑ ↓	↑ ↓				$1s^2\,2s^2$
$_5$B	↑ ↓	↑ ↓	↑			$1s^2\,2s^2\,2p^1$
$_6$C	↑ ↓	↑ ↓	↑	↑		$1s^2\,2s^2\,2p^2$
$_7$N	↑ ↓	↑ ↓	↑	↑	↑	$1s^2\,2s^2\,2p^3$
$_8$O	↑ ↓	↑ ↓	↑ ↓	↑	↑	$1s^2\,2s^2\,2p^4$
$_9$F	↑ ↓	↑ ↓	↑ ↓	↑ ↓	↑	$1s^2\,2s^2\,2p^5$
$_{10}$Ne	↑ ↓	↑ ↓	↑ ↓	↑ ↓	↑ ↓	$1s^2\,2s^2\,2p^6$

Electronic Configurations for Z = 11 - 20

[Ne] = $1s^2\,2s^2\,2p^6$ [Ar] = $1s^2\,2s^2\,2p^6\,3s^2\,3p^6$

Element	Configuration	Element	Configuration
$_{11}\text{Na}$	[Ne] $3s^1$	$_{16}\text{S}$	[Ne] $3s^2\,3p^4$
$_{12}\text{Mg}$	[Ne] $3s^2$	$_{17}\text{Cl}$	[Ne] $3s^2\,3p^5$
$_{13}\text{Al}$	[Ne] $3s^2\,3p^1$	$_{18}\text{Ar}$	[Ne] $3s^2\,3p^6$
$_{14}\text{Si}$	[Ne] $3s^2\,3p^2$	$_{19}\text{K}$	[Ar] $4s^1$
$_{15}\text{P}$	[Ne] $3s^2\,3p^3$	$_{20}\text{Ca}$	[Ar] $4s^2$

Electronic Configurations of the First Transition Series

Element	Configuration	Element	Configuration
$_{21}\mathrm{Sc}$	$[\mathrm{Ar}]\ 3d^{1}\ 4s^{2}$	$_{26}\mathrm{Fe}$	$[\mathrm{Ar}]\ 3d^{6}\ 4s^{2}$
$_{22}\mathrm{Ti}$	$[\mathrm{Ar}]\ 3d^{2}\ 4s^{2}$	$_{27}\mathrm{Co}$	$[\mathrm{Ar}]\ 3d^{7}\ 4s^{2}$
$_{23}\mathrm{V}$	$[\mathrm{Ar}]\ 3d^{3}\ 4s^{2}$	$_{28}\mathrm{Ni}$	$[\mathrm{Ar}]\ 3d^{8}\ 4s^{2}$
$_{24}\mathrm{Cr}$	$[\mathrm{Ar}]\ 3d^{5}\ 4s^{1}$	$_{29}\mathrm{Cu}$	$[\mathrm{Ar}]\ 3d^{10}\ 4s^{1}$
$_{25}\mathrm{Mn}$	$[\mathrm{Ar}]\ 3d^{5}\ 4s^{2}$	$_{30}\mathrm{Zn}$	$[\mathrm{Ar}]\ 3d^{10}\ 4s^{2}$

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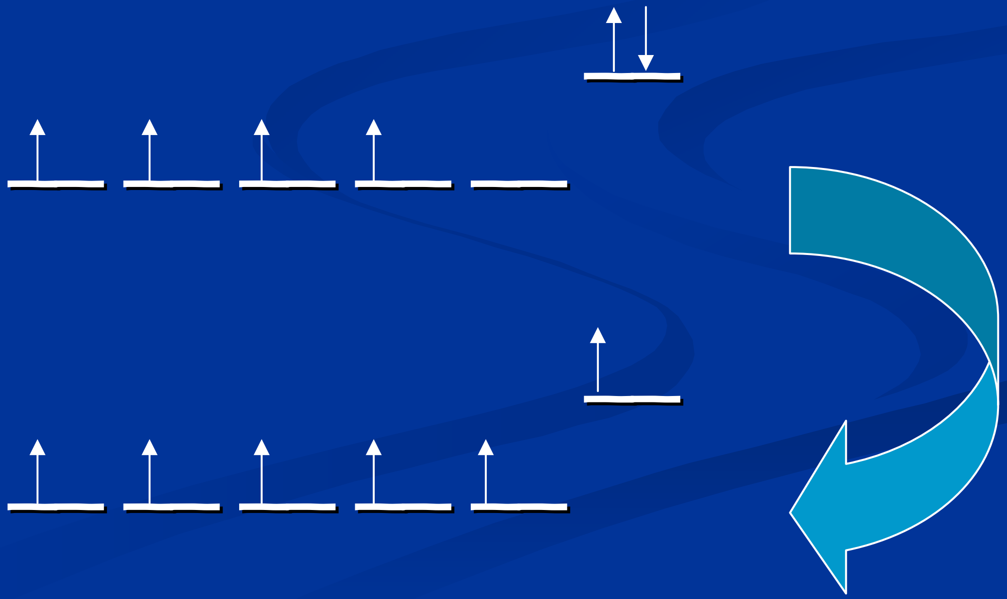
Cr $3d^5\,4s^1$ and Cu $3d^{10}\,4s^1$

The exchange energy bonus of a half- or fully-filled *d* subshell favors these configurations.

🚫 $3d^4\,4s^2$

🙂 Cr $3d^5\,4s^1$



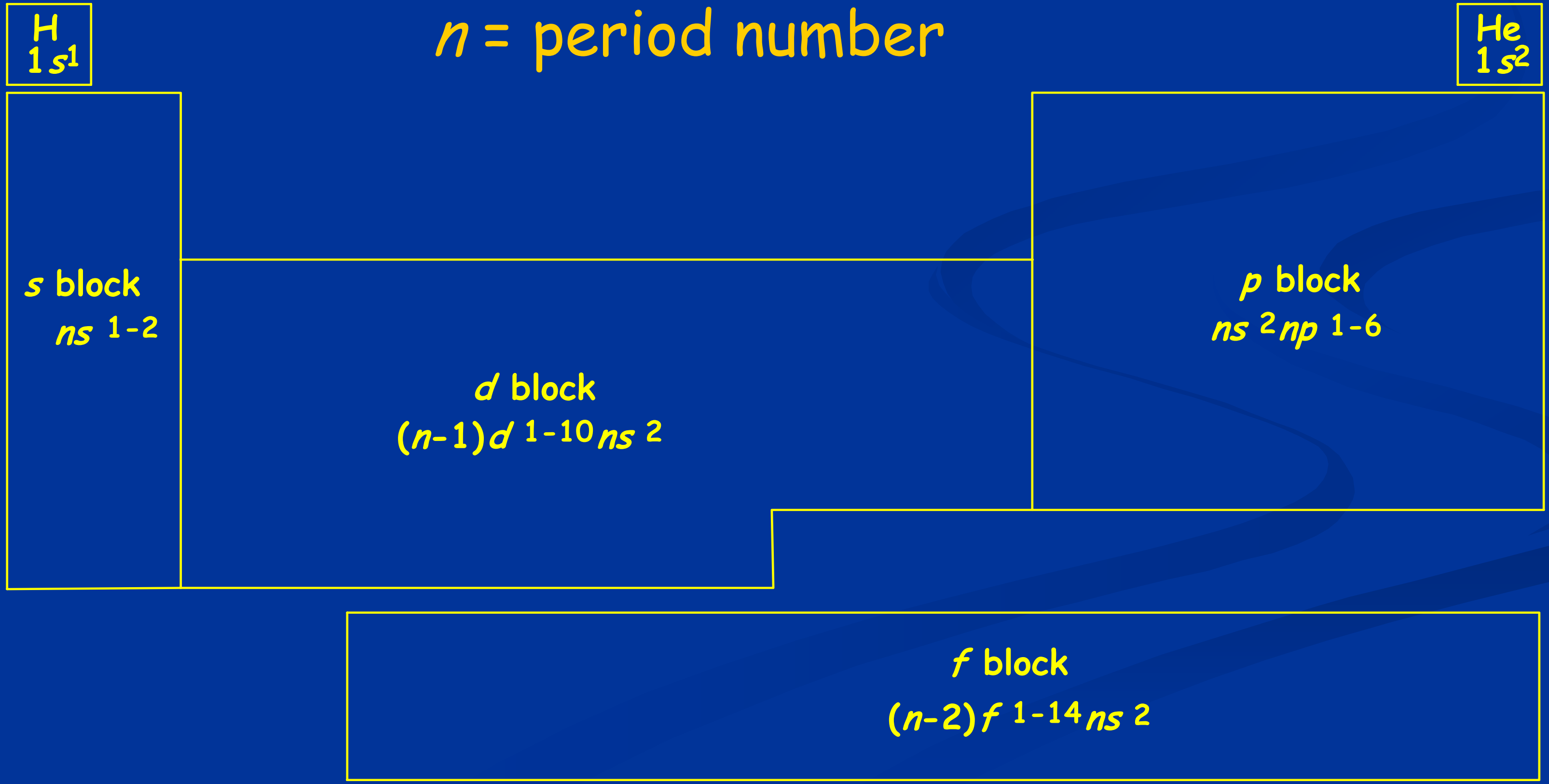
Strengths and Weaknesses of the Aufbau Predictions

Predictions for main group elements (groups 1, 2, 13-18) are always correct.

Predictions for transition elements are sometimes irregular, particularly in the 2nd and 3rd transition series.

Lanthanides and actinides are often irregular.

Valence Configurations (Aufbau Predictions) from Position in the Periodic Table



n = period number

H
$1s^1$

He
$1s^2$

s block
ns^{1-2}

d block
$(n-1)d^{1-10}ns^2$

p block
ns^2np^{1-6}

f block
$(n-2)f^{1-14}ns^2$

Configurations of Anions

$$A + ne^{-} \longrightarrow A^{n-}$$

Electrons are added to available orbitals within the lowest-energy valence subshell.

F	$2s^2\,2p^5$	F^-	$2s^2\,2p^6$ = [Ne]
S	$3s^2\,3p^4$	S^{2-}	$3s^2\,3p^6$ = [Ar]

Configurations of Non-Transition Metal Cations

$$\mathrm{M} \longrightarrow \mathrm{M}^{n+} + ne^{-}$$

Electrons are removed from the highest occupied subshell.

Mg $3s^2$ Mg^{2+} $3s^0 = [\mathrm{Ne}]$

Al $3s^2 3p^1$ Al^{3+} $3s^0 3p^0 = [\mathrm{Ne}]$

Configurations of Transition Metal Cations

$$\mathrm{M} \longrightarrow \mathrm{M}^{n+} + ne^{-}$$

The *ns* electrons are *always* removed first, before any (*n*-1)*d* electrons.

Fe $3d^6\,4s^2$

Fe^{2+} $3d^6\,(4s^0)$

Fe^{3+} $3d^5$

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Bohr is no more!