



CH-110 Advanced General Chemistry I

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Student questions

In this equation:

$$E_k = \frac{1}{2} m v^2 = \frac{(m v)^2}{2m} = \frac{(p)^2}{2m} = \frac{\left(\frac{h}{\lambda}\right)^2}{2m} = \frac{h^2}{2m \lambda^2}$$

Student question: Why is this condition valid « $\lambda = \frac{2L}{n}$, with $n = 1, 2, \dots$ »? And not: « $\lambda = \frac{nL}{2}$ »?

Because for $n=1$, half a wavelength fits into the box (see graph): $\lambda = \frac{1L}{2} = \frac{1}{2} L$

For $n=2$: $\lambda = \frac{2L}{2} = L$, for $n=3$: $\lambda = \frac{3L}{2}$ etc.

Answer: λ is not the number of wavelengths that fit into the box, but the length in box L units that corresponds to one wavelength (peak to peak). So for $n=1$, one wavelength corresponds to $2L$ ($\lambda = \frac{2L}{1}$) because half a wavelength fits into $\frac{1}{2} L$. For $n=2$, one wavelength corresponds to $1L$ ($\lambda = \frac{2L}{2}$), For $n=3$, one wavelength corresponds to $2/3$ of the box length ($\lambda = \frac{2L}{3}$).

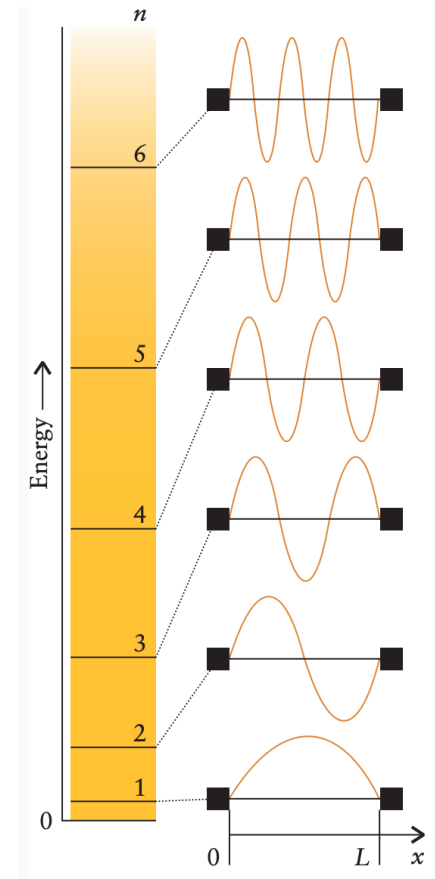


Figure 1C.3

The Hydrogen Atom

Topic 1D

Last week (Tue): Topic 1D.1 Energy levels

Last week (Tue): Topic 1D.2 Atomic orbitals

Last week (Fri): Topic 1D.3 Quantum numbers, shells, and subshells

Last week (Fri): Topic 1D.4 The shapes of orbitals

Topic 1D.5 Electron spin

Topic 1D.6 The electronic structure of hydrogen: a summary

WHY DO YOU NEED TO KNOW THIS MATERIAL?

- The hydrogen atom is the **simplest atom of all** and is used to discuss the **structures of all atoms**.
- It is therefore **central** to many explanations in chemistry.

WHAT DO YOU NEED TO KNOW ALREADY?

- Features of spectrum of atomic hydrogen (Topic 1A)
- Concepts of wavefunction and energy level in quantum mechanics (Topic 1C)

The Shapes of Orbitals

Topic 1D.4

Recap of last time:

Transition from particle in a box to atomic orbitals

Recap of Particle in a Box:

Particle in a box model: solution of the Schrödinger equation in 1D, derive wavefunctions and energy levels for confined particle, wavefunctions with specific standing wave patterns that describe the probability distribution of finding the particle within the box.

Extension to Three Dimensions:

Solve **3D Schrödinger equation**: closer to actual behavior of electrons in atoms, solutions to this equation yields wave functions that represent the electron's behavior in 3D space

Atomic Orbitals:

Wavefunctions for the hydrogen atom correspond to **atomic orbitals**. Orbitals describe regions in space where there is a high probability of finding the electron. Shape of atomic orbitals determined by the angular momentum of the electron.

Recap of last time:

Transition from particle in a box to atomic orbitals

Significance of Quantum Numbers:

Each wavefunction (= atomic orbital) is characterized by a set of **quantum numbers** that arise from the solution of the Schrödinger equation:

1. **Principal Quantum Number (n)**: energy level and size. Higher n values mean the electron is further from the nucleus.
2. **Orbital Angular Momentum Quantum Number (l)**: shape (s, p, d, f) and can take on integer values from 0 to $n-1$.
3. **Magnetic Quantum Number (m_l)**: Describes the orientation of the orbital in space and can take values from $-l$ to $+l$.
4. **Spin Quantum Number (m_s)**: Accounts for the intrinsic spin of the electron, which can be either $+1/2$ or $-1/2$.

Connecting Concepts:

Wavefunction in the particle in a box model described **specific standing wave patterns**

Wavefunction for atomic orbitals describe the **spatial distributions of electrons around the nucleus**.

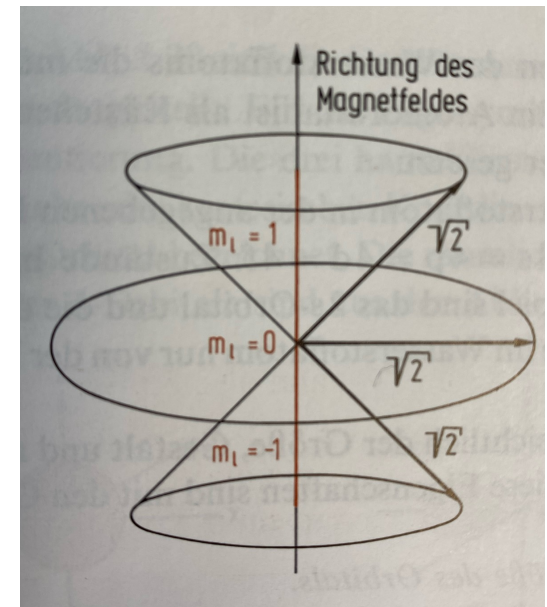
The quantum numbers serve as essential descriptors of these states, much like the integer n indicated the allowed energy levels in the particle in a box.

Recap of last time:

Orbital angular momentum quantum number vs. magnetic quantum number (m_l)

To remember:

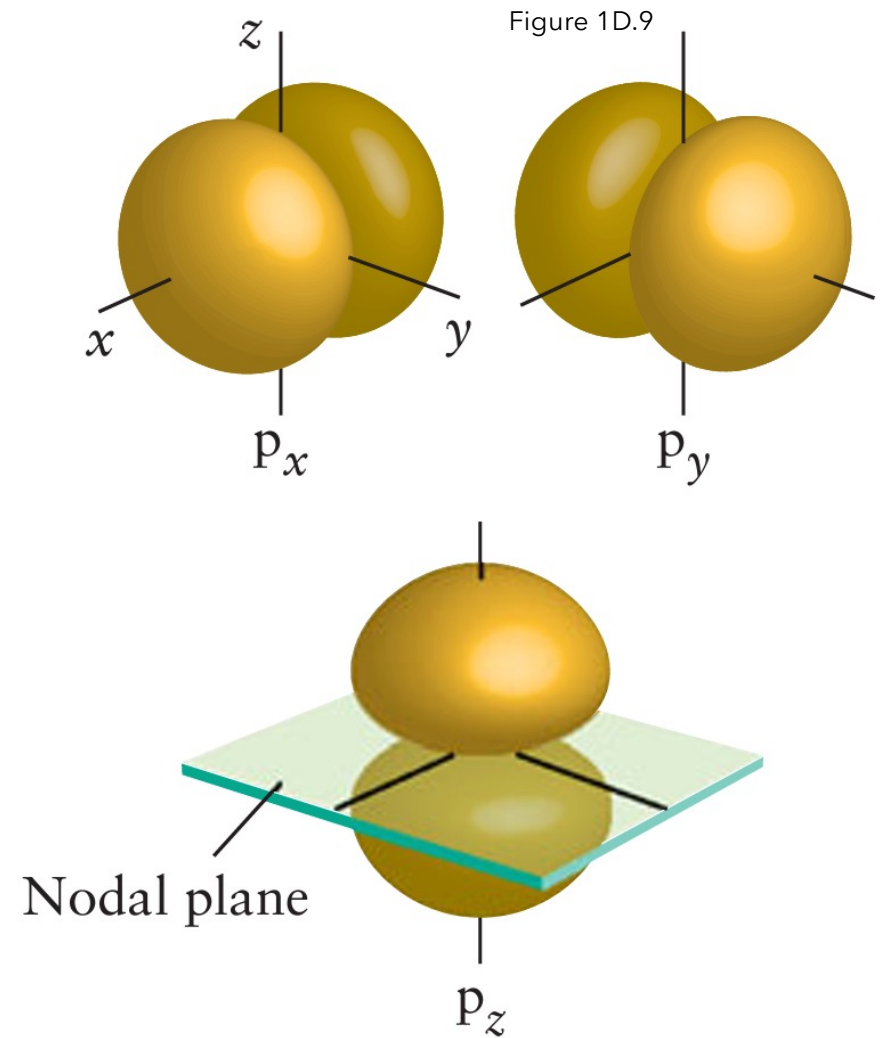
1. *Orbital angular momentum* = $\sqrt{l(l+1)}\hbar$. Think of an electron moving around the nucleus of an atom like a planet orbiting the sun. This movement gives the electron something called "orbital angular momentum," which is a measure of how much motion it has while orbiting.
2. The orbital angular momentum determines the **shape** of the orbital (quantum number l).
3. The projection of the orbital angular momentum along a specific axis (often the z-axis) is given by the magnetic quantum number m_l multiplied by $\hbar$. In other words: **The value of m_l tells us how the electron's motion is oriented in space.** m_l can take values from $-l$ to $+l$, determining the orientation of the orbital in space.



1D.4 The shapes of orbitals

p-orbitals

- Three p-orbitals in each subshell of an atom
- Quantum numbers $m_l = +1, 0, -1$
- Chemists refer to them according to the axes along which the lobes lie: p_x -, p_y -, p_z -orbitals
- p_z -orbital has $m_l = 0$
- p_x -, p_y -orbitals have $m_l = \pm 1$



1D.4 The shapes of orbitals

d-orbitals

- Subshell $l = 2$ consists of **five d-orbitals**
- Each d-orbital has four lobes, except d_{z^2}

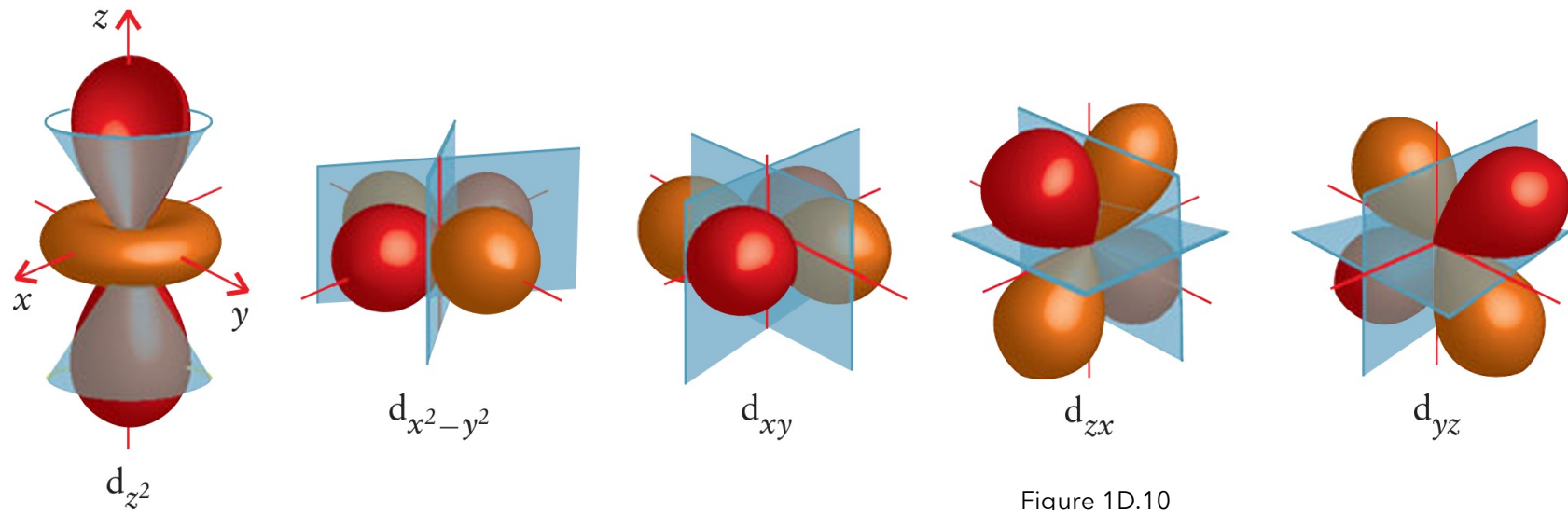


Figure 1D.10

1D.4 The shapes of orbitals

Summary

The shape of an atomic orbital depends on its quantum numbers and can be depicted by a boundary surface. The radial distribution function expresses the probability of finding an electron at a given radius regardless of its angular momentum.

Electron Spin

Topic 1D.5

1D.5 Electron spin

A spinning sphere

Tiny discrepancies were observed in the atomic spectrum of hydrogen.

Goudsmit and Uhlenbeck proposed these differences are due to the fact that an electron behaves like a spinning sphere (like a planet rotating around its axis).

This property is called spin.

Schrödinger's theory did not account for spin, and it emerged naturally when the British physicist Paul Dirac found a way (in 1928) to combine Einstein's theory of relativity with Schrödinger's approach.

According to quantum mechanics, an electron has two spin states represented by the **arrows** $\uparrow$ **and** $\downarrow$ or the Greek letters α and β .

1D.5 Electron spin

Spin $\uparrow$ and $\downarrow$

Think of an electron as being able to spin counterclockwise (the $\uparrow$ state) and clockwise (the $\downarrow$ state) at exactly the same rate.

These two spins are distinguished by a **fourth quantum number**, the spin magnetic quantum number, m_s .

This quantum number can have only one of two values: $+\frac{1}{2}$ ($\uparrow$) and $-\frac{1}{2}$ ($\downarrow$).

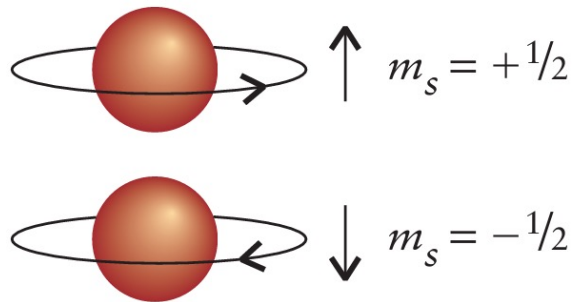


Figure 1D.12

1D.5 Electron spin

Summary

An electron has the property of spin;

the spin is described by the quantum number $m_s = \pm\frac{1}{2}$.

The Electronic Structure of Hydrogen: A Summary

Topic 1D.6

1D.6 The electronic structure of hydrogen: a summary

1) In the **ground state of hydrogen**:

$$n = 1, l = 0, m_l = 0, m_s = \pm \frac{1}{2}$$

Both values of m_s are possible, spin orientation does not affect energy.

This is an s-electron with specified spin.

2) When an atom **acquires enough energy** (by absorbing a photon) for its electron to reach $n=2$:

It can occupy any of the four orbitals in that shell: one 2s and three 2p orbitals (in hydrogen, they all have the same energy): 2s- or 2p-electron

Average distance of electron from nucleus increases with increasing n : atom is «swelling up» as it is excited energetically.

1D.6 The electronic structure of hydrogen: a summary

3) Atom acquires **even more energy**:

Electron can move to $n = 3$ shell

Atom is now even larger

Nine orbitals available (3s, 3p, 3d)

4) More energy still:

Electron can move to $n = 4$ shell with 16 available orbitals

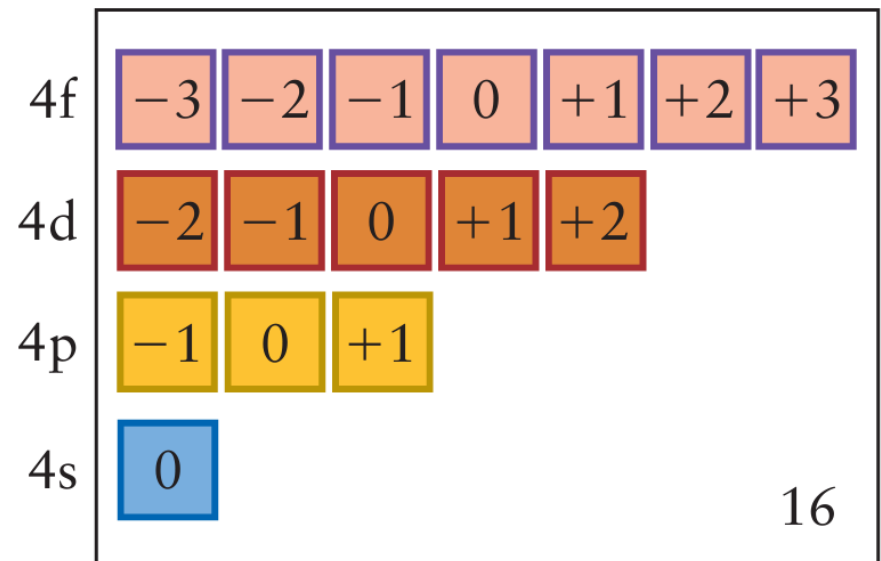


Figure 1D.13

1D.6 The electronic structure of hydrogen: a summary

TABLE 1.3 Quantum Numbers for Electrons in Atoms

Name	Symbol	Values	Specifies	Indicates
principal	n	$1, 2, \dots$	shell	size
orbital angular momentum*	l	$0, 1, \dots, n - 1$	subshell: $l = 0, 1, 2, 3, 4, \dots$ s, p, d, f, g, ...	shape
magnetic	m_l	$l, l - 1, \dots, -l$	orbitals of subshell	orientation
spin magnetic	m_s	$+\frac{1}{2}, -\frac{1}{2}$	spin state	spin direction

*Also called the azimuthal quantum number.

1D.6 The electronic structure of hydrogen: a summary

Summary

The state of an electron in a hydrogen atom is defined by the four quantum numbers n , l , m_l and m_s ; as the value of n increases, the size of the atom increases.

The skills you have mastered are the ability to

- ☐ Assess the relative probability of finding an electron at a given distance from the nucleus of an atom.
- ☐ Name and explain the relation of each of the four quantum numbers to the properties and relative energies of atomic orbitals.
- ☐ Describe the properties of electron spin.
- ☐ Describe the state of a hydrogen atom in its ground and excited states.

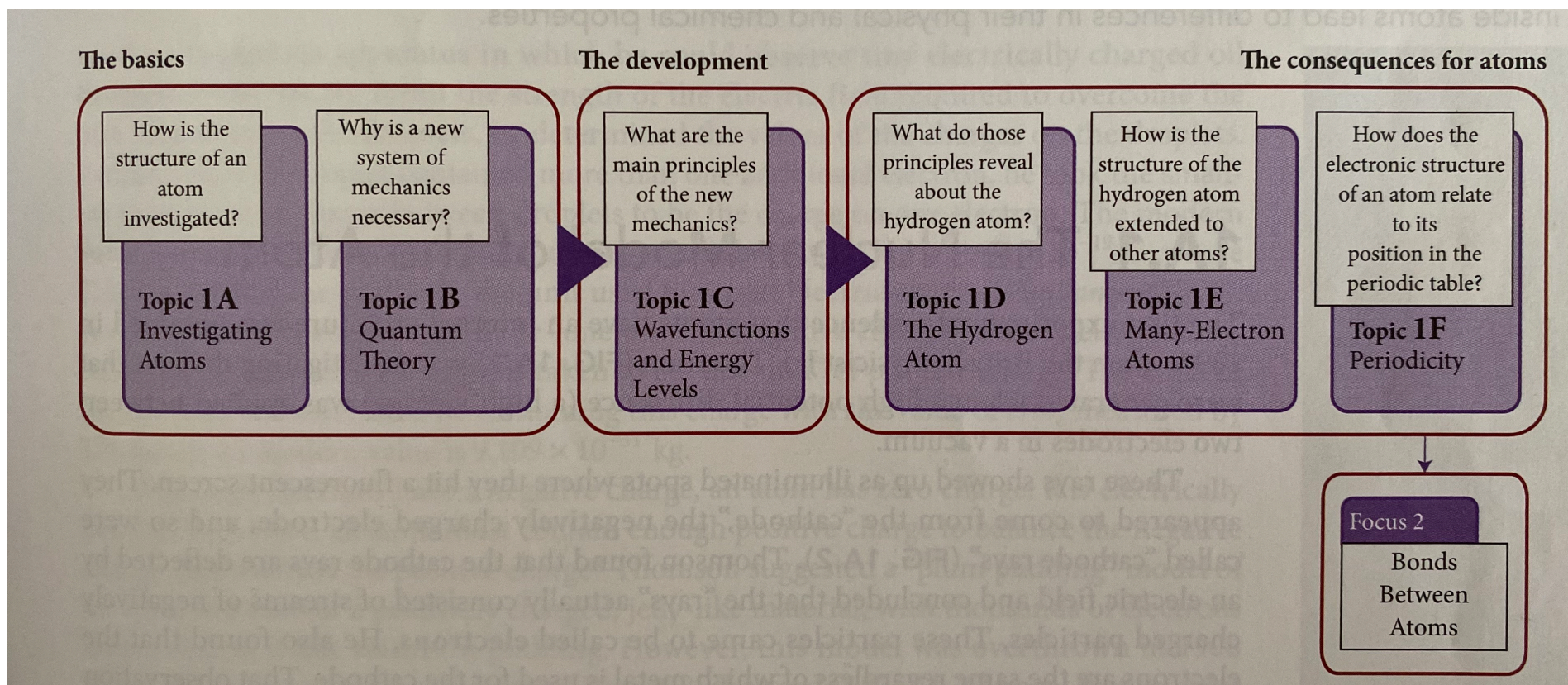
Summary: You have learned that an electron in a hydrogen atom is described by wavefunctions called atomic orbitals and that each orbital is specified by three quantum numbers: n , l , and m_l . You now know that the shape and energy of a given orbital is found by solving the Schrödinger equation for an electron attracted to a nucleus. You also now know that transitions between the allowed energy levels account for the observed patterns of spectroscopic lines. You have also encountered the property of “electron spin” and know that electron spin may have either of two orientations.

	Particle in a box	Hydrogen atom
Dimension of space	1D	3D
Walls	Physical walls	No physical walls, and electrons are confined by pull of the nucleus
Quantization	Energy quantized	
Potential energy	Potential energy inside the box is zero	Potential energy governed by Coulomb potential
Wave function shape	Sinusoidal functions (sine or cosine)	Wave functions (called orbitals) are more complex, often spherical or lobed in shape (spherical harmonics), with both radial and angular components.
Quantum numbers	One quantum number, n , which represents the energy level and is related to the number of nodes in the wave function.	Three quantum numbers: n : principal quantum number (energy level), l : angular momentum quantum number (shape of the orbital), m_l : magnetic quantum number (orientation of the orbital).
Degeneracy	No degeneracy: each energy level corresponds to one unique state.	Degeneracy in energy levels: for a given principal quantum number n , multiple different orbitals (characterized by l and m_l) have the same energy.
Boundary conditions	The wave function must go to zero at the walls of the box.	The wave function must go to zero at infinity, far from the nucleus.
Physical interpretation	The particle is free inside the box but cannot escape due to infinite potential at the walls.	The electron is bound to the nucleus due to the attractive Coulomb force, which confines the electron.

Many-Electron Atoms

Topic 1E

Overview Chapter 1 (Focus 1: Atoms)



Topic 1E.1 Orbital Energies

Topic 1E.2 The Building-Up Principle

WHY DO YOU NEED TO KNOW THIS MATERIAL?

- The electronic structures of many-electron atoms account for the **form** of chemistry's all-important **periodic table**.

WHAT DO YOU NEED TO KNOW ALREADY?

- Description of atomic orbitals of hydrogen (**Topic 1D**), especially their radial dependence and their angular shapes.
- Electron has a property called spin.
- General structure of the periodic table (**Fundamentals B**)

Orbital energies

Topic 1E.1

1E.1 Orbital energies

Most atoms have more than one electron

- A neutral atom other than hydrogen has more than one electron and is known as a many-electron atom (or polyelectron atom).
- In this topic 1E, we will learn how the presence of more than one electron affects the energies of atomic orbitals and how they are occupied.

1E.1 Orbital energies

Most atoms have more than one electron

- As with hydrogen, electrons in many-electron atoms **occupy orbitals**. Two main differences:
 1. Nucleus is more highly charged → attracts electrons more strongly → lowers energy
 2. Electrons repel one another → repulsion opposes nuclear attraction → raises energy

1E.1 Orbital energies

Energy for helium atom

For Helium, with two electrons, the charge of the nucleus is $+2e$, the total potential energy is given by three terms:

$$V \propto \underbrace{-\frac{2e^2}{r_1}}_{\text{Attraction of electron 1 to the nucleus}} - \underbrace{\frac{2e^2}{r_2}}_{\text{Attraction of electron 2 to the nucleus}} + \underbrace{\frac{e^2}{r_{12}}}_{\text{Repulsion between the two electron}}$$

With r_1 : the distance of electron 1 from nucleus, r_2 is the distance of electron 2 from nucleus, and r_{12} is the distance between the two electrons.

1E.1 Orbital energies

Solving the Schrödinger equation for the helium atom

- The Schrödinger equation based on the potential in the previous slide is impossibly **difficult to solve exactly**.
- Highly accurate **numerical solutions** can be obtained by using computers
- Today, chemists are among the **heavy users of computers**, utilizing them to calculate detailed electronic structures of atoms and molecules. (Alongside code breakers, weather forecasters, and molecular biologists, fields such as data science, machine learning, finance, and engineering have also become significant users of computational resources, driving the demand for sophisticated computational techniques to solve complex problems across diverse disciplines.)

1E.1 Orbital energies

Energy level differences in orbitals of the same shell

Hydrogen atom:

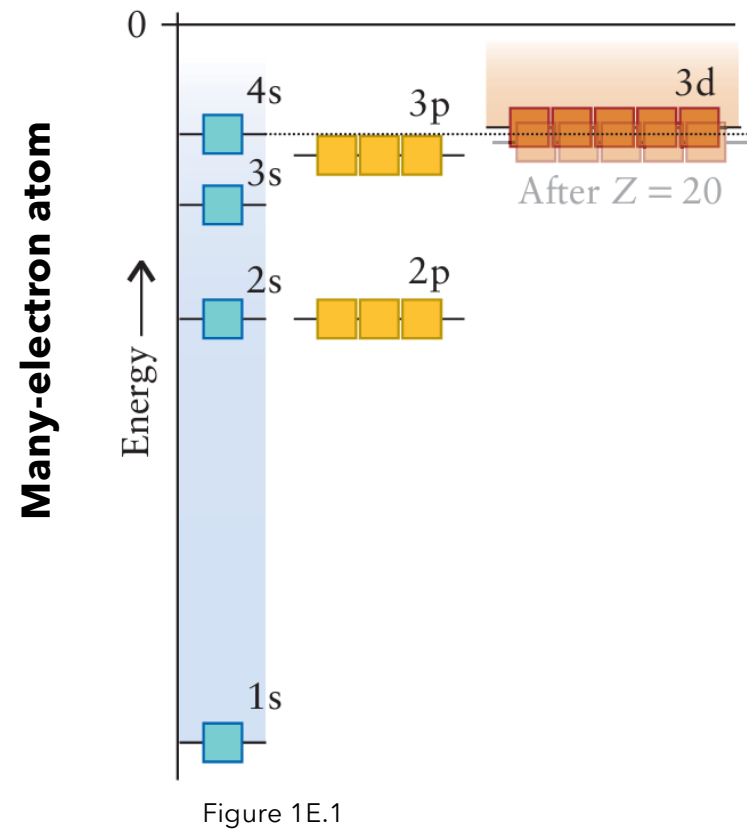
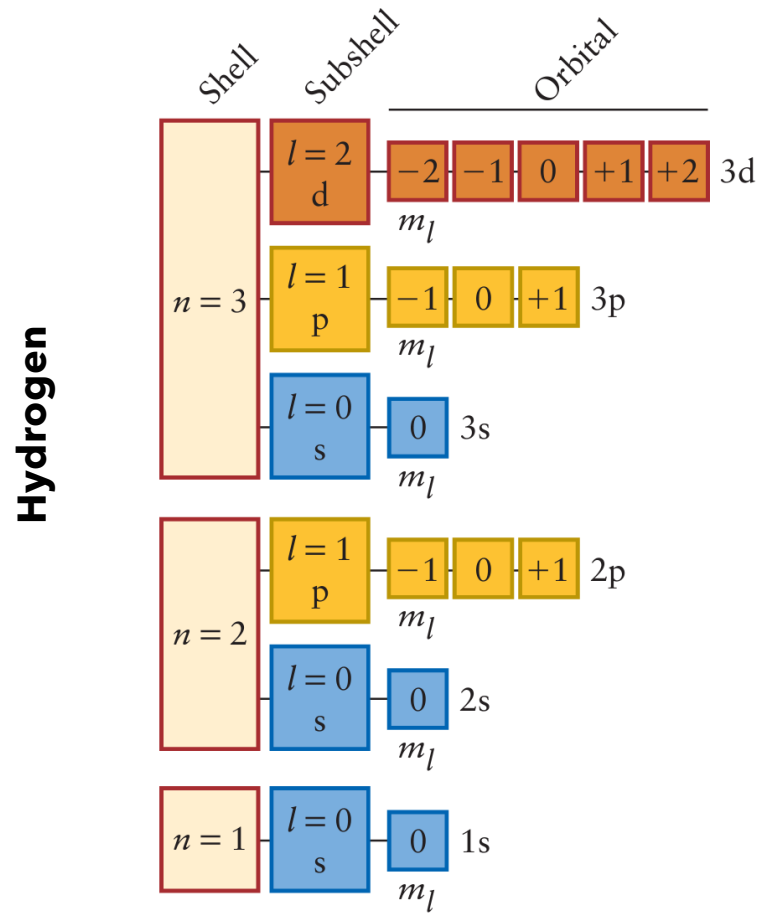
- One electron and **no electron-electron repulsions**
- All orbitals of a given shell are **degenerate** (have the same energy): 2s and all three 2p-orbitals have the same energy

Many-electron atoms:

- **Electron-electron repulsions** cause the energy of 2p-orbitals to be higher than that of the 2s-orbital.
- Same for $n=3$: 3d-orbitals higher than 3p, and 3p higher than 3s:

1E.1 Orbital energies

Energy level differences in orbitals of the same shell



1E.1 Orbital energies

Shielding

- Each electron is attracted by the nucleus and **repelled by the other electrons**.
- Electron is less tightly bound to the nucleus than it would be if those other electrons were absent: **electron is shielded from the full attraction of the nucleus** by the other electrons in the atom.
- Shield effect reduces pull of the nucleus on an electron.
- The effective nuclear charge, $Z_{eff}e$, experienced by the electron is always less than the actual nuclear charge, Ze . Electron-electron repulsions work against the pull of nucleus.
- Approximate form of the energy of an electron in a many-electron atom is a version of an equation given in topic 1D ($E_n = -Z^2hR/n^2$)

$$E_n = -\frac{Z_{eff}^2 hR}{n^2}$$

1E.1 Orbital energies

Shielding in different orbitals

- Extent of shielding depends on where electron is likely to be found → shape of the orbital
- A s-electron of any shell can be found very close to the nucleus: said to penetrate through the inner shells.
- A p-electron penetrates much less because its orbital angular momentum prevents it from approaching close to the nucleus.
- A p-electron has zero probability density at the nucleus.
- Because it penetrates less than an s-electron through the inner shells of the atom, it is more effectively shielded from the nucleus → **experiences a smaller effective nuclear charge than an s-electron**
- An s-electron is bound more tightly than a p-electron and has a slightly lower (more negative) energy.
- A d-electron is bound less tightly than a p-electron, has higher angular momentum

1E.1 Orbital energies

Radial distribution functions for s-, p-, and d-orbitals

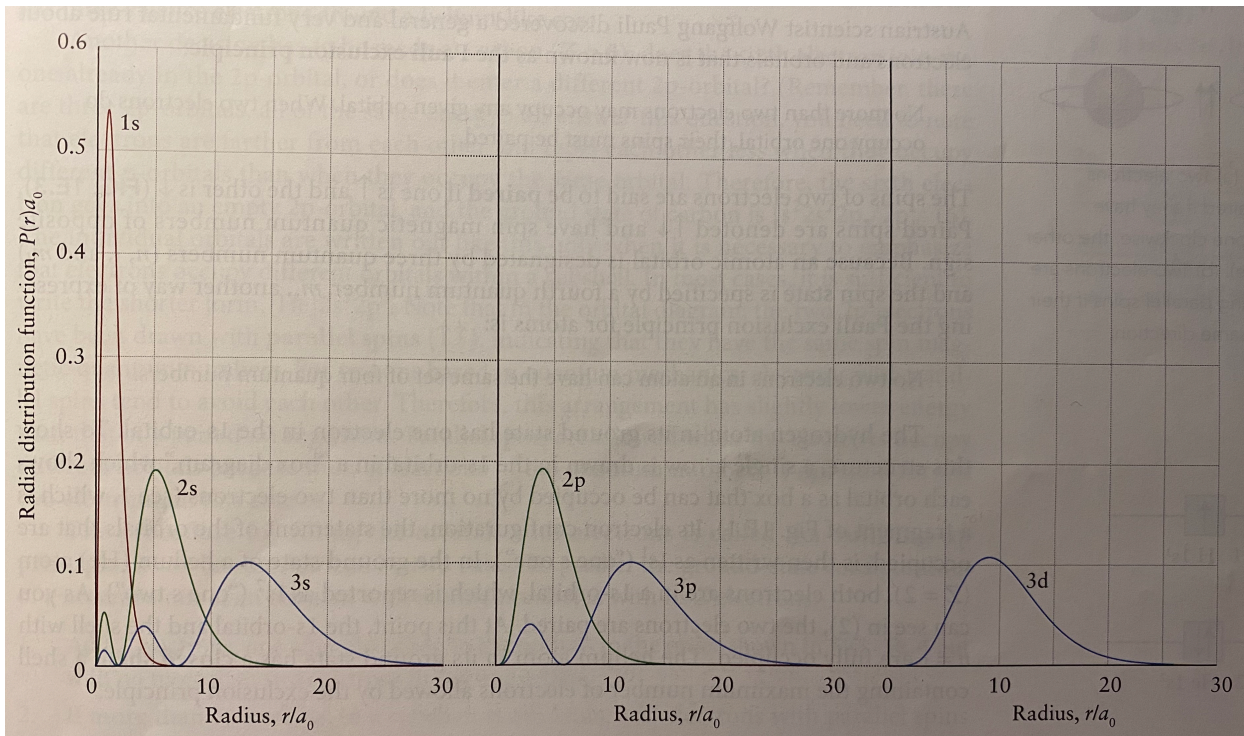


Figure 1E.2

- First three shells of hydrogen atom.
- Probability maxima for orbitals of the same shell are close to each other
- An electron in an ns -orbital has a higher probability of being found close to the nucleus than does an electron in an np - or an nd -orbital

1E.1 Orbital energies

Effects of shielding can be large

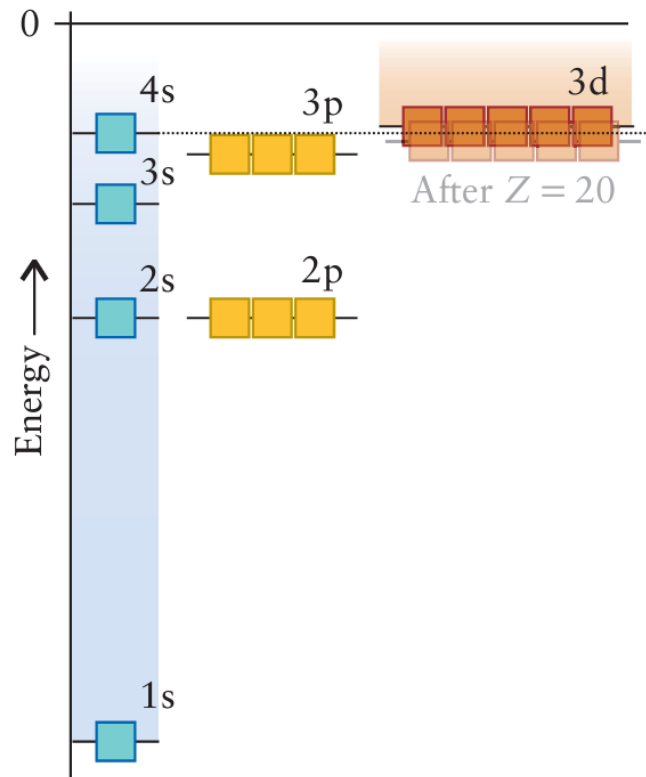


Figure 1E.1

- A 4s-electron has a much lower energy than a 3d-electron of the same atom.
- The precise ordering of the orbitals depends on the number of electrons in the atom as well as the effective nuclear charge experienced by the electrons
- See next section.

1E.1 Orbital energies

Summary

In a many-electron atom, because of the effects of penetration and shielding, the order of orbital energies in a given shell is $s < p < d < f$.

The Building-Up Principle

Topic 1E.2

1E.2 The building-up principle

Electronic structure of many-electron atoms

- Electronic structure of an atom determines chemical properties.
- **Electron configuration**: a list of all its occupied orbitals with the numbers of electrons that occupy each one.
- **Ground state** of a many-electron atom: electrons occupy atomic orbitals in such a way that the total energy of the atom is a minimum
- **Total energy of atom**: the sum of the kinetic energy of each electron, the attraction of each electron to the nucleus, repulsions between all the electrons
- First glance: lowest energy if all electrons are in lowest-energy orbital (1s)
- However: except for the hydrogen or helium atom (only up to two electrons), that can never happen.

1E.2 The building-up principle

The Pauli exclusion principle

- In 1925, Austrian scientist Wolfgang Pauli discovered a general and fundamental rule about electrons and orbitals:

No more than two electrons may occupy any given orbital. When two electrons do occupy one orbital, their spins must be paired.

- The two spins of electrons are paired if one is $\uparrow$ and $\downarrow$.
- Paired spins are denoted $\uparrow\downarrow$ and have spin magnetic quantum numbers of opposite signs.
- Another way to phrase the Pauli exclusion principle:

No two electrons in an atom can have the same set of four quantum numbers.

1E.2 The building-up principle

The Pauli exclusion principle

- (a) The two spins of electrons are paired if one is $\uparrow$ and $\downarrow$. They have opposite signs (one clockwise, the other counterclockwise).
- (b) Two electrons are classified as having parallel spins if their spins are in the same direction.

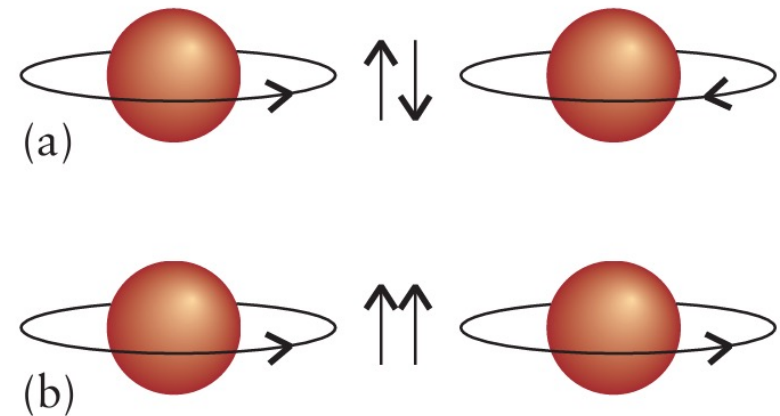
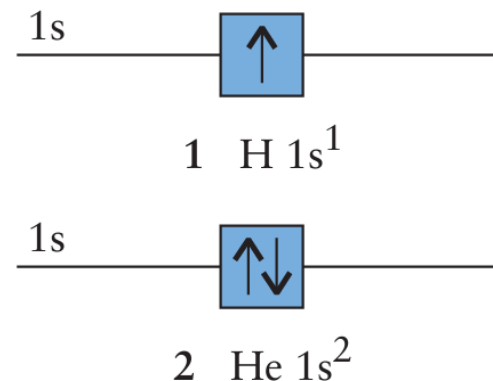


Figure 1E.3

1E.2 The building-up principle

Hydrogen and helium

- Hydrogen in the ground state: one electron in the 1s-orbital: a single arrow in the box diagram: $1s^1$
- Box indicates space for two electrons.
- Helium in the ground state: two electrons in the 1s-orbital: two paired electrons in box diagram: $1s^2$
- Helium has a fully occupied 1s orbital,
- Helium has **a closed shell**: a shell containing the maximum number of electrons allowed by the exclusion principle.



1E.2 The building-up principle

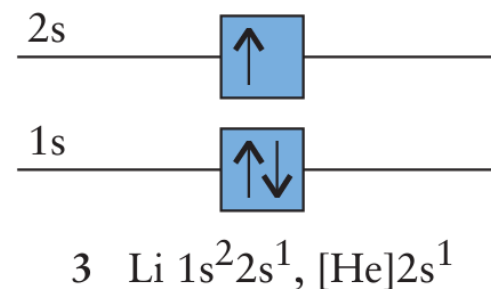
Valence electrons

- Filled, inner orbitals: **core**
- Outermost shell: **valence electrons**
- Valence electrons are involved in chemical reactions.
- Core electrons are in lower-energy orbitals and too tightly bound.
- The outermost electrons are used in the formation of chemical bonds (Topic 2A), and one theory of bond formation is called *valence-bond* theory, hence the name *valence electrons*.

1E.2 The building-up principle

Lithium (Li)

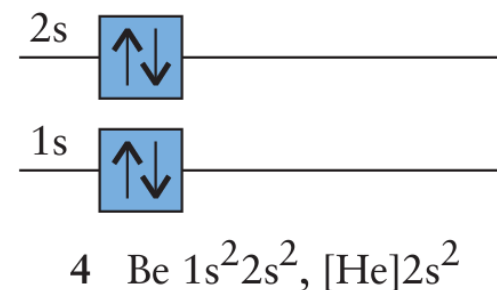
- Lithium ($Z = 3$) has three electrons: Two in 1s-, one in the 2s-orbital.
- Ground state of lithium: $1s^2 2s^1$
- Core for lithium: $1s^2 = [\text{He}]$
- With valence electrons: **$[\text{He}]2s^1$**
- Lithium only **loses one electron** when it forms compounds: Li^+ rather than Li^{2+} or Li^{3+}



1E.2 The building-up principle

Beryllium (Be)

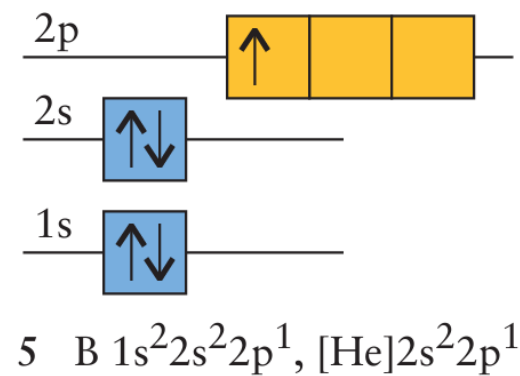
- Beryllium ($Z = 4$) has four electrons: Two in $1s$ -, two in the $2s$ -orbital.
- Ground state: $1s^2 2s^2$
- With valence electrons: **$[\text{He}]2s^2$**
- Be atom loses only valence shell electrons in chemical reactions: Be^{2+} ion



1E.2 The building-up principle

Boron (B)

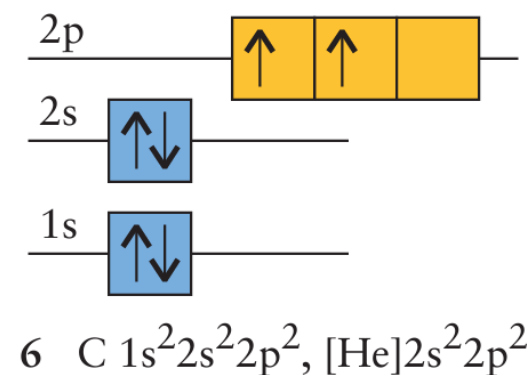
- Boron ($Z = 5$) has five electrons. Two in 1s-, two in the 2s-orbital, one in the 2p-orbital.
- Ground state: $1s^2 2s^2 2p^1$
- With valence electrons: $[\text{He}] 2s^2 2p^1$



1E.2 The building-up principle

Carbon (C)

- Carbon ($Z = 6$) has six electrons. Two in 1s-, two in the 2s-orbital, two in the 2p-orbital.
- Ground state: $1s^2 2s^2 2p^2$
- With valence electrons: $[\text{He}] 2s^2 2p^2$
- Decision: paired or parallel electrons in p-orbitals?
- Electrons are farther from each other and repell each other less when they occupy different p-orbitals than when they occupy the same orbital:
- $1s^2 2s^2 2p_x^2 2p_y^1$
- Parallel spins



1E.2 The building-up principle

The building-up principle and Hund's rule

Two rules:

1. Add Z electrons, one after the other, to the orbitals in the order shown in Fig. 1E.4 (next slide) but with no more than two electrons in any one orbital.
 2. If more than one orbital in a subshell is available, add electrons with parallel spins to different orbitals of that subshell rather than pairing two electrons in one of the orbitals. (**Hund's rule**, after German spectroscopist Friedrich Hund)
- **Configuration** of the atom at the **lowest total energy**: maximizes the attraction of the electrons to nucleus and minimizes their repulsion by one another

1E.2 The building-up principle

The periodic table

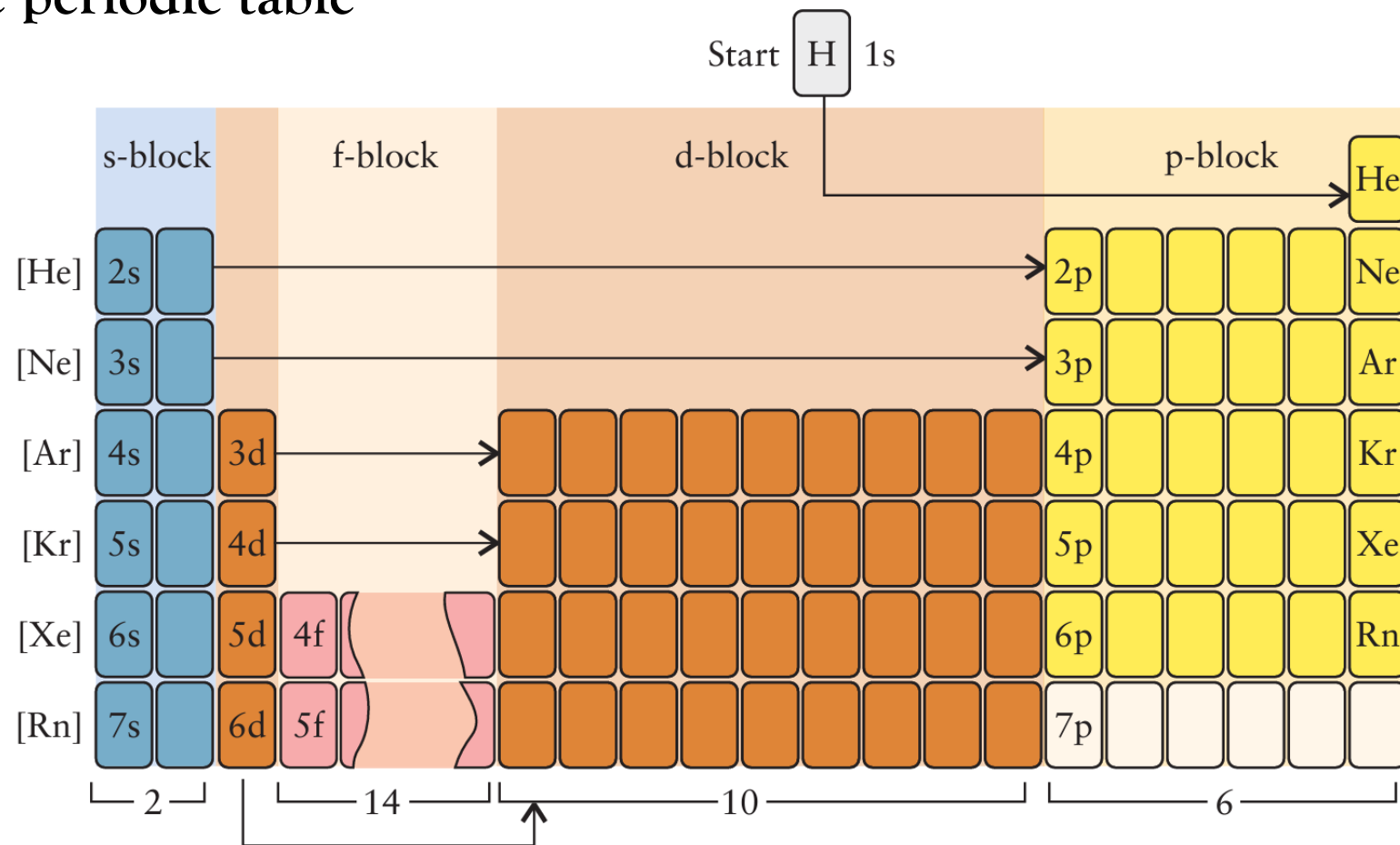


Figure 1E.4

1E.2 The building-up principle

Excited state

- An atom with electrons in higher energy states than predicted by the building-up principle is said to be in an excited state.
- For example: $[\text{He}]2s^12p^3$ represents an excited state of a carbon atom.
- An excited state is **unstable** and quickly **relaxes** back to the ground state as the electron returns to an orbital that restores the atom to a lower energy and **emits a photon**.

The building-up principle is also commonly called the **Aufbau principle** from the German word for «building up».

- Think of any atom: Noble-gas core surrounded by valence electrons.
- The **valence shell** is the occupied shell with the largest value of n .

1E.2 The building-up principle

The underlying organization: periods

- Rows are called periods
- All the atoms of the main-group elements in a given period have a valence shell with the same principal quantum number (equal to period number)
- E.g. Valence shell of elements in period 2 (lithium to neon) is the shell with $n=2$.
- All atoms in a given period have the same type of core but different numbers of valence electrons.
- Period 2: elements that have a helium-like $1s^2$ core, denoted [He]
- Period 3: elements with a neon-like $1s^2 2s^2 2p^6$ core, denoted [Ne]

1E.2 The building-up principle

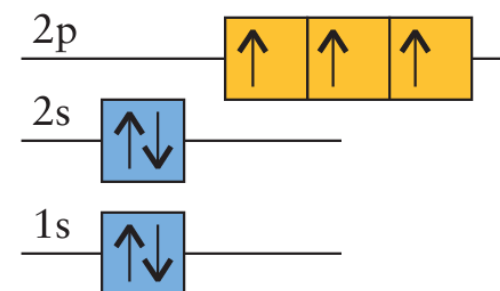
The underlying organization: groups

- Columns are groups: main groups 1, 2, 13-18
- Same group, analogous valence electron configurations, differ only in value of n
- E.g. all members of Group 1 have the valence configuration ns^1
- All members of Group 14 have the valence configuration ns^2np^2
- Similar electron configurations give the elements in a group similar chemical properties

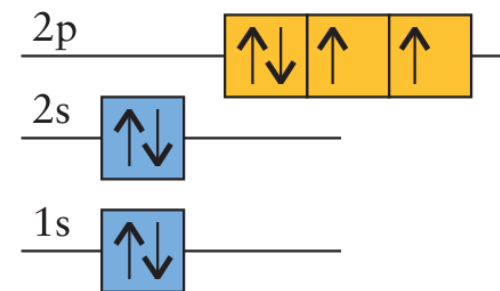
1E.2 The building-up principle

Nitrogen and oxygen

- **Nitrogen** ($Z = 7$) has seven electrons. Two in 1s-, two in the 2s-orbital, three in the 2p-orbital.
- Ground state: $1s^2 2s^2 2p^3$
- With valence electrons: $[\text{He}] 2s^2 2p^3$
- **Oxygen** ($Z = 8$) has eight electrons. Two in 1s-, two in the 2s-orbital, four in the 2p-orbital.
- Ground state: $1s^2 2s^2 2p^4$
- With valence electrons: $[\text{He}] 2s^2 2p^4$



7 N $1s^2 2s^2 2p^3$, $[\text{He}] 2s^2 2p^3$

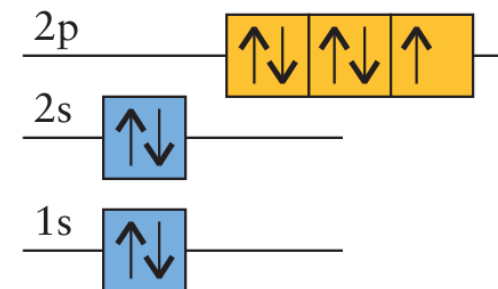


8 O $1s^2 2s^2 2p^4$, $[\text{He}] 2s^2 2p^4$

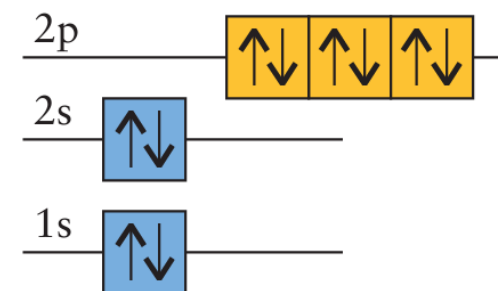
1E.2 The building-up principle

Fluorine and neon

- **Fluorine** ($Z = 9$) has nine electrons. Two in 1s-, two in the 2s-orbital, five in the 2p-orbital.
- Ground state: $1s^2 2s^2 2p^5$
- With valence electrons: $[\text{He}] 2s^2 2p^5$
- Only one unpaired electron
- **Neon** ($Z = 10$) has ten electrons. Two in 1s-, two in the 2s-orbital, six in the 2p-orbital.
- Ground state: $1s^2 2s^2 2p^6$
- With valence electrons: $[\text{He}] 2s^2 2p^6$
- No unpaired electrons (complete shell $n=2$)
- Next: sodium, Na ($Z = 11$): $[\text{Ne}] 3s^1$



9 F $1s^2 2s^2 2p^5$, $[\text{He}] 2s^2 2p^5$



10 Ne $1s^2 2s^2 2p^6$, $[\text{He}] 2s^2 2p^6$

1E.2 The building-up principle

After the 3p orbitals are filled...

- s- and p-orbitals of the shell with $n = 3$ full at **argon**: $[\text{Ne}]3s^23p^6$
- Next orbital 4s (not 3d!) because s-electrons penetrate through the inner-core electrons to a greater extent than p- or d-electrons → lower energy
- Potassium $[\text{Ar}]4s^1$ and calcium $[\text{Ar}]4s^2$ are next
- $[\text{Ar}]$ denotes $1s^22s^22p^63s^23p^6$ core
- Then 3d-orbitals are filled

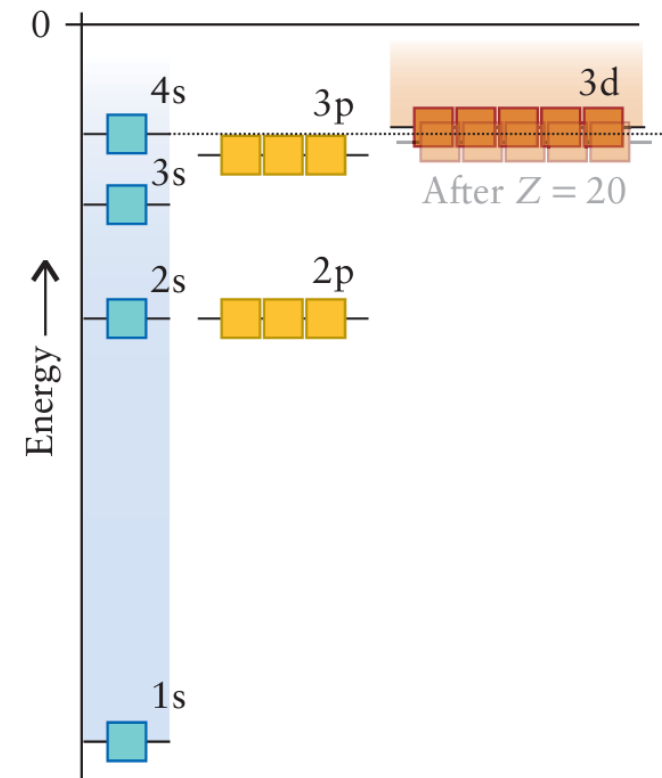


Figure 1E.1

1E.2 The building-up principle

After the 4s orbital is filled...

- Change of rhythm: 3d orbitals
- From $Z = 21$ to $Z = 30$ (scandium to zinc)
- Scandium ($Z = 21$): $[\text{Ar}]3d^14s^2$
- Titanium ($Z = 22$): $[\text{Ar}]3d^24s^2$
- Note: 3d-orbitals are written before 4s-orbitals because they become lower in energy compared to 4s **when filled with electrons**
- Same relation holds true for nd - and $(n+1)s$ -orbitals in subsequent periods.

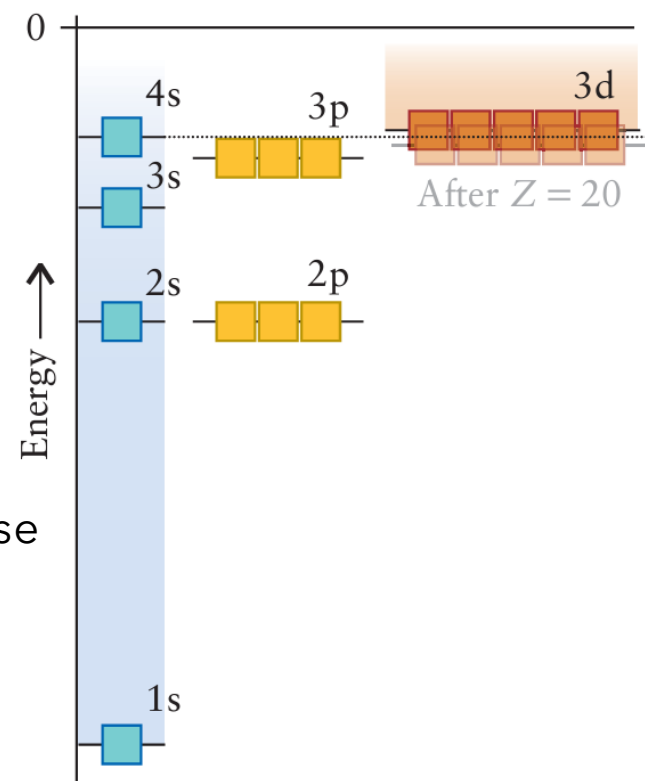


Figure 1E.1

1E.2 The building-up principle

After the 4s orbital is filled...

- Successive electrons are added to d-electrons as Z increases.
- With two exceptions:
- Chromium ($Z = 24$): $[\text{Ar}]3d^54s^1$ instead of $[\text{Ar}]3d^44s^2$
- Copper ($Z = 29$): $[\text{Ar}]3d^{10}4s^1$ instead of $[\text{Ar}]3d^94s^2$
- **Half-complete subshell configuration** d^5 and **complete subshell configuration** d^{10} have a lower energy
- More exceptions to the building-up principles can be found in Appendix 2C with a complete listing of electron configurations

1E.2 The building-up principle

After the 3d orbitals are filled...

- Note: Electron configurations are written in order of increasing energy, not in order of filling. For example, scandium is written $[\text{Ar}]3d^14s^2$ and not $[\text{Ar}]4s^23d^1$
- 4p-orbitals are next (see periodic table!)
- Germanium: $[\text{Ar}]3d^{10}4s^24p^2$
- Arsenic: $[\text{Ar}]3d^{10}4s^24p^3$
- Fourth period contains **18 elements**: 4s- and 4p-orbitals with 8 electrons and 3d-orbitals with 10 electrons
- Period four is the first **long period** of the periodic table

CONCEPTUAL BASIS

Electrons occupy orbitals in such a way as to minimize the total energy of an atom by maximizing attractions and minimizing repulsions in accord with the Pauli exclusion principle and Hund's rule.

PROCEDURE

We use the following rules of the building-up principle to assign a ground-state configuration to a neutral atom of an element with atomic number Z :

- 1 Add Z electrons, one after the other, to the orbitals in the order shown in Figs. 1.41 and 1.44 but with no more than two electrons in any one orbital (the Pauli exclusion principle).
- 2 If more than one orbital in a subshell is available, add electrons to different orbitals of the subshell before doubly occupying any of them (Hund's rule).
- 3 Write the labels of the orbitals in order of increasing energy, with a superscript that gives the number of electrons in that orbital. The configuration of a filled shell is represented by the symbol of the noble gas having that configuration, as in [He] for $1s^2$.

- 4 When drawing a box diagram, show the electrons in different orbitals of the same subshell with parallel spins; electrons sharing an orbital have paired spins.

In most cases this procedure gives the ground-state electron configuration of an atom, the arrangement with the lowest energy. Any arrangement other than the ground state corresponds to an excited state of the atom. Note that we can use the structure of the periodic table to predict the electron configurations of most elements once we realize which orbitals are being filled in each block of the periodic table (see Fig. 1.44).

A useful shortcut for atoms of elements with large numbers of electrons is to write the valence electron configuration from the group number, which gives the number of valence electrons in the ground state of the atom, and the period number, which gives the value of the principal quantum number of the valence shell. The core consists of the preceding noble-gas configuration together with any completed d- and f-subshells.

Example 1.10 shows how these rules are applied.

1E.2 The building-up principle

After the 4p orbitals are filled...

- Period 5: 5s-orbital is filled next, followed by 4d-orbitals
- As in Period 4, the energies of the 4d-orbitals fall below that of the 5s-orbitals after two electrons have been accommodated in the 5s-orbital
- Similar effect is seen in Period 6:
- Cerium: $[\text{Xe}]4f^15d^16s^2$
- Electrons then continue to occupy the seven 4f-orbitals, which are complete after 14 electrons have been added, at ytterbium, $[\text{Xe}]4f^{14}5d^{10}6s^26p^1$
- In Appendix 2C: seven apparent disruptions occur in the order in which the 4f-orbitals are filled (because 4f- and 5d-orbitals are close in energy)
- Despite exceptions, rules are good guidelines as a starting point.

1E.2 The building-up principle

Example 1E.1 Predicting the ground-state electron configuration of a heavy atom

EXAMPLE 1.10 Predicting the ground-state electron configuration of a heavy atom

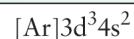
Predict the ground-state electron configuration of (a) a vanadium atom and (b) a lead atom.

Anticipate Because vanadium is a member of the d-block, we should expect its atoms to have a partially filled set of d-orbitals. Because lead is in the same group as carbon, we should expect the configuration of its valence electrons to be similar to that of carbon (s^2p^2).

PLAN Follow the procedure in Toolbox 1.1.

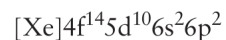
SOLVE

(a) Vanadium is in Period 4, and so it has an argon core. Add two electrons to the 4s-orbital, and the last three electrons to three separate 3d-orbitals.



Ar	2	3	4	5
K	Ca	Sc	Ti	V
s^1	s^2	d^1s^2	d^2s^2	d^3s^2

(b) Lead belongs to Group 14/IV and Period 6. It therefore has four electrons in its valence shell, two in a 6s-orbital and two in different 6p-orbitals. The atom has complete 5d- and 4f-subshells, and the preceding noble gas is xenon.



C			
Si			
Ge			
Sn			
Pb			

1E.2 The building-up principle

Example 1E.1 Predicting the ground-state electron configuration of a heavy atom

Evaluate As expected, vanadium has an incomplete set of d-electrons and the valence-shell configuration of lead is analogous to that of carbon.

Self-Test 1.12A Write the ground-state configuration of a bismuth atom.

[*Answer:* $[\text{Xe}]4f^{14}5d^{10}6s^26p^3$]

Self-Test 1.12B Write the ground-state configuration of an arsenic atom.

We account for the ground-state electron configuration of an atom by using the building-up principle in conjunction with Fig. 1.41, the Pauli exclusion principle, and Hund's rule.

1E.2 The building-up principle

Summary

The ground-state electron configuration of an atom is predicted by using the building-up principle in conjunction with Fig. 1E.1, the Pauli exclusion principle, and Hund's rule.

The skills you have mastered are the ability to

- ❑ Describe the factors affecting the energy of an electron in a many-electron atom.
- ❑ Write the ground-state electron configuration for an element.

Summary: You have learned that the structures of many-electron atoms are explained by the systematic occupation of orbitals by electrons, with the order determined by the effects of penetration and shielding in conjunction with the Pauli exclusion principle. The building-up principle is reflected in and in a sense accounts for the general structure of the periodic table.