CH-110 Advanced General Chemistry I

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Housekeeping notes

- Solutions book for exercises in the book: available at library, will be uploaded to Moodle
- Only odd number exercises (even are very similar)
- We also uploaded a study guide with a summary
- SESSION ID: 861684

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, derives **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

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**.

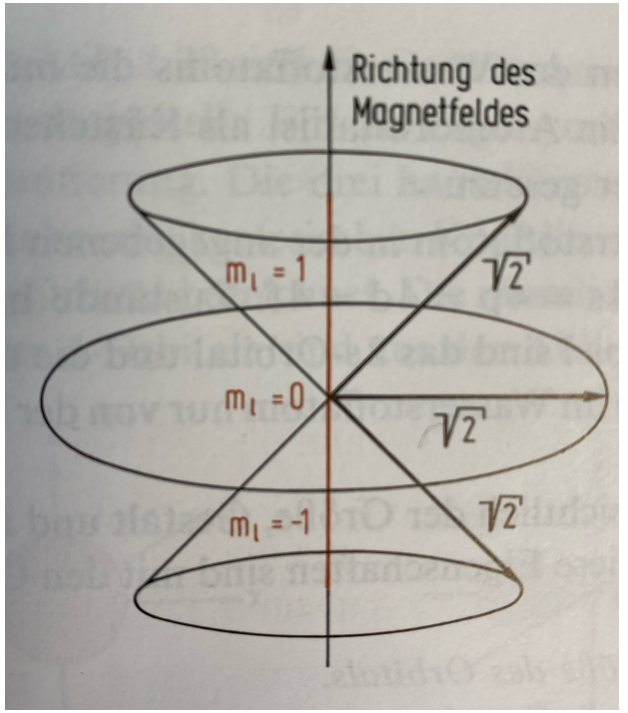
The quantum numbers serve as essential descriptors of these states, much like the integer n indicated the allowed energy levels in the particle in a box.

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.



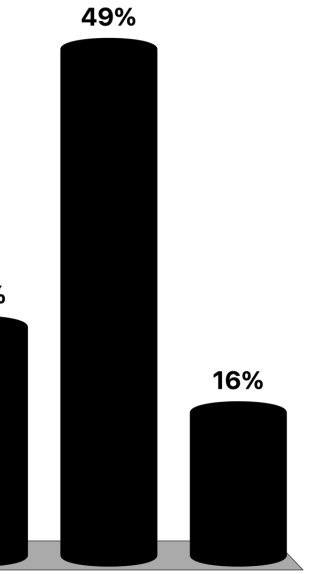
How would you expect a 1s-orbital of He^+ to differ from a 1s-orbital in H?

A. The 1s-orbital of He^+ has a higher energy than the 1s-orbital of H due to increased electron-electron repulsion.

B. The 1s-orbital of He^+ is larger and more diffuse than the 1s-orbital of H due to a greater number of protons in the nucleus.

C. The 1s-orbital of He^+ is lower in energy and smaller in size than the 1s-orbital of H due to a higher effective nuclear charge experienced by the electron. (CORRECT)

D. The 1s-orbital of He^+ has the same energy and size as the 1s-orbital of H because both have one electron.



1D.4 The shapes of orbitals

Question: How would you expect a 1s-orbital of He^+ to differ from a 1s-orbital in H?

$$E_n = -\frac{Z^2 hR}{n^2} \; with \; n = 1, 2, \ldots$$

Z is the atomic number. For H, $Z = 1$. For He, $Z = 2$.

- **Charge**: He^+ has a higher nuclear charge (+2e) than hydrogen (+1e).
- **Energy**: The 1s orbital in He^+ is lower in energy (more negative) compared to that in hydrogen.
- **Size**: The 1s orbital in He^+ is smaller and more compact than that in hydrogen due to greater electron-nucleus attraction.
- **Electron Density**: The electron density is more concentrated near the nucleus in He^+.

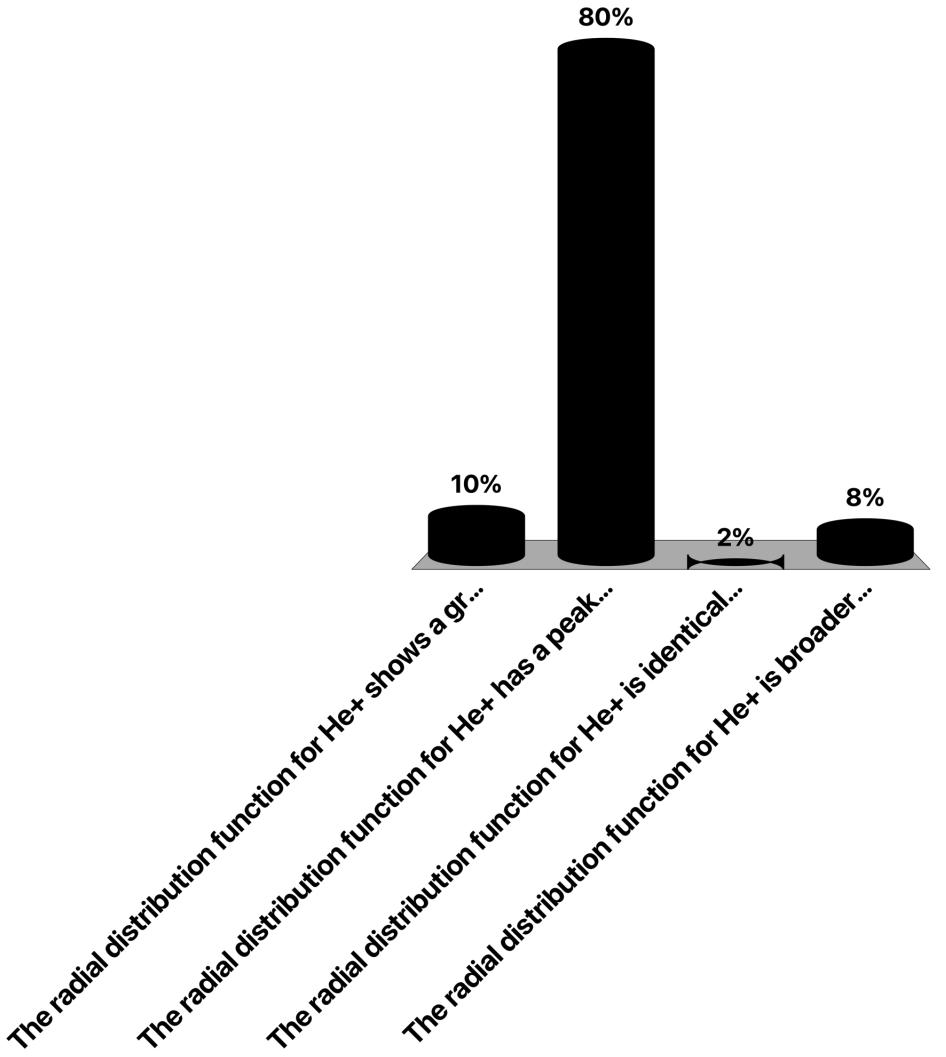
How does the radial distribution function for an electron in He+ differ from that of H itself?

A) The radial distribution function for He^+ shows a greater probability of finding the electron at larger distances from the nucleus compared to H.

B) The radial distribution function for He^+ has a peak at a smaller radius and is more sharply defined than that of H, indicating a higher probability density closer to the nucleus. (CORRECT)

C) The radial distribution function for He^+ is identical to that of H because both systems have the same number of protons.

D) The radial distribution function for He^+ is broader and more spread out than that of H, indicating a more diffuse electron cloud.



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Question: How does the radial distribution function for an electron in He^+ differ from that of H itself?

The correct answer is:

2) The radial distribution function for He^+ has a peak at a smaller radius and is more sharply defined than that of H, indicating a higher probability density closer to the nucleus.

Explanation:

He^+ is a hydrogen-like ion with one electron, but it has two protons in the nucleus, creating a stronger Coulomb attraction compared to hydrogen (H), which only has one proton.

Due to this increased nuclear charge (two protons in He^+ vs. one proton in H), the electron in He^+ experiences a stronger attractive force, pulling it closer to the nucleus.

As a result, the electron's wavefunction and radial distribution function are more concentrated near the nucleus, leading to a peak at a smaller radius and a higher probability density closer to the nucleus compared to hydrogen.

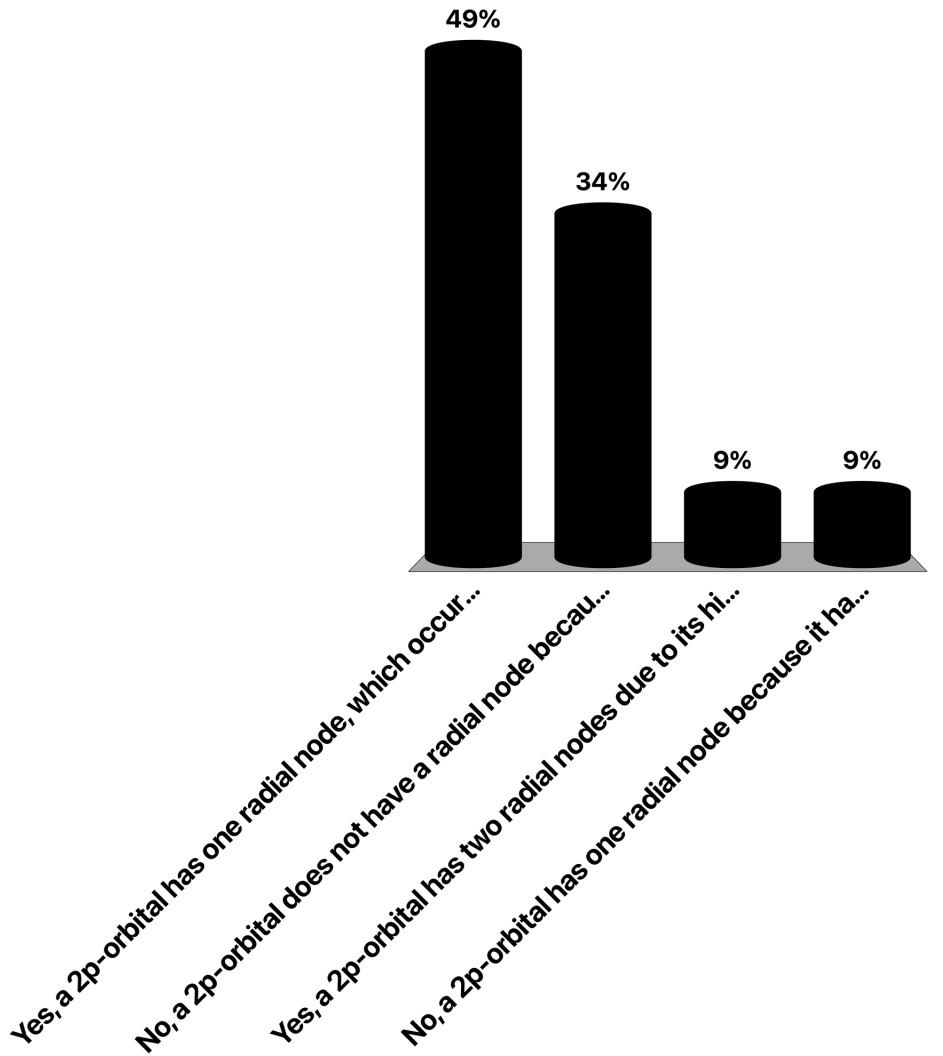
Does a 2p-orbital have a radial node? Hint: Think carefully about the definition of a radial node.

A) Yes, a 2p-orbital has one radial node, which occurs at a certain distance from the nucleus where the probability of finding an electron is zero.

B) No, a 2p-orbital does not have a radial node because it has zero radial nodes and only angular nodes. (CORRECT)

C) Yes, a 2p-orbital has two radial nodes due to its higher energy level compared to the 1s orbital.

D) No, a 2p-orbital has one radial node because it has one angular node.



1D.4 The shapes of orbitals

Question: Does a 2p-orbital have a radial node? Hint: Think carefully about the definition of a radial node.

The correct answer is:

No, a 2p-orbital does not have a radial node because it has zero radial nodes and only angular nodes.

Explanation:

Radial nodes occur when the radial part of the wavefunction goes to zero at certain distances from the nucleus. For an orbital to have a radial node, its radial wavefunction must cross zero.

The number of radial nodes is given by $n-l-1$

For a **2p-orbital**:

$n=2,\ l=1$

Using the formula for radial nodes:
$n-l-1=2-1-1=0$
Therefore, a 2p-orbital has **zero radial nodes**.

Angular nodes are determined by the azimuthal quantum number l, and for a p-orbital (l=1), there is **one angular node** (which corresponds to the plane where the probability of finding an electron is zero, like the xy-plane for a 2p orbital along the z-axis).

Thus, a **2p orbital** has **no radial nodes** but **one angular node**.

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** ↑ **and** ↓ or the Greek letters α and β.

1D.5 Electron spin

Spin ↑ and ↓

Think of an electron as being able to spin counterclockwise (the ↑ state) and clockwise (the ↓ 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: $+\frac{1}{2}$ (↑) and $-\frac{1}{2}$ (↓).

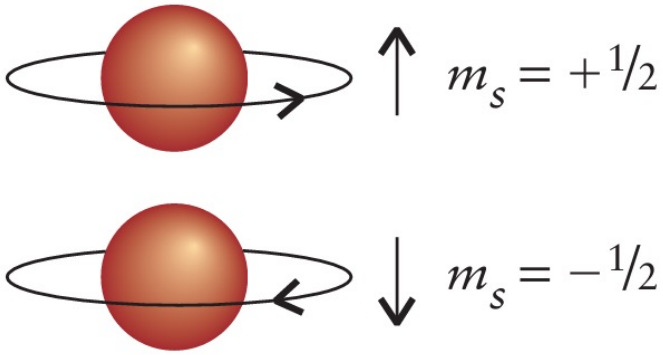


Figure 1D.12

1D.5 Electron spin

Summary

An electron has the property of spin;

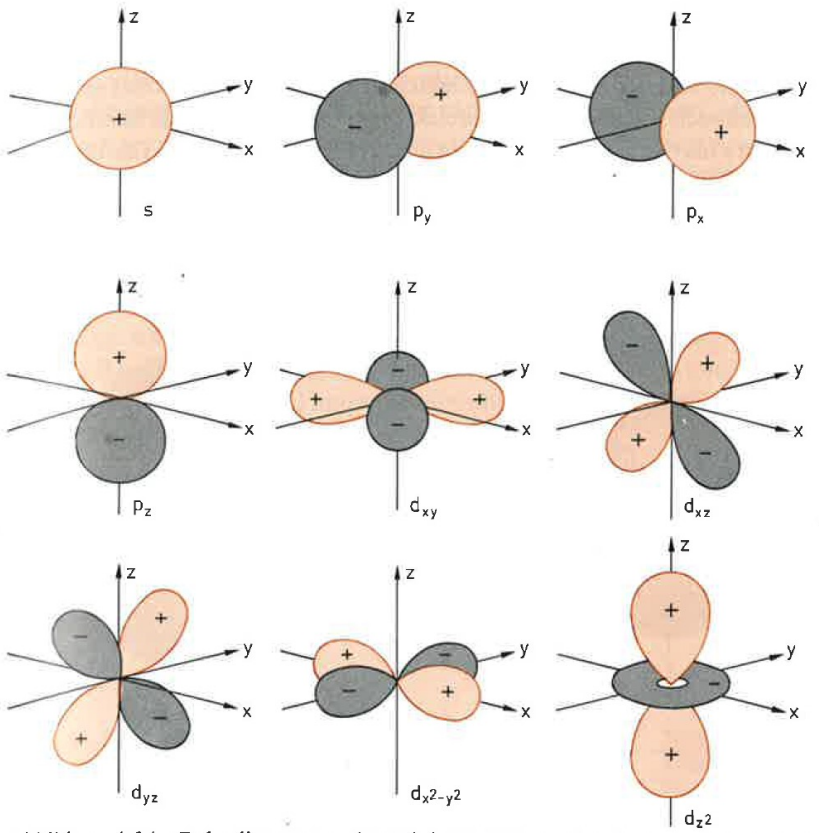
the spin is described by the quantum number $m_s = \pm\frac{1}{2}$.

The Electronic Structure of Hydrogen: A Summary

Topic 1D.6

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

Blackboard summary



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

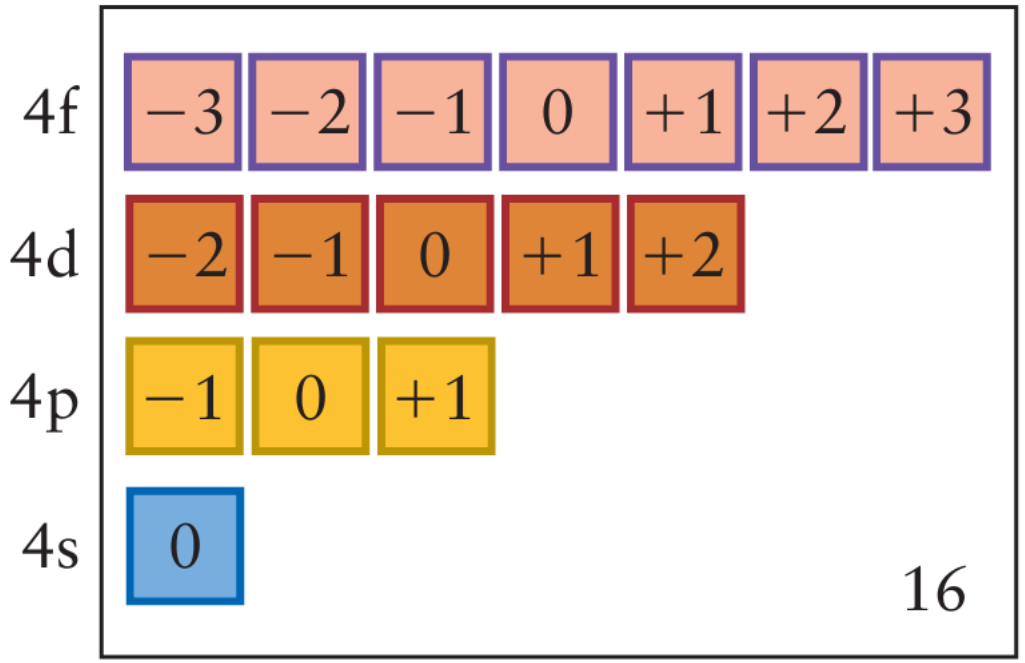


Figure 1D.13

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, . . .	shell	size
orbital angular momentum*	l	0, 1, . . ., $n - 1$	subshell: $l = 0, 1, 2, 3, 4, \ldots$ s, p, d, f, g, . . .	shape
magnetic	m_l	$l, l - 1, \ldots, -l$	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 ist ground and excited states.

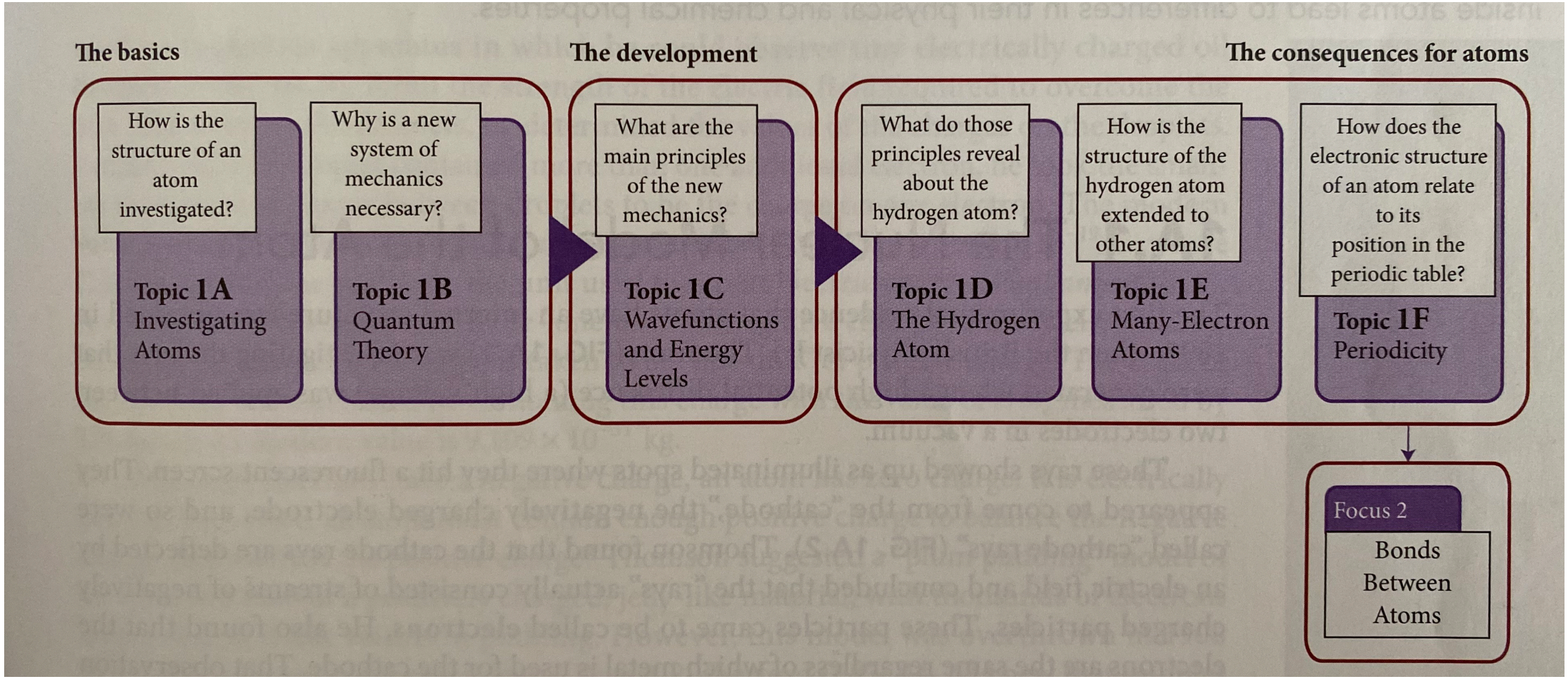
Summary: You have learned that an electron in a hydrogen atom is described by wavefunctions called atomic orbitals and that each orbital is specified by three quantum numers: n, l, and m_l. You now know that the shape and energy of a given orbital is found by solving the Schrödinger equation for an electron 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), $\boldsymbol{m_l}$: 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

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**.

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

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:

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

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.

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.)

Energies of hydrogen vs. many-electron atoms

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:

Energy level differences in orbitals of the same shell

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 ($E_n = -Z^2hR/n^2$)

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

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 the p-electron 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

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

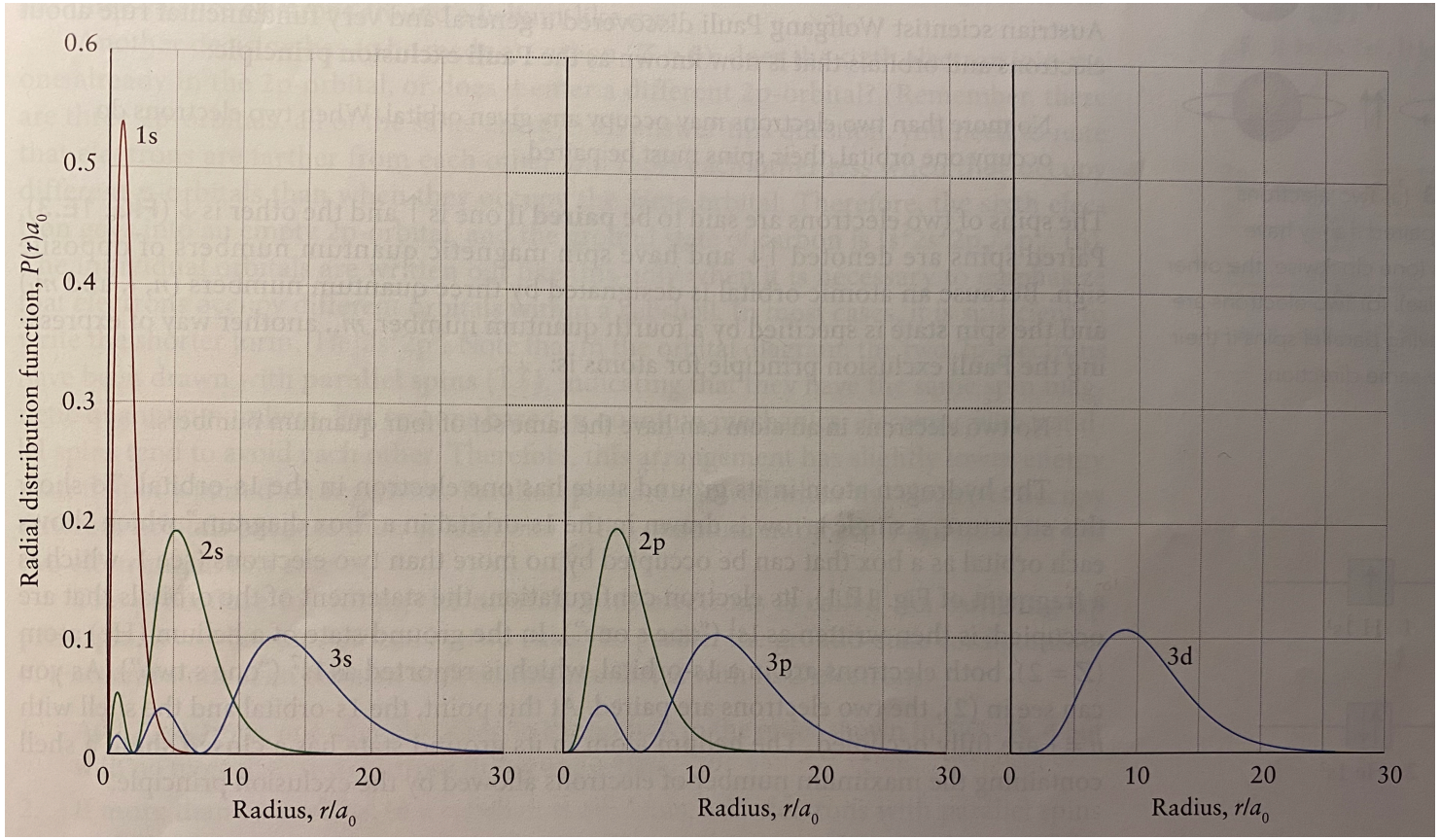


Figure 1E.2

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

Effects of shielding can be large

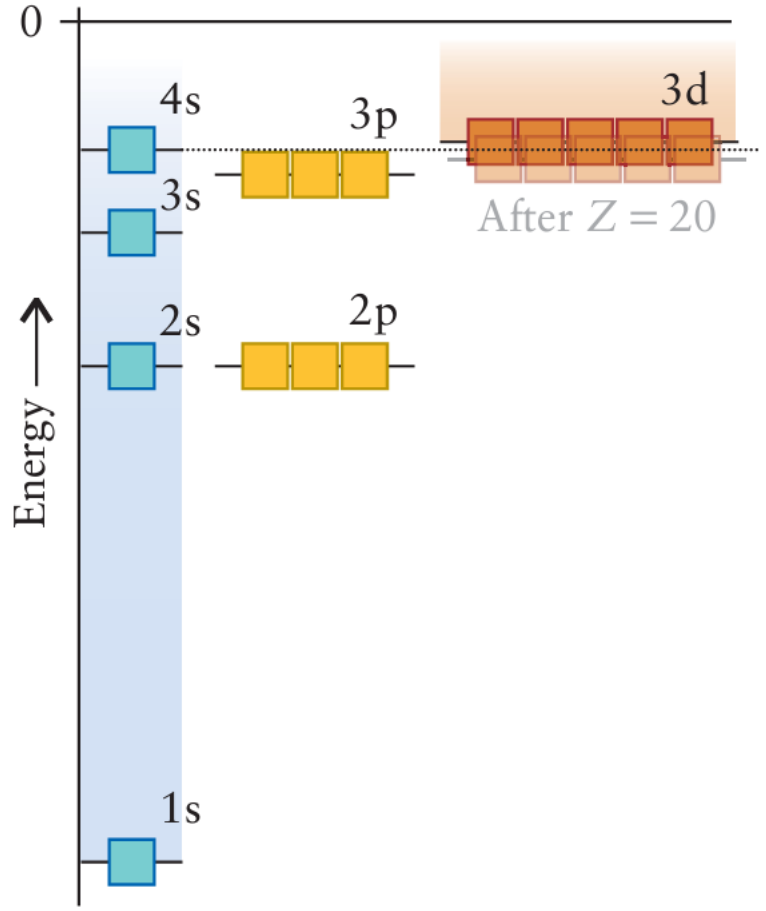


Figure 1E.1

- 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

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.

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 ↑ and ↓.
- Paired spins are denoted ↑↓ 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.

The Pauli exclusion principle

(a) The two spins of electrons are **paired** if one is ↑ and ↓. 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.

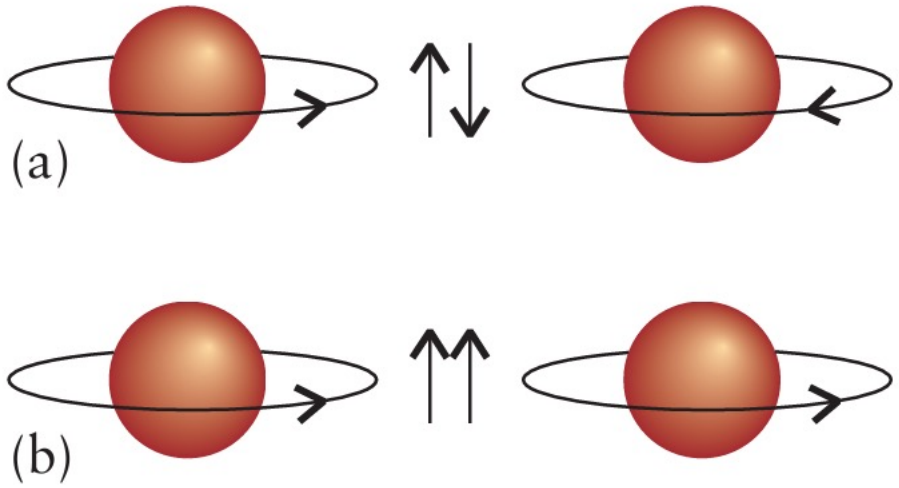
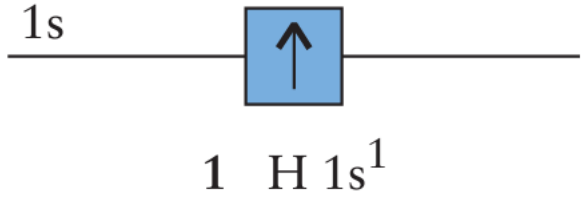
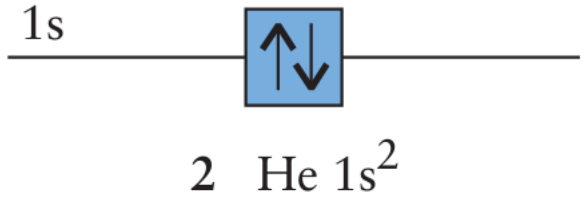


Figure 1E.3

Hydrogen and helium

- Hydrogen in the ground state: one electron in the 1s-orbital: a single arrow in the box diagram: $1s^1$ (electron configuration)
- 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.



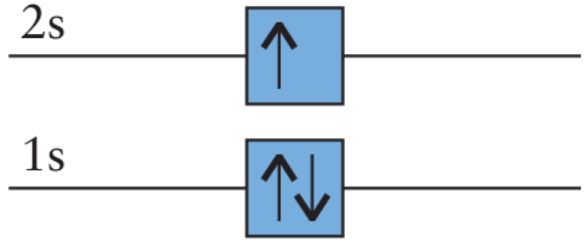


Valence electrons

- 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*.

Lithium (Li)

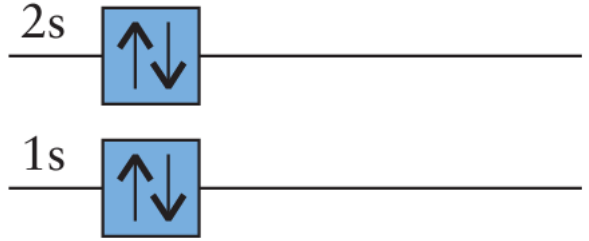
- Lithium (Z = 3) has three electrons: Two in 1s-, one in the 2s-orbital.
- Ground state of lithium: $1s^2 2s^1$
- Core for lithium: $1s^2$ = [He]
- With valence electrons: **[He]$2s^1$**
- Lithium only **loses one electron** when it forms compounds: Li^+ rather than Li^{2+} or Li^{3+}



3 Li $1s^2 2s^1$, [He]$2s^1$

Beryllium (Be)

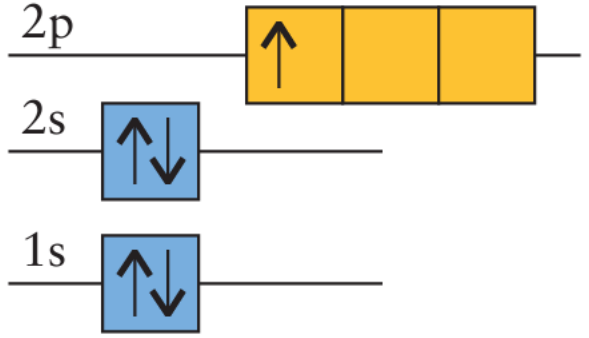
- Beryllium (Z = 4) has four electrons: Two in 1s-, two in the 2s-orbital.
- Ground state: $1s^2 2s^2$
- With valence electrons: **$[He]2s^2$**
- Be atom loses only valence shell electrons in chemical reactions: Be^{2+} ion



4 Be $1s^2 2s^2$, $[He]2s^2$

Boron (B)

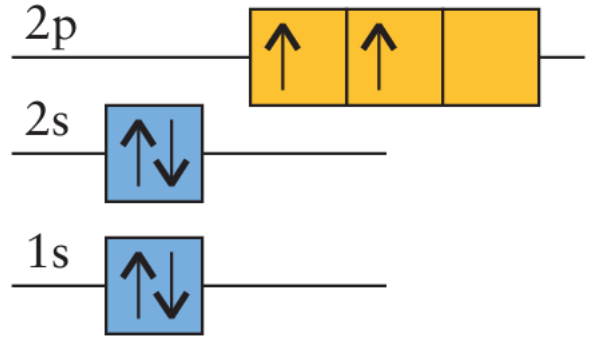
- Boron (Z = 5) has five electrons. Two in 1s-, two in the 2s-orbital, one in the 2p-orbital.
- Ground state: $1s^2 2s^2 2p^1$
- With valence electrons: $[He]2s^2 2p^1$



5 B $1s^2 2s^2 2p^1$, $[He]2s^2 2p^1$

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: $[He]2s^2 2p^2$
- 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:
- $1s^2 2s^2 2p_x^1 2p_y^1$
- Parallel spins



6 C $1s^2 2s^2 2p^2$, $[He]2s^2 2p^2$

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

The periodic table

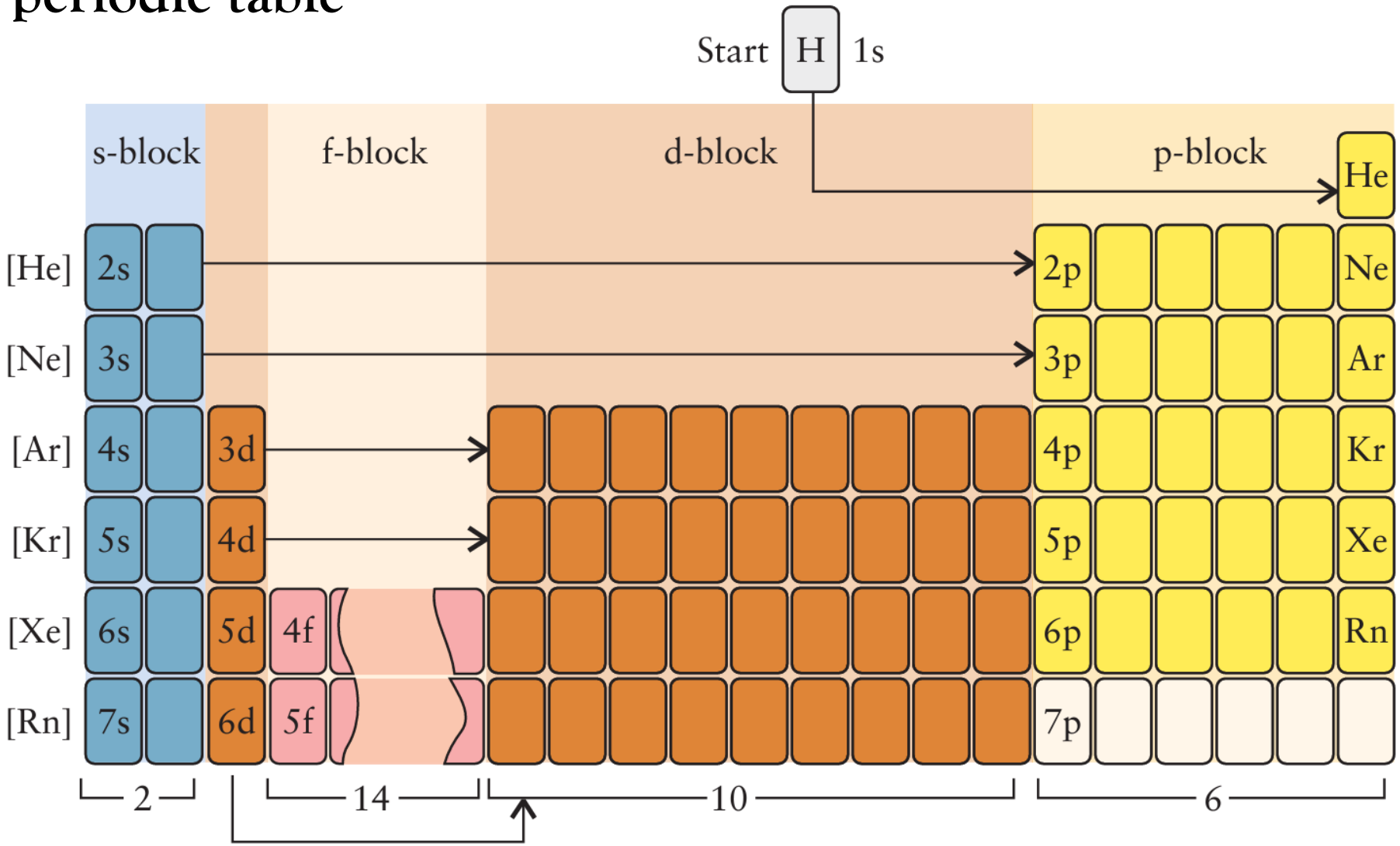


Figure 1E.4

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: [He]$2s^1 2p^3$ 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*.

The underlying organization: Periods

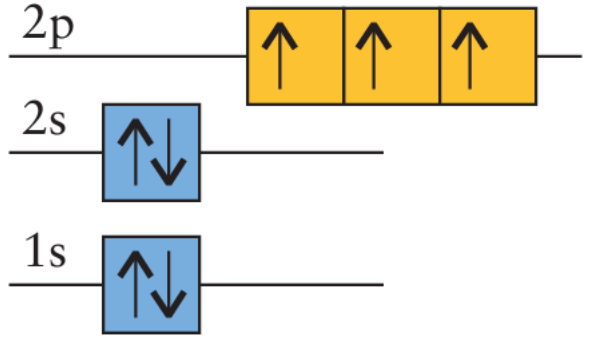
- Rows are called **periods**
- All the atoms of the **main-group elements** in a given period have a valence shell with the same principal quantum number (equal to period number)
- E.g. Valence shell of elements in period 2 (lithium to neon) is the shell with n=2.
- All atoms in a given period have 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]

The underlying organization: Groups

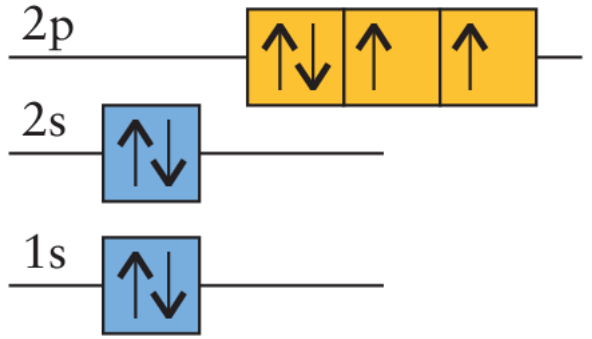
- **Columns** are **groups**: main groups 1, 2, 13-18
- Same group, analogous valence electron configurations, differ only in value of *n*
- E.g. all members of Group 1 have the valence configuration ns^1
- All members of Group 14 have the valence configuration ns^2np^2
- **Similar electron configurations**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

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: $[He]2s^2 2p^3$
- **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: $[He]2s^2 2p^4$



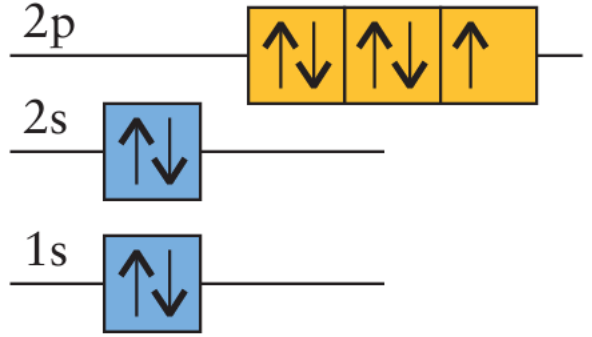
7 N $1s^2 2s^2 2p^3$, $[He]2s^2 2p^3$



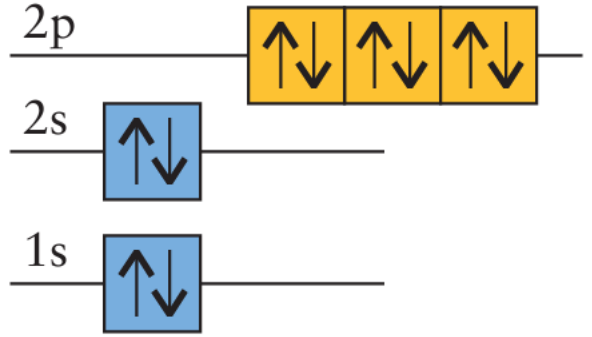
8 O $1s^2 2s^2 2p^4$, $[He]2s^2 2p^4$

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: $[He]2s^2 2p^5$
- 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: $[He]2s^2 2p^6$
- No unpaired electrons (complete shell n=2)
- Next: sodium, Na (Z = 11): $[Ne]3s^1$



9 F $1s^2 2s^2 2p^5$, $[He]2s^2 2p^5$



10 Ne $1s^2 2s^2 2p^6$, $[He]2s^2 2p^6$

After the 3p orbitals are filled...

- s- and p-orbitals of the shell with $n = 3$ full at **argon**: [Ne]$3s^2 3p^6$
- **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 [Ar]$4s^1$ and calcium [Ar]$4s^2$ are next
- [Ar] denotes $1s^2 2s^2 2p^6 3s^2 3p^6$ core
- Then 3d-orbitals are filled

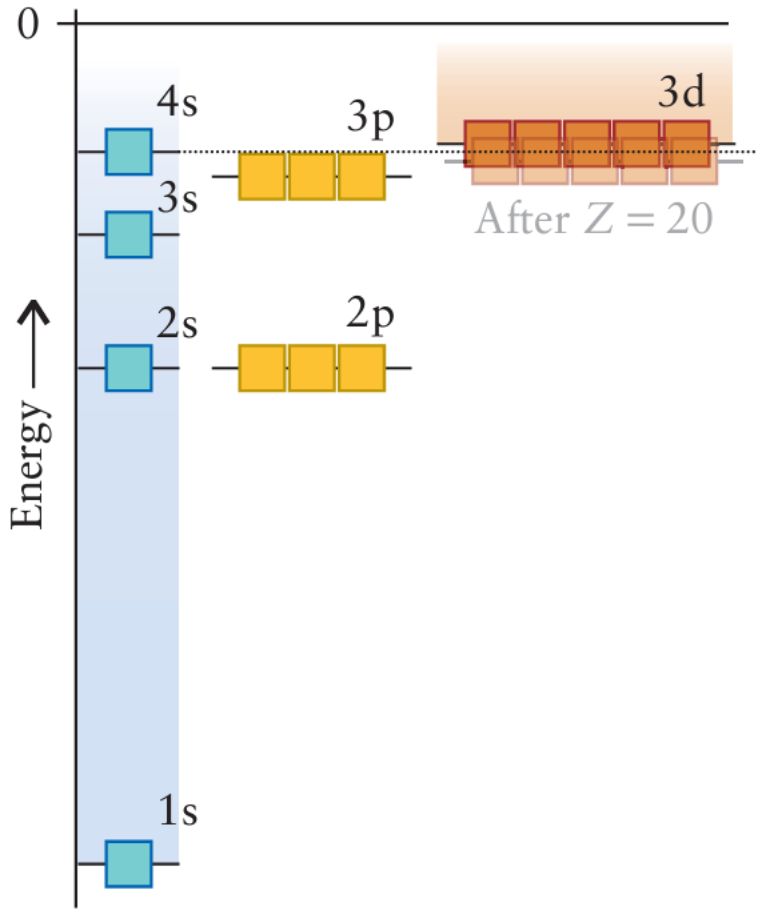


Figure 1E.1

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): $[Ar]3d^14s^2$
- Titanium (Z = 22): $[Ar]3d^24s^2$
- 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 *n*d- and (*n*+1)s-orbitals in subsequent periods.

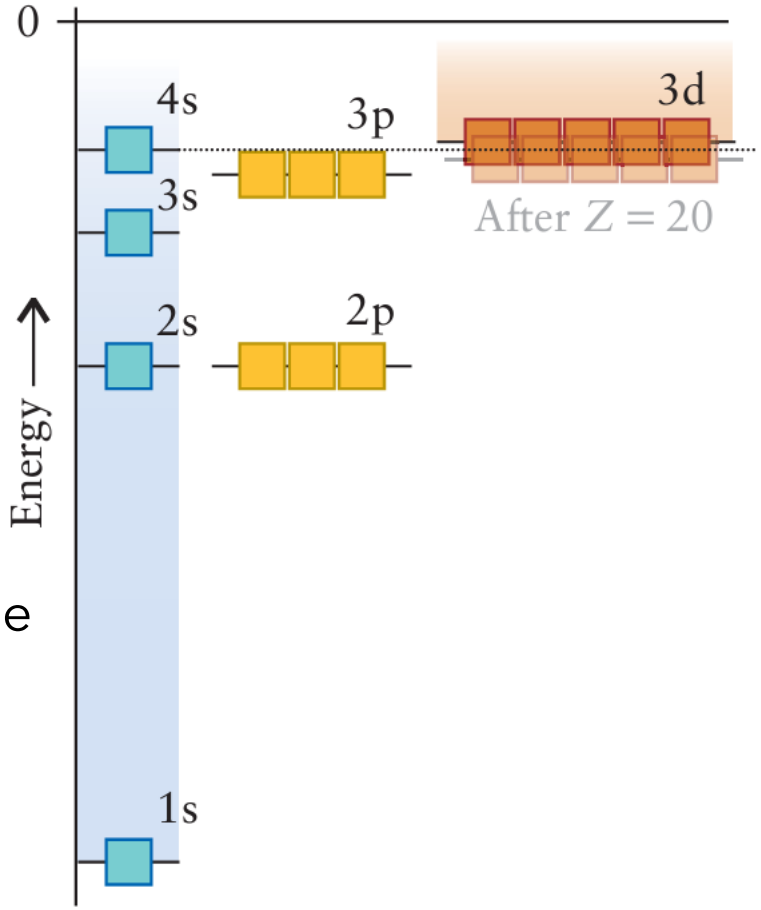


Figure 1E.1

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): $[Ar]3d^5 4s^1$ instead of $[Ar]3d^4 4s^2$
- Copper (Z = 29): $[Ar]3d^{10} 4s^1$ instead of $[Ar]3d^9 4s^2$
- **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 [Ar]$3d^1 4s^2$ and not [Ar]$4s^2 3d^1$
- 4p-orbitals are next (see periodic table!)
- Germanium: [Ar]$3d^{10} 4s^2 4p^2$
- Arsenic: [Ar]$3d^{10} 4s^2 4p^3$
- 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

TOOLBOX 1.1 HOW TO PREDICT THE GROUND-STATE ELECTRON CONFIGURATION OF AN ATOM

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).

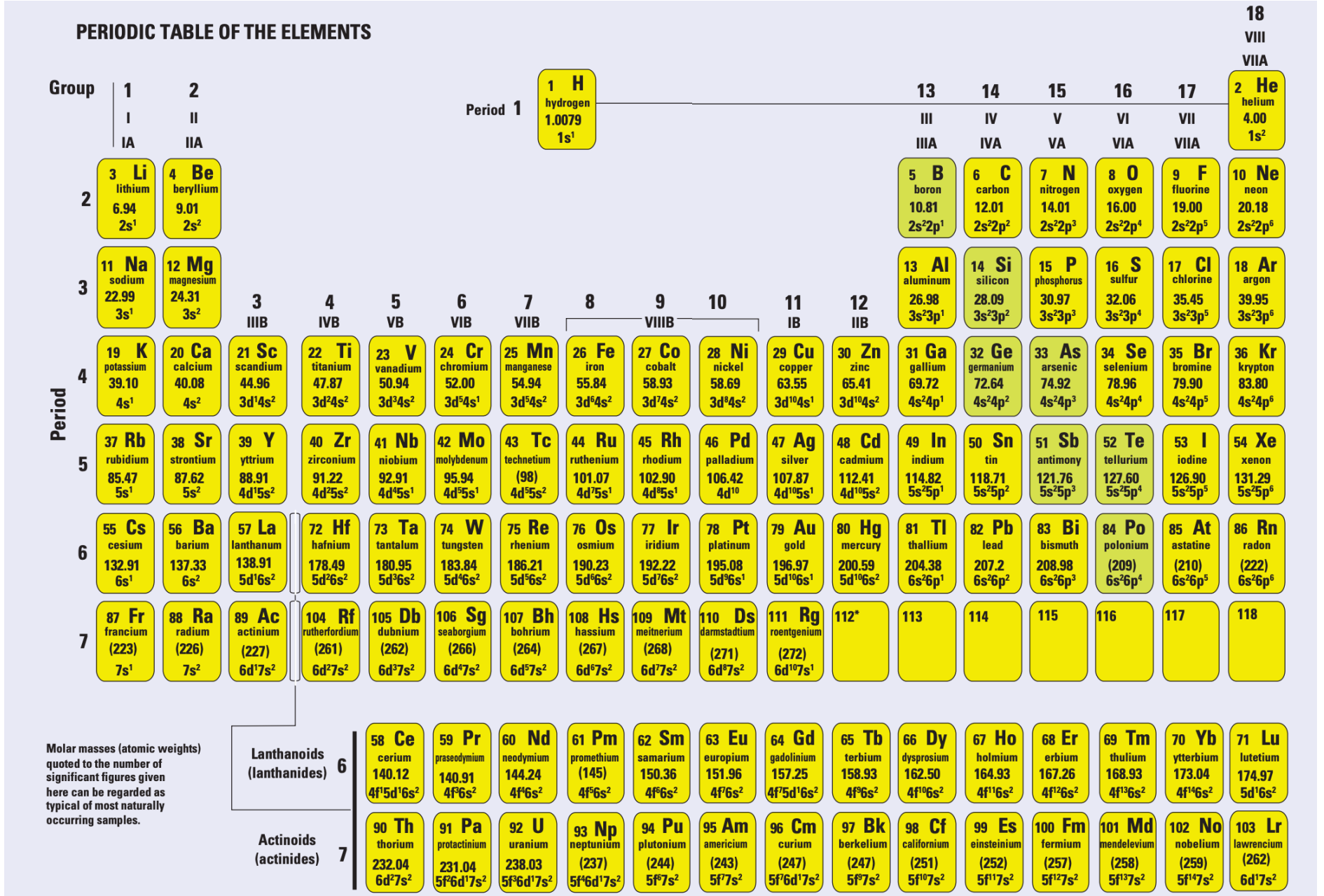
A useful shortcut for atoms of elements with large numbers of electrons is to write the valence electron configuration from the group number, which gives the number of valence electrons in the ground state of the atom, and the period number, which gives the value of the principal quantum number of the 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: $[Xe]4f^{1}5d^{1}6s^{2}$
- Electrons then continue to occupy the seven 4f-orbitals, which are complete after 14 electrons have been added, at ytterbium, $[Xe]4f^{14}5d^{10}6s^{2}6p^{1}$
- 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 as starting point.


PERIODIC TABLE OF THE ELEMENTS
Group
Period
1 I IA
2 II IIA
3 IIIB
4 IVB
5 VB
6 VIB
7 VIIB
8
9 VIIIB
10
11 IB
12 IIB
13 III IIIA
14 IV IVA
15 V VA
16 VI VIA
17 VII VIIA
18 VIII VIIA
1 H hydrogen 1.0079 1s1
2 He helium 4.00 1s2
3 Li lithium 6.94 2s1
4 Be beryllium 9.01 2s2
5 B boron 10.81 2s22p1
6 C carbon 12.01 2s22p2
7 N nitrogen 14.01 2s22p3
8 O oxygen 16.00 2s22p4
9 F fluorine 19.00 2s22p5
10 Ne neon 20.18 2s22p6
11 Na sodium 22.99 3s1
12 Mg magnesium 24.31 3s2
13 Al aluminum 26.98 3s23p1
14 Si silicon 28.09 3s23p2
15 P phosphorus 30.97 3s23p3
16 S sulfur 32.06 3s23p4
17 Cl chlorine 35.45 3s23p5
18 Ar argon 39.95 3s23p6
19 K potassium 39.10 4s1
20 Ca calcium 40.08 4s2
21 Sc scandium 44.96 3d14s2
22 Ti titanium 47.87 3d24s2
23 V vanadium 50.94 3d34s2
24 Cr chromium 52.00 3d54s1
25 Mn manganese 54.94 3d54s2
26 Fe iron 55.84 3d64s2
27 Co cobalt 58.93 3d74s2
28 Ni nickel 58.69 3d84s2
29 Cu copper 63.55 3d104s1
30 Zn zinc 65.41 3d104s2
31 Ga gallium 69.72 4s24p1
32 Ge germanium 72.64 4s24p2
33 As arsenic 74.92 4s24p3
34 Se selenium 78.96 4s24p4
35 Br bromine 79.90 4s24p5
36 Kr krypton 83.80 4s24p6
37 Rb rubidium 85.47 5s1
38 Sr strontium 87.62 5s2
39 Y yttrium 88.91 4d15s2
40 Zr zirconium 91.22 4d25s2
41 Nb niobium 92.91 4d45s1
42 Mo molybdenum 95.94 4d55s1
43 Tc technetium (98) 4d55s2
44 Ru ruthenium 101.07 4d75s1
45 Rh rhodium 102.90 4d85s1
46 Pd palladium 106.42 4d10
47 Ag silver 107.87 4d105s1
48 Cd cadmium 112.41 4d105s2
49 In indium 114.82 5s25p1
50 Sn tin 118.71 5s25p2
51 Sb antimony 121.76 5s25p3
52 Te tellurium 127.60 5s25p4
53 I iodine 126.90 5s25p5
54 Xe xenon 131.29 5s25p6
55 Cs cesium 132.91 6s1
56 Ba barium 137.33 6s2
57 La lanthanum 138.91 5d16s2
72 Hf hafnium 178.49 5d26s2
73 Ta tantalum 180.95 5d36s2
74 W tungsten 183.84 5d46s2
75 Re rhenium 186.21 5d56s2
76 Os osmium 190.23 5d66s2
77 Ir iridium 192.22 5d76s2
78 Pt platinum 195.08 5d96s1
79 Au gold 196.97 5d106s1
80 Hg mercury 200.59 5d106s2
81 Tl thallium 204.38 6s26p1
82 Pb lead 207.2 6s26p2
83 Bi bismuth 208.98 6s26p3
84 Po polonium (209) 6s26p4
85 At astatine (210) 6s26p5
86 Rn radon (222) 6s26p6
87 Fr francium (223) 7s1
88 Ra radium (226) 7s2
89 Ac actinium (227) 6d17s2
104 Rf rutherfordium (261) 6d27s2
105 Db dubnium (262) 6d37s2
106 Sg seaborgium (266) 6d47s2
107 Bh bohrium (264) 6d57s2
108 Hs hassium (267) 6d67s2
109 Mt meitnerium (268) 6d77s2
110 Ds darmstadtium (271) 6d87s2
111 Rg roentgenium (272) 6d107s1
112* 113 114 115 116 117 118
Molar masses (atomic weights) quoted to the number of significant figures given here can be regarded as typical of most naturally occurring samples.
Lanthanoids (lanthanides) 6
58 Ce cerium 140.12 4f15d16s2
59 Pr praseodymium 140.91 4f36s2
60 Nd neodymium 144.24 4f46s2
61 Pm promethium (145) 4f56s2
62 Sm samarium 150.36 4f66s2
63 Eu europium 151.96 4f76s2
64 Gd gadolinium 157.25 4f75d16s2
65 Tb terbium 158.93 4f96s2
66 Dy dysprosium 162.50 4f106s2
67 Ho holmium 164.93 4f116s2
68 Er erbium 167.26 4f126s2
69 Tm thulium 168.93 4f136s2
70 Yb ytterbium 173.04 4f146s2
71 Lu lutetium 174.97 5d16s2
Actinoids (actinides) 7
90 Th thorium 232.04 6d27s2
91 Pa protactinium 231.04 5f26d17s2
92 U uranium 238.03 5f36d17s2
93 Np neptunium (237) 5f46d17s2
94 Pu plutonium (244) 5f67s2
95 Am americium (243) 5f77s2
96 Cm curium (247) 5f76d17s2
97 Bk berkelium (247) 5f97s2
98 Cf californium (251) 5f107s2
99 Es einsteinium (252) 5f117s2
100 Fm fermium (257) 5f127s2
101 Md mendelevium (258) 5f137s2
102 No nobelium (259) 5f147s2
103 Lr lawrencium (262) 6d17s2
*The names of the elements 112 and higher have not yet been determined; both 112 and 114 have been confirmed.

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

- (a) vanadium
- (b) lead

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.

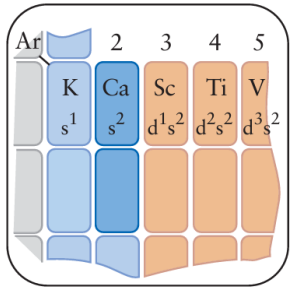
Anticipate Because vanadium is a member of the d-block, we should expect its atoms to have a partially filled set of d-orbitals. Because lead is in the same group as carbon, we should expect the configuration of its valence electrons to be similar to that of carbon (s^2p^2).

PLAN Follow the procedure in Toolbox 1.1.

SOLVE

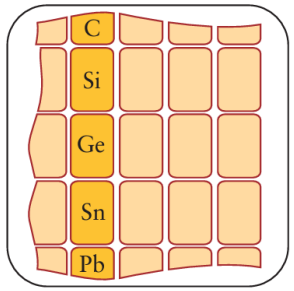
(a) Vanadium is in Period 4, and so it has an argon core. Add two electrons to the 4s-orbital, and the last three electrons to three separate 3d-orbitals.

$[Ar]3d^3 4s^2$



(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.

$[Xe]4f^{14}5d^{10}6s^2 6p^2$



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:*** $[Xe]4f^{14}5d^{10}6s^{2}6p^{3}$]

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 conjuction with Fig. 1E.1, the Pauli exclusion principle, and Hund's rule.

Student quotes

“CHEMISTRY CAN EXPLAIN THE WORLD IN WHICH WE LIVE, AND THERE IS LOT OF DIFFERENT THINGS WE CAN STUDY IN CHEMISTRY.”

“BECAUSE CHEMISTRY IS EVERYWHERE.”

"I CHOOSE CHEMISTRY BECAUSE IT'S A SCIENCE CLOSE FROM NATURE.”

“UNDERSTAND HOW THINGS WORK AND HOW TO CREATE NEW THINGS."

Connection to today’s lecture: These quotes relate to the **Aufbau principle** because they emphasize understanding how things work by building knowledge in a structured way, similar to how the Aufbau principle describes the stepwise filling of electron orbitals to explain the behavior of atoms and matter in the natural world.

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.

Student questions

In this equation:

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

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

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

For n=2: $\lambda = \frac{2\mathrm{L}}{2} = L$, for n=3: $\lambda = \frac{3\mathrm{L}}{2}$ 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 ($\lambda = \frac{2\mathrm{L}}{1}$) because half a wavelength fits into 1 L. For n=2, one wavelength corresponds to 1L ($\lambda = \frac{2\mathrm{L}}{2}$), For n=3, one wavelength corresponds to 2/3 of the box length ($\lambda = \frac{2\mathrm{L}}{3}$).

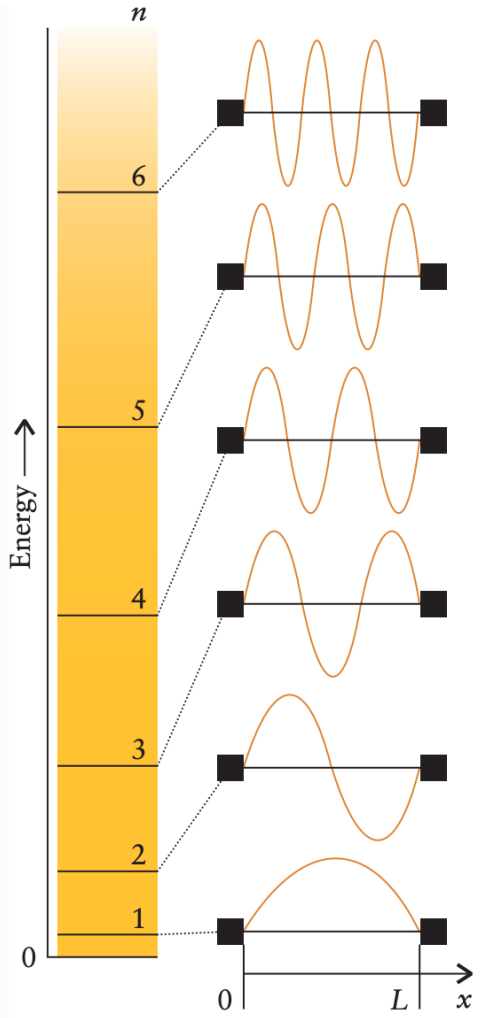


Figure 1C.3

Student questions

Angular vs. radial nodes?

Angular nodes are **planar** (e.g. all d-orbitals except $\boldsymbol{d_{z^2}}$ have two planar angular nodes) or **conical** regions ($\boldsymbol{d_{z^2}}$ has two angular conical nodes) where the probability of finding an electron is zero. Radial nodes are **spherical** surfaces where the probability of finding an electron is zero. The number of angular nodes is equal to the value of l for a given orbital. The number of radial nodes is calculated using this formula: $n - l - 1$

Student questions

What is a standing wave? Are atomic orbitals standing waves?

A standing wave is a wave that remains fixed in space with specific nodes and antinodes. Atomic orbitals can be thought of as standing waves because they are described by wavefunctions that define the probability distributions of electrons in atoms, with distinct nodes corresponding to areas of zero probability

Student questions

Radial distribution function vs. Radial wavefunction?

(1) Radial Wavefunction

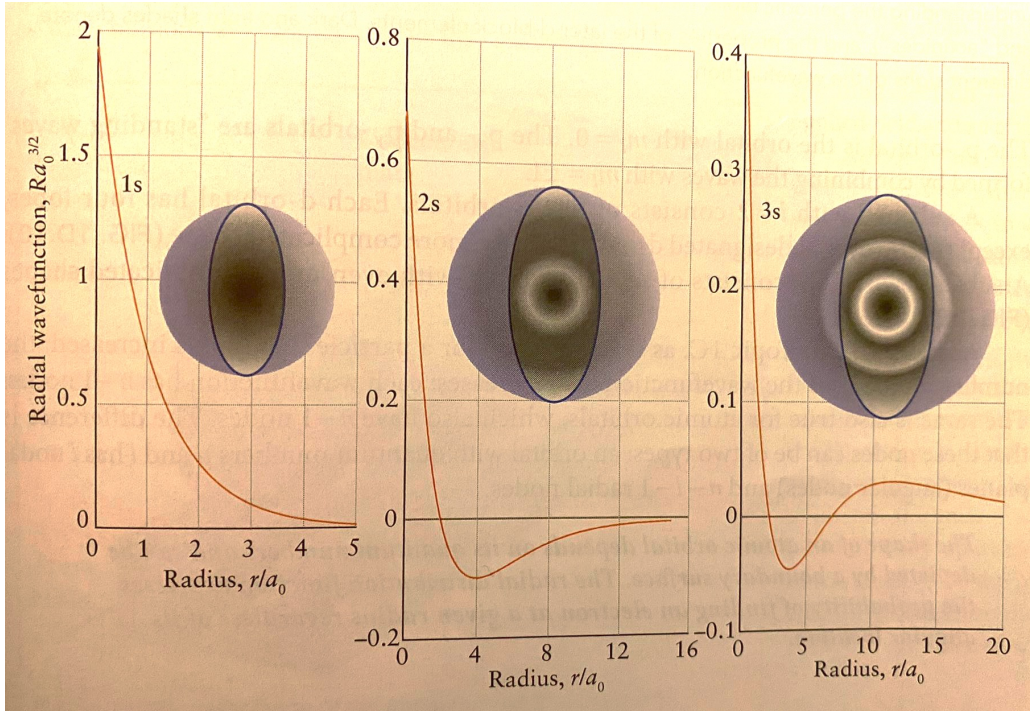
1. **Definition**: The radial wavefunction, often denoted as $R(r)$, is a part of the overall wavefunction $\psi(r, \theta, \varphi)$ for an electron in an atom, specifically in spherical coordinates. It describes how the **probability amplitude** of finding an electron varies with distance r from the nucleus.

2. **Mathematical Form**: The radial wavefunction is derived from the solution of the Schrödinger equation for the hydrogen atom (or hydrogen-like atoms). For example, for a 1s orbital:

$$\psi(r, \theta, \varphi) = \left(\frac{1}{\pi a_0^3}\right)^{\frac{1}{2}} e^{-\frac{r}{a_0}} \text{ where } a_0 \text{ is the Bohr radius}$$

1. **Interpretation**: The radial wavefunction itself does not directly give probabilities. It provides the amplitude of the wavefunction that varies with distance from the nucleus.

Figure 1D.7



Student questions

Radial distribution function vs. Radial wavefunction?

(2) Radial Distribution Function

1. **Definition**: The radial distribution function, often denoted as $P(r)$, represents the **probability of finding an electron within a thin spherical shell** between r and r + δr from the nucleus, accounting for the volume of that shell.

2. **Mathematical Form**: The radial distribution function is given by:

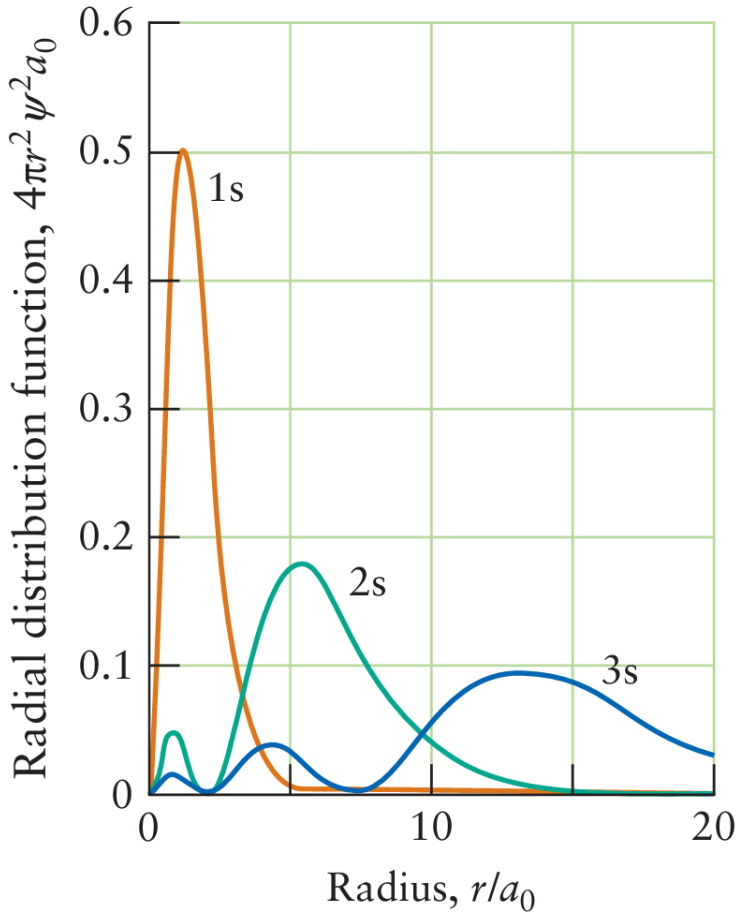
$$P(r) = r^2 R^2(r)$$

For s-orbitals: $P(r) = 4\pi r^2 \psi^2(r)$

Here, $R^2(r)$ is the probability density associated with the radial wavefunction, and r^2 accounts for the volume of the spherical shell, which grows with the square of the radius.

1. **Interpretation**: The radial distribution function provides a clearer picture of where electrons are likely to be found in space. It indicates the probability of locating an electron at a certain distance r from the nucleus, integrating the radial wavefunction's contributions over all angles.

Figure 1D.5



Student questions

What are the valence electrons in vanadium?

Outermost shell, not including noble gas core: $3d^3 4s^2$

Vanadium has five valence electrons, two in the 4s and three in the 3d orbital

Student questions

Why is potential energy negative for the hydrogen atom?

How can an energy be negative?

Because the potential energy is defined to be negative when the electron is bound to the nucleus (i.e., when r is finite and positive), **the energy becomes less than zero:**

$$V(r) = \frac{(-e)\times(+e)}{4\pi\varepsilon_0 r} = -\frac{e^2}{4\pi\varepsilon_0 r}$$

Negative energy levels indicate that the electron is **bound** to the nucleus. It requires energy to remove the electron completely from the influence of the nucleus, which is the point at which the potential energy would become zero.

The more negative the energy, the more stable and tightly bound the electron is to the nucleus.

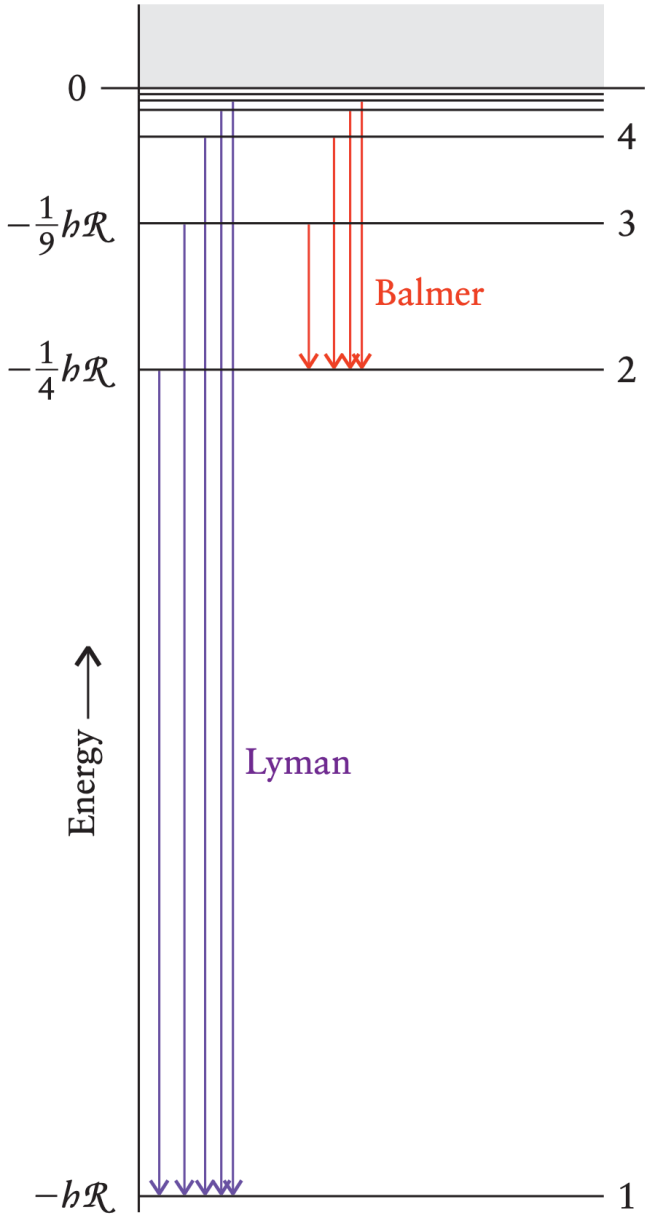


Figure 1D.1

Student questions

Is there a way to deduce the shapes of the x^2-y^2 and z^2 orbital logically?

Yes, if you solve the Schrödinger equation and look at the individual wavefunctions. However, this is beyond the scope of this class. What you should know that helps you deduce the shapes:

Each d-orbital has two angular nodes (either nodal planes or nodal cones)

- $\boldsymbol{d_{xy}}$, $\boldsymbol{d_{xz}}$, and $\boldsymbol{d_{yz}}$ have two nodal planes:
- For $\boldsymbol{d_{xy}}$, the nodal planes are the x- and y-axes.
- For $\boldsymbol{d_{xz}}$, the nodal planes are the x- and z-axes.
- For $\boldsymbol{d_{yz}}$, the nodal planes are the y- and z-axes.
- $\boldsymbol{d_{x^2-y^2}}$ has two angular nodes that are aligned along the diagonal planes y=x and y=−x.
- $\boldsymbol{d_{z^2}}$ has two **conical nodes**, which are cone-shaped regions around the z-axis.

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}

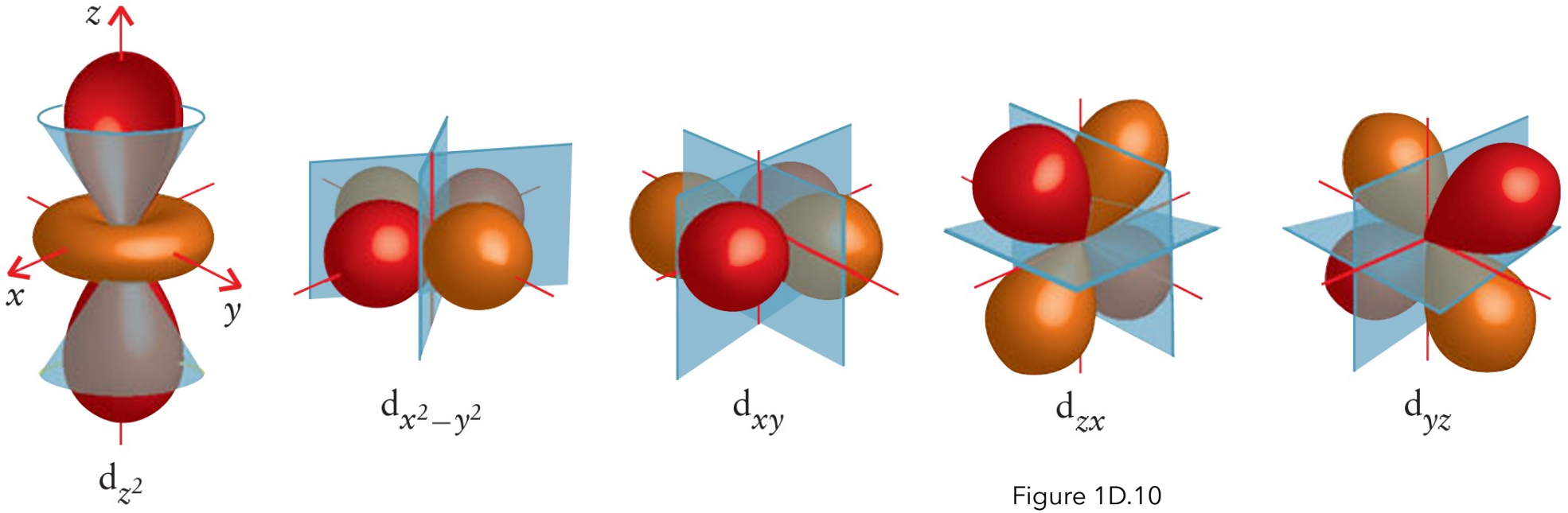


Figure 1D.10