CH-110 Advanced General Chemistry I

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Housekeeping notes

- You are allowed to write your answers **in French on the exam**.
- Exercises marked with **“requires calculus”** are not part of the material tested at the exam.
- **SESSION ID: 161855**

Student questions

Radial distribution function vs. Radial wavefunction?

(1) Radial Wavefunction

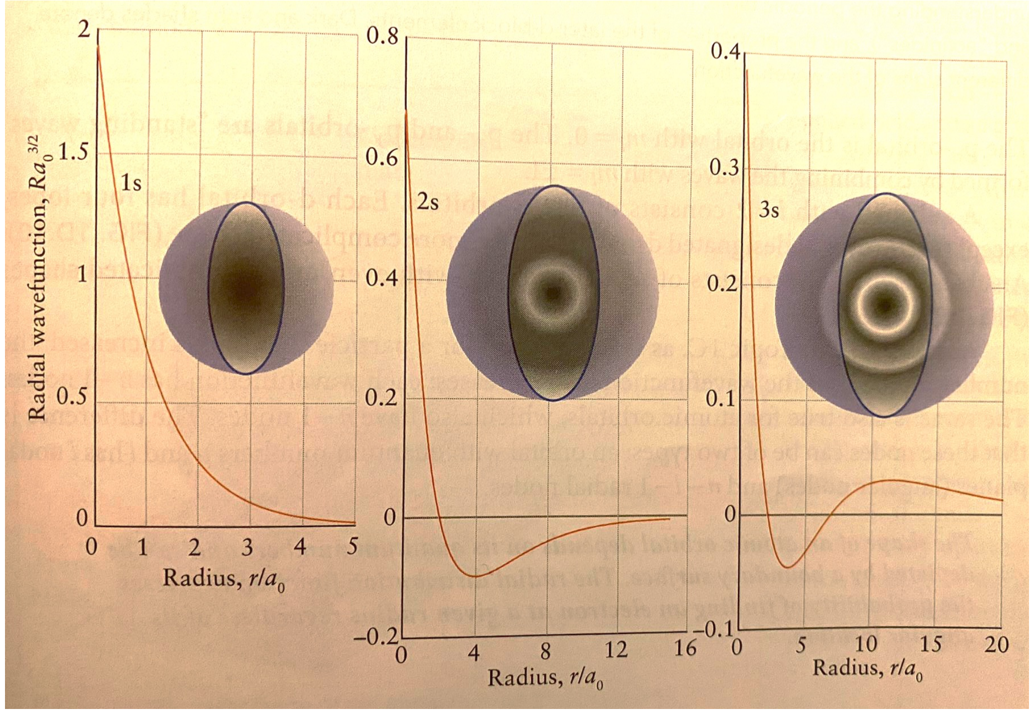
1. **Definition**: The radial wavefunction, often denoted as $R(r)$, is a part of the overall wavefunction $\psi(r,\theta,\varphi)$ for an electron in an atom, specifically in spherical coordinates. It describes how the **probability amplitude** of finding an electron varies with distance r from the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

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

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



$Ra_0^{\frac{3}{2}}$: **dimensionless** radial wavefunction

Student questions

Radial distribution function vs. Radial wavefunction?

(2) Radial Distribution Function

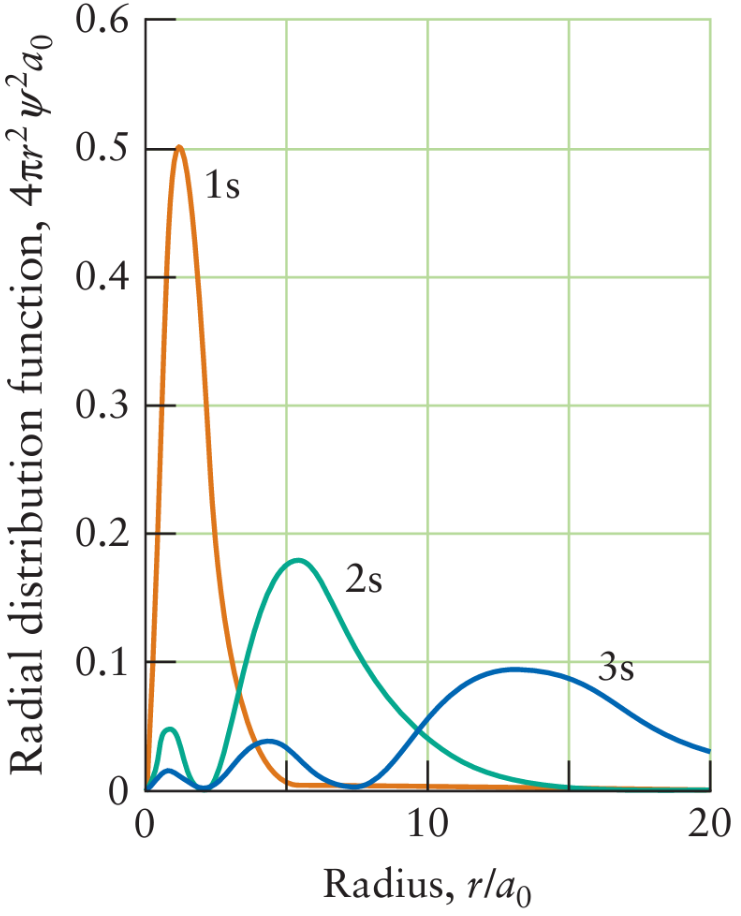
1. **Definition**: The radial distribution function, often denoted as $P(r)$, represents the **probability of finding an electron within a thin spherical shell** between r and r + δr from the nucleus, accounting for the volume of that shell.
2. **Mathematical Form**: The radial distribution function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

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

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

Radial distribution function vs. Radial wavefunction?

The relationship between the **radial wavefunction** $R(r)$ and the **radial distribution function** $P(r)$ is analogous to the relationship between the **wavefunction** $\psi(x)$ and the **probability density** $\psi(x)^{2.}$ Both pairs relate a more abstract, non-physical quantity (the wavefunction) to a physically meaningful probability (the distribution function or probability density).

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}

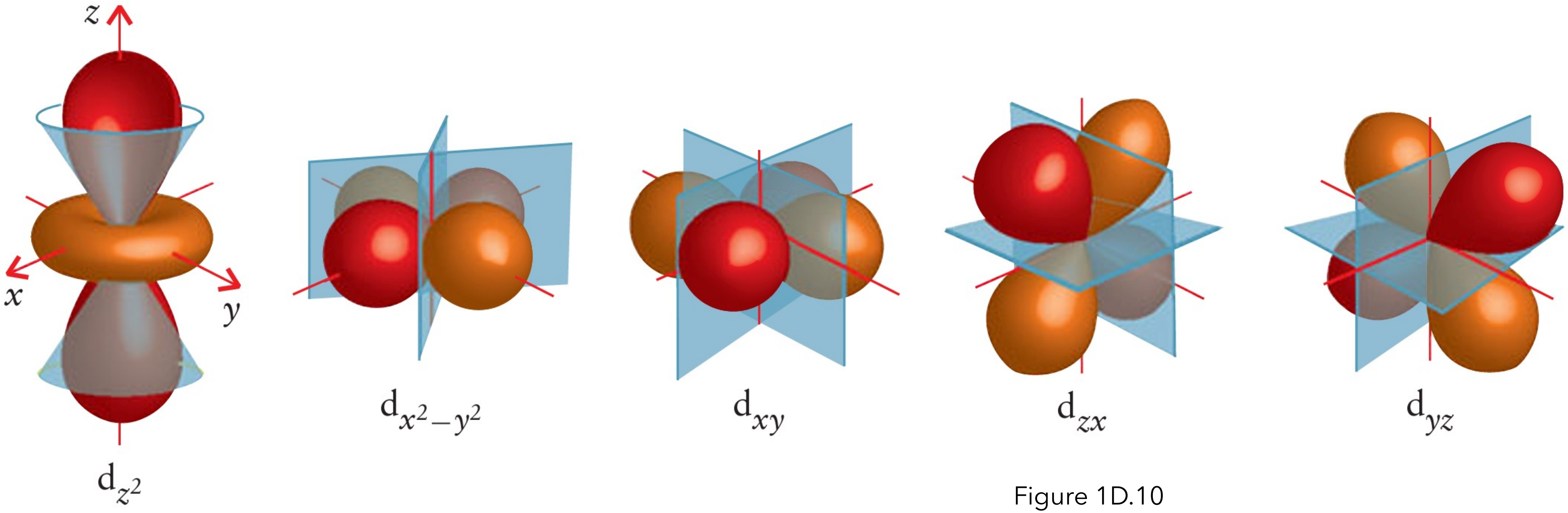
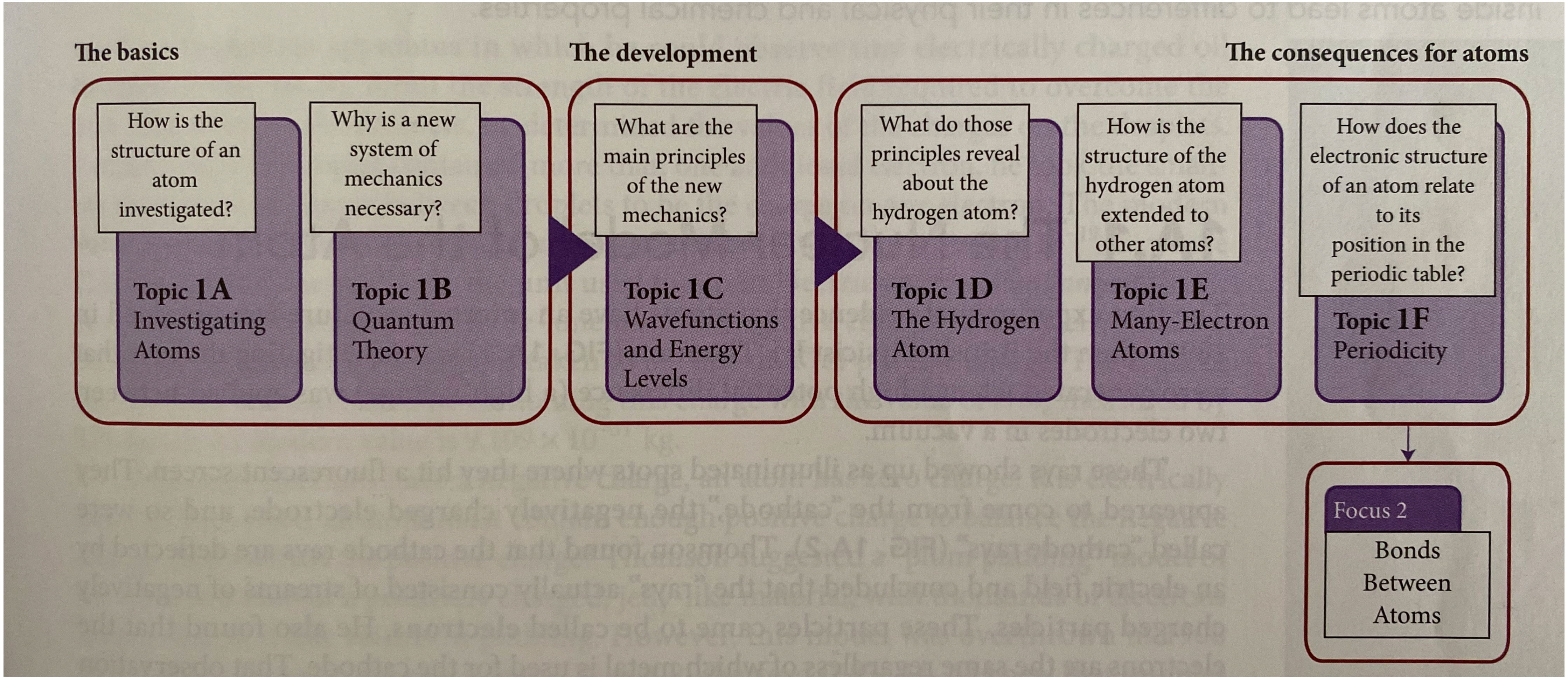


Figure 1D.10

Overview Chapter 1 (Focus 1: Atoms)



The basics

How is the structure of an atom investigated?

Topic 1A Investigating Atoms

Why is a new system of mechanics necessary?

Topic 1B Quantum Theory

The development

What are the main principles of the new mechanics?

Topic 1C Wavefunctions and Energy Levels

The consequences for atoms

What do those principles reveal about the hydrogen atom?

Topic 1D The Hydrogen Atom

How is the structure of the hydrogen atom extended to other atoms?

Topic 1E Many-Electron Atoms

How does the electronic structure of an atom relate to its position in the periodic table?

Topic 1F Periodicity

Focus 2

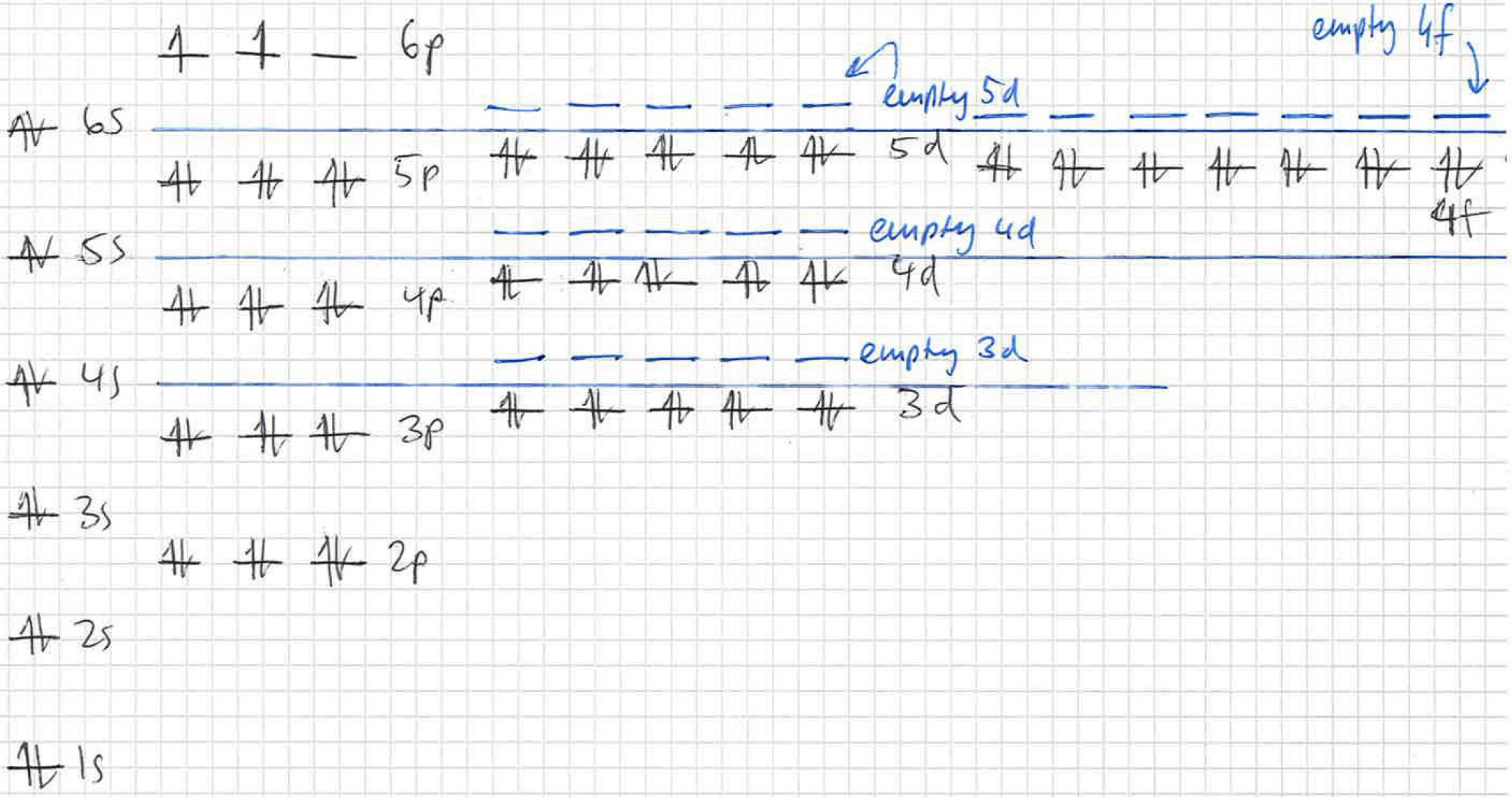
Bonds Between Atoms

1E.2 The building-up principle

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

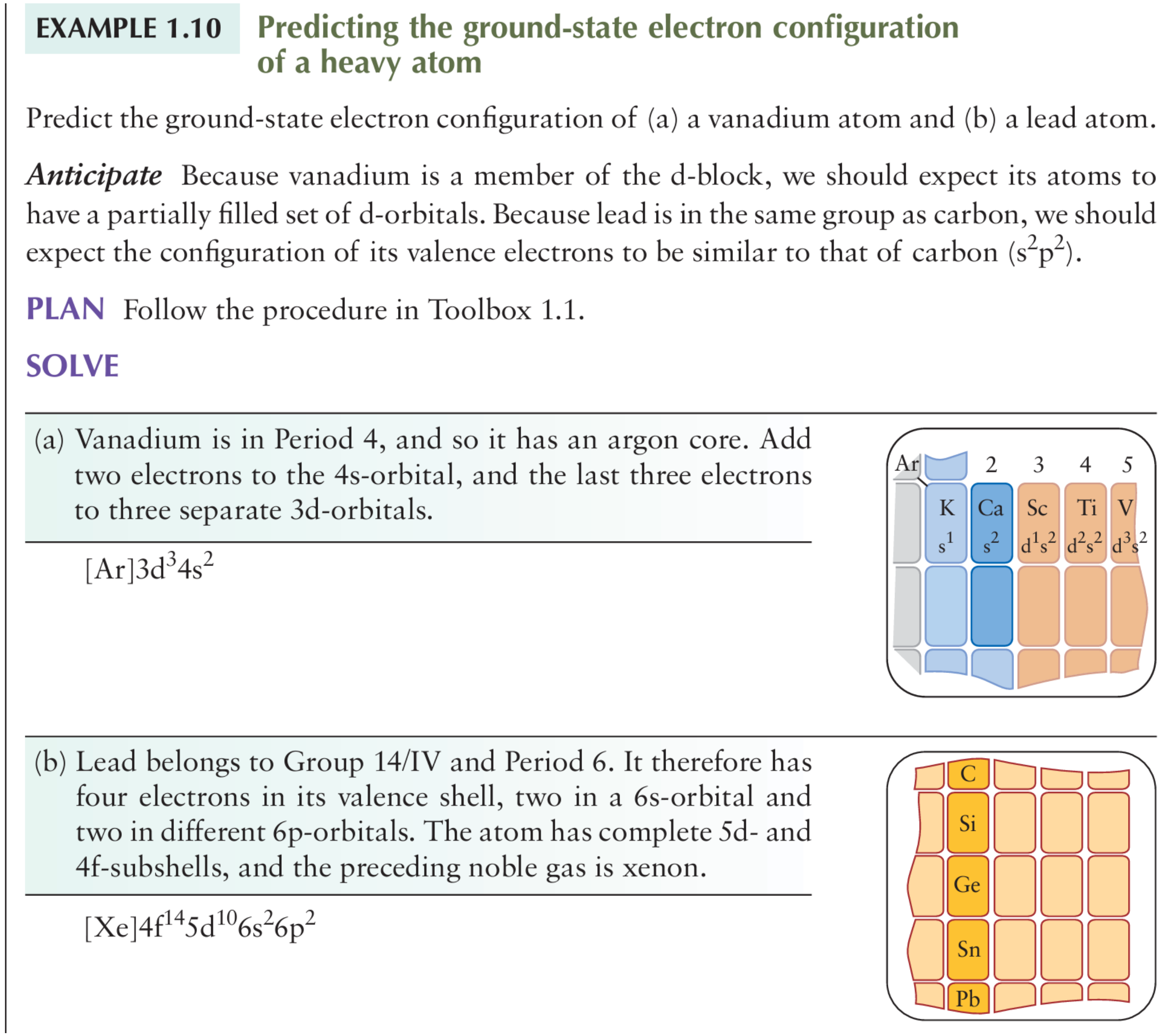
- (a) vanadium
- (b) lead

Pb : $Z = 82$ $[\mathrm{Xe}]\,4f^{14}5d^{10}6s^{2}6p^{2}$



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.

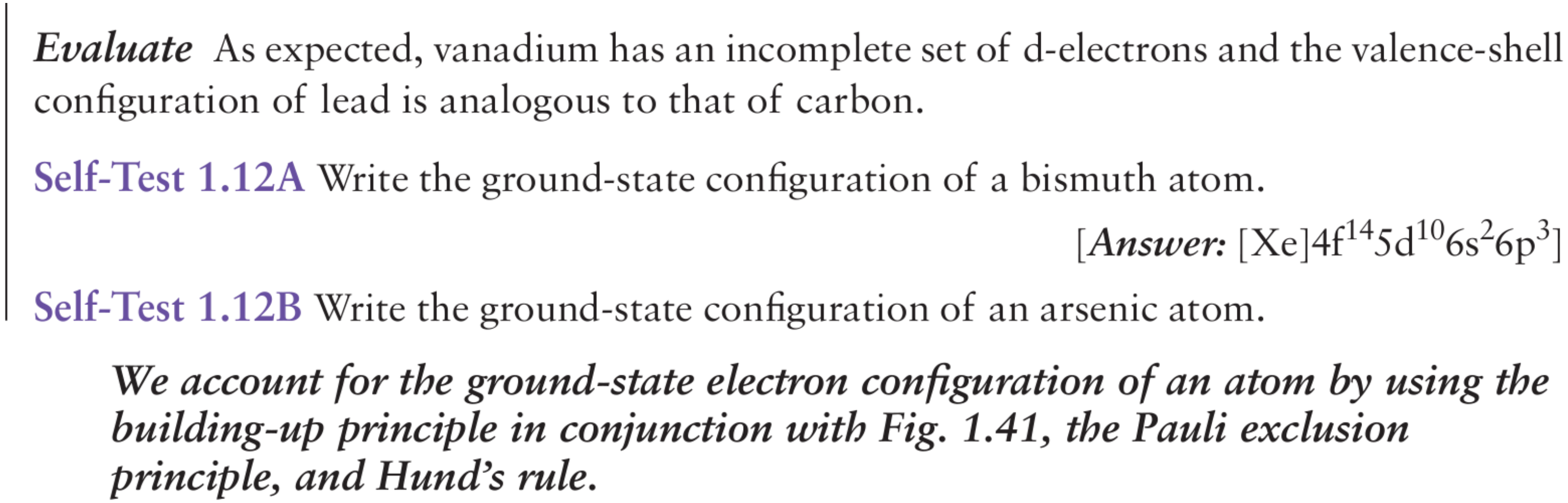
$[Ar]3d^3 4s^2$

(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.

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

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:*** [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.

Periodicity

Topic 1F

Topic 1F.1 Atomic radius
Topic 1F.2 Ionic radius
Topic 1F.3 Ionization energy
Topic 1F.4 Electron affinity
Topic 1F.5 Electronegativity
Topic 1F.6 The general properties of the elements

WHY DO YOU NEED TO KNOW THIS MATERIAL?

- The periodic table summarizes trends in the properties of the elements. The ability to **predict the properties of an element from its location** in the periodic table is a central skill of a chemist.

WHAT DO YOU NEED TO KNOW ALREADY?

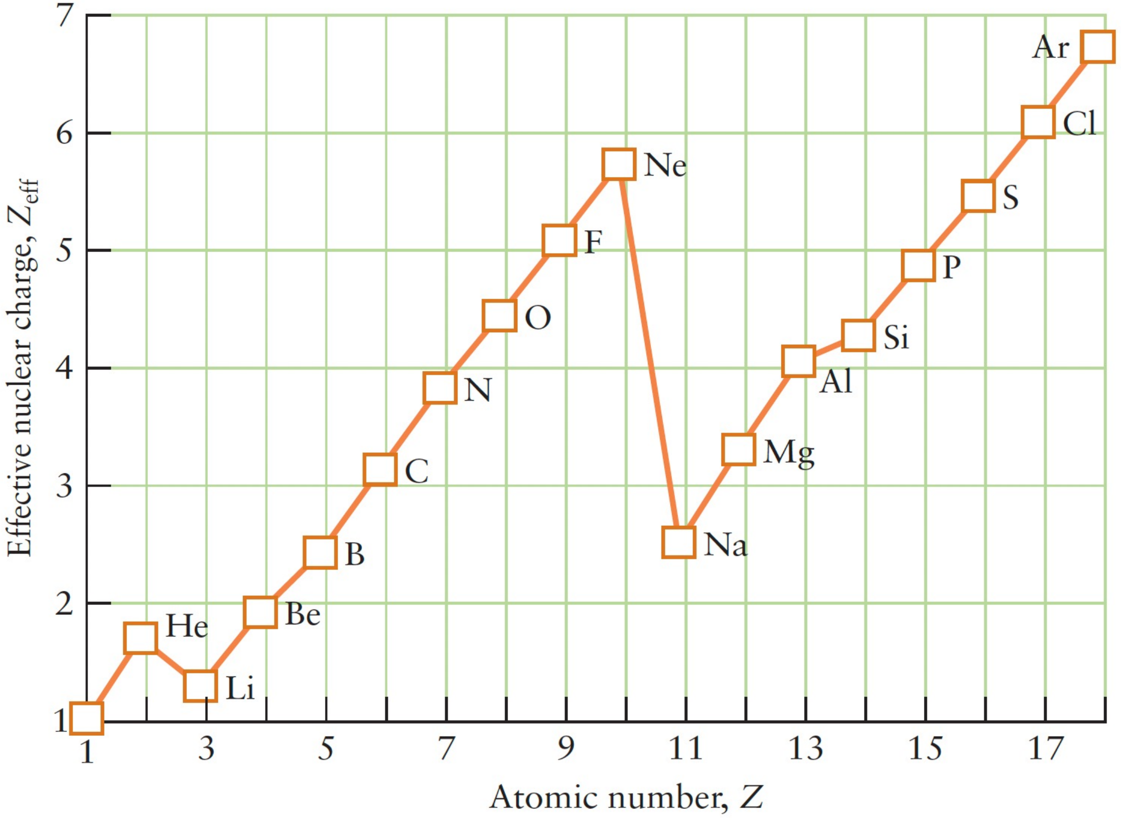
- The structure of the **periodic table**, the **building-up principle** (Topic 1E)
- **Oxidation state** (Fundamentals K)
- Definition of **ionization energy** (Topic 1D)

1F.1 Atomic radius

Effective nuclear charge, Z_{eff}

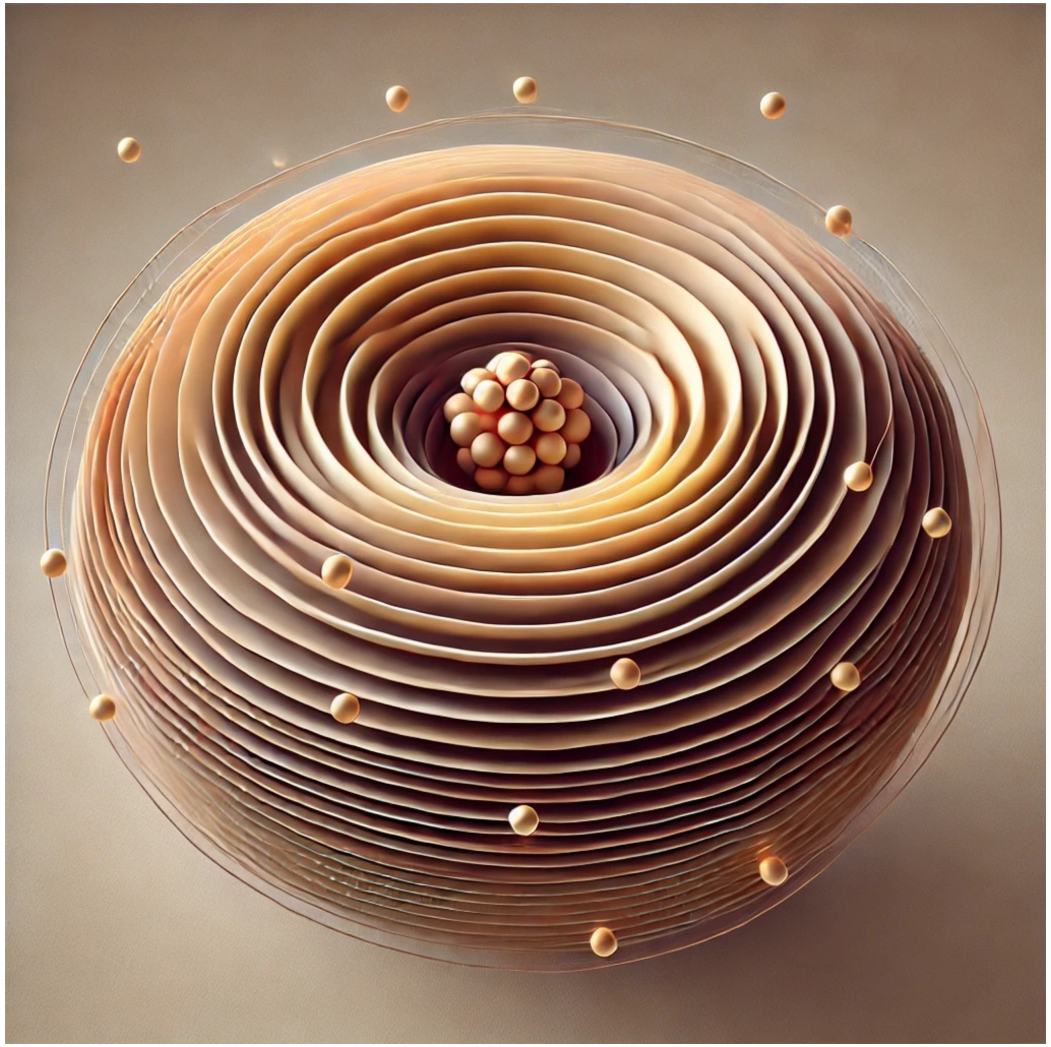
- The **effective nuclear charge** is the net positive charge that a valence electron actually feels after accounting for the shielding effect of inner electrons.
- The **effective nuclear charge**, $Z_{eff}e$, is always smaller than Ze.
- $Z_{eff}e$: To convert Z_{eff} into a **physical force** or **potential energy** that the electron experiences, you multiply Z_{eff} by the elementary charge e.

Figure 1F.1



1F.1 Atomic radius

Shielding



Atomic Radius

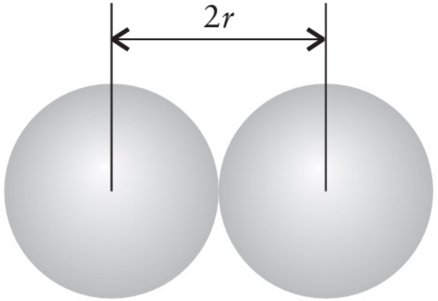
Topic 1F.1

1F.1 Atomic radius

Different types of radii

- Electron clouds don't have sharp boundaries → exact radius of an atom unknown
- **Edge of atom**: when electron density of atom falls off sharply = atomic radius
- The atomic radius of an element is defined as the half distance between the centers of neighbouring atoms.
- If the element is a **metal**, its **atomic radius** is taken to be half the distance between the centers of neighbouring atoms in a solid sample

E.g. the distance between two neighbouring nuclei in solid copper is 256 pm, the atomic radius of copper is 128 pm



Atomic radius

1F.1 Atomic radius

Different types of radii

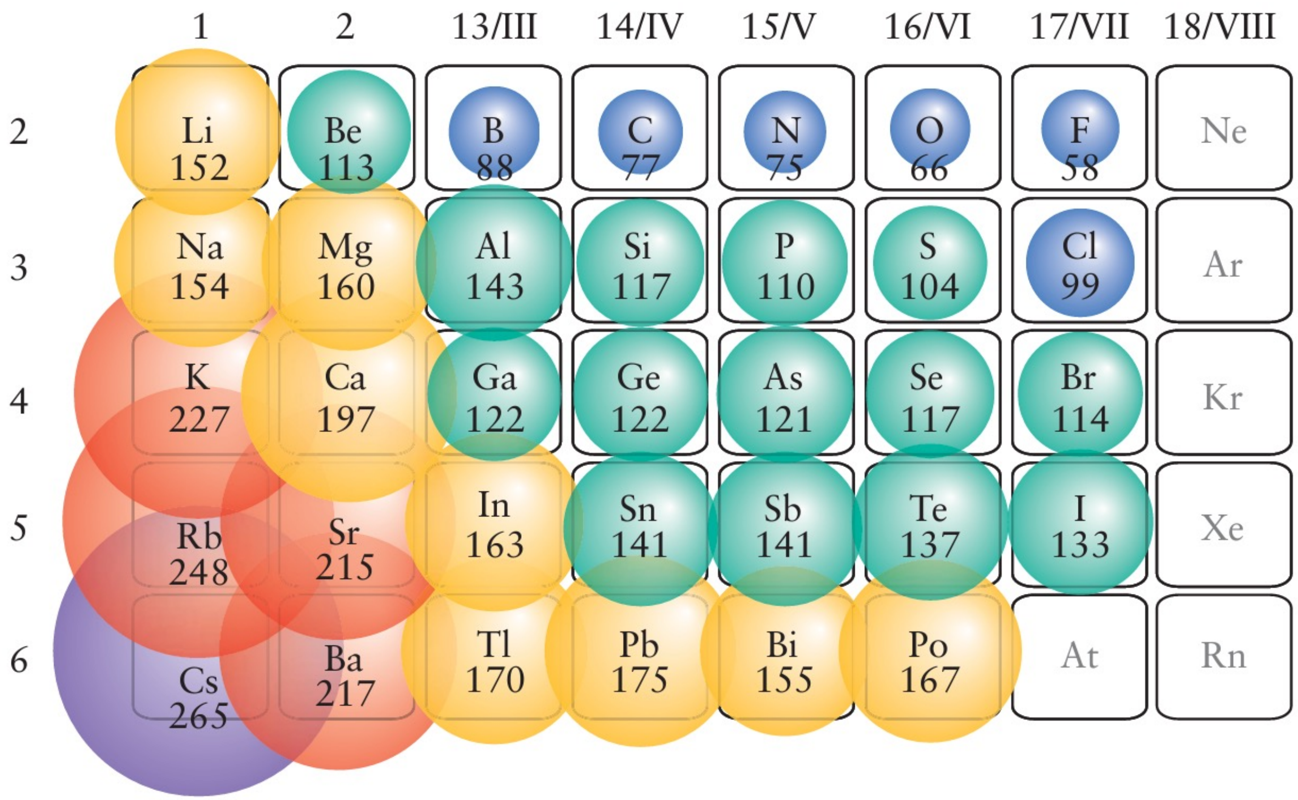
- If the element is a **nonmetal** or a **metalloid**, half the distance between the nuclei of atoms joined by a chemical bond is used; this radius is also called the **covalent radius** of the elements for reasons explained in Topic 2D.

E.g. the distance between the nuclei in Cl_2 is 198 pm, and so the covalent radius of chlorine is 99 pm.

- If the element is a noble gas, the **van der Waals radius** is used, which is half the distance between the centers of neighbouring atoms in a sample of the gas that has been solidified.
- Atoms are not bonded together in a noble gas, van der Waals radii are generally much larger than covalent radii → **not included in discussion of trends**

1F.1 Atomic radius

Atomic radii of main-group elements



	1	2	13/III	14/IV	15/V	16/VI	17/VII	18/VIII
2	Li 152	Be 113	B 88	C 77	N 75	O 66	F 58	Ne
3	Na 154	Mg 160	Al 143	Si 117	P 110	S 104	Cl 99	Ar
4	K 227	Ca 197	Ga 122	Ge 122	As 121	Se 117	Br 114	Kr
5	Rb 248	Sr 215	In 163	Sn 141	Sb 141	Te 137	I 133	Xe
6	Cs 265	Ba 217	Tl 170	Pb 175	Bi 155	Po 167	At	Rn

Figure 1F.2

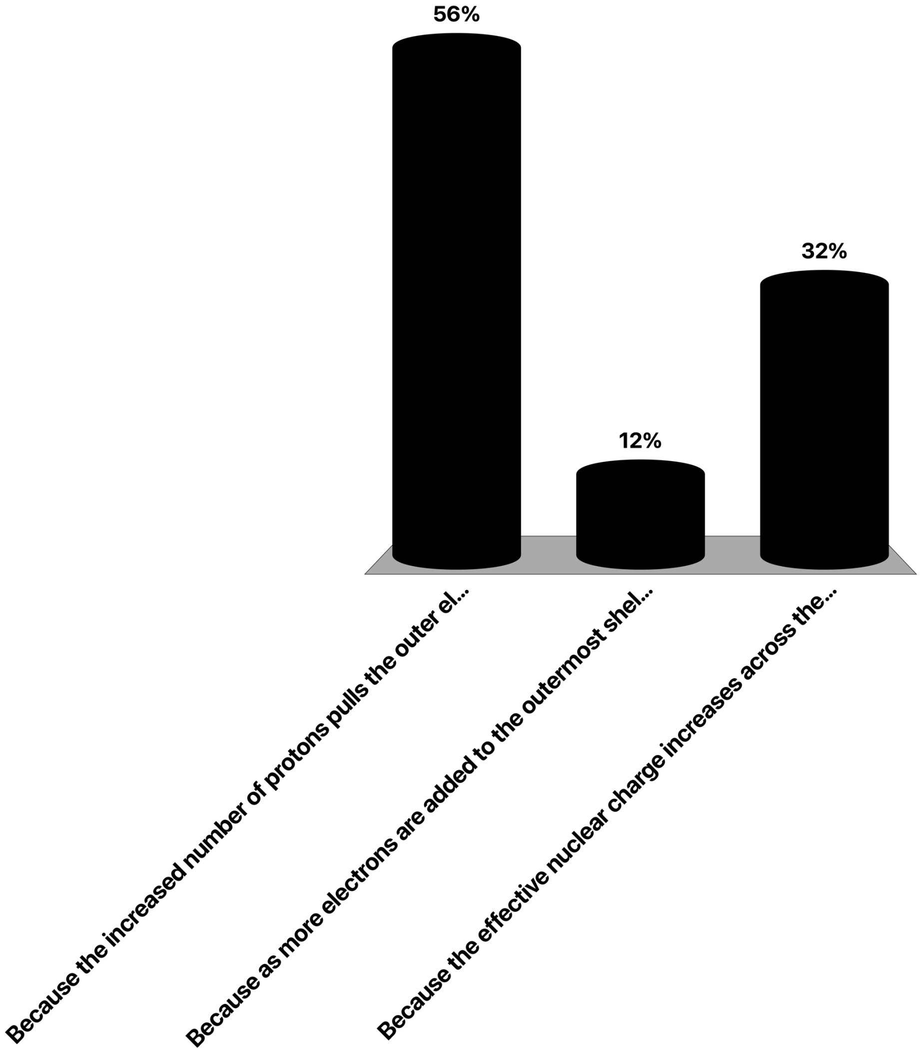
TREND: Atomic radius generally decreases from left to right across a period and increases down a group.

Why do atomic radii decrease across a period in the periodic table, even though the number of electrons and protons increases?

A) Because the increased number of protons pulls the outer electrons closer to the nucleus, and the added electrons do not effectively shield one another from the increased nuclear charge.

B) Because as more electrons are added to the outermost shell, they repel each other strongly, causing the nucleus to shrink.

C) Because the effective nuclear charge increases across the period



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Atomic radii of main-group elements

TREND: Atomic radius generally decreases from left to right across a period and increases down a group.

Increase down a group (e.g. from Li to Cs): with each new period, outermost electrons occupy shells with higher principal quantum numbers, farther and farther away from nucleus.

Decrease across period (e.g. From Li to Ne): surprising at first because number of electrons increases with number of protons. The new electrons are **in the same shell** of the atom and about as close to the nucleus as the other new electrons in the shell. However, because they are spread out in the shell, the electrons do not shield one another well from the nuclear charge, so the effective nuclear charge increases across the period.

The increasing effective nuclear charge on valence electrons draws the electrons in → the atom is more compact.

1F.1 Atomic radius

The periodic variation of the atomic radii of the elements

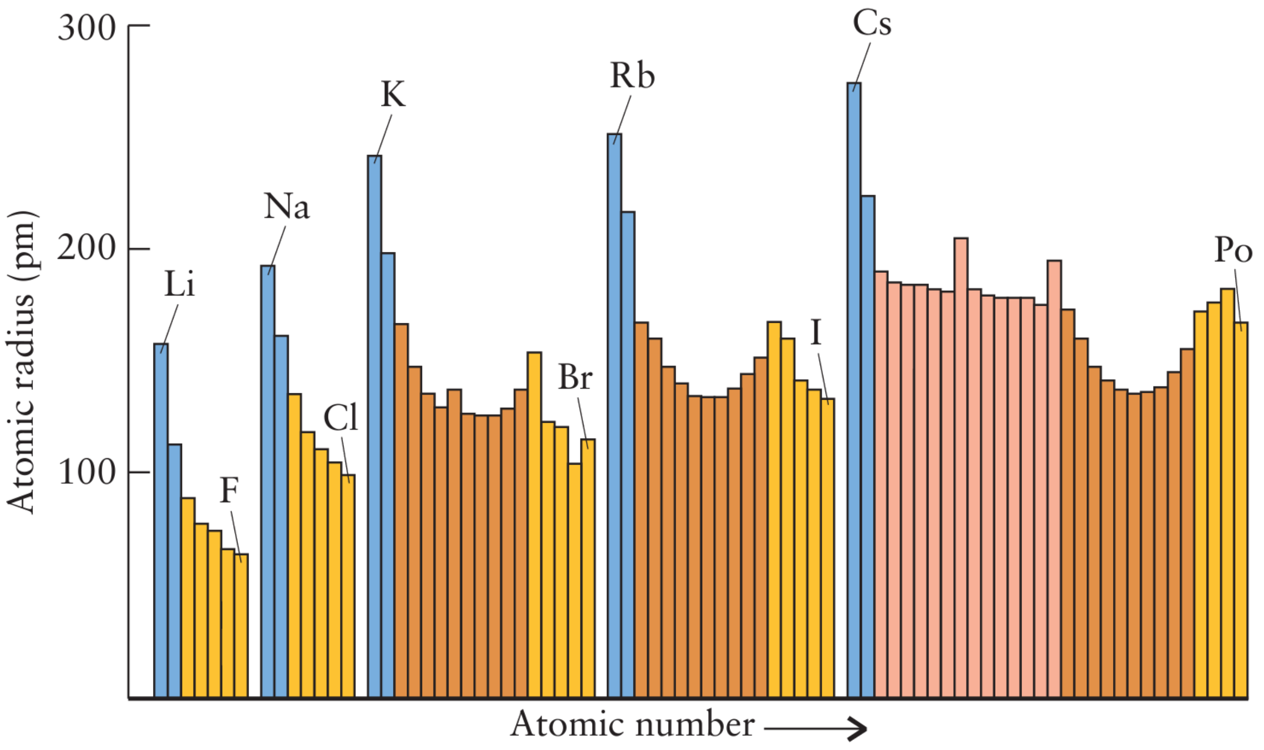


Figure 1F.3

Blue: s-block
Yellow: p-block
Orange: d-block
Salmon: f-block

TREND: Atomic radius generally decreases from left to right across a period and increases down a group.

1F.1 Atomic radius

Summary

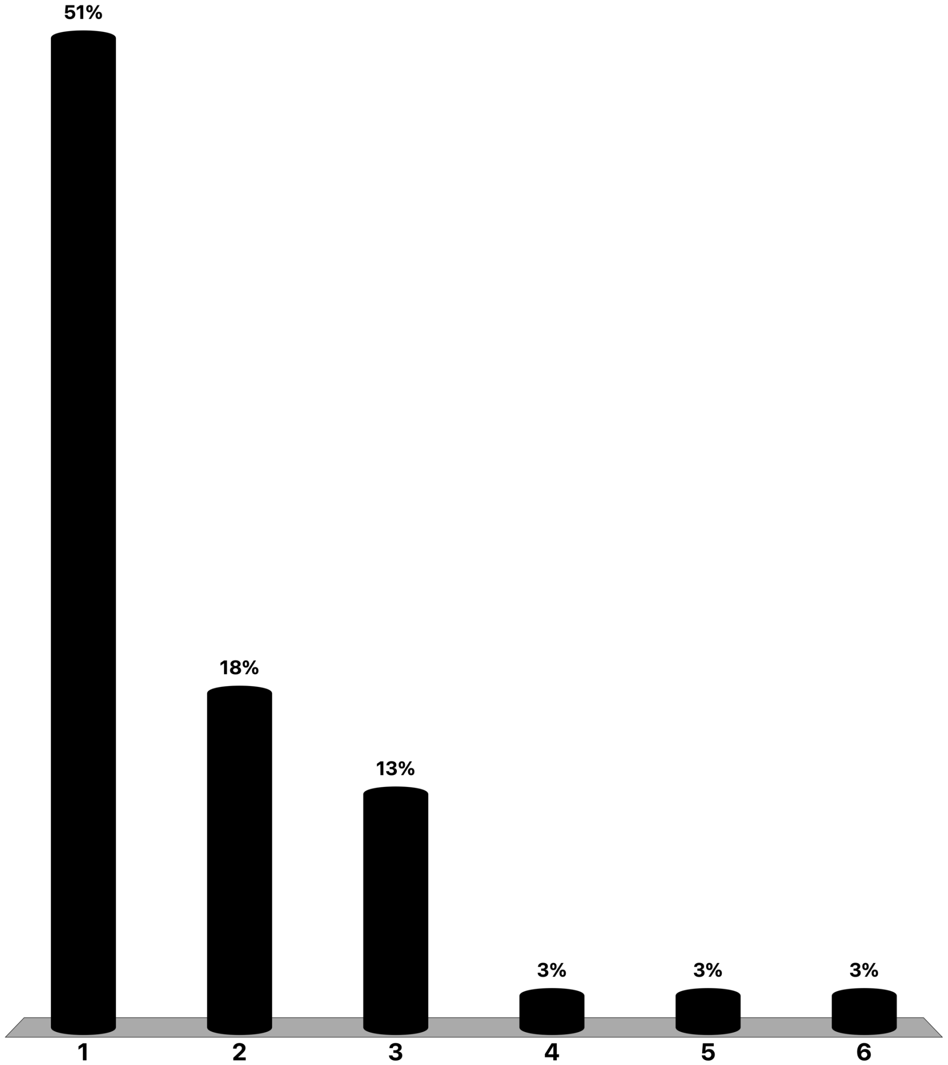
TREND: Atomic radii generally decrease from left to right across a period as the effective nuclear charge increases, and they increase down a group as successive shells are occupied.

What's the elemental symbol of the largest known element in the periodic table?

Rank	Responses
1	FR
2	CS
3	FRANCIUM
4	AC
5	FR
6	NOBLE GAS

Keyword: Fr

Keyword Matches: 20



1F.1 Atomic radius

Francium

Francium was discovered in 1939 by Marguerite Perey, a physicist at the Radium Institute in Paris, France. Photo kindly provided by Musée Curie (Coll. ACJC), Institut Curie, Centre National de la Recherche Scientifique, Paris, France.

87

Fr

Francium

(223)

Ionic Radius

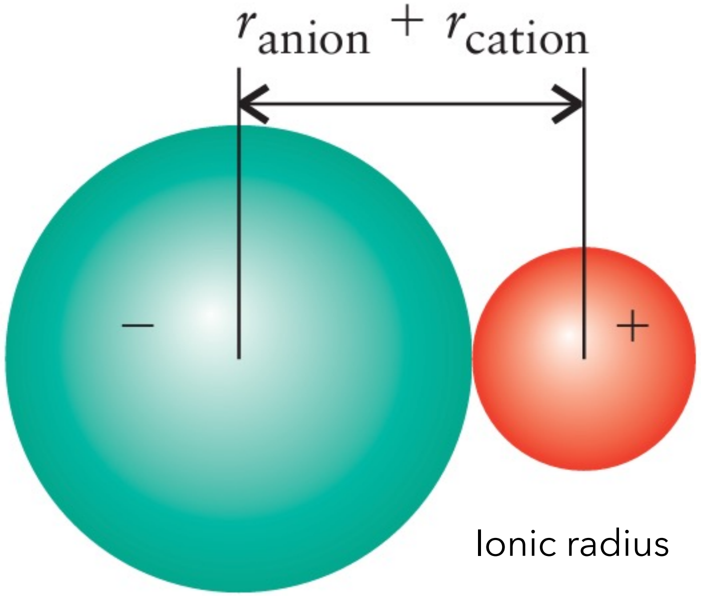
Topic 1F.2

Another type of radius: ionic radius

- The radii of ions are **very different** to the radii of their parent atoms.

How is it measured:

- Each ion in an ionic solid is surrounded by ions of opposite charge.
- The ionic radius of an element is its share of the distance between neighboring ions in an ionic solid.
- In practice, the radius of the oxide ion is taken to be 140. pm, and the radii of other atoms are calculated on the basis of that value.
- For example, Mg^{2+} and O^{2-} ions in magnesium is 212 pm, the radius of the Mg^2+ ion is reported as 212 - 140. pm = 72 pm.



Ionic radius

Ionic radii of the ions of the main-group elements

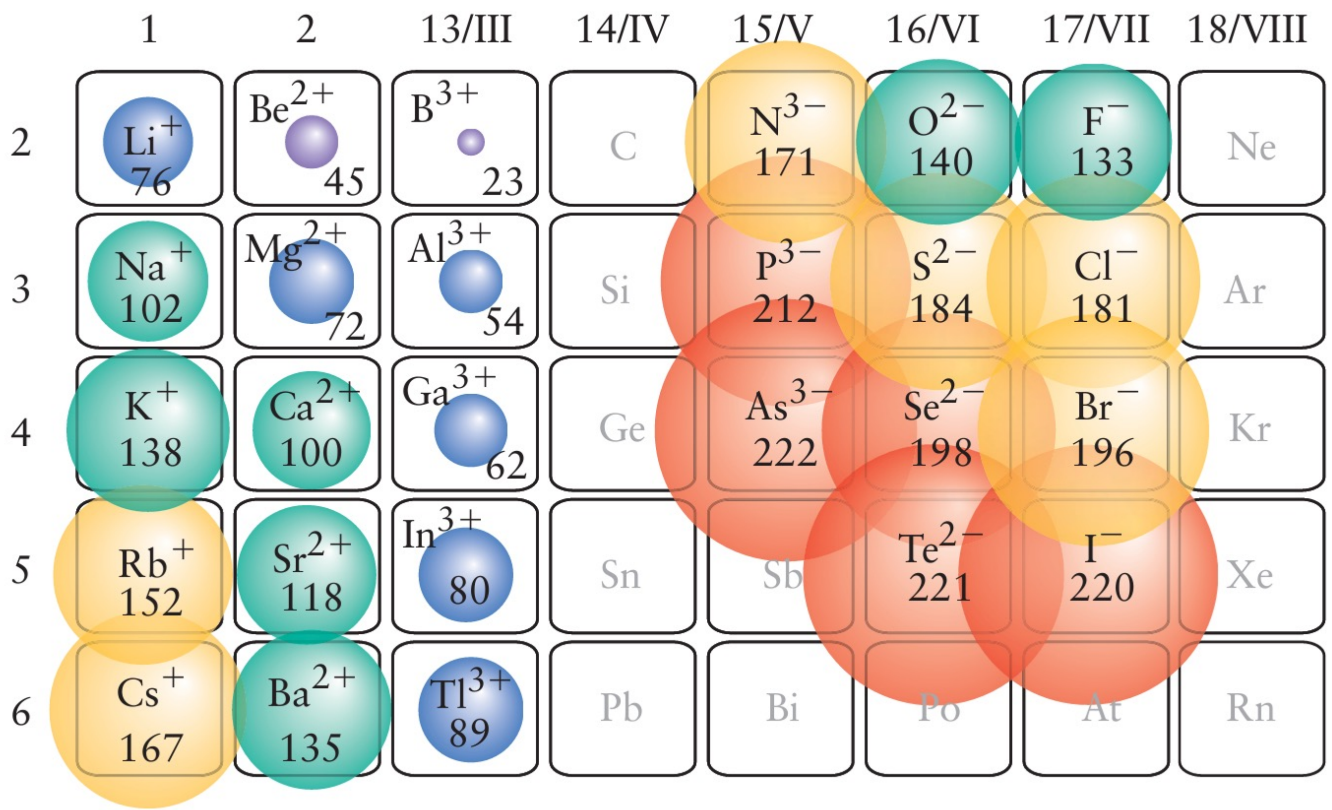


Figure 1F.4

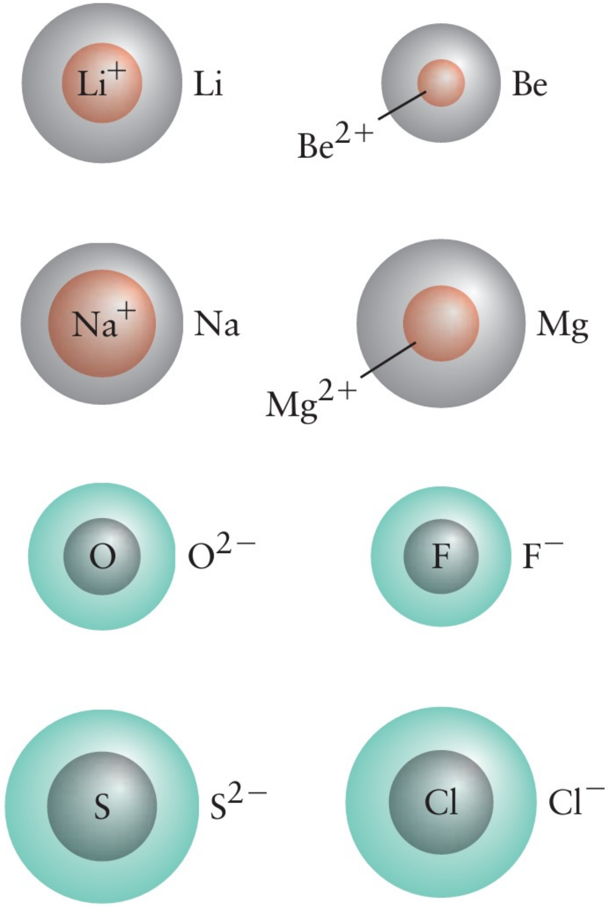
TREND: Cations are smaller than their parent atoms, whereas anions are larger.

1F.2 Ionic radius

Ionic radii of the ions of the main-group elements

- **Anions are larger than their parent atom**: increased number of electrons in the valence shell plus repulsive effects by electrons on one another.
- **Isoelectronic:** atoms and ions with the same number of electrons.
- Na^+, F^-, and Mg^{2+} are isoelectronic with their electronic configuration $[He]2s^22p^6$. Radii differ!

Figure 1F.5



TREND: Cations are smaller than their parent atoms, whereas anions are larger.

1F.2 Ionic radius

Example 1F.1 Predicting the relative sizes of ions

- Arrange each of the following pairs of ions in order of increasing ionic radius

(a) Mg^{2+} and Ca^{2+}

(b) O^{2-} and F^{-}

Example 1F.1 Predicting the relative sizes of ions

EXAMPLE 1.11 **Deciding the relative sizes of ions**

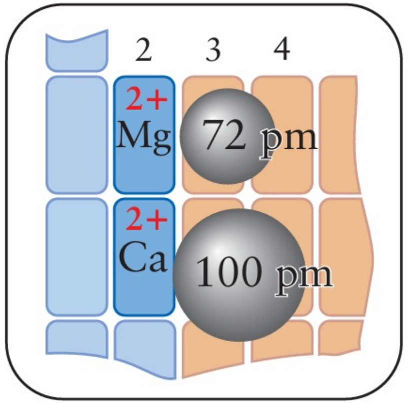
Arrange each of the following pairs of ions in order of increasing ionic radius: (a) Mg^{2+} and Ca^{2+}; (b) O^{2-} and F^{-}.

PLAN The smaller member of a pair of isoelectronic ions in the same period will be an ion of an element that lies farther to the right in a period, because that ion has the greater effective nuclear charge. If the two ions are in the same group, the smaller ion will be the one that lies higher in the group, because its outermost electrons are closer to the nucleus.

SOLVE

(a) Mg lies above Ca in Group 2.

Mg^{2+} has the smaller ionic radius.

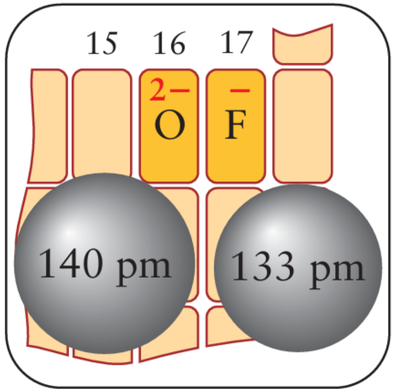


1F.2 Ionic radius

Example 1F.1 Predicting the relative sizes of ions

(b) F^- lies to the right of O in Period 2.

F^- has the smaller ionic radius.



Evaluate Appendix 2C shows that the actual values are (a) 72 pm for Mg^{2+} and 100 pm for Ca^{2+}; (b) 133 pm for F^- and 140 pm for O^{2-}.

Self-Test 1.13A Arrange each of the following pairs of ions in order of increasing ionic radius: (a) Mg^{2+} and Al^{3+}; (b) O^{2-} and S^{2-}.

[***Answer:*** (a) $r(Al^{3+}) < r(Mg^{2+})$; (b) $r(O^{2-}) < r(S^{2-})$]

Self-Test 1.13B Arrange each of the following pairs of ions in order of increasing ionic radius: (a) Ca^{2+} and K^+; (b) S^{2-} and Cl^-.

1F.2 Ionic radius

Summary

TREND: Ionic radii generally increase down a group and decrease from left to right across a period. Cations are smaller than their parent atoms, and anions are larger.

Student questions

1. Why does the 3d and 4f orbitals' energy get lowered when occupied? Do the 3p or 4p orbital energies also get lowered when occupied? Why does the 4p orbital not become lower compared to the 4s orbital when filled, similar to how the 3d orbital energy becomes lowered below the 4s orbital energy when filled?

Answer: Most orbitals become more stable when filled with electrons. The 3d orbitals in particular become lower in energy when filled because the added electrons experience stronger attraction to the nucleus (due to **increased effective nuclear charge**). This makes the 3d orbitals lower in energy than the 4s orbital after filling.

The question is how close in energy are the empty and filled orbitals to the other orbitals. The 3d orbitals are very close in energy to the 4s orbitals and only slightly higher than them when empty. The filling with electrons stabilizes the 3d orbitals and this stabilization happens to make them lower in energy than the 4s orbitals. The same trend can be observed for the 4f orbitals compared with the 6s orbitals.

The p-orbitals have a larger energy gap compared to the s-orbitals and even after filling them, they will not be close in energy to the s-orbitals.

Student questions

2. Exam question: «The difference between two successive energy levels of an electron in a one-dimensional box decreases as n decreases." Why false?

Answer: this statement is **true**, the solution online was incorrect. We fixed this.

3. Comment: There was a typo on last week's problem set solutions.

Answer: Exercise 4.9 mistakenly referred to argon instead of arsenic. We fixed this.

4. Comment: The answer in exercise 3.4 c) was misleading.

Answer: Please disregard this statement from the solution, it is incorrect: "This can lead to the electron moving faster within the atom or potentially being ejected from the atom entirely, a phenomenon known in atomic physics as the photoelectric effect. " We will fix this and upload a new version.

Student questions

5. Example 1D.1, why is the probability calculated by taking the ratio of $\psi(x)^2$ and not the ratio of $\psi(x)^2 \times dV$ because the probability is given by $P(x) = \psi(x)^2 \times dV$?

In Example 1D.1, we calculated the probability of finding an electron at a certain location. The **probability** $P(x, t)$ is the likelihood of finding the particle in a specific **region** of space, not just at a single point. To get the probability, you must integrate the **probability density** over that region.

For example, the probability of finding the particle in a very small volume element dV around point x is given by:

$$P(x) = \psi(x)^2 \times dV$$

In general, for any region R, the probability is calculated by summing (integrating) the probability density $\psi(x)^2$ over the entire region R:

$$P(R) = \int \psi(R)^2 dV$$

However, you are not expected to solve integrals or derivatives at the exam, thus, this example includes an approximation that does not require solving an integral: We focus on the relative probability of finding an electron in a small region a distance a_0 from the nucleus relative to the probability of finding it **in the same small region** located right at the nucleus. Since the volume element dV is the same in both cases, it cancels out, and the ratio of probabilities is given by:

$$\frac{P(r = a_0)}{P(r = 0)} = \frac{\Psi^2(a_0) \times dV}{\Psi^2(0) \times dV} = \frac{\Psi^2(a_0)}{\Psi^2(0)}$$