CHEM110 – Chapter 4
Atomic Energy Levels

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True or false: The position of a moving electron can always be known.

A. True
B. False

4.4 Quantisation and Quantum Numbers

- **Atoms have unique electronic energy levels → property of the bound electrons**

- **Quantized**

- **Bound electrons have properties relating to their energies and 'shapes' of their waves**

4.4 Quantisation and Quantum Numbers

- **Bound electrons**
  - **Can undergo transitions from one bound state to another**
  - **Quantized energies**

- **Free electrons**
  - **With enough energy electron can be removed**
  - **Can have any energies**

4.4 Quantisation and Quantum Numbers

- **Emission and absorption spectra → experimental values for quantised energies of electrons**

- **Quantum mechanics → mathematical links quantised energies with wave characteristics of electrons**

4.4 Quantisation and Quantum Numbers

Wave properties of atomic electrons are described by the

Schrödinger Equation

$$\boxed{\hat{H}\psi = E\psi}$$

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4.4 Quantisation and Quantum Numbers

Schrödinger Equation

$$\boxed{\hat{H}\psi = E\psi}$$

- Solutions only for specific energy values
- For each quantised energy value → Schrödinger equation generates a wavefunction (ψ) that gives information about an electrons position
- ψ^2 tells us how the electrons are distributed in space
- A one-electron wavefunction is called an orbital
- Orbitals have properties

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4.4 Quantisation and Quantum Numbers

- Each quantised property can be identified using a quantum number
- Each electron in an atom has three quantum numbers that specify properties
- A fourth number describes the spin

4.4 Quantisation and Quantum Numbers

- **Principal quantum number *n***
  - Positive integer (n = 1,2,3…)
  - n is correlated with orbital **size**
  - As n increases:
    - Energy of the electron increases
    - Electrons orbital gets bigger
    - Electron less tightly bound to the atom

4.4 Quantisation and Quantum Numbers

- **Azimuthal quantum number *l***
  - Indexes the angular momentum of the orbital
  - Identifies the **shape** of the **electron distribution within the orbital**
  - $l = 0, \ldots, n-1$

Value of *l*	*0*	*1*	*2*	*3*	*4*
Orbital designation	*s*	*p*	*d*	*f*	*g*

4.4 Quantisation and Quantum Numbers

- **Magnetic quantum number m_l**
  - Indexes the restricted numbers of possible orientations
  - m_l can be any positive or negative integer between 0 and l → $m_l = 0, \pm 1, \pm 2, \ldots$
  - $2l + 1$ possible values for m_l

4.4 Quantisation and Quantum Numbers

Magnetic quantum number m_l

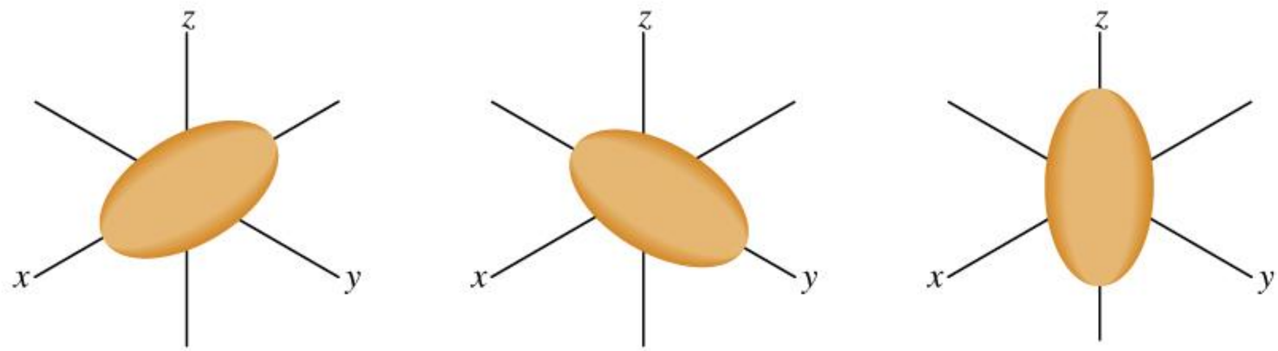

Figure 4.24 and 4.25

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4.4 Quantisation and Quantum Numbers

- **Spin quantum number m_s**
  - All electrons have a property called spin
  - This means that they can behave in one of two ways in a magnetic field
  - Spin quantum number indexes this behaviour
  - $m_s = \pm \frac{1}{2}$

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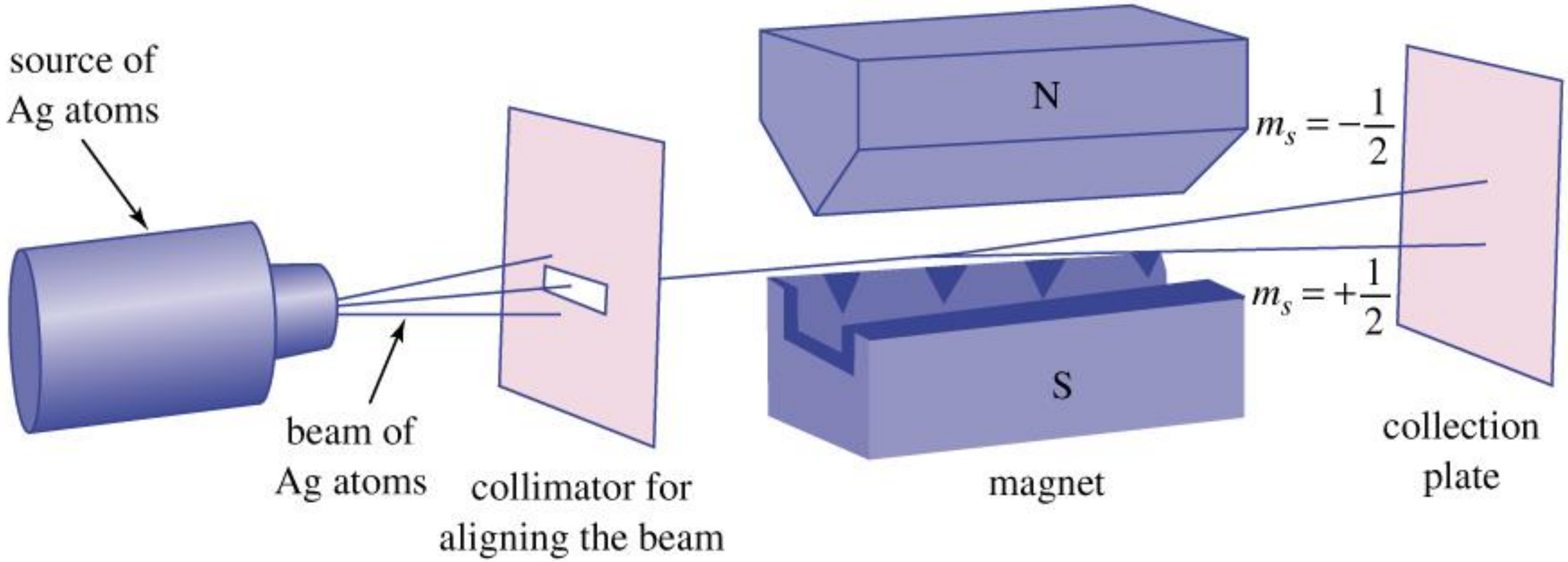
4.4 Quantisation and Quantum Numbers

Figure 4.26



4.4 Quantisation and Quantum Numbers

- **Pauli Exclusion Principle → each electron in an atom has a unique set of quantum numbers**

- **A direct consequence is that any orbital can contain a maximum of two electrons**

4.4 Quantisation and Quantum Numbers

Complete description of an atomic electron requires a set of four quantum numbers

TABLE 4.2 Restrictions on quantum numbers for electrons in atoms.

Quantum number	Restrictions	Range
n	positive integers	$1, 2, \ldots, \infty$
l	positive integers less than n	$0, 1, \ldots, (n-1)$
m_l	integers between $-l$ and l	$-l, \ldots, -1, 0, +1, \ldots, +l$
m_s	$-\frac{1}{2}$ or $+\frac{1}{2}$	$-\frac{1}{2}, +\frac{1}{2}$

Value of *l*	***0***	***1***	***2***	***3***	***4***
Orbital designation	***s***	***p***	***d***	***f***	***g***

Worked Example 4.8 – page 130

How many valid sets of quantum numbers exists for 4*d* orbitals? Give two examples.

4.5 Atomic Orbital Electron Distributions and Energies

- Chemical properties of atoms determined by behaviour of their electrons

- Atomic electrons are described by orbitals

- Electron interaction can be described by orbital interactions

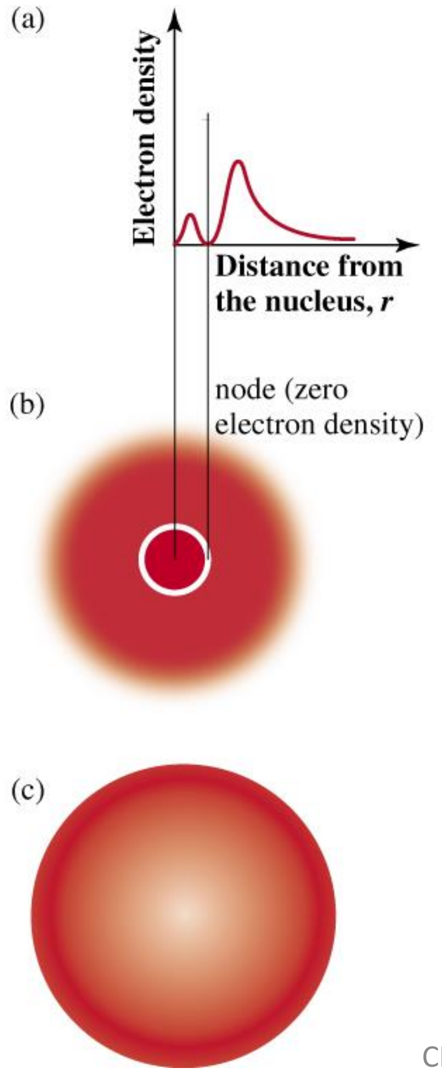
4.5 Atomic Orbital Electron Distributions and Energies

- Wave-like properties cause electrons to be smeared out → describe using electron density
- Where electrons are LIKELY to be found → HIGH electron density
- When energy of an electron changes → size and shape of its distribution changes

4.5 Atomic Orbital Electron Distributions and Energies

Figure 4.27

2s orbital



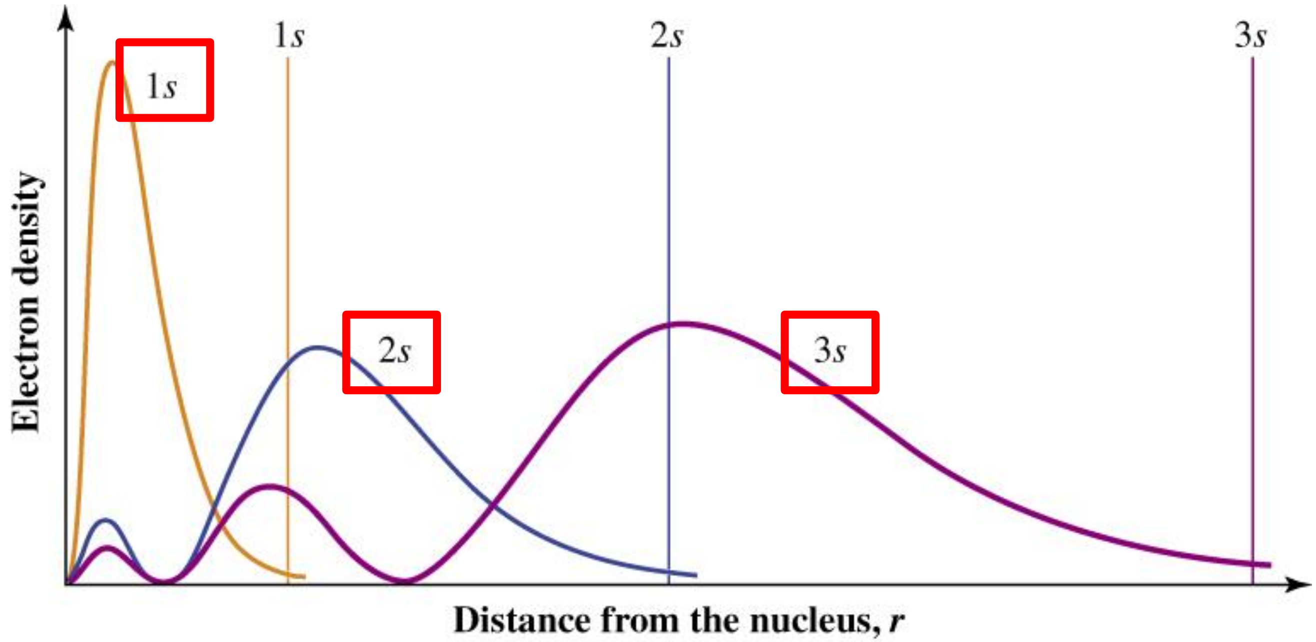
Electron density plot

Electron density picture

Boundary surface diagram

4.5 Atomic Orbital Electron Distributions and Energies

Figure 4.28



As *n* increases → orbitals get larger and # nodes increases

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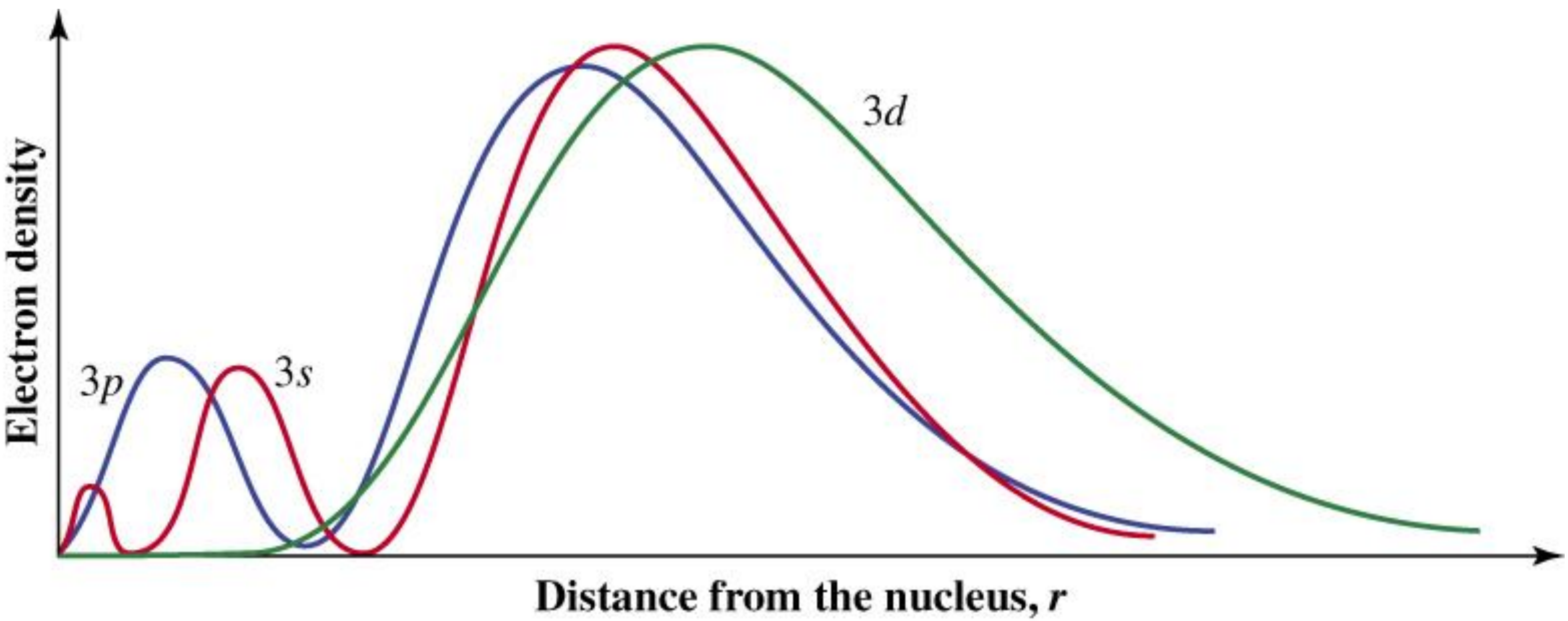
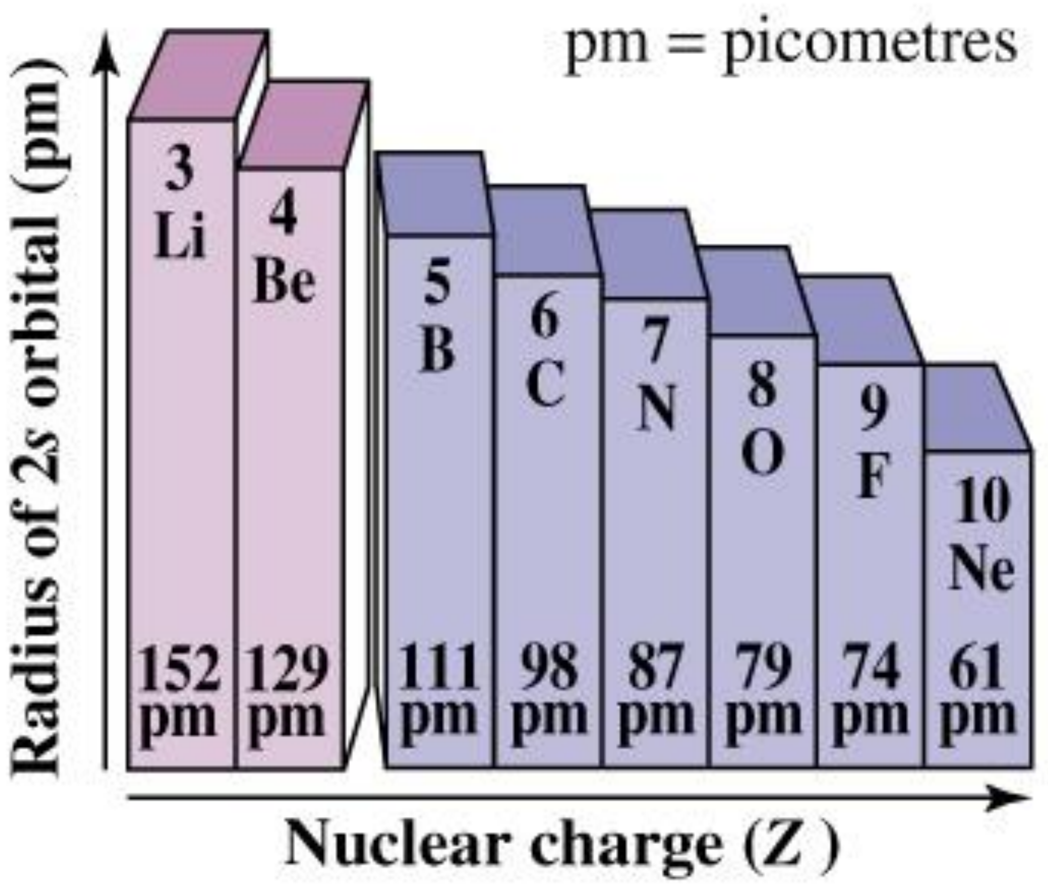
4.5 Atomic Orbital Electron Distributions and Energies

Figure 4.29



4.5 Atomic Orbital Electron Distributions and Energies

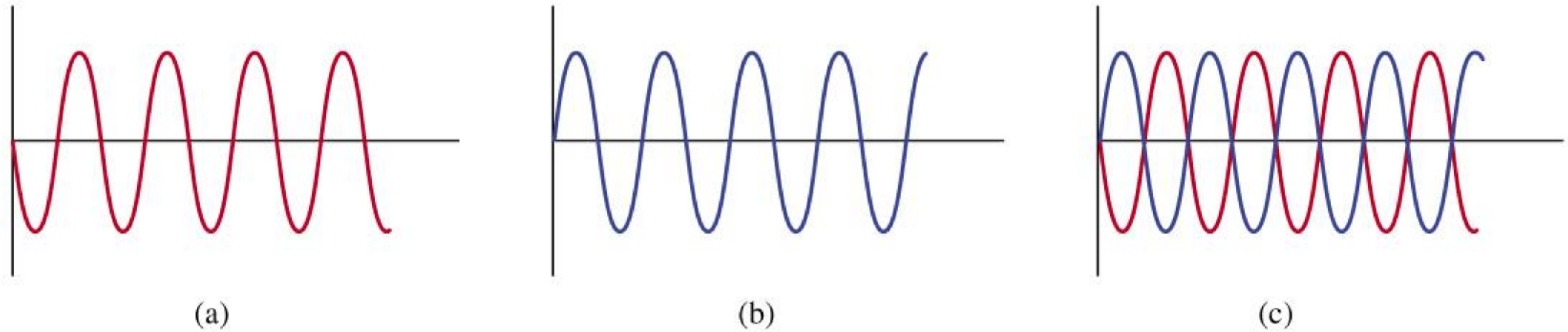


Specific orbitals become smaller as the atomic nuclear charge *Z* increases

4.5 Atomic Orbital Electron Distributions and Energies

- **Electron distribution → strongly influences chemical interactions**
- **Need a detailed picture of ELECTRON DISTRIBUTION**

4.5 Atomic Orbital Electron Distributions and Energies

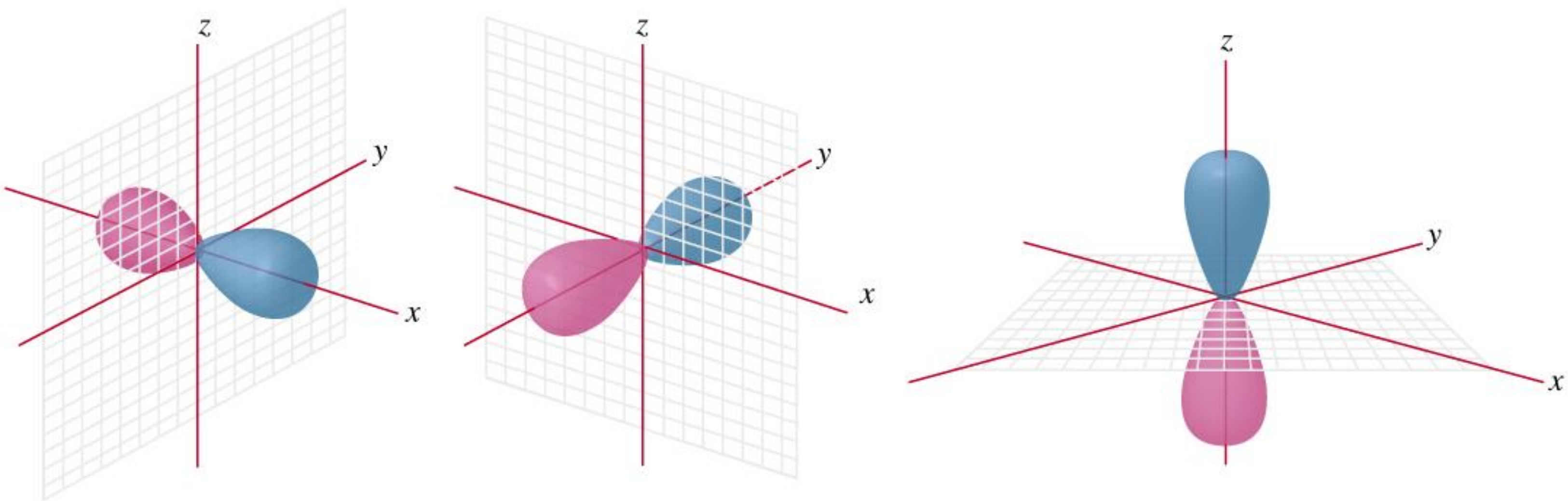


4.5 Atomic Orbital Electron Distributions and Energies

- $l = 0 \rightarrow s$ orbital
- $m_l = 0, \ldots, l - 1 \rightarrow m_l = 0$
- Single phase

4.5 Atomic Orbital Electron Distributions and Energies

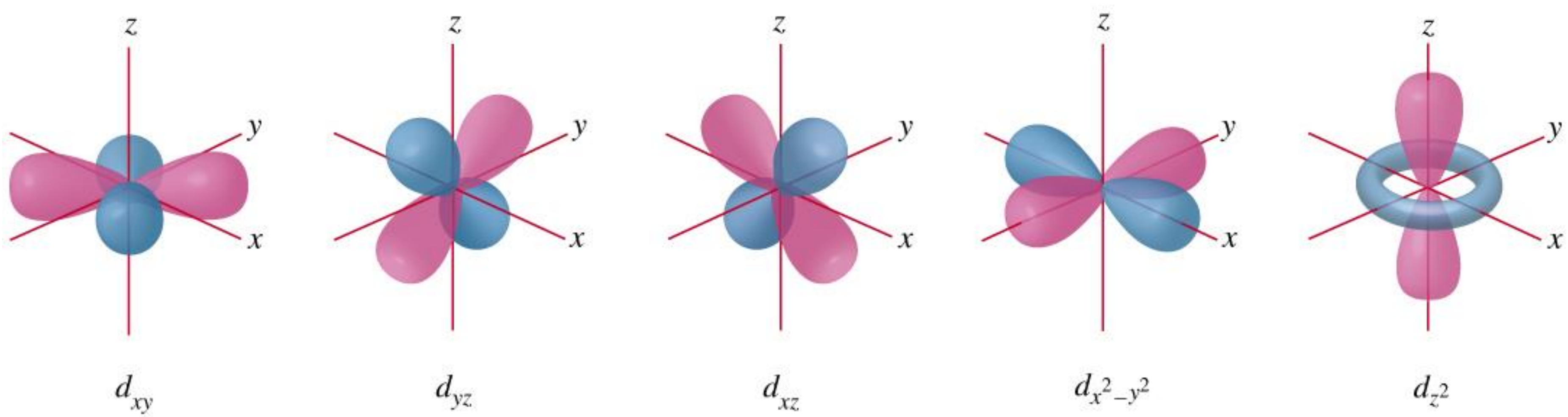
- $l = 1 \rightarrow p$ orbital
- $m_l = 0, \ldots, l - 1 \rightarrow m_l = -1, 0, 1$
- Two lobes have opposite phase



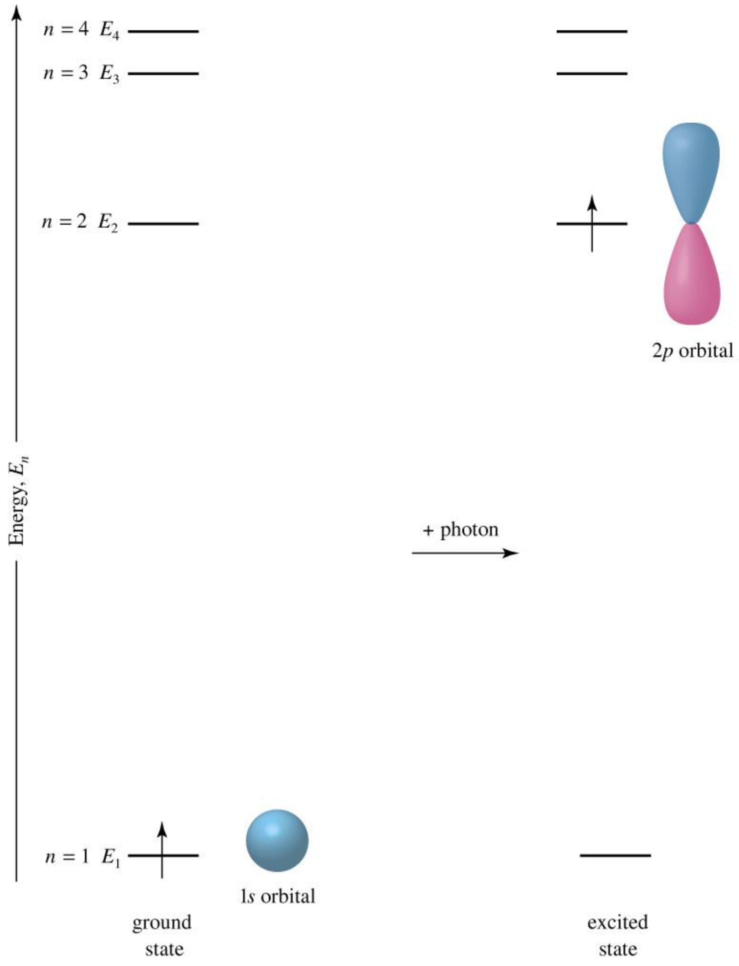
p_x p_y p_z

4.5 Atomic Orbital Electron Distributions and Energies

- **$l = 2 \rightarrow d$ orbital**
- **$m_l = 0, \ldots, l - 1 \rightarrow m_l = -2, -1, 0, 1, 2$**



4.5 Atomic Orbital Electron Distributions and Energies

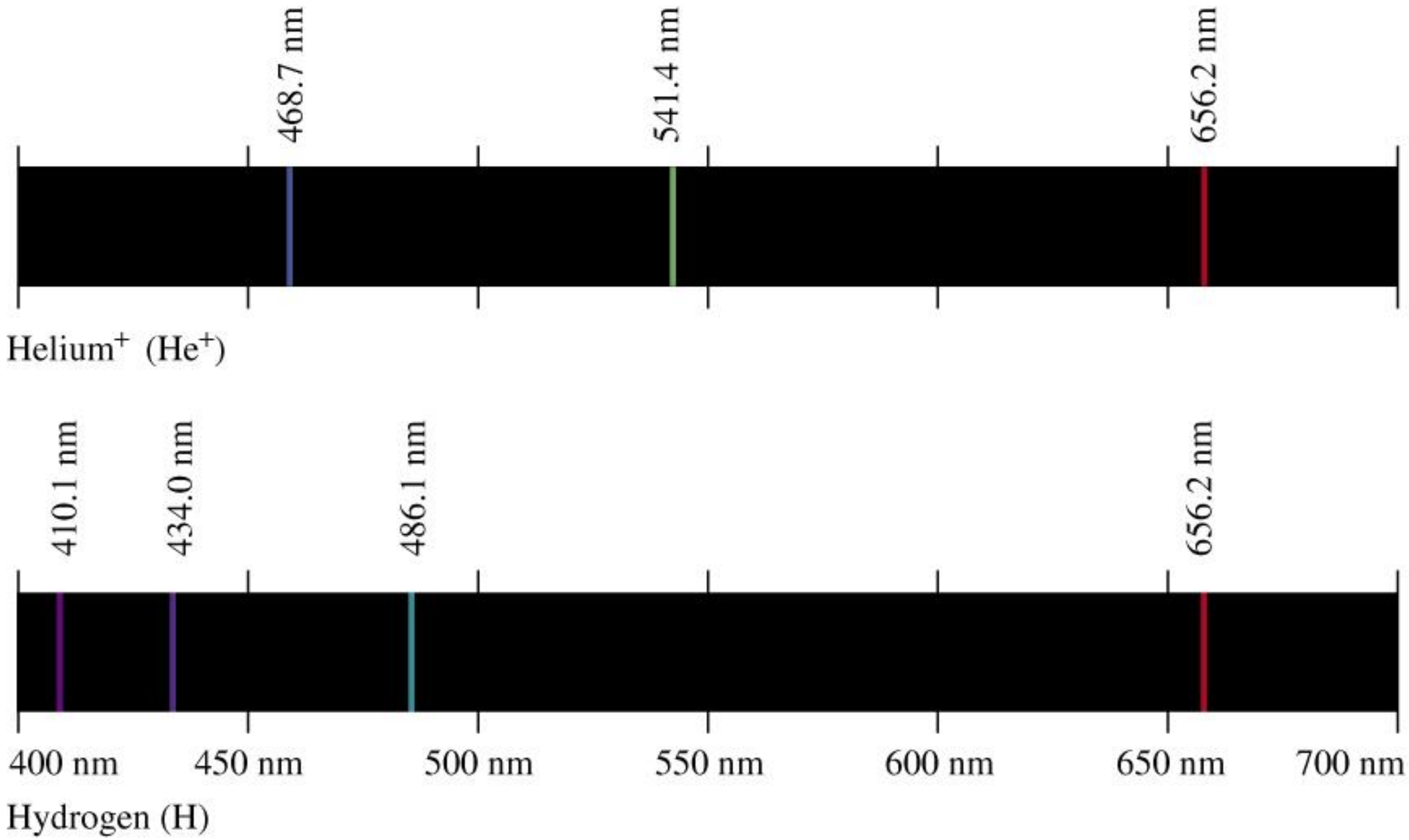


Hydrogen Atom

All orbitals corresponding to one level of *n* have the same energy and are said to be degenerate

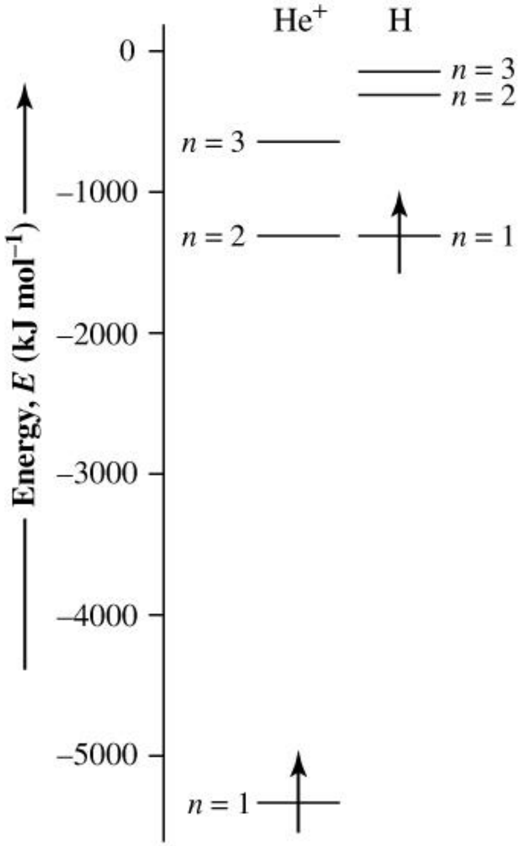
Figure 4.34

4.5 Atomic Orbital Electron Distributions and Energies



4.5 Atomic Orbital Electron Distributions and Energies

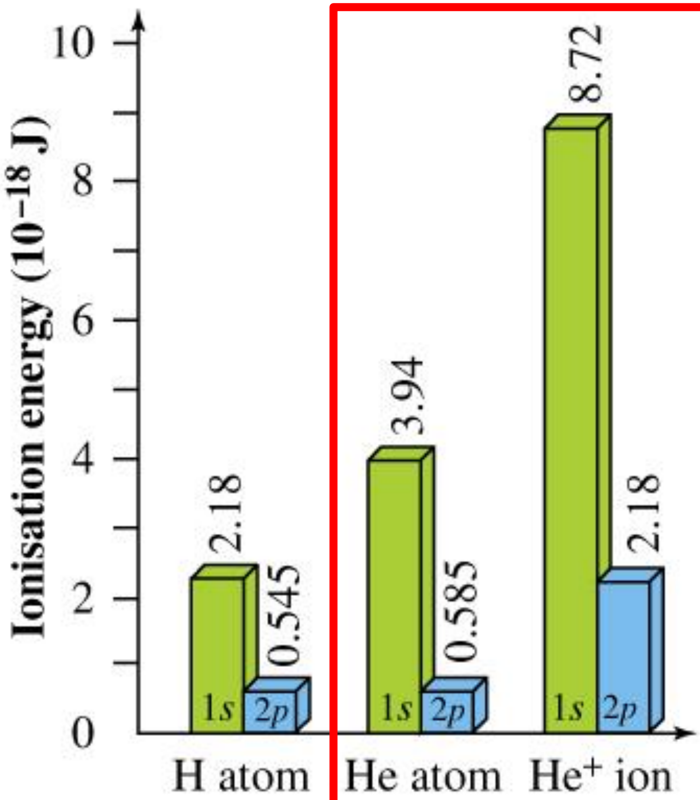
- The effect of nuclear charge
  - Energy of an orbital can be determined by measuring the amount of energy required to remove an electron completely
  - Ionisation energy → E_i



$H \rightarrow H^+ + e^-$ $\quad$ $E_{i\,H} = 2.18 \times 10^{-18}$ J

$He^+ \rightarrow He^{2+} + e^-$ $\quad$ $E_{i\,He^+} = 8.72 \times 10^{-18}$ J

4.5 Atomic Orbital Electron Distributions and Energies



1e⁻	2e⁻	1e⁻
Z=1	*Z*=2	*Z*=2

The effect of other electrons

- **Electrons affect each other's properties**
- **A given orbital is of higher energy (easier to remove electron) in a multi-electron atom than it is in a single-electron ion with the same nuclear charge**