CH-110 Advanced General Chemistry I

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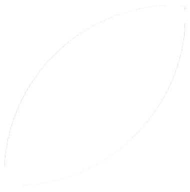
Wavefunctions and Energy Levels

Topic 1C



Topic 1C.1 The wavefunction and its interpretation
Topic 1C.2 The quantization of energy

WHY DO YOU NEED TO KNOW THIS MATERIAL?

- Whenever you are dealing with quantum mechanics, you have to consider the **properties of wavefunctions and the information they contain**.

WHAT DO YOU NEED TO KNOW ALREADY?

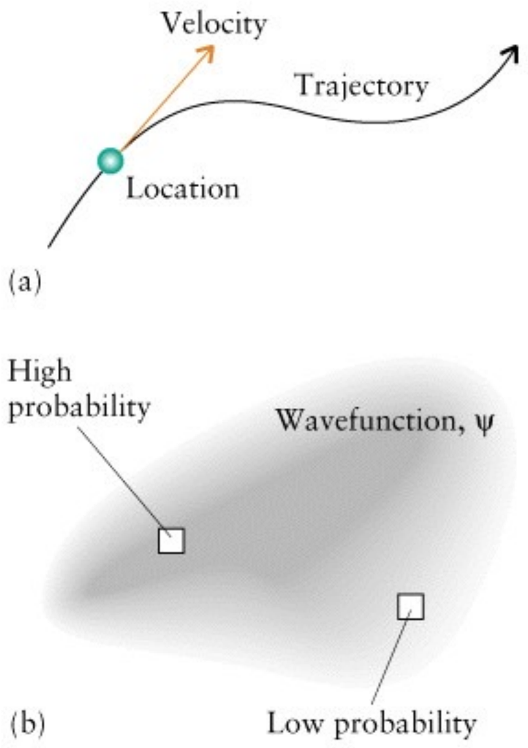
- Properties of sine functions (sin x)
- Concept of duality
- De Broglie relation between momentum and wavelength
- Heisenberg uncertainty principle

The Wavefunction and Its Interpretation

Topic 1C.1

1C.1 The wavefunction and its interpretation

Last time: Classical vs. quantum mechanics



- **Classical mechanics:** the location and velocity of a particle are known precisely at each point in time (trajectory), described by a path or position function.
- **Quantum mechanics**: the particle is better described by its wave-like character with a wavefunction ψ (position not defined).

1C.1 The wavefunction and its interpretation

Last time: The Schrödinger equation

- The Schrödinger equation is used to calculate the **wavefunction** for any **particle** **confined** to any region of space, including **electrons** **confined** within atoms and molecules.

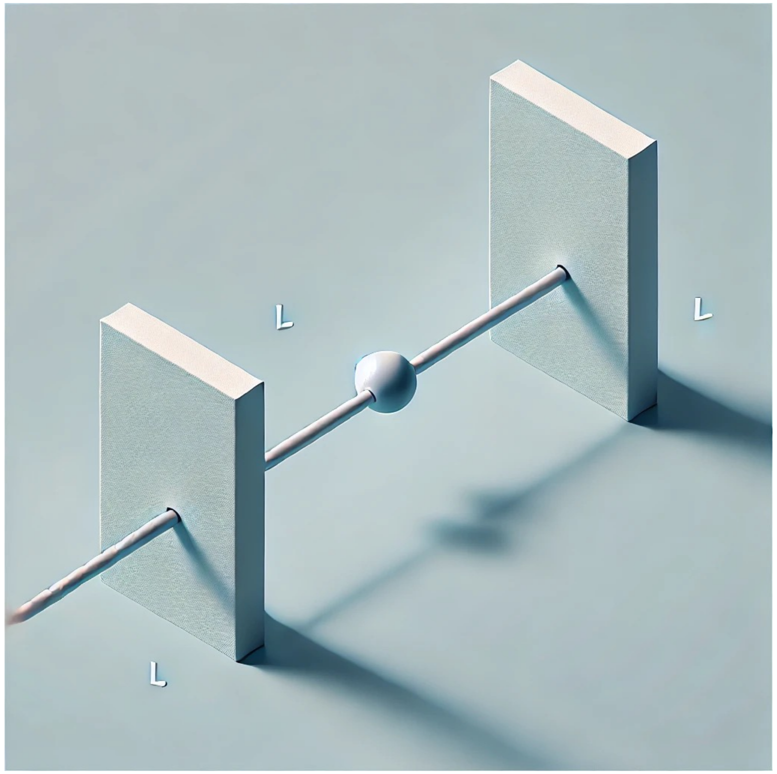
$$H\psi = E\psi$$

1C.1 The wavefunction and its interpretation

Last time: The particle-in-a-box model

- The Schrödinger equation is used to calculate both the **wavefunction ψ** and the corresponding **energy E**.

- Simple **model system**: a **single particle of mass m** confined in a **one-dimensional** «box» between two impenetrable walls a distance L apart.



1C.1 The wavefunction and its interpretation

Last time: The mathematical form of the particle in the box

Due to boundary conditions, only wavefunctions with **certain wavelengths** can exist in the box. The general solution for the wavefunction inside the box is:

$$\psi_n(x) = \left(\frac{2}{L}\right)^{\frac{1}{2}} \sin\left(\frac{n\pi x}{L}\right)$$

$$n = 1,2,\ldots$$

- For $\psi_n(x)$ to satisfy the boundary $\psi_n(L) = 0, \frac{n\pi x}{\mathrm{L}}$ must be an integer multiple of π when $x = L$, so that the sine function goes to zero. This only happens if n is a **positive integer** (1, 2, 3,...), because:
- $\sin(n\pi) = 0$ when n=1,2,3,…

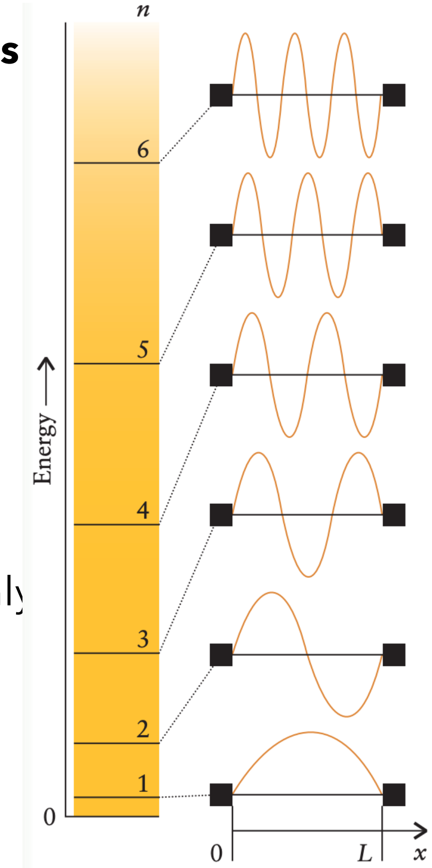


Figure 1C.3

1C.1 The wavefunction and its interpretation

Last time: The mathematical form of the particle in the box

A **quantum number**:

- Is an integer (or sometimes a half-integer, such as ½, see Topic 1D)
- Labels a wavefunction
- Specifies a state

The Quantization of Energy

Topic 1C.2

1C.2 The quantization of energy

Energies of a particle in a box

The wavefunctions associated with different quantum numbers also have different energies associated with them. How do we calculate these energies?

If the particle stays in the box, the potential energy is zero:

$$E_k = E_{total}$$

Use de Broglie relation:

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

1C.2 The quantization of energy

Energies of a particle in a box

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

Recognize, only **whole-number multiples of half-wavelengths** can fit into the box:

The wavelengths possible for a particle in a box of length L must meet the condition that $\lambda = 2L, L, \frac{2}{3}L, \ldots$

In other words, the allowed wavelengths are

$$\lambda = \frac{2\mathrm{L}}{\mathrm{n}}, \text{with } \mathrm{n} = 1,2, \ldots$$

Insert this expression for λ into the expression for energy:

$$E_n = \frac{h^2}{2m\lambda^2} = \frac{h^2}{2m\left(\frac{2L}{n}\right)^2} = \frac{n^2h^2}{8mL^2}$$

1C.2 The quantization of energy

What does this equation tell you?

$$E_n = \frac{h^2}{2m\lambda^2} = \frac{h^2}{2m\left(\frac{2L}{n}\right)^2} = \frac{n^2h^2}{8mL^2}$$

Mass in denominator: energy levels are lower and closer together for heavy particles than for light ones.

Length in denominator: as the walls become more confining (*L* smaller), the energy levels rise and become more widely spaced. In contrast, as the walls become less confining (*L* larger), the levels fall and get closer together.

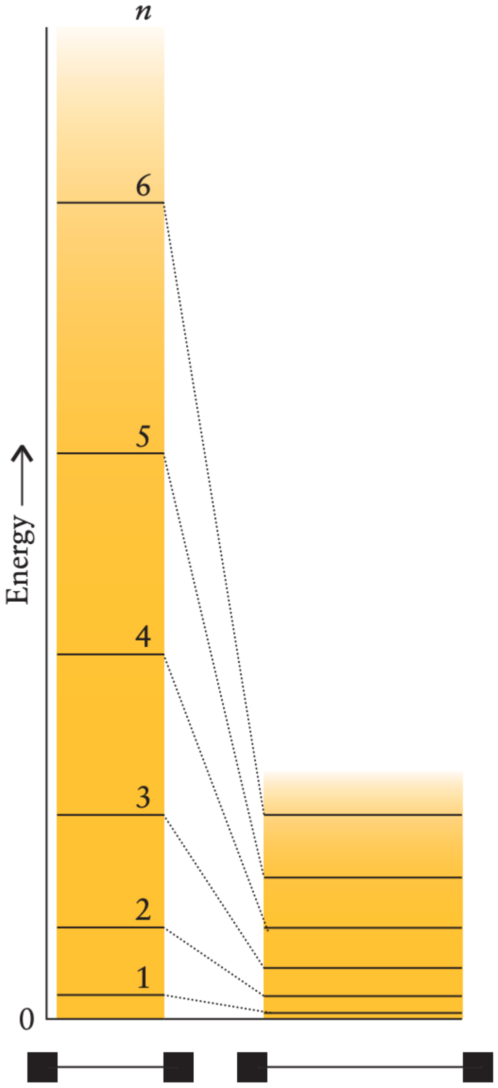


Figure 1C.4

1C.2 The quantization of energy

What does this equation tell you?

$$E_n = \frac{n^2 h^2}{8mL^2}$$

- n can only be integer values → **energy is quantized!**
- Energy quantization stems from the boundary conditions on the wavefunction.
- **Particle in a box translates to atoms:**
- Electrons must also satisfy certain boundary conditions, but now in three dimensions.
- We will revisit spectral lines in hydrogen absorption spectrum!

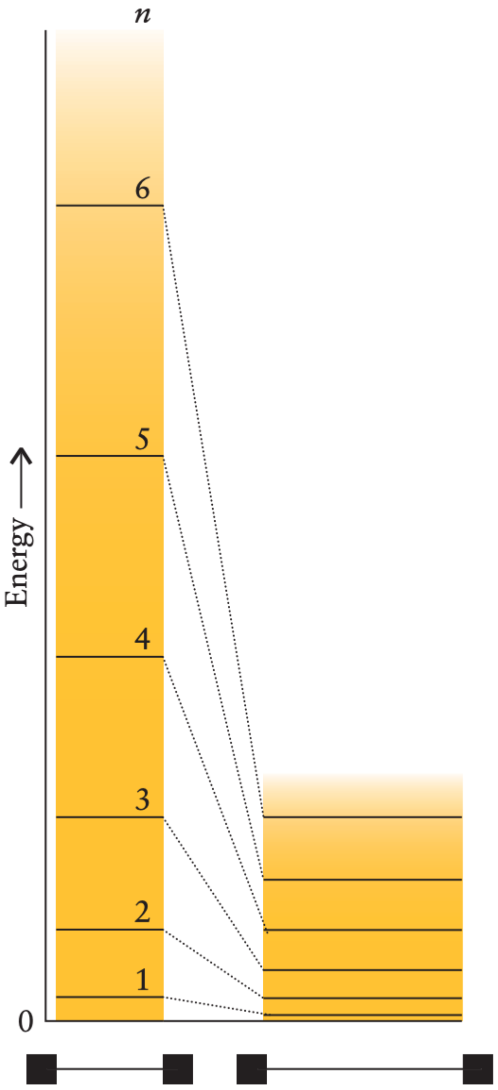


Figure 1C.4

1C.2 The quantization of energy

Energy separation between neighboring levels

$$E_{n+1} - E_n = \frac{(n+1)^2h^2}{8mL^2} - \frac{n^2h^2}{8mL^2}$$

$$= \{(n+1)^2 - n^2\}\frac{h^2}{8mL^2} = \frac{(2n+1)h^2}{8mL^2}$$

As *L* or *m* increases, the separation between neighboring energy levels decreases.

Macroscopic objects in ordinary-sized containers have energy levels that are extremely close together: **undetectable quantization**.

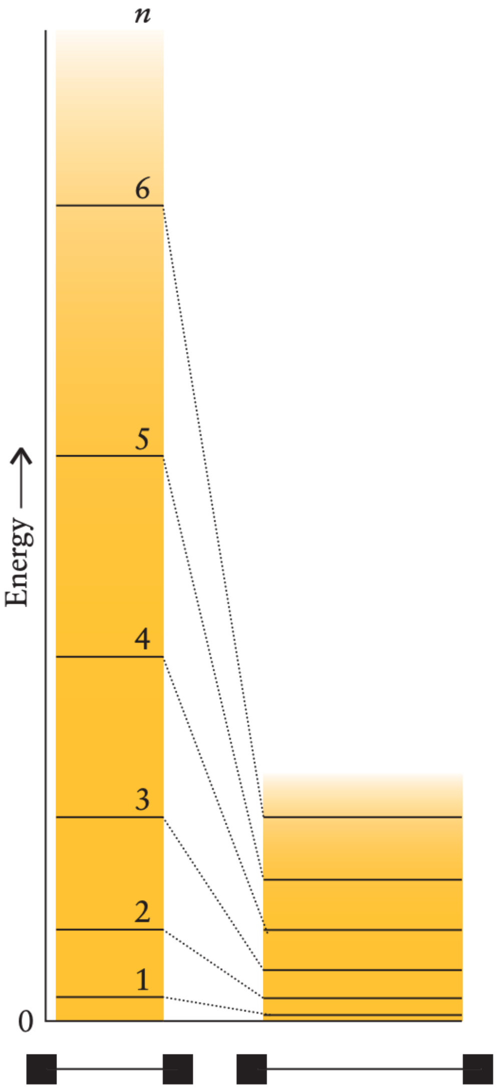


Figure 1C.4

1C.2 The quantization of energy

Quantization of energy and the atomic spectrum of hydrogen

Energy is quantized → this realization is key to understanding the **atomic spectrum of hydrogen** (Topic 1A).

Particle in a box	Hydrogen atom
1D	3D
Physical walls	No physical walls, and electrons are confined by pull of the nucleus
Energy quantized	

1C.2 The quantization of energy

What are these lines?!

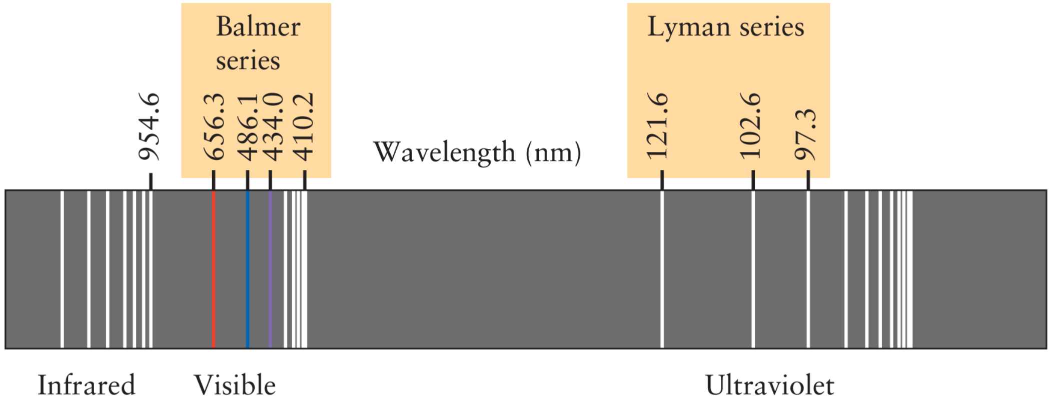


Figure 1A.10

A spectral line arises from a **transition of an electron between allowed energy levels**.

The difference in energy is carried away as a photon.

$$h\nu = E_{upper} - E_{lower} = \Delta E$$

This equation is known as the **Bohr frequency condition.**

1C.2 The quantization of energy

Example 1C.1: Calculating the energies of a particle in a box

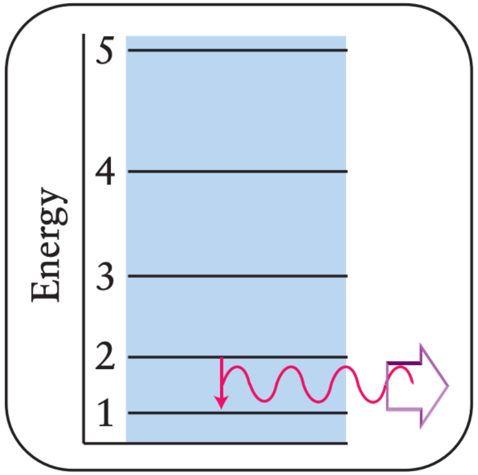
We will estimate the energies of the hydrogen atom.

Estimate: «back of the envelope» calculation

Treat hydrogen atom as a **one-dimensional box of length 150. pm** (the approximate diameter of the atom) with one electron.

Predict energy level separation **between the lowest and next higher** energy levels.

If the electron falls from the **upper level to the lower level**, what would be the wavelength of the radiation emitted as a photon?



1C.2 The quantization of energy

Example 1C.1: Calculating the energies of a particle in a box

1C.2 The quantization of energy

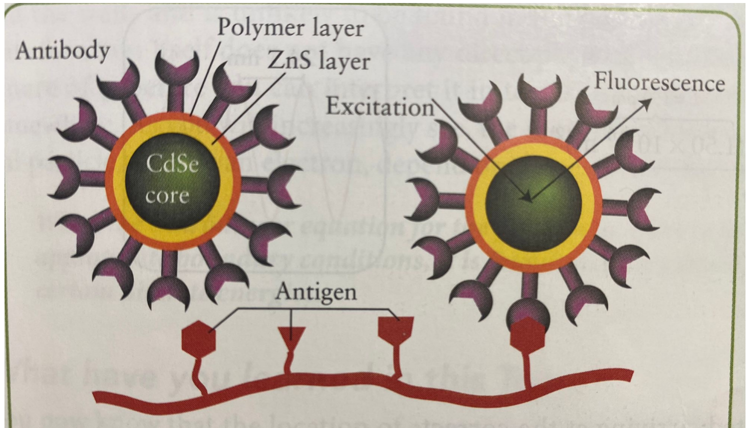
Nanocrystals

Electrons in nanoscale particles (1-100 nm diameter) made of semiconductor materials are **quantum confined** and behave like a particle in a box: Quantum dots or nanocrystals.

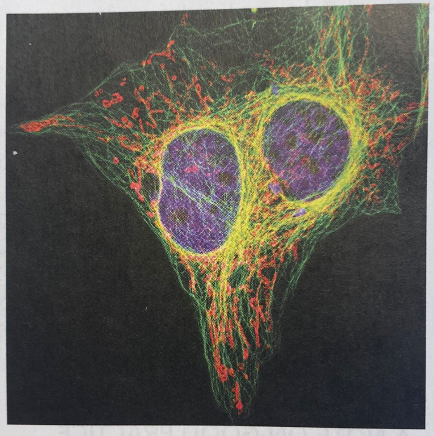
CdSe nanoparticles coated with shell of ZnS plus polymer, modified with antibodies.

Antigen-specific binding on cells.

Size of quantum dot will change emitted light wavelength: imaging at multiple wavelengths possible.



CdSe quantum dots with a shell of ZnS and polymer are linked to an antibody. The antibody binds to specific antigens within the cell.



Multicolor fluorescence micrograph of HeLa cells showing the location of the cytoskeleton (yellow and green) and the cell nucleus (purple). *(Dr. Gopal Murti/Science Source.)*

BOX 1C.1

1C.2 The quantization of energy

Particle in a box: zero-point energy

- Surprising implication of equation: $E_n = \frac{n^2h^2}{8mL^2}$
- A particle in a container **cannot have zero energy**.
- The lowest value of *n* is 1.
- Lowest energy is $E_1 = \frac{h^2}{8mL^2}$ (**Zero-point energy**)
- What this means: A particle can never be perfectly still when it is confined between two walls, it must always possess an energy, in this case, at least the kinetic energy $\frac{h^2}{8mL^2}$.

1C.2 The quantization of energy

Zero-point energy is consistent with uncertainty principle

The **Heisenberg uncertainty principle** states that there is a fundamental limit to how precisely we can simultaneously know a particle's **position** and **momentum**:

$$\Delta \mathrm{p} \times \Delta x \geq \frac{1}{2}\hbar$$

- The particle is confined within a box, so its **position uncertainty** Δx is on the order of the size of the box, L.

$$\Delta x \approx L$$

- Due to the **Uncertainty Principle**, if the particle's position is confined, the **momentum** p (and hence its velocity) cannot be zero. There must be some uncertainty in momentum $\Delta \mathrm{p}$, meaning the particle has a **nonzero minimum momentum**.

$$\Delta \mathrm{p} \geq \hbar/2L$$

- This nonzero momentum means the particle always has some **kinetic energy**, even in the ground state, and cannot be perfectly still. This nonzero energy is the **zero-point energy**.

1C.2 The quantization of energy

The shapes of the wavefunctions

- The shapes reveal interesting information.
- The two lowest-energy wavefunctions are displayed on the right, *n* = 1 and *n* = 2.
- **Density of shading**: likelihood of finding a particle (formally: probability density)
- For ψ_1 with energy $\mathrm{h}^2/8mL^2$: the particle is most likely found at the **center** of the box.
- For ψ_2 with energy $\mathrm{h}^2/2mL^2$: the particle is least likely found at the center of the box, most likely to be found in regions between the center and the walls.
- **The most likely locations of a quantum mechanical particle, such as an electron, depend on the quantum state it is in.**

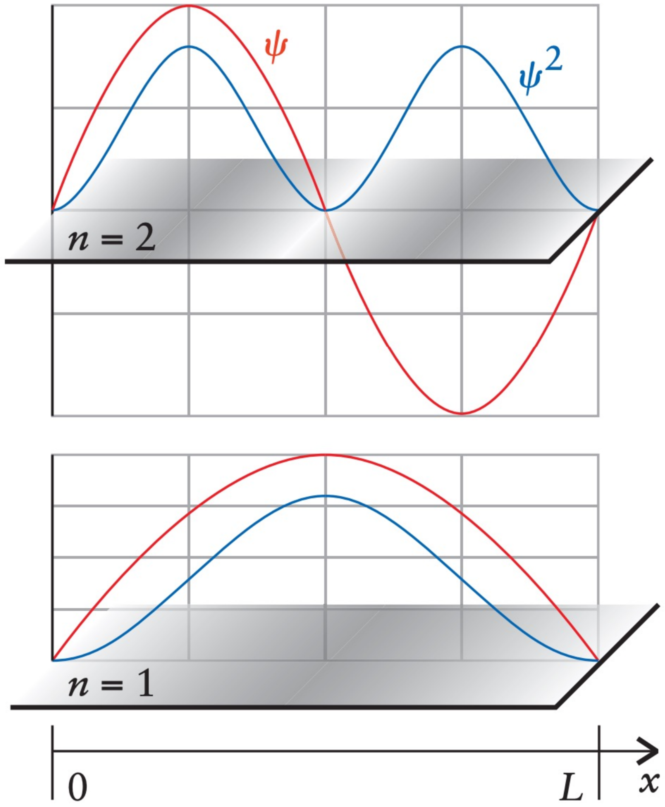


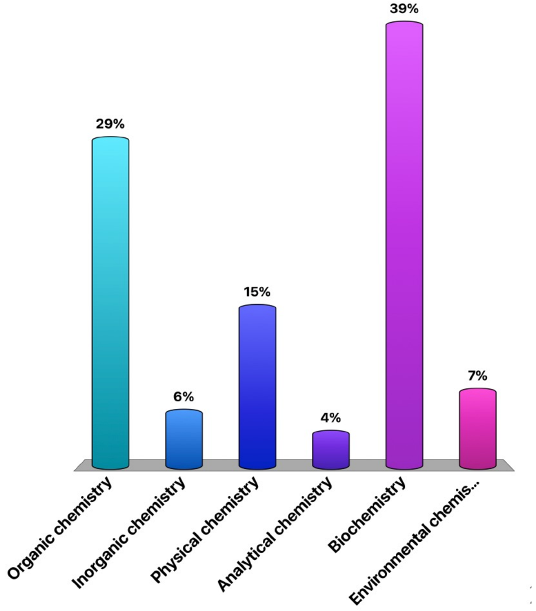
Figure 1C.5

1C.2 The quantization of energy

Why is this statement relevant for you even if you don't plan on studying quantum chemistry again?

The most likely locations of a quantum mechanical particle, such as an electron, depend on the quantum state it is in.

A. Organic chemistry
B. Inorganic chemistry
C. Physical chemistry
D. Analytical chemistry
E. Biochemistry
F. Environmental chemistry



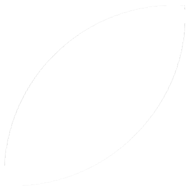
The skills you have mastered are the ability to

- ☐ Describe the origin and shapes of the wavefunctions of a particle in a box.
- ☐ Calculate the allowed energies of a particle in a box and explain how they depend on the length of the box and the mass of the particle.
- ☐ Explain what is meant by zero-point energy and accounts for its origin

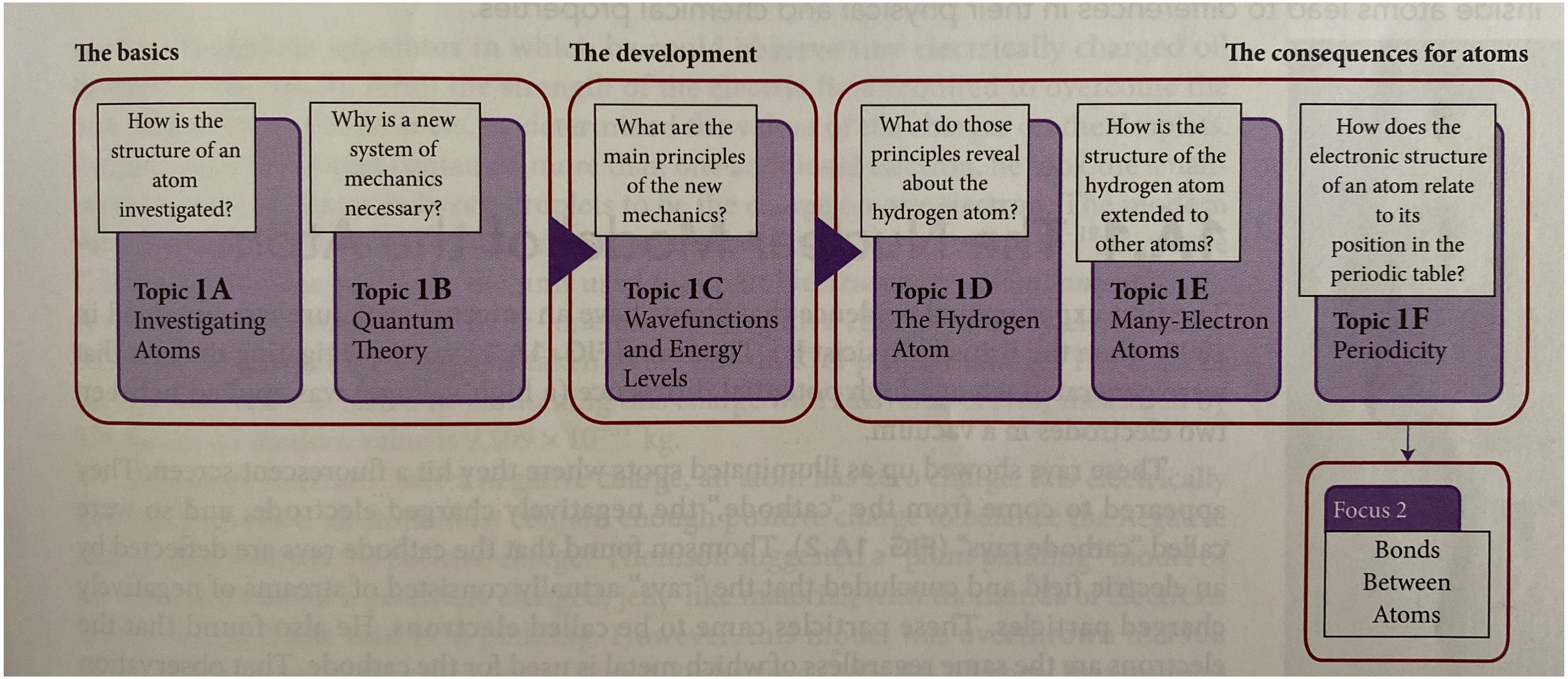
Summary: You now know that the location of a particle is expressed by a wavefunction, the square of which expresses the probability (as a probability density) that the particle will be found in each region of space. You also know that a wavefunction is found by solving the Schrödinger equation and that one consequence of the wavefunction having to fit into a region of space is that a particle confined to a region can have only certain discrete energies known as energy levels.

The Hydrogen Atom

Topic 1D



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

Topic 1D.1 Energy levels
Topic 1D.2 Atomic orbitals
Topic 1D.3 Quantum numbers, shells, and subshells
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)

1D The hydrogen atom

Setting the stage

In Topic 1A, we have seen this puzzle

$$\nu = R\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \; n_1 = 1,2, \ldots, n_2 = n_1 + 1, n_1 + 2, \ldots$$

Value of Rydberg constant, $R = 3.29 \text{ x } 10^{15} Hz$

- Why such a **pattern** and why does R have that **value**?
- Example 1C.1 gave clues: lines in spectrum are due to transitions between allowed energy levels of the atom, the difference in energy is carried awway by a photon of energy $h\nu$
- **Aim of this topic**: construct a quantum mechanical model of the hydrogen atom using the fact that an electron has wave-like properties and is described by a wavefunction, and has quantized energy levels.

Energy Levels

Topic 1D.1

1D.1 Energy levels

Setting the stage

- **Again:** an **electron** in an atom is like a **particle** in a box in the sense that it is confined within the atom, not by the **walls**, but by the **electrostatic pull of the nucleus**.
- It follows **boundary conditi**ons are also applicable for atom.
- Solving Schrödinger equation for the hydrogen atom will result in existence of **discrete energy levels**.

1D.1 Energy levels

Allowed energy levels for electron in hydrogen atom

To find allowed energy levels of an electron in a hydrogen atom, you need to solve appropriate Schrödinger equation. Consider:

1. Motion in three dimensions.
2. Coulomb potential energy of an electron of charge $-e$ at a distance r from the nucleus of charge $+e$:

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

ε_0: electric constant

1D.1 Energy levels

Allowed energy levels for electron in hydrogn atom

Schrödinger managed to solve his equation with this potential energy:

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

ε_0: electric constant

He found that the allowed energy levels of an electron in a hydrogen atom are:

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

$$R = \frac{m_e e^4}{8h^3\varepsilon_0^2} \text{ with } n = 1, 2, \ldots$$

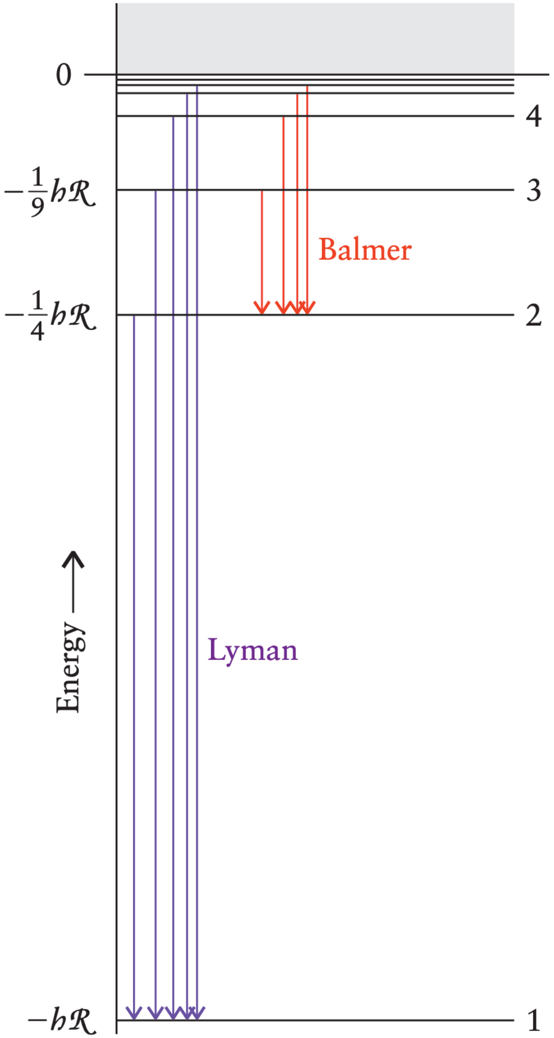


Figure 1D.1

1D.1 Energy levels

What does this equation tell you?

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

$$R = \frac{m_e e^4}{8h^3\varepsilon_0^2} \text{ with } n = 1, 2, \ldots$$

- All energies are **negative**: electron has a lower energy far from the nucleus, it takes energy to remove an electron from an atom.
- There is a **quantum number**, *n*, like for the particle in a box. Energy is quantized, can only have discrete values.
- *n* appears in the **denominator**: as *n* increases, the energies of successive levels increase (become less negative).
- As the energies approach zero, the electron is on the point of **escaping** from the atom.

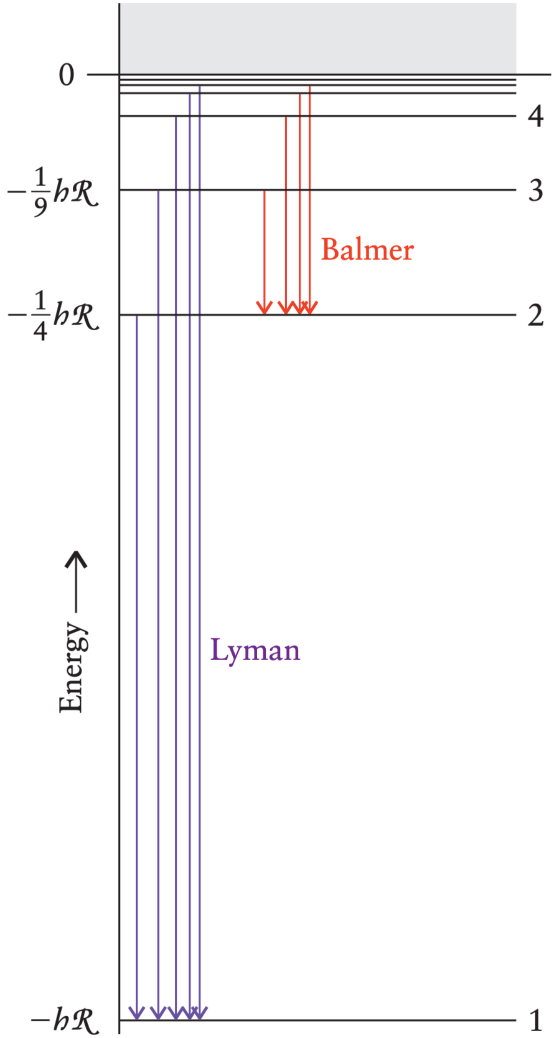


Figure 1D.1

Relationship to Bohr frequency condition

Bohr frequency condition:

$$h\nu = \Delta E$$

Insert into previous equation. In case of the hydrogen atom, if the electron falls from a level with quantum number n_2 to one with quantum number n_1, then:

$$h\nu = \Delta E = \left(-\frac{hR}{n_2^2}\right) - \left(\frac{hR}{n_1^2}\right) = hR\left\{\frac{1}{n_1^2} - \frac{1}{n_2^2}\right\}\ n_1 = 1,2, \dots, n_2 = n_1 + 1, n_1 + 2, \dots$$

Compare to previous Rydberg equation:

$$\nu = R\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)\ n_1 = 1,2, \dots, n_2 = n_1 + 1, n_1 + 2, \dots$$

1D.1 Energy levels

Finally, it makes sense

You can now see:

- Balmer series, for example, arises from transitions starting at $n_2 = 3, 4, 5 \ldots$ and all ending at $\boldsymbol{n_1 = 2}$
- Lyman series: $n_2 = 2, 3, 4, 5 \ldots$ to $\boldsymbol{n_1 = 1}$

Rydberg constant

$$R = \frac{m_e e^4}{8h^3\varepsilon_0^2} = \boldsymbol{3.29 \times 10^{15}\ Hz}$$

- Imagine Schrödinger calculating this constant!

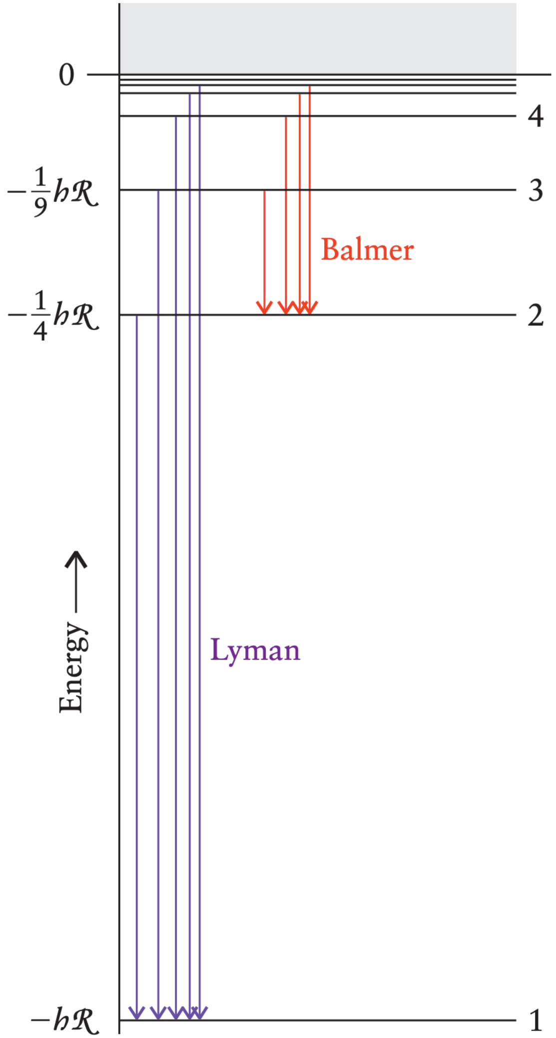


Figure 1D.1

1D.1 Energy levels

Generalization to other one-electron ions possible

Schrödinger was able to generalize this equation

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

$$R = \frac{m_e e^4}{8h^3 \varepsilon_0^2} \text{ with } n = 1, 2, \ldots$$

to other one-electron ions such as He^+ and even C^{5+}. For a nucleus with atomic number Z and charge Ze, the energy levels are:

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

Note: because Z appears in the **numerator**, the greater the value of the nuclear charge, the lower the energy (more negative) of the electron and the more tightly it is bound to the nucleus.

This equation can be used for **one-electron ions**, for many-electron atoms, see Topic 1E.

1D.1 Energy levels

The principal quantum number

- The integer $n = 1, 2, \ldots$ is called the **principal quantum number**.
- Coming soon: more quantum numbers.
- The lowest (most negative) energy possible for an electron in a hydrogen atom is obtained when $n = 1$ and E_n is equal to $-hR$: **ground state of the atom**.
- When the atom absorbs a **photon** or collides with other particles, it may be **excited from the ground state** to a level with a higher value of n.
- If collision are very energetic, n might reach infinity, a process called **ionization**. An electron is removed from the hydrogen atom.
- The minimum ionization energy starting from an electron in the ground state for a hydrogen atom is equal to hR. (numerical value:$2.18 \times 10^{-17} J$ or 13.6 eV).
- Any further energy beyond the ionization energy adds kinetic energy to the liberated electron.

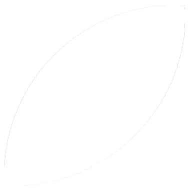
1D.1 Energy levels

Summary

The energy levels of a hydrogen atom are defined by the principal quantum number, $n = 1, 2, \ldots$, and form a converging ladder, as shown in Figure 1D.1. Spectroscopic lines arise from transitions between the levels.

Atomic Orbitals

Topic 1D.2



1D.2 Atomic orbitals

Wavefunction and atomic orbitals

The wavefunction of an electron in an atom is called an atomic orbital.

Less finite than «orbit» of an electron around the nucleus, to account for wave-like nature.

Again: the square of a wavefunction tells you the probability density of finding an electron an each point in space.

In context of hydrogen atom: imagine a cloud centered on the nucleus.

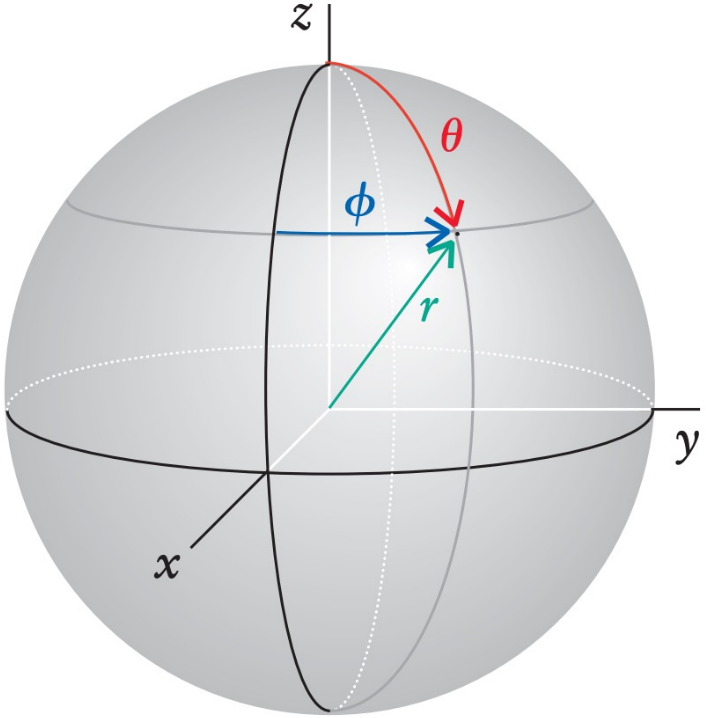
Dense regions: locations where the electron is most likely to be found.

1D.2 Atomic orbitals

Spherical polar coordinates

The atom is like a sphere (3D), spherical polar coordinates apply:

- *r* is the **radius**, the distance from the nucleus
- θ (theta) is the **colatitude**, the angle from the positive *z*-axis (the «north pole»), which can be thought of as playing the role of the geographical «latitude»
- ϕ (phi) is the **azimuth**, the angle about the *z*-axis, the geographical «longitude».



1D.2 Atomic orbitals

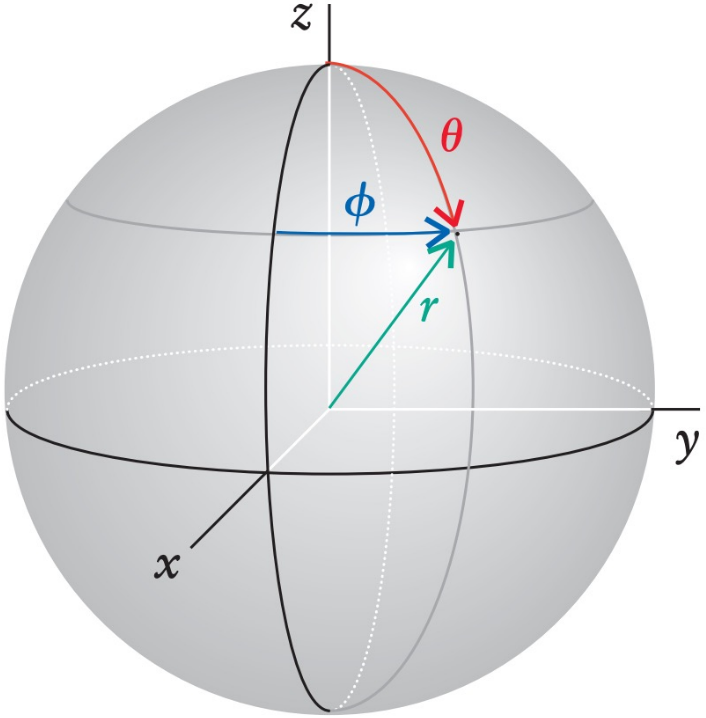
Wavefunction and atomic orbitals

Each wavefunction has a value that depends on these three coordinates and is therefore denoted as $\Psi(\mathrm{r}, \theta, \phi)$. You can also express it as the product of a function that depends only on *r* and another function that depends on the angles θ and ϕ:

$$\Psi(\mathrm{r}, \theta, \phi) = \mathrm{R(r)} \times Y(\theta, \phi)$$

$R(r)$**: radial wavefunction**, expresses how the wavefunction varies with distance from the nucleus.

$Y(\theta, \phi)$: **angular wavefunction**, expresses how the wavefunction varies as the angles θ and ϕ change.



1D.2 Atomic orbitals

Expressions for atomic orbitals

- Expressions for some atomic orbitals are shown in Table 1D.1a (see next slide)
- Looks complicated at first glance, do not worry about knowing these by heart.
- Some are not complicated, e.g. the wavefunction corresponding to the ground state of the hydrogen atom (*n* = 1) is:

$$\Psi(\mathrm{r},\theta,\phi)=\left(\frac{1}{\pi a_0^3}\right)^{\frac{1}{2}} e^{-\frac{r}{a_0}}$$

a_0: Bohr radius (52.9 pm)

- Wavefunction is spherically symmetric: independent of θ and ϕ and for a given radius, ist value is the same in all directions.
- Wavefunction decays exponentially toward zero as *r* increases. Probability density is highest close to the nucleus (at r = 0, e^0 = 1)
- In contrast to particle in a box: no physical, confining walls for electron in atom, but the pull of nucleus weakens with distance.

1D.2 Atomic orbitals

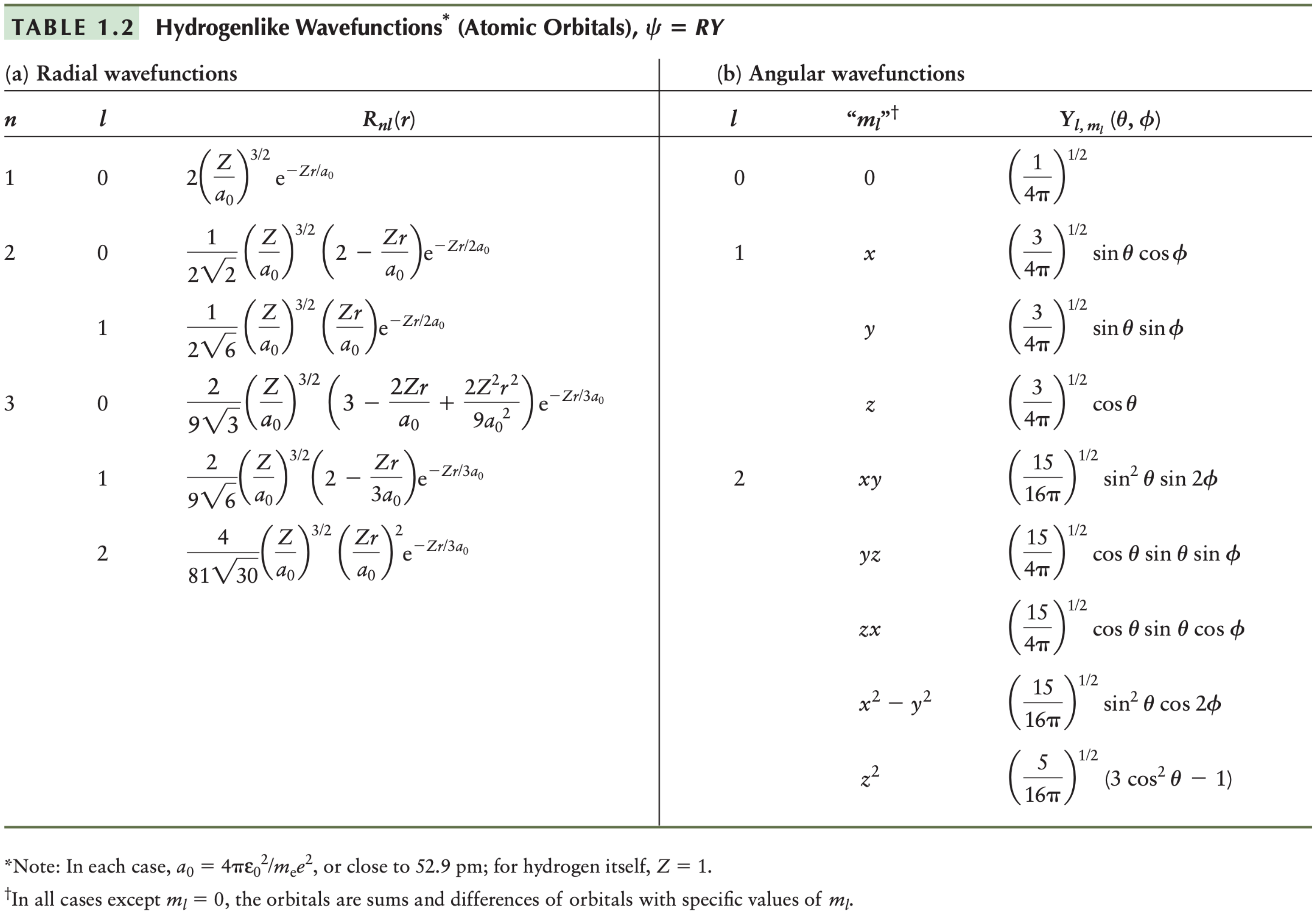


TABLE 1.2 **Hydrogenlike Wavefunctions* (Atomic Orbitals), $\psi = RY$**

(a) Radial wavefunctions			(b) Angular wavefunctions		
n	l	$R_{nl}(r)$	l	"m_l"[†]	$Y_{l,m_l}(\theta,\phi)$
1	0	$2\left(\frac{Z}{a_0}\right)^{3/2} e^{-Zr/a_0}$	0	0	$\left(\frac{1}{4\pi}\right)^{1/2}$
2	0	$\frac{1}{2\sqrt{2}}\left(\frac{Z}{a_0}\right)^{3/2}\left(2-\frac{Zr}{a_0}\right)e^{-Zr/2a_0}$	1	x	$\left(\frac{3}{4\pi}\right)^{1/2}\sin\theta\cos\phi$
	1	$\frac{1}{2\sqrt{6}}\left(\frac{Z}{a_0}\right)^{3/2}\left(\frac{Zr}{a_0}\right)e^{-Zr/2a_0}$		y	$\left(\frac{3}{4\pi}\right)^{1/2}\sin\theta\sin\phi$
3	0	$\frac{2}{9\sqrt{3}}\left(\frac{Z}{a_0}\right)^{3/2}\left(3-\frac{2Zr}{a_0}+\frac{2Z^2r^2}{9a_0^2}\right)e^{-Zr/3a_0}$		z	$\left(\frac{3}{4\pi}\right)^{1/2}\cos\theta$
	1	$\frac{2}{9\sqrt{6}}\left(\frac{Z}{a_0}\right)^{3/2}\left(2-\frac{Zr}{3a_0}\right)e^{-Zr/3a_0}$	2	xy	$\left(\frac{15}{16\pi}\right)^{1/2}\sin^2\theta\sin 2\phi$
	2	$\frac{4}{81\sqrt{30}}\left(\frac{Z}{a_0}\right)^{3/2}\left(\frac{Zr}{a_0}\right)^2 e^{-Zr/3a_0}$		yz	$\left(\frac{15}{4\pi}\right)^{1/2}\cos\theta\sin\theta\sin\phi$
				zx	$\left(\frac{15}{4\pi}\right)^{1/2}\cos\theta\sin\theta\cos\phi$
				x^2-y^2	$\left(\frac{15}{16\pi}\right)^{1/2}\sin^2\theta\cos 2\phi$
				z^2	$\left(\frac{5}{16\pi}\right)^{1/2}(3\cos^2\theta-1)$

*Note: In each case, $a_0 = 4\pi\varepsilon_0{}^2/m_e e^2$, or close to 52.9 pm; for hydrogen itself, $Z = 1$.

[†] In all cases except $m_l = 0$, the orbitals are sums and differences of orbitals with specific values of m_l.

1D.2 Atomic orbitals

Example from Table 1D.1

- For example, a 2p$_x$-orbital (n = 2, l = 1, «m_l» = x) of hydrogen (Z = 1) is

$$\Psi(\mathrm{r},\theta,\phi) = R_{2,1}(r)\times Y_{1,x}(\theta,\phi) = \frac{1}{2\sqrt{6}}\left(\frac{1}{\mathrm{a}_0}\right)^{\frac{3}{2}}\frac{r}{a_0}\,e^{-\frac{r}{2a_0}}\times\left(\frac{3}{4\pi}\right)^{\frac{1}{2}}\sin(\theta)\cos(\phi)$$

1D.2 Atomic orbitals

Summary

The distribution of an electron in an atom is described by a wavefunction known as an atomic orbital.