CH-110 Advanced General Chemistry I

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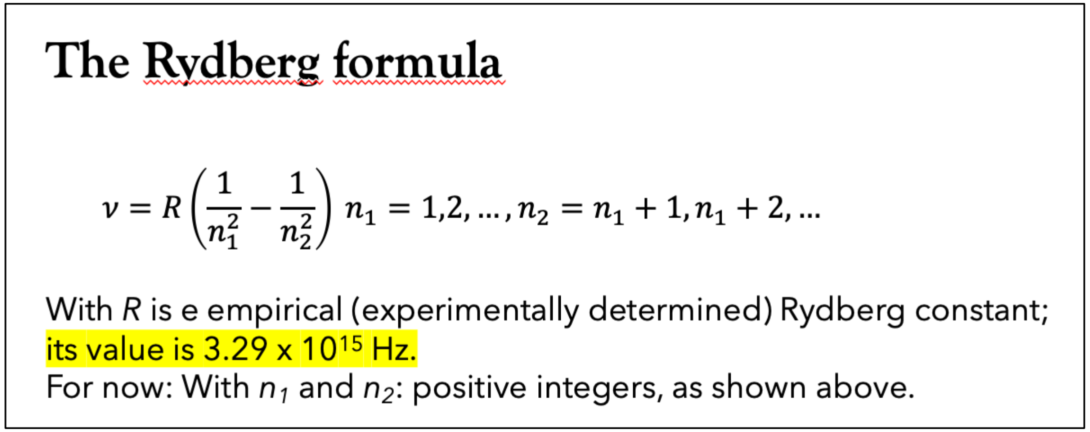
Housekeeping notes

- **Typo** slides in Topic 1A, slide #38 (corrected version was uploaded):



The Rydberg formula

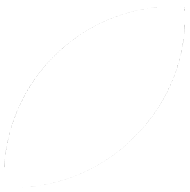
$$\nu = R\left(\frac{1}{n_1^2}-\frac{1}{n_2^2}\right) \quad n_1 = 1,2,\dots, n_2 = n_1+1, n_1+2,\dots$$

With *R* is e empirical (experimentally determined) Rydberg constant; its value is 3.29×10^{15} Hz.
For now: With n_1 and n_2: positive integers, as shown above.

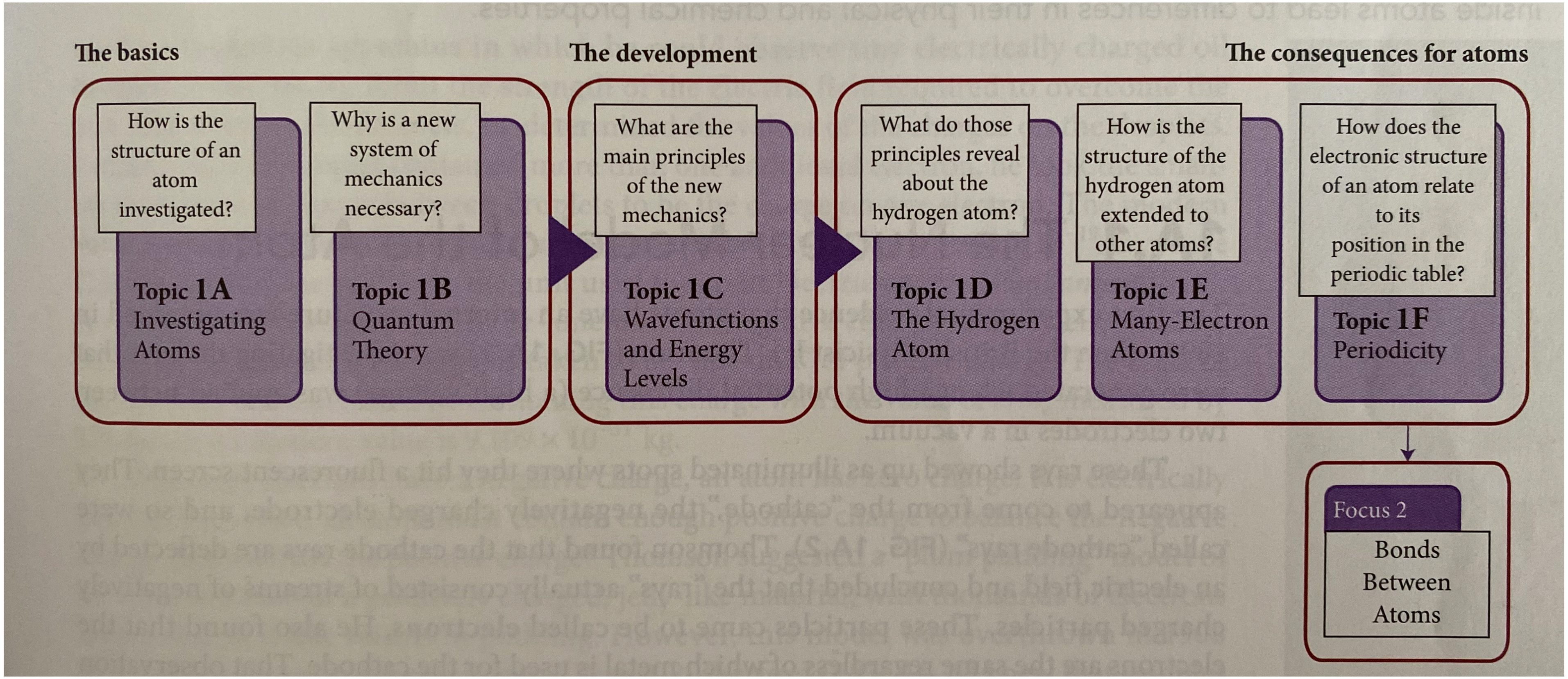
- **Calculator at exam**: non-programmable. If you have any doubts, you can post a photo of your calculator in the Ed discussion forum and we will let you know if this calculator is okay.

Wavefunctions and Energy Levels

Topic 1C



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 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

Last week:

Matter has wave-like properties: The de Broglie relation

If electromagnetic radiation, long thought as a wave, has dual character, **could it be that matter,** which has been though as consisting of particles, **also has wave-like properties?**

In 1924, **Louis de Broglie** proposes that all particles should be regarded as having wave-like properties.

He suggested, the wavelength associated with a **«matter wave»** is inversely proportional to the particle's mass, *m*, and speed, *v*, and that

$$\lambda = \frac{h}{mv}$$

With $mv = p$, the linear momentum:

$$\lambda = \frac{h}{p}$$

The Wavefunction and Its Interpretation

Topic 1C.1

1C.1 The wavefunction and its interpretation

Setting the stage

- Classical mechanics treats particles as ”point-like” objects: precise paths with definite velocities at each point.
- **Electrons** have wave-like properties: **how do you define their path?** Electrons don’t have a well-defined location.

1C.1 The wavefunction and its interpretation

The wavefunction, ψ

- Precise trajectory of a particle is replaced by the wavefunction, ψ (the Greek letter psi)
- In 1927 by Erwin Schrödinger

The wavefunction is a mathematical function with values that depend on position (and can depend on other variables).

- Or in other words:

The wavefunction is a mathematical tool that contains all the information about a particle's state.

Its values don't directly tell us anything measurable.

- Waves are described with **sine functions** (sin x): it can have positive, negative, and complex values.
- Note: in more complex quantum mechanics, you will see that wavefunctions may be "complex" in the technical sense involving $i = \sqrt{-1}$. We ignore this possibility here.

Erwin Schrödinger, now featuring his signature round glasses, along with the wavefunction background in the Vienna Secessionist style.

1C.1 The wavefunction and its interpretation

Born interpretation of the wave function

- Max Born suggested how a wavefunction should be interpreted physically.
- Why? Because the wave function ψ itself does not directly represent a physical quantity.
- **Born interpretation**: The probability of finding the particle in a region of space is proportional to the value of ψ^2 in that region.
- **ψ^2 is a probability density**, **the probability that a particle will be found in a small region divided by the volume of the region.**
- If ψ^2 is large, the particle has a high probability density.
- If ψ^2 is small, the particle has a low probability density.
- To calculate the probability that a particle will be found in a region, the probability density in that region is multiplied by the volume of the region.

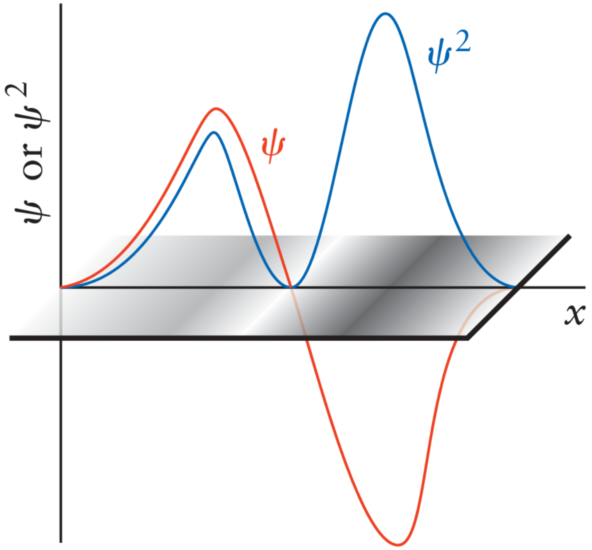


Figure 1C.2

1C.1 The wavefunction and its interpretation

Probability vs. probability density

- Probability: **unitless**, can have values between 0 (certainly not there) and 1 (certainly there)
- Probability density: units are **1/volume**

1C.1 The wavefunction and its interpretation

Physical density analogy

- Imagine you have a block of material, like a piece of metal, and you know its **density** is 10 grams per cubic centimeter (g/cm³). This density tells you how much **mass** is packed into each cubic centimeter of the metal.
- Now, to find out how much **total mass** is in a specific region of the block (let's say a small section of the metal), you would **multiply** the **density** (10 g/cm³) by the **volume** of the region (in cubic centimeters). This gives you the **total mass** in that region.

Quantum Probability Density:

- In quantum mechanics, **probability density** ψ^2 works in a similar way. The probability density tells you how **likely** it is to find a particle in a small region of space—just like the physical density tells you how much mass is in a certain volume.
- To find the **total probability** of finding the particle in a certain region, you multiply the **probability density** ψ^2 by the **volume** of that region. This gives you the **total probability** of finding the particle in that space.

1C.1 The wavefunction and its interpretation

Example: Physical density analogy

Physical density: If the density is 10 g/cm³ and you have a 2 cm³ region, the total mass in that region is:

- Mass = Density × Volume = 10 g/cm³ × 2 cm³ = 20 g

Probability density: If the probability density is 0.5 per cubic centimeter and you have a region of 2 cm³, the total probability of finding the particle in that region is:

- Probability = ψ^2 × Volume = 0.5 per cm³ × 2 cm³ = 1
- In this case, the particle is very likely to be in that region!

Key Takeaway:

- Just like multiplying physical density by volume gives you the **mass** in that region, multiplying **probability density** by the volume gives you the **probability** of finding the particle in that region. Both involve spreading a certain amount (mass or probability) over space and calculating how much is in a specific part of that space.

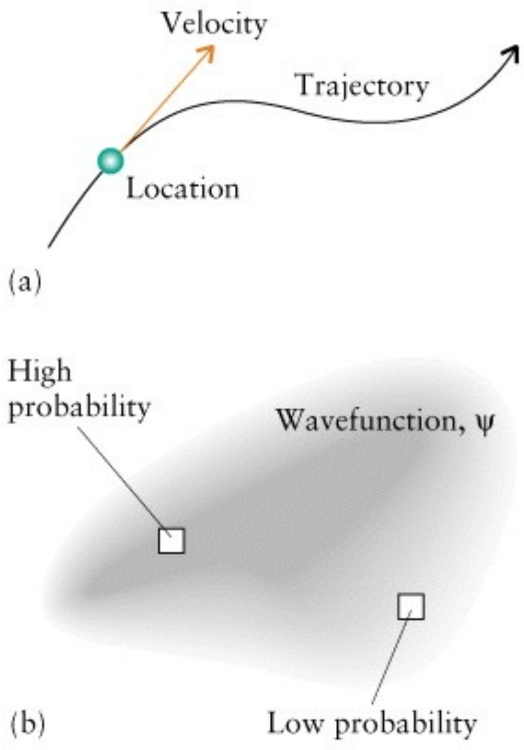
1C.1 The wavefunction and its interpretation

ψ is a wave

- The value of ψ can be positive (above the center line) or negative (below the center line)
- This results in **constructive** or **destructive** interference
- The square of a function is **never negative** → ψ^2, or the probability density, is never negative
- Places where ψ has a **large positive** or **large negative** value → places where a particle is **likely** to be **found**
- $\psi = 0$ with $\psi^2 = 0$: the particle has zero probability density, meaning the particle will **not be found** there
- A location where ψ **passes through zero** (not just reaches zero) is called a **node**, a particle has zero probability density wherever the wavefunction has nodes

1C.1 The wavefunction and its interpretation

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

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.
- Equation not used directly in this class.
- You will need to know the form of some of its solutions, but not how these solutions are found.

1C.1 The wavefunction and its interpretation

The Schrödinger equation

- For a particle of mass m moving in one dimension in a region where the potential energy is $V(x)$, the equation is

$$\underbrace{-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2}}_{\text{Kinetic energy}} + \underbrace{V(x)\psi}_{\text{Potential energy}} = \underbrace{E\psi}_{\text{Total energy}}$$

$\frac{d^2\psi}{dx^2}$: this term indicates how sharply the wavefunction is curved: sharply curved wave function is characteristic of a particle with high kinetic energy.

$$\underbrace{-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + V(x)\psi}_{H\psi} = E\psi$$

1C.1 The wavefunction and its interpretation

The Schrödinger equation

- H is called the hamiltonian of the system.
- The hamiltonian is an operator, it «operates on» the wavefunction ψ.
- In terms of H, the equation takes the deceptively simple form

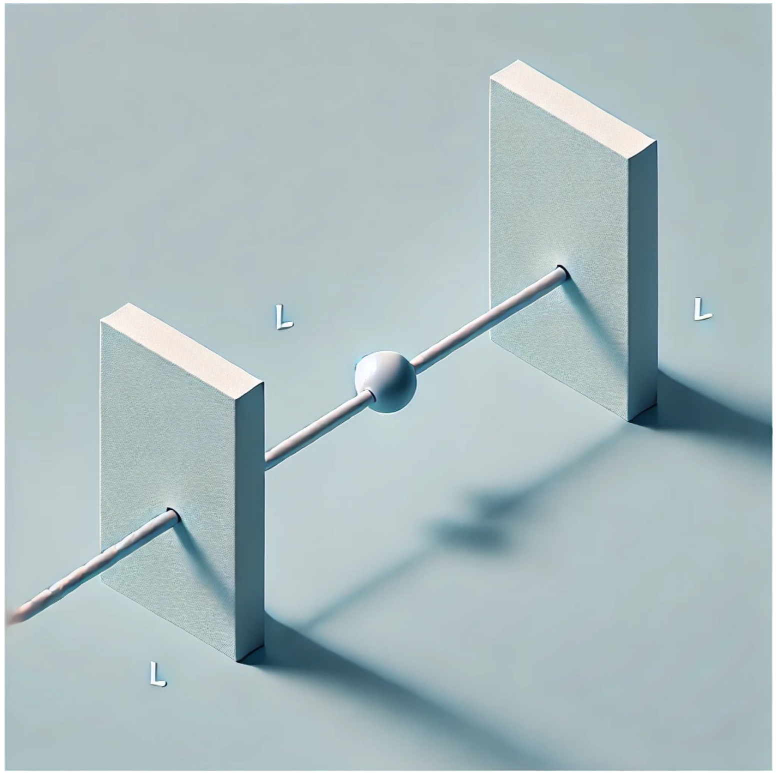
$$H\psi = E\psi$$

- Because H is an operator, you cannot simply divide by ψ from both sides.
- The Schrödinger equation is a «**differential equation**», an equation that relates the «derivatives» of a function (in this case the second derivative of ψ, $d^2\psi/\mathrm{dx}^2$) to the value of a function at each point. You will go more deeply into this topic later in your studies.
- The Schrödinger equation is used to calculate both the **wavefunction $\boldsymbol{\psi}$** and the corresponding **energy $\boldsymbol{E}$**.

1C.1 The wavefunction and its interpretation

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.
- **Physical analog**: a bead free to slide along a rigid rod lying between two walls a distance *L* apart.
- **Classical mechanics**: the bead has the same probability of being found on the rod at any point inside the box, any speed, any kinetic energy



1C.1 The wavefunction and its interpretation

Boundary conditions

The quantum mechanical solution:

- The particle must be inside the box: **boundary conditions**
- Boundary conditions are statements about the values a wavefunction must have at certain locations.
- A probability density—and therefore a wavefunction—cannot jump abruptly from one value to another: it varies **smoothly** and **continuously**.
- Therefore: because the particle cannot be found outside the walls, its wavefunction must be zero just inside the walls.
- The boundary conditions for a particle in a box are that **its wavefunction must be zero** at each end of the box, at $\boldsymbol{x = 0}$ and $\boldsymbol{x = L}$.

1C.1 The wavefunction and its interpretation

Wavefunctions vs. guitar strings

Because the particle acts like a wave with zero amplitude at each end of the box

- → Only wavefunctions with **certain wavelengths** can exist in the box
- → Think of a **guitar string**: because it is tied down at each end, it can support only shapes like the ones shown in Fig. 1C.3.
- → The shapes of the wavefunctions for the particle in the box are the same as the displacements of a vibrating string.

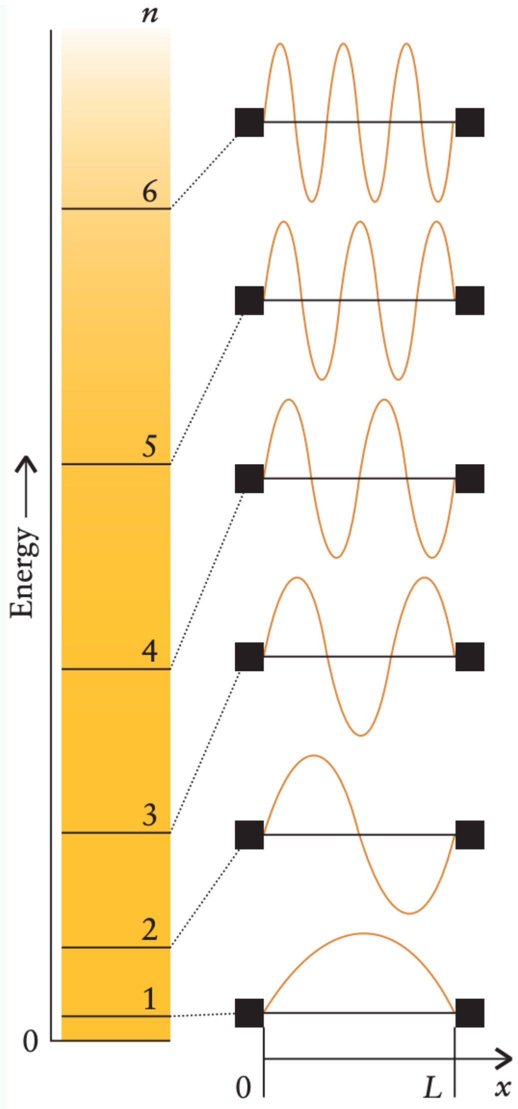
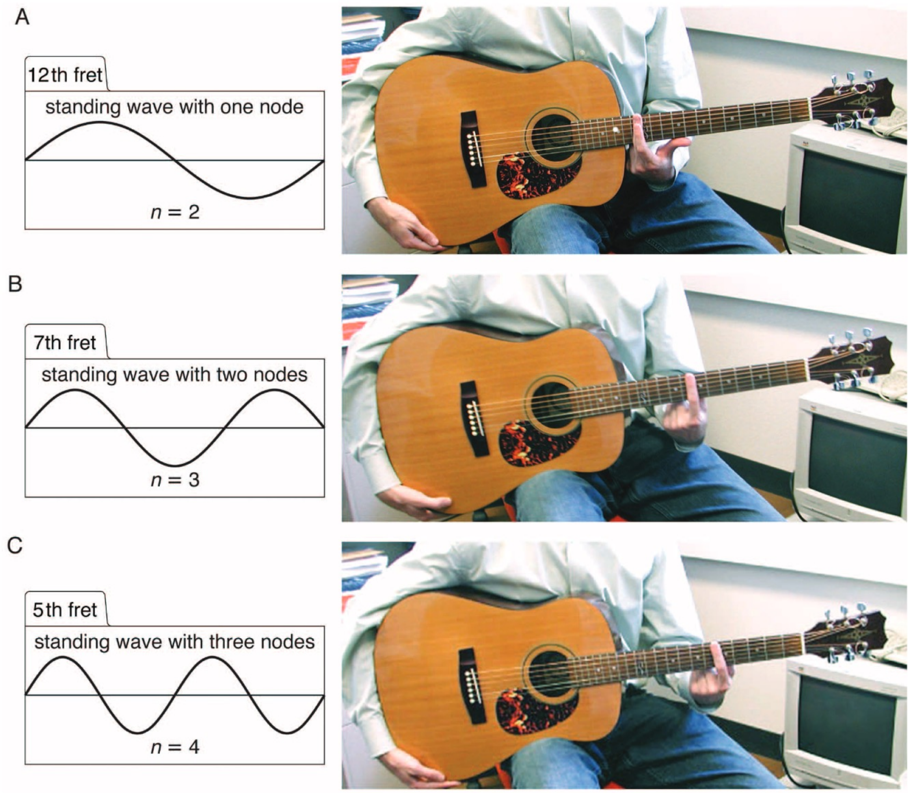


Figure 1C.3

1C.1 The wavefunction and its interpretation

Wavefunctions vs. guitar strings



Michael Davis, Journal of Chemical Education **2007**, 1287.

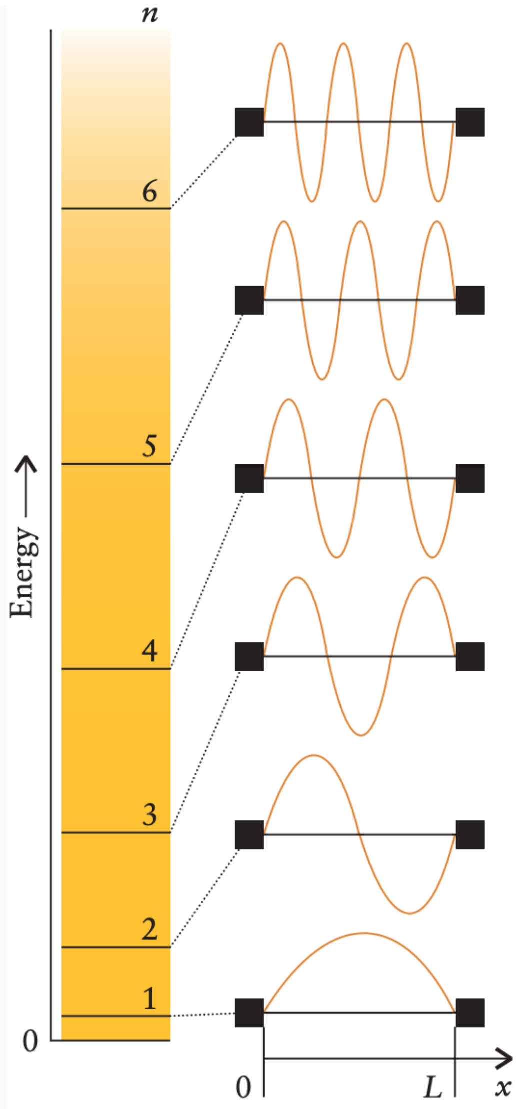


Figure 1C.3

1C.1 The wavefunction and its interpretation

The mathematical form of the particle in the box

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

- The integer n labels the wavefunctions and is called a "quantum number".

A **quantum number**:

- Is an integer (or sometimes a half-integer, such as ½, see Topic 1D)
- Labels a wavefunction
- Specifies a state
- Can sometimes be used to calculate the value of a property of the system, e.g. energy.

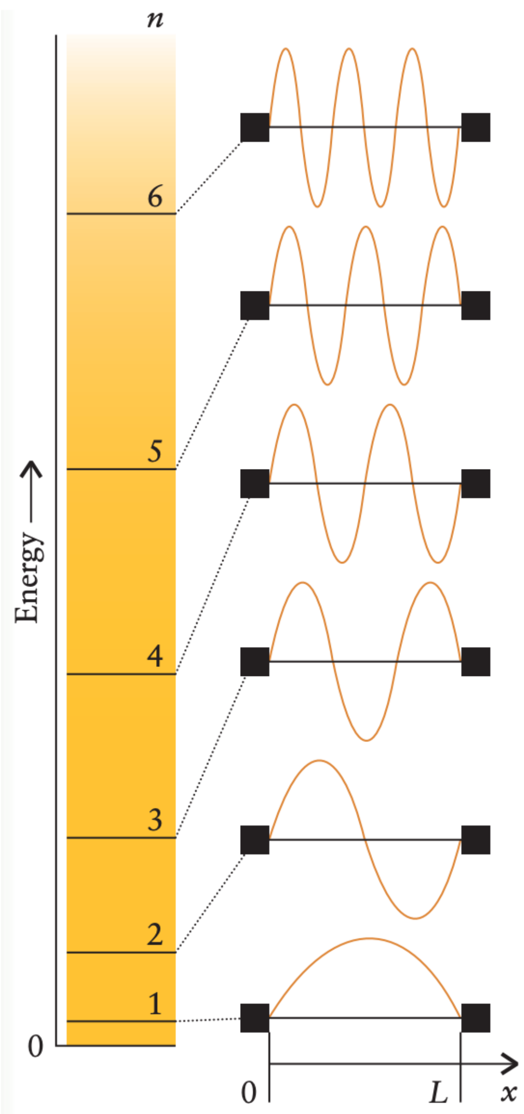


Figure 1C.3

1C.1 The wavefunction and its interpretation

Summary

The **probability density** for a particle at a location is proportional to the square of the wavefunction at that point; places where the wavefunction passes through zero are called **nodes**, and the particle will not be found there. A wavefunction is found by **solving the Schrödinger equation** for the particle and recognizing the existence of certain **boundary conditions**.

URL

Quantum mechanics and guitars

Figure 1C.3