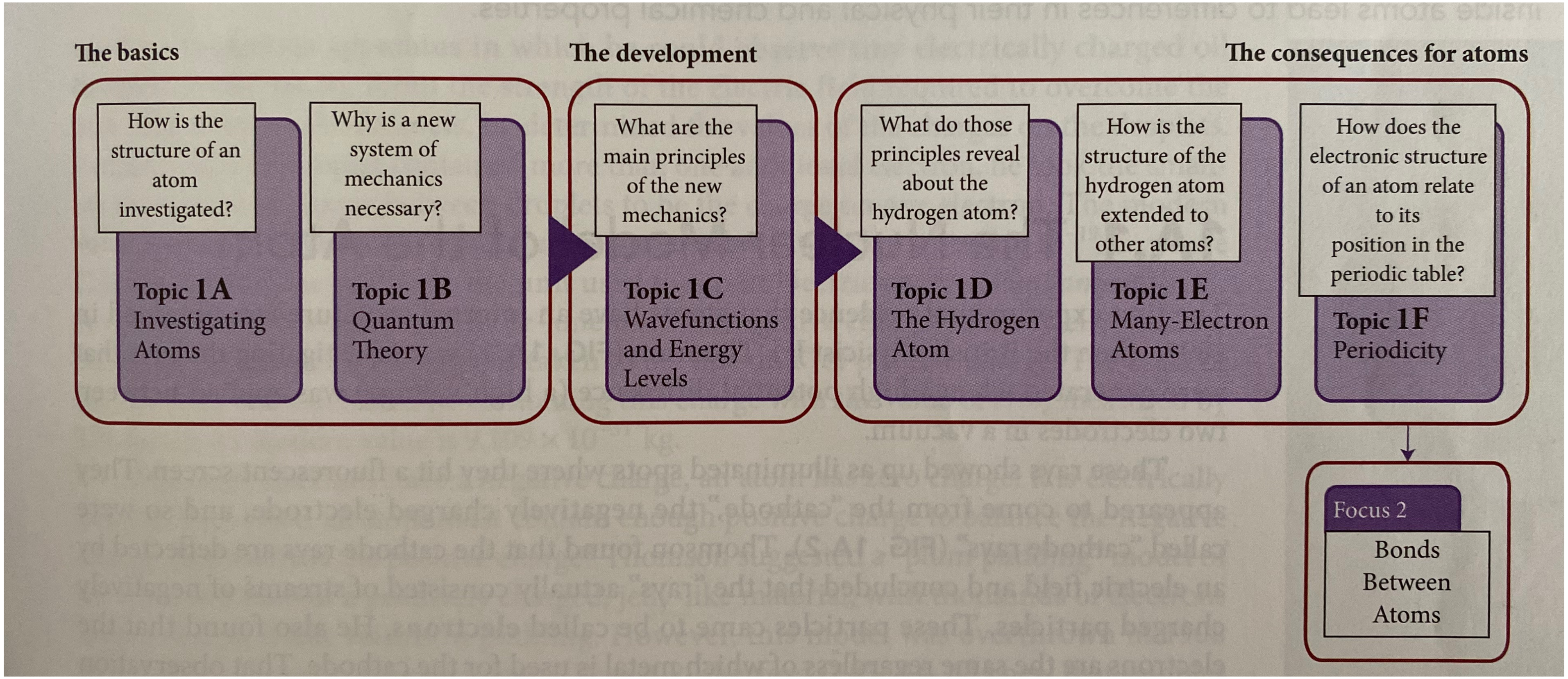
CH-110 Advanced General Chemistry I

Prof. A. Steinauer
angela.steinauer@epfl.ch

Wavefunctions and Energy Levels

Topic 1C

Overview Chapter 1 (Focus 1: Atoms)



The Wavefunction and Its Interpretation

Topic 1C.1

Classical mechanics:

Fixed predictable path

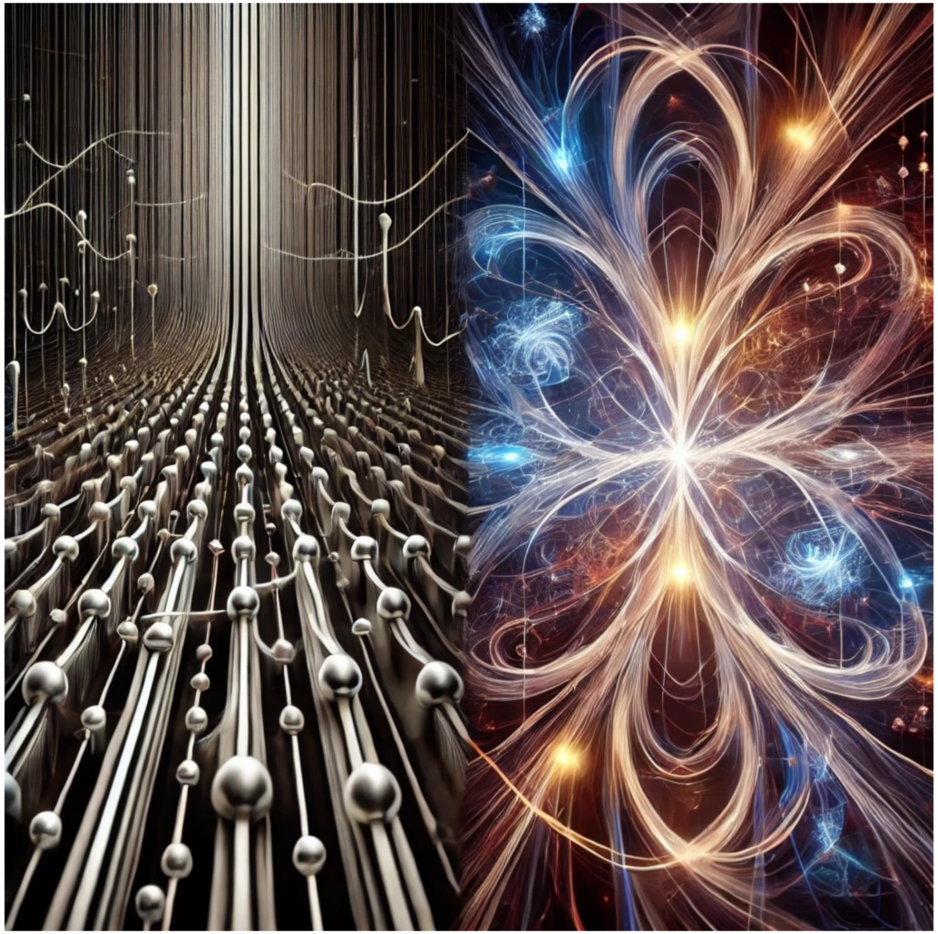


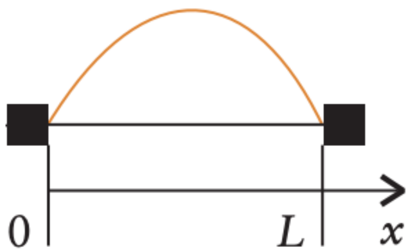
Image source: ChatGPT.
Classical vs. quantum paths.

Quantum mechanics:

Probability distribution

1C.1 The wavefunction and its interpretation

The particle-in-a-box model



The wavefunction of the particle in its lowest-energy state (**ground state, *n* = 1**):

$$\psi_1(x) = \left(\frac{2}{L}\right)^{\frac{1}{2}} \sin\left(\frac{\pi x}{L}\right)$$

And therefore:

$$\psi_1^2(x) = \left(\left(\frac{2}{L}\right)^{\frac{1}{2}} \sin\left(\frac{\pi x}{L}\right)\right)^2 = \frac{2}{L}\, sin^2\left(\frac{\pi x}{L}\right)$$

And P(x=0) = P(x=L) = 0

1C.1 The wavefunction and its interpretation

The particle-in-a-box model

- **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

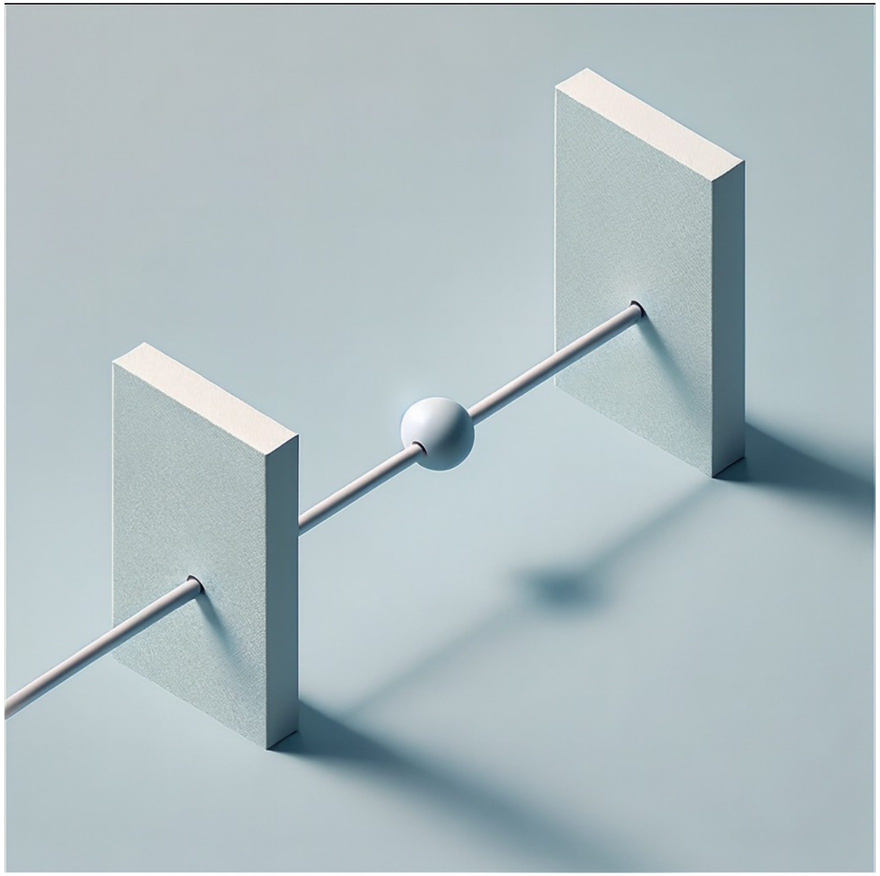


Image source: ChatGPT.
Bead on a rigid rod..

1C.1 The wavefunction and its interpretation

The particle-in-a-box model: n<1

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

- 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.

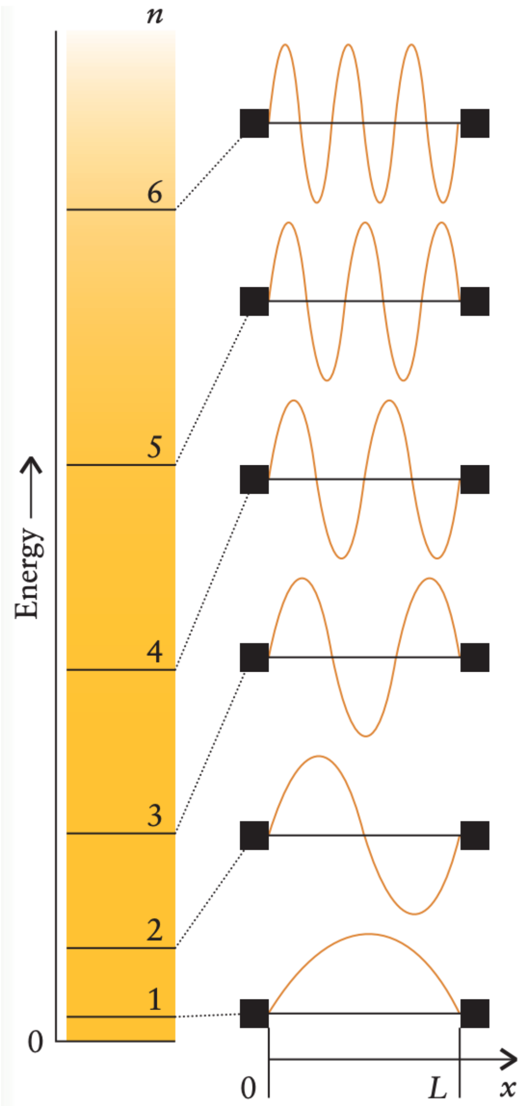


Figure 1C.3

1C.1 The wavefunction and its interpretation

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.
- → The shapes of the wavefunctions for the particle in the box are the same as the displacements of a vibrating string.

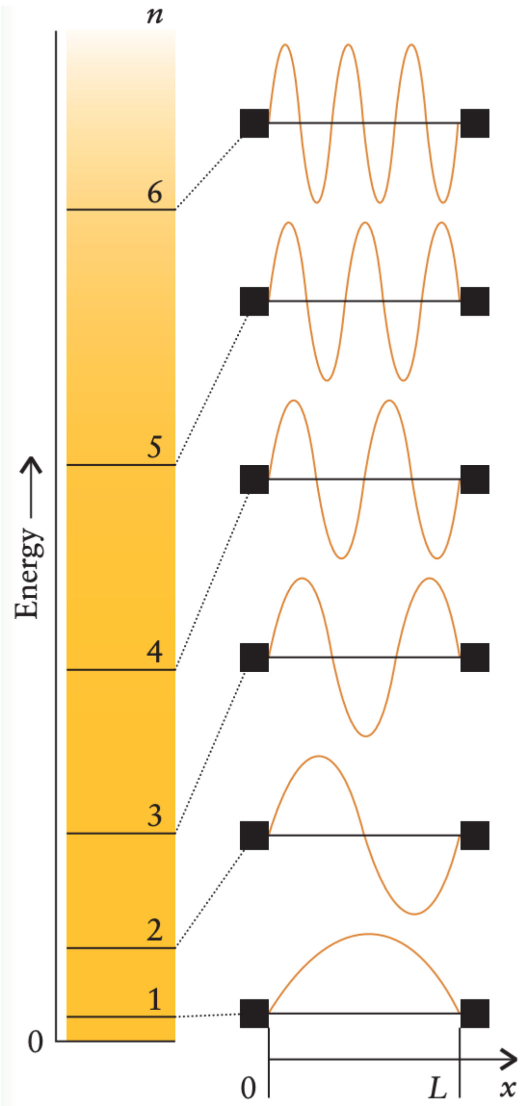
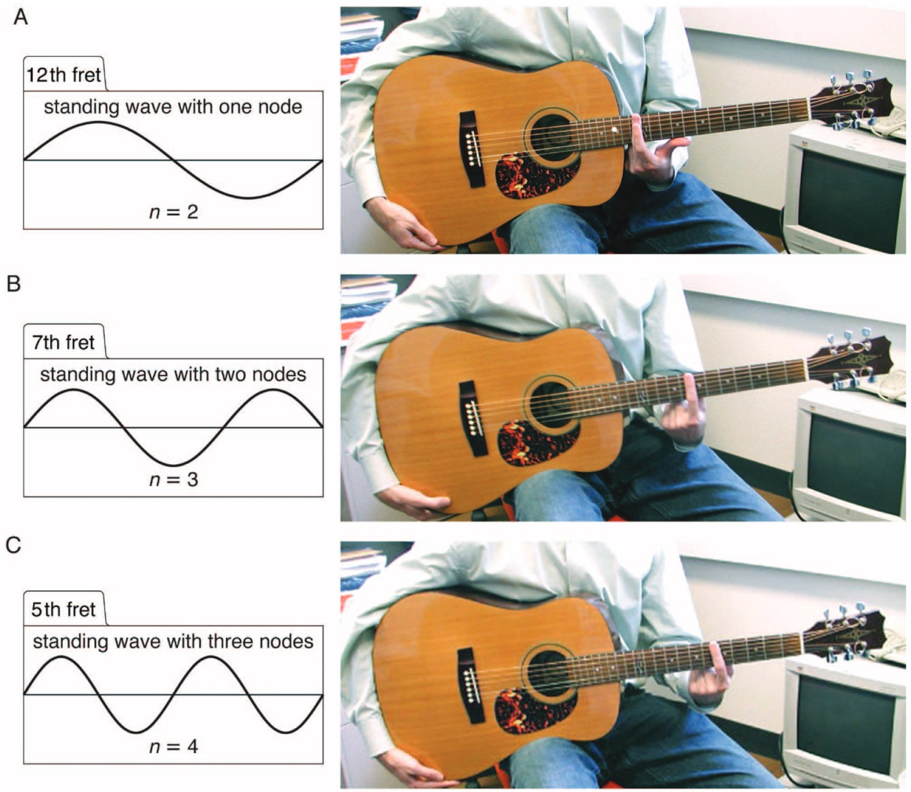


Figure 1C.3

1C.1 The wavefunction and its interpretation

Wavefunctions vs. guitar strings



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

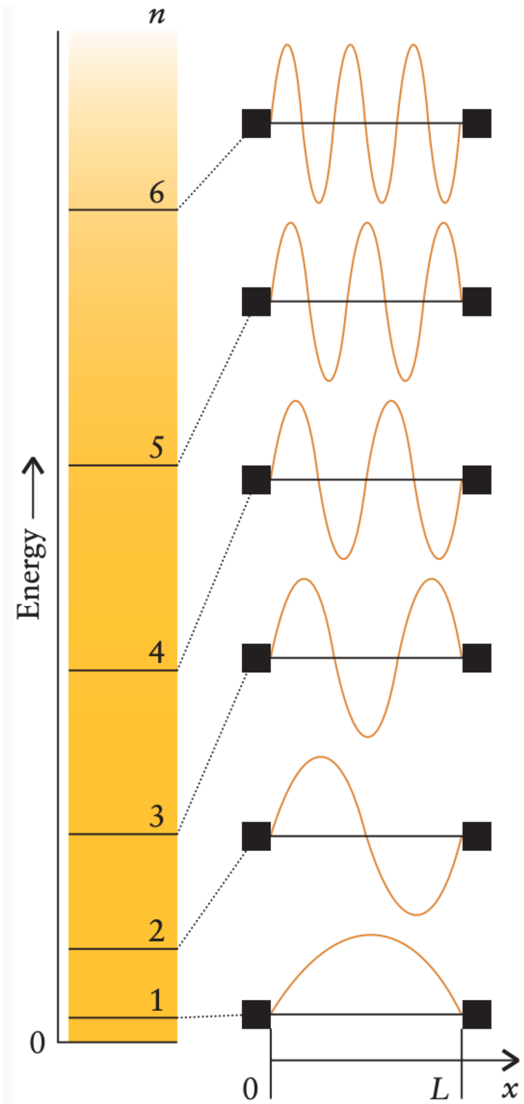


Figure 1C.3

1C.1 The wavefunction and its interpretation

Connecting concepts across Topics 1B and 1C

- **Planck and Einstein:** energy is quantized → light behaves as particles (photons)
- **De Broglie:** matter particles (e.g. electrons) have wave nature
- **Quantum chemistry**: focus on most probable position, not exact location.
- **Schrödinger**: equation provides wavefunction (ψ) and energy of a system.
- **Goal**: knowing $\psi(r)$ and E gives all electron properties; information extracted through probability.

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

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 $\left(\lambda = \frac{h}{p}\right)$:

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

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:

- For n = 1: exactly half a wavelength fits into the box, so $\lambda = 2L$.
- For n = 2: one full wavelength fits, so $\lambda = L$.
- For N = 3: one and a half wavelengths fit, so $\lambda = \frac{2L}{3}$.

Thus, 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?

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

Important formula.
Need to know how to apply.

- **Mass in denominator:** Heavier particles → lower, closer energy levels. Lighter particles → higher, more widely spaced levels.
  Box length effect: Smaller box (L↓) → higher, more widely spaced levels. Larger box (L↑) → lower, closer levels.
- n can only be integer values → **energy is quantized!**

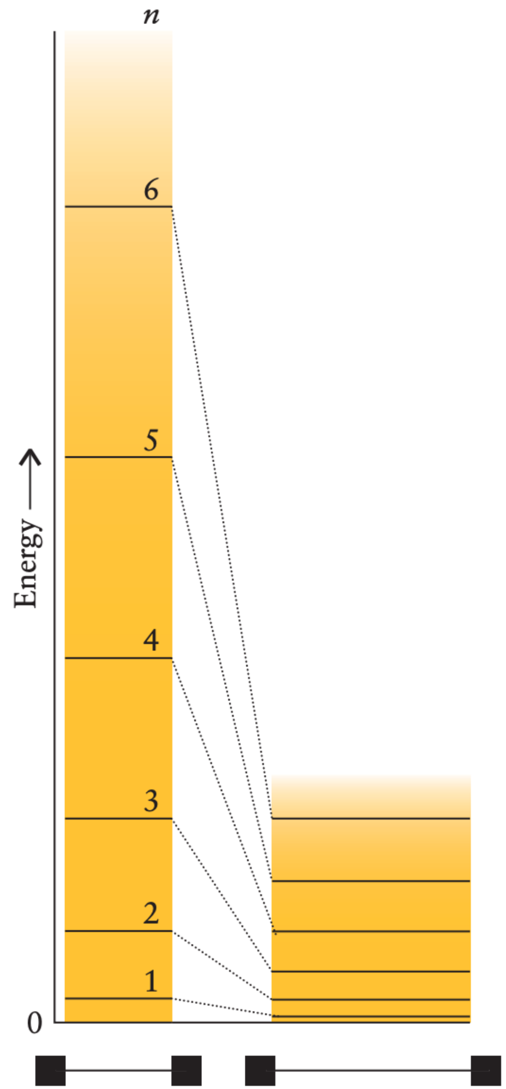


Figure 1C.4

1C.2 The quantization of energy

Energy separation between neighboring levels

Important formula.
Need to know
how to apply.

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

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

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

→ For large *m* or *L* (macroscopic systems), the levels are so close together they appear continuous.

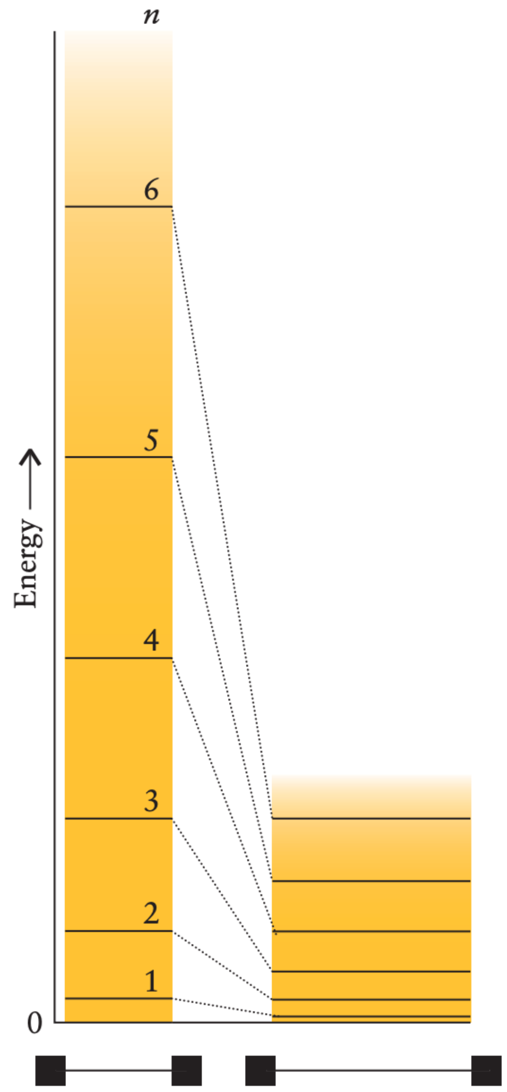


Figure 1C.4

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?!

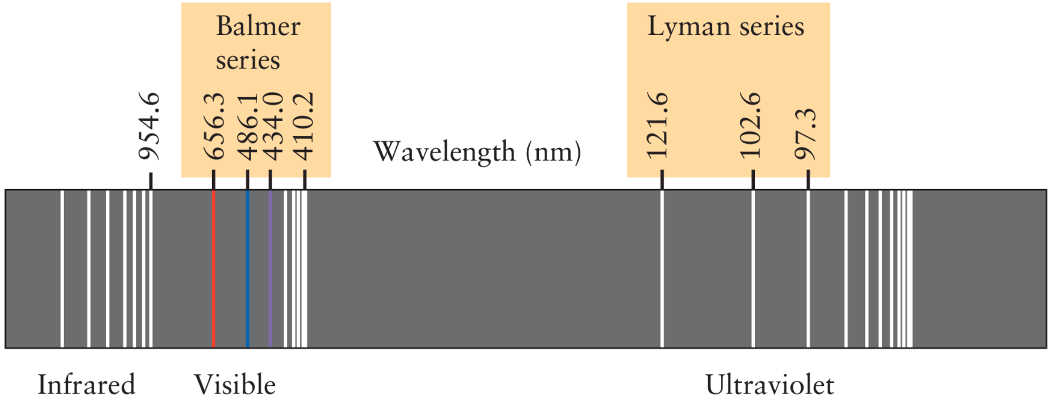


Figure 1A.10

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

The difference in energy is carried away as a photon.

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

Important formula.
Need to know how to apply.

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

1C.2 The quantization of energy

Terminology

- **Ground state**: The lowest energy state of an atom.
- **Excited state**: Any higher energy state above the ground state.
- **Excitation**: Moving to a higher energy state
  1. **Radiative excitation** (**<u>photon absorption</u>**): photon absorbed, electron promoted.
  2. Nonradiative excitation: energy gained from collisions, chemical reactions, or electric fields.
- **Relaxation:** General term for return from an excited state to a lower state.
  1. **Radiative relaxation** (**<u>photon emission</u>**): energy released as a photon .
  2. Nonradiative relaxation: energy released in other forms (e.g., vibrations, heat).

1C.2 The quantization of energy

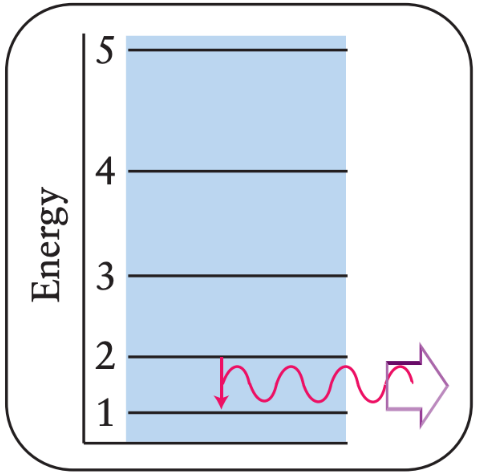
Example 1C.1: Calculating the energies of a particle in a box

We will estimate the energies of the hydrogen atom.

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.

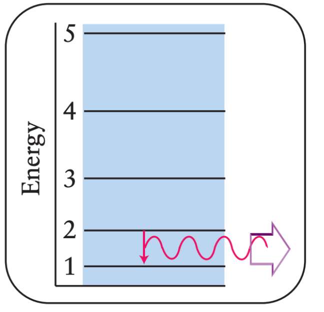
If the electron falls from the **upper level to the lower level**, what would be the wavelength of the radiation emitted as a photon?



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

SOLVE The mass of the electron is found inside the back cover.

From Eq. 12 with $n = 1$, $2n + 1 = 3$,



$$E_2 - E_1 = \frac{3h^2}{8m_eL^2}$$

From $E_2 - E_1 = h\nu$,

$$h\nu = \frac{3h^2}{8m_eL^2}, \quad \text{so } \nu = \frac{3h}{8m_eL^2}$$

From $\lambda = c/\nu$,

$$\lambda = \frac{c}{(3h/8m_eL^2)} = \frac{8m_ecL^2}{3h}$$

1C.2 The quantization of energy

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

Now substitute the data:

$$\lambda = \frac{8 \times \overbrace{(9.109\,39 \times 10^{-31}\ \mathrm{kg})}^{m_e} \times \overbrace{(2.998 \times 10^{8}\ \mathrm{m\cdot s^{-1}})}^{c} \times \overbrace{(1.50 \times 10^{-10}\ \mathrm{m})}^{L=150\ \mathrm{pm}}{}^2}{3 \times \underbrace{(6.626 \times 10^{-34}\ \mathrm{J\cdot s})}_{h}}$$

$$= \frac{8 \times 9.109\,39 \times 10^{-31} \times 2.998 \times 10^{8} \times (1.50 \times 10^{-10})^2}{3 \times 6.626 \times 10^{-34}} \frac{\mathrm{kg\cdot m\cdot s^{-1}\cdot m^2}}{\underbrace{\mathrm{kg\cdot m^2\cdot s^{-2}}}_{\mathrm{J}}\mathrm{\cdot s}}$$

$$= 2.47 \times 10^{-8}\ \mathrm{m}$$

A note on good practice: Note once again how the complicated collection of units is treated: arriving at the correct units for the answer is a sign that you have set up the equation correctly. As usual, it is good practice to go as far as possible symbolically and then to insert numerical values at the last possible stage.

1C.2 The quantization of energy

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

Evaluate This wavelength corresponds to 24.7 nm. The experimental value for the actual transition in a hydrogen atom is 122 nm. Although there is a big discrepancy, an atom does not have the hard boundaries that confine a particle in a box, and is three-dimensional. The fact that the predicted wavelength has nearly the same order of magnitude as the actual value suggests that a quantum theory of the atom, based on a more realistic three-dimensional model, should give good agreement.

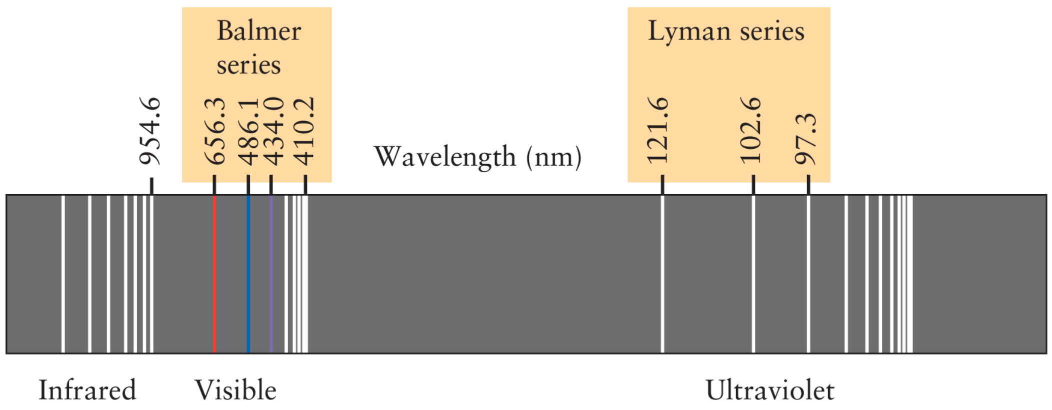


Figure 1A.10

1C.2 The quantization of energy

Particle in a box: zero-point energy

- Surprising implication of equation: $E_n = \frac{n^2 h^2}{8mL^2}$
- 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

The shapes of the wavefunctions

- The first two wavefunctions ($n = 1{,}2$) illustrate how **particle location depends on quantum state**.
- $n = 1$ with $E = h^2/8mL^2$**:** Particle most likely at the center.
- $n = 2$**,** $E = h^2/2mL^2$**:** Particle least likely at the center, most likely between center and walls.
- Shading indicates probability density – the likelihood of finding the particle at each position.

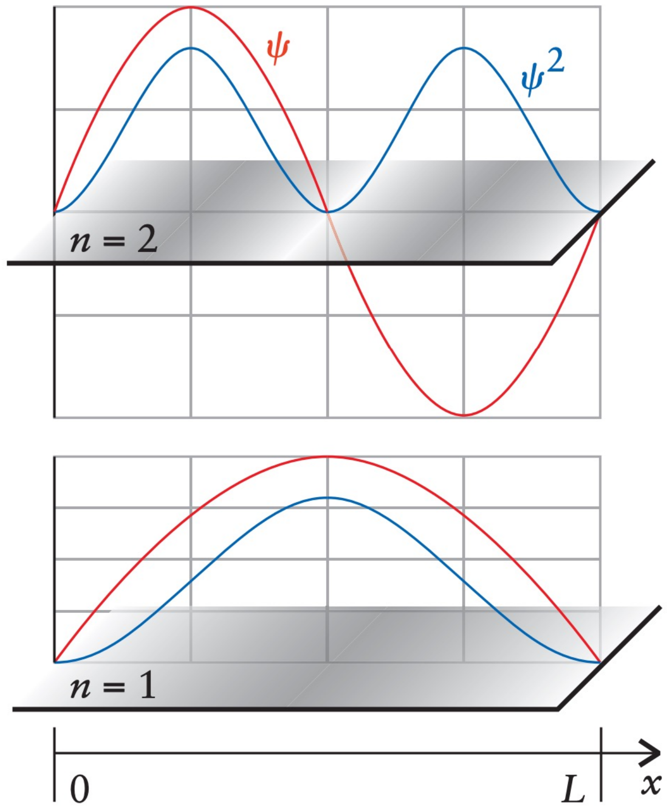


Figure 1C.5

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.