

Chapter 19

Quantum Matter Waves and Bound States

First Edition

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Preface

This chapter develops the first fully worked *bound quantum systems* in this volume. Earlier material introduced photons, de Broglie waves, particle interference and uncertainty. Here the question becomes constructive: if a particle is confined by a potential, which states can it occupy, and what can we predict about measurements?

Confinement turns matter-wave behaviour into a spectrum of allowed states. Boundary conditions and normalization select wavefunctions and their energies. The one-dimensional box makes this mechanism transparent; finite wells, rectangular traps and hydrogen show which conclusions survive when the potential changes.

For engineering, Technical Physics, Computer Science and applied-science students, the chapter connects these models to optical spectra, tunnelling currents, semiconductor confinement and numerical eigenvalue calculations. The core uses introductory calculus and differential equations. Mathematical abstraction is introduced only where it clarifies a physical question.

Reading routes. Begin with probability, boundary conditions, the infinite and finite wells, rectangular traps and hydrogen. The applications and numerical sections connect these ideas to measurement and design. Section 19.20 provides optional enrichment on operators, approximations, computational methods and data analysis. In the broad Physics II course, instructors can select a core route and representative problems; the enrichment is not all required syllabus content.

The Guideline

Before calculating, identify the potential energy, spatial domain, boundary and normalization conditions, and requested observable. Then check dimensions and limiting behaviour. Keep the quantum state distinct from a classical trajectory.

Pedagogical boundary

The models are nonrelativistic and describe one particle, or relative two-body motion, in specified potentials. Spin, identical particles, many-body theory and relativistic corrections require further structure and belong to later study.

Conventions and notation

The complete time-dependent wavefunction of a single nonrelativistic particle is denoted by $\Psi(\mathbf{r}, t)$. For a stationary state, the spatial factor is written $\psi_n(\mathbf{r})$ and the complete time dependence is

$$\Psi_n(\mathbf{r}, t) = \psi_n(\mathbf{r}) \exp\left(-\frac{iE_n t}{\hbar}\right). \quad (0.1)$$

The probability density is $|\Psi|^2 = \Psi^* \Psi$. A wavefunction is not itself a probability. In one dimension, the probability of detecting the particle between $x = a$ and $x = b$ is

$$P(a < x < b) = \int_a^b |\psi(x)|^2 dx, \quad (0.2)$$

provided ψ is normalized.

We use

$$\hbar = \frac{h}{2\pi}, \quad h = 6.62607015 \times 10^{-34} \text{ J s}, \quad (0.3)$$

and the electronvolt

$$1 \text{ eV} = 1.602176634 \times 10^{-19} \text{ J}. \quad (0.4)$$

The elementary charge magnitude is $e = 1.602176634 \times 10^{-19} \text{ C}$ and the electron mass is $m_e \approx 9.109 \times 10^{-31} \text{ kg}$. Electronvolts are used for microscopic energies because they keep numerical values readable; SI joules are used when dimensional checks are especially important.

The one-dimensional time-independent Schrödinger equation is

$$-\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} + V(x)\psi(x) = E\psi(x). \quad (0.5)$$

Here m is the particle mass, $V(x)$ is its potential energy, and E is the total energy eigenvalue. We preserve the chapter's conventional quantum-mechanics symbol V for energy (J or eV); it is not the electric potential in volts used in the electrostatics chapters. For a charge q in an electric potential φ , the contribution is $V = q\varphi$. In three dimensions,

$$-\frac{\hbar^2}{2m} \nabla^2 \psi(\mathbf{r}) + V(\mathbf{r})\psi(\mathbf{r}) = E\psi(\mathbf{r}). \quad (0.6)$$

Appendix A collects the symbols and their units. In particular, a normalized wavefunction has units $\text{m}^{-1/2}$ in one dimension and $\text{m}^{-3/2}$ in three dimensions; its squared magnitude becomes a probability only after integration over the corresponding measure.

Caution

Two different symbols that look similar have very different meanings: m denotes particle mass, while m_ℓ is a dimensionless magnetic quantum number in the hydrogen atom. Likewise, n labels a box eigenstate and also labels the principal hydrogen level, but the physical degeneracies and wavefunctions associated with n are not the same in the two systems.

Chapter 19

Quantum Matter Waves and Bound States

19.1 Motivation and roadmap

Classical mechanics allows a particle in a box to have any nonnegative kinetic energy. If the particle is at rest, its kinetic energy can even be exactly zero. A matter wave cannot generally satisfy the same freedom once it is spatially confined. Just as a string fixed at both ends supports only standing waves whose wavelengths fit the boundary conditions, a confined quantum particle supports only certain stationary wave patterns. The allowed spatial wave numbers determine the kinetic-energy scale and therefore the allowed energies. A confined energy eigenstate is not a state of definite signed momentum.

This mechanism is not a mathematical curiosity. Nanostructures confine electrons on length scales of a few nanometres, producing energy separations large enough to affect optical absorption, emission and charge transport. Semiconductor quantum wells and quantum dots exploit exactly this principle. Atomic spectra are a more fundamental example: the electron in hydrogen is bound by the attractive Coulomb potential, and its discrete energies lead to sharply defined spectral lines.

The progression from confinement to measurable spectra is summarized in Figure 19.1.

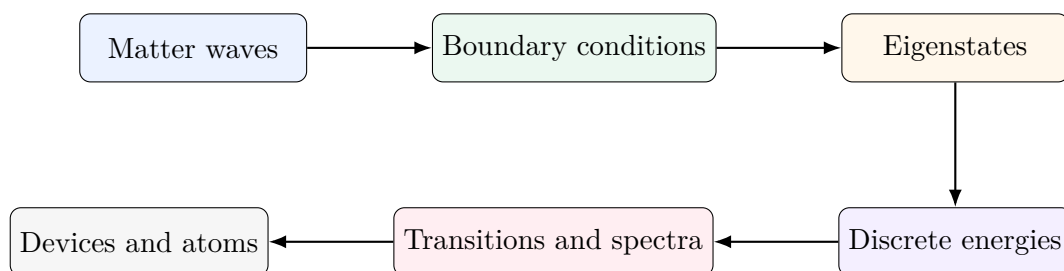


Figure 19.1: Conceptual roadmap for Chapter 19. Confinement constrains matter waves; the resulting eigenstates have discrete energies whose differences are observed through transitions and exploited in nanoscale devices.

Learning goals

After studying this chapter, the student should be able to:

- explain why confinement produces discrete stationary states;
- interpret ψ as a probability amplitude and $|\psi|^2$ as a probability density;
- normalize simple one-dimensional wavefunctions;
- use the time-independent Schrödinger equation for piecewise-constant potentials;
- derive the normalized eigenfunctions and energies of the one-dimensional infinite square well;

- calculate position probabilities and identify nodes for box eigenstates;
- interpret quantum transitions and calculate photon energies and wavelengths;
- explain qualitatively how a finite well differs from an infinite well and why wavefunctions penetrate classically forbidden regions;
- calculate energy levels in rectangular two- and three-dimensional boxes and identify simple degeneracies;
- describe the hydrogen atom as a Coulomb bound-state problem and distinguish the Bohr model from the modern Schrödinger description;
- interpret the quantum numbers n , ℓ and m_ℓ without turning them into classical orbital trajectories;
- connect bound-state physics to quantum wells, quantum dots, semiconductor lasers and scanning tunnelling microscopy;
- implement a basic finite-difference eigenvalue calculation for a one-dimensional potential and perform numerical consistency checks.

Key message

Quantization is not imposed by declaring that “nature likes integers.” In bound systems it emerges because only certain wavefunctions simultaneously satisfy the differential equation, the physical boundary conditions, and normalization.

19.2 From de Broglie waves to stationary states

The de Broglie relation associates wavelength with momentum,

$$\lambda = \frac{h}{p}, \quad (19.1)$$

for a nonrelativistic or relativistic particle whenever p is interpreted as the particle momentum. In the nonrelativistic regime, $K = p^2/(2m)$, so a free particle with a well-defined momentum can be associated with a wavelength

$$\lambda = \frac{h}{\sqrt{2mK}}. \quad (19.2)$$

A perfectly monochromatic matter wave extends throughout space and therefore does not represent a localized particle. Localized wave packets require a superposition of wave numbers. Bound stationary states are different again: the particle is spatially confined, and the allowed spatial patterns are selected by the potential and its boundary conditions.

The analogy with standing waves on a string is useful if it is handled carefully. For a string of length L fixed at both ends, the displacement must vanish at $x = 0$ and $x = L$, so the allowed wavelengths are

$$\lambda_n = \frac{2L}{n}, \quad n = 1, 2, 3, \dots \quad (19.3)$$

A particle in an infinite one-dimensional well obeys mathematically similar endpoint conditions. Substituting the allowed matter-wave wavelengths into the de Broglie relation gives

$$p_n = \frac{nh}{2L}, \quad (19.4)$$

and therefore

$$E_n = \frac{p_n^2}{2m} = \frac{n^2 h^2}{8mL^2}. \quad (19.5)$$

Here $p_n = \hbar k_n$ denotes a characteristic momentum magnitude, or equivalently $\sqrt{\langle p_x^2 \rangle}$ for the box eigenstate. It is not the statement that a momentum measurement has one certain outcome. The spatial sine wave is confined to a finite interval; its full momentum distribution is discussed in Section 19.20.3. This argument predicts the correct spectrum, but it is not yet a complete quantum calculation because it does not establish the probability interpretation, normalization, or the actual eigenfunctions. Those come from the Schrödinger equation.

The string analogy also has a dynamical limit: a vibrating string has a frequency proportional to wave number for an ideal nondispersive medium, whereas a free nonrelativistic particle has $E = \hbar^2 k^2 / (2m)$. Similar boundary conditions therefore need not imply identical frequency spectra.

Guided checks

1. If the width L of a box doubles while the particle mass is unchanged, by what factor does every energy level change?
2. If the particle mass becomes four times larger while L is fixed, what happens to the level spacing?
3. Why does the standing-wave analogy suggest a nonzero lowest energy even before the Schrödinger equation is introduced?

Answers: energies scale as L^{-2} , so they become one quarter as large; they scale as m^{-1} , so the spectrum becomes four times denser; the longest allowed standing wavelength is finite, so the lowest kinetic-energy scale is nonzero.

Caution

A matter wave is not a mechanical vibration of a material medium. The wavefunction is a probability amplitude. The standing-wave analogy is powerful for boundary conditions and quantization, but it must not be interpreted as an electron literally wiggling up and down like a string.

19.3 Wavefunctions, probability density and normalization

Quantum mechanics predicts probabilities for measurement outcomes. The wavefunction $\Psi(\mathbf{r}, t)$ contains the information needed to construct those probabilities. The Born rule states that

$$|\Psi(\mathbf{r}, t)|^2 d^3r \quad (19.6)$$

is the probability of detecting the particle inside the infinitesimal volume element d^3r centred at $\mathbf{r}$ at time t . In one dimension,

$$|\Psi(x, t)|^2 dx \quad (19.7)$$

is the corresponding position probability in an interval of length dx .

Because the particle must be detected somewhere if a complete position measurement is made, an acceptable single-particle wavefunction is normalized:

$$\int_{-\infty}^{\infty} |\Psi(x, t)|^2 dx = 1 \quad (19.8)$$

in one dimension, or

$$\int_{\mathbb{R}^3} |\Psi(\mathbf{r}, t)|^2 d^3r = 1 \quad (19.9)$$

in three dimensions. The wavefunction itself may be positive, negative, or complex.

A probability density can exceed 1 in its chosen units; only its integral over a region is a probability constrained to $[0, 1]$. For an ordinary continuous position distribution, the probability of one exact

point is zero, including at a maximum of the density. A detector samples a finite spatial interval or volume. A constant overall phase does not change any physical prediction; relative phases between components can change interference.

For a normalized one-dimensional wavefunction, the probability of detecting the particle between a and b is

$$P(a < x < b) = \int_a^b |\Psi(x, t)|^2 dx. \quad (19.10)$$

The result must be dimensionless and lie between 0 and 1. Since dx has units of length, $|\Psi|^2$ has units of inverse length in a one-dimensional model, and Ψ has units of length^{-1/2}.

Definition 19.1: Node

In one dimension, an interior *node* of a stationary-state wavefunction is a point inside the domain at which $\psi(x) = 0$. In more dimensions the zero set can include lines or surfaces. The probability density also vanishes there. Nodes are features of a stationary spatial pattern; they are not impenetrable walls unless the potential itself imposes a wall.

Example 19.1: Normalizing a trial wavefunction on a finite interval

Suppose a particle is known to lie in $0 < x < L$ and is described by the trial wavefunction

$$\psi(x) = Ax(L - x), \quad 0 < x < L,$$

with $\psi = 0$ outside. Determine A if the wavefunction is normalized.

Solution. Apply Eq. (19.8):

$$\begin{aligned} 1 &= |A|^2 \int_0^L x^2(L - x)^2 dx \\ &= |A|^2 \int_0^L (L^2x^2 - 2Lx^3 + x^4) dx \\ &= |A|^2 L^5 \left(\frac{1}{3} - \frac{1}{2} + \frac{1}{5} \right) = |A|^2 \frac{L^5}{30}. \end{aligned}$$

Hence

$$A = \frac{\sqrt{30}}{L^{5/2}},$$

where the positive sign is chosen for convenience; an overall minus sign would describe the same position probability density.

Check. Since $x(L - x)$ has units L^2 , A must carry units $L^{-5/2}$ so that ψ has units $L^{-1/2}$. The dimensions are consistent.

Method

For every normalization or probability integral, perform three checks: (1) the integrand must be $|\psi|^2$, not ψ ; (2) the integration limits must correspond to the physical region asked for; and (3) the final probability must be dimensionless and between 0 and 1.

19.4 The time-independent Schrödinger equation

For a classical nonrelativistic particle moving in a potential $V(x)$,

$$E = \frac{p^2}{2m} + V(x). \quad (19.11)$$

Quantum mechanics replaces the classical momentum observable by the differential operator

$$\hat{p}_x = -i\hbar \frac{d}{dx}. \quad (19.12)$$

Acting twice gives $\hat{p}_x^2 = -\hbar^2 d^2/dx^2$. The corresponding Hamiltonian operator is

$$\hat{H} = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + V(x). \quad (19.13)$$

Stationary states satisfy the eigenvalue equation

$$\hat{H}\psi = E\psi, \quad (19.14)$$

which is the one-dimensional time-independent Schrödinger equation,

$$-\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} + V(x)\psi = E\psi. \quad (19.15)$$

This equation is a postulate of nonrelativistic quantum theory, motivated by the energy and momentum relations, not a theorem derivable from Newton's laws. Its connection with time evolution is particularly useful. For a time-independent potential, insert $\Psi(x, t) = \psi(x)f(t)$ in

$$i\hbar \frac{\partial \Psi}{\partial t} = \hat{H}\Psi. \quad (19.16)$$

Dividing by ψf where they are nonzero separates a function of time from a function of position:

$$i\hbar \frac{f'}{f} = \frac{\hat{H}\psi}{\psi} = E.$$

Both sides must equal the same constant, giving $f(t) = \exp(-iEt/\hbar)$ and $\hat{H}\psi = E\psi$. The phase evolves while $|\Psi|^2$ stays fixed. A linear combination of different energy eigenfunctions solves the time-dependent equation when each component carries its own phase; it does not solve the stationary equation with a single energy.

Equation (19.15) is a second-order linear differential equation. Its solutions are strongly constrained by physical acceptability. For a bounded, piecewise continuous potential and a constant mass, ψ and its first derivative are continuous at a finite interface. A bound state is square-integrable and can be normalized. Ideal scattering waves instead use flux normalization or wave packets; one must not try to normalize a plane wave over all space to unity. At an ideal infinite wall the wavefunction vanishes at the boundary. For bound states, ψ must decay sufficiently rapidly as $|x| \rightarrow \infty$ whenever the classically allowed region is finite.

The kinetic-energy term is related to curvature. Rearranging gives

$$\frac{d^2\psi}{dx^2} = -\frac{2m}{\hbar^2}[E - V(x)]\psi. \quad (19.17)$$

For constant V with $E > V$, sine and cosine solutions follow; for constant V with $E < V$, the solutions are growing and decaying exponentials. For varying V , the equation still determines local curvature, but these elementary functions are not generally exact solutions. A normalizable bound state selects the decaying behaviour far from the well.

Key message

The Schrödinger equation does not by itself quantize every system. A free particle can have a continuous range of energies. Discrete energies arise when the differential equation is combined with boundary conditions and normalizability appropriate to a bound system.

Guided checks

1. In a region where V is constant and $E > V$, why do sine and cosine functions naturally appear?
2. In a region where $E < V$, why is a decaying exponential physically acceptable but an exponentially growing solution usually not acceptable for a bound state extending to infinity?
3. What dimensions must the factor $2m(E - V)/\hbar^2$ have in Eq. (19.17)?

Answer to the dimensional check: inverse length squared, because it multiplies ψ to produce $d^2\psi/dx^2$.

19.5 Boundary conditions, continuity and reading potential diagrams

The Schrödinger equation is a differential equation, but a physically acceptable solution is determined only after boundary conditions are imposed. In bound-state problems these conditions encode the geometry of the confinement and the requirement that probabilities remain finite.

For a finite potential step at $x = x_0$, the usual one-particle Schrödinger equation with a constant mass requires both the wavefunction and its first derivative to be continuous:

$$\psi(x_0^-) = \psi(x_0^+), \quad \psi'(x_0^-) = \psi'(x_0^+). \quad (19.18)$$

The reason can be seen by integrating the Schrödinger equation across a very narrow interval from $x_0 - \epsilon$ to $x_0 + \epsilon$:

$$-\frac{\hbar^2}{2m} \int_{x_0-\epsilon}^{x_0+\epsilon} \psi''(x) dx + \int_{x_0-\epsilon}^{x_0+\epsilon} (V - E)\psi dx = 0. \quad (19.19)$$

If V remains finite, the second integral vanishes as $\epsilon \rightarrow 0$, leaving

$$\psi'(x_0^+) - \psi'(x_0^-) = 0.$$

A discontinuity in ψ itself would generate still more singular derivatives and would be incompatible with the ordinary finite-potential equation.

The infinite wall is different. It is an idealized limiting potential, not a finite step. The wavefunction must vanish at the wall and outside it, and the derivative need not match smoothly to the identically zero exterior solution. This distinction is important when moving from the infinite well to a finite well.

Caution

Do not impose $\psi = 0$ at every abrupt change in potential. A finite potential step normally requires continuity of ψ and ψ' , whereas an ideal infinite wall enforces $\psi = 0$ at the boundary.

Potential-energy diagrams also deserve careful reading. The vertical axis represents *potential energy*, not force and not necessarily electric potential. For a constant-potential segment, an energy line above $V(x)$ implies sinusoidal solutions, while a line below $V(x)$ implies exponentials. In a varying potential this is a local qualitative guide; at $E = V$ the local curvature vanishes. This simple graphical rule allows a qualitative wavefunction sketch before any algebra is performed.

Guided checks

A student sketches a finite-well bound state that jumps discontinuously at the wall but has the correct exponential decay outside. What is wrong with the sketch? How would the sketch change if the wall were truly infinite?

Answer. Both ψ and ψ' must match at a finite step for constant mass. At an infinite wall ψ vanishes, but its derivative need not join the zero exterior derivative. Figure 19.5 shows a correctly matched finite-well example.

19.6 The one-dimensional infinite square well

The infinite square well is the cleanest model of spatial confinement. Let

$$V(x) = \begin{cases} 0, & 0 < x < L, \\ \infty, & x \leq 0 \text{ or } x \geq L. \end{cases} \quad (19.20)$$

The particle has zero probability of being found outside the interval, so the wavefunction obeys

$$\psi(0) = \psi(L) = 0. \quad (19.21)$$

Inside the box, $V = 0$, and Eq. (19.15) becomes

$$\frac{d^2\psi}{dx^2} + k^2\psi = 0, \quad k^2 = \frac{2mE}{\hbar^2}. \quad (19.22)$$

The general solution is

$$\psi(x) = A \sin(kx) + B \cos(kx). \quad (19.23)$$

The condition $\psi(0) = 0$ forces $B = 0$. The condition $\psi(L) = 0$ then gives

$$\sin(kL) = 0, \quad (19.24)$$

so

$$kL = n\pi, \quad n = 1, 2, 3, \dots \quad (19.25)$$

The value $n = 0$ would produce the identically zero function, which is not a physical state because it cannot be normalized to probability one.

Thus

$$k_n = \frac{n\pi}{L}, \quad (19.26)$$

and

$$E_n = \frac{\hbar^2 k_n^2}{2m} = \frac{n^2 \pi^2 \hbar^2}{2mL^2} = \frac{n^2 h^2}{8mL^2}. \quad (19.27)$$

Normalization determines the remaining amplitude:

$$1 = |A|^2 \int_0^L \sin^2\left(\frac{n\pi x}{L}\right) dx = |A|^2 \frac{L}{2}, \quad (19.28)$$

so a convenient real choice is

$$\boxed{\psi_n(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right)}, \quad 0 < x < L. \quad (19.29)$$

The boundary conditions and node counts can be inspected in Figure 19.2.

The energy spectrum scales as n^2 . Therefore adjacent levels become farther apart as n increases:

$$E_{n+1} - E_n = (2n + 1)E_1. \quad (19.30)$$

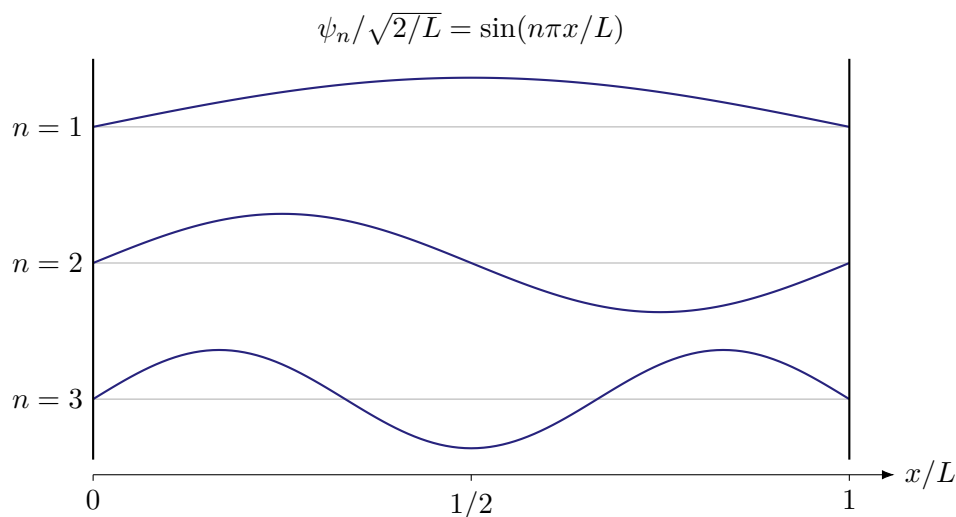


Figure 19.2: Infinite-well eigenfunctions with separate zero baselines and a common amplitude scale. The vertical offsets do not represent energies. State n has $n - 1$ interior nodes; every curve vanishes at the physical walls.

The ground-state energy

$$E_1 = \frac{h^2}{8mL^2} \quad (19.31)$$

is strictly positive. This is often called the zero-point energy of the box.

The energy is quoted relative to the well bottom. Adding a constant C to V shifts every E_n by C without changing the wavefunctions, energy differences or probabilities. The zero-point statement is therefore about a positive kinetic energy and an energy above the minimum, not about an absolute, experimentally privileged zero.

Caution

The nonzero ground-state energy is not an arbitrary “quantum correction” added to a classical answer. It follows directly from the impossibility of satisfying both confinement and normalization with a constant zero-momentum wavefunction. A wavefunction that is constant inside the box and zero outside would also fail the required boundary behaviour at the walls.

Example 19.2: Electron confined to a one-nanometre box

An electron is confined to an ideal one-dimensional well of width $L = 1.00$ nm. Find the first three energies relative to the well bottom.

Solution. Using Eq. (19.27),

$$E_1 = \frac{h^2}{8m_e L^2} = 0.376 \text{ eV}.$$

Because $E_n = n^2 E_1$,

$$E_2 = 4E_1 = 1.50 \text{ eV}, \quad E_3 = 9E_1 = 3.38 \text{ eV}.$$

Interpretation. The electron cannot have 0.80 eV while remaining in a stationary state of this ideal well; that value lies between the allowed eigenenergies.

Scale check. Sub-electronvolt to few-electronvolt spacings are entirely plausible for nanometre confinement. This is why quantum confinement is technologically important in semiconductor nanostructures.

Example 19.3: Mass scaling: electron versus proton

An electron and a proton are separately confined in identical one-dimensional wells of width L . Compare their ground-state energies.

Solution. Since $E_1 \propto 1/m$,

$$\frac{E_{1,e}}{E_{1,p}} = \frac{m_p}{m_e} \approx 1836.$$

The electron has a ground-state confinement energy roughly 1836 times larger than the proton in the same geometric box.

Physical meaning. Quantum confinement is especially conspicuous for light particles. The same dimensional feature can strongly quantize electrons while having much smaller effects on heavier atoms or nuclei.

Guided checks

1. How many interior nodes does ψ_5 have?
2. Does the probability density distinguish ψ_n from $-\psi_n$?
3. If L decreases from 2 nm to 1 nm, what happens to E_1 ?
4. Why is $n = 0$ excluded?

Answers: four nodes; no; E_1 increases by a factor of four; $n = 0$ gives the zero function, not a normalizable physical state.

19.7 Position probabilities in the infinite well

For the normalized box eigenstate of Eq. (19.29), the probability density is

$$|\psi_n(x)|^2 = \frac{2}{L} \sin^2\left(\frac{n\pi x}{L}\right). \quad (19.32)$$

It is stationary: the complete state acquires the phase factor $\exp(-iE_n t/\hbar)$, but its magnitude squared is independent of time. This is the precise meaning of a stationary state.

The probability of finding the particle between $x = a$ and $x = b$ is

$$P(a < x < b) = \frac{2}{L} \int_a^b \sin^2\left(\frac{n\pi x}{L}\right) dx \quad (19.33)$$

$$= \frac{b-a}{L} - \frac{1}{2n\pi} \left[\sin\left(\frac{2n\pi b}{L}\right) - \sin\left(\frac{2n\pi a}{L}\right) \right]. \quad (19.34)$$

This formula makes clear that quantum probability need not be proportional to interval length. It depends on the spatial structure of the state.

The dependence of probability density on the quantum state is visible in Figure 19.3.

Example 19.4: Probability in the left and middle thirds

A particle is in the ground state of an infinite well extending from 0 to L . Find the probability of detecting it in (a) the left third, $0 < x < L/3$, and (b) the middle third, $L/3 < x < 2L/3$.

Solution. Set $n = 1$ in Eq. (19.34). For the left third,

$$P_{\text{left}} = \frac{1}{3} - \frac{1}{2\pi} \sin\left(\frac{2\pi}{3}\right) \approx 0.1955.$$

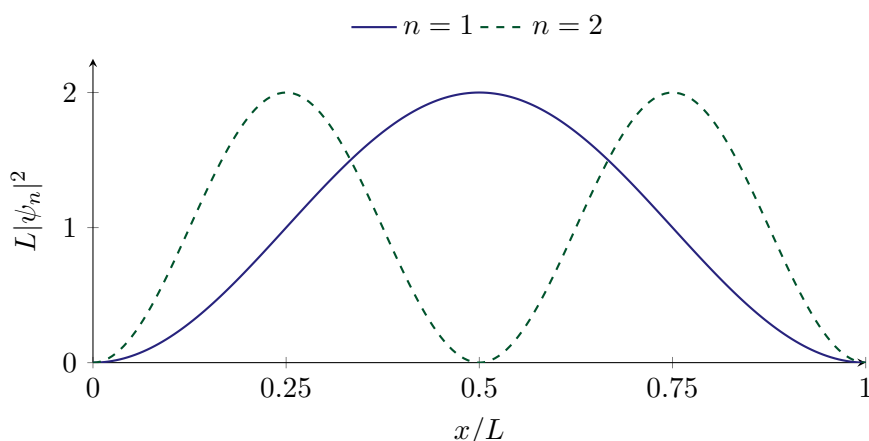


Figure 19.3: Calculated dimensionless probability densities. Both have unit area in the coordinate x/L , although their maxima reach 2. The zero at the centre for $n = 2$ changes interval probabilities; negative wavefunction lobes never create negative probability.

By symmetry the right-third probability is the same. Therefore

$$P_{\text{middle}} = 1 - 2P_{\text{left}} \approx 0.6090.$$

Interpretation. The middle third occupies one third of the geometric length but contains about 61% of the ground-state position probability because the ground-state density peaks near the centre.

Example 19.5: A node changes the probability pattern

For the first excited state $n = 2$, calculate the probability of finding the particle in the middle third of the same box.

Solution. Using Eq. (19.34) with $n = 2$, $a = L/3$, and $b = 2L/3$ gives

$$P_{\text{middle}} \approx 0.1955.$$

The central node at $x = L/2$ suppresses probability density in the middle of the box, so the middle-third probability is much smaller than for the ground state.

Lesson. Knowing only the box width is not enough to predict position probabilities. The quantum state matters.

Method

When interpreting a wavefunction graph, first identify whether the vertical axis shows ψ , $|\psi|$, or $|\psi|^2$. A graph of ψ may cross zero and become negative; a graph of $|\psi|^2$ cannot. Nodes occur at the same positions in both, but signs and interference information are contained in ψ , not in $|\psi|^2$ alone.

19.7.1 How to read and interpret wavefunction graphs

Quantum-mechanics exercises often provide a graph rather than an explicit formula. Reading such a graph requires more care than reading a classical trajectory. The horizontal coordinate usually labels position, while the vertical curve can represent several different quantities. The caption or axis label must be checked first.

If the graph is $\psi(x)$, then positive and negative lobes carry phase information, nodes are zero crossings, and the magnitude alone does not directly give a probability for a finite interval. If the graph is $|\psi(x)|^2$, all values are nonnegative and the area under the curve over an interval is the probability for that interval. If wavefunctions are plotted on an energy-level diagram, they are often vertically shifted and rescaled for visibility; their vertical coordinate should not then be interpreted as the physical value of ψ .

For a one-dimensional bound state in a smooth or piecewise finite potential, the number of nodes provides a strong ordering clue: the ground state has no internal node, the first excited state has one, and so on. This node theorem is more general than the infinite-well formula and is extremely useful for checking numerical eigenvectors.

Method

When given a wavefunction plot, use the following order: identify the plotted quantity; locate the physical boundaries; count nodes; inspect symmetry or parity; compare the tail behaviour with the potential; only then infer the likely quantum-state ordering.

Example 19.6: Inferring the state from a graph

A numerical calculation for a symmetric one-dimensional well produces a real eigenfunction that is antisymmetric, crosses zero at the centre, has no other internal zero, and decays exponentially outside the well. The absence of additional nodes means it is the first excited bound state. The antisymmetry is consistent with the parity sequence of a symmetric well: an even ground state followed by an odd first excited state.

A probability-density plot hides the sign changes of ψ . For example, the $n = 2$ and a hypothetical everywhere-positive curve could have similar lobe locations in $|\psi|^2$ while representing very different amplitudes. Sign and phase become essential when states interfere or when transition matrix elements are evaluated.

19.7.2 Measurement, expectation values and ensembles

The word “measurement” has a specific role in quantum physics. A normalized state predicts probabilities for possible outcomes. In an energy eigenstate, an ideal energy measurement returns the corresponding eigenvalue with certainty. In a superposition, several energy outcomes are possible.

It is useful to distinguish a single measurement from an ensemble average. Suppose an observable A can return values A_i with probabilities p_i . Repeating the same preparation many times gives the expectation value

$$\langle A \rangle = \sum_i p_i A_i \quad (19.35)$$

in a discrete case. This number need not be one of the possible single-shot outcomes.

Position is continuous. The probability density $|\psi(x)|^2$ plays the role of a continuous probability distribution, and

$$\langle x \rangle = \int x |\psi(x)|^2 dx. \quad (19.36)$$

For the infinite well, symmetry gives $\langle x \rangle = L/2$ for every stationary state, even though the states have very different density patterns.

Example 19.7: Mean position versus most probable position

In the $n = 2$ infinite-well state, the density has two equal maxima, one in each half of the well, while the density vanishes at the centre. Nevertheless, symmetry gives

$$\langle x \rangle = L/2.$$

Thus the expectation value lies exactly at a point where the probability density is zero. There is no contradiction: an expectation value is an ensemble mean, not necessarily the most probable outcome.

Key message

Do not interpret $\langle x \rangle$ as “where the particle really is” before measurement. It is the mean of the position probability distribution for an ensemble of identically prepared systems.

This distinction is especially important for engineering students accustomed to deterministic state variables. Quantum predictions are still precise, but what is predicted precisely may be a distribution rather than one trajectory.

19.8 Energy measurements, transitions and photons

If a particle is in a stationary energy eigenstate ψ_n , an ideal measurement of energy returns E_n with certainty. A transition to another stationary state changes the system energy by

$$\Delta E = E_f - E_i. \quad (19.37)$$

When the transition is caused by absorption of a single photon,

$$hf = E_f - E_i > 0. \quad (19.38)$$

For spontaneous or stimulated emission from a higher energy E_i to a lower energy E_f ,

$$hf = E_i - E_f > 0. \quad (19.39)$$

Equivalently,

$$\lambda = \frac{hc}{|E_f - E_i|}. \quad (19.40)$$

The sign bookkeeping belongs to the system energy change; the photon energy itself is positive.

The wavelength here is the vacuum wavelength. Atomic recoil is neglected in the simple relation $E_\gamma = |E_i - E_f|$; for a freely moving atom, energy and momentum conservation also transfer a small amount of energy to recoil. An isolated stationary state of a time-independent one-particle Hamiltonian does not decay by itself: radiative transitions require coupling to the electromagnetic field.

For an infinite square well,

$$\Delta E = E_1(n_f^2 - n_i^2). \quad (19.41)$$

Therefore the transition spectrum is discrete. The mere existence of an energy difference does not guarantee that every possible transition occurs with equal strength; selection rules depend on the interaction and wavefunction symmetry. We postpone that issue to the advanced enrichment section.

In the centred infinite well an electric-dipole transition couples opposite-parity states, corresponding to $n_i + n_f$ odd. Thus $3 \rightarrow 2$ is allowed in this approximation, whereas $3 \rightarrow 1$ is forbidden even

though the energy gap is well defined. Higher multipoles, symmetry breaking or other interactions require separate analysis.

The unequal spacings and two dipole-allowed transitions are shown in Figure 19.4.

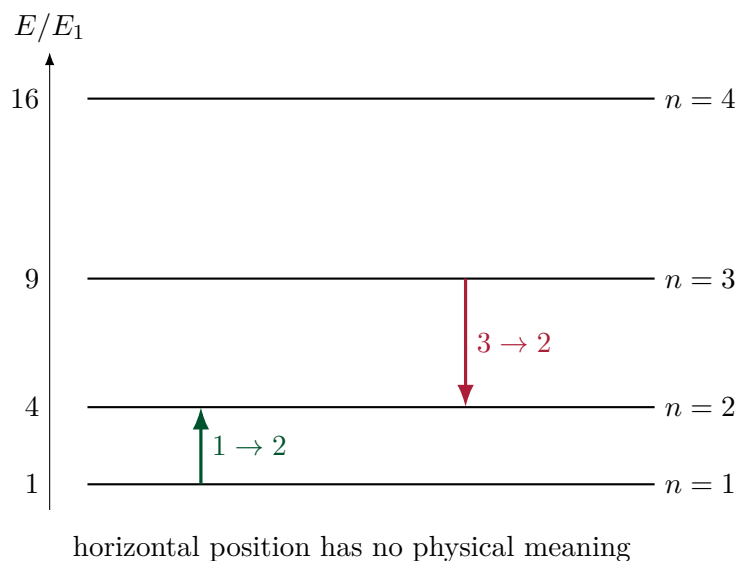


Figure 19.4: Quantitative infinite-well energy spacing in units of E_1 . The arrows show absorption $1 \rightarrow 2$ and emission $3 \rightarrow 2$, both allowed by the electric-dipole parity condition. An energy gap alone does not establish transition strength.

Example 19.8: Photon emitted in a box transition

An electron in a 1.00 nm infinite well falls from $n = 3$ to $n = 2$. Find the emitted photon energy and wavelength.

Solution. From Example 19.2, $E_1 = 0.376$ eV. Hence

$$E_3 - E_2 = (9 - 4)E_1 = 1.880 \text{ eV}.$$

Using $hc \approx 1239.84$ eV nm,

$$\lambda = \frac{1239.84 \text{ eV nm}}{1.880 \text{ eV}} \approx 660 \text{ nm}.$$

The photon lies in the red part of the visible spectrum.

Caveat. This result concerns an idealized one-dimensional electron well. Real semiconductor structures include band offsets, effective masses, Coulomb interactions, and selection rules.

Guided checks

For a $1 \rightarrow 2$ transition, does the system absorb or emit energy? For a $4 \rightarrow 1$ transition, which is larger: the emitted photon energy or the energy emitted in a $2 \rightarrow 1$ transition? Explain without calculation.

Answer. $1 \rightarrow 2$ is absorption. Because $E_n \propto n^2$, the $4 \rightarrow 1$ energy difference is much larger than the $2 \rightarrow 1$ difference.

19.9 Finite square wells: confinement without infinite walls

Real confining potentials are finite. A useful model is a symmetric finite square well,

$$V(x) = \begin{cases} 0, & |x| < a, \\ V_0, & |x| \geq a, \end{cases} \quad V_0 > 0. \quad (19.42)$$

Bound states satisfy

$$0 < E < V_0 \quad (19.43)$$

for this choice of zero energy. Inside the well, $E > V$, so the solutions oscillate. Outside, $E < V_0$, so the wavefunction decays exponentially. Define

$$k = \frac{\sqrt{2mE}}{\hbar}, \quad \kappa = \frac{\sqrt{2m(V_0 - E)}}{\hbar}. \quad (19.44)$$

Then a bound-state wavefunction behaves schematically as

$$\psi(x) \sim \begin{cases} \text{oscillatory}, & |x| < a, \\ \exp[-\kappa(|x| - a)], & |x| > a. \end{cases} \quad (19.45)$$

The important physical result is that ψ does not abruptly become zero at a finite barrier. It penetrates into the classically forbidden region. For a constant exterior potential, the density decays exactly as $\exp[-2\kappa(|x| - a)]$ multiplied by its interface value. This phenomenon is sometimes called *evanescent leakage* for a bound state.

The word leakage describes spatial penetration, not a loss of probability with time. A stationary bound state has a time-independent tail and no outward flux at infinity. Escape requires a scattering channel at the same total energy or an interaction that changes the state.

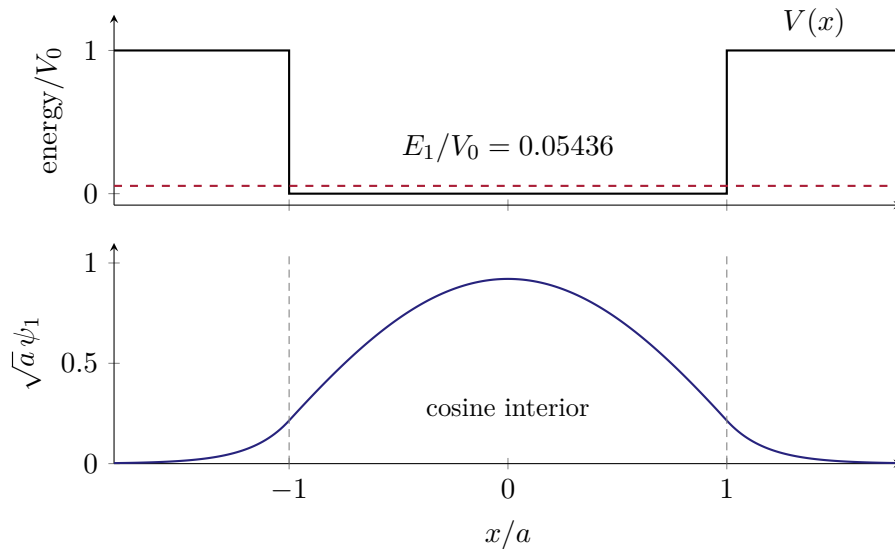


Figure 19.5: Finite-well ground state for an electron, $2a = 1.00$ nm and $V_0 = 5.00$ eV. Energy and amplitude have separate axes. The plotted state is obtained from the matching equation with $ka = 1.33547658$ and $\kappa a = 5.57001394$; both amplitude and slope are continuous. The tails are stationary probability penetration, not a continuous escape process.

A finite well has two major differences from an infinite well. First, it supports only a finite number of bound states for fixed depth and width. Second, its bound-state energies are lower than those of an infinite well with the same interior width because the wavefunction spreads beyond the nominal edges, reducing the curvature and therefore the kinetic-energy scale.

The comparison holds at fixed interior energy reference and for corresponding states. If V_0 is lowered with $V = 0$ retained inside, the eigenenergies also decrease, while the continuum threshold decreases faster. The binding energy $V_0 - E$ becomes smaller. Confusing energy relative to the bottom with binding relative to the outside reverses this conclusion.

Caution

“Classically forbidden” does not mean “quantum mechanically impossible.” It means that classical energy conservation would require negative kinetic energy there. Quantum mechanics replaces the trajectory picture with a wavefunction, and a bound-state wavefunction can have an exponentially decaying tail in such a region.

Example 19.9: Decay length outside a finite well

An electron has energy $E = 1.0$ eV in a region where the potential rises to $V_0 = 4.0$ eV. Estimate the evanescent amplitude decay length $1/\kappa$.

Solution. The energy deficit is $V_0 - E = 3.0$ eV. Therefore

$$\kappa = \frac{\sqrt{2m_e(3.0 \text{ eV})}}{\hbar} \approx 8.87 \times 10^9 \text{ m}^{-1}.$$

Thus

$$\frac{1}{\kappa} \approx 1.13 \times 10^{-10} \text{ m} = 0.113 \text{ nm}.$$

The wavefunction amplitude decreases by a factor e over only about one tenth of a nanometre.

Interpretation. Exponential penetration is short-ranged for electronvolt-scale barriers, yet at atomic distances it is large enough to produce measurable tunnelling currents.

19.10 Barrier penetration and quantum tunnelling

A finite well shows that a bound-state wavefunction can extend into a classically forbidden region. A closely related phenomenon occurs when a particle approaches a finite barrier that has another allowed region on the far side. Classically, a particle with $E < V_0$ cannot cross the barrier. Quantum mechanically, an incident wave can produce a transmitted component.

For a rectangular barrier of height V_0 and width d , with $E < V_0$, the wavefunction inside the barrier contains exponentials with decay constant

$$\kappa = \frac{\sqrt{2m(V_0 - E)}}{\hbar}. \quad (19.46)$$

When the barrier is sufficiently wide or high, the transmission probability has the dominant dependence

$$T \propto \exp(-2\kappa d). \quad (19.47)$$

The omitted prefactor depends on the detailed matching conditions. Equation (19.47) is therefore a useful scaling law, not a universal exact formula.

This extreme sensitivity to distance is exploited by the scanning tunnelling microscope (STM). A conducting tip is brought within roughly an atomic distance of a conducting surface. Electrons tunnel through the vacuum gap. As the tip scans laterally, a feedback system adjusts the height to maintain a chosen current, producing information about surface topography and electronic structure.

Example 19.10: Why STM is sensitive to sub-nanometre distance changes

Take an effective vacuum barrier of 4.0 eV for an electron and approximate

$$\kappa = \frac{\sqrt{2m_e\Phi}}{\hbar}.$$

Estimate the factor by which the tunnelling current changes if the tip–sample spacing increases by 0.10 nm, assuming $I \propto e^{-2\kappa d}$.

Solution. For $\Phi = 4.0$ eV,

$$\kappa \approx 10.25 \text{ nm}^{-1}.$$

Thus

$$\frac{I(d + 0.10 \text{ nm})}{I(d)} = \exp[-2\kappa(0.10 \text{ nm})] \approx 0.129.$$

An increase of only one tenth of a nanometre reduces the current to roughly 13% of its previous value.

Engineering significance. Such exponential sensitivity is the source of STM's remarkable vertical resolution, but it also demands excellent vibration isolation and feedback control.

Guided checks

If the barrier height increases while E and d are fixed, does tunnelling become more or less likely? What if the particle mass increases? Use the dependence of κ to justify both answers.

Answer. Both a larger barrier deficit $V_0 - E$ and a larger mass increase κ , so the exponential suppression becomes stronger.

19.11 Two- and three-dimensional rectangular traps

Many devices confine particles in more than one direction. Consider a two-dimensional rectangular infinite well with sides L_x and L_y . Inside the rectangle, separation of variables allows

$$\psi(x, y) = X(x)Y(y), \quad (19.48)$$

and the normalized eigenfunctions are

$$\psi_{n_x n_y}(x, y) = \frac{2}{\sqrt{L_x L_y}} \sin\left(\frac{n_x \pi x}{L_x}\right) \sin\left(\frac{n_y \pi y}{L_y}\right), \quad (19.49)$$

with $n_x, n_y = 1, 2, 3, \dots$ and

energies obtained by dividing the separated equation by XY :

$$-\frac{\hbar^2}{2m} \frac{X''}{X} - \frac{\hbar^2}{2m} \frac{Y''}{Y} = E_x + E_y = E.$$

The two terms depend on different coordinates and are independently constant. Applying the one-dimensional boundary conditions in each direction gives

$$E_{n_x n_y} = \frac{h^2}{8m} \left(\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} \right). \quad (19.50)$$

For a three-dimensional rectangular box,

$$E_{n_x n_y n_z} = \frac{h^2}{8m} \left(\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} + \frac{n_z^2}{L_z^2} \right). \quad (19.51)$$

The ground state is $(1, 1, 1)$, not $(0, 0, 0)$.

The normalized three-dimensional state is the product of the three normalized sine factors, with overall coefficient $\sqrt{8/(L_x L_y L_z)}$. Product normalization follows because the three integrals separate. All degeneracies quoted for these boxes count spatial states only; electron spin would add a separate factor of two when no spin-dependent interaction is present.

If two distinct sets of quantum numbers have the same energy, the level is *degenerate*. Degeneracy is especially common when the geometry has symmetry. In a cubic box with $L_x = L_y = L_z = L$, the states $(1, 1, 2)$, $(1, 2, 1)$ and $(2, 1, 1)$ have equal energy because Eq. (19.51) depends only on $n_x^2 + n_y^2 + n_z^2$.

A sign-domain map makes the product-state geometry explicit in Figure 19.6.

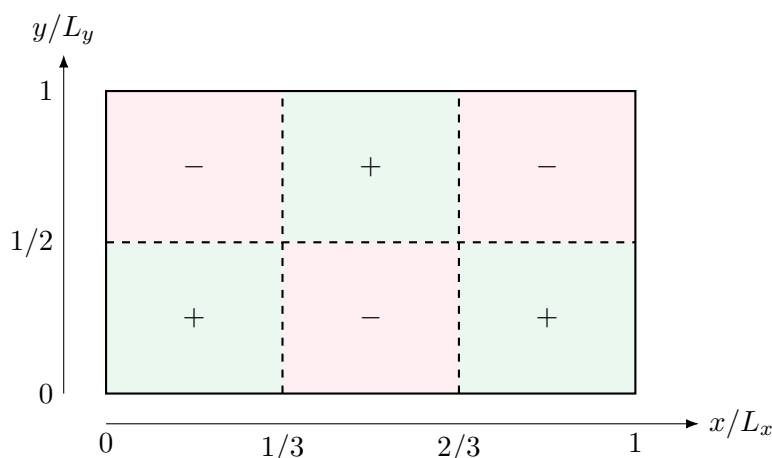


Figure 19.6: Sign domains of the real product state $(n_x, n_y) = (3, 2)$. Dashed lines are exact interior nodes at $x = L_x/3, 2L_x/3$ and $y = L_y/2$. Uniform shading shows the sign only, not the magnitude of probability density. The two-dimensional domain is not a one-dimensional wave drawn on a trajectory.

Example 19.11: Electron in a rectangular two-dimensional nanostructure

An electron is confined in a two-dimensional infinite rectangle with $L_x = 4.0$ nm and $L_y = 6.0$ nm. Find the energies of the states $(n_x, n_y) = (1, 1)$, $(1, 2)$ and $(2, 1)$.

Solution. Equation (19.50) gives

$$E_{11} = 0.0339 \text{ eV}, \quad E_{12} = 0.0653 \text{ eV}, \quad E_{21} = 0.104 \text{ eV}.$$

The $(1, 2)$ and $(2, 1)$ levels are not degenerate because $L_x \neq L_y$. The geometry has broken the interchange symmetry between the two directions.

Design lesson. Changing lateral dimensions changes not only the absolute confinement scale but also degeneracy patterns. This is one way nanostructure geometry controls electronic spectra.

Example 19.12: Threefold degeneracy in a cubic quantum dot model

Model an electron in a cubic infinite box of side $L = 5.0$ nm. Compare the ground state $(1, 1, 1)$ with the three states obtained by replacing one of the 1s by 2.

Solution. For this cube, the one-dimensional factor $\hbar^2/(8m_e L^2)$ is 0.01504 eV. Therefore

$$E_{111} = 3(0.01504) = 0.04512 \text{ eV},$$

while

$$E_{112} = E_{121} = E_{211} = 6(0.01504) = 0.09025 \text{ eV}.$$

The latter energy is threefold degenerate in the ideal cubic model.

Caveat. Real quantum dots have finite barriers, non-cubic shapes, effective masses, strain and Coulomb interactions, all of which can shift or split idealized degeneracies.

Key message

Quantum numbers label independent standing-wave structure in each confined direction. Symmetry can make physically distinct spatial patterns share the same energy, producing degeneracy.

19.12 Hydrogen as a three-dimensional Coulomb bound state

The hydrogen atom consists of a proton and an electron interacting primarily through the attractive Coulomb potential. The interaction potential energy in the relative coordinate is

$$V(r) = -\frac{e^2}{4\pi\epsilon_0 r}, \quad (19.52)$$

where r is the electron–proton separation. The negative sign is essential: the interaction is attractive, and the zero of potential energy is conventionally chosen at infinite separation.

A bound state has total energy $E < 0$. The value $E = 0$ marks the ionization threshold in this convention. The nonrelativistic Schrödinger equation is

$$-\frac{\hbar^2}{2\mu}\nabla^2\psi - \frac{e^2}{4\pi\epsilon_0 r}\psi = E\psi, \quad (19.53)$$

where $\mu = m_e m_p / (m_e + m_p)$ is the reduced mass. For many introductory calculations one sets $\mu \approx m_e$, but the reduced mass gives a more accurate treatment of the relative motion.

The exact bound spectrum within this nonrelativistic two-body Coulomb model is

$$E_n = -\frac{\mu e^4}{2(4\pi\epsilon_0)^2 \hbar^2 n^2}. \quad (19.54)$$

With $\mu \simeq m_e$ and a rounded energy coefficient, this becomes

$$E_n = -\frac{13.6 \text{ eV}}{n^2}, \quad n = 1, 2, 3, \dots \quad (19.55)$$

The coefficient 13.6 eV is a three-significant-figure teaching approximation, not a precision hydrogen line standard. The ground state is $E_1 = -13.6 \text{ eV}$. The negative sign does not mean that the electron has “negative kinetic energy.” It means that the total energy lies below the chosen zero corresponding to a separated electron and proton.

The crowding of levels near ionization is shown in Figure 19.7.

The level spacings become progressively smaller as n increases. This behaviour differs from the infinite box, for which $E_n \propto n^2$ and levels spread farther apart. The contrast reflects the different potential shapes. There is no universal rule that all quantum spectra must become closer together or farther apart; the spectrum is a property of the Hamiltonian.

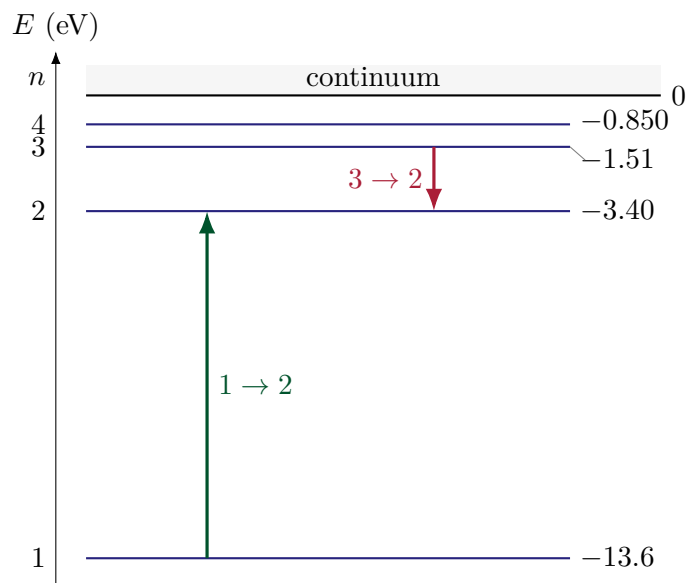


Figure 19.7: Hydrogen principal levels calculated from $E_n = -13.6 \text{ eV}/n^2$, with a linear energy scale and the ionization threshold at zero. Only the first four levels are drawn; higher levels accumulate below the continuum. Arrows indicate energy differences, while sublevel selection rules determine allowed radiative channels.

Guided checks

1. Which hydrogen state is more strongly bound: $n = 1$ or $n = 3$?
2. Why does the ionization threshold correspond to $E = 0$ rather than $+13.6 \text{ eV}$?
3. As n becomes large, do adjacent hydrogen levels move closer together or farther apart?

Answers: $n = 1$ is more strongly bound; energy zero is a chosen reference at infinite separation; adjacent levels crowd toward zero.

19.13 The Bohr model: historically useful, physically limited

Before modern quantum mechanics was formulated, the Bohr model provided a remarkably successful description of the hydrogen energy spectrum. It combined the classical Coulomb force with the postulate of quantized angular momentum,

$$L = n\hbar. \quad (19.56)$$

For a circular orbit, balancing Coulomb attraction against centripetal acceleration gives

$$\frac{m_e v^2}{r} = \frac{e^2}{4\pi\epsilon_0 r^2}. \quad (19.57)$$

Together with $m_e v r = n\hbar$, this leads to the Bohr radii

$$r_n = n^2 a_0, \quad (19.58)$$

where

$$a_0 = \frac{4\pi\epsilon_0 \hbar^2}{m_e e^2} \approx 5.29 \times 10^{-11} \text{ m} \quad (19.59)$$

and to the same principal energy pattern

$$E_n = -\frac{13.6 \text{ eV}}{n^2} \quad (19.60)$$

for ideal hydrogen.

For clarity, the Bohr energy follows by writing $C = e^2/(4\pi\epsilon_0)$: force balance gives $m_e v^2 = C/r$, so $K = C/(2r)$ and $V = -C/r$. Hence $E = -C/(2r)$; substitution of $r_n = n^2\hbar^2/(m_e C)$ gives the displayed spectrum. This derivation explains the scale but not the modern angular-momentum structure. In particular, the Schrödinger ground state has $\ell = 0$ and $L = 0$, whereas the Bohr ground orbit assigns $L = \hbar$.

The agreement of the energy formula can make the Bohr picture seem more complete than it is. Modern quantum mechanics does not describe the electron as a tiny object travelling along a definite circular orbit. The Schrödinger solution gives spatial probability amplitudes. The labels n , ℓ and m_ℓ characterize stationary states and angular-momentum properties, not classical trajectories.

Caution

The Bohr model is a historical approximation and a useful scale-setting tool, not the modern description of atomic electron motion. Phrases such as “the electron orbits the nucleus at radius a_0 ” should be avoided when discussing a Schrödinger eigenstate. For the ground state, a_0 is the natural length scale of the probability distribution, not the radius of a literal circular path.

A negative total Coulomb energy is compatible with a positive kinetic energy: binding means that work must be supplied to reach the separated-particle threshold.

Example 19.13: Hydrogen Balmer- α wavelength

Calculate the wavelength emitted in the hydrogen transition $n_i = 3 \rightarrow n_f = 2$ using the ideal nonrelativistic level formula.

Solution. The photon energy is

$$\begin{aligned}\Delta E &= 13.6 \text{ eV} \left(\frac{1}{2^2} - \frac{1}{3^2} \right) \\ &= 1.889 \text{ eV}.\end{aligned}$$

Hence

$$\lambda = \frac{hc}{\Delta E} \approx 656.4 \text{ nm}.$$

This is the familiar red Balmer- α line.

Validity. The value neglects fine structure, hyperfine structure, radiative corrections and other small effects. Those refinements are not needed at the level of this chapter.

Example 19.14: Ionization energy from an excited hydrogen level

How much energy is required to ionize an ideal hydrogen atom from $n = 4$?

Solution. Ionization raises the energy from

$$E_4 = -\frac{13.6 \text{ eV}}{16} = -0.850 \text{ eV}$$

to $E = 0$. Therefore

$$\Delta E = 0.850 \text{ eV}.$$

An excited atom is less strongly bound and therefore easier to ionize than an atom in its ground state.

19.14 Schrödinger's hydrogen atom and quantum numbers

Because the Coulomb potential depends only on r , hydrogen has spherical symmetry. In spherical coordinates the spatial wavefunction can be separated as

$$\psi_{n\ell m_\ell}(r, \theta, \phi) = R_{n\ell}(r)Y_\ell^{m_\ell}(\theta, \phi). \quad (19.61)$$

The radial function $R_{n\ell}$ controls the dependence on distance from the nucleus, while the spherical harmonic $Y_\ell^{m_\ell}$ controls angular dependence.

Three quantum numbers appear:

$$n = 1, 2, 3, \dots, \quad (19.62)$$

$$\ell = 0, 1, 2, \dots, n-1, \quad (19.63)$$

$$m_\ell = -\ell, -\ell+1, \dots, +\ell. \quad (19.64)$$

At the nonrelativistic Coulomb level, the energy depends only on n , which gives a substantial degeneracy. The orbital angular-momentum magnitude is

$$L = \sqrt{\ell(\ell+1)}\hbar, \quad (19.65)$$

and its z component is

$$L_z = m_\ell \hbar. \quad (19.66)$$

The older spectroscopic notation identifies $\ell = 0, 1, 2, 3$ with s, p, d, f , respectively.

For the hydrogen ground state, $n = 1$, $\ell = 0$, $m_\ell = 0$.

In the following wavefunction formulas we use the fixed-proton approximation. For a finite nuclear mass replace a_0 by $a_\mu = (m_e/\mu)a_0$. Its normalized spatial wavefunction is

$$\psi_{100}(r) = \frac{1}{\sqrt{\pi a_0^3}} \exp\left(-\frac{r}{a_0}\right). \quad (19.67)$$

The probability density is spherically symmetric,

$$|\psi_{100}(r)|^2 = \frac{1}{\pi a_0^3} \exp\left(-\frac{2r}{a_0}\right). \quad (19.68)$$

However, the probability of finding the electron between radii r and $r+dr$ is not simply proportional to $|\psi|^2 dr$. The spherical shell volume contributes a factor $4\pi r^2$:

$$P(r)dr = 4\pi r^2 |\psi_{100}(r)|^2 dr. \quad (19.69)$$

The radial probability distribution peaks at $r = a_0$, which helps explain why the Bohr radius remains a useful atomic length scale even though the classical orbit picture is abandoned.

To see why two different maxima occur, compare equal small volumes with equal thin shells. At the nucleus, the probability per unit volume $|\psi_{100}|^2$ is largest. But a spherical shell near $r = 0$ has very little volume. Multiplication by $4\pi r^2$ initially outweighs the decrease in local density, and only farther out does the exponential dominate. Figure 19.8 keeps these two distributions distinct.

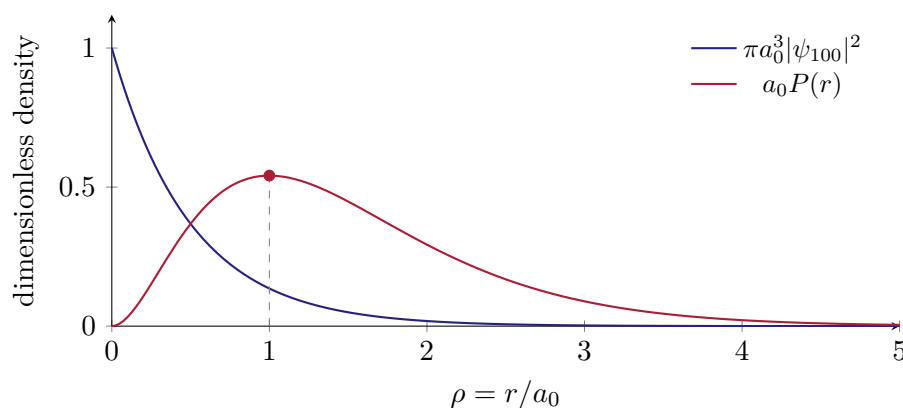


Figure 19.8: Hydrogen 1s volume density and radial density from the same wavefunction. The radial curve has unit integral with respect to ρ ; the scaled volume-density curve does not. Their maxima answer different questions.

Example 19.15: How much of the hydrogen ground state lies beyond a chosen radius?

In the fixed-proton model, find the probability that an electron in the 1s state is detected outside $r = 2a_0$.

Strategy. Integrate over spherical shells, not along one radial line. With $\rho = r/a_0$, normalization reduces the question to a dimensionless integral:

$$P(r > 2a_0) = 4 \int_2^\infty \rho^2 e^{-2\rho} d\rho.$$

Two integrations by parts give the general tail probability

$$P(r > Ra_0) = e^{-2R}(1 + 2R + 2R^2).$$

Therefore $P(r > 2a_0) = 13e^{-4} \simeq 0.238$.

Interpretation and checks. About 24% of detections occur beyond twice the Bohr radius, even though the most probable radius is a_0 . The atom has no hard outer surface. The expression tends to one at $R = 0$ and to zero for $R \rightarrow \infty$, as required. The factors r^2 and dr are essential to both normalization and dimensions.

Angular symmetry and nodal planes are illustrated in Figure 19.9.

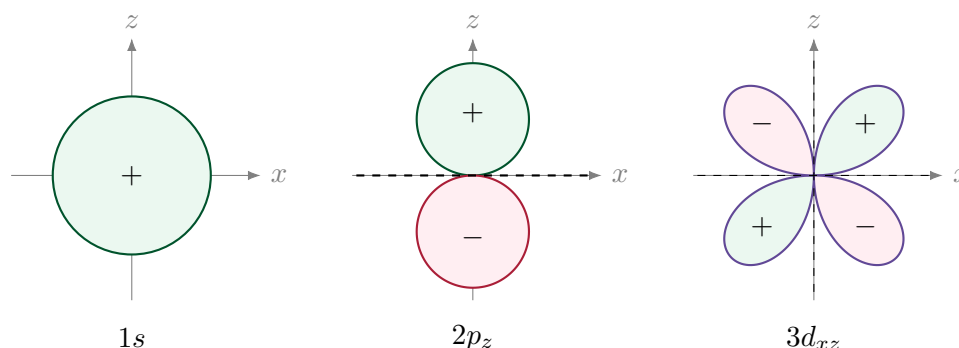


Figure 19.9: Angular-amplitude guides for real orbitals in an xz section: constant s , $|\cos\theta|$ for p_z , and $|\sin 2\theta|$ for d_{xz} , each rescaled for visibility. Signs label real wavefunction lobes; all probabilities are nonnegative. Dashed traces identify nodal planes. These polar guides are not spatial density contours or electron paths; the radial dependence is omitted. The real d_{xz} orbital is a combination of magnetic-quantum-number states.

Key message

An atomic orbital is a stationary-state wavefunction, not an orbit. Quantum numbers classify the spatial state and angular momentum. Measurement probabilities are constructed from the wavefunction; no definite classical path is implied.

Guided checks

For $n = 3$, what values of ℓ are allowed? For $\ell = 2$, what values of m_ℓ are allowed? Can a hydrogen state have $n = 2$, $\ell = 2$?

Answer. For $n = 3$, $\ell = 0, 1, 2$. For $\ell = 2$, $m_\ell = -2, -1, 0, 1, 2$. The combination $n = 2$, $\ell = 2$ is not allowed because $\ell \leq n - 1$.

19.15 Atomic transitions and line spectra

A hydrogen emission line occurs when the atom loses energy and a photon carries away the difference between two allowed atomic energies. At the simplest level,

$$hf = E_{n_i} - E_{n_f}, \quad n_i > n_f. \quad (19.70)$$

Combining Eq. (19.55) with $f = c/\lambda$ gives the Rydberg form

$$\frac{1}{\lambda} = R_H \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right), \quad (19.71)$$

where R_H is the hydrogen Rydberg constant when the appropriate reduced-mass correction is included.

The Lyman series has $n_f = 1$ and lies in the ultraviolet. The Balmer series has $n_f = 2$ and includes visible lines. Higher series converge toward their respective ionization limits.

A subtle but important point is that energy conservation is necessary but not sufficient to determine transition intensity. The interaction between matter and the electromagnetic field introduces matrix elements and selection rules. At the introductory level, it is enough to know that not every pair of energy eigenstates is connected equally strongly by an electric-dipole transition. The advanced section develops the qualitative origin of the common rules $\Delta\ell = \pm 1$ and $\Delta m_\ell = 0, \pm 1$.

Example 19.16: Compare two hydrogen photons

Compare the wavelengths for the ideal hydrogen transitions $4 \rightarrow 2$ and $3 \rightarrow 2$.

Solution. For $4 \rightarrow 2$,

$$\Delta E = 13.6 \text{ eV} \left(\frac{1}{4} - \frac{1}{16} \right) = 2.55 \text{ eV},$$

so

$$\lambda_{4 \rightarrow 2} \approx 486.2 \text{ nm}.$$

For $3 \rightarrow 2$, Example 19.13 gave

$$\lambda_{3 \rightarrow 2} \approx 656.4 \text{ nm}.$$

The transition with the larger energy difference emits the shorter-wavelength photon.

Caution

Do not insert negative photon energies because hydrogen bound-state energies are negative. For emission, use the positive difference $E_i - E_f$. For absorption, use the positive difference $E_f - E_i$.

19.15.1 Spectroscopy as a measurement of quantum energy differences

One of the most direct experimental signatures of quantized energy is a line spectrum. If an atom emits a photon when making a transition from E_i to a lower E_f , then

$$E_\gamma = E_i - E_f = hf = \frac{hc}{\lambda}.$$

A spectrometer therefore converts measured wavelengths into energy differences.

The ideal formula predicts a single wavelength for a single isolated transition, but real spectral lines have finite width. Several effects can contribute: instrumental resolution, Doppler broadening from thermal motion, collision or pressure broadening, finite excited-state lifetimes, unresolved fine structure and environmental fields. At the level of this chapter, the central lesson is that a measured line has both a centre and a width, and the width should not automatically be interpreted as uncertainty in the theoretical level formula.

The first four Balmer lines in the rounded model are compared in Figure 19.10.

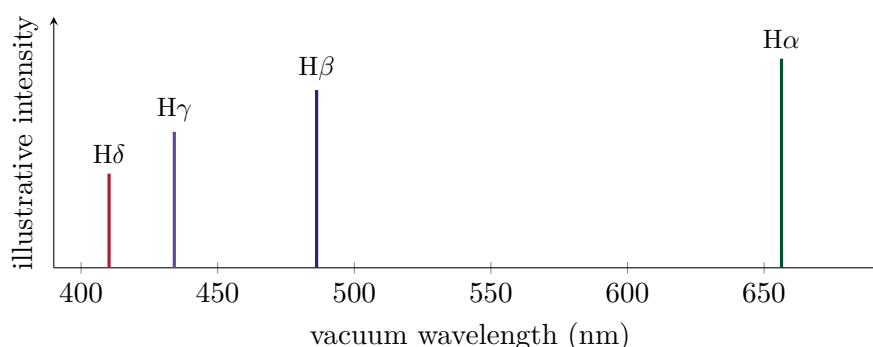


Figure 19.10: Balmer lines calculated consistently with the rounded 13.6 eV level model and $hc = 1239.84 \text{ eV nm}$. The line heights are illustrative, not measured intensities or predictions of transition rates. These approximate positions must not be used as precision wavelength calibration standards.

A calibration is required before a laboratory instrument can return trustworthy wavelengths. A simple calibration model may relate detector pixel coordinate p to wavelength by a polynomial,

$$\lambda(p) = b_0 + b_1 p + b_2 p^2 + \dots \quad (19.72)$$

Known reference lines determine the coefficients.

The calibration coefficients b_j are unrelated to the Bohr radius a_0 . All model wavelengths here are vacuum wavelengths. A spectrometer calibrated against wavelengths in air must use the same convention on both sides of a comparison: $\lambda_{\text{vac}} = n_{\text{air}} \lambda_{\text{air}}$. Use the refractive index appropriate to the measurement conditions for precision work, and use a reduced-mass or higher-accuracy line model when the uncertainty warrants it. At visible wavelengths the air–vacuum difference can compete with a sub-nanometre error budget. The calibrated wavelengths can then be compared with the Rydberg relation.

Example 19.17: From wavelength uncertainty to energy uncertainty

A line near $\lambda = 656.3 \text{ nm}$ is measured with an uncertainty $\delta\lambda = 0.2 \text{ nm}$. Since

$$E = \frac{hc}{\lambda},$$

small-uncertainty propagation gives

$$\frac{\delta E}{E} \approx \frac{\delta\lambda}{\lambda}.$$

With $E \approx 1.89 \text{ eV}$,

$$\delta E \approx 1.89 \text{ eV} \times \frac{0.2}{656.3} \approx 5.8 \times 10^{-4} \text{ eV}.$$

Thus a sub-nanometre wavelength uncertainty corresponds to a sub-meV energy uncertainty at this wavelength.

Guided checks

If a measured hydrogen line is broader than the spectrometer resolution, does that by itself prove a breakdown of the energy-level model? List at least three physical broadening mechanisms that should be considered first.

19.15.2 Laboratory connection: a hydrogen-spectrum data-analysis workflow

A practical teaching laboratory can connect the abstract energy-level picture to direct data. A hydrogen discharge tube, diffraction grating or compact spectrometer, and wavelength-calibration source are sufficient for a qualitative or quantitative Balmer-series study.

A careful workflow is:

1. record a dark spectrum to estimate detector background;
2. record one or more calibration sources with known line positions;
3. determine the wavelength calibration and its residuals;
4. acquire the hydrogen spectrum without saturating the detector;
5. subtract background and identify candidate Balmer peaks;
6. estimate each peak centre and statistical fitting uncertainty;
7. combine fitting and calibration uncertainties conservatively;
8. convert wavelengths to photon energies;
9. compare with $13.6 \text{ eV}(1/4 - 1/n_i^2)$ for $n_f = 2$;
10. inspect residuals rather than quoting only percent agreement.

For stronger students, the Rydberg constant can be estimated from a linearized relation. For Balmer transitions,

$$\frac{1}{\lambda} = R_H \left(\frac{1}{4} - \frac{1}{n_i^2} \right). \quad (19.73)$$

Define

$$x_i = \frac{1}{4} - \frac{1}{n_i^2}, \quad y_i = \frac{1}{\lambda_i}.$$

A fit through the origin has slope R_H in the ideal model. If a free intercept is used as a diagnostic, an intercept inconsistent with zero can signal calibration bias or an inadequate uncertainty model.

Method

A good laboratory comparison reports measured values, uncertainties, model predictions and residuals. “The values look close” is not a quantitative conclusion.

Example 19.18: Residual analysis for a Balmer line

Suppose a calibrated spectrometer reports $\lambda_{\text{meas}} = 486.5 \pm 0.3 \text{ nm}$ for a line identified as the $4 \rightarrow 2$ transition. The simple hydrogen model predicts approximately 486.2 nm. The residual is

$$r = 486.5 - 486.2 = 0.3 \text{ nm}.$$

Measured in units of the quoted experimental uncertainty, $r/(0.3 \text{ nm}) \approx 1$. The observation is therefore compatible with the simple prediction at this level of precision. The exercise illustrates why a residual normalized by uncertainty is more informative than a bare wavelength difference.

Example 19.19: Hydrogen series limit as an ionization threshold

For Balmer emission, $n_f = 2$ and n_i can increase without bound. The largest possible emitted photon energy in this series is

$$E_{\text{max}} = 13.6 \text{ eV} \left(\frac{1}{4} - 0 \right) = 3.40 \text{ eV}.$$

Therefore

$$\lambda_{\text{min}} = \frac{1240 \text{ eV nm}}{3.40 \text{ eV}} \approx 365 \text{ nm}.$$

The series converges because highly excited hydrogen levels crowd toward the ionization threshold $E = 0$.

19.16 Engineering and applied-science connections

19.16.1 Semiconductor quantum wells

A semiconductor heterostructure can create an effective potential well for conduction-band electrons or valence-band holes. For example, a conduction-band minimum in a thin layer between higher conduction-band edges confines electrons. Holes have their own effective potential and valence-band offsets; the sign must be interpreted in the hole-energy convention. Carriers may then be confined in the growth direction while remaining relatively free in the plane. The result is a quantum well: quantized motion in one direction combined with approximately continuous motion in two others.

The infinite-well energy scale

$$E_1 \sim \frac{\pi^2 \hbar^2}{2m^* L^2} \quad (19.74)$$

is a useful first estimate, where m^* is the carrier effective mass. Real heterostructures require finite barriers, material-dependent effective masses and band offsets. Nevertheless, the L^{-2} scaling explains why a small change in layer thickness can significantly shift optical transition energies.

19.16.2 Quantum dots

A quantum dot confines carriers in all three spatial directions. Its discrete states are sometimes described loosely as “artificial atom” levels. The phrase is useful because both systems have discrete spectra, but the confining mechanisms differ: atoms are bound mainly by Coulomb attraction, whereas semiconductor dots are engineered through band offsets, electrostatic gates, strain, or combinations of these mechanisms.

Changing the dot size changes the confinement energy. Smaller dots generally have larger level spacings in simple models. This size dependence underlies the tunable emission colours of many semiconductor nanocrystals, although quantitative predictions also require band structure, finite barriers, electron–hole interactions and material parameters.

19.16.3 Quantum-well lasers and light-emitting structures

In semiconductor light emitters, electrons and holes can occupy quantized subbands. Radiative recombination between electron and hole states produces photons. Confinement modifies the electronic density of states and can improve control over gain and emission energy. A full laser model also requires population inversion, carrier injection, optical modes, losses and stimulated emission; the bound-state physics developed here supplies only the quantum-confinement part of that larger system.

19.16.4 Scanning tunnelling microscopy

The STM example in Section 19.10 shows how an exponentially distance-sensitive tunnelling current can become a measurement tool. From an engineering perspective, the instrument combines quantum mechanics with feedback control, vibration isolation, piezoelectric positioning, low-noise electronics and signal processing. The quantum effect is essential, but successful measurement depends equally on careful system design.

19.16.5 Nanoscale sensors and confinement as a design parameter

Confinement energies can shift when a device geometry, electrostatic potential, material composition or external field changes. This allows bound states to function as sensitive probes. Quantum-dot charge sensors, resonant tunnelling structures and spectroscopic detectors all use the dependence of eigenenergies and transition probabilities on controllable parameters.

Key message

In nanoscale engineering, geometry becomes an energy-design variable. A dimension measured in nanometres can determine a level spacing measured in electronvolts or millielectronvolts.

19.16.6 Confinement energy scales: when is quantization experimentally visible?

A useful engineering question is whether the level spacing is large compared with other energy scales. In an infinite well,

$$E_1 = \frac{h^2}{8mL^2}.$$

For electrons confined over nanometres, E_1 can lie in the meV-to-eV range. For macroscopic masses and centimetre scales, the same formula produces fantastically small energies.

Thermal energy provides one comparison scale:

$$k_B T \approx 25.9 \text{ meV} \quad \text{at } T = 300 \text{ K.} \quad (19.75)$$

If a device has level spacings much smaller than $k_B T$, thermal occupation can smear discrete-level effects. If the spacings are much larger, individual levels can remain spectroscopically distinct more easily. This is not a universal criterion because coupling, linewidths, carrier statistics and nonequilibrium conditions also matter, but it is an excellent first scale comparison.

Example 19.20: A room-temperature scale comparison

For an ideal well with $L = 10.0 \text{ nm}$ and $m^* = 0.067m_e$, use

$$E_1 = 0.376 \text{ eV} \frac{m_e}{m^*} \left(\frac{1 \text{ nm}}{L} \right)^2 \simeq 56.1 \text{ meV}, \quad E_2 - E_1 = 3E_1 \simeq 168 \text{ meV}.$$

These are confinement energies relative to the well bottom. Both scales are larger than $k_B T \approx 26 \text{ meV}$ at room temperature, especially the first excitation gap. This does not by itself predict device performance, but it shows that the confinement energy scale is not negligible compared with thermal energy.

A second comparison scale is experimental resolution. A spectrometer with 10 meV resolution cannot resolve two otherwise sharp levels separated by 1 meV . Quantization may exist physically yet remain invisible to a particular instrument.

A third scale is lifetime broadening. A state with a very short lifetime tends to have a larger natural energy width, a point revisited in the advanced section. The general engineering lesson is to compare the predicted quantum spacing with *all* relevant broadening and resolution scales.

Example 19.21: How small must an electron box be for an eV-scale ground energy?

Set $E_1 = 1.00 \text{ eV}$ and solve

$$L = \frac{h}{\sqrt{8m_e E_1}}.$$

Using the known 1 nm scale $E_1 \approx 0.376 \text{ eV}$ is even faster:

$$\frac{1.00}{0.376} = \left(\frac{1 \text{ nm}}{L} \right)^2.$$

Thus

$$L \approx 0.613 \text{ nm}.$$

Atomic-scale confinement is therefore required for an electron's simplest box ground energy to reach the eV scale.

19.17 Laboratory and computational connection: solving a one-dimensional Schrödinger problem numerically

Analytical solutions exist for only a limited set of potentials. Numerical methods turn the stationary Schrödinger equation into an eigenvalue problem that can be solved on a computer. This is an especially natural connection to Computer Science, numerical methods and engineering simulation.

Choose a uniform grid

$$x_j = x_{\min} + j\Delta x, \quad j = 1, 2, \dots, N. \quad (19.76)$$

Here N counts interior points, $\Delta x = (x_{\max} - x_{\min})/(N + 1)$, and the boundary values are $\psi_0 = \psi_{N+1} = 0$. For an infinite well these are physical walls; for a finite well they are artificial boundaries that must lie far into the decaying tails. Approximate the second derivative by the central finite

difference

$$\left. \frac{d^2\psi}{dx^2} \right|_{x_j} \approx \frac{\psi_{j+1} - 2\psi_j + \psi_{j-1}}{(\Delta x)^2}. \quad (19.77)$$

Substituting into Eq. (19.15) gives a matrix equation

$$\mathbf{H}\psi = E\psi. \quad (19.78)$$

For interior points, the Hamiltonian matrix has diagonal entries

$$H_{jj} = \frac{\hbar^2}{m(\Delta x)^2} + V(x_j), \quad (19.79)$$

and nearest-neighbour entries

$$H_{j,j\pm 1} = -\frac{\hbar^2}{2m(\Delta x)^2}. \quad (19.80)$$

All other entries are zero for this simplest discretization.

If a library normalizes an eigenvector v by $\sum_j |v_j|^2 = 1$, the wavefunction samples are $\psi_j = v_j/\sqrt{\Delta x}$. Forgetting this conversion changes physical probability integrals even if the eigenvalues are correct. The matrix is real and symmetric for a real potential, so its eigenvalues are real and its eigenvectors can be chosen orthogonal.

The finite-difference coupling is illustrated in Figure 19.11.

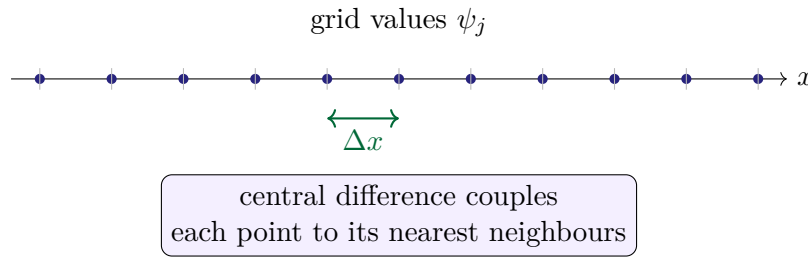


Figure 19.11: Finite-difference grid for the one-dimensional Schrödinger equation. The second derivative produces a tridiagonal kinetic-energy matrix.

A minimal computational workflow is:

1. choose a domain large enough to contain the bound-state tails;
2. choose N or Δx ;
3. sample the potential $V(x_j)$;
4. construct the tridiagonal Hamiltonian;
5. diagonalize it numerically;
6. sort the eigenvalues and normalize eigenvectors with the discrete approximation $\sum_j |\psi_j|^2 \Delta x = 1$;
7. repeat with a finer grid and a larger domain to test convergence.

Method

A numerical eigenvalue is not trustworthy merely because a library routine returned it. At minimum, test grid refinement, domain-size dependence, normalization, orthogonality, and agreement with an analytical benchmark such as the infinite square well.

Example 19.22: Grid-convergence strategy for a numerical box

Suppose a program approximates the first three energies of a 1 nm infinite electron well. Describe a professional validation procedure.

Solution strategy.

1. Compare the numerical values against $E_n = n^2 h^2 / (8m_e L^2)$.
2. Run, for example, $N = 100, 200, 400$ and 800 interior points.
3. Record the relative error $|E_n^{\text{num}} - E_n^{\text{exact}}| / E_n^{\text{exact}}$ for each state.
4. Verify that the error decreases systematically as Δx decreases.
5. Check that the discrete eigenvectors satisfy normalization and near-zero mutual overlap.
6. Plot the first few eigenvectors and verify the expected node counts.

A calculation that passes all of these checks is much more informative than a single unvalidated numerical output.

For a discontinuous finite-well potential, interface placement on the grid adds a separate error. Refine the grid with a documented edge convention, and check that any apparent convergence is not simply the result of moving the effective well width.

Example 19.23: Synthesis: diagnosing an unphysical numerical state

A finite-well code reports a “bound state” with energy $E = 5.2$ eV when the outside potential is $V_0 = 5.0$ eV and the computational wavefunction is forced to zero at distant artificial boundaries. The eigenvector is square-integrable on the finite numerical box, but physically it is not a true bound state of the isolated finite well because $E > V_0$ permits propagating behaviour outside the well. The artificial outer box has discretized continuum-like states. The correct diagnosis comes from comparing the eigenvalue with the asymptotic potential and examining domain-size dependence.

19.17.1 An exact benchmark for the discrete Hamiltonian

A particularly useful verification result can be derived analytically for the standard second-difference Hamiltonian. Let the interval $0 < x < L$ contain N interior grid points with spacing

$$\Delta x = \frac{L}{N+1},$$

and impose $\psi_0 = \psi_{N+1} = 0$. With $V = 0$, the discrete eigenvalue equation is

$$-\frac{\hbar^2}{2m(\Delta x)^2}(\psi_{i+1} - 2\psi_i + \psi_{i-1}) = E\psi_i.$$

Try the discrete sine vector

$$\psi_i^{(n)} = \sin\left(\frac{n\pi i}{N+1}\right), \quad n = 1, \dots, N.$$

Using

$$\sin(\theta + \alpha) + \sin(\theta - \alpha) = 2 \sin \theta \cos \alpha,$$

one obtains the exact matrix eigenvalues

$$E_n^{(N)} = \frac{\hbar^2}{m(\Delta x)^2} \left[1 - \cos\left(\frac{n\pi}{N+1}\right) \right]. \quad (19.81)$$

For small $n/(N+1)$, expand $1 - \cos u = u^2/2 - u^4/24 + \dots$:

$$\begin{aligned} E_n^{(N)} &= \frac{\hbar^2 (N+1)^2}{m L^2} \left[\frac{1}{2} \left(\frac{n\pi}{N+1} \right)^2 - \frac{1}{24} \left(\frac{n\pi}{N+1} \right)^4 + \dots \right] \\ &= \frac{n^2 \pi^2 \hbar^2}{2m L^2} \left[1 - \frac{n^2 \pi^2}{12(N+1)^2} + \dots \right]. \end{aligned}$$

The leading relative error is therefore proportional to $1/(N+1)^2$, exactly as expected for a second-order finite-difference method. This provides a rare and valuable case in which the numerical discretization error itself can be checked analytically.

Since $\sin u/u < 1$ for $0 < u < \pi$, these discrete box energies approach the continuum result from below. This does not contradict the variational upper bound: the finite-difference matrix is a different operator, not simply the exact continuum Hamiltonian restricted to a trial-function subspace. For fixed low n , doubling $N+1$ approximately divides the leading error by four.

Interior points N	$n = 1$ error (%)	$n = 2$ error (%)	$n = 3$ error (%)
24	0.131525	0.525272	1.178756
49	0.032894	0.131525	0.295738
99	0.008224	0.032894	0.074000
199	0.002056	0.008224	0.018504

The table is calculated from Eq. (19.81); error means $100(E_n - E_n^{(N)})/E_n$. It is a benchmark calculation, not experimental data.

19.17.2 A reproducible computation: box benchmark and finite-well states

The following Python program requires NumPy and SciPy. It uses energies in eV and positions in nm, so $\hbar^2/(2m_e) = 0.0380998 \text{ eV nm}^2$ is sufficient at the displayed precision. The eigensolver uses the two diagonals directly rather than allocating a dense matrix.

```
import numpy as np
from scipy.linalg import eigh_tridiagonal

C = 0.0380998 # hbar^2/(2 m_e), eV nm^2

def solve(xmin, xmax, N, potential, nlevels=4):
    dx = (xmax - xmin)/(N + 1)
    x = xmin + dx*np.arange(1, N + 1)
    kinetic = C/dx**2
    diagonal = 2*kinetic + potential(x)
    off = -kinetic*np.ones(N - 1)
    E, v = eigh_tridiagonal(diagonal, off, select="i",
                           select_range=(0, nlevels - 1))
    psi = v/np.sqrt(dx)
    return x, dx, E, psi

for N in (24, 49, 99, 199):
    x, dx, E, psi = solve(0., 1., N, np.zeros_like, 3)
    n = np.arange(1, 4)
    exact = C*(n*np.pi)**2
    print(N, 100*(exact-E)/exact)

# Finite well: width 1 nm, barrier 5 eV, zero inside.
```

```
# Interface points use V=V0/2 to define the step consistently.
for edge, N in ((1.5, 599), (1.5, 1199), (2.5, 1999)):
    def V(x):
        values = np.where(np.abs(x) < 0.5, 0., 5.)
        return np.where(np.isclose(np.abs(x), 0.5), 2.5, values)
    x, dx, E, psi = solve(-edge, edge, N, V)
    bound = E < 5.0
    overlap = dx*psi.T @ psi
    print(edge, N, E[bound], np.diag(overlap))
```

For the finite well, compare the output with the matching roots of Example 19.27. The lowest four energies approach 0.2718, 1.0774, 2.3792 and 4.0593 eV. The first two runs test grid refinement; the last two have the same spacing and test the outer boundary. To plot physically normalized functions, use the returned ψ , not the raw eigenvectors. Arbitrary eigenvector signs have no effect on probabilities.

Key message

A strong numerical-physics workflow does not merely compare code with the continuum analytic answer. When possible, derive what the discretized algorithm should produce. This separates implementation errors from the known approximation error of the numerical method.

19.18 Common mistakes and how to avoid them

1. **Using $|\psi|$ as a probability.** Probability density is $|\psi|^2$, and probability requires integration over a region.
2. **Forgetting normalization.** A shape that solves the differential equation may still need a multiplicative normalization constant.
3. **Allowing $n = 0$ in the infinite well.** It gives the zero wavefunction, which cannot represent a particle.
4. **Treating a node as a permanent barrier.** A node is a zero of a particular stationary-state wavefunction, not necessarily a physical wall.
5. **Assuming all quantum spectra are equally spaced.** The spectrum depends on the potential. Infinite-well energies grow as n^2 ; hydrogen energies scale as $-1/n^2$.
6. **Forgetting the sign convention for bound hydrogen energies.** With $V(\infty) = 0$, bound states have $E < 0$.
7. **Drawing electrons on definite hydrogen orbits.** Orbitals are wavefunctions or probability distributions, not trajectories.
8. **Assuming finite barriers force $\psi = 0$.** Wavefunctions generally penetrate finite classically forbidden regions.
9. **Applying the infinite-well formula to every nanosystem.** It is a model and often a first estimate; real devices may require finite barriers and effective masses.
10. **Interpreting every energy difference as an equally strong optical line.** Transition strengths depend on coupling and selection rules.
11. **Ignoring dimensionality.** A quantum well, wire and dot confine different numbers of spatial directions and therefore have different spectra and density-of-states behaviour.

12. **Trusting numerical diagonalization without convergence tests.** Discretization and finite-domain errors can create convincing but inaccurate results.

Caution

Classical language remains useful for energy scales and limiting arguments, but it becomes dangerous when it silently reintroduces a definite trajectory. In this chapter, speak about states, probability densities, expectation values and measurement outcomes unless a classical approximation is explicitly being made.

19.19 Main chapter summary

Summary

- A bound quantum state is determined by a potential, the Schrödinger equation, boundary conditions and normalization.
- The wavefunction ψ is a probability amplitude. Position probability density is $|\psi|^2$.
- In a one-dimensional infinite well, $\psi_n = \sqrt{2/L} \sin(n\pi x/L)$ and $E_n = n^2 h^2 / (8mL^2)$.
- The ground-state energy of an infinite well is nonzero because a nontrivial confined stationary state cannot have zero spatial variation.
- Finite wells permit exponential penetration into classically forbidden regions and support only finitely many bound states for fixed depth and width.
- Tunnelling through a finite barrier is exponentially sensitive to barrier width, height and particle mass.
- In rectangular multidimensional traps, energies are sums of independent confinement contributions; symmetry can produce degeneracy.
- Hydrogen is a Coulomb bound-state problem with $E_n \approx -13.6 \text{ eV}/n^2$ in the simplest nonrelativistic treatment.
- The Bohr model reproduces the principal hydrogen energy scale but should not be interpreted as the modern trajectory picture.
- Schrödinger hydrogen states are labelled by quantum numbers and described by spatial probability amplitudes called orbitals.
- Bound-state ideas underpin quantum wells, quantum dots, semiconductor optoelectronics and scanning tunnelling microscopy.
- Numerical finite-difference methods convert the Schrödinger equation into a matrix eigenvalue problem and must be validated by convergence and physical checks.

The consolidated formulas and their assumptions are collected in Appendix B.

19.20 Advanced Topics for Technical and Engineering Students

The main chapter developed bound states primarily through concrete models. This section revisits the same physics from a more structural viewpoint. The aim is not to turn an introductory chapter into a full quantum-mechanics course, but to show strong students how the familiar box, finite well and hydrogen examples fit into a broader mathematical framework and into modern device modelling.

Pedagogical boundary

The enrichment material introduces operator language, expectation values, exact finite-well matching equations, density-of-states ideas and hydrogen radial equations. Spin, identical-particle statistics, perturbation theory, relativistic quantum mechanics and many-electron atomic structure are mentioned only where they clarify the present topic; they belong to later or more specialized courses.

19.20.1 Energy eigenstates, operators and orthogonality

Equation (19.15) can be written compactly as

$$\hat{H}\psi = E\psi, \quad (19.82)$$

where the one-dimensional Hamiltonian operator is

$$\hat{H} = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + V(x). \quad (19.83)$$

This is an *eigenvalue equation*. The task is not to choose an arbitrary energy and then find any function that satisfies the differential equation. Instead, one seeks pairs (E, ψ) that simultaneously satisfy the differential equation, boundary conditions and normalizability. For confining potentials this combination commonly restricts E to a discrete set.

The language is closely related to engineering eigenvalue problems. A vibrating beam, a resonant electromagnetic cavity and a quantum particle in a trap all possess special spatial patterns selected by a differential equation and boundary conditions. Their mathematical structures are similar even though the physical meanings of the eigenfunctions and eigenvalues are different.

Key message

Quantization is often an eigenvalue phenomenon. Boundary conditions and normalizability do not merely modify an already chosen classical motion; they select the admissible states of the quantum system.

For a normalized state, the expectation value of an observable represented by an operator $\hat{A}$ is

$$\langle A \rangle = \int \psi^*(x) \hat{A}\psi(x) dx, \quad (19.84)$$

where the integral extends over the allowed spatial domain. Two especially important operators are

$$\hat{x} = x, \quad \hat{p}_x = -i\hbar \frac{d}{dx}. \quad (19.85)$$

The Hamiltonian itself represents energy, so a stationary energy eigenstate satisfies $\langle H \rangle = E$.

Guided checks

Why can a classical energy take a continuous range in a box while the corresponding quantum stationary-state energies are discrete? Which extra mathematical requirements appear in the quantum problem?

Orthogonality and expansion coefficients

Eigenstates of a self-adjoint Hamiltonian with distinct energies are orthogonal. Within a degenerate eigenspace an orthonormal basis can be chosen; arbitrary vectors in that space need not be orthogonal. The one-dimensional box spectrum is nondegenerate. For the infinite well,

$$\int_0^L \psi_m^*(x) \psi_n(x) dx = \delta_{mn}, \quad (19.86)$$

where δ_{mn} is the Kronecker delta: it equals one for $m = n$ and zero otherwise.

Using Eq. (19.29),

$$\int_0^L \psi_m \psi_n dx = \frac{2}{L} \int_0^L \sin\left(\frac{m\pi x}{L}\right) \sin\left(\frac{n\pi x}{L}\right) dx. \quad (19.87)$$

The trigonometric identity

also verifies the special case directly. More generally, self-adjointness gives $(E_n - E_m)\langle m|n\rangle = 0$: integrate the difference $\psi_m^* H \psi_n - (H \psi_m)^* \psi_n$, and the boundary term vanishes for the stated boundary conditions. Thus different energies imply zero overlap. For the box the identity

$$2 \sin A \sin B = \cos(A - B) - \cos(A + B)$$

shows immediately that the integral vanishes when $m \neq n$ and equals one when $m = n$.

Orthogonality is useful because a sufficiently well-behaved wavefunction in the well can be expanded as

$$\Psi(x, 0) = \sum_{n=1}^{\infty} c_n \psi_n(x), \quad c_n = \int_0^L \psi_n^*(x) \Psi(x, 0) dx. \quad (19.88)$$

For a normalized state,

$$\sum_{n=1}^{\infty} |c_n|^2 = 1. \quad (19.89)$$

The quantity $|c_n|^2$ is the probability of obtaining E_n in an ideal energy measurement.

Method

When a state is given as a linear combination of energy eigenstates, first normalize the coefficients, then read energy probabilities from $|c_n|^2$. Only after that should you calculate expectation values such as $\langle E \rangle = \sum_n |c_n|^2 E_n$.

Example 19.24: Energy measurement for a two-state superposition

An electron in a one-dimensional infinite well is prepared in

$$\Psi(x, 0) = \frac{1}{\sqrt{5}} \psi_1(x) + \frac{2}{\sqrt{5}} \psi_2(x).$$

The orthonormality of the eigenstates guarantees normalization because $1/5 + 4/5 = 1$. An energy measurement gives E_1 with probability 0.20 and E_2 with probability 0.80. The mean energy is

$$\langle E \rangle = \frac{1}{5} E_1 + \frac{4}{5} E_2 = \frac{1}{5} E_1 + \frac{4}{5} (4E_1) = \frac{17}{5} E_1.$$

For a 1.00 nm electron box, $E_1 \approx 0.376$ eV, so

$$\langle E \rangle \approx 1.28 \text{ eV.}$$

Notice that 1.28 eV is not itself an allowed measured energy in this two-state preparation; it is an ensemble average.

19.20.2 Time evolution and quantum beating in a superposition

A stationary spatial eigenfunction acquires only a phase factor in time,

$$\Psi_n(x, t) = \psi_n(x)e^{-iE_nt/\hbar}. \quad (19.90)$$

Therefore its probability density is time independent:

$$|\Psi_n(x, t)|^2 = |\psi_n(x)|^2.$$

A superposition behaves differently. If

$$\Psi(x, t) = c_1\psi_1(x)e^{-iE_1t/\hbar} + c_2\psi_2(x)e^{-iE_2t/\hbar}, \quad (19.91)$$

then $|\Psi|^2$ contains an interference term oscillating with angular frequency

$$\omega_{21} = \frac{E_2 - E_1}{\hbar}. \quad (19.92)$$

This is a clean connection between energy differences and time-dependent quantum behaviour.

For equal real initial coefficients, the density is

$$|\Psi|^2 = \frac{1}{2}(\psi_1^2 + \psi_2^2) + \psi_1\psi_2 \cos(\omega_{21}t).$$

The interference term integrates to zero by orthogonality, so the moving density remains normalized. Energy probabilities stay at 1/2 and 1/2: time-dependent position statistics do not require time-dependent total energy. Figure 19.12 shows this redistribution.

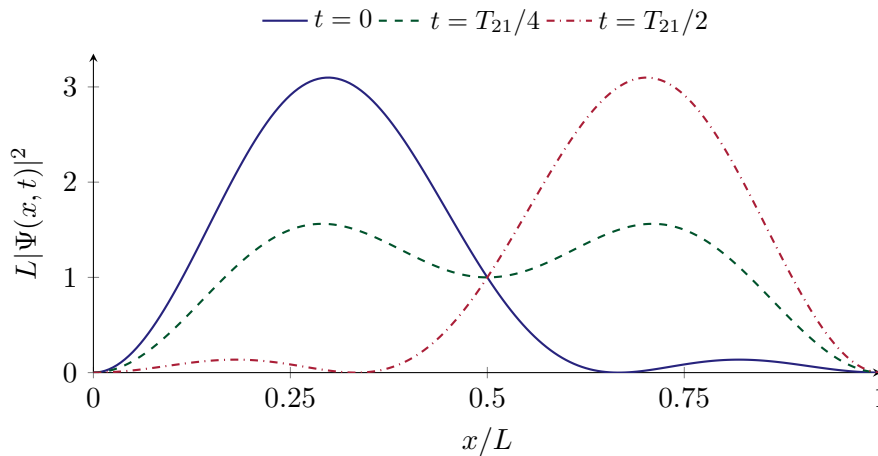


Figure 19.12: Calculated density for the coherent state $(\psi_1 + \psi_2)/\sqrt{2}$ with its two stationary time factors. Relative phase moves probability from one side to the other without changing the energy probabilities. The dashed curve also equals the position density of an incoherent equal mixture, which would remain unchanged at all times.

Example 19.25: Characteristic beating time in a nanometre box

For an electron in a 1.00 nm infinite well,

$$E_2 - E_1 = 3E_1 \approx 1.128 \text{ eV}.$$

The relative phase completes one cycle in

$$T_{21} = \frac{2\pi}{\omega_{21}} = \frac{h}{E_2 - E_1}.$$

Using $h = 4.1357 \times 10^{-15} \text{ eV s}$ gives

$$T_{21} \approx 3.67 \times 10^{-15} \text{ s}.$$

Thus nanoscale confinement naturally produces femtosecond dynamical time scales.

Note

The global phase of a wavefunction has no observable effect on $|\Psi|^2$. Relative phases between different components do matter because they control interference.

19.20.3 Expectation values and the uncertainty product in the infinite well

For the normalized state ψ_n in a well $0 < x < L$, symmetry about $x = L/2$ gives

$$\langle x \rangle = \frac{L}{2}. \quad (19.93)$$

A direct integration yields

$$\langle x^2 \rangle = L^2 \left(\frac{1}{3} - \frac{1}{2n^2\pi^2} \right), \quad (19.94)$$

so

$$\Delta x = L \sqrt{\frac{1}{12} - \frac{1}{2n^2\pi^2}}. \quad (19.95)$$

For the same real stationary states,

$$\langle p_x \rangle = 0, \quad (19.96)$$

while

$$\langle p_x^2 \rangle = \left(\frac{n\pi\hbar}{L} \right)^2, \quad (19.97)$$

which gives

$$\Delta p_x = \frac{n\pi\hbar}{L}. \quad (19.98)$$

The product is therefore

$$\Delta x \Delta p_x = n\pi\hbar \sqrt{\frac{1}{12} - \frac{1}{2n^2\pi^2}} \geq \frac{\hbar}{2}. \quad (19.99)$$

Example 19.26: Ground-state uncertainty product

For $n = 1$,

$$\frac{\Delta x}{L} = \sqrt{\frac{1}{12} - \frac{1}{2\pi^2}} \approx 0.1808,$$

and

$$\Delta p_x = \frac{\pi \hbar}{L}.$$

Hence

$$\Delta x \Delta p_x \approx 0.568 \hbar,$$

which is safely above the Heisenberg lower bound $\hbar/2$.

Guided checks

The expectation value $\langle p_x \rangle$ is zero in a stationary infinite-well state, but the kinetic energy is not zero. Explain how this is possible by distinguishing $\langle p_x \rangle$ from $\langle p_x^2 \rangle$.

Momentum-space intuition and Fourier content

A position-space wavefunction can be viewed as a superposition of plane-wave components. In a more advanced course this relation is expressed by a Fourier transform. Schematically,

$$\phi(p) = \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} \Psi(x) e^{-ipx/\hbar} dx. \quad (19.100)$$

The momentum-space probability density is $|\phi(p)|^2$.

This viewpoint gives a useful physical explanation of the uncertainty relation. A spatially broad, nearly sinusoidal wave contains a narrow range of wave numbers. A sharply localized wave packet requires many wave numbers and therefore many momenta. Confinement in position space broadens momentum content.

For the box state extended by zero outside $0 < x < L$, define $q = pL/\hbar$. The integral can be evaluated explicitly:

$$\phi_n(p) = \sqrt{\frac{L}{\pi\hbar}} \frac{n\pi[1 - (-1)^n e^{-iq}]}{n^2\pi^2 - q^2}. \quad (19.101)$$

The apparent singularities at $q = \pm n\pi$ are removable; use the integral or a limit there. This distribution describes a free momentum measurement immediately after an ideal sudden removal of the walls, before the position wavefunction changes. It is continuous, symmetric in p and normalized over dp . The natural scale of its spread is $\hbar/L$, consistent with the second moment already calculated. This measurement interpretation avoids assigning a self-adjoint signed-momentum observable with the same Dirichlet domain as the hard-wall Hamiltonian.

For an ideal infinite-well state, it is tempting to say that the particle has exactly the two momenta $\pm n\pi\hbar/L$ because a sine can be decomposed into two exponentials. That statement is too naive: the abrupt truncation at the walls modifies the full momentum-space distribution. Nevertheless, the characteristic momentum scale $n\pi\hbar/L$ correctly appears in $\langle p^2 \rangle$.

Caution

A standing wave is not evidence that a quantum particle literally bounces back and forth along a definite classical trajectory. The traveling-wave decomposition is mathematically useful, but a stationary state is described by one quantum state, not by a hidden classical path.

19.20.4 Parity and the centred square well

Symmetry becomes more transparent if an infinite well of width L is centred at the origin:

$$V(x) = 0 \quad \text{for } |x| < L/2, \quad V = \infty \quad \text{otherwise.}$$

The potential obeys $V(-x) = V(x)$. Energy eigenstates can then be chosen with definite parity:

$$\psi(-x) = +\psi(x) \quad (\text{even}), \quad \psi(-x) = -\psi(x) \quad (\text{odd}). \quad (19.102)$$

Even and odd states alternate as the energy rises. The physics and spectrum are identical to the $0 < x < L$ description; only the coordinate origin has changed.

Parity is not merely a plotting convenience. If an integrand is odd over a symmetric interval, its integral vanishes. This observation becomes a powerful shortcut in expectation values and transition matrix elements.

19.20.5 The finite square well as an exact matching problem

Consider a symmetric well of half-width a ,

$$V(x) = \begin{cases} 0, & |x| < a, \\ V_0, & |x| \geq a, \end{cases} \quad 0 < E < V_0. \quad (19.103)$$

Inside the well define

$$k = \frac{\sqrt{2mE}}{\hbar},$$

and outside define

$$\kappa = \frac{\sqrt{2m(V_0 - E)}}{\hbar}.$$

For the even solution, continuity can be built into the wavefunction before differentiating:

$$\psi_e(x) = A \begin{cases} \cos(kx), & |x| \leq a, \\ \cos(ka)e^{-\kappa(|x|-a)}, & |x| > a. \end{cases} \quad (19.104)$$

At $x = a$, derivative continuity is $-Ak \sin(ka) = -A\kappa \cos(ka)$. Dividing by the nonzero interface amplitude gives $k \tan(ka) = \kappa$. An odd state has $B \sin(kx)$ inside and $B \operatorname{sgn}(x) \sin(ka)e^{-\kappa(|x|-a)}$ outside; matching derivatives gives $k \cos(ka) = -\kappa \sin(ka)$.

Normalization must include both tails. For the even state,

$$1 = A^2 \left[a + \frac{\sin(2ka)}{2k} + \frac{\cos^2(ka)}{\kappa} \right], \quad (19.105)$$

$$P_{\text{out}} = \frac{A^2 \cos^2(ka)}{\kappa}. \quad (19.106)$$

The bracket has units of length, so A has the required units $\text{m}^{-1/2}$. For the odd state replace the bracket by $a - \sin(2ka)/(2k) + \sin^2(ka)/\kappa$. These expressions make the physical distinction from an infinite well quantitative: the interior probability alone is less than one.

Because the potential is even, bound eigenstates have even or odd parity. Matching both ψ and $d\psi/dx$ at $x = \pm a$ gives

$$k \tan(ka) = \kappa \quad (\text{even states}), \quad (19.107)$$

$$-k \cot(ka) = \kappa \quad (\text{odd states}). \quad (19.108)$$

Introduce dimensionless variables

$$z = ka, \quad y = \kappa a, \quad z_0 = \frac{a\sqrt{2mV_0}}{\hbar}. \quad (19.109)$$

Then

$$z^2 + y^2 = z_0^2, \quad (19.110)$$

with the transcendental conditions

$$z \tan z = \sqrt{z_0^2 - z^2}, \quad \text{even,} \quad (19.111)$$

$$-z \cot z = \sqrt{z_0^2 - z^2}, \quad \text{odd.} \quad (19.112)$$

Unlike the infinite well, these equations generally require numerical solution.

The roots can be located graphically in Figure 19.13.

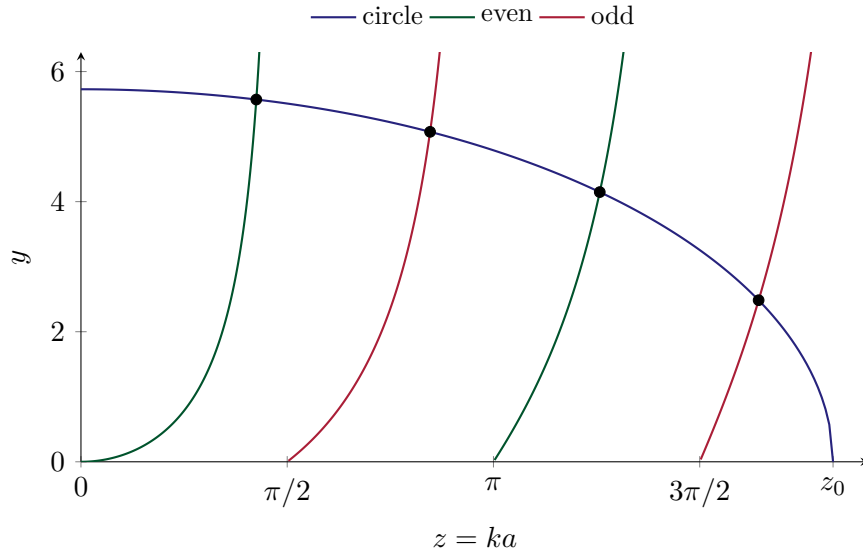


Figure 19.13: Quantitative matching curves for $z_0 = 5.727875$. Four intersections select the four bound states. Each tangent or cotangent branch is plotted separately and clipped at the frame; no horizontal plateau is part of the physical function. Values at trigonometric poles are excluded.

Example 19.27: Numerical finite-well eigenvalues

Take an electron in a well of total width $2a = 1.00$ nm and depth $V_0 = 5.00$ eV, with the inside potential defined as zero. The dimensionless depth is

$$z_0 = \frac{a\sqrt{2m_e V_0}}{\hbar} \approx 5.73.$$

Numerical solution of Eqs. (19.108) gives approximately

state parity	z	E (eV)
even	1.335	0.272
odd	2.659	1.077
even	3.951	2.379
odd	5.161	4.059

All four energies lie below the outside potential $V_0 = 5$ eV. The corresponding infinite-well ground energy for the same geometric width is 0.376 eV, higher than the finite-well value because the finite-barrier wavefunction spreads beyond the nominal width. Greater spatial extent reduces the kinetic-energy cost of confinement.

For the ground-state root, $\sqrt{a}A = 0.920757$ and Eq. (19.106) gives $P_{\text{out}} = 0.00827$. Less than one percent of the probability lies beyond the interfaces for this particular ground state; higher states have larger penetration. Substituting the root into the derivative condition gives the independently checkable equality $z \tan z = \sqrt{z_0^2 - z^2}$.

Key message

A finite well illustrates two important facts at once: the spectrum is still discrete for bound states, but the energies and wavefunctions are determined by boundary matching rather than by a simple integer-wavelength rule.

How many bound states can a finite well support?

Unlike the infinite well, a finite well has only a finite number of bound states. The dimensionless depth parameter

$$z_0 = \frac{a\sqrt{2mV_0}}{\hbar}$$

controls how many intersections appear in the graphical equations of Sec. 19.20.5. Increasing a , m or V_0 increases z_0 and generally allows more bound states.

There is an exact count for this one-dimensional square well. The positive matching branches begin at $z = j\pi/2$ for $j = 0, 1, 2, \dots$, alternating even and odd. A branch contributes one normalizable state only if its left endpoint lies strictly below z_0 . Therefore

$$N_{\text{bound}} = \left\lceil \frac{2z_0}{\pi} \right\rceil, \quad z_0 > 0. \quad (19.113)$$

At an exact threshold $z_0 = j\pi/2$, the new root would have $\kappa = 0$ and a nondecaying exterior; it is not a normalizable bound state and is excluded by this formula. Any nonzero square well therefore has at least one bound state in one dimension. This conclusion is not universal in three dimensions. For the worked well, $2z_0/\pi \simeq 3.65$, giving four states. A comparison with infinite-well levels is only a rough guide and can undercount states near threshold.

Guided checks

Why do larger mass, larger width and greater depth all tend to increase the number of finite-well bound states? Answer using both the dimensionless parameter z_0 and the physical idea of confinement energy.

Root finding without crossing a pole

The transcendental equations are simple to write but can be numerically troublesome near poles of $\tan z$ and $\cot z$. A robust root-finding strategy should respect the known branch structure.

For a given z_0 , define

$$\begin{aligned} f_e(z) &= z \tan z - \sqrt{z_0^2 - z^2}, \\ f_o(z) &= -z \cot z - \sqrt{z_0^2 - z^2}. \end{aligned}$$

Search only on intervals with $0 < z < z_0$ that do not cross a trigonometric pole. For the even function, useful branches lie between the poles of $\tan z$; for the odd function, between the poles of $\cot z$. Within each allowed branch:

1. evaluate the function slightly away from each endpoint;
2. verify a sign change before invoking a bracketing solver;
3. use bisection or Brent's method rather than an unconstrained Newton step as the first choice;
4. convert the root to energy using

$$E = \frac{\hbar^2 z^2}{2ma^2};$$

5. verify $0 < E < V_0$;
6. reconstruct and normalize the wavefunction;
7. count nodes and check the expected parity.

Why not simply apply Newton's method from a random initial value? Near a tangent pole, a large derivative can send the iteration to a different branch or outside the physical interval. A root returned by a numerical routine is not automatically the root one intended to find.

For the 1.00 nm-wide, 5.00 eV electron well, the roots listed earlier,

$$z \approx 1.335, 2.659, 3.951, 5.161,$$

alternate even and odd parity. Reconstructing the states should show zero, one, two and three internal nodes respectively. Node count is therefore an independent diagnostic of root ordering.

19.20.6 Probability current and local conservation

Probability density does not merely exist; in a time-dependent state it can flow through space. The one-dimensional probability current is

$$j(x, t) = \frac{\hbar}{2mi} \left(\Psi^* \frac{\partial \Psi}{\partial x} - \Psi \frac{\partial \Psi^*}{\partial x} \right) = \frac{\hbar}{m} \text{Im} \left(\Psi^* \frac{\partial \Psi}{\partial x} \right). \quad (19.114)$$

Together with $\rho = |\Psi|^2$, it satisfies a continuity equation,

$$\frac{\partial \rho}{\partial t} + \frac{\partial j}{\partial x} = 0. \quad (19.115)$$

This has the same mathematical form as local conservation laws for electric charge or fluid mass.

A short derivation is illuminating. Start with the time-dependent Schrödinger equation and its complex conjugate,

$$\begin{aligned} i\hbar \frac{\partial \Psi}{\partial t} &= -\frac{\hbar^2}{2m} \frac{\partial^2 \Psi}{\partial x^2} + V\Psi, \\ -i\hbar \frac{\partial \Psi^*}{\partial t} &= -\frac{\hbar^2}{2m} \frac{\partial^2 \Psi^*}{\partial x^2} + V\Psi^*. \end{aligned}$$

Multiply the first by Ψ^* , the second by Ψ , subtract appropriately, and recognize

$$\frac{\partial}{\partial t} |\Psi|^2 = \Psi^* \frac{\partial \Psi}{\partial t} + \Psi \frac{\partial \Psi^*}{\partial t}.$$

For a real potential, the V terms cancel and Eq. (19.115) follows.

For a plane wave

$$\Psi = Ae^{i(kx - \omega t)},$$

the current is

$$j = \frac{\hbar k}{m} |A|^2. \quad (19.116)$$

A left-moving wave has negative current. A real standing wave can have $j = 0$ even though it contains nonzero momentum components. This is another reason that “zero current” should not be confused with “zero kinetic energy.”

Key message

The continuity equation expresses conservation of total probability. In scattering problems, transmission and reflection coefficients are most cleanly defined as ratios of probability currents, not merely ratios of wave amplitudes.

Reflection and transmission as current ratios

For a barrier-scattering problem with an incident wave from the left,

$$\begin{aligned}\Psi_{\text{left}} &= Ae^{ikx} + Be^{-ikx}, \\ \Psi_{\text{right}} &= Fe^{ikx},\end{aligned}$$

when the asymptotic potentials and masses are the same on both sides. The incident, reflected and transmitted currents are proportional to $|A|^2$, $-|B|^2$ and $|F|^2$, respectively. Therefore

$$R = \frac{|j_{\text{refl}}|}{j_{\text{inc}}} = \frac{|B|^2}{|A|^2}, \quad T = \frac{j_{\text{trans}}}{j_{\text{inc}}} = \frac{|F|^2}{|A|^2}, \quad (19.117)$$

and conservation gives

$$R + T = 1. \quad (19.118)$$

If the wave numbers or effective masses differ on the two sides, the amplitude ratios alone are insufficient; the velocity/current factors must be included.

Caution

A transmission amplitude and a transmission probability are different quantities. In the simplest equal-medium case $T = |F/A|^2$, but in general current factors are required. Always define T from transmitted flux divided by incident flux.

19.20.7 Rectangular-barrier transmission beyond the exponential estimate

For a rectangular barrier of height V_0 and width d , with the same zero potential on both sides and $0 < E < V_0$, matching the wavefunction and its derivative gives the transmission probability

$$T = \left[1 + \frac{V_0^2 \sinh^2(\kappa d)}{4E(V_0 - E)} \right]^{-1}, \quad \kappa = \frac{\sqrt{2m(V_0 - E)}}{\hbar}. \quad (19.119)$$

For $\kappa d \gg 1$, since $\sinh(\kappa d) \approx \frac{1}{2}e^{\kappa d}$,

$$T \approx \frac{16E(V_0 - E)}{V_0^2} e^{-2\kappa d}. \quad (19.120)$$

The exponential dependence used earlier is therefore the dominant thick-barrier behaviour, while the prefactor contains additional energy dependence.

Example 19.28: Comparing exact and exponential tunnelling estimates

Let an electron with $E = 1.00$ eV encounter a $V_0 = 4.00$ eV barrier of width $d = 0.50$ nm. From the main chapter, $\kappa \approx 8.87$ nm⁻¹, so $\kappa d \approx 4.44$. Using unrounded constants, Eq. (19.119) gives $T = 4.2006 \times 10^{-4}$. The exponential alone is 1.4004×10^{-4} , while the matching prefactor is $16E(V_0 - E)/V_0^2 = 3$. Including it gives 4.2012×10^{-4} , within 0.02% of the exact result. The extra digits here compare the two model formulas; they do not imply precision knowledge of a real barrier.

Caution

The rectangular-barrier formula assumes piecewise constant potentials and coherent one-particle quantum mechanics. Real tunnel junctions can require effective masses, image-potential corrections, bias-dependent barrier shapes, many-electron effects and material-specific electronic structure.

19.20.8 Transfer-matrix thinking for layered quantum structures

A multilayer semiconductor heterostructure contains many interfaces. In each layer of constant potential, the Schrödinger equation has elementary exponential or sinusoidal solutions. The amplitudes on one side of an interface can be related linearly to those on the other side. Repeating this interface propagation leads naturally to a matrix product,

$$\begin{pmatrix} A_R \\ B_R \end{pmatrix} = M_N M_{N-1} \cdots M_2 M_1 \begin{pmatrix} A_L \\ B_L \end{pmatrix}. \quad (19.121)$$

This *transfer-matrix* idea is widely used for quantum barriers, optical thin films, transmission lines and acoustic multilayers. The physical equations differ, but the engineering logic of propagating amplitudes through layered media is strikingly similar.

For thick evanescent layers, naive transfer matrices may become numerically ill-conditioned because exponentially growing and decaying components coexist. More stable scattering-matrix formulations are often preferred in precision software. This is an example of a general computational lesson: mathematically equivalent formulations need not be numerically equivalent.

19.20.9 Coupled wells and level splitting

Two separated identical finite wells provide a bridge from isolated bound states to molecules, quantum-dot pairs and superlattices. If the barrier between the wells is extremely wide, each well has nearly the same isolated ground state and the pair is nearly degenerate. When the barrier is finite, the tails overlap and the two localized states couple.

The lowest pair of eigenstates then becomes approximately

$$\psi_+ \approx \frac{1}{\sqrt{2}}(\psi_L + \psi_R), \quad \psi_- \approx \frac{1}{\sqrt{2}}(\psi_L - \psi_R), \quad (19.122)$$

where ψ_L and ψ_R are normalized states localized mainly in the left and right wells, with overlap neglected (or removed by orthogonalization). The symmetric combination usually has lower energy because it can remain smoother through the central barrier, reducing kinetic-energy curvature. The antisymmetric combination has a node between the wells and lies higher.

Define the splitting

$$\Delta E = E_- - E_+. \quad (19.123)$$

As the barrier becomes wider or higher, overlap decreases and ΔE typically becomes exponentially small. This connects directly with the tunnelling scale developed earlier.

The low-lying double-well splitting is illustrated in Figure 19.14.

Example 19.29: Coherent transfer time from a two-level splitting

If a particle is initially localized mainly in one well, it can be written as a superposition of the symmetric and antisymmetric eigenstates. Within the isolated, orthonormal two-state model, the probability of finding it in the other well is

$$P_R(t) = \sin^2\left(\frac{\Delta E t}{2\hbar}\right).$$

The first complete transfer occurs at $\tau = \pi\hbar/\Delta E$. Coupling to other levels or loss of coherence can reduce the transfer in a real device. If $\Delta E = 1.0$ meV, then

$$\tau = \frac{\pi(6.582 \times 10^{-16} \text{ eV s})}{10^{-3} \text{ eV}} \approx 2.1 \text{ ps}.$$

The example shows how a small energy splitting sets a dynamical tunnelling time scale.

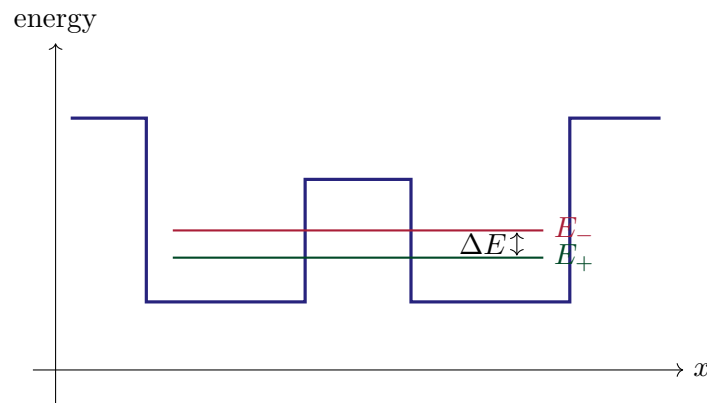


Figure 19.14: Schematic symmetric double well. Coupling through the central barrier splits a nearly degenerate isolated-well level into symmetric and antisymmetric combinations.

From a finite well to a superlattice: qualitative band formation

Imagine many identical finite wells separated by barriers. If the wells are far apart, each supports nearly independent localized states. As the barriers become thinner, wavefunction tails overlap. States that were nearly degenerate can split into closely spaced combinations extending over several wells. In a long periodic array, these split levels develop into minibands.

This provides a bridge from the bound-state language of this chapter to the band-structure language used for solids. The key physical mechanism is overlap and coupling between neighboring localized states. The same qualitative idea appears in molecular orbital formation and in tight-binding descriptions of crystals.

Pedagogical boundary

A quantitative derivation of Bloch's theorem and solid-state band structure is postponed. Here the finite-well picture is used only to motivate how coupling many localized quantum states can broaden discrete levels into allowed energy bands.

19.20.10 Resonant tunnelling and quasi-bound states

A double-barrier structure can trap a wave temporarily in the central region. If the incident energy aligns with a quasi-bound level of that region, multiple reflections between the barriers interfere constructively and the transmission can become much larger than the single-barrier expectation. This phenomenon is *resonant tunnelling*.

The idea is analogous to optical Fabry-Pérot resonance. A cavity transmits strongly when the round-trip phase satisfies a constructive-interference condition. In a quantum resonant-tunnelling structure, the central well plays the role of a matter-wave cavity.

Real resonant-tunnelling diodes exploit related physics in semiconductor heterostructures. Their current-voltage characteristic can display a region of negative differential resistance when a resonant level moves out of alignment with occupied emitter states. A realistic device analysis requires carrier distributions, electrostatics and scattering, but the core resonance mechanism is already visible in the one-particle barrier model.

Pedagogical boundary

A quasi-bound state is not a perfectly stable bound state. Because it is coupled to propagating regions, it has a finite lifetime and a finite resonance width. A full treatment uses scattering theory and open-system boundary conditions.

19.20.11 Quantum wells, wires and dots: dimensionality as a design variable

Confinement can act in one, two or three spatial directions. The terminology is conventional:

Structure	Confined directions	Approximately free directions	Spectrum character
Quantum well	1	2	discrete subbands plus in-plane continuum
Quantum wire	2	1	transverse subbands plus axial continuum
Quantum dot	3	0	fully discrete levels

In a simple effective-mass model, a quantum-well subband has

$$E_n(k_x, k_y) = E_n^\perp + \frac{\hbar^2(k_x^2 + k_y^2)}{2m^*}, \quad (19.124)$$

where m^* is the semiconductor effective mass and $E_n^\perp$ is the confinement energy in the growth direction.

The ability to engineer L , barrier height and material composition makes quantum confinement a practical design tool rather than a purely conceptual effect. Quantum-well lasers, infrared photodetectors and nanostructured light emitters exploit such engineered spectra.

Density of states from three dimensions to zero dimensions

The *density of states* (DOS) tells how many one-particle states are available per energy interval. For a parabolic band with energy

$$E = E_c + \frac{\hbar^2 k^2}{2m^*},$$

the ideal three-dimensional DOS per unit volume, including a factor two for spin degeneracy, is

$$g_{3D}(E) = \frac{1}{2\pi^2} \left(\frac{2m^*}{\hbar^2} \right)^{3/2} \sqrt{E - E_c}, \quad E \geq E_c. \quad (19.125)$$

For an ideal two-dimensional subband, the DOS per unit area is constant above each subband edge,

$$g_{2D}(E) = \frac{m^*}{\pi \hbar^2} \Theta(E - E_n^\perp) \quad \text{for one subband}, \quad (19.126)$$

again using spin degeneracy two.

Here Θ is zero below the subband edge and one above it. DOS counts available states whether or not they are occupied; carrier occupation requires a separate distribution function. Additional valley degeneracy is not included. In one dimension the DOS has inverse-square-root singularities at subband edges, while in an ideal zero-dimensional dot the spectrum is a set of discrete lines.

The different DOS shapes are compared in Figure 19.15.

The power laws follow from state counting. In d free directions with a parabolic dispersion, the number of states inside a k -space ball scales as k^d , and $k^2 \propto E - E_c$. Hence $N(E) \propto (E - E_c)^{d/2}$ and

$g(E) \propto (E - E_c)^{d/2-1}$. The proportionality changes at every subband threshold; occupation is not part of this argument. In two dimensions, periodic boundaries of area A give $N(k) = 2A\pi k^2/(2\pi)^2$, so $A^{-1}dN/dE = m^*/(\pi\hbar^2)$, including spin two. This also checks the units: states per area per energy.

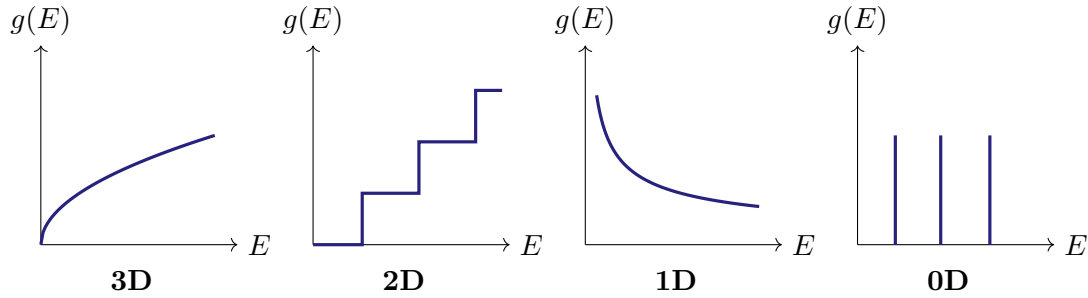


Figure 19.15: Idealized density-of-states shapes for parabolic-band systems of different effective dimensionality. The sketches use independent arbitrary vertical scales: DOS units differ with dimensionality. The 0D sticks indicate delta-function levels of equal illustrative degeneracy, not finite-width peaks. Broadening and many-body effects are omitted.

Key message

Reducing dimensionality changes not only the spacing of discrete levels but also the number of states available near a given energy. This is one reason nanostructuring can strongly modify optical and transport properties.

19.20.12 Effective mass and finite barriers in semiconductor wells

Electrons moving through a periodic crystal do not generally respond to applied forces as free electrons of mass m_e . Near a simple parabolic band extremum, their dynamics can often be described using an *effective mass* m^* . In a one-band envelope-function approximation one writes

$$-\frac{\hbar^2}{2} \frac{d}{dz} \left[\frac{1}{m^*(z)} \frac{d\psi}{dz} \right] + V(z)\psi = E\psi. \quad (19.127)$$

The position dependence allows different semiconductor layers to have different effective masses. Interface matching is then more subtle than simply matching ψ' ; in a commonly used model, ψ and $(1/m^*)\psi'$ are continuous.

These conditions follow by integrating Eq. (19.127) across a finite interface and requiring a continuous envelope. They conserve the normal current $j = (\hbar/m^*)\text{Im}(\psi^*\psi')$. They are conditions for this specified one-band Hamiltonian, not universal microscopic boundary conditions for every heterostructure.

The conduction-band confinement model is illustrated in Figure 19.16.

The model makes an important pedagogical point: the infinite square well is often a useful first estimate, but device-level calculations typically require finite band offsets and material-specific parameters.

Optical transitions in a simple semiconductor quantum well

A simplified semiconductor quantum well can confine both conduction-band electrons and valence-band holes, each described relative to its own band edge. In an infinite-well approximation, their

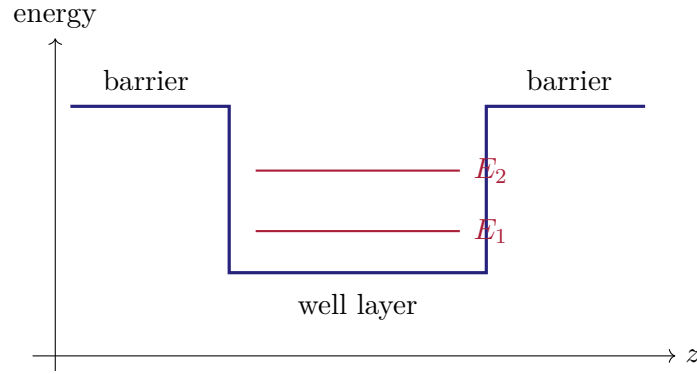


Figure 19.16: Schematic conduction-band profile of a semiconductor quantum well. The horizontal lines represent confined subband energies in the growth direction. Real heterostructures require material-dependent offsets and effective masses.

confinement energies scale inversely with their respective effective masses:

$$E_{e,n}^{\text{conf}} = \frac{n^2 \hbar^2}{8m_e^* L^2}, \quad (19.128)$$

$$E_{h,n}^{\text{conf}} = \frac{n^2 \hbar^2}{8m_h^* L^2}. \quad (19.129)$$

A crude interband transition energy can then be estimated as

$$E_\gamma \approx E_g + E_{e,n}^{\text{conf}} + E_{h,m}^{\text{conf}}, \quad (19.130)$$

where E_g is the bulk band gap. Real systems require finite barriers, band mixing, Coulomb attraction between electron and hole, strain and selection rules, but Eq. (19.130) captures the basic blue-shift caused by confinement.

For ideal wells of the same width, the envelope overlap $\int_0^L \psi_{e,n} \psi_{h,m} dz$ vanishes for $n \neq m$ because the sine functions are orthogonal. Thus even this crude model must pair the energy-gap calculation with an optical matrix element. A common further correction is a subtraction of a positive exciton binding energy; it should not be confused with the individual electron confinement energy.

Example 19.30: Why a narrower well can emit higher-energy photons

If the well width decreases from L to $0.8L$, each ideal confinement contribution increases by

$$\frac{1}{0.8^2} = 1.5625.$$

The transition energy therefore increases in the simplest model. The corresponding emitted wavelength decreases. This is the quantum-confinement origin of a blue shift, although real device shifts are not determined by box energies alone.

19.20.13 A numerical strategy: nondimensionalization before discretization

Numerical work becomes more stable and more transparent when variables are scaled before constructing matrices. Choose a characteristic length L_0 and define

$$\xi = \frac{x}{L_0}, \quad \epsilon = \frac{E}{E_0}, \quad u(\xi) = \frac{V(x)}{E_0}, \quad (19.131)$$

with the natural energy scale

$$E_0 = \frac{\hbar^2}{2mL_0^2}. \quad (19.132)$$

Then the one-dimensional Schrödinger equation becomes

$$-\frac{d^2\psi}{d\xi^2} + u(\xi)\psi = \epsilon\psi. \quad (19.133)$$

Scaling removes small SI constants and makes parameters easier to compare. Matrix entries are not generally of order unity: the kinetic diagonal grows as $2/(\Delta\xi)^2$ and the off-diagonals as $-1/(\Delta\xi)^2$ when the grid is refined.

Method

For computational physics, scale first and discretize second. Keep one explicit conversion layer between dimensionless numerical variables and SI or eV-based physical outputs. This makes unit tests much easier.

Grid convergence, domain truncation and numerical credibility

A computed eigenvalue is not trustworthy merely because a library routine returned many digits. At least four checks should be made:

1. **Grid convergence:** halve Δx and verify that low-lying energies stabilize.
2. **Domain convergence:** for finite wells, move artificial outer boundaries farther away and verify stability.
3. **Normalization and orthogonality:** numerical eigenvectors should satisfy discrete analogues of Eqs. (19.8) and (19.86).
4. **Benchmarking:** reproduce an analytic problem, such as the infinite well, before trusting a new potential.

For the central second-difference stencil, low-lying eigenvalues typically approach the continuum result with an error scaling approximately as $(\Delta x)^2$ when the solution is smooth and other errors are controlled.

A useful convergence estimator from two grid spacings h and $h/2$ is

$$\delta_E \approx |E(h/2) - E(h)|. \quad (19.134)$$

For a second-order scheme, comparing a third grid can reveal whether the asymptotic h^2 regime has actually been reached.

Guided checks

Suppose two successive grid refinements change the ground-state energy by 2% and then 0.5%. Is the first quoted result accurate to four significant figures? What additional test would you perform before reporting a precision claim?

Numerical, parameter and model uncertainty

Consider a calculated transition energy for a nanostructure. Three distinct uncertainty categories should not be mixed:

Numerical uncertainty: finite grid spacing, finite domain, eigensolver tolerance and numerical quadrature.

Parameter uncertainty: uncertain well width, effective mass, band offset, dielectric constant or temperature.

Model discrepancy: physics omitted from the chosen equations, such as many-body interactions, nonparabolicity or interface roughness.

A simulation can have tiny numerical uncertainty while still being physically inaccurate because of parameter or model uncertainty. Conversely, an excellent physical model can be undermined by poor numerical convergence.

For professional reporting, one should state which category is being estimated. “The result is accurate to 0.1%” is ambiguous unless the basis for that claim is specified.

19.20.14 The variational principle: estimating a ground-state energy

Another broadly useful method is the variational principle. For any normalized trial function ϕ satisfying the required boundary conditions,

$$E_{\text{trial}} = \langle \phi | \hat{H} | \phi \rangle \geq E_0, \quad (19.135)$$

where E_0 denotes the true ground-state energy in this subsection (the box ground state elsewhere is labelled E_1). A well-chosen trial function can therefore provide both an estimate and an upper bound.

The trial state must lie in the Hamiltonian’s quadratic-form domain and have finite kinetic energy. Expanding in energy eigenstates makes the inequality transparent: $\langle H \rangle = \sum_n |c_n|^2 E_n \geq E_0 \sum_n |c_n|^2 = E_0$, with the continuum contribution included if present.

Consider the infinite well $0 < x < L$ with the simple trial function

$$\phi(x) = Ax(L - x), \quad (19.136)$$

which automatically vanishes at both walls. Normalization gives

$$A = \sqrt{\frac{30}{L^5}}.$$

Because $V = 0$ inside the well, the energy expectation can be evaluated from the kinetic-energy form

$$E_{\text{trial}} = \frac{\hbar^2}{2m} \int_0^L |\phi'(x)|^2 dx. \quad (19.137)$$

Since $\phi' = A(L - 2x)$,

$$\int_0^L |\phi'|^2 dx = A^2 \frac{L^3}{3} = \frac{10}{L^2}.$$

Thus

$$E_{\text{trial}} = \frac{5\hbar^2}{mL^2}. \quad (19.138)$$

The exact ground energy is

$$E_1 = \frac{\pi^2 \hbar^2}{2mL^2} \approx 4.935 \frac{\hbar^2}{mL^2}.$$

Therefore

$$\frac{E_{\text{trial}}}{E_1} = \frac{10}{\pi^2} \approx 1.013.$$

A simple parabola already estimates the exact ground energy to about 1.3% from above.

Method

Choose a trial function satisfying the essential boundaries and reflecting the expected shape. Enlarging a nested trial family cannot raise its optimized energy, which remains an upper bound to the ground energy.

19.20.15 A second canonical bound system: the quantum harmonic oscillator

Near a stable minimum, many smooth potentials can be approximated by a parabola. If $x = 0$ is the equilibrium point,

$$V(x) \approx V(0) + \frac{1}{2}m\omega^2 x^2. \quad (19.139)$$

Choose the energy zero so that $V(0) = 0$. The corresponding quantum harmonic oscillator has the exact spectrum

$$E_n = \left(n + \frac{1}{2}\right) \hbar\omega, \quad n = 0, 1, 2, \dots \quad (19.140)$$

and a Gaussian ground state,

$$\psi_0(x) = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} \exp\left(-\frac{m\omega x^2}{2\hbar}\right). \quad (19.141)$$

The zero-point energy is $E_0 = \hbar\omega/2$.

This result can be checked without solving the complete spectrum. Write $\psi_0 = A \exp(-\alpha x^2/2)$. Then $\psi_0'' = (\alpha^2 x^2 - \alpha)\psi_0$; choosing $\alpha = m\omega/\hbar$ cancels the x^2 terms in $H\psi_0$, leaving $H\psi_0 = (\hbar\omega/2)\psi_0$. The normalized Gaussian has $\Delta x = \sqrt{\hbar/(2m\omega)}$ and $\Delta p = \sqrt{m\hbar\omega/2}$, so it saturates $\Delta x \Delta p = \hbar/2$, unlike a box eigenstate.

This system is included here only as a comparison. It shows that discrete bound-state energies do not always scale as n^2 and that the infinite-well spectrum is not universal. In the oscillator, adjacent levels are equally spaced. The form of $V(x)$ determines the spectrum.

The oscillator also appears as a local approximation to molecular vibrations, lattice vibrations and small-amplitude modes of many physical systems. Its full algebraic treatment belongs to a dedicated quantum-mechanics course.

Guided checks

Compare three spectra: infinite well $E_n \propto n^2$, harmonic oscillator $E_n \propto n + 1/2$, hydrogen $E_n \propto -1/n^2$. What does this comparison teach about the relationship between a potential and its quantum spectrum?

19.20.16 The WKB approximation: local wavelength in a slowly varying potential

The square well is exactly solvable because the potential is piecewise constant. Many realistic potentials vary continuously and cannot be solved in elementary functions. A powerful semiclassical approximation is the Wentzel–Kramers–Brillouin (WKB) method.

Define a local classical momentum in an allowed region,

$$p(x) = \sqrt{2m[E - V(x)]}. \quad (19.142)$$

When the potential changes slowly over a local de Broglie wavelength,

more precisely $\hbar|p'(x)| \ll p(x)^2$ away from turning points, the wavefunction is approximately

$$\psi(x) \approx \frac{C}{\sqrt{p(x)}} \exp\left(\pm \frac{i}{\hbar} \int^x p(x') dx'\right). \quad (19.143)$$

In a forbidden region, define

$$|p(x)| = \sqrt{2m[V(x) - E]},$$

and the WKB form becomes exponential,

$$\psi(x) \sim \frac{1}{\sqrt{|p(x)|}} \exp\left(-\frac{1}{\hbar} \int |p(x)| dx\right). \quad (19.144)$$

This generalizes the rectangular-barrier factor $e^{-\kappa d}$ to barriers of arbitrary smooth shape.

For two smooth classical turning points x_1 and x_2 , an approximate bound-state quantization condition is

$$\int_{x_1}^{x_2} p(x) dx \approx \left(n + \frac{1}{2}\right) \pi \hbar, \quad n = 0, 1, 2, \dots \quad (19.145)$$

with the indexing convention shown. The additional one-half reflects phase changes near smooth turning points. Hard infinite walls have different boundary-phase behaviour, so the square-well formula should not be obtained by blindly substituting its discontinuous walls into Eq. (19.145).

Key message

WKB expresses a deep correspondence idea: where the potential varies slowly, the matter wave behaves locally like a wave with wavelength $\lambda(x) = h/p(x)$. Quantization arises when the accumulated phase fits the boundary/turning-point conditions.

WKB tunnelling through a nonrectangular barrier

If x_1 and x_2 are turning points of a smooth barrier with $V(x) > E$ between them, WKB predicts the dominant exponential transmission scale

$$T \sim \exp\left[-2 \int_{x_1}^{x_2} \frac{\sqrt{2m[V(x) - E]}}{\hbar} dx\right]. \quad (19.146)$$

For a rectangular barrier, the integrand is constant and Eq. (19.146) reduces to the familiar $e^{-2\kappa d}$ dependence.

This form is useful in field emission, alpha-decay intuition, tunnel junctions and semiconductor barriers. The exact prefactor depends on the detailed matching and is not contained in the simple exponential estimate.

Example 19.31: Triangular-barrier scaling

Suppose a barrier decreases linearly from height V_0 at $x = 0$ to the particle energy E at $x = d$:

$$V(x) - E = (V_0 - E) \left(1 - \frac{x}{d}\right).$$

The WKB exponent contains

$$\begin{aligned} \int_0^d \sqrt{2m[V(x) - E]} dx &= \sqrt{2m(V_0 - E)} \int_0^d \sqrt{1 - x/d} dx \\ &= \frac{2d}{3} \sqrt{2m(V_0 - E)}. \end{aligned}$$

Therefore the dominant transmission factor is

$$T \sim \exp\left[-\frac{4d}{3\hbar} \sqrt{2m(V_0 - E)}\right].$$

The exponent differs from that of a rectangular barrier because the particle sees a smaller average forbidden-region momentum.

Classical turning points and quantum tails

A classical turning point satisfies

$$E = V(x_t). \quad (19.147)$$

Classically, motion reverses there because the kinetic energy $E - V$ reaches zero. Quantum mechanically, a bound-state wavefunction does not generally stop abruptly at x_t . It extends into the classically forbidden region and decays over a scale determined by the local value of $V - E$.

For a smooth potential, the WKB amplitude formally becomes singular at a turning point because $p(x_t) = 0$. This signals failure of the naive local approximation, not a physical divergence of the true wavefunction. More careful matching through the turning-point region restores a finite solution and generates the phase corrections that appear in the WKB quantization condition.

The turning-point concept is useful when interpreting molecular vibrations, oscillator states and slowly varying quantum wells. It also reinforces a recurring lesson: classical concepts can organize intuition, but quantum boundary behaviour must be obtained from the wave equation.

19.20.17 Basis-set diagonalization: turning differential equations into linear algebra

Instead of representing ψ by values on a spatial grid, one can expand it in known basis functions,

$$\psi(x) = \sum_{n=1}^N c_n \phi_n(x). \quad (19.148)$$

Substitution into the Schrödinger equation and projection onto the basis gives a matrix eigenproblem,

$$\sum_n H_{mn} c_n = E c_m, \quad H_{mn} = \int \phi_m^* \hat{H} \phi_n \, dx, \quad (19.149)$$

for an orthonormal basis.

For a potential confined to a finite interval, the infinite-well eigenfunctions can form a convenient basis. The kinetic-energy matrix is then diagonal, while the potential contributes integrals

$$V_{mn} = \int_0^L \phi_m(x) V(x) \phi_n(x) \, dx.$$

Increasing N improves the representation if the basis is appropriate. This approach connects quantum mechanics directly to numerical linear algebra and spectral methods.

A poor basis may converge slowly. Good computational physics therefore combines mathematical completeness with physical insight about the shape and symmetry of the expected states.

19.20.18 The hydrogen radial equation and effective potential

For a central potential, write

$$\psi(r, \theta, \phi) = R_{n\ell}(r) Y_{\ell}^{m_{\ell}}(\theta, \phi).$$

Defining

$$u(r) = r R(r) \quad (19.150)$$

converts the radial Schrödinger equation into a one-dimensional-looking form,

$$-\frac{\hbar^2}{2\mu} \frac{d^2 u}{dr^2} + V_{\text{eff}}(r) u = E u, \quad (19.151)$$

with

$$V_{\text{eff}}(r) = -\frac{e^2}{4\pi\epsilon_0 r} + \frac{\hbar^2 \ell(\ell+1)}{2\mu r^2}. \quad (19.152)$$

The second term is the centrifugal contribution. It vanishes for s states ($\ell = 0$) and pushes higher- ℓ probability away from the origin.

The radial effective-potential picture is shown in Figure 19.17.

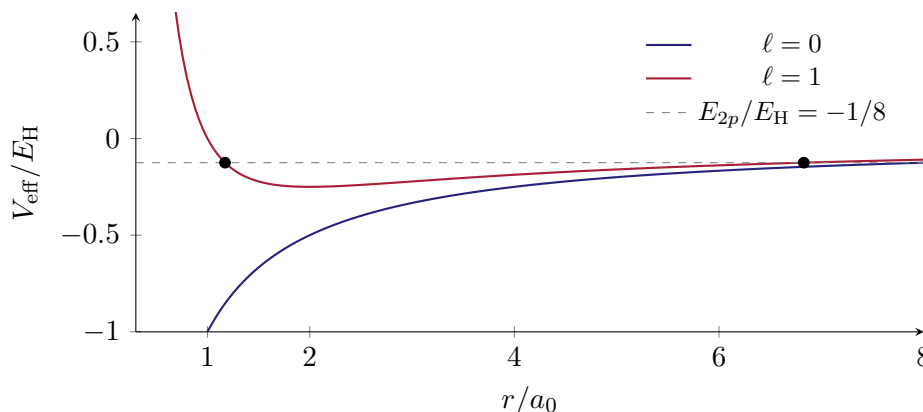


Figure 19.17: Calculated fixed-proton Coulomb effective potentials, using $E_H = \hbar^2/(m_e a_0^2) \simeq 27.2 \text{ eV}$. The centrifugal term gives $V_{\text{eff}}/E_H = -1/\rho + \ell(\ell+1)/(2\rho^2)$ with $\rho = r/a_0$. Dots mark the two radial classical turning points for the $2p$ energy in the $\ell = 1$ effective potential. The quantum radial wavefunction has tails beyond these points.

Key message

The hydrogen atom is a three-dimensional bound-state problem, but spherical symmetry separates it into angular eigenfunctions and a radial equation. The quantum number ℓ enters the radial dynamics through an effective centrifugal term.

Nodes in hydrogenic orbitals

For hydrogenic orbitals, the number of radial nodes is

$$N_{\text{radial}} = n - \ell - 1, \quad (19.153)$$

and the usual real orbital basis has ℓ angular nodal surfaces. In that convention, radial plus angular nodal-surface counts add to $n - 1$. This geometric counting must not be applied without qualification to complex $Y_\ell^{m_\ell}$: their phase and zero sets can have a different representation. For example, the complex $m_\ell = \pm 1$ p states have no real nodal plane of the p_x or p_y type.

Examples are instructive:

Orbital	n	ℓ	radial nodes	angular nodes
$1s$	1	0	0	0
$2s$	2	0	1	0
$2p$	2	1	0	1
$3s$	3	0	2	0
$3p$	3	1	1	1
$3d$	3	2	0	2

A node is a zero of the wavefunction and probability density. Across a nodal surface a real orbital commonly changes sign; a complex wavefunction has phase rather than a simple positive/negative sign. The sign of the wavefunction matters for interference and matrix elements even though the position probability depends on $|\psi|^2$.

19.20.19 Hydrogen ground-state expectation values

The normalized hydrogen ground-state wavefunction is

$$\psi_{100}(r) = \frac{1}{\sqrt{\pi a_0^3}} e^{-r/a_0}.$$

Because it is spherically symmetric, radial expectation values use

$$\langle f(r) \rangle = 4\pi \int_0^\infty r^2 |\psi_{100}(r)|^2 f(r) dr. \quad (19.154)$$

For example,

$$\langle r \rangle = \frac{4}{a_0^3} \int_0^\infty r^3 e^{-2r/a_0} dr = \frac{3a_0}{2}, \quad (19.155)$$

$$\left\langle \frac{1}{r} \right\rangle = \frac{4}{a_0^3} \int_0^\infty r e^{-2r/a_0} dr = \frac{1}{a_0}. \quad (19.156)$$

The most probable radius, found earlier from the radial probability density, is a_0 , whereas the mean radius is $3a_0/2$. These are different statistical descriptors of the same distribution.

Using Eq. (19.156), the mean Coulomb potential energy is

$$\langle V \rangle = -\frac{e^2}{4\pi\epsilon_0 a_0}. \quad (19.157)$$

The virial theorem then gives $\langle T \rangle = -\langle V \rangle/2$ and reproduces the negative total ground-state energy.

Key message

A quantum state does not have one unique “radius.” The most probable radius, mean radius and root-mean-square radius are distinct quantities derived from the radial probability distribution.

The virial theorem as a consistency check for Coulomb binding

For a bound stationary state of a homogeneous potential proportional to r^k , with convergent expectation values and no additional hard-wall boundary term, the quantum virial theorem gives

$$2\langle T \rangle = k\langle V \rangle. \quad (19.158)$$

For the Coulomb potential $V \propto r^{-1}$, $k = -1$, so

$$2\langle T \rangle = -\langle V \rangle. \quad (19.159)$$

Consequently,

$$E = \langle T \rangle + \langle V \rangle = -\langle T \rangle = \frac{1}{2}\langle V \rangle. \quad (19.160)$$

The total energy is negative because the attractive potential contribution has twice the magnitude of the positive kinetic contribution.

This theorem is useful as a conceptual and computational check. If a numerical hydrogen-like calculation produces a supposedly converged bound state for which $2\langle T \rangle + \langle V \rangle$ is far from zero, something deserves investigation.

19.20.20 Reduced mass and the precision of the hydrogen energy scale

The finite-mass proton cannot be treated as immovable in a precision calculation. Separating centre-of-mass and relative coordinates gives a free centre-of-mass motion and an internal Coulomb problem. The relative-coordinate problem uses the reduced mass

$$\mu = \frac{m_e m_p}{m_e + m_p}. \quad (19.161)$$

Because μ is slightly smaller than m_e , the actual nonrelativistic hydrogen Rydberg energy is slightly smaller in magnitude than the value obtained with an infinitely heavy nucleus.

This correction also explains why hydrogen and deuterium have slightly different spectral wavelengths: replacing the proton by a deuteron changes the reduced mass. Such isotope shifts are experimentally measurable. A high-precision treatment additionally requires relativistic, spin and quantum-electrodynamic corrections, all beyond the scope of this chapter.

Caution

The familiar $-13.6 \text{ eV}/n^2$ formula is an excellent introductory result, not the complete precision spectrum of real hydrogen. State clearly which approximation is being used whenever sub-meV effects matter.

19.20.21 Degeneracy, symmetry and what can lift it

A degeneracy occurs when distinct quantum states share the same energy. In a cubic infinite box, permutations of (n_x, n_y, n_z) can produce the same sum $n_x^2 + n_y^2 + n_z^2$. In the ideal nonrelativistic Coulomb problem, the hydrogen energy in Eq. (19.55) depends only on n , producing a larger degeneracy among different ℓ and m_ℓ values.

Degeneracy is strongly connected to symmetry. If the symmetry is reduced, the degeneracy may be partially or completely lifted. Examples include:

- changing a cubic box into a rectangular box with unequal side lengths;
- applying an electric field, producing Stark shifts;
- applying a magnetic field, producing Zeeman shifts;
- including relativistic and spin-dependent corrections in atomic spectra.

A full calculation of these effects requires methods beyond this chapter, but the symmetry principle already gives useful qualitative predictions.

19.20.22 Transition matrix elements and qualitative selection rules

An atomic transition is not determined solely by energy conservation. In the electric-dipole approximation, the transition amplitude contains a matrix element of the position operator,

$$\mathbf{d}_{fi} = -e \langle f | \mathbf{r} | i \rangle = -e \int \psi_f^*(\mathbf{r}) \mathbf{r} \psi_i(\mathbf{r}) d^3r. \quad (19.162)$$

If symmetry makes this integral vanish, the electric-dipole transition is forbidden at that approximation level even when the photon energy matches $E_i - E_f$.

For hydrogenic states, the familiar electric-dipole rules are

$$\Delta \ell = \pm 1, \quad \Delta m_\ell = 0, \pm 1, \quad (19.163)$$

with additional restrictions when spin and total angular momentum are treated properly.

Parity gives an intuitive explanation of part of this result. The vector $\mathbf{r}$ is odd under spatial inversion. Therefore an electric-dipole matrix element can be nonzero only when the initial and final spatial states have opposite parity.

Guided checks

Energy conservation says whether a photon of a given frequency can match a level separation. A transition matrix element addresses a different question: how strongly the electromagnetic field couples those two states. Explain why these are logically separate requirements.

19.20.23 Lifetime, linewidth and the energy–time scale

Suppose an isolated upper state has an exponentially decaying survival probability $P(t) = e^{-t/\tau}$, and the lower level is sharp. The amplitude is proportional to $e^{-t/(2\tau)}e^{-iE_0t/\hbar}$ for $t \geq 0$. Its Fourier transform gives a Lorentzian energy profile,

$$I(E) \propto \frac{1}{(E - E_0)^2 + (\hbar/2\tau)^2}.$$

The full width at half maximum is consequently

$$\Gamma_E = \frac{\hbar}{\tau}, \quad \Gamma_f = \frac{1}{2\pi\tau}. \quad (19.164)$$

This is a linewidth for the stated exponential-decay model, not an energy standard deviation (an ideal Lorentzian has no finite variance). It is also not a universal operator uncertainty relation involving a time observable. Broadening of both levels, collisions, Doppler effects and the instrument response can change an observed line profile.

Example 19.32: Lifetime scale and natural width

If an excited state has lifetime $\tau = 10$ ns, then

$$\frac{\hbar}{\tau} = \frac{6.582 \times 10^{-16} \text{ eV s}}{10^{-8} \text{ s}} \approx 6.6 \times 10^{-8} \text{ eV}.$$

This is extremely narrow compared with an eV-scale transition energy. In many laboratory spectra, Doppler or instrumental broadening can therefore dominate the observed linewidth.

19.20.24 Extracting the Rydberg constant from measured line data

Suppose measured Balmer wavelengths λ_i correspond to upper quantum numbers $n_i = 3, 4, 5, \dots$. Write

$$y_i = \frac{1}{\lambda_i}, \quad x_i = \frac{1}{4} - \frac{1}{n_i^2}.$$

The ideal model is

$$y_i = R_H x_i. \quad (19.165)$$

With uncertainties σ_{y_i} , a weighted least-squares estimate minimizes

$$\chi^2(R_H) = \sum_i \frac{(y_i - R_H x_i)^2}{\sigma_{y_i}^2}. \quad (19.166)$$

The best-fit slope has the analytic form

for independent Gaussian y_i errors

$$\hat{R}_H = \frac{\sum_i x_i y_i / \sigma_{y_i}^2}{\sum_i x_i^2 / \sigma_{y_i}^2}. \quad (19.167)$$

This is a valuable bridge between introductory quantum physics and data analysis: a theoretical level formula becomes a fit model whose residuals can be inspected experimentally.

For small wavelength uncertainties, $\sigma_{y_i} \simeq \sigma_{\lambda_i}/\lambda_i^2$, and the fitted slope uncertainty is $\sigma_R = (\sum_i x_i^2/\sigma_{y_i}^2)^{-1/2}$ under the stated independent-error model. A shared wavelength calibration creates correlations; then use a covariance matrix C and $\hat{R} = (x^T C^{-1} y)/(x^T C^{-1} x)$, with variance $(x^T C^{-1} x)^{-1}$. More lines do not average away a common calibration offset. A fit to the rounded 13.6 eV model tests that approximation; extracting a precision physical R_H requires consistent vacuum wavelengths, reduced mass and resolved corrections.

A free-intercept fit,

$$y = a + Rx,$$

can be useful as a systematic diagnostic, but a should be physically consistent with zero in the ideal model. One should not automatically improve the theoretical model merely because an extra fit parameter lowers the residual sum.

19.20.25 Confinement from the uncertainty principle: an energy-scale estimate

The exact infinite-well spectrum comes from solving the Schrödinger equation, but the uncertainty principle already predicts the correct scale of the ground-state energy. If a particle is localized to a region of characteristic width L , then one expects

$$\Delta x \sim L, \quad \Delta p \gtrsim \frac{\hbar}{2L}.$$

A corresponding kinetic-energy scale is

$$E_{\text{kin}} \sim \frac{(\Delta p)^2}{2m} \sim \frac{\hbar^2}{8mL^2}. \quad (19.168)$$

The exact infinite-well ground energy is

$$E_1 = \frac{\pi^2 \hbar^2}{2mL^2},$$

which differs by a numerical factor but has precisely the same mass and length dependence.

This scaling argument is powerful because it does not depend on a square well. Any attempt to localize a quantum particle more tightly generally increases the momentum spread and therefore raises a kinetic-energy cost. The balance between this kinetic cost and attractive potential energy is central to the stability and size of bound systems.

Example 19.33: Why an atom is not arbitrarily small

As a crude scaling model, localize an electron within radius r around a proton. Estimate

$$T \sim \frac{\hbar^2}{2m_e r^2}, \quad V \sim -\frac{e^2}{4\pi\epsilon_0 r}.$$

The total scale is

$$E(r) \sim \frac{\hbar^2}{2m_e r^2} - \frac{e^2}{4\pi\epsilon_0 r}.$$

The kinetic term diverges as $1/r^2$ while the attractive Coulomb term grows only as $-1/r$. Minimizing the estimate gives a radius of the order of the Bohr radius. The argument is not a substitute for solving hydrogen, but it explains qualitatively why quantum kinetic energy prevents collapse to $r = 0$ in this nonrelativistic model.

19.20.26 Semiclassical intuition: when does a spectrum look nearly continuous?

For the one-dimensional infinite well,

$$E_n = n^2 E_1, \quad E_{n+1} - E_n = (2n + 1)E_1.$$

The absolute spacing grows with n , but the *relative* spacing behaves as

$$\frac{E_{n+1} - E_n}{E_n} = \frac{2n + 1}{n^2} \approx \frac{2}{n} \quad (n \gg 1). \quad (19.169)$$

Thus neighboring levels become close compared with the total energy at large quantum number. This is one manifestation of the correspondence principle: suitably coarse observations of highly excited quantum systems can approach classical behaviour.

A complementary position-space limit follows directly from the normalized box states:

$$P_n(a < x < b) = \frac{b - a}{L} - \frac{\sin(2n\pi b/L) - \sin(2n\pi a/L)}{2n\pi}.$$

For any fixed interval, the correction has magnitude at most $1/(n\pi)$ and vanishes as $n \rightarrow \infty$. Thus finite-resolution position measurements approach the uniform classical distribution of a particle moving at constant speed between reflecting walls. The oscillatory density itself does not converge pointwise to a constant; averaging is essential.

The same idea explains why quantization is conspicuous in nanometre structures but usually invisible for everyday macroscopic containers. Because confinement energies scale as $1/(mL^2)$, large masses and large dimensions make quantum spacings extraordinarily small.

19.20.27 Advanced synthesis: one set of ideas across several systems

The examples in this chapter can be organized by a common sequence:

System	Potential and symmetry	Mathematical selection mechanism	Physical consequence
Infinite well	hard boundaries	zeros of ψ at walls	exact discrete n^2 spectrum
Finite well	finite barriers, often parity	continuity of ψ and derivative	discrete bound states with leakage
Rectangular 2D/3D box	separable boundaries	independent quantum numbers	additive energies and degeneracies
Hydrogen	spherical Coulomb potential	normalizable radial and angular eigenfunctions	(n, ℓ, m_ℓ) quantum numbers and line spectra
Quantum well device	finite band offsets, effective mass	interface matching and confinement	subbands used in optoelectronics
Tunnel junction	finite barrier	evanescent wave matching	transmission exponentially sensitive to barrier

The table highlights a transferable problem-solving strategy: identify the potential, exploit symmetry, solve in each region, impose physical boundary conditions, normalize, interpret the eigenvalues and finally connect calculated quantities to measurements.

Take-home message

The unifying message of bound-state quantum mechanics is not a single formula. It is a modelling workflow: *potential* $\rightarrow$ *Schrödinger equation* $\rightarrow$ *boundary conditions* $\rightarrow$ *eigenstates* $\rightarrow$ *probabilities and observables* $\rightarrow$ *experiment or device behaviour*.

19.21 Original Practice Problems

The following problems are original exercises prepared for this chapter. Unless stated otherwise, use $m_e = 9.109 \times 10^{-31}$ kg, $h = 6.626 \times 10^{-34}$ J s, $\hbar = h/(2\pi)$, $1 \text{ eV} = 1.602 \times 10^{-19}$ J and $hc \approx 1240 \text{ eV nm}$. Show units and state modelling assumptions.

Conceptual questions

- C1. Explain why the wavefunction itself is not a probability density. Give one physical consequence of the fact that ψ can be negative or complex while $|\psi|^2$ cannot.
- C2. A student says, “The electron in an infinite well is at rest in the ground state because its probability density does not change with time.” Identify the error in this reasoning.
- C3. Why is $n = 0$ excluded from the infinite-well spectrum? Answer both mathematically and physically.
- C4. A finite-well wavefunction extends into a region in which $E < V$. Why does this not violate energy conservation?
- C5. Distinguish *penetration into a finite barrier* from *transmission through a finite barrier*.
- C6. What is meant by degeneracy? Give one example from a cubic box and one from ideal nonrelativistic hydrogen.
- C7. Explain why the Bohr model should not be presented as an electron moving on a literally known circular path in modern quantum mechanics.
- C8. In hydrogen, what is the physical meaning of a negative bound-state energy when the zero of potential energy is chosen at infinite separation?
- C9. Energy conservation fixes the photon frequency for an ideal transition. Why does it not, by itself, determine the transition probability?
- C10. A numerical solver returns ten eigenvalues to twelve decimal places. List at least four checks required before trusting those digits physically.

Analytical problems

- A1. Starting from the boundary conditions $\psi(0) = \psi(L) = 0$, derive the allowed wave numbers and energy levels for a one-dimensional infinite square well.
- A2. For the ground state of a one-dimensional infinite well, derive an exact expression for the probability of finding the particle in the interval $0 < x < L/4$.
- A3. Show directly that ψ_1 and ψ_2 of the infinite well are orthogonal.
- A4. For an infinite well, derive $E_{n+1} - E_n = (2n + 1)E_1$ and show that the relative spacing approaches $2/n$ at large n .
- A5. Derive $\langle x \rangle = L/2$ for any infinite-well stationary state using symmetry. Then verify it explicitly for $n = 1$.
- A6. Starting from ψ_n , derive $\langle p_x^2 \rangle = (n\pi\hbar/L)^2$ without evaluating a Fourier transform.
- A7. A normalized state is $\Psi = (\sqrt{3}/2)\psi_1 + (1/2)\psi_3$. Find the possible measured energies, their probabilities and $\langle E \rangle$.

- A8.** For the state in the previous problem, write $\Psi(x, t)$ and identify the angular frequency of the interference term in $|\Psi|^2$.
- A9.** Show that a finite-well bound-state tail of the form $Ae^{-\kappa x}$ has a probability density that decays with characteristic length $1/(2\kappa)$, while the amplitude decays with characteristic length $1/\kappa$.
- A10.** In a two-dimensional square box of side L , list all states with $n_x^2 + n_y^2 \leq 10$ and identify degeneracies.
- A11.** Show that the ground-state hydrogen radial probability density is proportional to $r^2 e^{-2r/a_0}$ and find the radius at which it is maximal.
- A12.** Use the Coulomb virial theorem to express $\langle T \rangle$ and $\langle V \rangle$ in terms of the total bound-state energy E .

Numerical and computational problems

- N1.** Calculate the first four energy levels of an electron in a 2.00 nm infinite well. Express the answers in eV.
- N2.** An electron is in the $n = 3$ state of a 0.80 nm infinite well. Calculate the vacuum wavelengths associated with the gaps to $n = 2$ and $n = 1$. Use parity to decide which transition is electric-dipole allowed in the ideal symmetric well; do not infer emission from an energy difference alone.
- N3.** An electron with $E = 1.50$ eV encounters a region with $V_0 = 5.00$ eV. Calculate κ and the amplitude penetration length $1/\kappa$.
- N4.** For the barrier in the previous problem, compare the exponential tunnelling factors $e^{-2\kappa d}$ for $d = 0.30$ nm and $d = 0.50$ nm. Report their ratio.
- N5.** Use Eq. (19.119) to compute the exact rectangular-barrier transmission for an electron with $E = 2.00$ eV, $V_0 = 6.00$ eV and $d = 0.40$ nm. Compare with the thick-barrier approximation.
- N6.** Calculate the four lowest distinct energy values and associated degeneracies for an electron in a cubic 4.00 nm box.
- N7.** An electron is confined in a 2D rectangular box with $L_x = 3.00$ nm and $L_y = 5.00$ nm. Compute E_{11} , E_{12} , E_{21} and E_{22} and order them.
- N8.** Write a short program that constructs the tridiagonal finite-difference Hamiltonian for an infinite well. Demonstrate convergence of the lowest three energies as N is increased.
- N9.** Modify the program in the previous problem to solve a symmetric finite well. Plot the potential, the lowest bound-state energies and wavefunctions. Compare with the infinite-well limit as V_0 is increased.
- N10.** Use a numerical root finder to solve the even and odd transcendental equations for the 1.00 nm, 5.00 eV finite well discussed in Example 19.27. Reproduce the stated eigenvalues to at least three significant figures.

Engineering and applied-science problems

- E1.** A simplified semiconductor quantum well has effective electron mass $m^* = 0.067m_e$ and width $L = 10.0$ nm. Estimate its infinite-well confinement energies E_1 and E_2 . Why does the small effective mass matter?

- E2.** A quantum-dot model uses a cubic box of side 6.0 nm with $m^* = 0.10m_e$. Estimate the ground confinement energy E_{111} relative to the bottom of the well.
- E3.** In a tunnel sensor, the current changes by a factor of 5 for a small displacement. Assuming $I \propto e^{-2\kappa d}$ with $\kappa = 10 \text{ nm}^{-1}$, estimate the displacement magnitude.
- E4.** An STM feedback controller maintains constant current while scanning. If the local barrier height decreases but geometric height is unchanged, in which direction must the tip move to restore the original current in the simple model? Explain.
- E5.** A finite quantum well is made shallower while its width and effective mass remain fixed. Predict qualitatively how the number of bound states and the penetration depth change.
- E6.** A heterostructure model uses a discontinuous effective mass. Explain why simply imposing continuity of ψ' may be inconsistent with Eq. (19.127).
- E7.** A finite-difference solver agrees with the analytic infinite-well ground energy to 0.02% but disagrees with an experimental quantum-well transition by 8%. Give at least four modelling effects that might explain the discrepancy without blaming the eigensolver.
- E8. Synthetic spectroscopy.** An ideal calibration has $\lambda = 400.0 \text{ nm} + (0.5000 \text{ nm/pixel})p$. A synthetic hydrogen peak is at $p = 173.0 \pm 0.4$ pixels, with an independent calibration uncertainty 0.10 nm. Find the wavelength, its combined standard uncertainty, and the photon energy. Compare with the rounded-model $4 \rightarrow 2$ prediction 486.21 nm using a normalized residual. Assume all wavelengths are in vacuum.
- E9. Photoionization from a finite well.** For the 1.00 nm, 5.00 eV finite well, take $E_1 = 0.2718 \text{ eV}$ relative to its bottom. Find the minimum photon energy for escape and the longest threshold wavelength. If a 200 nm photon is absorbed into a continuum state, find the asymptotic kinetic energy. Neglect recoil and assume a nonzero absorption matrix element.
- E10. Uncertainty in a confinement design.** For $E_1 \propto (m^*L^2)^{-1}$, derive the fractional change in E_1 for small signed changes in m^* and L . Then propagate independent standard uncertainties of 3% in m^* and 1% in L . Compare the physical uncertainty with a numerical discretization error of 0.02%.

Challenge problems for strong students

- H1.** A particle in an infinite well is prepared in $\Psi(x, 0) = A[\psi_1(x) + i\psi_2(x)]$. Find A , the energy probabilities, $\langle E \rangle$, and the time-dependent probability density. Identify the interference term explicitly.
- H2.** For the same state, determine whether $\langle x \rangle$ is time dependent. Set up the required matrix element and evaluate it.
- H3.** Derive the one-dimensional infinite-well uncertainty product in Eq. (19.99) from first principles.
- H4.** For a centred symmetric finite well, explain graphically why deeper or wider wells support more bound states. Use the dimensionless parameter z_0 to organize your argument.
- H5.** Derive the 2D density of states for a parabolic band by counting k -states in a large square with periodic boundary conditions. State where spin degeneracy enters.
- H6.** For hydrogen, use the explicit ground-state wavefunction to calculate $\langle r \rangle$ and compare it with the most probable radius.

- H7.** Use parity to determine whether the position matrix element $\langle m|x|n \rangle$ in a centred infinite well can be nonzero when the two states have the same parity. Connect the result to qualitative selection rules.
- H8.** Construct a numerical double-well potential and investigate how the splitting between the two lowest energies depends on barrier width. Test whether the splitting is approximately exponential over a useful parameter range.

19.22 Selected Solutions to Representative Problems

The purpose of these selected solutions is to model professional reasoning and checking, not to replace independent work on the full problem set.

Solution to C2: stationary density does not mean zero kinetic energy

The statement confuses time independence of the probability density with absence of motion or momentum content. In the ground state,

$$\Psi_1(x, t) = \psi_1(x)e^{-iE_1 t/\hbar},$$

so $|\Psi_1|^2 = |\psi_1|^2$ is time independent. However,

$$\langle p \rangle = 0, \quad \langle p^2 \rangle = \left(\frac{\pi \hbar}{L} \right)^2,$$

and therefore

$$\langle T \rangle = \frac{\langle p^2 \rangle}{2m} = E_1 > 0.$$

A stationary state means a state with a time-independent probability distribution and definite energy, not a classical particle sitting motionless at one point.

Solution to A2: ground-state probability in the left quarter

For $n = 1$,

$$P\left(0 < x < \frac{L}{4}\right) = \frac{2}{L} \int_0^{L/4} \sin^2\left(\frac{\pi x}{L}\right) dx.$$

Using $\sin^2 u = (1 - \cos 2u)/2$,

$$\begin{aligned} P &= \left[\frac{x}{L} - \frac{1}{2\pi} \sin\left(\frac{2\pi x}{L}\right) \right]_0^{L/4} \\ &= \frac{1}{4} - \frac{1}{2\pi}. \end{aligned}$$

Thus

$$\boxed{P \approx 0.0908.}$$

The small value is physically reasonable because the ground-state density peaks at the centre and vanishes at the wall.

Solution to A7: energy probabilities in a superposition

The state

$$\Psi = \frac{\sqrt{3}}{2}\psi_1 + \frac{1}{2}\psi_3$$

is normalized because $3/4 + 1/4 = 1$. Therefore

$$P(E_1) = \frac{3}{4}, \quad P(E_3) = \frac{1}{4}.$$

Since $E_3 = 9E_1$,

$$\langle E \rangle = \frac{3}{4}E_1 + \frac{1}{4}(9E_1) = 3E_1.$$

The mean value $3E_1$ is not one of the two possible outcomes. Repeated energy measurements on identically prepared systems return either E_1 or E_3 with the probabilities above.

Solution to A11: most probable radius in hydrogen ground state

For the hydrogen ground state,

$$|\psi_{100}|^2 = \frac{1}{\pi a_0^3} e^{-2r/a_0}.$$

The probability in a spherical shell of radius r and thickness dr is proportional to

$$P_r(r)dr \propto 4\pi r^2 |\psi_{100}|^2 dr,$$

so the radial density is proportional to

$$f(r) = r^2 e^{-2r/a_0}.$$

Differentiate:

$$f'(r) = e^{-2r/a_0} \left(2r - \frac{2r^2}{a_0} \right) = 2r e^{-2r/a_0} \left(1 - \frac{r}{a_0} \right).$$

The nonzero maximum occurs at

$$r = a_0.$$

This is the most probable *radius*, not a fixed orbital radius followed by an electron trajectory.

Solution to N1: four levels in a 2.00 nm electron well

For an electron,

$$E_1 = \frac{h^2}{8m_e L^2}.$$

With $L = 2.00$ nm,

$$E_1 \approx 0.0940 \text{ eV}.$$

Therefore

$$E_1 = 0.0940 \text{ eV}, \quad E_2 = 0.376 \text{ eV}, \quad E_3 = 0.846 \text{ eV}, \quad E_4 = 1.504 \text{ eV}.$$

The n^2 pattern is immediately visible. Compared with a 1 nm well, all energies are smaller by a factor of four.

Solution to N2: energy gaps and selection rules for the $n = 3$ state

For a 0.80 nm electron well,

$$E_1 = 0.376 \text{ eV} \left(\frac{1.00}{0.80} \right)^2 \approx 0.5875 \text{ eV}.$$

The $3 \rightarrow 2$ energy difference is

$$\Delta E_{32} = (9 - 4)E_1 = 5E_1 \approx 2.94 \text{ eV},$$

so

$$\lambda_{32} \approx \frac{1240}{2.94} \text{ nm} \approx 422 \text{ nm}.$$

For $3 \rightarrow 1$,

$$\Delta E_{31} = 8E_1 \approx 4.70 \text{ eV},$$

and

$$\lambda_{31} \approx 264 \text{ nm.}$$

The $3 \rightarrow 1$ gap corresponds to the larger photon energy, but the direct electric-dipole transition is forbidden: states 3 and 1 have the same parity. The $3 \rightarrow 2$ transition is electric-dipole allowed. The 264 nm value is therefore an energy-gap wavelength, not a predicted strong emission line.

Solution to N5: exact and asymptotic barrier transmission

For $E = 2.00 \text{ eV}$ and $V_0 = 6.00 \text{ eV}$,

$$V_0 - E = 4.00 \text{ eV}, \quad \kappa \approx 10.25 \text{ nm}^{-1}.$$

With $d = 0.40 \text{ nm}$,

$$\kappa d \approx 4.10.$$

The exact rectangular-barrier expression gives

$$T \approx 9.790 \times 10^{-4}.$$

The thick-barrier approximation gives

$$T_{\text{approx}} \approx 9.794 \times 10^{-4}.$$

The close agreement is expected because κd is already substantially larger than unity.

Solution to N6: the first four distinct energy groups in a cubic 4.00 nm box

For a cube,

$$E = E_0(n_x^2 + n_y^2 + n_z^2), \quad E_0 = \frac{h^2}{8m_e L^2}.$$

At $L = 4.00 \text{ nm}$,

$$E_0 \approx 0.02350 \text{ eV}.$$

The lowest sums and degeneracies are

S	representative state	E (eV)	g
3	(1, 1, 1)	0.0705	1
6	(1, 1, 2)	0.1410	3
9	(1, 2, 2)	0.2115	3
11	(1, 1, 3)	0.2585	3

The factor of three occurs because the unequal quantum number can occupy any one of the three Cartesian directions.

Solution to E1: effective-mass quantum well

The infinite-well energy scales as $1/m^*$. For $m^* = 0.067m_e$ and $L = 10.0 \text{ nm}$,

$$E_1 = \frac{h^2}{8m^* L^2} \approx 0.0561 \text{ eV},$$

so

$$E_1 \approx 56.1 \text{ meV}, \quad E_2 \approx 224 \text{ meV}.$$

The small effective mass raises the confinement energies relative to a free-electron-mass estimate by the factor $m_e/m^* \approx 14.9$.

Solution to E3: displacement inferred from tunnel-current change

With

$$I \propto e^{-2\kappa d},$$

a factor of five corresponds to

$$5 = e^{2\kappa|\Delta d|}.$$

Therefore

$$|\Delta d| = \frac{\ln 5}{2\kappa} = \frac{1.609}{20 \text{ nm}^{-1}} \approx 0.0805 \text{ nm}.$$

Thus

$$|\Delta d| \approx 8.1 \times 10^{-2} \text{ nm}.$$

The result illustrates why tunnelling can serve as an extremely sensitive displacement transducer.

Solution to E5: making a finite well shallower

Reducing the well depth while holding width and mass fixed has several consequences:

1. the dimensionless depth parameter $z_0 \propto \sqrt{V_0}$ decreases;
2. the number of bound-state intersections in the matching equations decreases or stays the same, never increases;
3. each surviving bound state moves *downward* relative to the fixed zero at the well bottom;
4. the difference $V_0 - E$ for a near-threshold state becomes smaller, so $\kappa = \sqrt{2m(V_0 - E)}/\hbar$ decreases;
5. therefore the evanescent tail penetrates farther into the barrier.

A sufficiently shallow well may support only one bound state in one dimension.

A sharper check is the Hellmann–Feynman relation for this fixed-bottom convention:

$$\frac{dE_n}{dV_0} = \int_{|x|>a} |\psi_n|^2 dx = P_{\text{out}}, \quad 0 < P_{\text{out}} < 1.$$

Thus lowering V_0 lowers E_n , and $d(V_0 - E_n)/dV_0 = 1 - P_{\text{out}} > 0$ shows that the binding relative to the threshold decreases as well. A claimed upward energy shift relative to the bottom would contradict this result.

Solution to H1: complex two-state superposition

The state is

$$\Psi(x, 0) = A[\psi_1(x) + i\psi_2(x)].$$

Orthogonality gives

$$1 = |A|^2(1 + 1),$$

so choose

$$A = \frac{1}{\sqrt{2}}.$$

The energy probabilities are 1/2 for E_1 and 1/2 for E_2 , hence

$$\langle E \rangle = \frac{1}{2}(E_1 + E_2) = \frac{5}{2}E_1.$$

The time-dependent state is

$$\Psi(x, t) = \frac{1}{\sqrt{2}} \left[\psi_1(x) e^{-iE_1 t/\hbar} + i\psi_2(x) e^{-iE_2 t/\hbar} \right].$$

For real box eigenfunctions,

$$|\Psi|^2 = \frac{1}{2} \psi_1^2 + \frac{1}{2} \psi_2^2 + \psi_1 \psi_2 \sin\left(\frac{E_2 - E_1}{\hbar} t\right).$$

The cross term oscillates with angular frequency $(E_2 - E_1)/\hbar$. At $t = 0$ it vanishes because of the relative phase i .

Challenge solution H2: time-dependent mean position in a two-state superposition

For H1,

$$\Psi(x, t) = \frac{1}{\sqrt{2}} \left[\psi_1(x) e^{-iE_1 t/\hbar} + i\psi_2(x) e^{-iE_2 t/\hbar} \right].$$

The expectation value is

$$\langle x \rangle = \int_0^L \Psi^* x \Psi dx.$$

The diagonal terms contribute

$$\frac{1}{2} \langle 1|x|1 \rangle + \frac{1}{2} \langle 2|x|2 \rangle = \frac{1}{2} \frac{L}{2} + \frac{1}{2} \frac{L}{2} = \frac{L}{2}.$$

The off-diagonal matrix element is

$$\begin{aligned} x_{12} &= \frac{2}{L} \int_0^L x \sin\left(\frac{\pi x}{L}\right) \sin\left(\frac{2\pi x}{L}\right) dx \\ &= -\frac{16L}{9\pi^2}. \end{aligned}$$

Let $\omega_{21} = (E_2 - E_1)/\hbar$. The cross terms produce

$$2 \operatorname{Re} \left[\frac{i}{2} e^{-i\omega_{21} t} x_{12} \right] = x_{12} \sin(\omega_{21} t).$$

Therefore

$$\boxed{\langle x \rangle(t) = \frac{L}{2} - \frac{16L}{9\pi^2} \sin(\omega_{21} t).} \quad (19.170)$$

The mean position oscillates even though neither individual stationary state has a time-dependent density. The motion of the expectation value is created by interference between the two energy components.

The amplitude of the oscillation is

$$\frac{16L}{9\pi^2} \approx 0.180L,$$

so the mean position always remains inside the well. The example is an elementary demonstration that time-dependent quantum motion can arise entirely from relative phase evolution.

Solution to H7: parity and a position matrix element

In a centred well, suppose $|m\rangle$ and $|n\rangle$ have the same parity. Their product $\psi_m^* \psi_n$ is even. Because x is odd, the full integrand

$$\psi_m^*(x) x \psi_n(x)$$

is odd. Its integral over the symmetric interval $[-L/2, L/2]$ therefore vanishes:

$$\boxed{\langle m|x|n \rangle = 0 \quad \text{for states of the same parity.}}$$

A nonzero electric-dipole position matrix element requires opposite spatial parity in this simple setting. This is a necessary condition; the remaining integral must still be checked. This is the same symmetry logic that underlies electric-dipole selection rules in atoms.

Solution to E8: synthetic spectroscopy and uncertainty

The calibrated wavelength is $400.0 + 0.5000(173.0) = 486.50 \text{ nm}$. Pixel fitting contributes $0.5000(0.4) = 0.20 \text{ nm}$, so independent standard uncertainties combine as

$$\sigma_\lambda = \sqrt{(0.20)^2 + (0.10)^2} \text{ nm} = 0.224 \text{ nm}.$$

Thus $E_\gamma = 1239.84/486.50 = 2.5485 \text{ eV}$ and $\sigma_E = E_\gamma \sigma_\lambda / \lambda \simeq 0.00117 \text{ eV}$. Report approximately $2.5485 \pm 0.0012 \text{ eV}$. Against the specified rounded model, the normalized residual is $(486.50 - 486.21)/0.224 = 1.30$. This is a modest residual in the assumed error model, not evidence of a failure of quantum theory. The numbers are synthetic; they are not an experimental determination of a hydrogen constant. A precision interpretation would also include uncertainty or discrepancy in the physical model.

19.23 Bridge to the Next Modern-Physics Chapter

This chapter established how quantum boundary conditions generate discrete bound states and how the Coulomb potential leads to hydrogenic quantum numbers and line spectra. Chapter 20, *Atomic Physics and Lasers*, develops spin, exclusion, real atoms and stimulated emission. Chapter 21, *Electrical Conduction in Solids*, develops the band and carrier physics previewed here.

The conceptual bridge is direct. The single-particle Schrödinger equation provides a basis of states; transitions connect those states through electromagnetic interactions; multiple electrons introduce additional quantum numbers, spin and the Pauli principle; many atoms brought together produce molecules and solids, where overlapping states develop into bands. Thus the bound-state language developed here is not an isolated topic. It is the mathematical foundation for much of atomic, molecular, optical and condensed-matter physics.

Chapter A

Notation Dictionary

Symbol	Meaning	Typical unit
$\psi(x)$	one-dimensional stationary-state wavefunction	$\text{m}^{-1/2}$
$\Psi(\mathbf{r}, t)$	time-dependent wavefunction	$\text{m}^{-3/2}$ in 3D
$ \psi ^2$	position probability density in 1D	m^{-1}
E	total energy eigenvalue	J or eV
V	potential energy	J or eV
m	particle mass	kg
m^*	effective mass in a material model	kg or multiple of m_e
μ	reduced mass	kg
h	Planck constant	J s
$\hbar$	reduced Planck constant, $h/(2\pi)$	J s
k	wave number in an oscillatory region	m^{-1}
κ	evanescent decay constant	m^{-1}
L (box)	well or box width	m
L (angular)	magnitude of orbital angular momentum	J s
a	finite-well half-width	m
a_0	Bohr radius	m
n	principal or one-dimensional quantum number	dimensionless
n_x, n_y, n_z	rectangular-box quantum numbers	dimensionless
ℓ	orbital angular-momentum quantum number	dimensionless
m_ℓ	magnetic quantum number	dimensionless
$Y_\ell^{m_\ell}$	spherical harmonic	dimensionless
$R_{n\ell}(r)$	radial factor with $\int Y_\ell^{m_\ell} ^2 d\Omega = 1$	$\text{m}^{-3/2}$
$u(r)$	reduced radial function, $u = rR$, normalized by $\int u ^2 dr = 1$	$\text{m}^{-1/2}$
T	barrier transmission probability	dimensionless
P	probability	dimensionless
$P(r)$	radial probability density, integrated with dr	m^{-1}
$\hat{H}$	Hamiltonian operator	energy operator
$\langle A \rangle$	expectation value of observable A	unit of A
ΔA	standard deviation/uncertainty of A	unit of A

Chapter B

Compact Formula Sheet

All Schrödinger models below are nonrelativistic and single-particle or relative-coordinate models. Infinite boxes have hard walls and a zero interior potential. Finite-well formulas use the same constant mass on both sides unless stated otherwise. Hydrogen's 13.6 eV coefficient is rounded; transition wavelengths are in vacuum, with recoil neglected. Transmission scaling requires $\kappa d \gg 1$ and is not an exact coefficient.

Formula summary

Probability and normalization

$$\begin{aligned}\int |\psi(x)|^2 dx &= 1, \\ P(a < x < b) &= \int_a^b |\psi(x)|^2 dx, \\ \langle A \rangle &= \int \psi^* \hat{A} \psi dx.\end{aligned}$$

Schrödinger equation

$$\begin{aligned}-\frac{\hbar^2}{2m} \frac{d^2 \psi}{dx^2} + V\psi &= E\psi, \\ \left[-\frac{\hbar^2}{2m} \nabla^2 + V(\mathbf{r}) \right] \psi &= E\psi.\end{aligned}$$

One-dimensional infinite well, $0 < x < L$

$$\begin{aligned}\psi_n(x) &= \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right), \\ E_n &= \frac{n^2 \hbar^2}{8mL^2} = \frac{n^2 \pi^2 \hbar^2}{2mL^2}.\end{aligned}$$

Finite barrier and well

$$\begin{aligned}k &= \frac{\sqrt{2mE}}{\hbar}, \\ \kappa &= \frac{\sqrt{2m(V_0 - E)}}{\hbar}, \\ T_{\text{thick}} &\propto e^{-2\kappa d}.\end{aligned}$$

Rectangular boxes

$$\begin{aligned}E_{n_x n_y} &= \frac{\hbar^2}{8m} \left(\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} \right), \\ E_{n_x n_y n_z} &= \frac{\hbar^2}{8m} \left(\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} + \frac{n_z^2}{L_z^2} \right).\end{aligned}$$

Hydrogen

$$\begin{aligned}V(r) &= -\frac{e^2}{4\pi\epsilon_0 r}, \\E_n &\approx -\frac{13.6 \text{ eV}}{n^2}, \\ \ell &= 0, 1, \dots, n-1, \\ m_\ell &= -\ell, \dots, +\ell, \\ L &= \sqrt{\ell(\ell+1)}\hbar, \\ L_z &= m_\ell\hbar.\end{aligned}$$

Transitions

$$\begin{aligned}E_\gamma &= |E_i - E_f| = hf = \frac{hc}{\lambda}, \\ \frac{1}{\lambda} &= R_H \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right) \quad (n_i > n_f).\end{aligned}$$

Chapter C

Useful Constants and Unit Conversions

Quantity	Symbol	Value
Planck constant	h	$6.62607015 \times 10^{-34} \text{ J s}$
Reduced Planck constant	$\hbar$	$1.054571817 \times 10^{-34} \text{ J s}$
Electron mass	m_e	$9.1093837 \times 10^{-31} \text{ kg}$
Proton mass	m_p	$1.6726219 \times 10^{-27} \text{ kg}$
Elementary charge	e	$1.602176634 \times 10^{-19} \text{ C}$
Vacuum permittivity	ε_0	$8.8541878 \times 10^{-12} \text{ F m}^{-1}$
Speed of light	c	$2.99792458 \times 10^8 \text{ m s}^{-1}$
Energy conversion	1 eV	$1.602176634 \times 10^{-19} \text{ J}$
Photon conversion	hc	1239.84 eV nm
Bohr radius	a_0	$5.29177 \times 10^{-11} \text{ m}$

The SI values of h , e and c are exact; the other displayed numerical values are rounded. For classroom calculations, retain enough digits internally and round the final result to the stated input precision.

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