The quantum view of the world 2

Electrons and waves

Modern physics for engineers

David Miller

De Broglie’s hypothesis

De Broglie's hypothesis

In 1924, Louis de Broglie proposed that

a particle with mass

also behaves as a wave with wavelength λ

now of the particle, not of electromagnetic waves

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

where p is the particle's momentum

which can fit with Bohr's orbital idea

Matrices and waves

Following from the successful but *ad hoc* Bohr model

and de Broglie's hypothesis

can we construct a solid mathematical approach?

Matrices and waves

Werner Heisenberg (1925)

- matrix formulation of quantum mechanics

Erwin Schrödinger (1926)

- wave equation

More key contributions by

- Max Born, Wolfgang Pauli, Paul Dirac, John von Neumann, …

Schrödinger’s wave equation

Schrödinger’s equation

The next step in quantum mechanics

- Schrödinger’s equation
  - solves the hydrogen atom
    - giving us the basis of chemical elements
      - and starting the rest of the quantum mechanics of materials

How do we get to Schrödinger’s equation?

Electrons as waves

de Broglie's hypothesis is that the electron wavelength λ is given by

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

where p is the electron momentum and

h is Planck's constant

$$h = 6.62606957 \times 10^{-34}\ J\ s$$

Now we want to use this to help construct a wave equation

A Helmholtz wave equation

If we are considering only waves of one wavelength λ for the moment

i.e., monochromatic waves

we can choose a Helmholtz wave equation

$$\frac{d^2\psi}{dz^2} = -k^2\psi \quad \text{with} \quad k = \frac{2\pi}{\lambda}$$

which we know works for simple waves

with solutions like

$\sin(kz)$, $\cos(kz)$, and $\exp(ikz)$

(and $\sin(-kz)$, $\cos(-kz)$, and $\exp(-ikz)$)

Use and notation for complex exponentials

We will need to use the complex exponential more in quantum mechanics

and we will use both notations $\exp(i\theta) \equiv e^{i\theta}$

We will also use the scientific notation $i \equiv \sqrt{-1}$

rather than the j more common in engineering

We remember Euler's formula

which here would give, for example

$$\exp(ikz) = \cos kz + i \sin kz$$

A Helmholtz wave equation

In three dimensions, we can write this as

$$\nabla^2\psi \equiv \frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2} = -k^2\psi$$

which has solutions like

$\sin(\mathbf{k}\cdot\mathbf{r})$, $\cos(\mathbf{k}\cdot\mathbf{r})$, and $\exp(i\mathbf{k}\cdot\mathbf{r})$

(and $\sin(-\mathbf{k}\cdot\mathbf{r})$, $\cos(-\mathbf{k}\cdot\mathbf{r})$, and $\exp(-i\mathbf{k}\cdot\mathbf{r})$)

where $\mathbf{k}$ and $\mathbf{r}$ are vectors

From Helmholtz to Schrödinger

With de Broglie's hypothesis $\lambda = h / p$

and the definition $k = 2\pi / \lambda$

then $k = 2\pi p / h = p / \hbar$

where we have defined $\hbar \equiv h / 2\pi$

so $k^2 = p^2 / \hbar^2$

Hence we can rewrite our Helmholtz equation

$$\nabla^2 \psi = -\frac{p^2}{\hbar^2} \psi$$

or

$$-\hbar^2 \nabla^2 \psi = p^2 \psi$$

From Helmholtz to Schrödinger

For some particle of mass m (e.g., an electron)

we can divide both sides by the particle mass m

$$-\frac{\hbar^2}{2m}\nabla^2\psi = \frac{p^2}{2m}\psi$$

But we know from classical mechanics that

$$\frac{p^2}{2m} \equiv \text{kinetic energy of the particle}$$

and in general

Total energy (E)=Kinetic energy + Potential energy ($V(\mathbf{r})$)

From Helmholtz to Schrödinger

So Kinetic energy = $p^2/2m$

= Total energy (E) - Potential energy ($V(\mathbf{r})$)

Hence our Helmholtz equation $$-\frac{\hbar^2}{2m}\nabla^2\psi = \frac{p^2}{2m}\psi$$

becomes the Schrödinger equation $$-\frac{\hbar^2}{2m}\nabla^2\psi = \left(E - V(\mathbf{r})\right)\psi$$

or equivalently

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

Schrödinger's time-independent equation

We can postulate a Schrödinger equation for any particle of mass m

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

Formally, this is the

time-independent Schrödinger equation

Schrödinger’s time-independent equation

- Note that we have not “derived” Schrödinger’s equation
  - We suggested it as an equation that agrees with at least one experiment
- There is no way to derive Schrödinger’s equation from first principles
  - Schrödinger’s equation has to be postulated
    - The <u>only</u> justification for making such a postulate is that it works!
- But what does the “wave” mean?

Probability densities

Born's postulate is that

the probability $P(\mathbf{r})$ of finding an electron near any specific point $\mathbf{r}$ in space

is proportional to the modulus squared $|\psi(\mathbf{r})|^2$ of the wave amplitude $\psi(\mathbf{r})$

$|\psi(\mathbf{r})|^2$ can therefore be viewed as a

"probability density"

with $\psi(\mathbf{r})$ called a "probability amplitude"

or a "quantum mechanical amplitude"

Electron waves and diffraction

Electron waves and diffraction

- de Broglie's hypothesis and Schrödinger's wave equation
  - were proposed before any evidence of electron waves
- In 1927, diffraction experiments with electrons
  - from nickel by Clinton Davisson and Lester Germer
  - and with gold films by George Thomson
    - showed clear wave behavior

Electron waves and diffraction

Diffraction of electrons by crystal surfaces

is a routine diagnostic technique today

Electron microscopes use the short wavelengths of accelerated electrons

down even to the size scales of atoms themselves

Electron wave phenomena

also expose many of the conceptual aspects of quantum mechanics

such as the uncertainty principle

and the measurement problem

The quantum view of the world 2

Solving Schrödinger’s equation – a particle in a box

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Particle in a box

We consider a particle of mass m

with a spatially-varying potential $V(z)$ in the z direction

so we have a Schrödinger equation

$$-\frac{\hbar^2}{2m}\frac{d^2\psi(z)}{dz^2}+V(z)\psi(z)=E\psi(z)$$

where E is the energy of the particle

and $\psi(z)$ is the wavefunction

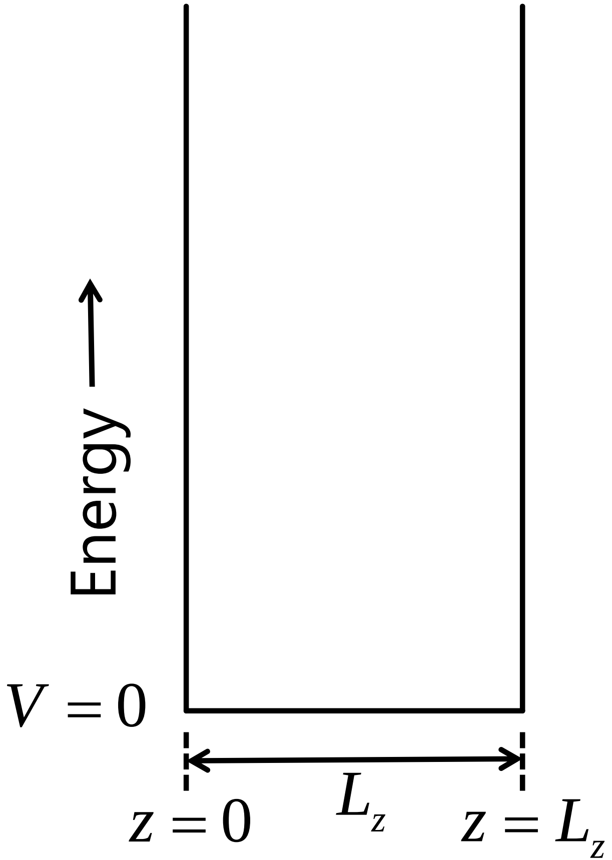
Particle in a box

Suppose the potential energy is a simple "rectangular" potential well

- thickness L_z
- Potential energy is constant inside
  - we choose $V = 0$ there
- rising to infinity at the walls
  - i.e., at $z = 0$ and $z = L_z$

We will sometimes call this

- an infinite or infinitely deep (potential) well



Particle in a box

Because these potentials at $z = 0$ and at $z = L_z$ are infinitely high

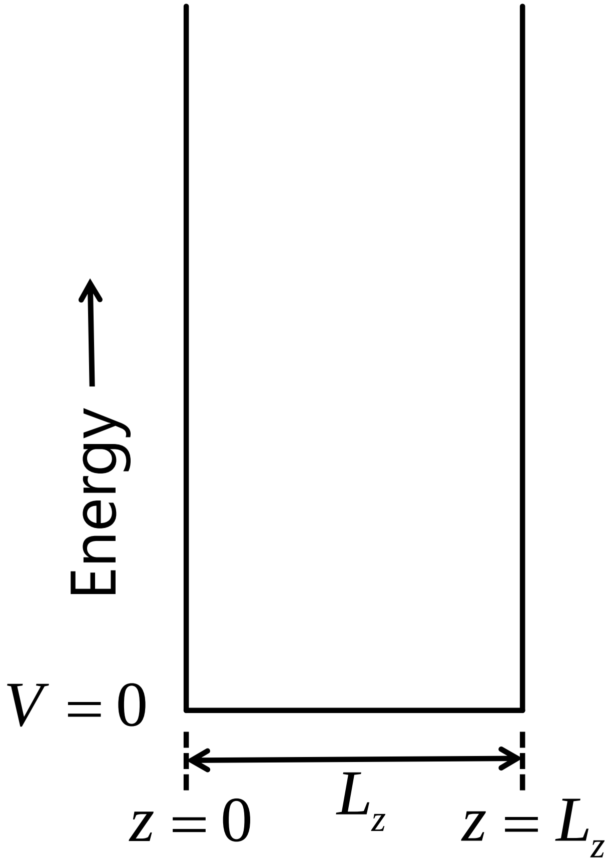
but the particle's energy E is presumably finite

we presume there is no possibility of finding the particle outside

i.e., for $z < 0$ or $z > L_z$

so the wavefunction ψ is 0 there

so ψ should be 0 at the walls



Particle in a box

With these choices

inside the well

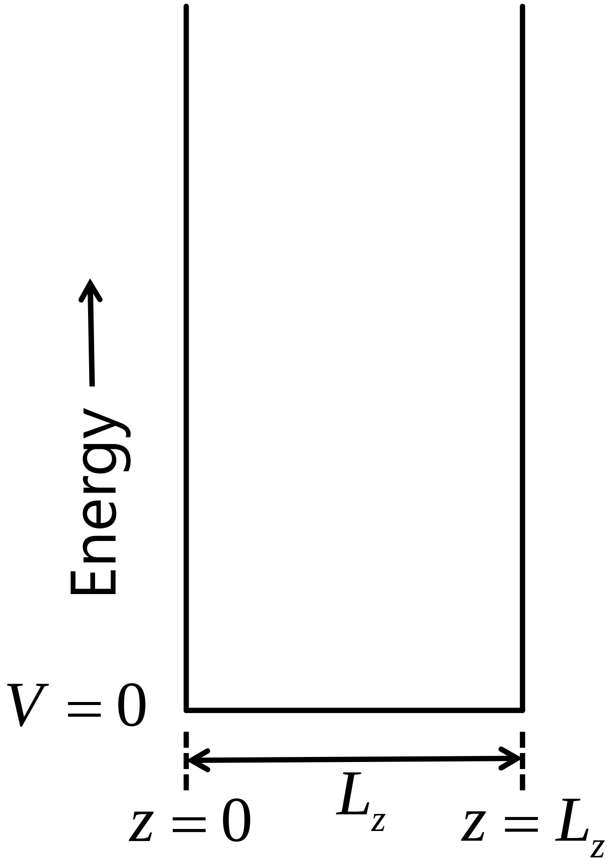
the Schrödinger equation

$$-\frac{\hbar^2}{2m}\frac{d^2\psi(z)}{dz^2}+V(z)\psi(z)=E\psi(z)$$

becomes $$-\frac{\hbar^2}{2m}\frac{d^2\psi(z)}{dz^2}=E\psi(z)$$

with the boundary conditions

$\psi(0)=0$ and $\psi(L_z)=0$



Particle in a box

The general solution to the equation

$$-\frac{\hbar^2}{2m}\frac{d^2\psi(z)}{dz^2} = E\psi(z)$$

is of the form

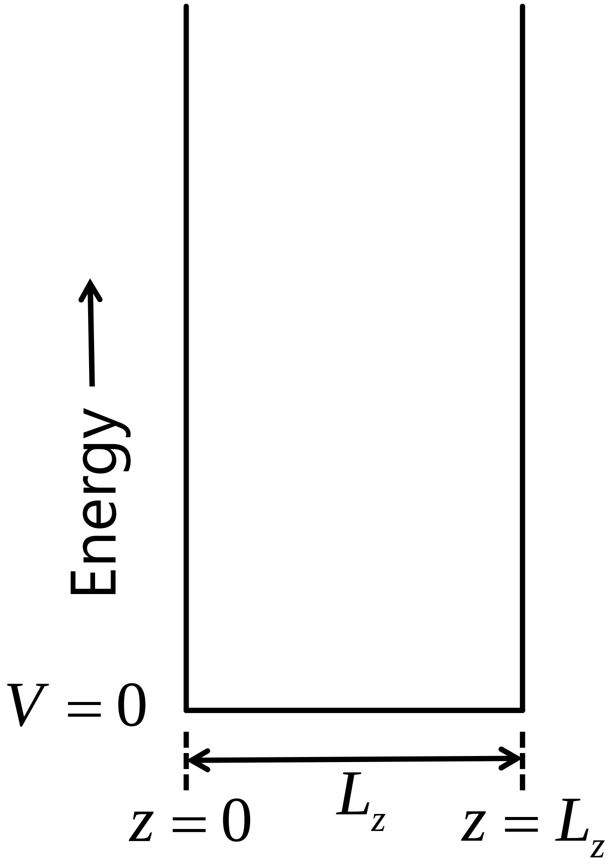
$$\psi(z) = A\sin(kz) + B\cos(kz)$$

where A and B are constants

and $k = \sqrt{2mE/\hbar^2}$

The boundary condition $\psi(0) = 0$

means $B = 0$ because $\cos(0) = 1$



Particle in a box

With now $\psi(z) = A\sin(kz)$

and the condition $\psi(L_z) = 0$

kz must be a multiple of π, i.e.,

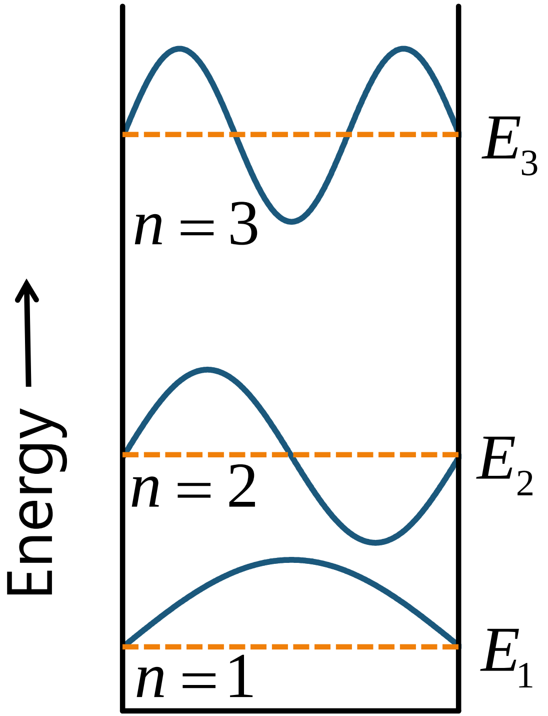
$$k = \sqrt{2mE/\hbar^2} = n\pi / L_z$$

where n is an integer

Since, therefore, $E = \frac{\hbar^2 k^2}{2m}$

the solutions are

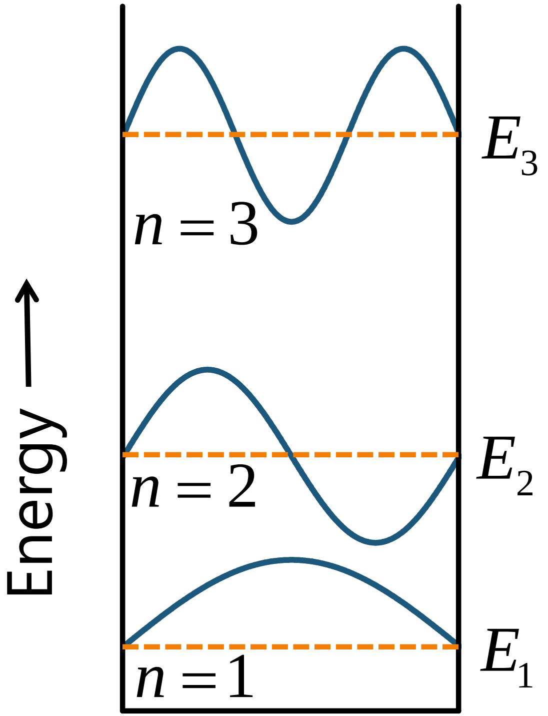
$$\psi_n(z) = A_n \sin\left(\frac{n\pi z}{L_z}\right) \text{ with } E_n = \frac{\hbar^2}{2m}\left(\frac{n\pi}{L_z}\right)^2$$



Particle in a box

We restrict n to positive integers $n = 1, 2, \ldots$ for the following reasons

- Since $\sin(-a) = -\sin(a)$ for any real number a
  - the wavefunctions with negative n are the same as those with positive n
    - within an arbitrary factor, here -1
  - the wavefunction for $n = 0$ is trivial
    - the wavefunction is 0 everywhere



$$\psi_n(z) = A_n \sin\left(\frac{n\pi z}{L_z}\right)$$

The quantum view of the world 2

Normalization and probability

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Normalizing wavefunctions

So far, if we integrate the modulus squared of the wavefunction

we do not get 1

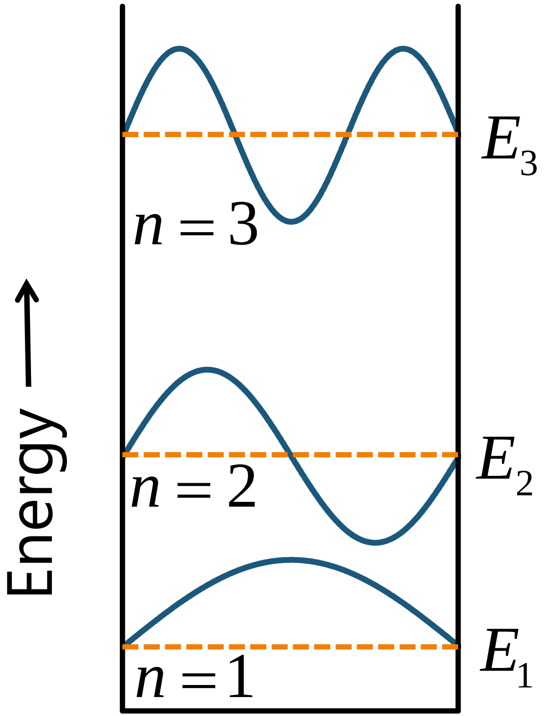
Specifically

$$\int_0^{L_z} |\psi_n(z)|^2 \, dz = \int_0^{L_z} |A_n|^2 \sin^2\left(\frac{n\pi z}{L_z}\right) dz = |A_n|^2 \frac{L_z}{2}$$

We prefer to "normalize"

so this integral does give 1

Then $|\psi_n(z)|^2$ will correspond to probability density per unit length



Normalizing wavefunctions

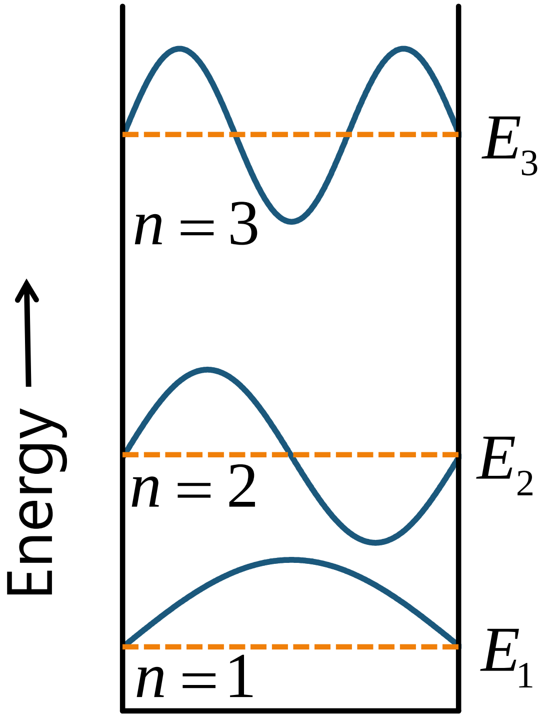
To have this integral equal 1, i.e.

$$\int_0^{L_z} |A_n|^2 \sin^2\left(\frac{n\pi z}{L_z}\right) dz = |A_n|^2 \frac{L_z}{2} = 1$$

we choose $|A_n| = \sqrt{2/L_z}$

Note A_n can be complex

All such solutions are arbitrary within a unit complex factor



Normalizing wavefunctions

Conventionally

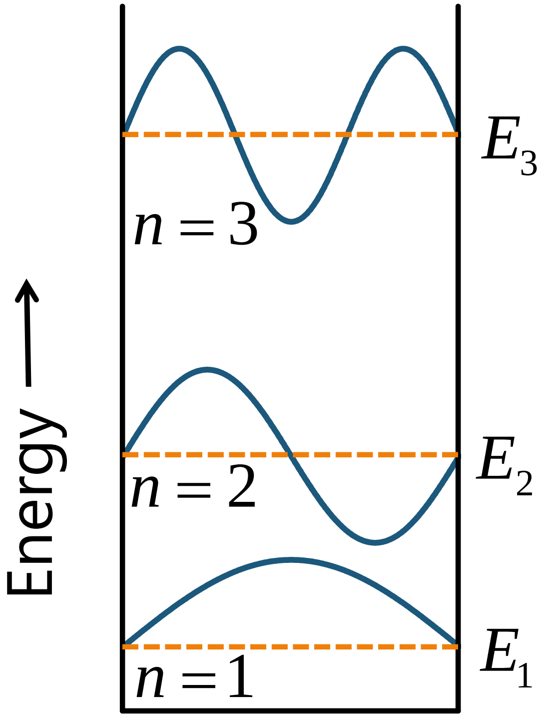
- we choose A_n real for simplicity
  - so we choose $A_n = \sqrt{2/L_z}$

Note that in this specific case

- the normalization coefficient is the same for all states

That will not typically be the case

- Normalization coefficients will often be different for different states



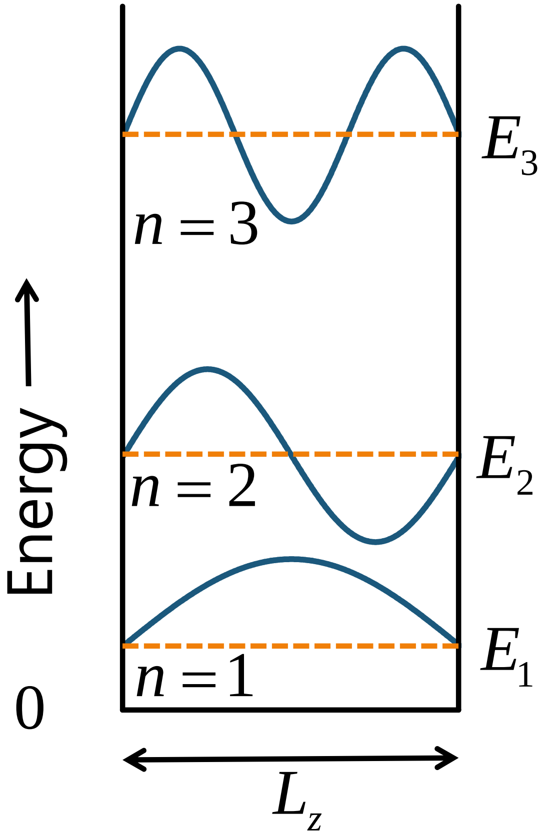
Particle in a box solutions

The normalized solutions for the particle in a box problem are

$$E_n = \frac{\hbar^2}{2m}\left(\frac{n\pi}{L_z}\right)^2$$

$$\psi_n(z) = \sqrt{\frac{2}{L_z}}\sin\left(\frac{n\pi z}{L_z}\right)$$

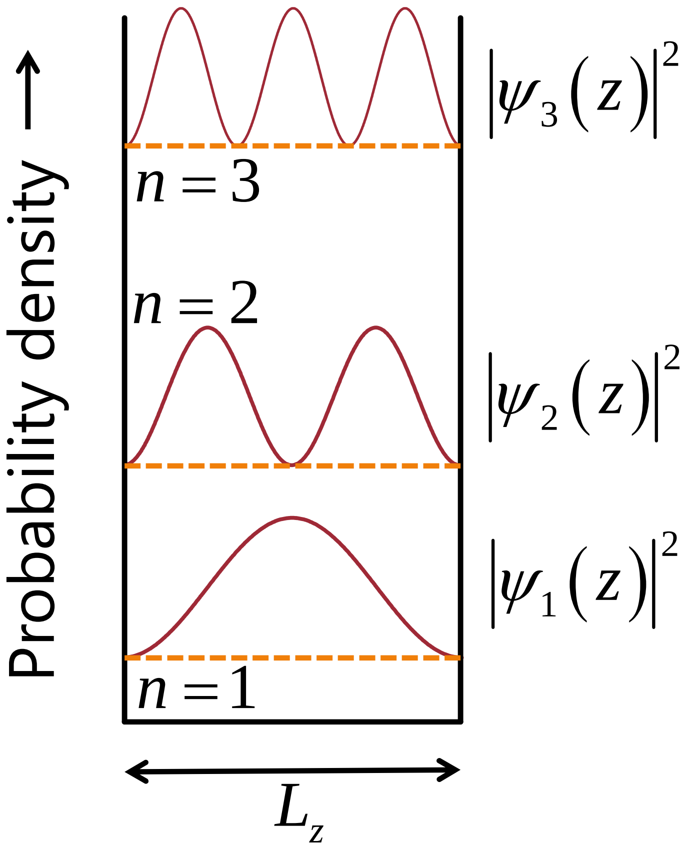
$$n = 1, 2, \ldots$$



Probability density

We can plot the probability densities
  for each state

When we use normalized wavefunctions
  the area under each such curve is 1



Probability

For the probability of finding a particle in a region

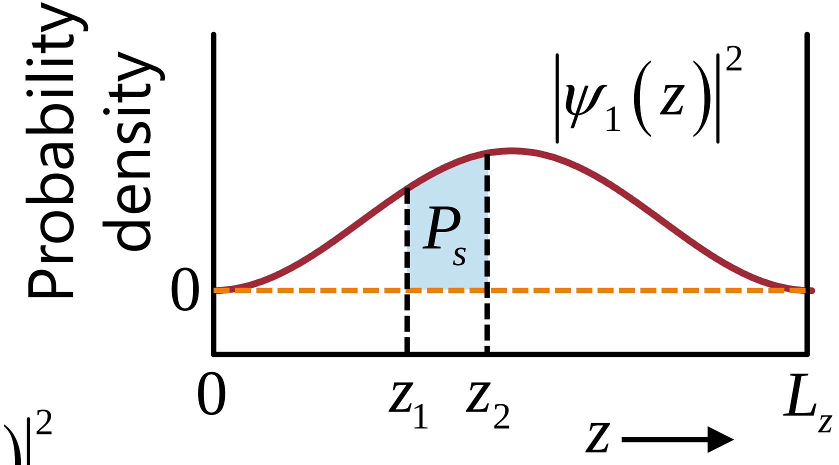
integrate the probability density over the region

For a particle in state $n = 1$ in our box

for the probability of finding the particle between z_1 and z_2

integrate the normalized $\left|\psi_1(z)\right|^2$

between these limits



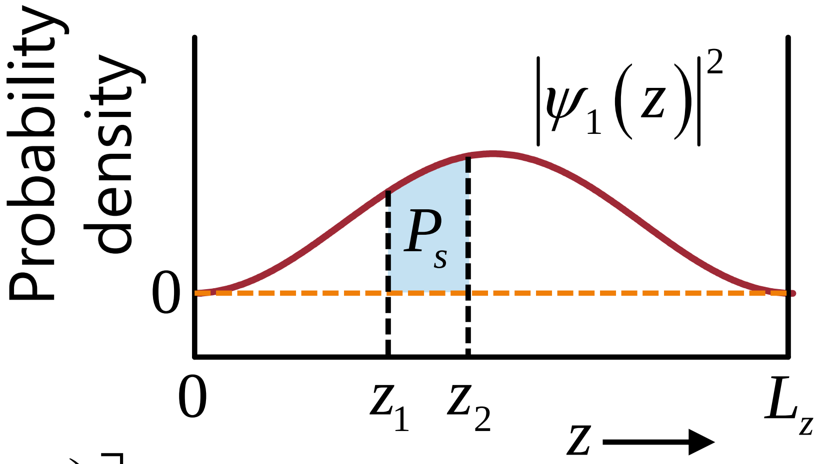
Probability

$$P_s = \int_{z_1}^{z_2} \left(\sqrt{\frac{2}{L_z}}\right)^2 \sin^2\left(\frac{\pi z}{L_z}\right) dz = \frac{2}{L_z}\int_{z_1}^{z_2} \frac{1}{2}\left[1 - \cos\left(\frac{2\pi z}{L_z}\right)\right] dz$$

$$= \frac{1}{L_z}\int_{z_1}^{z_2} 1\, dz - \frac{1}{L_z}\int_{z_1}^{z_2} \cos\left(\frac{2\pi z}{L_z}\right) dz$$

$$= \frac{1}{L_z}\left[z\right]_{z_1}^{z_2} - \frac{1}{L_z}\frac{L_z}{2\pi}\left[\sin\left(\frac{2\pi z}{L_z}\right)\right]_{z_1}^{z_2}$$

$$= \frac{(z_2 - z_1)}{L_z} - \frac{1}{2\pi}\left[\sin\left(\frac{2\pi z_2}{L_z}\right) - \sin\left(\frac{2\pi z_1}{L_z}\right)\right]$$



The quantum view of the world 2

The nature of the particle-in-a-box solutions

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Eigenvalues and eigenfunctions

As in classical wave problems

- solutions with a specific set of allowed values of a parameter (here energy)
  - the eigenvalues
- and with a particular function associated with each such value
  - the eigenfunctions

can be called eigensolutions

$$E_n = \frac{\hbar^2}{2m}\left(\frac{n\pi}{L_z}\right)^2$$

$$\psi_n(z) = \sqrt{\frac{2}{L_z}}\sin\left(\frac{n\pi z}{L_z}\right)$$

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

Eigenvalues and eigenfunctions

Compared to the classical world

- at least in this example problem
  - asking for solutions with definite energy E
    - leads to the conclusion that
      - only very specific, discrete values of that energy are possible
        - unlike classical models of matter

$$E_n = \frac{\hbar^2}{2m}\left(\frac{n\pi}{L_z}\right)^2$$

$$\psi_n(z) = \sqrt{\frac{2}{L_z}}\sin\left(\frac{n\pi z}{L_z}\right)$$

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

Eigenvalues and eigenfunctions

Here, since the parameter is an energy

- we can call the eigenvalues
  - eigenenergies
- the eigenfunctions are
  - energy eigenfunctions
- and we call n a
  - quantum number

The eigenenergy, eigenfunction, and quantum number

- are attributes of the particle's "state"

$$E_n = \frac{\hbar^2}{2m}\left(\frac{n\pi}{L_z}\right)^2$$

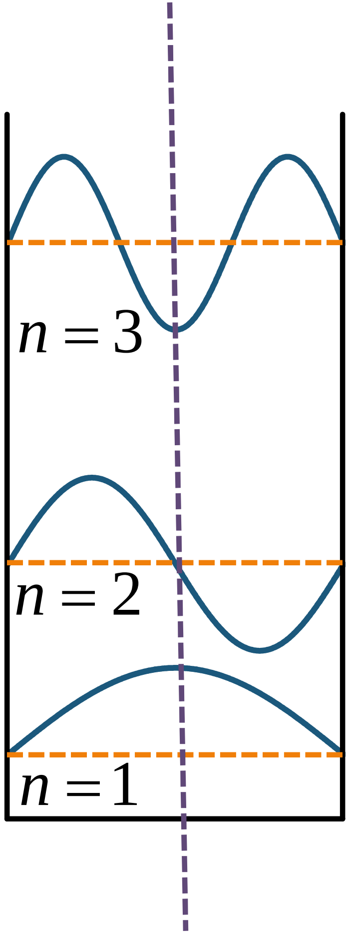
$$\psi_n(z) = \sqrt{\frac{2}{L_z}}\sin\left(\frac{n\pi z}{L_z}\right)$$

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

Parity of wavefunctions

Note these eigenfunctions have definite symmetry

- the $n = 1$ function is the mirror image on the left of what it is on the right
  - such a function has "even parity"
  - or is said to be an "even function"
- The $n = 3$ eigenfunction is also even
- The $n = 2$ eigenfunction
  - has "odd parity"
  - or is said to be an "odd function"



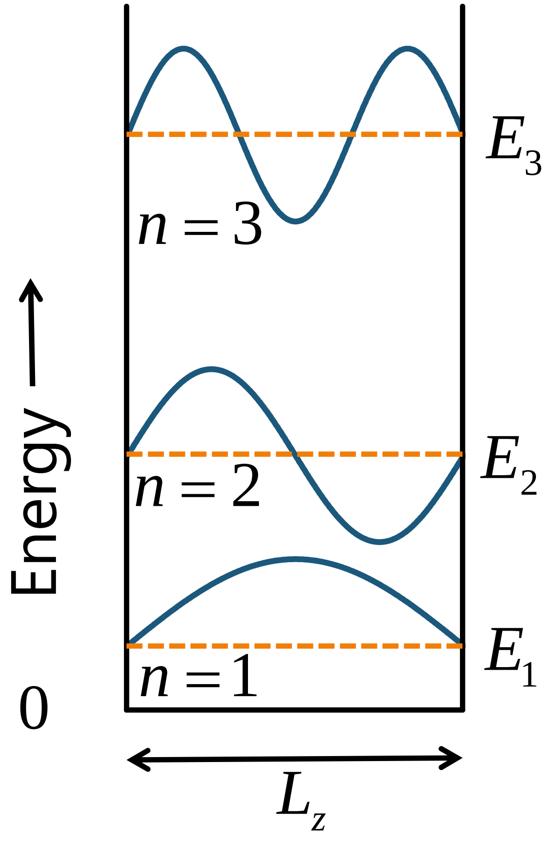
Zeros in eigenfunctions

Note that

- each successively higher energy state
  - has one more "zero" in the eigenfunction

This is very common behavior in quantum mechanics

- and is a common result of requiring mathematically "orthogonal" functions



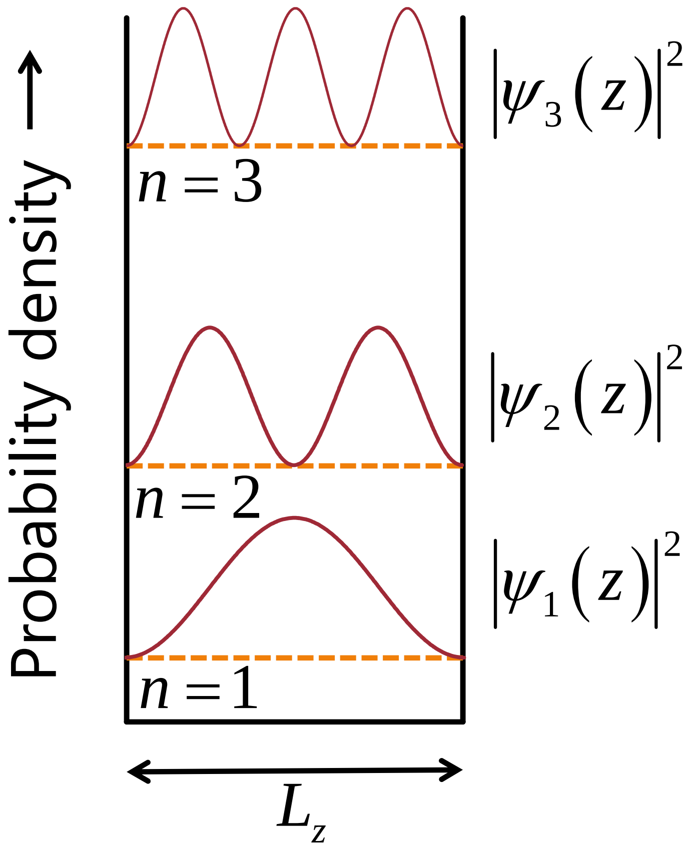
Probability density

In the lowest state $(n = 1)$

- the particle is most likely to be found near the center of the box

In higher states

- there are points inside the box where the particle will never be found



Quantum confinement

This particle-in-a-box behavior is very different from the classical case in at least 3 ways

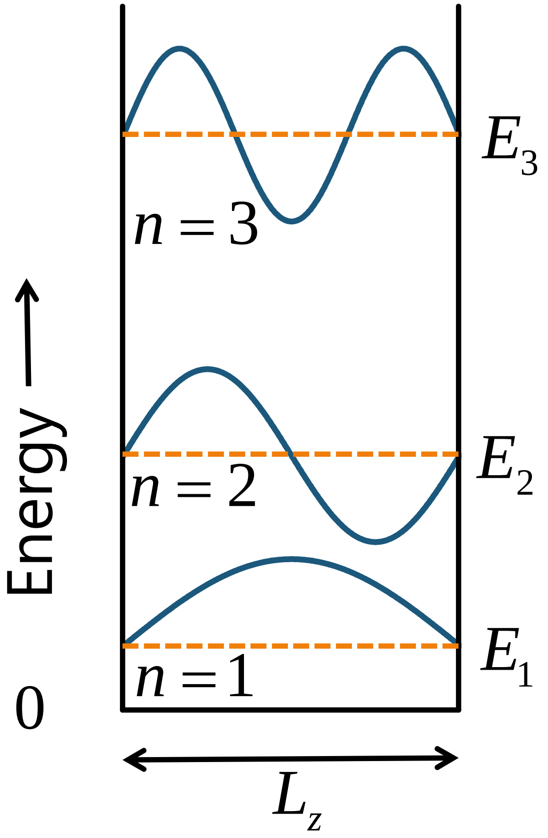
1 – there is only a discrete set of possible values for the energy

2 – there is a minimum possible energy for the particle

here corresponding to $n = 1$

here $E_1 = \left(\hbar^2 / 2m\right)\left(\pi / L_z\right)^2$

sometimes called a "zero-point energy"



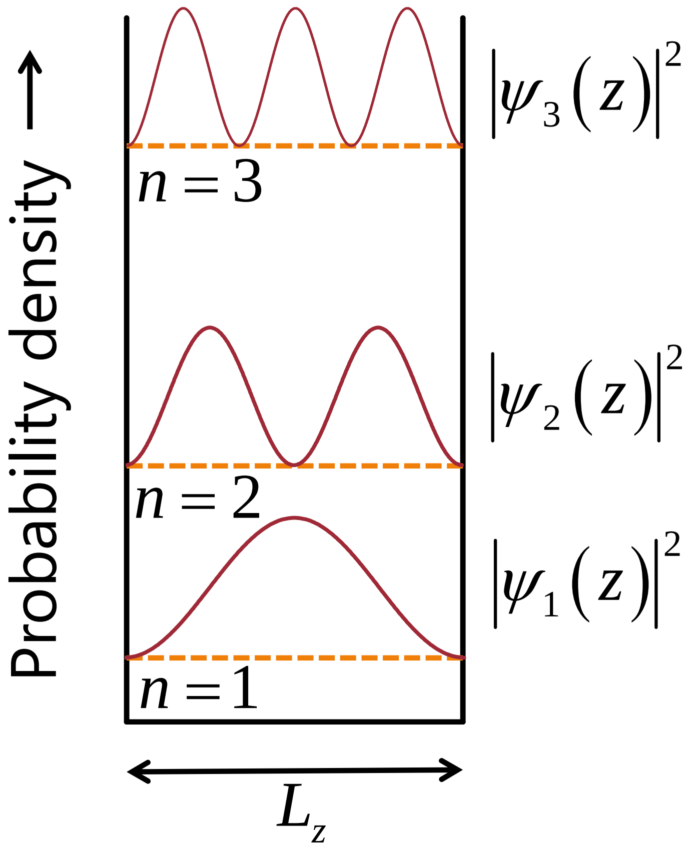
Quantum confinement

3 - the particle is not uniformly distributed over the box, and

its distribution is different for different energies

It is almost never found very near to the walls of the box

The probability obeys a standing wave pattern



Orders of magnitude

E.g., confine an electron in a 5 Å (0.5 nm) thick box

The first allowed level for the electron is

$$E_1 = \left(\hbar^2 / 2m_e\right)\left(\pi / 5\times10^{-10}\right)^2 \cong 2.4\times10^{-19}\ \text{J} \cong 1.5\ \text{eV}$$

The separation between the first and second allowed energies ($E_2 - E_1 \simeq 3E_1$) is $\simeq 4.5$ eV

which is a characteristic size of major energy separations between levels in an atom

Note that visible photons also have energies in the single eV range

so light-matter interaction is quantum mechanical