CHAPTER 6
Quantum Mechanics II

- 6.0 Partial differentials John von Neumann: ”Young man, in mathematics you don’t understand things. You just get used to them.”

- **6.1 The Schrödinger Wave Equation, Operators**
- **6.2 Expectation Values**
- 6.3 Infinite Square-Well Potential slide 29
- 6.5 Three-Dimensional Infinite-Potential Well
- 6.4 Finite Square-Well Potential
- 6.6 Simple Harmonic Oscillator
- 6.7 Barriers and Tunneling in some books an extra chapter due to its immense technical importance

I think it is safe to say that no one understands quantum mechanics. Do not keep saying to yourself, if you can possibly avoid it, “But how can it be like that?” because you will get “down the drain” into a blind alley from which nobody has yet escaped. Nobody knows how it can be like that.

- Richard Feynman

$$f(x,y) = yx^2$$

y will often be time *t* for 1D wave functions

$$\frac{\partial f(x,y)}{\partial x} = \{\frac{\partial f(x,y)}{\partial x}\}_{y=cons.} = 2yx \qquad \frac{\partial^2 f(x,y)}{\partial x^2} = \frac{\partial}{\partial x}\{\frac{\partial f(x,y)}{\partial x}\}_{y=cons.} = 2y$$

$$\frac{\partial f(x,y)}{\partial y} = \{\frac{\partial f(x,y)}{\partial y}\}_{x=cons.} = x^2 \qquad \frac{\partial^2 f(x,y)}{\partial y^2} = \frac{\partial}{\partial y}\{\frac{\partial f(x,y)}{\partial y}\}_{x=cons.} = 0$$

$$\nabla^2 f(x,y) = \frac{\partial^2}{\partial x^2} f(x,y) + \frac{\partial^2}{\partial y^2}(f(x,y) = 2y$$

[4]Obtaining solutions to partial differential equations in separable form is called *separation of variables*. On separating variables, a partial differential equation in, say, *N* variables is reduced to *N* ordinary differential equations, each involving only a single variable. The technique is a general one which may be applied to many (but not all!) of the partial differential equations encountered in science and engineering applications.

$$\partial \rightarrow d$$

$$\frac{1}{i} = -i$$

$$\frac{d}{dx}(e^{ax}) = a \cdot e^{ax} \qquad \frac{d}{dx}(e^{iax}) = ia \cdot e^{iax}$$

$$\frac{d}{dx}(\sin ax) = a \cdot \cos ax$$

$$\frac{d}{dx}(\cos ax) = -a \cdot \sin ax$$

complex conjugate pair

$$\cos(k_n x) = \frac{e^{ik_n x} + e^{-ik_n x}}{2}$$

$$e^{i\theta} = \cos\theta + i\sin\theta$$

$$e^{-i\theta} = \cos\theta - i\sin\theta$$

$$\sin(k_n x) = \frac{e^{ik_n x} - e^{-ik_n x}}{2i}$$

Felix Bloch

. . . in one of the next colloquia, Schrödinger gave a beautifully clear account of how de Broglie associated a wave with a particle and how he [i.e., de Broglie] could obtain the quantization rules . . . by demanding that an integer number of waves should be fitted along a stationary orbit. When he had finished Debye[2] casually remarked that he thought this way of talking was rather childish . . . [that to] deal properly with waves, one had to have a wave equation.

1. Felix Bloch (1905–1983), Swiss American physicist. He was a student at the University of Zurich and attended the colloquium referred to. The quote is from an address before the American Physical Society in 1976. Bloch shared the 1952 Nobel Prize in Physics for measuring the magnetic moment of the neutron, using a method that he invented that led to the development of the analytical technique of nuclear magnetic resonance (NMR) spectroscopy.

2. Peter J. W. Debye (1884–1966), Dutch American physical chemist. He succeeded Einstein in the chair of theoretical physics at the University of Zurich and received the Nobel Prize in Chemistry in 1936.

As a function of 3D space and time, separate

$$i\hbar\frac{\partial\Psi}{\partial t} = -\frac{\hbar^2}{2m}\left(\frac{\partial^2\Psi}{\partial x^2}+\frac{\partial^2\Psi}{\partial y^2}+\frac{\partial^2\Psi}{\partial z^2}\right)+V\Psi(x,y,z,t)$$

V=V(x,y,z,t)

Total energy

As a function of 3D space only, stationary state, small

$$-\frac{\hbar^2}{2m}\nabla^2\psi + V\psi = E\psi$$

Light "wavicals" are special, they obey the time dependent Helmholtz (wave) equation

$$\frac{\partial^2 \mathcal{E}}{\partial x^2} = \frac{1}{c^2}\frac{\partial^2 \mathcal{E}}{\partial t^2} \qquad \mathcal{E}(x,t) = \mathcal{E}_0 \cos(kx - \omega t)$$

Plane wave for electric field vector

$$\frac{\partial^2 \mathcal{E}}{\partial x^2} = -k^2 \mathcal{E}(x,t) \qquad \frac{\partial^2 \mathcal{E}}{\partial t^2} = -\omega^2 \mathcal{E}_0 \cos(kx - \omega t) = -\omega^2 \mathcal{E}(x,t)$$

$$-k^2 = -\frac{\omega^2}{c^2} \qquad \omega = kc \qquad c = \lambda f$$

Using $\omega = E/\hbar$ and $p = \hbar k$ for electromagnetic radiation, we have

$$p = \hbar k = h/\lambda \qquad E = pc$$

As we already know from special relativity, a massless particle has momentum

A light wave is its own probability density wave, idea by Einstein

Solve the steady state version of his equation for an electron acted upon by the Coulomb force that is due to a close by proton, and you have a model of the hydrogen atom - Energy quantization and 3 quantum numbers just follows from the mathematical process !!

$$\mathbf{F}_1 = k_e \frac{q_1 q_2}{|\mathbf{r}_{21}|^2} \qquad \mathbf{F}_2 = -\mathbf{F}_1$$

$$k_e = 1/(4\pi\varepsilon_0)$$

3. Erwin R. J. A. Schrödinger (1887–1961), Austrian physicist. He succeeded Planck in the chair of theoretical physics at the University of Berlin in 1928 following Planck's retirement and two years after publishing in rapid succession six papers that set forth the theory of wave mechanics. For that work he shared the Nobel Prize in Physics with P. A. M. Dirac in 1933. He left Nazi-controlled Europe in 1940, moving his household to Ireland.

1933 for Oxford, later on Graz, Italy, Ireland

Loved his pipe, wine, and many mistresses, kind of started biophysics in 1944 with his booklet “What is life?”

left the top theoretical physics position in all of Germany (at Berlin University) on his own account in 1933, .., 1938 after Austria was annexed, he left Graz despite orders to stay, his mother was half-English, …Republic of Ireland remained neutral during WW II

6.1. The Schrödinger Wave Equation

- The Schrödinger wave equation in its time-dependent form for a particle subject to a potential energy function *V* in one dimension is

$$i\hbar\frac{\partial\Psi(x,t)}{\partial t}=-\frac{\hbar^2}{2m}\frac{\partial^2\Psi(x,t)}{\partial x^2}+V\Psi(x,t)$$

m = mass of electron, more precisely reduced mass

$$V(x,t)=V_2(x,t)-V_1(x.t)=-\int_1^2\vec{F}(t)\cdot d\vec{x}$$

Equivalent to time dependent Helmholtz (wave) equation, which can be derived from Newton's force laws, BUT Schrödinger equation cannot be derived from anything else !!!

- The extension into three dimensions is

$$i\hbar\frac{\partial\Psi}{\partial t}=-\frac{\hbar^2}{2m}\left(\frac{\partial^2\Psi}{\partial x^2}+\frac{\partial^2\Psi}{\partial y^2}+\frac{\partial^2\Psi}{\partial z^2}\right)+V\Psi(x,y,z,t)$$

where $i=\sqrt{-1}$

The statement is in both cases that operators act on the wave function, V = V(x,t) in the first equation for 1D, V = V(x,y,z,t) in the second equation for 3D, non-relativistic

Comparison of Classical and Quantum Mechanics

Non-relativistic, m is constant and taken out of the differential d(m,v)

$$\vec{F} = {d\vec{p}}\Big/_{dt} = m \cdot {d\vec{v}}\Big/_{dt} = m \cdot \left({d\vec{x}}\Big/_{dt}\right) {d\vec{x}}\Big/_{dt} = m \cdot {d^2\vec{x}}\Big/_{dt^2} = m \cdot \vec{a}$$

- Newton’s second law and Schrödinger’s wave equation are both differential equations.
- Newton’s second law can be derived from the Schrödinger wave equation, so the latter is the more fundamental – cannot be derived from anything else.
- Classical mechanics only appears to be more precise because it deals with macroscopic phenomena. The underlying uncertainties in macroscopic measurements are just too small to be significant, the un-correctable “systematic residual/rest error” that is due to the uncertainty principle is too small to be noticed for heavy objects

Free particle solution of the Schrödinger wave equation, harmonic/plane matter wave, V = 0 or constant

- The wave function for a plane wave

$$\Psi(x,t) = Ae^{i(kx-\omega t)} = A[\cos(kx - \omega t) + i\sin(kx - \omega t)]$$

which describes a wave moving in the *x* direction to the right from minus infinity to plus infinity (left it you change the sign). In general the amplitude (A) may also be complex. Out of the sum of infinitely many different plane matter waves, we can create wave packets, just as we did for classical waves earlier

- Wave functions are also not restricted to being real. All traveling matter waves are complex. Note that the sine term has an imaginary number in front of it. Only physically measurable quantities must be real. These include the probability of finding the particle someplace (either at some particular time or all the time), momentum, energy, … anything you want to know

If V ≠ 0 or not constant with time, it is no longer a free particle, then we can and need to normalize, setting the scale for all measurements by operators

$$-\frac{\hbar^2}{2m}\frac{\partial^2\Psi(x,t)}{\partial x^2} + V(x,t)\Psi(x,t) = i\hbar\frac{\partial\Psi(x,t)}{\partial t}$$

Free particle is analog of Newton's first law

$\Psi(x,t) = Ae^{i(kx-\omega t)}$ = ideal free particle, $V_0 = 0$

$$= A[\cos(kx - \omega t) + i\sin(kx - \omega t)]$$

$$\frac{\partial^2\Psi}{\partial x^2} = (ik)^2 Ae^{i(kx-\omega t)} = -k^2\Psi \qquad \frac{\partial\Psi}{\partial t} = -i\omega Ae^{i(kx-\omega t)} = -i\omega\Psi$$

Substituting these derivatives into the Schrödinger equation with $V(x,t) = V_0$ gives

$$\frac{-\hbar^2}{2m}(-k^2\Psi) + V_0\Psi = i\hbar(-i\omega)\Psi$$

or

$$\frac{\hbar^2k^2}{2m} + V_0 = \hbar\omega$$

The potential energy function does not vary in space and time, it's a constant, either zero or any value

Quasi-Free particle wave function solves the Schrödinger equation with a constant potential, that can be set zero, postulating validity for $V_0 \neq 0$, i.e. as any function of time was quite a stretch

$$-\frac{\hbar^2}{2m}\frac{\partial^2\Psi}{\partial x^2} + U(x)\Psi = i\hbar\frac{\partial\Psi}{\partial t} = E\cdot\Psi(x,t) = \hbar\omega\cdot\Psi(x,t)$$

Ψ(x,t) is eigenfunction of time dependent total energy operator

$$\hbar\omega = \frac{\hbar^2k^2}{2m} + V \qquad E = \frac{p^2}{2m} + V$$

For a single plane wave, $\Psi = Ae^{i(kx-\omega t)}$, representing a "completely spread-out" particle

$$-\frac{\hbar^2}{2m}\frac{\partial^2\Psi(x,t)}{\partial x^2} + V(x,t)\Psi(x,t) = i\hbar\frac{\partial\Psi(x,t)}{\partial t} = E\cdot\Psi(x,t)$$

Total energy = kinetic energy + potential energy in operator form, i.e. total energy is conserved on average, we ignore rest energy/special relativity, always need to make sure that particles move with v < 0.01 c or better $^1/_\alpha \approx {}^1/_{137}$

while there are undetectable energy fluctuations within the uncertainty limit, wave particle duality is taken care of by the ***i***, *i.e. going complex, into Hilbert space*

Eigenfunctions of total energy E_n solve Schroedinger equation, E_n are **eigenvalues** (you may remember algebra of matrices, solving linear systems of equations)

Normalization and Probability

- The probability density $P(x)\,dx$ of a particle being found between x and x +-dx was given in the equation

complex conjugate

$$P(x)\,dx = \Psi^*(x,t)\Psi(x,t)\,dx$$

- The probability of the particle being found between x_1 and x_2 is given by

$$P = \int_{x_1}^{x_2} \Psi^*\Psi\,dx$$

- The wave function must be normalized so that the probability of the particle being found somewhere on the x axis (or within Δx) is 1 (100%).

$$\int_{-\infty}^{\infty} \Psi^*(x,t)\Psi(x,t)\,dx = 1$$

Compare previous chapter !!!

Since the only things we are allowed to know are all calculated from the wave function for a particular physical scenario V(x,t) function, normalization sets the scale for all other predictions/calculations

Need to fulfill this condition,

$$\int_{-\infty}^{\infty} \Psi^*(x,t)\Psi(x,t)\,dx = 1$$

Ψ(x,t) and Ψ^*(x,t) both needs to have the same prefactor that is the square root of the reciprocal value of the integral when multiplied

$$\int_{-\infty}^{\infty} \Psi^*(x,t)\Psi(x,t)\,dx = \text{something finite}$$

It is going to be 1/Sqrt whatever the integral comes to

$$\int_{-\infty}^{\infty} \frac{1}{\sqrt{something\_finite}}\Psi^* \bullet \frac{1}{\sqrt{something\_finite}}\Psi \bullet dx = 1$$

since Schrödinger equation is linear, a prefactor on both sides changes nothing

$$-\frac{\hbar^2}{2m}\frac{\partial^2\Psi(x,t)}{\partial x^2} + V(x,t)\Psi(x,t) = i\hbar\frac{\partial\Psi(x,t)}{\partial t}$$

try to normalize the wave function for a free particle

$$\Psi(x,t) = Ae^{i(kx-\omega t)} = A[\cos(kx-\omega t) + i\sin(kx-\omega t)]$$

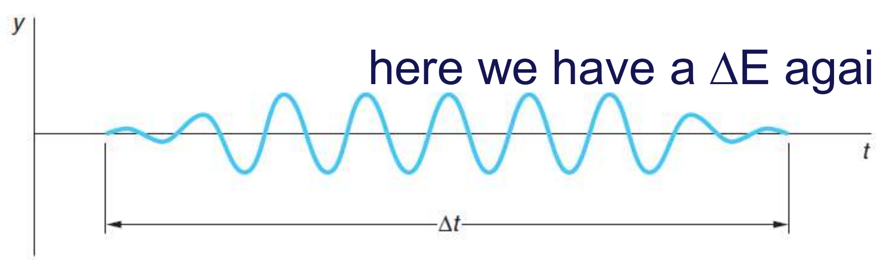
$$\int_{-\infty}^{\infty} \Psi^*(x,t)\Psi(x,t)\,dx = \infty$$

What does this mean?

Probability of fining the particle is in each finite unit segment identical and finite, adding all of these unit segments together gives infinity – so the particle is to be found everywhere at any one time, better: one does not know where it is to be found at all

But $\Delta E \Delta t \geq \frac{\hbar}{2}$ ***no longer apply, definite and arbitrary E and p***

$\Delta p_x \Delta x \geq \frac{\hbar}{2}$



here we have a ΔE again

No big deal, just a useful model, superposing of infinitely many plane waves with the right properties leads to any wave packet that we may need to normalize in order to set the physical scale right

$$\Psi(x,t) = \int_{-\infty}^{\infty} a(k)\, e^{i\{kx-\omega(k)t\}}\, dk$$

Properties of valid wave functions

I. Boundary conditions, to make the mathematics work

1) In order to avoid infinite probabilities, the wave function must be finite everywhere.
2) In order to avoid multiple values of the probability, the wave function must be single valued everywhere.
3) For finite potentials, the wave function and its derivative must be continuous. This is required because the second-order derivative term in the wave equation must be single valued. (There are exceptions to this rule when *V* is approximated to be infinite – last chapter.)
4) In order to be able to normalize wave functions, they must approach zero as *x* approaches infinity.

$\psi(x) \to 0$ fast enough as $x \to \pm\infty$ so that the normalization integral, Equation 6-20, remains bounded.

- Wave functions that do not posses these mathematical properties do not correspond to physically realizable circumstances. **BUT physics of the problem also needs to be captured by the boundary conditions**

$$P(x,t)\,dx = \Psi^*(x,t)\Psi(x,t)\,dx = |\Psi(x,t)|^2\,dx$$

Properties of valid wave functions II

II. Boundary condition, to bring the physics in

- Every problem has its specific wave function (that surely needs to get the maths of the Schrödinger equation right)

- it all depends on the potential energy function, the physics of the problem to be solved is encoded there
- we need a function, not a vector so instead of force we use its scalar product with position

gradient of potential energy function = - force

$$\Delta V = V_2 - V_1 = -\int_1^2 \vec{F} \cdot d\vec{x} \qquad V(x) = U(x) = \frac{kx^2}{2} \qquad \frac{d}{dx}\left(\frac{kx^2}{2}\right) = k|\vec{x}| = -|\vec{F}|$$

e.g. potential energy function of a spring, does not depend on time

V_1 can be set zero

Hooke's law in Newton's formulation

Probability *P* and probability density *P(x)* of finding a particle

Two ways of dealing with

$$P(x)\,dx = \Psi^*(x,t)\Psi(x,t)\,dx$$

$$P(x)\,\cancel{dx} = \Psi^*(x,t)\Psi(x,t)\,\cancel{dx}$$

Cancel dx on both sides, and you get a formulae for the probability density at any x

$$P = \int_{x_1}^{x_2} \Psi^* \Psi \, dx$$

Integrate both sides over some region of space and you get the probability of finding that “wavicel” in that region

In both cases, the wave function needs to be normalized, otherwise the result will be just proportional to finding the wavicel

Time-Independent Schrödinger Equation – separation of space and time variables

- The potential in many cases will not depend on time, stationary states.
- In all of these cases, the wavefunction can be rewritten

$$\Psi(x,t) = \psi(x) f(t)$$

- And we can derive the time independent Schrödinger equation, take

$$i\hbar\,\psi(x)\frac{\partial f(t)}{\partial t} = -\frac{\hbar^2 f(t)}{2m}\frac{\partial^2\psi(x)}{\partial x^2} + V(x)\psi(x)f(t)$$

divide by $\psi(x)f(t)$ yields:

$$i\hbar\frac{1}{f(t)}\frac{df(t)}{dt} = -\frac{\hbar^2}{2m}\frac{1}{\psi(x)}\frac{d^2\psi(x)}{dx^2} + V(x)$$

The left side depends only on time, and the right side depends only on spatial coordinates. Hence each side must be equal to the same constant. The time dependent side is

$$i\hbar\frac{1}{f}\frac{df}{dt} = B$$

What might this B possibly be? The Schrödinger equation is a statement on the conservation of total energy, which is constant in a stationary state, i.e. does not change with time

Time-Independent Schrödinger Equation Continued

$$i\hbar\frac{1}{f}\frac{df}{dt} = B$$

- We integrate both sides and find: $i\hbar\int\frac{df}{f} = \int B\,dt \qquad i\hbar\ln f = Bt + C$

  where *C* is an integration constant that we choose to be 0. Therefore

$$\ln f = \frac{Bt}{i\hbar}$$

This determines *f* to be $f(t) = e^{Bt/i\hbar} = e^{-iBt/\hbar}$

In order to do this, *f(t)* needs to be eigenfunction

$$i\hbar\frac{1}{f(t)}\frac{df(t)}{dt} = E$$

Total energy operator

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

Dimensional analysis of the exponent leads to E ! What else could B possibly be? given the fact that the Schrödinger equation is a statement on the conservation of total energy, we also know from slide 10 that wavefunctions that solve the Schrödinger equation are eigenfunctions of the total energy operator

- This is known as the **time-independent Schrödinger equation**, and it is a fundamental equation in quantum mechanics.

Note that we now use (little) ψ(x) instead of (big) Ψ(x,t)

Stationary State

Remember when you see E think ω (or frequency) and vice versa

- The wave function can be written as: $\Psi(x,t) = \psi(x)e^{-i\omega t}$
- Whenever the potential energy function is not time dependent
- Integrand in probability density integral $\Psi^*\Psi = \psi^2(x)(e^{i\omega t}e^{-i\omega t})$

  becomes: $\Psi^*\Psi = \psi^2(x)$

- The probability distributions are constant in time. This is a standing wave phenomena that is called a stationary state.

$$E = \hbar \cdot \omega$$

So whenever you see circular frequency omega, you can also think total energy divided by h-bar

$$p = \hbar k = h/\lambda$$

So whenever you see the wave number, you can also think linear momentum divided by h-bar

6.2: Expectation Values, what one will measure on average is derived from correct wave function for a problem

- The **expectation value** is the expected result of the average of many measurements of a given quantity of many identical systems. The expectation value of *x* is denoted by <*x*>
- Any measurable quantity for which we can calculate the expectation value is called a **physical observable**. The expectation values of physical observables (for example, position, linear momentum, angular momentum, and energy) must be real, because the experimental results of measurements are real.
- The average value of *x* is

$$\bar{x} = \frac{N_1 x_1 + N_2 x_2 + N_3 x_3 + N_4 x_4 + \ldots}{N_1 + N_2 + N_3 + N_4 + \ldots} = \frac{\sum_i N_i x_i}{\sum_i N_i}$$

Continuous Expectation Values

- We can change from discrete to continuous variables by using the probability density *P*(*x*,*t*) of observing the particle at a particular *x and t*.

$$\overline{x} = \frac{\int_{-\infty}^{\infty} xP(x)\,dx}{\int_{-\infty}^{\infty} P(x)\,dx}$$

- Using a normalized wave function, the expectation value is:

$$\langle x \rangle = \int_{-\infty}^{+\infty} \Psi^*(x,t) x \Psi(x,t)\,dx$$

$$\langle x \rangle = \frac{\int_{-\infty}^{\infty} x\Psi^*(x,t)\Psi(x,t)\,dx}{\int_{-\infty}^{\infty} \Psi^*(x,t)\Psi(x,t)\,dx}$$

- The expectation value of any observable, represented by an operator *g*(*x,t*), for a normalized wave function

$$\langle g(x) \rangle = \int_{-\infty}^{\infty} \Psi^*(x,t) g(x) \Psi(x,t)\,dx$$

x, g(x), and g(x,t) are operators !!!, x could also have been in the middle of conjugate complex wave function times wave function as it is the rule for all operators, where it is in this particular product does not mater

Momentum Operator

- To find the expectation value of *p*, we first need to represent *p* in terms of *x* and *t*. Consider the derivative of the wave function of a free particle with respect to *x*:

$$\frac{\partial \Psi}{\partial x} = \frac{\partial}{\partial x}[e^{i(kx-\omega t)}] = ike^{i(kx-\omega t)} = ik\Psi$$

$$p = \hbar k = h/\lambda$$

With $k = p / \hbar$ we have $\frac{\partial \Psi}{\partial x} = i\frac{p}{\hbar}\Psi$

$$\frac{1}{i} = -i$$

This yields $p^*[\Psi(x,t)] = -i\hbar\frac{\partial \Psi(x,t)}{\partial x}$

- This means we have derived the momentum operator $\hat{p} = -i\hbar\frac{\partial}{\partial x}$
.

- The expectation value of the momentum is

$$\langle p \rangle = -i\hbar\int_{-\infty}^{\infty}\Psi^*(x,t)\frac{\partial \Psi(x,t)}{\partial x}dx$$

$$\langle p \rangle = \int_{-\infty}^{+\infty}\Psi^*\left(\frac{\hbar}{i}\frac{\partial}{\partial x}\right)\Psi\, dx$$

$$\langle p^2 \rangle = \int_{-\infty}^{+\infty}\Psi^*\left(\frac{\hbar}{i}\frac{\partial}{\partial x}\right)\left(\frac{\hbar}{i}\frac{\partial}{\partial x}\right)\Psi\, dx$$

Position and Energy Operators

- The position *x* is its own operator [x] or x hat.
- The time derivative of the free-particle wave function is

$$\frac{\partial \Psi}{\partial t} = \frac{\partial}{\partial t}\left[e^{i(kx-\omega t)}\right] = -i\omega e^{i(kx-\omega t)} = -i\omega\Psi$$

$$E = \hbar \cdot \omega$$

Substituting $\omega = E / \hbar$ yields $\overset{*}{E}[\Psi(x,t)] = i\hbar \frac{\partial \Psi(x,t)}{\partial t}$

- The time dependent total energy operator is $\hat{E} = i\hbar \frac{\partial}{\partial t}$ $\qquad \frac{1}{-i} = i$

- The expectation value of the total energy is

$$\langle E \rangle = i\hbar \int_{-\infty}^{\infty} \Psi^*(x,t) \frac{\partial \Psi(x,t)}{\partial t} dx$$

A wavefunction that solves the Schroedinger equation is also an eigenfunction of the total energy operator (both in its time and position dependent forms, left and right hand side of Schrödinger equation)

Table 6-1 Some quantum-mechanical operators

Symbol	Physical quantity	Operator
$f(x)$	Any function of x—e.g., the position x, the potential energy $V(x)$, etc.	$f(x)$
p_x	x component of momentum	$\frac{\hbar}{i}\frac{\partial}{\partial x}$
p_y	y component of momentum	$\frac{\hbar}{i}\frac{\partial}{\partial y}$
p_z	z component of momentum	$\frac{\hbar}{i}\frac{\partial}{\partial z}$
H = E	Hamiltonian (time independent)	$\frac{p_{op}^2}{2m} + V(x)$ Total energy
E	Total energy (time dependent)	$i\hbar\frac{\partial}{\partial t}$
E_k	kinetic energy	$-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}$
L_z	z component of angular momentum	$-i\hbar\frac{\partial}{\partial \phi}$

$$\hat{p} = -i\hbar\frac{\partial}{\partial x}$$

$$\frac{1}{-i} = i$$

For anything you want to know (and are allowed to know), there is an operator, the procedure is always the same to get the information out of the wave function that represents your problem, just let the correct operator loose on it, it's that simple

Only three operators are fundamental

If you need an operator, make it up from the classical physics equation by replacing x, p, E(t) with their operators

The new operator will have the same functional relationship for the x, p, E(t) operators as the classical physics equation,

example kinetic energy operator

$$KE = \tfrac{1}{2} m v^2 = \frac{p^2}{2m}$$

$$[KE] = K\hat{E} = KE_{op} = \frac{\hat{p}^2}{2m} = \tfrac{1}{2m} \cdot (-i\hbar \frac{\partial}{\partial x}) \cdot (-i\hbar \frac{\partial}{\partial x}) = -\frac{\hbar^2}{2m} \cdot \frac{\partial^2}{\partial x^2}$$

$$x = \hat{x} = [x]$$

Some expectation values are sharp some others fuzzy

Table 6.1 Hypothetical Data Set for Position of a Particle as Recorded in Repeated Trials

Trial	Position (arbitrary units)	Trial	Position (arbitrary units)	Trial	Position (arbitrary units)
1	$x_1 = 2.5$	7	$x_7 = 8.0$	13	$x_{13} = 4.2$
2	$x_2 = 3.7$	8	$x_8 = 6.4$	14	$x_{14} = 8.8$
3	$x_3 = 1.4$	9	$x_9 = 4.1$	15	$x_{15} = 6.2$
4	$x_4 = 7.9$	10	$x_{10} = 5.4$	16	$x_{16} = 7.1$
5	$x_5 = 6.2$	11	$x_{11} = 7.0$	17	$x_{17} = 5.4$
6	$x_6 = 5.4$	12	$x_{12} = 3.3$	18	$x_{18} = 5.3$

$$\overline{x} = <x>$$

$$\neq \hat{x} = [x]$$

How operators are typically written

$$x = \hat{x} = [x]$$

$$\overline{x} = \frac{(2.5 + 3.7 + 1.4 + \cdots + 5.4 + 5.3)}{18} = 5.46$$

$$\langle x \rangle = \int_{-\infty}^{\infty} x |\Psi(x, t)|^2 \, dx$$

Since there is scatter in the actual positions (x), the calculated expectation value will have an uncertainty, fuzziness. (Note that x is its own operator.)

$$\int_{-\infty}^{+\infty} \Psi^* \Psi \, dx = 1$$

Normalizing condition, note its effect !

Some expectation values are sharp some others fuzzy, continued I

In classical physics all observables are sharp.[13]

[13]We discount in this discussion any random errors of measurement. In principle at least, the imprecision resulting from such errors can be reduced to arbitrarily low levels.

standard deviation, σ, of the data, defined as

$$\sigma = \sqrt{\frac{\Sigma(x_i - \overline{x})^2}{N}}$$

$$\sigma = \sqrt{\overline{(x^2)} - (\overline{x})^2}$$

Writing out the square under the radical gives

$$\frac{\Sigma(x_i)^2}{N} - 2(\overline{x})\frac{\Sigma(x_i)}{N} + (\overline{x})^2\Sigma\left(\frac{1}{N}\right) = \overline{(x^2)} - 2(\overline{x})(\overline{x}) + (\overline{x})^2$$
$$= \overline{(x^2)} - (\overline{x})^2$$

x may as well stand for any kind of operator Q

Δx, is often called the *uncertainty* in position $\Delta x = \sqrt{\langle x^2\rangle - \langle x\rangle^2}$

The degree to which particle position is fuzzy is given by the magnitude of Δx;

For any observable, fuzzy or not

$$\Delta Q = \sqrt{\langle Q^2\rangle - \langle Q\rangle^2}$$

If not fuzzy, $\Delta Q = 0$

Because $<Q^2>= <Q>^2$

Eigenvalues of the wavefunctions that solved the Schroedinger equation are never fuzzy. How come?

Some expectation values are sharp some others fuzzy, continued II

- Eigenvalues of operators are always sharp (an actual – physical - measurement may give some variation in the result – random error, but the calculation gives zero (systematic) fuzziness
- Say Q is the Hamiltonian operator

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + U(x)\psi(x) = E\psi(x)$$

$$U(x) = \hat{U} = [U] = \hat{V} = [V]$$

A wave function that solves this equation is an eigenfunction of this operator, E is the corresponding eigenvalue, apply this operator twice and you get E^2 – which sure is the same as squaring to result of applying it once (E)

[14]The eigenvalue problem for any operator $[Q]$ is $[Q]\psi = q\psi$; that is, the result of the operation $[Q]$ on some function ψ is simply to return a multiple q of the same function. This is possible only for certain special functions ψ, the *eigenfunctions*, and then only for certain special values of q, the *eigenvalues*. Generally, $[Q]$ is known; the eigenfunctions and eigenvalues are found by imposing the eigenvalue condition.

So if the time independent potential energy operator acts to confine a particle of mass *m*, we will have a discrete set of stationary states with total energies, E_1, E_2, ..

Free to move, persist to exist, so it must be a standing wave, interference of two moving particles, let's consider it $\psi(x)$ as V is not V(t)

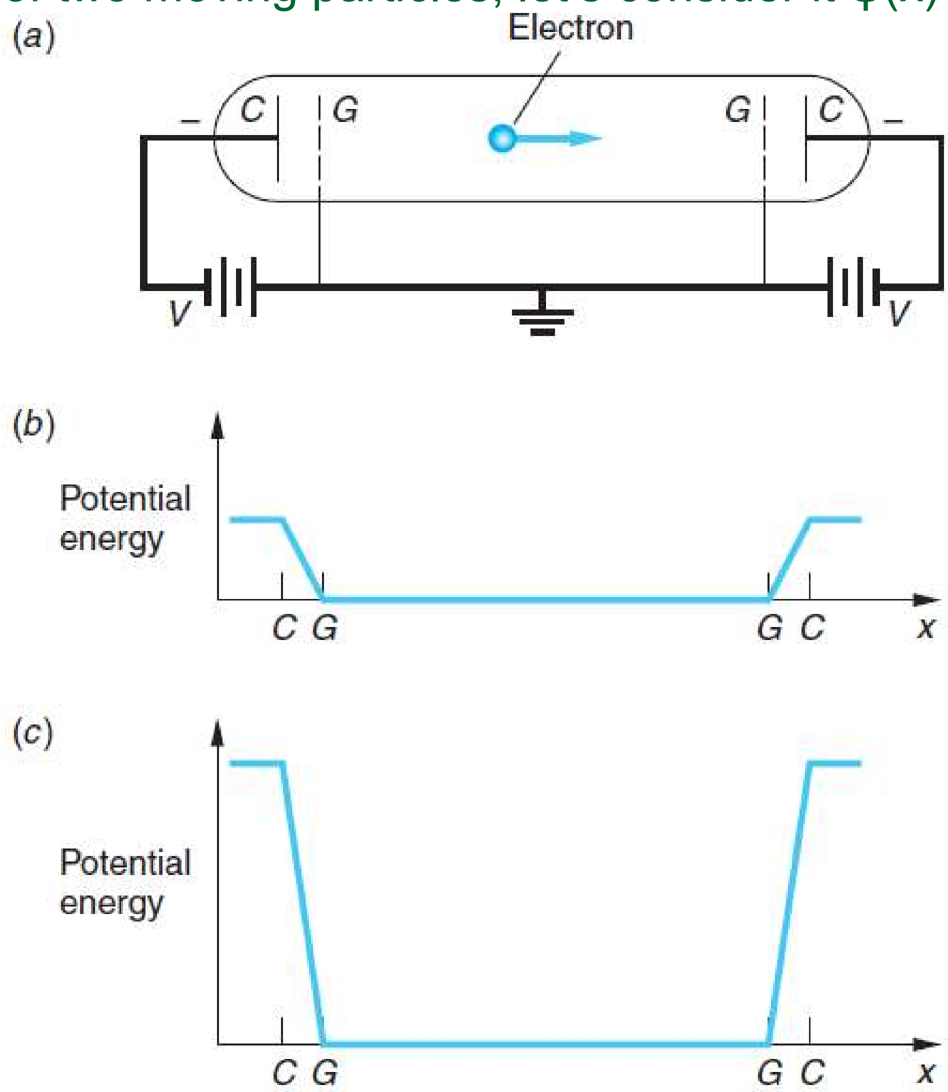


Figure 6-1 (*a*) The electron placed between the two sets of electrodes *C* and grids *G* experiences no force in the region between the grids, which are at ground potential. However, in the regions between each *C* and *G* is a repelling electric field whose strength depends upon the magnitude of *V*. (*b*) If *V* is small, then the electron's potential energy versus *x* has low, sloping "walls." (*c*) If *V* is large, the "walls" become very high and steep, becoming infinitely high for $V \to \infty$.

If distance C to G is very short and voltage very high an infinitely deep square well will model this experiment pretty well, introduced in last chapter

Physical boundary condition particle in box

- Boundary conditions of the potential dictate that the wave function must be zero at $x = 0$ and $x = L$. This yields valid solutions for integer values of n such that $kL = n\pi$.

$$k_n = 2\pi/\lambda_n$$

an integral number of half wavelengths fit into the length L

- The wave function is $$\psi_n(x) = A\sin\left(\frac{n\pi x}{L}\right) \qquad n\frac{\lambda}{2} = L \qquad n = 1, 2, 3, \ldots$$
- We normalize the wave function

$$\int_{-\infty}^{\infty} \psi_n^*(x)\psi_n(x)\,dx = 1 \qquad A^2 \int_0^L \sin^2\left(\frac{n\pi x}{L}\right) dx = 1$$

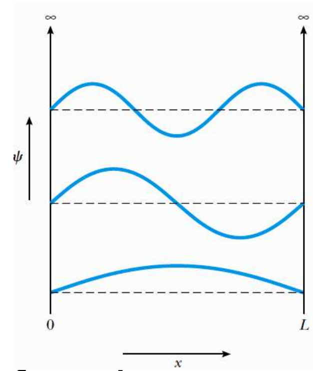
- The normalized wave function becomes
- $$\psi_n(x) = \sqrt{\frac{2}{L}}\sin\left(\frac{n\pi x}{L}\right)$$
- These functions are identical to those obtained for a vibrating string with fixed ends (we could as well have solved the Helmholtz equation)

We obtain E_n either from the solution to the Schrödinger equation with U(x) = 0 as eigenvalues, all expectation values are calculated by the procedure with the corresponding operators from the wave functions for the different states

6.3: Infinite Square-Well Potential

- a particle trapped in a box with "infinitely hard" walls that the particle cannot penetrate. This potential is called an infinite square well and is given by

$$V(x) = \begin{cases} \infty & x \le 0, x \ge L \\ 0 & 0 < x < L \end{cases} \qquad n\frac{\lambda}{2} = L \qquad n = 1, 2, 3, \ldots$$



- Clearly the wave function must be zero where the potential is infinite,

there will be infinitely many E_n eigenvaules with their matching eigenfunctions

- Where the potential energy is zero inside the box, the Schrödinger equation becomes

$$\frac{d^2\psi}{dx^2} = -\frac{2mE}{\hbar^2}\psi = -k^2\psi$$

where $k = \sqrt{2mE/\hbar^2}$. $k = 2\pi/\lambda$

- The general solution is

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

$$\sin(k_n x) = \frac{e^{ik_n x} - e^{-ik_n x}}{2i}$$

B = 0, as just the sine term will do $\qquad k_n = 2\pi/\lambda_n$

Note that this wave function is real because we are considering a standing wave, that is the sum (interference) of two waves moving in opposite directions

Hamiltonian operator is just kinetic energy operator for this particular zero-potential (no force inside the infinitely deep well with infinitely wide barriers)

Wavefunction

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

It's also an eigenfunction of both the total energy operator and the Hamiltonian

that passes the Schrödinger equation test corresponds to a meaningful physical scenario in which kinetic (and total) energy is conserved

Let's derive the formulae for the kinetic energy (which is an observable) - so we apply the kinetic energy operator to the physically meaningful wavefunciton

$$-\frac{\hbar^2}{2m} \cdot \frac{d^2\psi_n(x)}{dx^2} = -\frac{\hbar^2}{2m} \cdot \frac{n\pi}{L} \cdot \frac{n\pi}{L} \cdot -1 \cdot \sqrt{\frac{2}{L}} \sin(\frac{n\pi x}{L})$$

$$= E_n \cdot \sqrt{\frac{2}{L}} \sin(\frac{n\pi x}{L})$$

From E_n we move to k_n $\quad k = \sqrt{2mE/\hbar^2}$

We could also have derived this formula over the expectation value approach

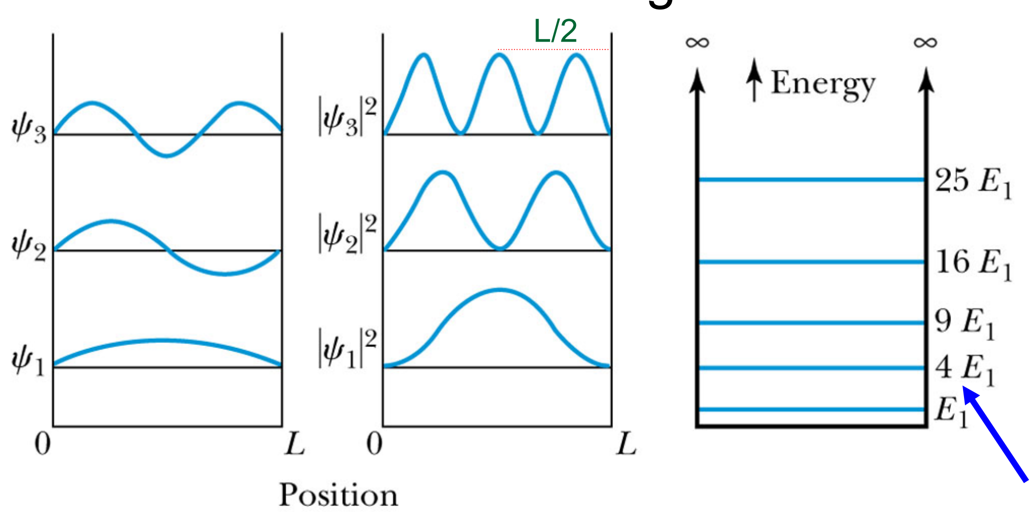
Quantized Energy

- The quantized wave number now becomes $k_n = \frac{n\pi}{L} = \sqrt{\frac{2mE_n}{\hbar^2}}$
- Solving for the total energy (in this case all kinetic) yields

$$E_n = n^2 \frac{\pi^2 \hbar^2}{2mL^2} \qquad (n = 1, 2, 3, \ldots)$$

Remember the nπ/L term twice in the product on last slide

- Note that the energy depends on the integer values of *n*. Hence the energy is quantized and nonzero for the ground state.
- The special case of *n* = 1 is called the ground state energy. $E_1 = \frac{\pi^2 \hbar^2}{2mL^2}$



Ground state energy, zero point energy, there is no n = 0 for this potential energy distribution

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same sequence as in the Bohr model

There is an infinite number of energy levels, because the potential barrier is infinitely high, only an approximation, more like a model (limit) to think about

EXAMPLE 6.5 Energy Quantization for a Macroscopic Object

A small object of mass 1.00 mg is confined to move between two rigid walls separated by 1.00 cm. (a) Calculate the minimum speed of the object. (b) If the speed of the object is 3.00 cm/s, find the corresponding value of n.

Solution Treating this as a particle in a box, the energy of the particle can only be one of the values given by Equation 6.17, or

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

The minimum energy results from taking $n = 1$. For $m = 1.00$ mg and $L = 1.00$ cm, we calculate

$$E_1 = \frac{(6.626 \times 10^{-34}\ \mathrm{J\cdot s})^2}{8.00 \times 10^{-10}\ \mathrm{kg\cdot m^2}} = 5.49 \times 10^{-58}\ \mathrm{J}$$

Because the energy is all kinetic, $E_1 = mv_1^2/2$ and the minimum speed v_1 of the particle is

$$v_1 = \sqrt{2(5.49 \times 10^{-58}\ \mathrm{J})/(1.00 \times 10^{-6}\ \mathrm{kg})}$$
$$= 3.31 \times 10^{-26}\ \mathrm{m/s}$$

This speed is immeasurably small, so that for practical purposes the object can be considered to be at rest. Indeed, the time required for an object with this speed to move the 1.00 cm separating the walls is about 3×10^{23} s, or about 1 million times the present age of the Universe! It is reassuring to verify that quantum mechanics applied to macroscopic objects does not contradict our everyday experiences.

If, instead, the speed of the particle is $v = 3.00$ cm/s, then its energy is

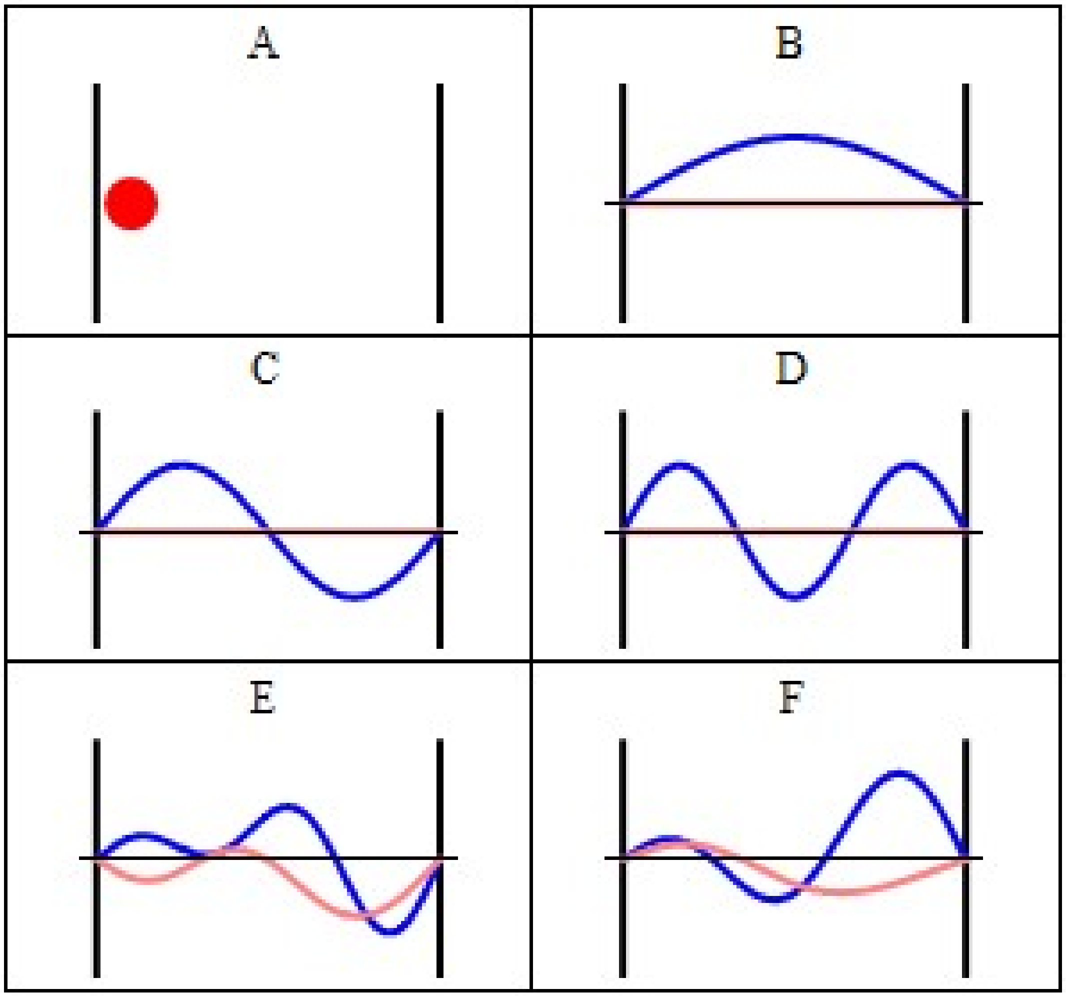
$$E = \frac{mv^2}{2} = \frac{(1.00 \times 10^{-6}\ \mathrm{kg})(3.00 \times 10^{-2}\ \mathrm{m/s})^2}{2}$$
$$= 4.50 \times 10^{-10}\ \mathrm{J}$$

This, too, must be one of the special values E_n. To find which one, we solve for the quantum number n, obtaining

$$n = \frac{\sqrt{8mL^2E}}{h}$$
$$= \frac{\sqrt{(8.00 \times 10^{-10}\ \mathrm{kg\cdot m^2})(4.50 \times 10^{-10}\ \mathrm{J})}}{6.626 \times 10^{-34}\ \mathrm{J\cdot s}}$$
$$= 9.05 \times 10^{23}$$

Niels Bohr’s correspondence principle

http://en.wikipedia.org/wiki/Particle_in_a_box



$$\psi_n(x,t) = \begin{cases} A\sin(k_n x)e^{-i\omega_n t}, & 0 \\ 0 & \text{ot} \end{cases}$$

$$k_n = \frac{n\pi}{L}, \quad \text{where} \quad n = \{1,2,3$$

$$E_n = \frac{n^2\hbar^2\pi^2}{2mL^2} =$$

$$\sin(k_n x) = \frac{e^{ik_n x} - e^{-ik_n x}}{2i}$$

$$E = \hbar\omega = \frac{\hbar^2}{2}$$

no potential energy in this scenario, there is a discrete set of wave numbers since an integral number of half-wavelength need to fit into the box. Infinitely many states.

for any kind of other calculation normalize

$$|A| = \sqrt{}$$

Some “trajectories” of a particle in a box (infinite square well/ infinitely deep well) according to Newton's laws of classical mechanics (A), and according to the Schrödinger equation of quantum mechanics. In (B-F), the horizontal axis is position, and the vertical axis is the real part (blue) and imaginary part (red) of the wavefunction. The states (B,C,D) are energy eigenstates, but (E,F) are not.

Normalization, to set the scale of a wave function

$$\int_{-\infty}^{+\infty} \Psi^*\Psi \, dx = 1$$

The integral is evaluated with the help of the trigonometric identity $2\sin^2\theta = 1 - \cos 2\theta$:

$$\int_0^L \sin^2\left(\frac{n\pi x}{L}\right) dx = \frac{1}{2}\int_0^L [1 - \cos(2n\pi x/L)]\, dx$$

Only the first term contributes to the integral, because the cosine integrates to $\sin(2n\pi x/L)$, which vanishes at the limits 0 and L. Thus, normalization requires $1 = A^2L/2$, or

$$A = \sqrt{\frac{2}{L}} \tag{6.19}$$

EXAMPLE 6.7 Probabilities for a Particle in a Box

A particle is known to be in the ground state of an infinite square well with length L. Calculate the probability that this particle will be found in the middle half of the well, that is, between $x = L/4$ and $x = 3L/4$.

Solution The probability density is given by $|\psi_n|^2$ with $n = 1$ for the ground state. Thus, the probability is

$$P = \int_{L/4}^{3L/4} |\psi_1|^2\, dx = \left(\frac{2}{L}\right)\int_{L/4}^{3L/4} \sin^2(\pi x/L)\, dx$$

$$= \left(\frac{1}{L}\right)\int_{L/4}^{3L/4} [1 - \cos(2\pi x/L)]\, dx$$

$$= \left(\frac{1}{L}\right)\left[\frac{L}{2} - \left(\frac{L}{2\pi}\right)\sin(2\pi x/L)\Big|_{L/4}^{3L/4}\right]$$

$$= \frac{1}{2} - \left(\frac{1}{2\pi}\right)[-1 - 1] = 0.818\ldots$$

Notice that this is considerably larger than $\frac{1}{2}$, which would be expected for a classical particle that spends equal time in all parts of the well.

if we had not used a normalized wave function, the probability of finding the particle in the box would not be unity, and we would not have obtained our ~ 81.8% result about 1.7 percent

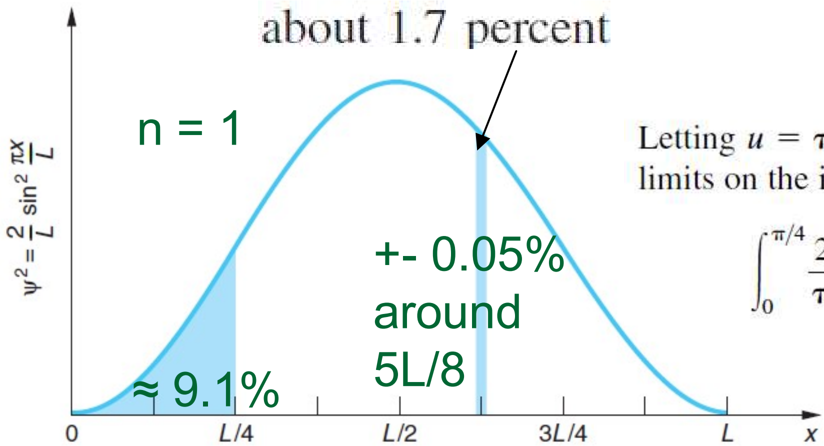


Figure 6-6 The probability density $\psi^2(x)$ versus x for a particle in the ground state of an infinite square well potential. The probability of finding the particle in the region $0 < x < L/4$ is represented by the larger shaded area. The narrow shaded band illustrates the probability of finding the particle within $\Delta x = 0.01L$ around the point where $x = 5L/8$.

$$\int_0^{L/4} P_1(x)\,dx = \int_0^{L/4} \frac{2}{L}\sin^2\left(\frac{\pi x}{L}\right) dx$$

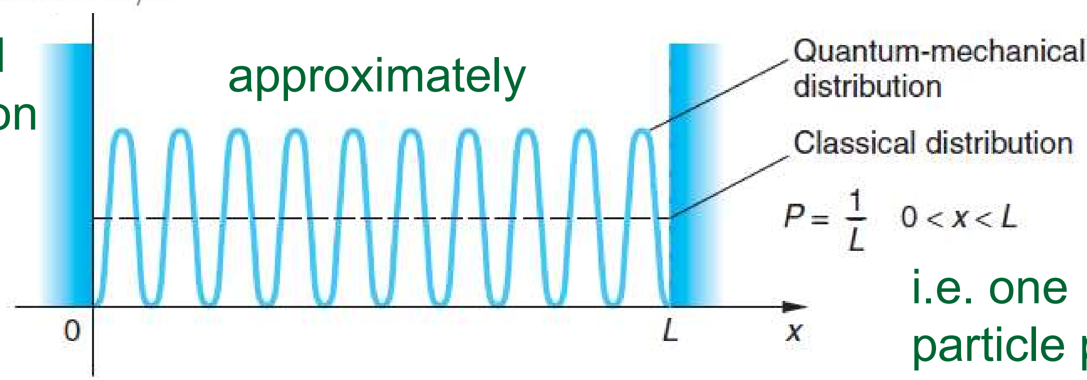
Letting $u = \pi x/L$, hence $dx = L\,du/\pi$, and noting the appropriate change in the limits on the integral, we have that

$$\int_0^{\pi/4} \frac{2}{\pi}\sin^2 u\,du = \frac{2}{\pi}\left(\frac{u}{2} - \frac{\sin 2u}{4}\right)\Bigg|_0^{\pi/4} = \frac{2}{\pi}\left(\frac{\pi}{8} - \frac{1}{4}\right) = 0.091$$

The lowest quantum states, smallest *n* are those that give results which are far from what one would expect from classical physics

If Δx <= 1% L ≈ dx, no need to integrate for approximation

approximately



Number of "wiggles" of ψ^2 = n

i.e. one particle per L

Bohr's correspondence principle

Figure 6-5 Probability distribution for $n = 10$ for the infinite square well potential. The dashed line is the classical probability density $P = 1/L$, which is equal to the quantum-mechanical distribution averaged over a region Δx containing several oscillations. A physical measurement with resolution Δx will yield the classical result if n is so large that $\psi^2(x)$ has many oscillations in Δx.

Equal and constant probability density for classical particle, in case *n* is going to infinity

Probability density of finding the particle in the second exited state at x = $^1/_6$ L and $^1/_3$ L

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

n = 3

$$\Psi^* \Psi = \psi^2(x)(e^{i\omega t} e^{-i\omega t})$$

$$\Psi^* \Psi = \psi^2(x)$$

$$P(x)\, \cancel{dx} = \Psi^*(x,t)\Psi(x,t)\, \cancel{dx}$$

$$\sqrt{\frac{2}{L}} \sin\left(\frac{3\pi \cdot {}^1\!/_6 L}{L}\right) \cdot \sqrt{\frac{2}{L}} \sin\left(\frac{3\pi \cdot {}^1\!/_6 L}{L}\right) = \frac{2}{L} = \max$$

Twice as high as classically expected, strange

$$\sqrt{\frac{2}{L}} \sin\left(\frac{3\pi \cdot {}^1\!/_3 L}{L}\right) \cdot \sqrt{\frac{2}{L}} \sin\left(\frac{3\pi \cdot {}^1\!/_3 L}{L}\right) = 0 = \min$$

classically not expected, but it is not classical particles we are dealing with !!

Why divided by L (dimension reciprocal meter) ?

Obviously because they are probability densities !!

Probability of finding the particle in the second exited state in an x = +-$^1/_{1000}$ L segment centered around $^1/_6$ L and $^1/_3$ L

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

n = 3

$$\Psi^* \Psi = \psi^2(x)(e^{i\omega t} e^{-i\omega t})$$

$$\Psi^* \Psi = \psi^2(x)$$

$$P(x)\,dx = \Psi^*(x,t)\Psi(x,t)\,dx$$

this time, let's do the integrals

$$P = \int_{x1=(\frac{1}{6}-\frac{1}{1000})L}^{x2=(\frac{1}{6}+\frac{1}{1000})L} \sqrt{\frac{2}{L}} \sin\left(\frac{3\pi \cdot x_{in\_units\_of\_L}}{L}\right) \cdot \sqrt{\frac{2}{L}} \sin\left(\frac{3\pi \cdot x_{in\_units\_of\_L}}{L}\right) \cdot dx = ?$$

What will be the dimension?

$$P = \frac{2}{L} \int_{\frac{1}{3}L-\frac{1}{1000}L}^{\frac{1}{3}L+\frac{1}{1000}L} \sin^2\left(\frac{3\pi \cdot x_{in\_units\_of\_L}}{L}\right) \cdot dx = \frac{2}{L} \cdot \left\{\frac{x_{in\_units\_of\_L}}{2} - \frac{L}{6\pi} \cdot \sin(\ldots)\right\} \Big|_{\frac{1}{3}L-\frac{1}{1000}L}^{\frac{1}{3}L+\frac{1}{1000}L}$$

Sure these results must be dimensionless as they are probabilities, smaller than 1 or (smaller than 100%) due to normalization

Sure, if the region/segment for which we want to calculate the probability of finding the particle there is very small, we can expand dx to Δx and obtain an approximate result (and get rid of dx that way, but beware P(x) ‡ 0 for sensible results

$$P = P(x)\,\Delta x = \frac{2}{L}\sin^2\frac{\pi x}{L}\Delta x$$

n is set 1 here, but sure that is not a precondition for the approximation to work

At the previous example, $\Delta x = {}^{2}/_{1000}$ L, for n = 3, and at x = ${}^{1}/_{6}$ L and ${}^{1}/_{3}$ L

$$P_{segment}\cdot\Delta x = \sqrt{\frac{2}{L}}\sin\left(\frac{3\pi\cdot {}^{1}/_{6}L}{L}\right)\cdot\sqrt{\frac{2}{L}}\sin\left(\frac{3\pi\cdot {}^{1}/_{6}L}{L}\right)\cdot\Delta x = \frac{2}{L}\cdot 1\cdot 1\cdot 0.002L = 0.4\%$$

Too large by only ≈1.2 10^{-5} %

Sure it is a very small segment of L for which we want to know the probability of finding the particle. For this very small segment, the probability of finding the quantum mechanical particle is quite high !

$$P_{segment}\cdot\Delta x = \sqrt{\frac{2}{L}}\sin\left(\frac{3\pi\cdot {}^{1}/_{3}L}{L}\right)\cdot\sqrt{\frac{2}{L}}\sin\left(\frac{3\pi\cdot {}^{1}/_{3}L}{L}\right)\cdot\Delta x = \frac{2}{L}\cdot 0\cdot 0.002L = 0$$

Instead of ≈ 1.2 10^{-5} %

Sure this approximation doesn't make sense if the probability density on which it is based is actually zero, there will nevertheless be a very small probability of finding the particle there when the integral is done

$$P_{1_{ab}} = \frac{2}{L}\int_a^b \sin^2\left(\frac{\pi x}{L}\right)dx$$

$$\approx \frac{2}{L}\int_a^b \sin^2\left(\frac{\pi(a+b)}{2L}\right)dx$$

$$\approx \frac{2}{L}\sin^2\left(\frac{\pi(a+b)}{2L}\right)x\Big|_a^b$$

dx → Δx

For Δx = +- 0.01 L example around x = 5/8 L with n = 1 (given as index of P), take the average of the two limiting values

$$\int_a^b A\cdot dx = A\cdot\int_a^b dx = A\cdot x\,\Big|_a^b$$

$$P_{1_{\frac{5L}{8}\pm\frac{L}{100}}} \approx \frac{2}{L}\sin^2\left(\frac{5\pi}{8}\right)x\Big|_{\frac{5L}{8}-\frac{L}{100}}^{\frac{5L}{8}+\frac{L}{100}}$$

$$\approx 2\sin^2\left(\frac{5\pi}{8}\right)\frac{2}{100}$$

$$\approx 3.41421\%$$

Solved integral, exact solution

$$P_{1_{\frac{5L}{8}\pm\frac{L}{100}}} = \frac{1}{L}\left[x - \frac{L}{2\pi}\sin\left(\frac{2\pi x}{L}\right)\right]_{\frac{5L}{8}-\frac{L}{100}}^{\frac{5L}{8}+\frac{L}{100}}$$

$$= \frac{2}{100} - \frac{1}{2\pi}\sin\left(\frac{5\pi}{4}+\frac{2\pi}{100}\right) + \frac{1}{2\pi}\sin\left(\frac{5\pi}{4}-\frac{2\pi}{100}\right)$$

$$\approx 3.41328\%$$

So a pretty good approximation, physics is the art of knowing which theory and approximation to use for a given problem

Find the probability that a particle trapped in a box L wide can be found between $0.45L$ and $0.55L$ for the ground and first excited states.

Solution

This part of the box is one-tenth of the box's width and is centered on the middle of the box (Fig. 5.6). Classically we would expect the particle to be in this region 10 percent of the time. Quantum mechanics gives quite different predictions that depend on the quantum number of the particle's state. From Eqs. (5.2) and (5.46) the probability of finding the particle between x_1 and x_2 when it is in the nth state is

$$P_{x_1,x_2} = \int_{x_1}^{x_2} |\psi_n|^2 \, dx = \frac{2}{L} \int_{x_1}^{x_2} \sin^2 \frac{n\pi x}{L} \, dx$$

$$= \left[\frac{x}{L} - \frac{1}{2n\pi} \sin \frac{2n\pi x}{L} \right]_{x_1}^{x_2}$$

Here $x_1 = 0.45L$ and $x_2 = 0.55L$. For the ground state, which corresponds to $n = 1$, we have

$$P_{x_1,x_2} = 0.198 = 19.8 \text{ percent}$$

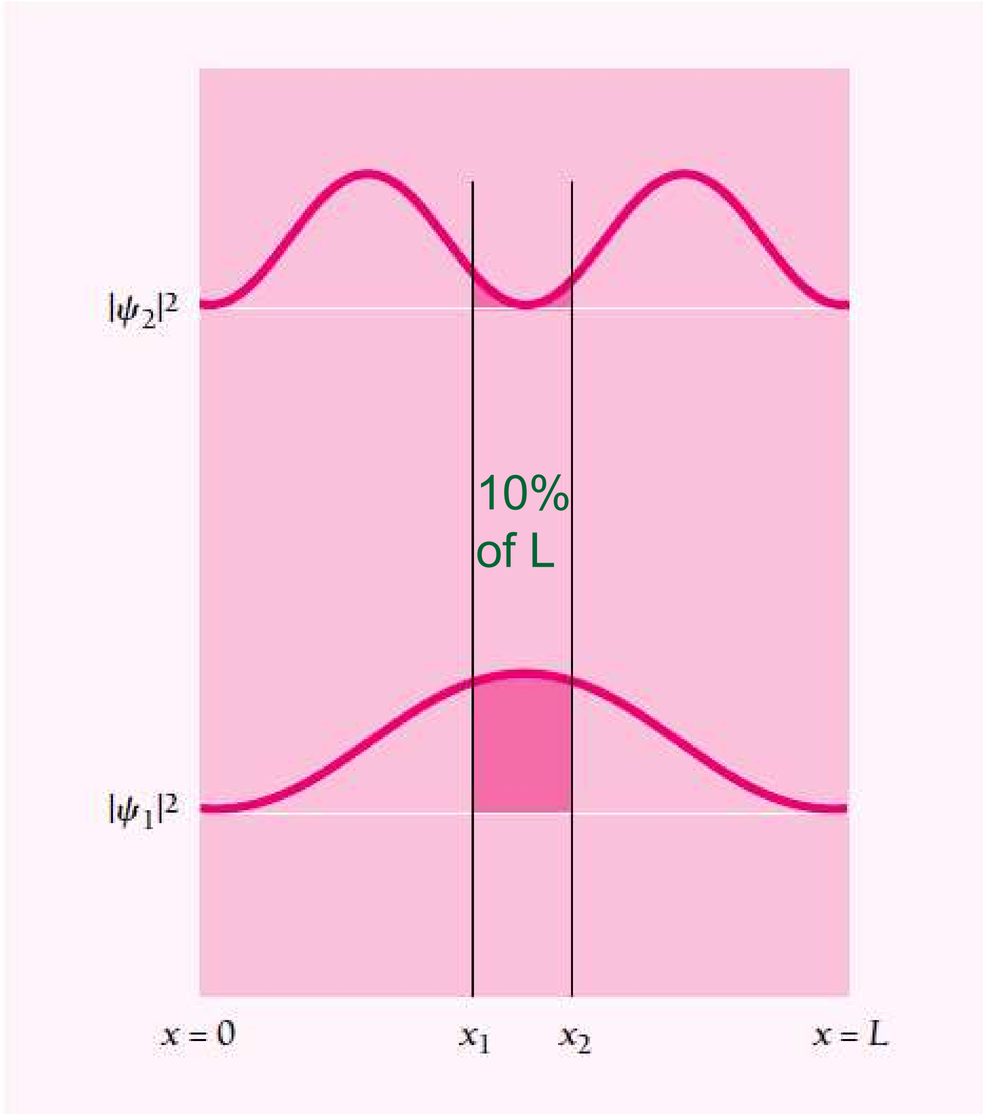
Approximation from last slide would give 20%

This is about twice the classical probability. For the first excited state, which corresponds to $n = 2$, we have

$$P_{x_1,x_2} = 0.0065 = 0.65 \text{ percent}$$

This low figure is consistent with the probability density of $|\psi_n|^2 = 0$ at $x = 0.5L$.

Visualization of calculation in previous slides



At point x = 0.5 L for n = 1, quantum probability density is twice as high (2/L) as classical probability density (1/L)
So for a +- 5% of L wide region around x = 0.5 L, we should expect something less than 20%

– **Figure 5.6** The probability P_{x_1,x_2} of finding a particle in the box of Fig. 5.5 between $x_1 = 0.45L$ and $x_2 = 0.55L$ is equal to the area under the $|\psi|^2$ curves between these limits.

Important difference: expectation value of x and probability density of finding the particle at x or (in region around x)

- Take the first exited state, n = 2, wavefunction has node (zero amplitude) at the middle of the box, so particle can never be found there …

$$\psi_2 = \sqrt{\frac{2}{L}}\sin(\frac{2\pi x}{L})$$

for x = ½ L

$$\psi_2 = \sqrt{\frac{2}{L}}\sin(\frac{2\pi x}{L}) = \sqrt{\frac{2}{L}}\sin(\frac{2\pi \frac{1}{2} L}{L}) = 0$$

No need to do an integral as we asked just for finding the particle at one specific position

$$P_{0.5L} = \psi_2 {}^* \psi_2 = \{\sqrt{\frac{2}{L}}\sin(\frac{2\pi x}{L})\}^2 = \frac{2}{L}\sin^2(\frac{2\pi \frac{1}{2} L}{L}) = 0$$

- BUT, what is the expectation value of x (independent of position and time)?

$$< x >_{n=2} = \frac{2}{L}\int_0^L \sin(\frac{2\pi x}{L}) \cdot x \cdot \sin(\frac{2\pi x}{L}) \cdot dx = \frac{L}{2}$$

Sure, we expect to find the particle on average (most often) in the middle of the box

What would have happened if our wavefunction was not normalized? We simply got a “quite useless result” that is only proportional to $L/_2$ with an **unknown factor of probability**

Given the stationary wave functions

$$\psi_n(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right) e^{-i\omega_n t}$$

$$k_n = \frac{n\pi}{L} = \sqrt{\frac{2mE_n}{\hbar^2}}$$

EXAMPLE 6-5 Expectation Values for p and p^2 Find $\langle p \rangle$ and $\langle p^2 \rangle$ for the ground-state wave function of the infinite square well. (Before we calculate them, what do you think the results will be?)

lets do it for all states

$$\sin(k_n x) = \frac{e^{ik_n x} - e^{-ik_n x}}{2i}$$

SOLUTION

Note misprints in Tippler/Lewellyn !!

We can ignore the time dependence of Ψ, in which case we have

$$\langle p \rangle = \int_0^L \left(\sqrt{\frac{2}{L}} \sin\frac{nx}{L}\right)\left(\frac{\hbar}{i}\frac{\partial}{\partial x}\right)\left(\sqrt{\frac{2}{L}} \sin\frac{nx}{L}\right) dx$$

π

n = 1

$$= \frac{\hbar}{i}\frac{2}{L}\frac{\pi}{L}\int_0^L \sin\frac{\pi x}{L}\cos\frac{\pi x}{L}\,dx = 0$$

No surprise, momentum is a vector, goes back and forth with same value but different sign

The particle is equally as likely to be moving in the $-x$ as in the $+x$ direction, so its *average* momentum is zero.

Similarly, since

n² n

$$\frac{\hbar}{i}\frac{\partial}{\partial x}\left(\frac{\hbar}{i}\frac{\partial}{\partial x}\right)\psi = -\hbar^2\frac{\partial^2\psi}{\partial x^2} = -\hbar^2\left(-\frac{\pi^2}{L^2}\sqrt{\frac{2}{L}}\sin\frac{\pi x}{L}\right)$$

$$= +\frac{\hbar^2\pi^2}{L^2}\psi \quad n^2$$

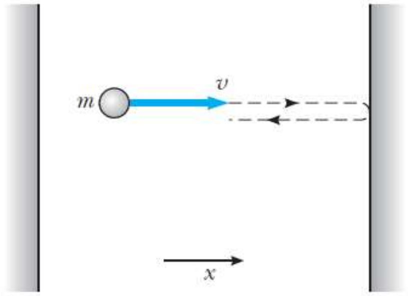


Figure 6.5 A particle of mass m and speed v bouncing elastically between two impenetrable walls.

Take the square root of this and you have the magnitude of the momentum

we have

n²

$$\langle p^2 \rangle = \frac{\hbar^2\pi^2}{L^2}\int_0^L \psi^*\psi\,dx = \frac{\hbar^2\pi^2}{L^2}\,n^2$$

$$\Delta Q = \sqrt{\langle Q^2 \rangle - \langle Q \rangle^2}$$

square of momentum is related to kinetic energy ≠ 0, momentum has a spread due to uncertainty principle !!

So is p sharp?

$2^2 = n^2$

$$\Delta p_{n=2} = \sqrt{(<p^2> - <p>^2} = \sqrt{\frac{4\pi^2\hbar^2}{L^2} - 0}$$

Nope, just look at the result of the calculation

full result for all n: $\bar{p}$ = <p> = 0 ± $|\vec{p}|$ = 0 ± sqroot <p^2>

which is of course just a statement of the uncertainty principle

$$\Delta x_2 \Delta p_2 \geq \frac{\hbar}{2}$$

For n = 2

$$\Delta x_2 = \sqrt{\langle x^2 \rangle_2 - \langle x \rangle_2^2}$$

$$\approx \sqrt{0.3207L^2 - \left(\frac{L}{2}\right)^2}$$

$$\approx 0.2658L$$

$$0.2658L \frac{2\pi\hbar}{L} \geq \frac{\hbar}{2}$$

The "stronger" the confinement, i.e. smaller L, the larger the uncertainty in x on the other hand, the "weaker" the confinement the less uncertainty of momentum

Must p^2 be sharp?

absolutely, because p^2 = KE times 2m, no potential energy in the infinitely deep square well, so KE must be sharp (one value for each *n* only without any spread) because total E is sharp

$$\Delta p^2 = \sqrt{(< p^4 > - < p^2 >^2} = 0$$

Remember, our wave function solved the Schroedinger equation

$$\Delta(KE \cdot 2m) = \sqrt{< (KE \cdot 2m)^2 > - < (KE \cdot 2m) >^2} = 0$$

It is, therefore, an eigenfunction of the Hamiltonian operator, which is in this case just the kinetic energy operator,

Each time the kinetic energy operator operates on an eigenfunction, it returns the unchanged eigenfunction multiplied by the eigenvalue,

$$\sin(k_n x) = \frac{e^{ik_n x} - e^{-ik_n x}}{2i}$$

sine wave function can be replaced by “sum” of two complex wave functions divided by 2 *i*, these wave functions are actually the eigenfunctions of the momentum operator

$$\hat{p} = -i\hbar \frac{\partial}{\partial x}$$

as it is a standing wave no time dependency needs to be considered, d/dx

$$i\hbar \frac{\partial}{\partial x} e^{ik_n x} = i\hbar \cdot ik_n e^{ik_n x} = -\hbar k_n e^{ik_n x} = -p_n e^{ik_n x}$$

that’s how we derived that operator earlier

$$(i\hbar \frac{\partial}{\partial x})^2 (e^{ik_n x}) = i^2 \hbar^2 \frac{\partial^2}{\partial x^2} (e^{ik_n x}) = (i\hbar \cdot ik_n)^2 e^{ik_n x} = (-\hbar k_n)^2 e^{ik_n x} = p_n{}^2 e^{ik_n x}$$

Applying the operator to an eigenfunction twice gives you the square of the eigenvalue

---

$<p^2>$ = $\int \psi^* (-i\hbar \frac{d}{dx^2})(-i\hbar \frac{d}{dx^2})\psi \cdot dx$

$$\Delta p^2 = \sqrt{(< p^4 > - < p^2 >^2} = 0$$

kind of result of doing something 4 times is equal of doing it 2^2 times

$<p^4>$ = $\int \psi^* (-i\hbar \frac{d}{dx^2})(-i\hbar \frac{d}{dx^2})(-i\hbar \frac{d}{dx^2})(-i\hbar \frac{d}{dx^2})\psi \cdot dx$

$$e^{-i\omega_n t}$$

Adding this factor or both sides of the wavefunction changes nothing as the partial differential is with respect to x and not t

Momentum eigenvalues for a particle in an infinitely deep well

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

Eigenfunctions of the momentum operator

$$\sin(k_n x) = \frac{e^{ik_n x} - e^{-ik_n x}}{2i}$$

$$\psi_n^+ = \frac{1}{2i}e^{in\pi x/L} \quad \text{and} \quad \psi_n^- = -\frac{1}{2i}e^{-in\pi x/L}$$

$$\hat{p}_n\psi_n^+ = p_n^+\psi_n^+ \quad \text{and} \quad \hat{p}_n\psi_n^- = p_n^-\psi_n^-$$

$$\frac{\hbar}{i}\frac{d}{dx}\psi_n^+ = \frac{\hbar}{i\cdot 2i}\frac{in\pi}{L}e^{in\pi x/L} = \frac{n\pi\hbar}{2iL}\psi_n^+ = p_n^+\psi_n^+ \qquad p_n^+ = \frac{n\pi\hbar}{L}$$

$$\frac{\hbar}{i}\frac{d}{dx}\psi_n^- = -\frac{\hbar}{i\cdot 2i}\frac{in\pi}{L}e^{-in\pi x/L} = -\frac{n\pi\hbar}{2iL}\psi_n^- = p_n^-\psi_n^- \qquad p_n^- = -\frac{n\pi\hbar}{L}$$

Eigenvalues of the momentum operator

Eigenvalues have no spread, a set of discrete values and function of integer n

$$|\vec{p}_n| = \pm\sqrt{2mE_n} = \pm\frac{n\pi\hbar}{L} = \pm k\hbar$$ from boundary conditions $$k_n = \frac{n\pi}{L} = \sqrt{\frac{2mE_n}{\hbar^2}}$$

Because the Schrödinger equation is linear: At any given instant in time, the wave function Ψ of a particle (or an isolated system) can be expressed as a linear superposition of a complete ortho-normal set $\{\Psi_n\}$ of wave functions:

$$\mathbf{\Psi = c_1\,\Psi_1 + c_2\,\Psi_2 + c_3\,\Psi_3 + c_4\,\Psi_4 + \ldots = \Sigma\, c_n\,\Psi_n}$$

Where prefactor $a_n = |c_n|^2$ represents the probability that the system will be found in state Ψ_n

$$\sqrt{2}\sin(k_n x) = \sqrt{2}\left(\frac{e^{ik_n x} - e^{-ik_n x}}{2i}\right) = \frac{\sqrt{2}e^{ik_n x}}{2i} + \frac{-\sqrt{2}e^{-ik_n x}}{2i}$$

$$\left[\sqrt{2}\sin(k_n x)\right]^2 = -\frac{1}{2}\left[e^{ik_n x}\right]^2 + \frac{1}{2}\left[e^{-ik_n x}\right]^2$$

½ = 50 %

So half of the time the system is found with momentum: $p_n^{\,+} = \frac{n\pi\hbar}{L}$

And the other half of the time: $p_n^{\,-} = -\frac{n\pi\hbar}{L}$

Usages of Particles in boxes

A possible application of ion traps that many scientists dream of is the quantum computer. In present-day classical computers the smallest unit of information is a bit that takes the value of either 1 or 0. In a quantum computer, however, the basic unit of information – a quantum bit or qubit – can be 1 and 0 at the same time. Two quantum bits can simultaneously take on four values – 00, 01, 10 and 11 – and each additional qubit doubles the amount of possible states. For n quantum bits there are 2^n possible states, and a quantum computer of only 300 qubits could hold 2^{300} values simultaneously, more than the number of atoms in the universe.

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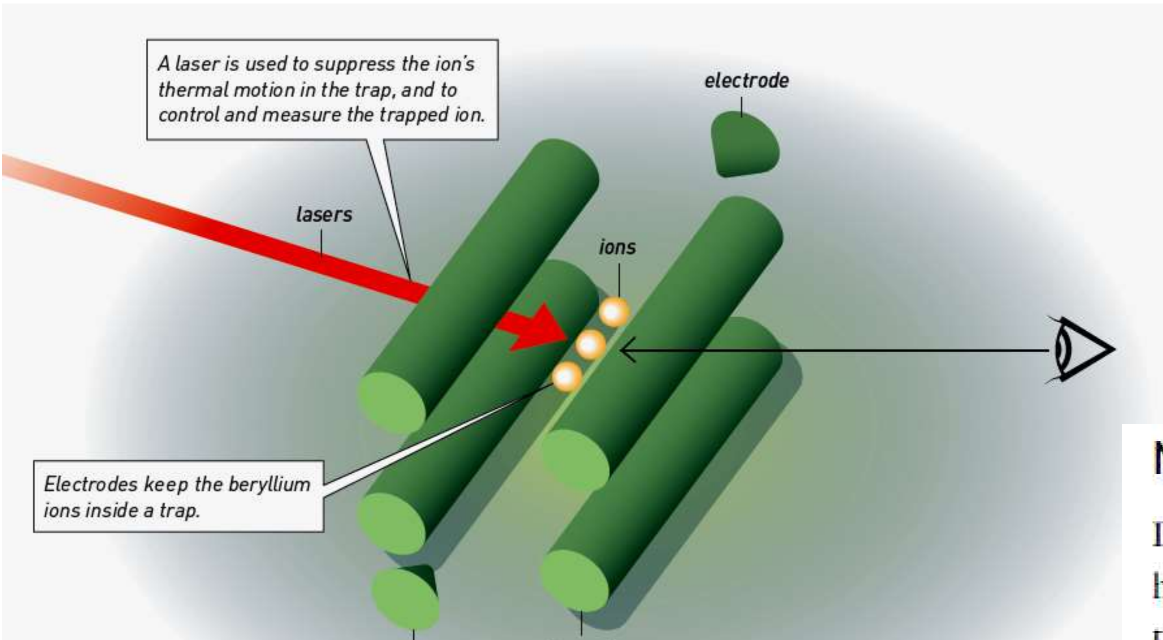
Superposition of states? Let's use it for quantum computing 2012



$$\Psi_n(x,t) = \frac{1}{2i}\sqrt{\frac{2}{L}}\,[e^{i(k_n x - \omega_n t)} - e^{-i(k_n x + \omega_n t)}]$$

Figure 2. In David Wineland's laboratory in Boulder, Colorado, electrically charged atoms or ions are kept inside a trap by surrounding electric fields. One of the secrets behind Wineland's breakthrough is mastery of the art of using laser beams and creating laser pulses. A laser is used to put the ion in its lowest energy state and thus enabling the study of quantum phenomena with the trapped ion.

DAVID J. WINELAND

U.S. citizen. Born 1944 in Milwaukee, WI, USA. Ph.D. 1970 from Harvard University, Cambridge, MA, USA. Group Leader and NIST Fellow at National Institute of Standards and Technology (NIST) and University of Colorado Boulder, CO, USA.

www.nist.gov/pml/div688/grp10/index.cfm

New clocks

David Wineland and his team of researchers have also used ions in a trap to build a clock that is a hundred times more precise than the caesium-based atomic clocks which are currently the standard for our measurement of time. T

Remember general relativity

GPS we rely on time signals from satellites with clocks that are routinely calibrated, because gravity is somewhat weaker several hundred kilometres up in the sky. With an optical clock it is possible to measure a difference in the passage of time when the clocks speed is changed by less than 10 metres per second, or when gravity is altered as a consequence of a difference in height of only 30 centimetres.

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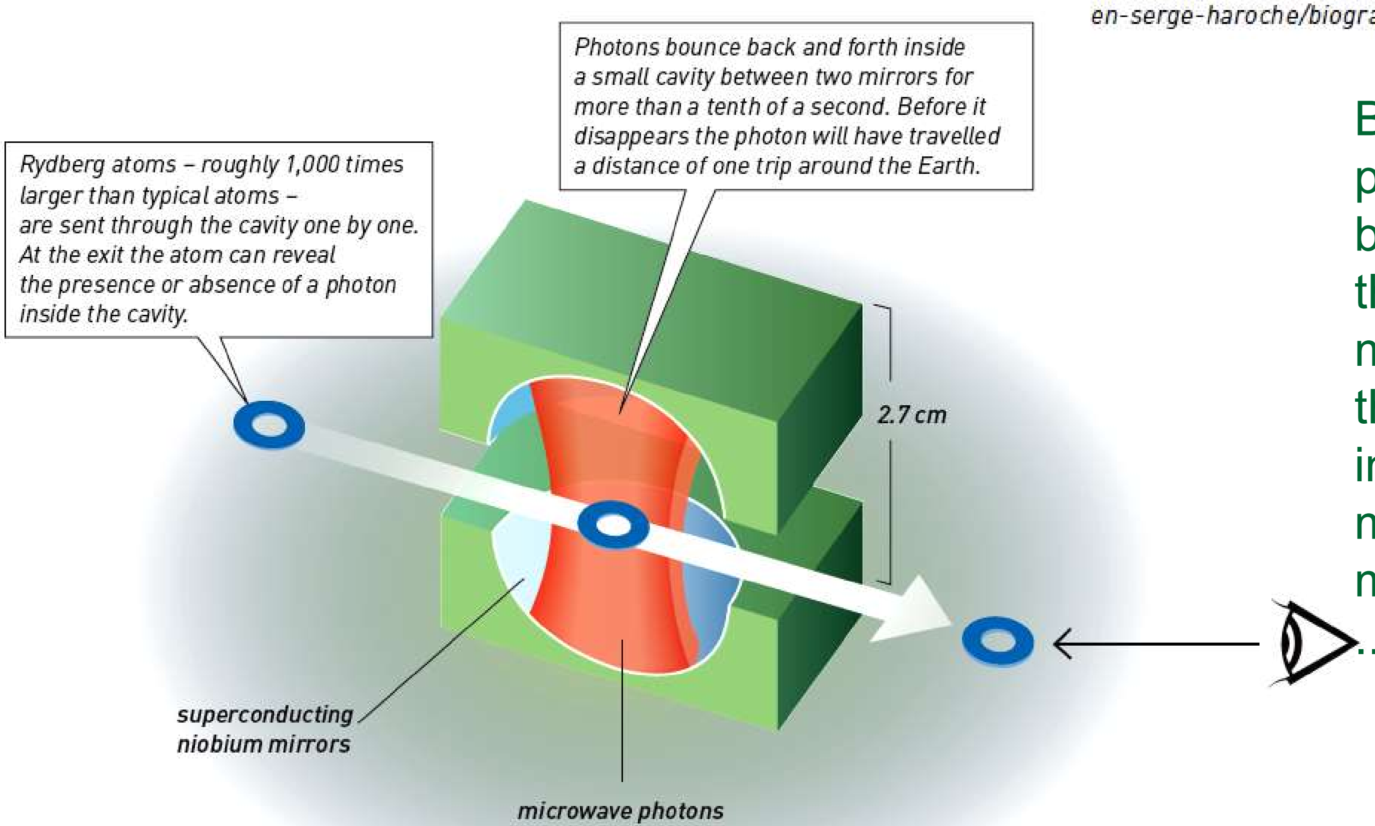
2012

Usages of Particles in a box

SERGE HAROCHE

French citizen. Born 1944 in Casablanca, Morocco. Ph.D. 1971 from Université Pierre et Marie Curie, Paris, France. Professor at Collège de France and Ecole Normale Supérieure, Paris, France.

www.college-de-france.fr/site/en-serge-haroche/biography.htm



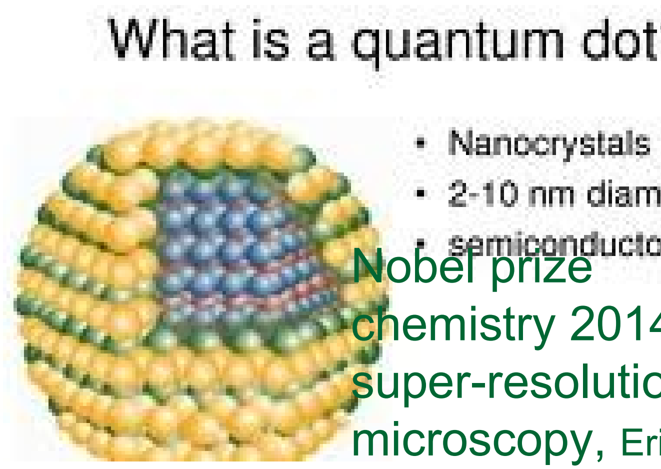
Bringing photons into a box, releasing them and manipulating them there, including measuring how many are there ..

Figure 3. In the Serge Haroche laboratory in Paris, in vacuum and at a temperature of almost absolute zero, the microwave photons bounce back and forth inside a small cavity between two mirrors. The mirrors are so reflective that a single photon stays for more than a tenth of a second before it is lost. During its long life time, many quantum manipulations can be performed with the trapped photon without destroying it.

Quantum Wells

Development of techniques for fabricating devices whose dimensions are of the order of nanometers, called *nanostructures*, has made possible the construction of *quantum wells*. These are finite potential wells of one, two, and three dimensions that can channel electron movement in selected directions. A one-dimensional quantum well is a thin layer of material that confines particles to within the dimension perpendicular to the layer's surface but does not restrict motion in the other two dimensions. In the case of three-dimensional wells, called *quantum dots*, electrons are restricted entirely to quantized energy states within the well. A ubiquitous current application of quantum wells is the diode lasers that read CDs, DVDs, and bar codes. Quantum dots have potential applications in data storage and *quantum computers*, devices that may greatly enhance computing power and speed.

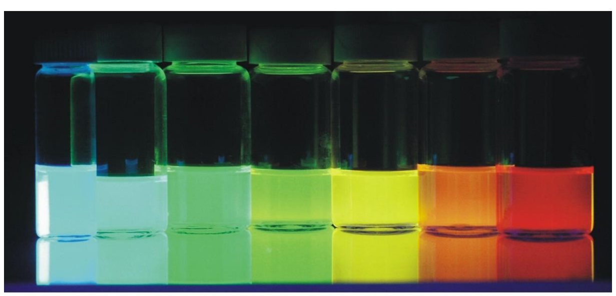
One-dimensional quantum wells, called *quantum wires*, offer the possibility of dramatically increasing the speed that electrons move through a device in selected directions. This in turn would increase the speed with which signals move between circuit elements in computer systems. Figure 6-15 is an outline of how such a well might be formed.



Nobel prize chemistry 2014, super-resolution microscopy, Eric Betzig, Stefan W. Hell, William E. Moerner

Quantum wires

Quantum dots



2.3 → 5.5

Size (nanometers)

CdS_2

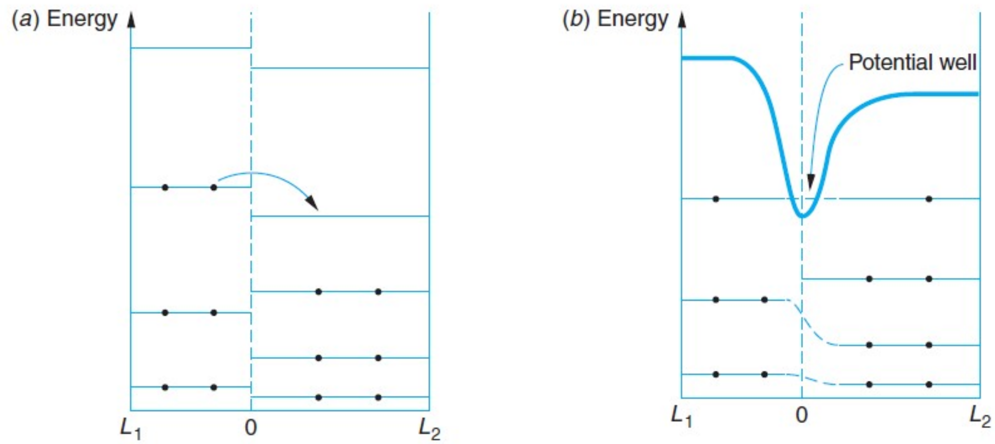


Figure 6-15 (*a*) Two infinite square wells of different widths L_1 and L_2, each containing the same number of electrons, are put together. An electron from well 1 moves to the lowest empty level of well 2. (*b*) The energies of the two highest electrons are equalized, but the unequal charge in the two wells distorts the energy-level structure. The distortion of the lowest empty levels in each well results in a potential well at the junction between the wells. The orientation of the newly formed well is perpendicular to the plane of the figure.

6.5: Three-Dimensional Infinite-Potential Well

- The wave function must be a function of all three spatial coordinates.

  We begin with the conservation of energy $E = K + V = \frac{p^2}{2m} + V$
- Multiply this by the wave function that depends on three spatial variables to get

$$\frac{p^2}{2m}\psi + V\psi = E\psi$$

- Now consider momentum as an operator acting on the wave function. In this case, the operator must act twice on each dimension. Given:

$$p^2 = p_x^{\ 2} + p_y^{\ 2} + p_z^{\ 2}, \text{ and} \quad \hat{p}_x\psi = -i\hbar\frac{\partial\psi}{\partial x} \quad \hat{p}_y\psi = -i\hbar\frac{\partial\psi}{\partial y} \quad \hat{p}_z\psi = -i\hbar\frac{\partial\psi}{\partial z}$$

- The (time independent) three dimensional Schrödinger equation

$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2}\right) + V\psi = E\psi \quad \text{or} \quad -\frac{\hbar^2}{2m}\nabla^2\psi + V\psi = E\psi$$

V = U(x) but not of time

First slide in this chapter

$$\psi(x, y, z) = \psi_1(x)\psi_2(y)\psi_3(z)$$

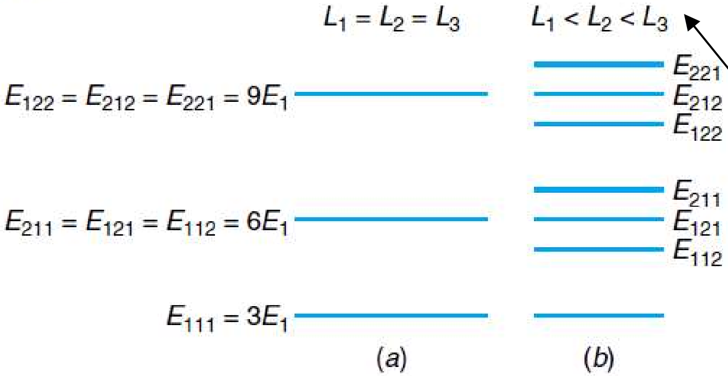
Separation of variables, δ → d

$$\psi(x, y, z) = A \sin k_1 x \sin k_2 y \sin k_3 z \qquad k_i = n_i \pi / L$$

$$E = \frac{\hbar^2}{2m}(k_1^2 + k_2^2 + k_3^2) \qquad E = \frac{(p_x^2 + p_y^2 + p_z^2)}{2m} \qquad p_x = \hbar k_1 \text{ and so forth}$$

Many “things” are there three times, three dimensions, three sine functions, three k, three p, much depends on the “symmetry” of the potential

$$E_{n_1 n_2 n_3} = \frac{\hbar^2 \pi^2}{2mL^2}(n_1^2 + n_2^2 + n_3^2)$$ Cubic box



$$\psi_{211} = A \sin\frac{2\pi x}{L_x} \sin\frac{\pi y}{L_y} \sin\frac{\pi z}{L_z}$$

$$E_{n_1 n_2 n_3} = \frac{\hbar^2 \pi^2}{2m}\left(\frac{n_1^2}{L_1^2} + \frac{n_2^2}{L_2^2} + \frac{n_3^2}{L_3^2}\right)$$

Figure 7-1 Energy-level diagram for (*a*) cubic infinite square well potential and (*b*) noncubic infinite square well. In the cubic well, the energy levels above the ground state are threefold degenerate; i.e., there are three wave functions having the same energy. The degeneracy is removed when the symmetry of the potential is removed, as in (*b*). The diagram is only schematic, and none of the levels in (*b*) necessarily has the same value of the energy as any level in (*a*).

Degeneracy

- Analysis of the Schrödinger equation in three dimensions introduces three quantum numbers that quantize the energy in bound systems in 3D.

- **A quantum state is degenerate when there is more than one wave function** (eigenfunction) **for a given energy** (eigenvalue).

- Degeneracy results from particular ***symmetry*** properties of the potential energy function that describes the system. A perturbation of the potential energy can remove the degeneracy.

  For a cubic box $L_1 = L_2 = L_3$

- Effects of external magnetic field will split spectral lines in atoms, predicted by Hendrik Lorentz, observed by his assistant Pieter Zeeman, joint Nobel prize 1902, mentioned on the introductory slides of several chapters

Table 8.1 Quantum Numbers and Degeneracies of the Energy Levels for a Particle Confined to a Cubic Box*

n_1	n_2	n_3	n^2	Degeneracy
1	1	1	3	None
1	1	2	6	Threefold
1	2	1	6	
2	1	1	6	
1	2	2	9	Threefold
2	1	2	9	
2	2	1	9	
1	1	3	11	Threefold
1	3	1	11	
3	1	1	11	
2	2	2	12	None

**Note:* $n^2 = n_1^2 + n_2^2 + n_3^2$.

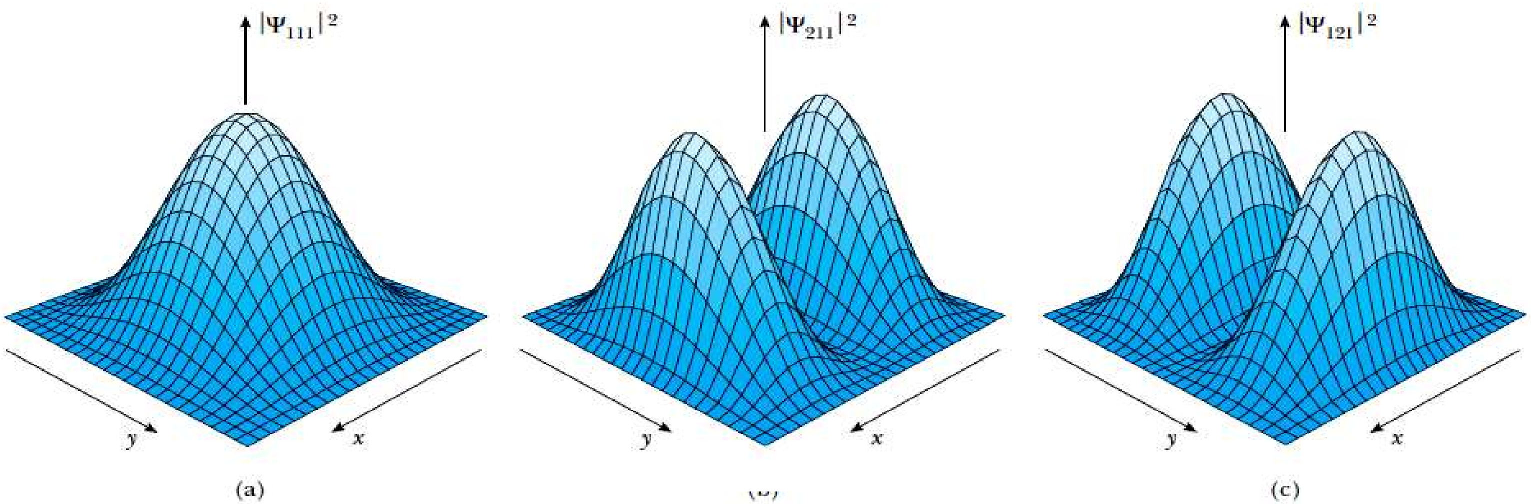
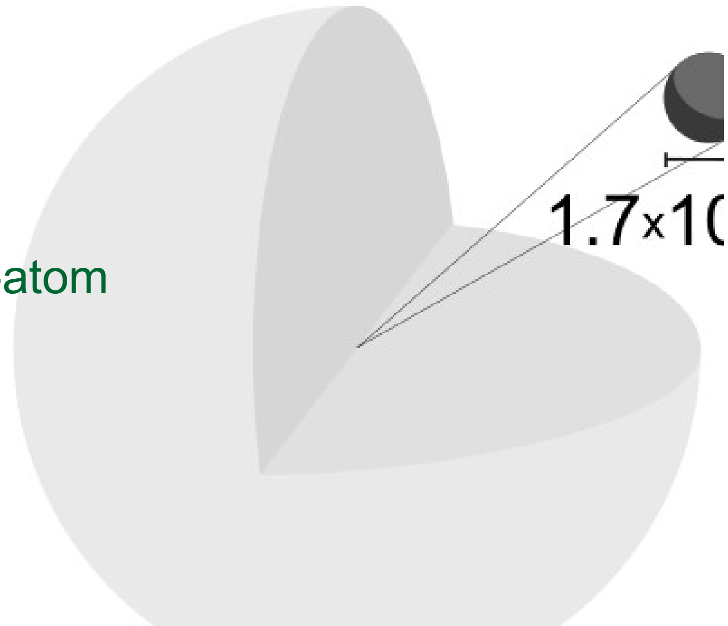
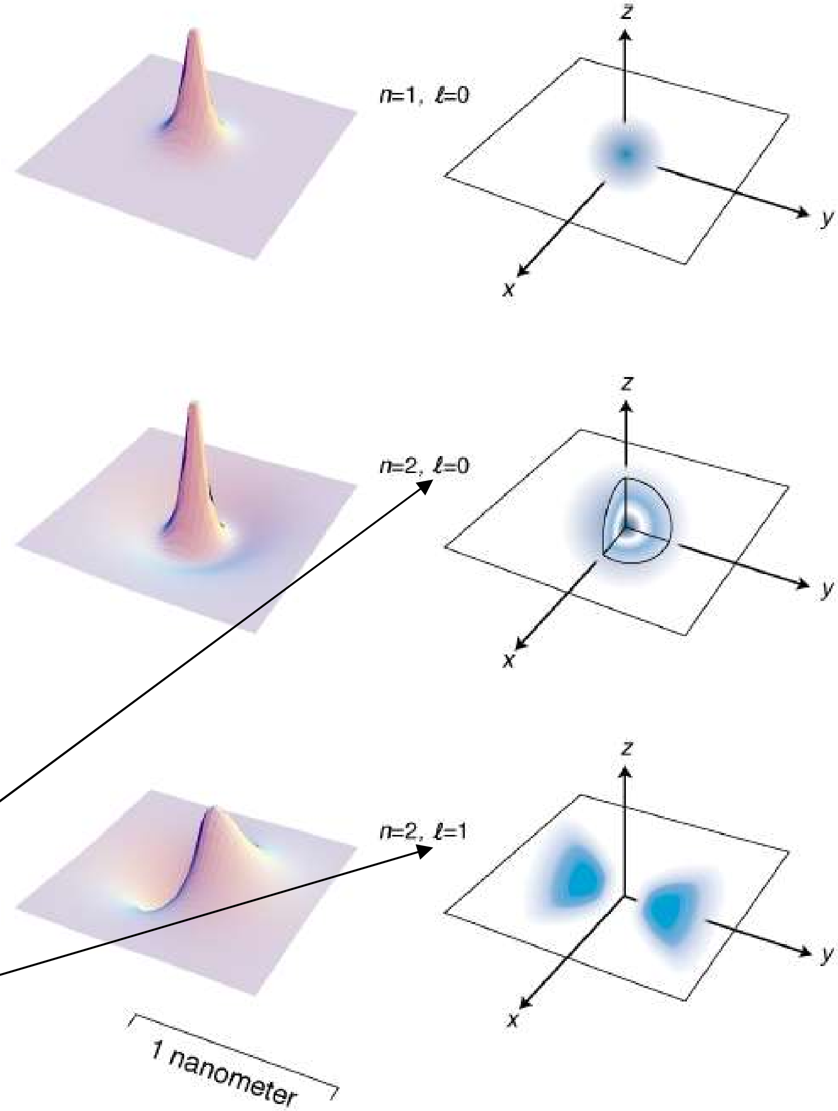


Figure 8.4 Probability density (unnormalized) for a particle in a box: (a) ground state, $|\Psi_{111}|^2$; (b) and (c) first excited states, $|\Psi_{211}|^2$ and $|\Psi_{121}|^2$. Plots are for $|\Psi|^2$ in the plane $z = \frac{1}{2}L$. In this plane, $|\Psi_{112}|^2$ (not shown) is indistinguishable from $|\Psi_{111}|^2$.

Central Coulomb force potential for hydrogen atom possesses highest possible 3D point symmetry

H-atom





The three lowest-energy states of hydrogen.

Spherical potential, very high symmetry, a lot of degeneracy

More next chapter $e^{i\theta} = \cos\theta + i\sin\theta$ $e^{-i\theta} = \cos\theta - i\sin\theta$

6.4: Finite Square-Well Potential

- The finite square-well potential is $V(x) = \begin{cases} V_0 & x \le 0 & \text{region I} \\ 0 & 0 < x < L & \text{region II} \\ V_0 & x \ge L & \text{region III} \end{cases}$

- The Schrödinger equation outside the finite well in regions I and III is

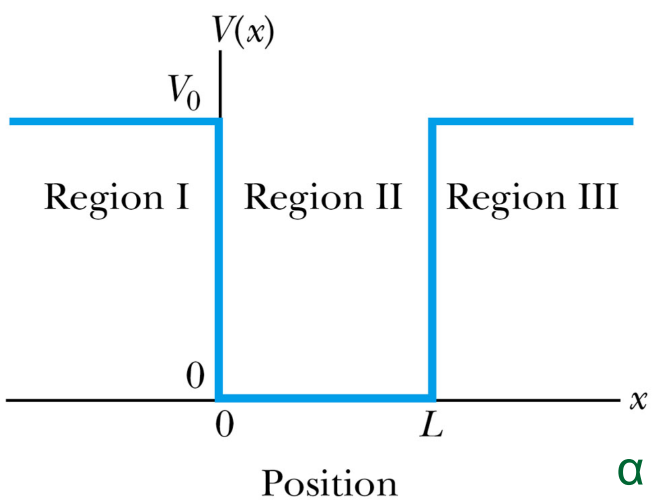
$-\frac{\hbar^2}{2m}\frac{1}{\psi}\frac{d^2\psi}{dx^2} = E - V_0$ regions I, III or using $\alpha^2 = 2m(V_0 - E)/\hbar^2$

Note the importance of the sign in the Schrödinger equation

yields $\frac{d^2\psi}{dx^2} = \alpha^2\psi$. Considering that the wave function must be zero at infinity, the solutions for this equation are

$\psi_{\text{I}}(x) = Ae^{\alpha x}$ region I, $x < 0$

$\psi_{\text{III}}(x) = Be^{-\alpha x}$ region III, $x > L$



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We need four constants to "stitch" the wave function together, here we have A and B

α modified wave number "equivalent" of k in infinite deep square well

Finite Square-Well Solution

$$\sin(kx) = \frac{e^{ikx} - e^{-ikx}}{2i} \qquad \cos(kx) = \frac{e^{ikx} + e^{-ikx}}{2}$$

- Inside the square well, where the potential energy function *V* is zero, the Schrödinger equation becomes $\frac{d^2\psi}{dx^2} = -k^2\psi \qquad k = \sqrt{(2mE)/\hbar^2}$

- Instead of one sinusoidal solution we use

$\psi(x)_{II} = C\sin kx + D\cos kx \quad \text{for } 0 < x < L$ or $\psi_{II} = Ce^{ikx} + De^{-ikx} \qquad \text{region II, } 0 < x < L$

- The boundary conditions require that

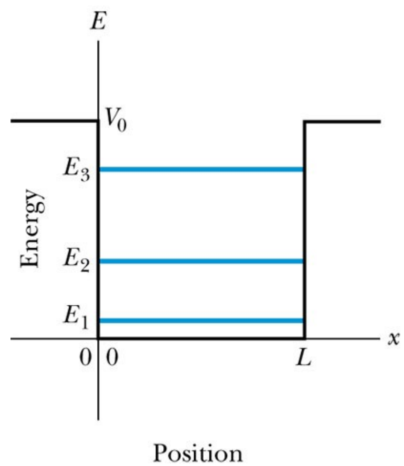
  $\psi_I = \psi_{II}$ at $x = 0$ and $\psi_{II} = \psi_{III}$ at $x = L$

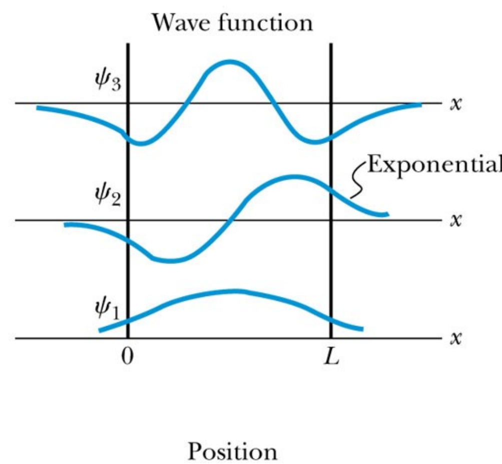
  and the wave function must be smooth where the regions meet.

We are gaining two more constant to fix !

first derivatives with respect to x need to match

- Note that the wave function is nonzero outside of the box.





There is a finite number of energy levels, because the potential barrier is finite in height, however shallow the well, there is at least one energy level

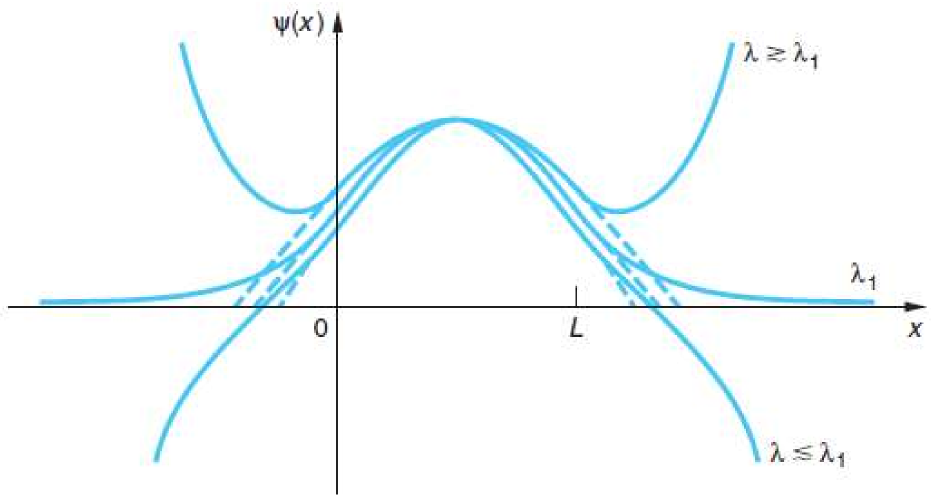


Figure 6-11 Functions satisfying the Schrödinger equation with wavelengths near the critical wavelength λ_1. If λ is slightly greater than λ_1, the function approaches infinity like that in Figure 6-10. At the wavelength λ_1, the function and its slope approach zero together. This is an acceptable wave function corresponding to the energy $E_1 = h^2/2m\lambda_1^2$. If λ is slightly less than λ_1, the function crosses the x axis while the slope is still negative. The slope becomes more negative because its rate of change ψ'' is now negative. This function approaches negative infinity at large x. [*This computer-generated plot courtesy of Paul Doherty, The Exploratorium.*]

While physical boundary conditions were set by the shape of the potential energy function, mathematical boundary conditions emerge from the necessity of stitching the wave function together from the 3 spatial parts in the physical problem

More

In most cases the solution of finite well problems involves transcendental equations and is very difficult. For some finite potentials, however, graphical solutions are relatively simple and provide both insights and numerical results. As an example, we have included the *Graphical Solution of the Finite Square Well* on the home page: www.whfreeman.com/tiplermodernphysics5e. See also Equations 6-36 through 6-43 and Figure 6-14 here.

Penetration Depth

- The penetration depth is the distance outside the potential well where the probability density significantly decreases. It is given by

$$\delta \approx \frac{1}{\alpha} = \frac{\hbar}{\sqrt{2m(V_0 - E)}}$$

$$\delta = \frac{1}{\alpha} = \frac{\hbar}{\sqrt{2m(U - E)}}$$

- It should not be surprising to find that the penetration distance that violates classical physics is proportional to Planck's constant.

The higher n, the higher the leakage of the wave function into the barrier, so the higher energy levels can also be quite counterintuitive

$$E_n \approx \frac{n^2\pi^2\hbar^2}{2m(L + 2\delta)^2} \qquad n = 1, 2, \ldots$$

Estimate the ground-state energy for an electron confined to a potential well of width 0.200 nm and height 100 eV.

Solution We solve Equations 6.21 and 6.22 together, using an iterative procedure. Because we expect $E \ll U(= 100\text{ eV})$, we estimate the decay length δ by first neglecting E to get

$$\delta \approx \frac{\hbar}{\sqrt{2mU}} = \frac{(197.3\text{ eV}\cdot\text{nm}/c)}{\sqrt{2(511\times 10^3\text{ eV}/c^2)(100\text{ eV})}}$$
$$= 0.0195\text{ nm}$$

Thus, the effective width of the (infinite) well is $L + 2\delta = 0.239$ nm, for which we calculate the ground-state energy:

$$E \approx \frac{\pi^2(197.3\text{ eV}\cdot\text{nm}/c)^2}{2(511\times 10^3\text{ eV}/c^2)(0.239\text{ nm})^2} = 6.58\text{ eV}$$

From this E we calculate $U - E = 93.42$ eV and a new decay length

$$\delta \approx \frac{(197.3\text{ eV}\cdot\text{nm}/c)}{\sqrt{2(511\times 10^3\text{ eV}/c^2)(93.42\text{ eV})}} = 0.0202\text{ nm}$$

This, in turn, increases the effective well width to 0.240 nm and lowers the ground-state energy to $E = 6.53$ eV. The iterative process is repeated until the desired accuracy is achieved. Another iteration gives the same result to the accuracy reported. This is in excellent agreement with the exact value, about 6.52 eV for this case.

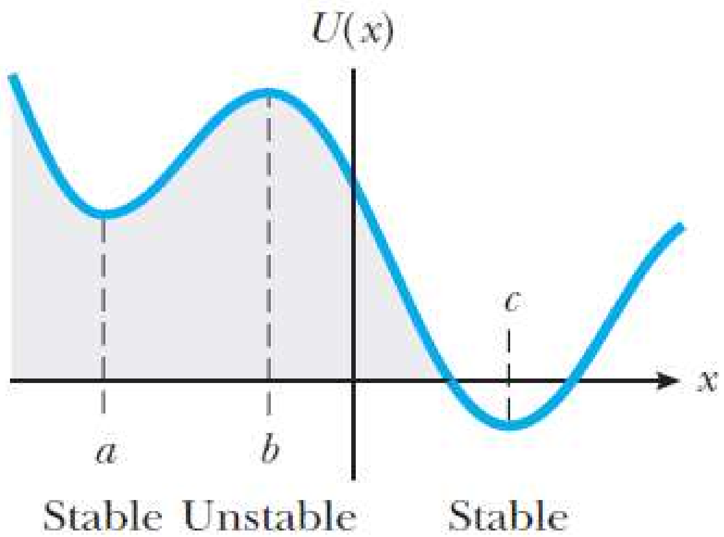


Figure 6.17 A general potential function $U(x)$. The points labeled a and c are positions of stable equilibrium, for which $dU/dx = 0$ and $d^2U/dx^2 > 0$. Point b is a position of unstable equilibrium, for which $dU/dx = 0$ and $d^2U/dx^2 < 0$.

Idea of stitching wave functions together for different regions of the problem.

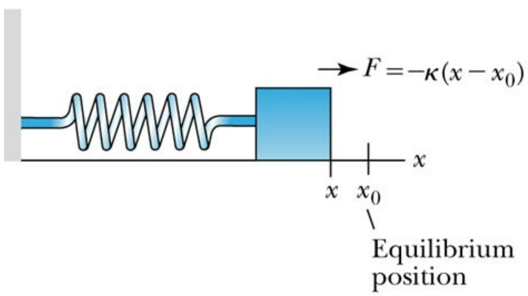
The regions around the troughs in this figure can be modeled by a parabolic function that facilitate harmonic oscillations

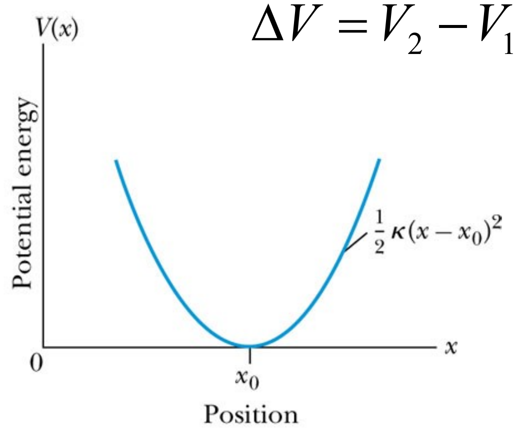
6.6: Simple Harmonic Oscillator

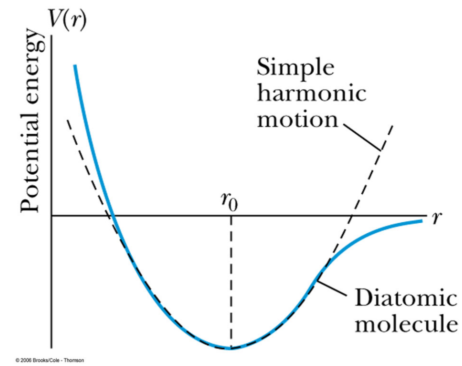
- Simple harmonic oscillators describe many physical situations: springs, diatomic molecules, and atoms in a crystal ***approximately***

$$\Delta V = V_2 - V_1 = -\int_1^2 \vec{F} \cdot d\vec{x}$$

set $V_1 = 0$







- "Hooke's potential" $V(x) = U(x) = \dfrac{\kappa x^2}{2} \neq U(t) = V(t)$

$$\frac{d^2\psi}{dx^2} = -\frac{2m}{\hbar^2}\left(E - \frac{\kappa x^2}{2}\right)\psi = \left(-\frac{2mE}{\hbar^2} + \frac{m\kappa x^2}{\hbar^2}\right)\psi$$

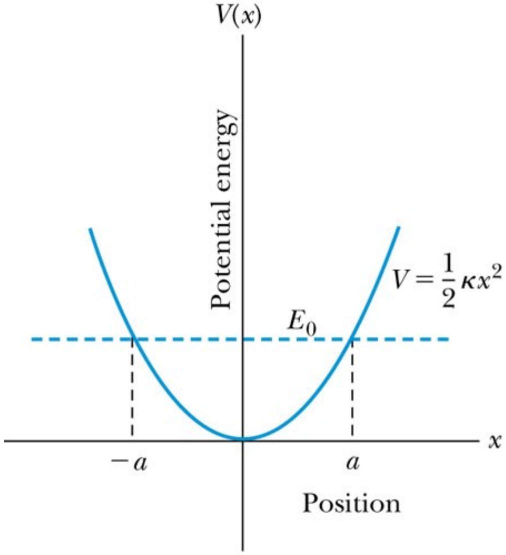
Schrödinger equation for stationary states

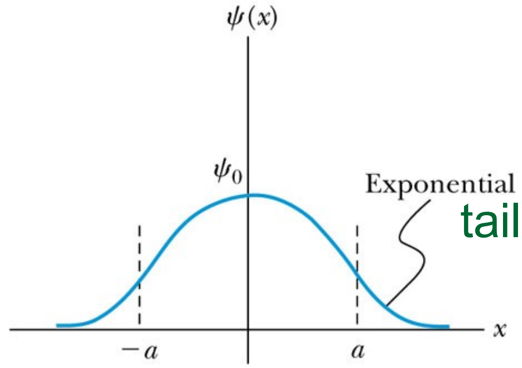
Let $\alpha^2 = \dfrac{m\kappa}{\hbar^2}$ and $\beta = \dfrac{2mE}{\hbar^2}$ which yields $\dfrac{d^2\psi}{dx^2} = (\alpha^2 x^2 - \beta)\psi$

Classically: $\omega = \sqrt{\dfrac{\kappa}{m}}$ The smaller the mass and the "stiffer" the spring, the higher the frequency

Parabolic Potential Well

Gaussian function resulting in an uncertainty $\Delta x \Delta p = \hbar/2$





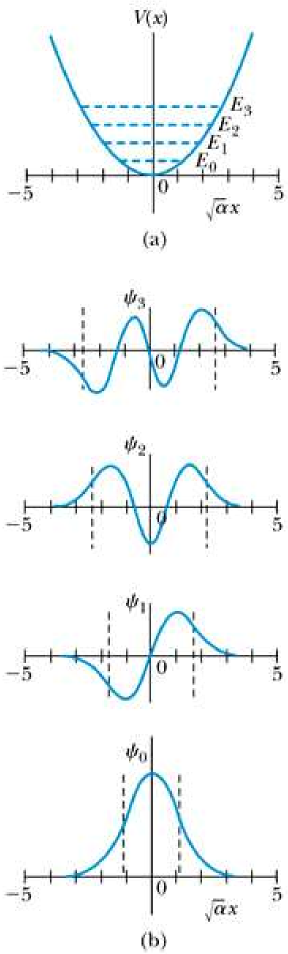
$$\psi_0 = A \cdot e^{-\frac{\sqrt{m\kappa}\cdot x^2}{2\hbar}}$$

$$p(x) = \frac{1}{\sqrt{2\sigma\pi}} e^{-\frac{(x-\mu)^2}{2\sigma^2}}$$

μ: mean (average)
σ: standard deviation

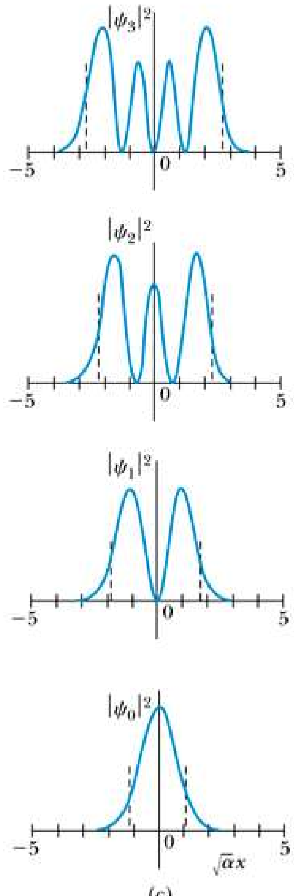
- Lowest energy level E_0 cannot be zero, would violate uncertainty principle.
- The wave function solutions are $\psi_n = H_n(x) e^{-\alpha x^2/2}$ where $H_n(x)$ are Hermite polynomials of order *n*. $H_0(x) = 1$, so the lowest quantum number is 0, the ground state wave function is a Gaussian
- In contrast to the particle in a box, where the oscillatory wave function is a sinusoidal curve, in this case the oscillatory behavior is due to the polynomial, which dominates at small *x*. The exponential tail is provided by the Gaussian function, which dominates at large *x*.

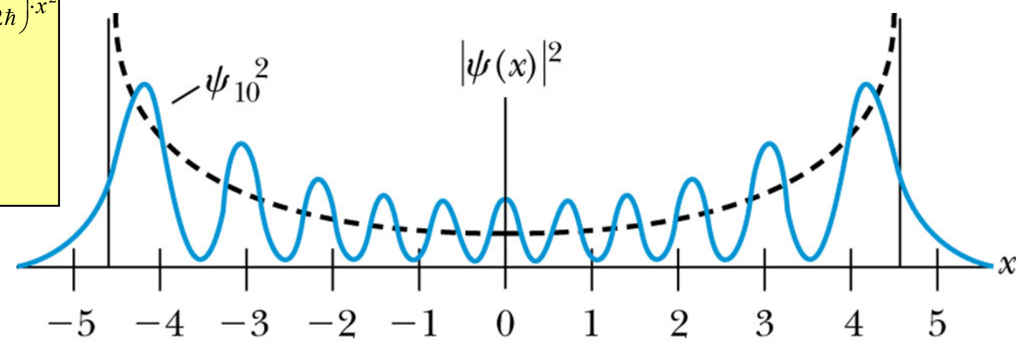
Analysis of the Parabolic Potential Well



$$\psi(x) = \left(\frac{m\kappa}{\pi^2\hbar^2}\right)^{1/8} e^{-\left(\sqrt{m\kappa}/2\hbar\right)\cdot x^2}$$

Ground state, n = 0, is Gaussian





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- The energy levels are given by

$$E_n = (n + \tfrac{1}{2})\hbar\sqrt{\kappa / m} = (n + \tfrac{1}{2})\hbar\omega$$

- The zero point energy is called the Heisenberg limit:

$$E_0 = \frac{1}{2}\hbar\omega$$

- Classically, the probability of finding the mass is greatest at the ends of motion and smallest at the center (that is, proportional to the amount of time the mass spends at each position).
- Contrary to the classical oscillator, the largest probability density for the lowest energy state is for the particle to be at the center.

Again leakage into barrier !

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Remember Max Planck derived ΔE = Δn hf for his resonators with Δn = +-1 correctly, didn't know about zero point energy and Heisenberg's principle

A property of these wave functions that we will state without proof is that

$$\int_{-\infty}^{+\infty} \psi_n^* x \psi_m \, dx = 0 \quad \text{unless} \quad n = m \pm 1 \qquad \textbf{6-59}$$

Oscillating expectation value between m and n quantum state

This property places a condition on transitions that may occur between allowed states. This condition, called a *selection rule*, limits the amount by which n can change for (electric dipole) radiation emitted or absorbed by a simple harmonic oscillator:

The quantum number of the final state must be 1 less than or 1 greater than that of the initial state.

This selection rule is usually written

$$\Delta n = \pm 1 \qquad \textbf{6-60}$$

We will have ***selection rules*** again when we apply the Schrödinger equation to the hydrogen atom

Since the difference in energy between two successive states is $\hbar\omega$, this is the energy of the photon emitted or absorbed in an electric dipole transition. The frequency of the photon is therefore equal to the classical frequency of the oscillator, as was assumed by Planck in his derivation of the blackbody radiation formula. Figure 6-20 shows an energy level diagram for the simple harmonic oscillator, with the allowed energy transitions indicated by vertical arrows.

$$E_n = (n + \tfrac{1}{2})\hbar\omega \qquad n = 0, 1, 2, \ldots$$

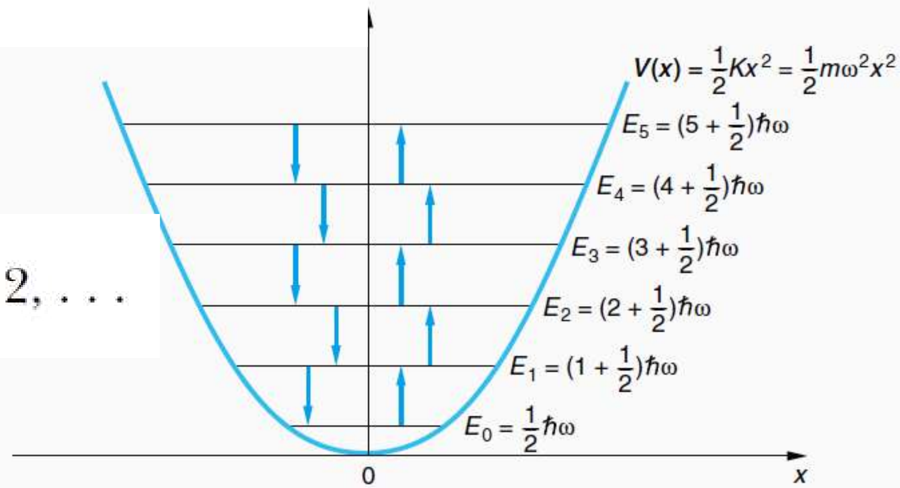
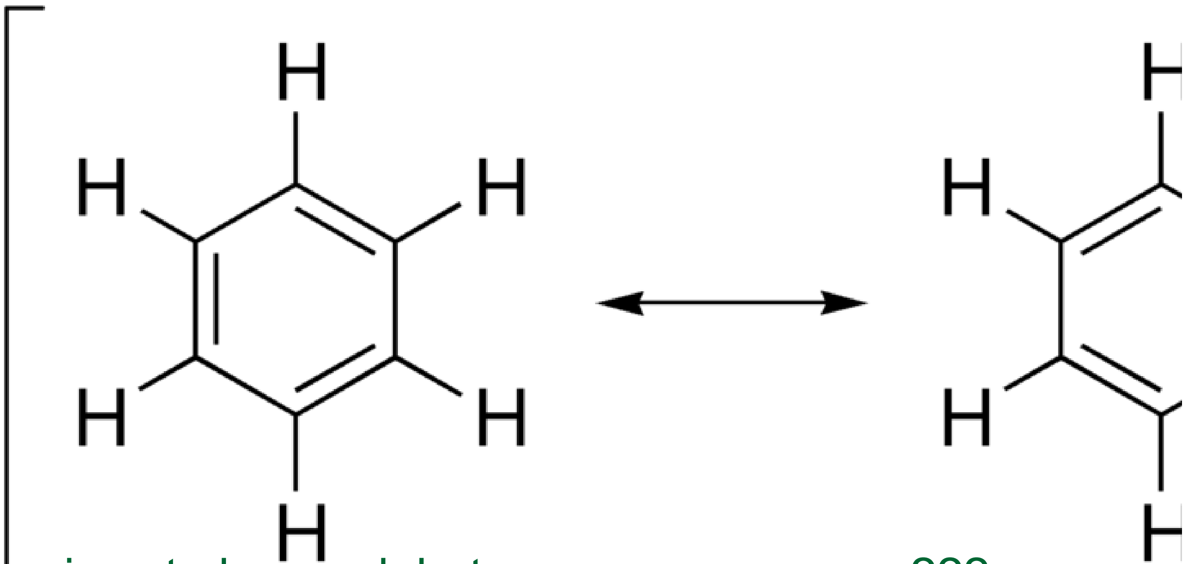
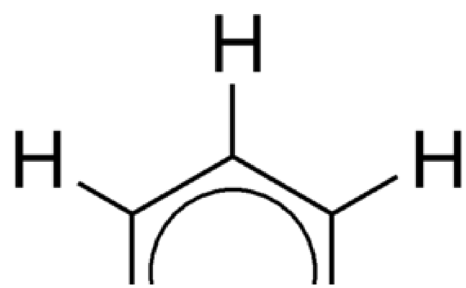


Figure 6-20 Energy levels in the simple harmonic oscillator potential. Transitions obeying the selection rule $\Delta n = \pm 1$ are indicated by the arrows (those pointing up indicate absorption). Since the levels have equal spacing, the same energy $\hbar\omega$ is emitted or absorbed in all allowed transitions. For this special potential, the frequency of the emitted or absorbed photon equals the frequency of oscillation, as predicted by classical theory.

If you have a chemistry background, did you ever wondered why



is not observed, but ???



Quantum oscillations and tunneling !!! So no good chemistry without modern physics !!!

6.7: Barriers and Tunneling

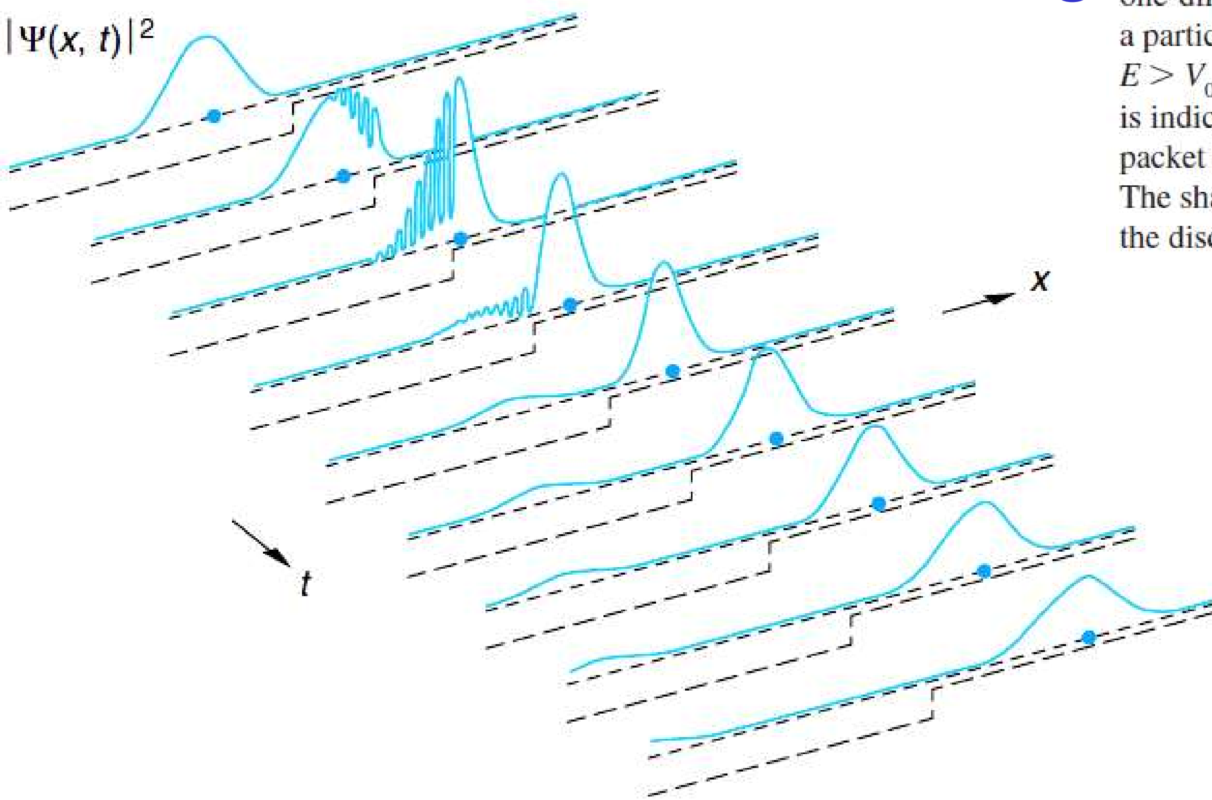


Figure 6-23 Time development of a one-dimensional wave packet representing a particle incident on a step potential for $E > V_0$. The position of a classical particle is indicated by the dot. Note that part of the packet is transmitted and part is reflected. The sharp spikes that appear are artifacts of the discontinuity in the slope of $V(x)$ at $x = 0$.

also note the dispersion of the pulse, all matter waves disperse – but the group velocity of the wavepacket is the same as the velocity of the particle (wavicel)

We are not interested in time dependent details, so just use the time independent Schrödinger equation (as we are not interested in how exactly all of the wiggles move back), calculate just how much probability there is for a wave to get transmitted (i.e. how many of the incoming wavicles get through) and how many are reflected, no particle gets lost

E > U_0 for infinite and very large "step thickness", so L does not show up in formulae, we get approximately

Finally, we express the probabilities in terms of U_0 and E. Using the definitions of k and k', we have

$$T = 4\frac{\sqrt{E(E-U_0)}}{\left(\sqrt{E}+\sqrt{E-U_0}\right)^2} \qquad R = \frac{\left(\sqrt{E}-\sqrt{E-U_0}\right)^2}{\left(\sqrt{E}+\sqrt{E-U_0}\right)^2} \tag{6-7}$$

Notably, expressions (6-7) are essentially identical to those giving reflected and transmitted intensities of a light wave normally incident on the interface between two media. Those for light differ only in that $\sqrt{E}$ and $\sqrt{E-U_0}$, proportional to the speeds in the two regions, are replaced by the speeds c/n, where n is the medium's refractive index. The behaviors are completely analogous. The most important point here is that, contrary to the classical expectation, the reflection probability is nonzero.

Only condition is that the De Broglie wavelength (or wavelength of electromagnetic wave) is on the same order of magnitude than the region where the U_0 (refractive index) changes !!!

Why is there no direct reference to Planck's constant ??

$E < U_0$ $\longrightarrow \infty$

Always reflection

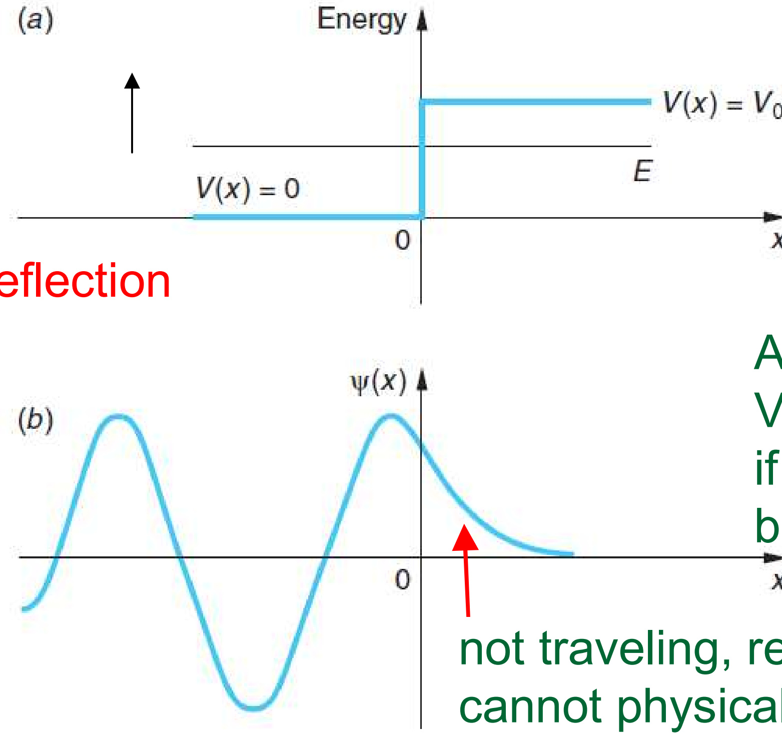


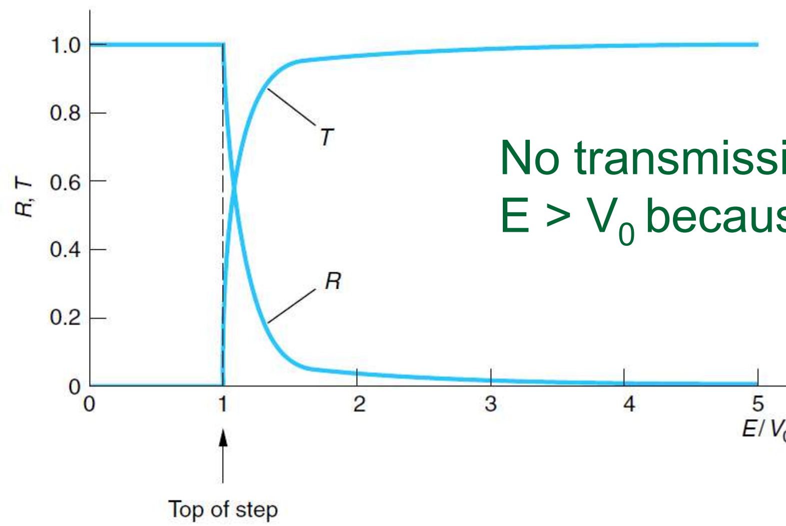
Figure 6-24 (*a*) A potential step. Particles are incident on the step from the left moving toward the right, each with total energy $E < V_0$. (*b*) The wave transmitted into region II is a decreasing exponential. However, the value of R in this case is 1 and no net energy is transmitted.

As long as $E < V_0$ only reflection if infinitely wide barrier $L \longrightarrow \infty$

not traveling, real, but you cannot physically detect it there

Only two regions for Schrödinger equation

If $E < V_0$ there is complete reflection ***as long as barrier is infinitely thick***



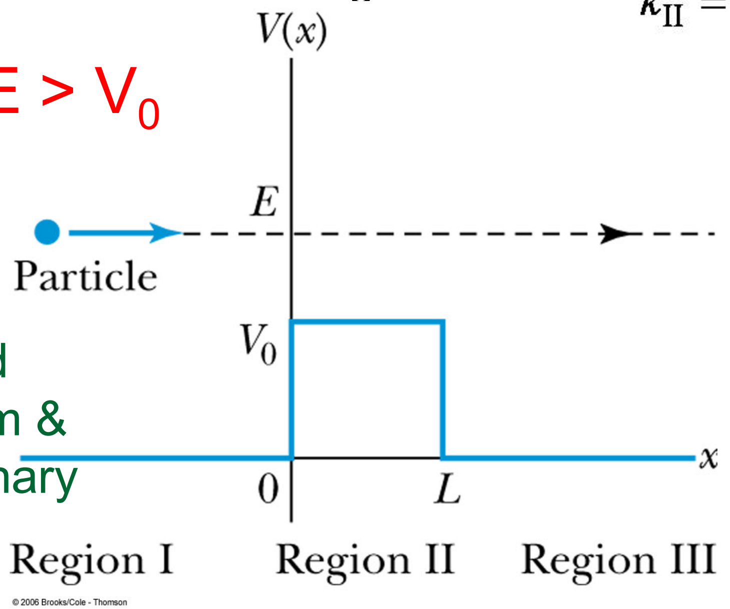
No transmission resonances for $E > V_0$ because L infinite

Figure 6-25 Reflection coefficient R and transmission coefficient T for a potential step V_0 high versus energy E (in units of V_0).

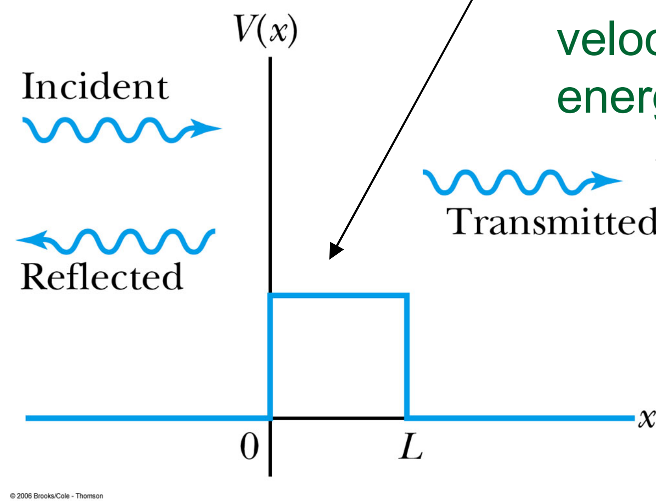
- Consider a particle of total energy E approaching a potential barrier of height V_0 and widths L and the potential (energy) everywhere else is zero.
- We will first consider the case when the **energy is greater than the potential barrier.**
- In regions I and III the wave numbers are: $k_I = k_{III} = \frac{\sqrt{2mE}}{\hbar}$ $k = 2\pi/\lambda$ $k\hbar = p$
- In the barrier region we have $k_{II} = \frac{\sqrt{2m(E-V_0)}}{\hbar}$ where $V = V_0$

i.e. λ is longer, smaller momentum, velocity, and total energy $p = \hbar k$

E > V_0



Bound system & stationary state



for $$E_n = V_0 + \frac{n^2\pi^2\hbar^2}{2mL^2}$$

Anyone remembers this term?

We can have resonant transmission, when wave that gets reflected at the second step cancels the wave that got reflected at the first step, so 100% transmission for precise E_n, e.g. optical coatings

n = 1, 2, 3 … Bohr's correspondence principle

Square step (or ditch)

- The wave function will consist of an incident wave, a reflected wave, and a transmitted wave for simplicity (no mechanism for ditch or step region)
- The potential energies and the Schrödinger wave equation for the three regions are as follows:

E > V_0 in a general sense valid for ditch and step of length L

Region I $(x<0)$	$V=0$	$\frac{d^2\psi_1}{dx^2}+\frac{2m}{\hbar^2}E\psi_1=0$
Region II $(0<x<L)$	$V=V_0$	$\frac{d^2\psi_{II}}{dx^2}+\frac{2m}{\hbar^2}(E-V_0)\psi_{II}=0$
Region III $(x>L)$	$V=0$	$\frac{d^2\psi_{III}}{dx^2}+\frac{2m}{\hbar^2}E\psi_{III}=0$

(E - -V_0) ditch

- The corresponding solutions are:

Region I $(x<0)$	$\psi_I = Ae^{ik_I x}+Be^{-ik_I x}$
Region II $(0<x<L)$	$\psi_{II} = Ce^{ik_{II} x}+De^{-ik_{II} x}$
Region III $(x>L)$	$\psi_{III} = Fe^{ik_I x}+Ge^{-ik_I x}$

$k_{II} > k_1 = k_3 = k_I$ for finite ditch reverse relation for finite step

- As the wave moves from left to right, we can specify the wave functions to:

Incident wave	$\psi_I(\text{incident}) = Ae^{ik_I x}$
Reflected wave	$\psi_I(\text{reflected}) = Be^{-ik_I x}$
Transmitted wave	$\psi_{III}(\text{transmitted}) = Fe^{ik_I x}$

Same wave as in Region I, but different amplitude

Probability of Reflection and Transmission for square step potential (barrier) with final width L

- The probability of the particles being reflected *R* or transmitted *T* is:

$$R = \frac{|\psi_{\mathrm{I}}(\text{reflected})|^2}{|\psi_{\mathrm{I}}(\text{incident})|^2} = \frac{B^* B}{A^* A}$$

$$T = \frac{|\psi_{\mathrm{III}}(\text{transmitted})|^2}{|\psi_{\mathrm{I}}(\text{incident})|^2} = \frac{F^* F}{A^* A}$$

Same traveling wave in both regions

- Because the particles must be either reflected or transmitted we have: *R* + *T* = 1 (no particle gets stuck in a barrier ever)

- We have enough information to derive transmission probability

$$T = \left[1 + \frac{V_0{}^2 \sin^2(k_{\mathrm{II}} L)}{4E(E - V_0)}\right]^{-1} \qquad k_{\mathrm{II}} = \frac{\sqrt{2m(E - V_0)}}{\hbar}$$

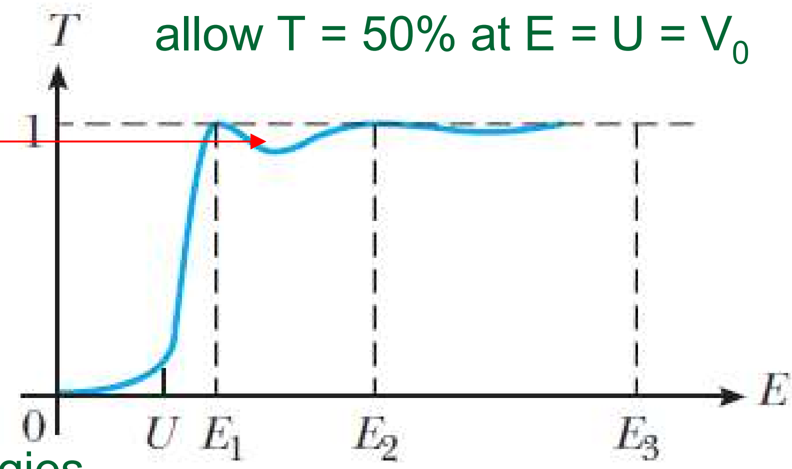
E higher than potential energy barrier $V_o = U_o$

Note that there is no h-bar directly, results carry over to any kind of classical wave,
but there is now a L in an oscillating term

$$T=\left[1+\frac{V_0^{\,2}\sin^2(k_{\mathrm{II}}L)}{4E(E-V_0)}\right]^{-1}$$

sin nπ = 0

for some L, that does not allow T = 50% at E = U = V_0



T = 1 when sine-term zero for resonance energies E_1, E_2, E_3 which are a function of L

$$k_{\mathrm{II}}=\frac{\sqrt{2m(E-V_0)}}{\hbar} \qquad E_n=V_0+\frac{n^2\pi^2\hbar^2}{2mL^2}$$

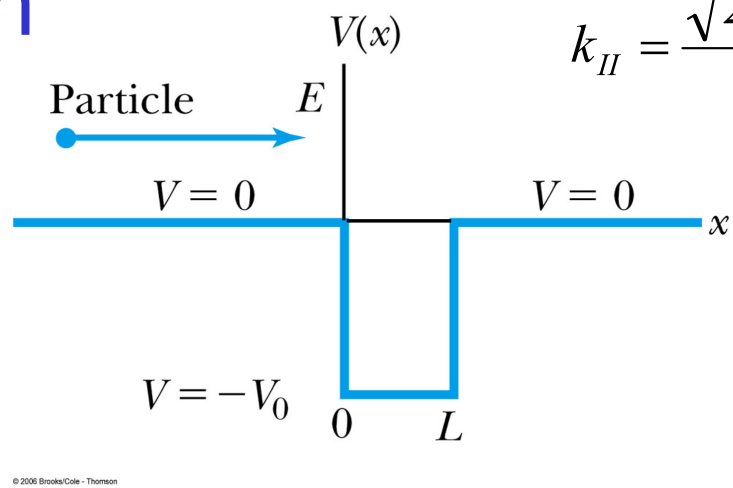
Figure 7.3 A sketch of the transmission coefficient $T(E)$ for a square barrier. Oscillation in $T(E)$ with E, and the transmission resonances at E_1, E_2, and E_3, are further evidence for the wave nature of matter.

Transmission and Reflection must always add up to 100% (nothing gets stuck in the barrier)

Different books:

U = V_0 also k_{II} = κ so look for the context

Square ditch



$$k_{II} = \frac{\sqrt{2m(\{E-(-V_0)\}}}{\hbar} > k_{I\_and\_III}$$

so λ shorter because k larger, higher momentum, velocity, kinetic energy

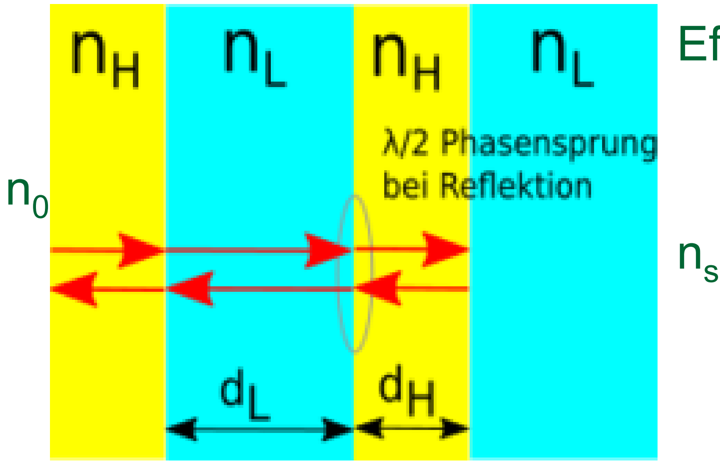
- Consider a particle passing through a potential well region rather than through a potential barrier.
- particle speeds up passing the ditch region, because $K = mv^2 / 2 = E + V_0$.

According to quantum mechanics, reflection and transmission occur as a matter of principle, and the wavelength above the potential ditch is smaller than outside. When the width of the potential well is precisely equal to half-integral or integral units of the wavelength, the reflected waves are out of phase or in phase with the original wave, and cancellations or resonances may occur. The reflection/cancellation effects lead theoretically to pure transmission or pure reflection for certain wavelengths. (Theoretically because the stationary state does not continue forever so that E is absolutely sharp, uncertainty principle again)

For example, at the second boundary ($x = L$) for a wave on the right-hand side, the wave may reflect and be out of phase with the incident wave. The effect would be a cancellation inside the ditch.

Distributed Bragg reflector, for light and wavicels, using the ditch

top view



Effect of each layer corresponds to “optical length” $\lambda_0/4$

There is a phase change on reflection

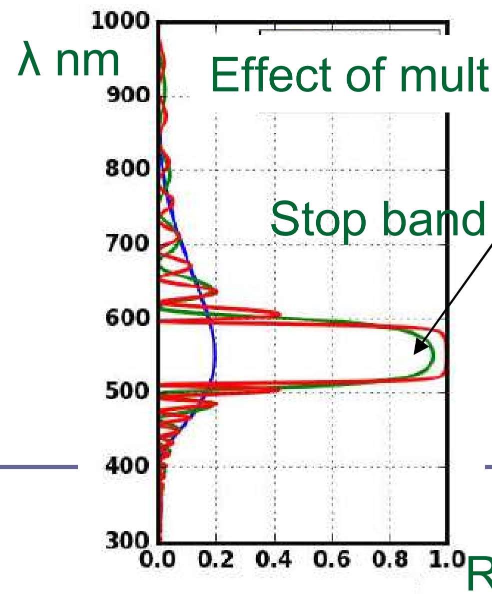
$\lambda_0/2$

$$2n_L d_L + \frac{\lambda}{2} = 2n_H d_H + \frac{\lambda}{2} = m\lambda$$

Condition for **constructive** interference, maximal transmission

$$n_H d_H = n_L d_L = \frac{(2m-1)\lambda}{4}$$

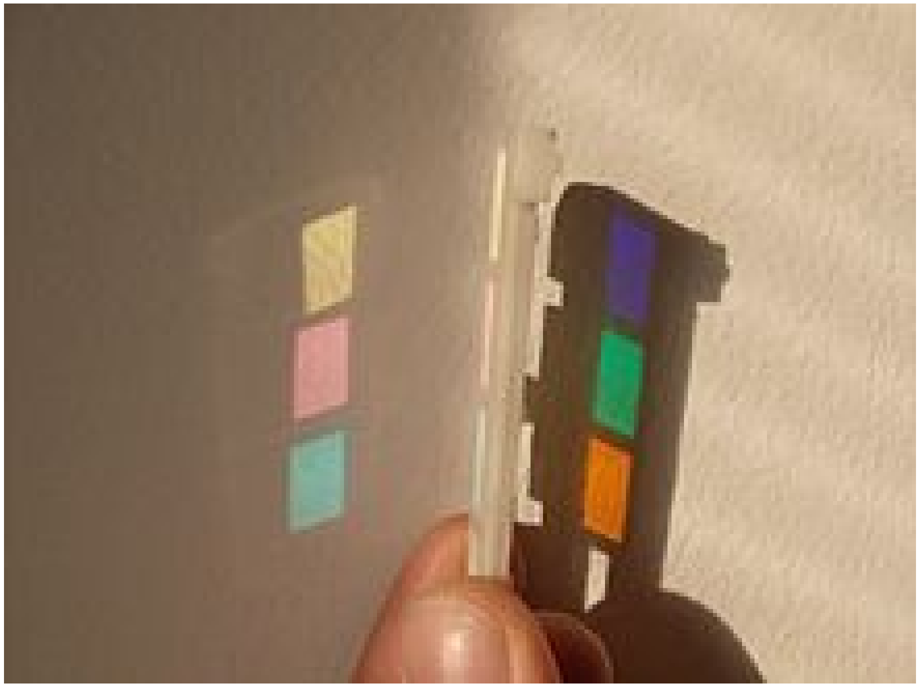
Condition for destructive interference for several wavelengths simultaneously fulfilled with integer m > 1, several layers necessary to create an nearly total reflector



$$R = \left[\frac{n_o (n_2)^{2N} - n_s (n_1)^{2N}}{n_o (n_2)^{2N} + n_s (n_1)^{2N}} \right]^2 \qquad \lim_{N \to \infty} R = 1$$

n_0 for air ≈ 1, $n_2 = n_{high}$, $n_1 = n_{low}$, n_s for substrate on which layers were deposited

Weak transmitted light in complementary colors ←



White light ←

Strong reflected light →

R + T = 1, nothing gets stuck in the ditch/barrier

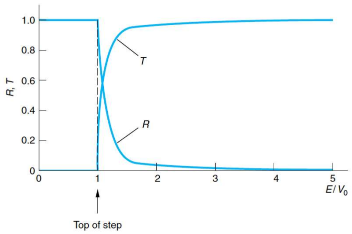
Wavicels behave just like Maxwellian light waves – which are also streams of photons

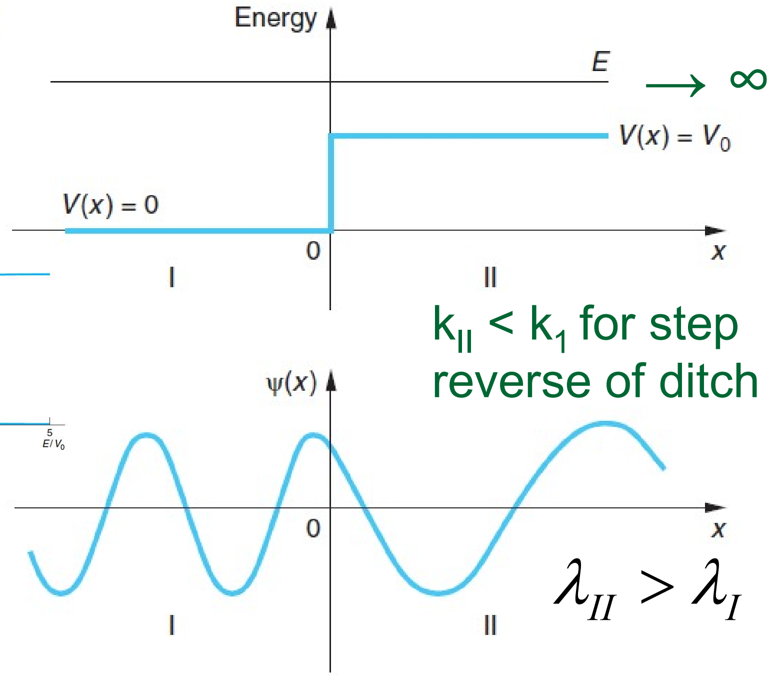
https://en.wikipedia.org/wiki/Distributed_Bragg_reflector

Two different scenarios

$E > V_0$

no L





$\rightarrow \infty$

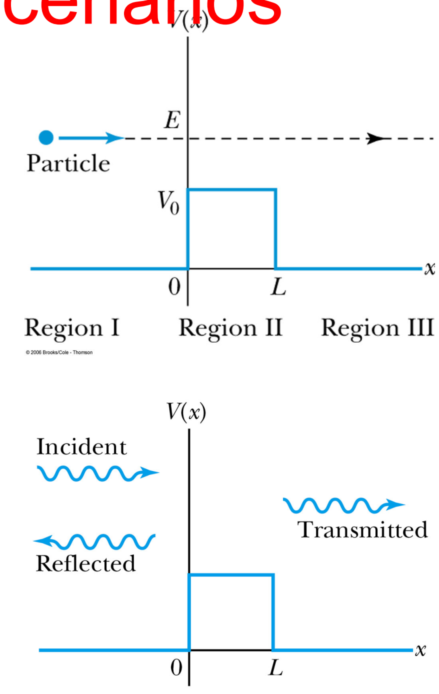
$k_{II} < k_1$ for step
reverse of ditch

$\lambda_{II} > \lambda_I$

Figure 6-22 (*a*) A potential step. Particles are incident on the step from the left toward the right, each with total energy $E > V_0$. (*b*) The wavelength of the incident wave (Region I) is shorter than that of the transmitted wave (Region II). Since $k_2 < k_1$, $|C|^2 > |A|^2$; however, the transmission coefficient $T < 1$.

(b)

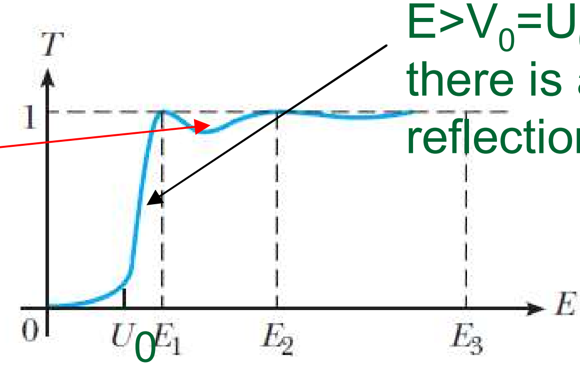
L



For ***barrier of finite widths***, there will be reflection and transmission on both x = 0 and x = L

$$R = \frac{\sin^2\left[\sqrt{2m(E - U_0)}\, L/\hbar\right]}{\sin^2\left[\sqrt{2m(E - U_0)}\, L/\hbar\right] + 4(E/U_0)\left[(E/U_0) - 1\right]}$$

$$T = \frac{4(E/U_0)\left[(E/U_0) - 1\right]}{\sin^2\left[\sqrt{2m(E - U_0)}\, L/\hbar\right] + 4(E/U_0)\left[(E/U_0) - 1\right]}$$



$E>V_0=U_0$, but there is also reflection

Reflection and transmission on each side of the barrier all the time (same for any discontinuity at step or ditch over which the wavical goes)

Optimization for transmission: choosing V_0 and L so that reflected wave and transmitted wave inside the barrier region (discontinuity) are **in phase** and **reinforce** each other, effect: **strong attenuation of reflected wave**

Both are modeled as quasi-traveling wavicals (i.e. complex, free particle with varying amplitudes but we do not care about time dependent details so we use just real functions to describe what is going on), anyway their superposition makes for a real valued function above the ditch or step

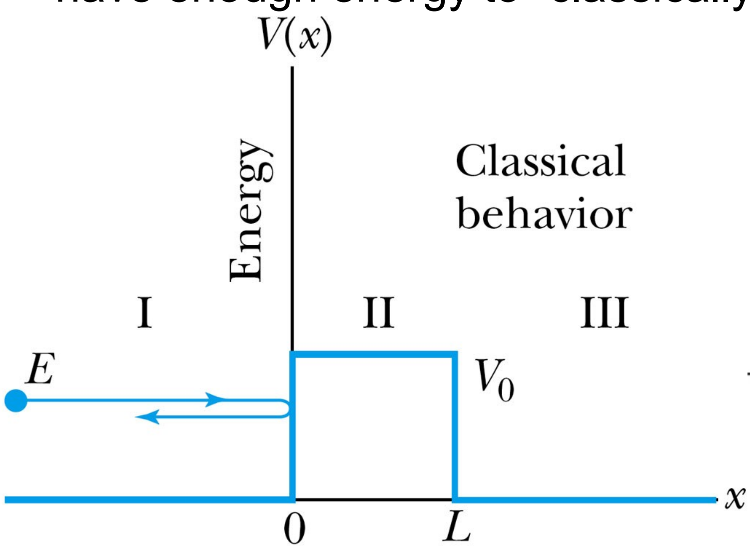
In order to calculate the amplitude of the transmitted wave, we need to fix 4 unknown by 4 equations, wavefunction has to be continuous and its first derivative has to be smooth (just as we did for the finite square well) – but now multiple times as the first reflected wave in the barrier region gets transmitted to the left as well and reflected again …

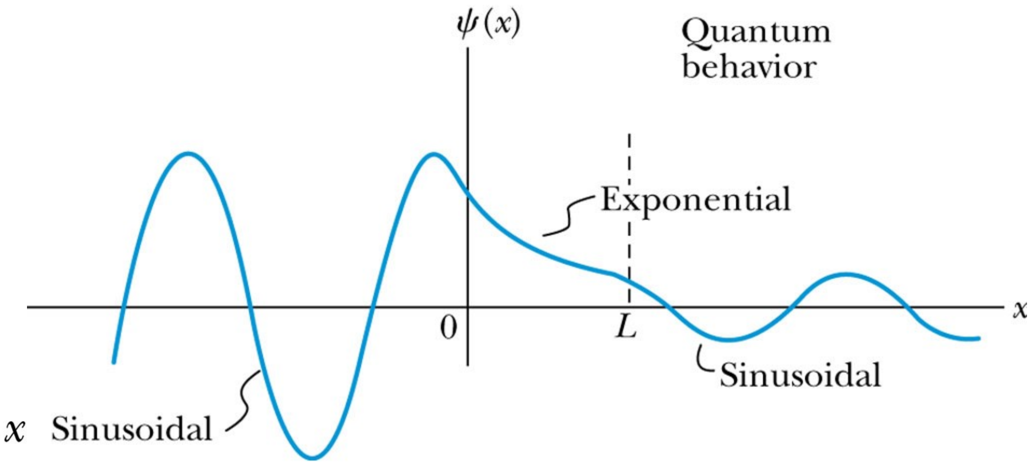
Tunneling

Now it is about evanescent wave in barrier

$$\sinh x = \frac{e^x - e^{-x}}{2} = \frac{e^{2x} - 1}{2e^x} = \cdots$$

- Now we contrast classical and quantum physics, classically the particle does not have enough energy to "classically overcome" the potential energy barrier, $E < V_0$.





- The quantum mechanical result, however, is one of the most remarkable features of modern physics, and there is ample experimental proof of its existence. There is a finite probability that the particle penetrates the barrier and emerges on the other side (no mechanistic description in the barrier).
- The wave function in region II becomes $\psi_{II} = Ce^{\kappa x} + De^{-\kappa x}$ where $\kappa = \frac{\sqrt{2m(V_0 - E)}}{\hbar}$

Note that this wave is not traveling, just rapidly decaying

- The transmission probability that describes the phenomenon of **tunneling** is

$$T = \left[1 + \frac{V_0^2 \sinh^2(\kappa L)}{4E(V_0 - E)}\right]^{-1}$$

when $\kappa L >> 1$

$$T = 16\frac{E}{V_0}\left(1 - \frac{E}{V_0}\right)e^{-2\kappa L}$$

Note that this wave is not traveling, just rapidly decaying, but in the region of L we must have *"formally"* negative kinetic energy because energy is conserved (stationary state), *the time – energy uncertainty principle allows for this negative kinetic energy to be "intellectually neutralized", loosely speaking*

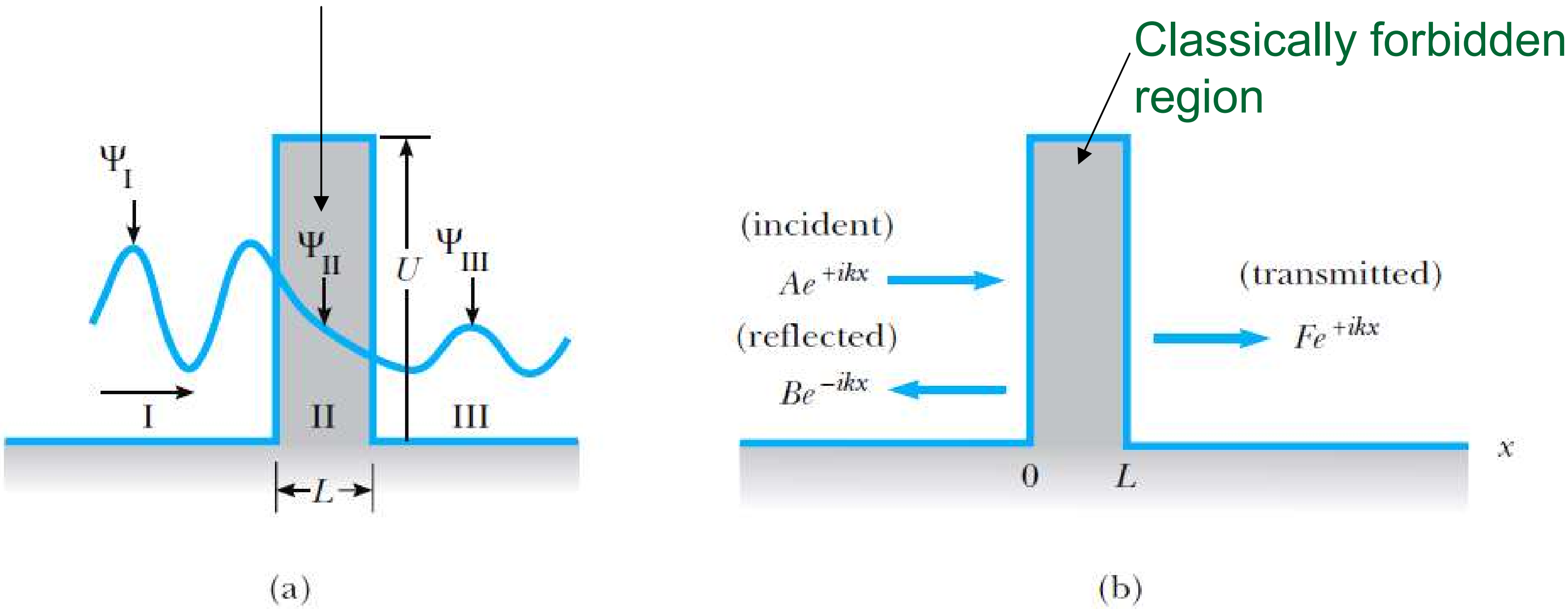


Figure 7.2 (a) A typical stationary-state wave for a particle in the presence of a square barrier. The energy E of the particle is less than the barrier height U. Since the wave amplitude is nonzero in the barrier, there is some probability of finding the particle there. (b) Decomposition of the stationary wave into incident, reflected, and transmitted waves.

E = KE + U, if E < U (as in barrier) KE is formally negative, no big deal, we have seen strange things before

Potential energy of barrier larger than total energy of particle, which is all kinetic

$$T(E) = \left\{1 + \frac{1}{4}\left[\frac{U^2}{E(U-E)}\right]\sinh^2\alpha L\right\}^{-1}$$

$$\alpha = \frac{\sqrt{2m(U-E)}}{\hbar} = \kappa = k_{II}$$

$$R = \frac{\sinh^2\left[\sqrt{2m(U_0 - E)}\,L/\hbar\right]}{\sinh^2\left[\sqrt{2m(U_0 - E)}\,L/\hbar\right] + 4(E/U_0)(1 - E/U_0)}$$

$$T = \frac{4(E/U_0)(1 - E/U_0)}{\sinh^2\left[\sqrt{2m(U_0 - E)}\,L/\hbar\right] + 4(E/U_0)(1 - E/U_0)}$$

Different books use different symbols, give different versions of the same formulae

summary

Both are, in general, nonzero—a particle can escape through a barrier that it can't surmount classically. It is important to grasp that it can do this *not* due to some mysterious fluctuation in its energy, allowing it to go "over the top." On the contrary, from the start, we assumed a stationary state, in which energy is well defined. *The particle never has sufficient energy to surmount the barrier.* Instead, it "tunnels" through, and the principles of quantum mechanics demand that there be such a possibility. The solution to the left of the barrier is some combination of incident and reflected waves, of positive and negative momentum. At $x = 0$, it smoothly joins a function inside the barrier that tends to die off (the C in the exponentially decreasing $Ce^{-\alpha x}$ being usually quite small). And at $x = L$, this smoothly joins a transmitted wave of positive momentum. There is no physically acceptable solution that is identically zero beyond the barrier.

Figure 6.7 shows wave functions (real part) for particles of different energies incident on a barrier from the left. Note that the wavelengths decrease as kinetic energy increases. At energy E_1, the exponential decay within the barrier is rapid, and little transmission occurs. At E_2, barely below the barrier height, the wave decays less rapidly, leaving a larger transmitted "tail." Energy E_3 is above the barrier, but we see evidence of significant reflection—the wave is of smaller amplitude to the right of the barrier than to the left. Also, the wavelength is longer when it is "over" the barrier, because the speed is smaller there. Energy E_4 happens to be the first transmission resonance—the wave on the right is of precisely the same amplitude as on the left. Note that the barrier's width is $\frac{1}{2}\lambda$. Not coincidentally, this is just the condition we would expect for maximum transmission of a light wave through a thin film surrounded by air. At E_5, though not a transmission resonance, little reflection occurs—the amplitude on the right is only slightly less than on the left.

Figure 6.8 shows reflection and transmission probabilities for all energies incident on the same barrier as in Figure 6.7, with the above energies E_1 to E_5 indicated by dashed lines. Although reflection dominates for $E < U_0$ and transmission for $E > U_0$, both occur at all energies except transmission resonances. In the limit $L \to \infty$, the barrier becomes a step and Figure 6.8 becomes Figure 6.4. Error in otherwise very good Harris book

Figure 6.7 Wave functions for particles of different energies incident from the left on a potential barrier.

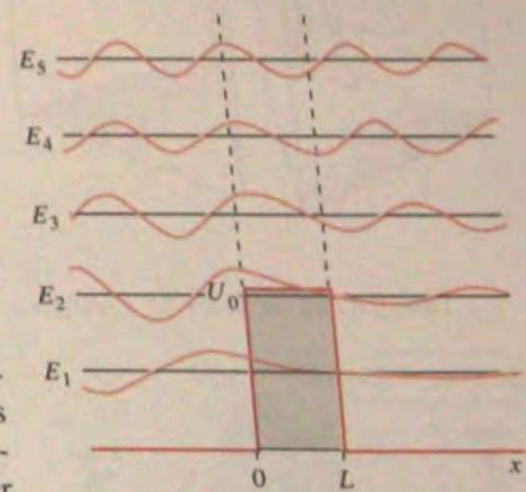
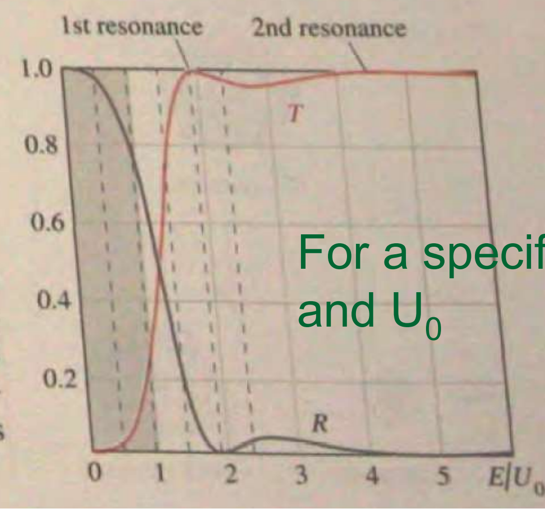


Figure 6.8 Reflection and transmission probabilities for a potential barrier.



For a specific L and U_0

EXAMPLE 7.1 Transmission Coefficient for an Oxide Layer

Two copper conducting wires are separated by an insulating oxide layer (CuO). Modeling the oxide layer as a square barrier of height 10.0 eV, estimate the transmission coefficient for penetration by 7.00-eV electrons (a) if the layer thickness is 5.00 nm and (b) if the layer thickness is 1.00 nm.

Solution From Equation 7.6 we calculate α for this case, using $\hbar = 1.973\ \text{keV}\cdot\text{Å}/c$ and $m_e = 511\ \text{keV}/c^2$ for electrons to get

$$\alpha = \frac{\sqrt{2m_e(U-E)}}{\hbar}$$

$$= \frac{\sqrt{2(511\ \text{keV}/c^2)(3.00\times 10^{-3}\ \text{keV})}}{1.973\ \text{keV}\cdot\text{Å}/c} = 0.8875\ \text{Å}^{-1}$$

The transmission coefficient from Equation 7.9 is then

$$T = \left\{1 + \frac{1}{4}\left[\frac{10^2}{7(3)}\right]\sinh^2(0.8875\ \text{Å}^{-1})L\right\}^{-1}$$

Substituting $L = 50.0$ Å (5.00 nm) gives

$$T = 0.963 \times 10^{-38}$$

a fantastically small number on the order of 10^{-38}! With $L = 10.0$ Å (1.00 nm), however, we find

$$T = 0.657 \times 10^{-7}$$

We see that reducing the layer thickness by a factor of 5 enhances the likelihood of penetration by nearly 31 orders of magnitude!

$$T(E) = \left\{1 + \frac{1}{4}\left[\frac{U^2}{E(U-E)}\right]\sinh^2\alpha L\right\}^{-1}$$

where sinh denotes the hyperbolic sine function: $\sinh x = (e^x - e^{-x})/2$.

Approximate transmission coefficient of a barrier with arbitrary shape

$$T(E) \approx \exp\left(-\frac{2}{\hbar}\sqrt{2m}\int\sqrt{U(x)-E}\,dx\right) \tag{7.10}$$

The integral in Equation 7.10 is taken over the range of x where $U(x) > E$, called the **classically forbidden region** because a classical particle in this interval would have to have a negative value of kinetic energy (an impossibility!).

GEOPHYSICAL RESEARCH LETTERS, VOL. 32, L10602, doi:10.1029/2005GL022834, 2005

Reflection and tunneling of ocean waves observed at a submarine canyon

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Naval Postgraduate School, Monterey, California, USA

Water surface waves are faster above a ditch

“As much as 60% of the energy of waves approaching the canyon normal to its axis was reflected, except for waves twice as long as the canyon width, which were transmitted across with no reflection. ***… analogous to the quantum tunneling of a free particle through a classically impenetrable barrier.”***

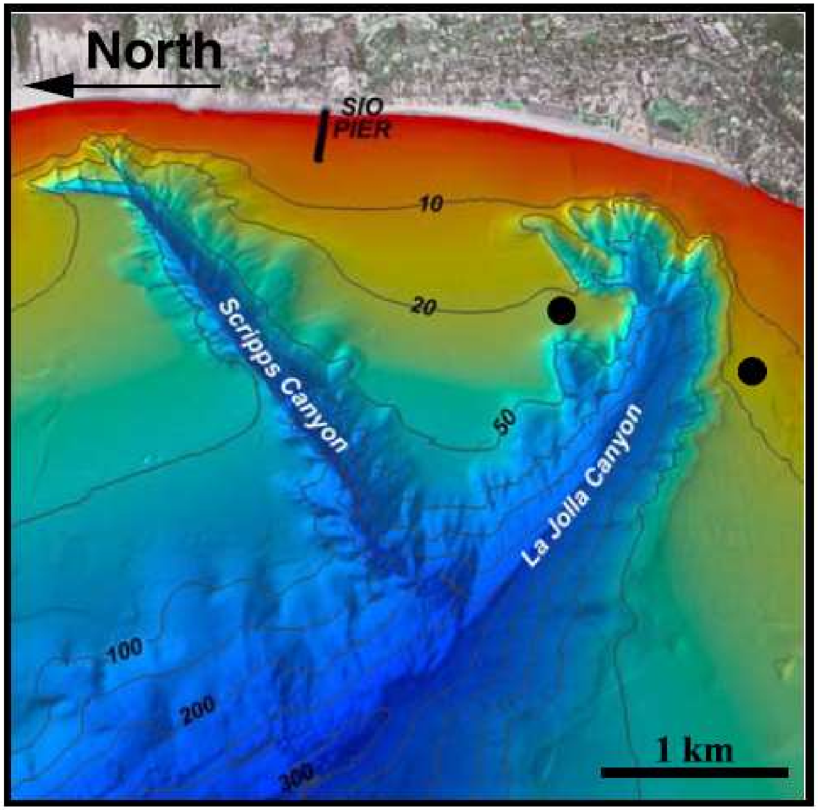

Figure 1. Map of underwater bathymetry (curves are depth contours in m below mean sea level) and aerial photograph of the adjacent land near two submarine canyons on the Southern California coast. The Scripps Institution of Oceanography (SIO) pier is between Scripps (the narrow canyon north of the pier) and La Jolla (the wider canyon south of the pier) submarine canyons. The circles on either side of La Jolla submarine canyon are locations of pressure gauges and current meters mounted 1 m above the seafloor for 4 weeks during fall of 2003.

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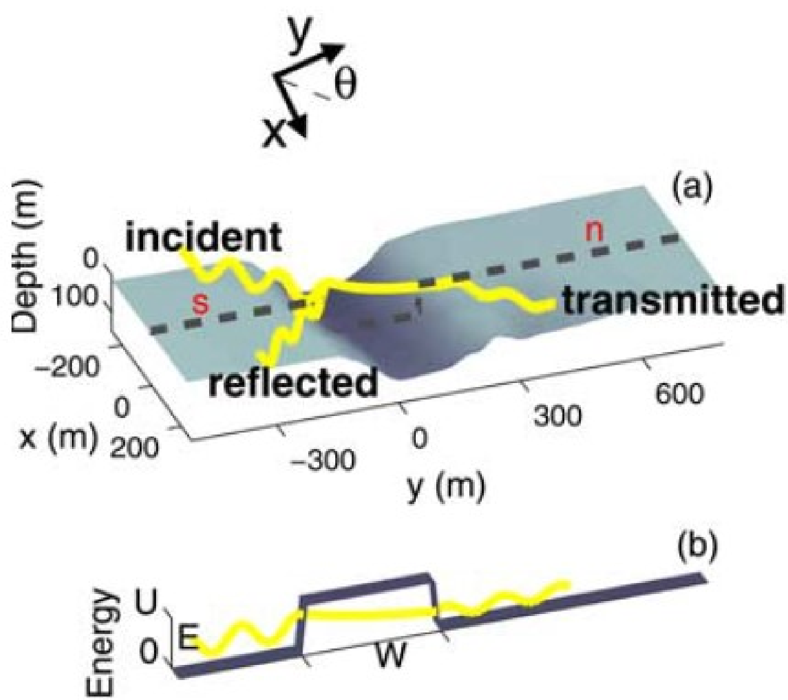
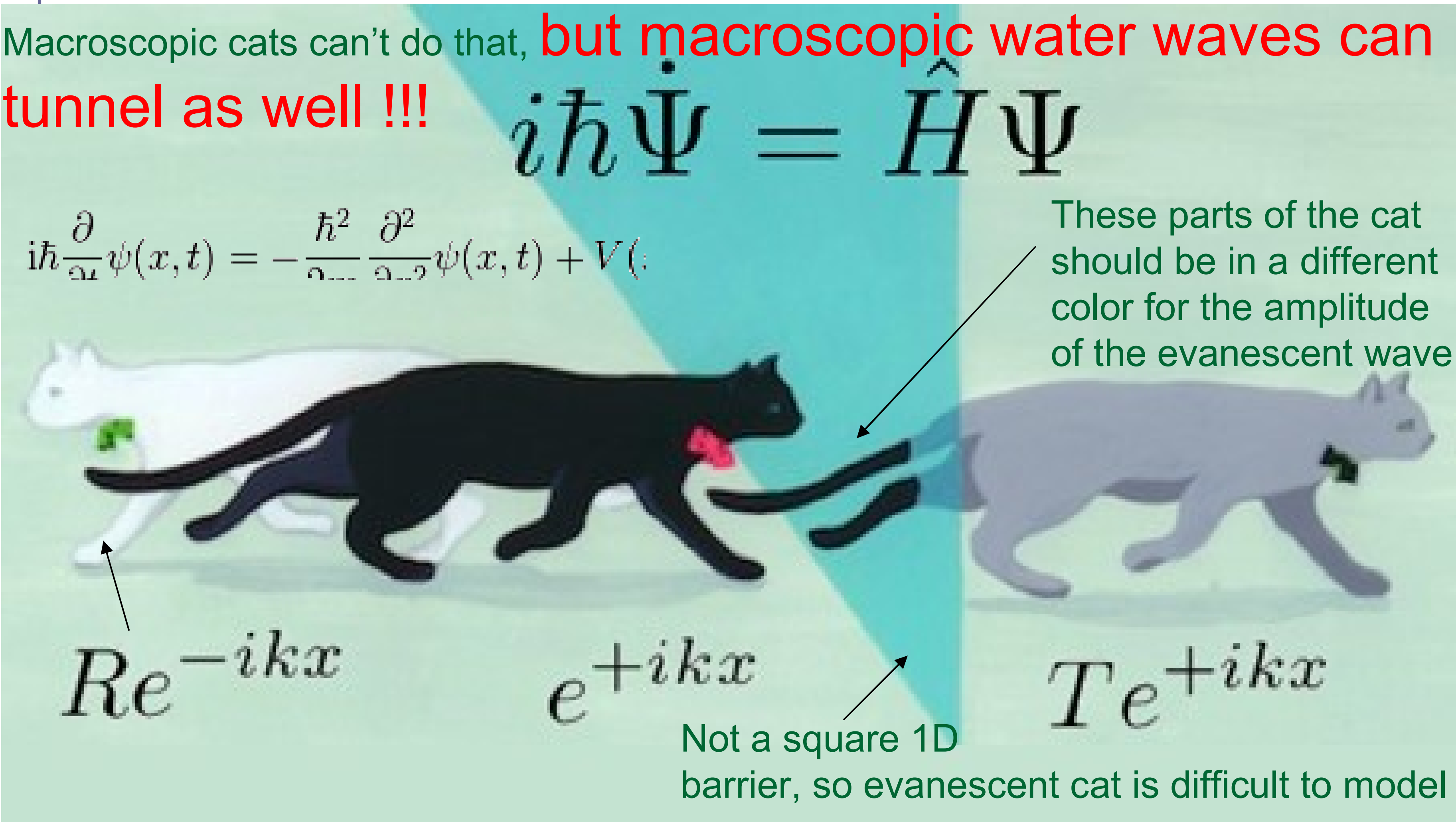


Figure 3. Schematic diagrams showing partial reflection of an oblique wave by a submarine canyon and quantum tunneling across an energy barrier. (a) Partial reflection of an obliquely incident wave (yellow curve) over the measured canyon bathymetry (shaded surface). A decaying wave over the canyon excites a transmitted wave on the far side, even though there is no propagation within the canyon. The transmitted wave preserves the angle θ relative to the cross-canyon coordinate *y*, while the reflected wave reverses the angle. Depth is measured in meters below mean sea level, and a rectangular idealization of the canyon cross-section with $h = 20$ m, $h_c = 115$ m, and $W = 365$ m is shown as a grey dashed line between the south (s) and north (n) instrument sites. (b) Quantum tunneling of a free particle (yellow curve) with energy E through a finite width W region of potential energy U, where $E < U$ and the region is classically forbidden. The scale of the decaying solution in the forbidden region is set by the de Broglie wavelength of the particle.

Quasi-particles because the quantum mechanics formalism is so successful



$$\Delta x \, \Delta p_x \gtrsim h \qquad \sigma_x \sigma_p \geq \frac{\hbar}{2}$$

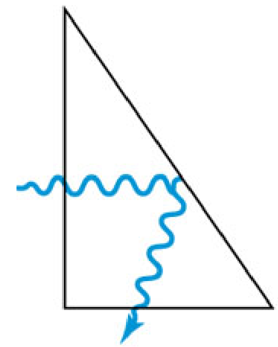
funny Quantum energy bank: your "quantum self" can get a no interest loan ΔE for a certain time Δt as long as ΔE Δt < h

where $\hbar = h/2\pi$, and σ_x, σ_p are the standard deviations of position and momentum

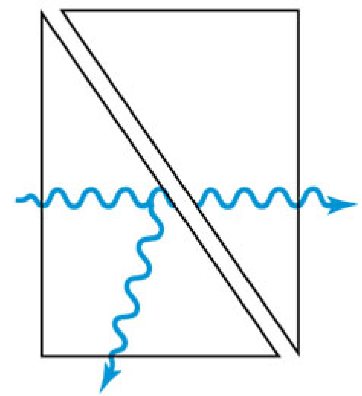
Analogy with Wave Optics

- If light passing through a glass prism reflects from an internal surface with an angle greater than the critical angle, total internal reflection occurs. However, the electromagnetic field is not exactly zero just outside the prism. If we bring another prism very close to the first one, experiments show that the electromagnetic wave (light) appears in the second prism.

- The situation is analogous to the tunneling described here. This effect was observed by Newton and can be demonstrated with two prisms and a laser. The intensity of the second light beam decreases exponentially as the distance between the two prisms increases.



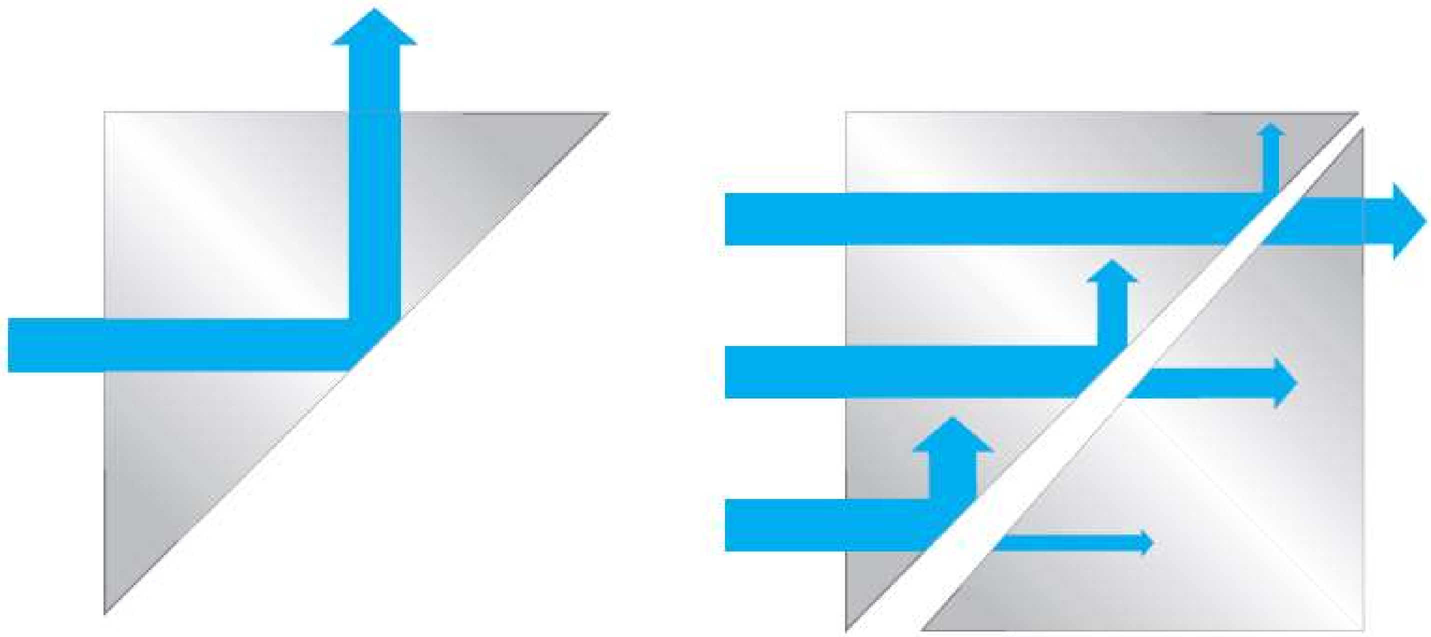
(a)



(b)

© 2006 Brooks/Cole - Thomson

Tunneling is just what waves like to do, observed macroscopically as well



(a) (b)

Figure 7.5 (a) Total internal reflection of light waves at a glass–air boundary. An evanescent wave penetrates into the space beyond the reflecting surface. (b) Frustrated total internal reflection. The evanescent wave is "picked up" by a neighboring surface, resulting in transmission across the gap. Notice that the light beam *does not* appear in the gap.

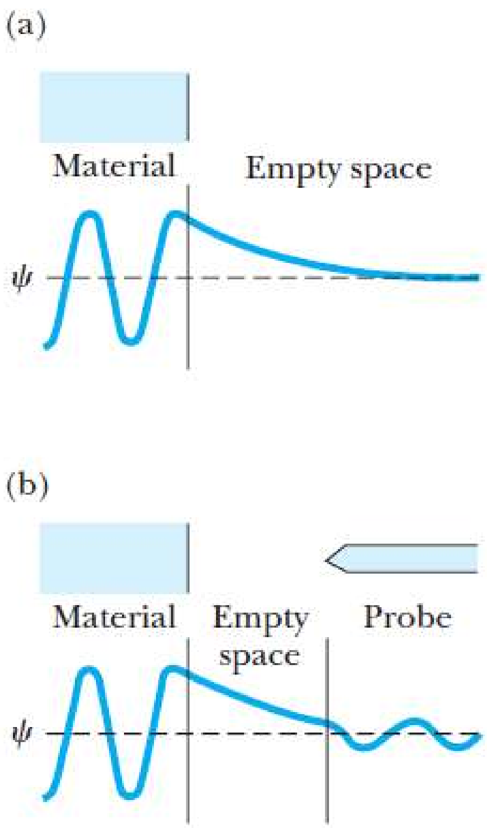


Figure 3 (a) The wavefunction of an electron in the surface of the material to be studied. The wavefunction extends beyond the surface into the empty region. (b) The sharp tip of a conducting probe is brought close to the surface. The wavefunction of a surface electron penetrates into the tip, so that the electron can "tunnel" from surface to tip. Compare this figure to Figure 7.2a.

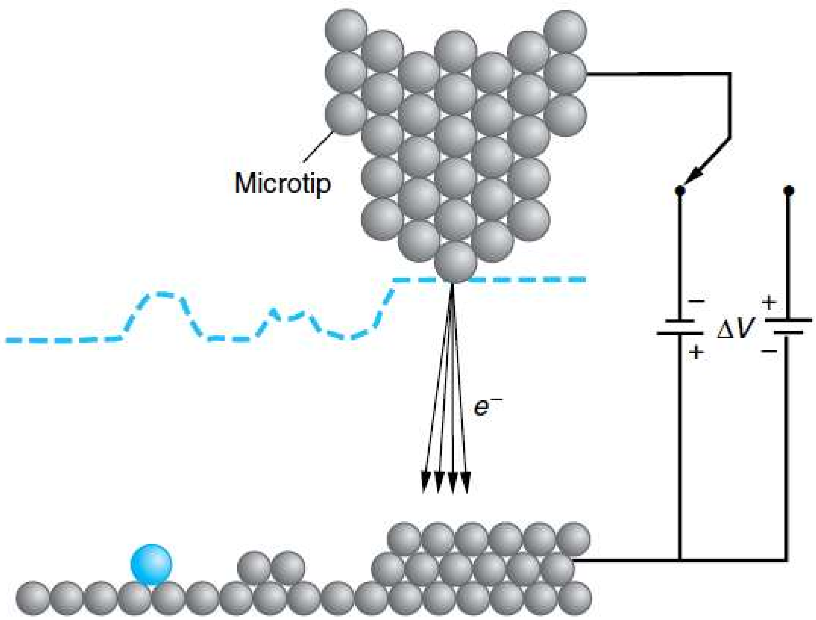
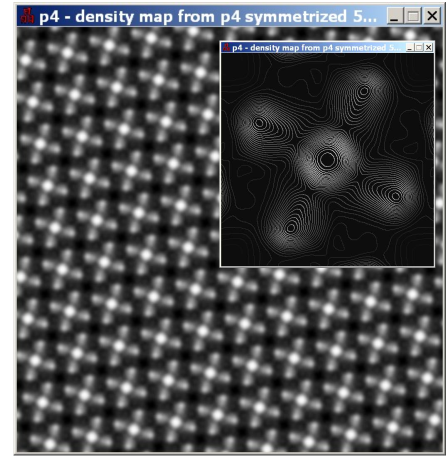
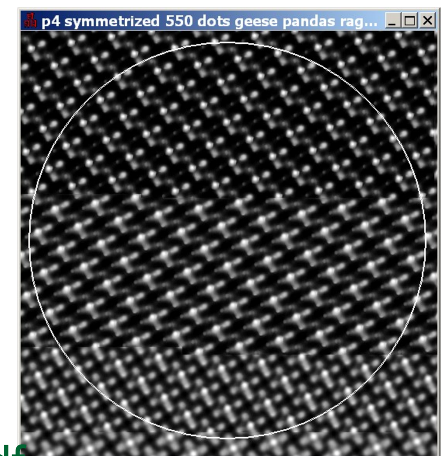


Figure 6-29 Schematic illustration of the path of the probe of an STM (dashed line) scanned across the surface of a sample while maintaining constant tunneling current. The probe has an extremely sharp microtip of atomic dimensions. Tunneling occurs over a small area across the narrow gap, allowing very small features (even individual atoms) to be imaged, as indicated by the dashed line.



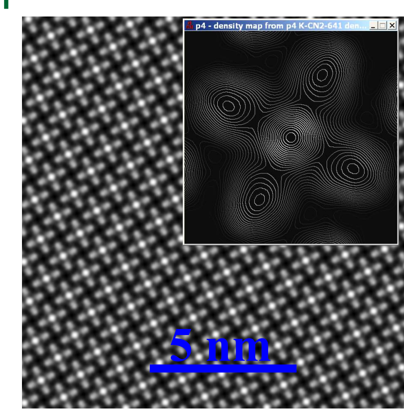


http://www.ascimaging.com/content/pdf/s40679-015-0014-6.pdf

*arXiv:*2009.08539

MS project Andrew Dempsey: *arXiv:*2009.08539

Doi: 10.3390/sym10050133 magnus opus

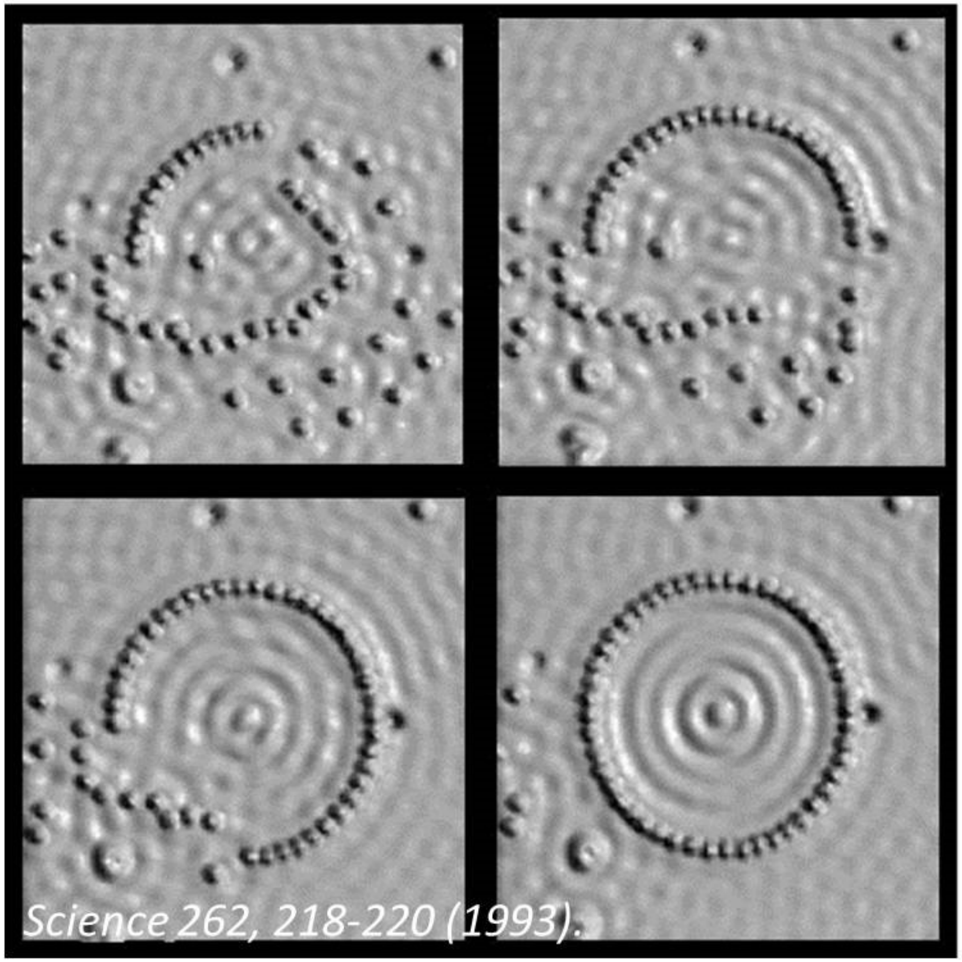


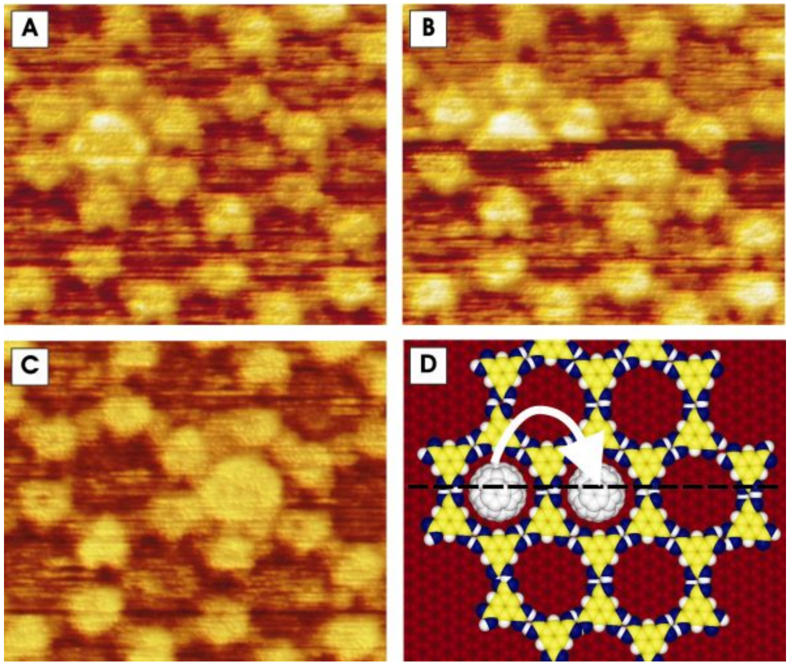
My research groups' work

Doi: 10.1109/nnano.2019.2946597

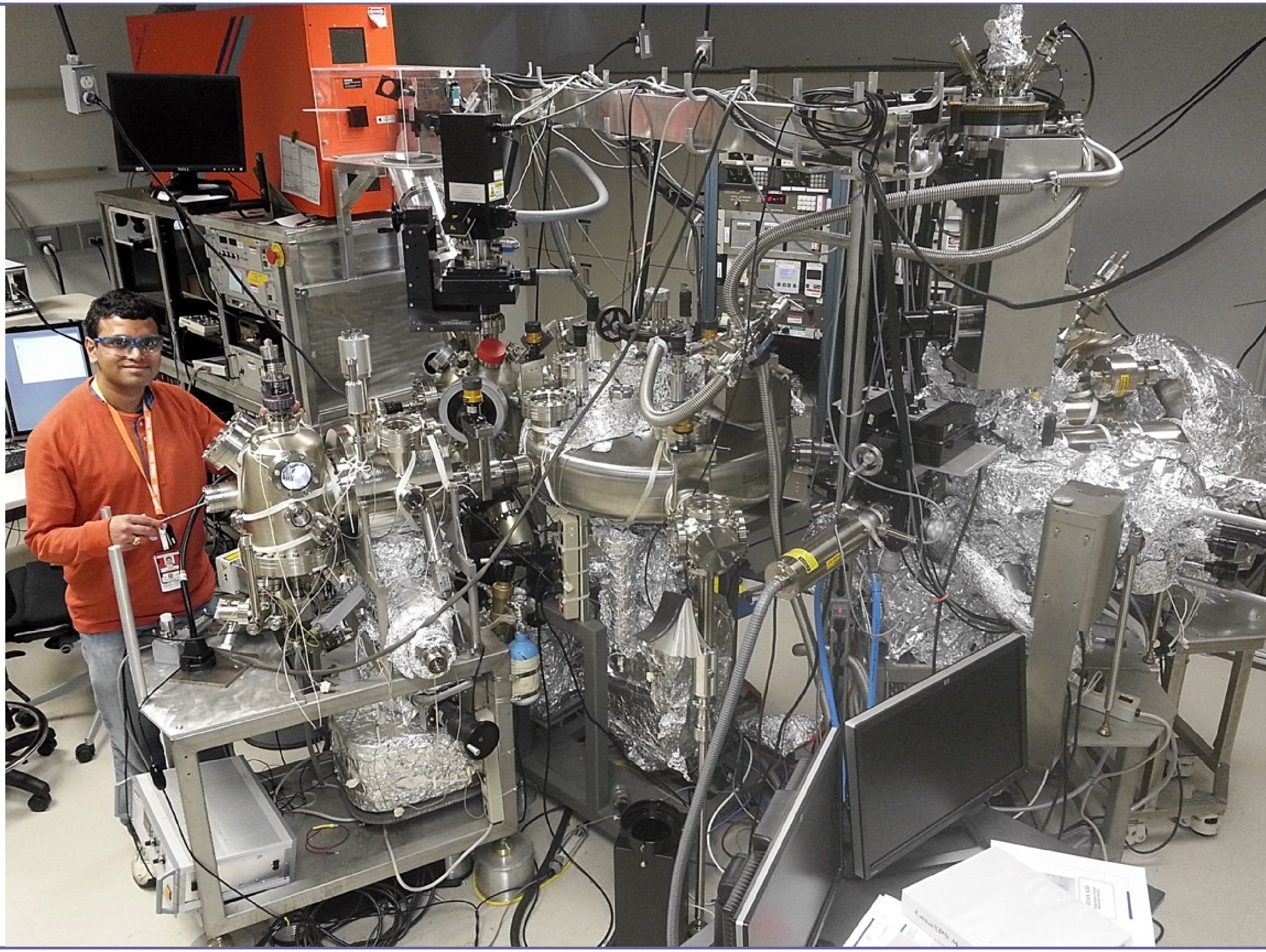
Doi: 10.1107/S2053273322000845

arXiv:2108.00829

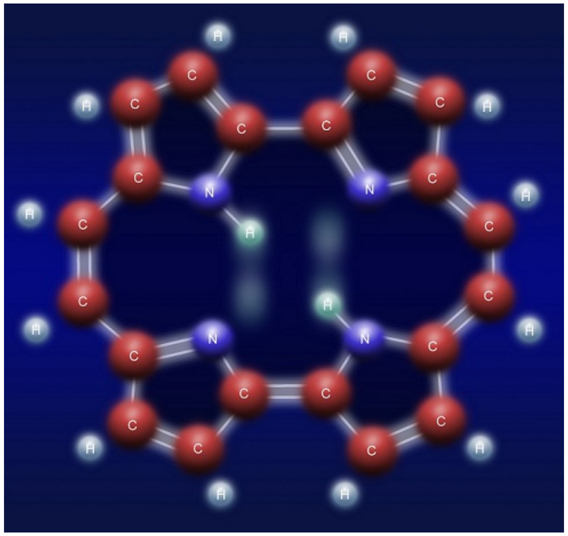




What Michael Hietscholdt's group the last time Germany was world champion in soccer, tunneling observed while scanning !! The popular press called it nano-soccer, but it is just a statistical process



Center for Nano-phase Materials Science, CNMS, Oak Ridge National Lab.
MS project with Tyler Bortel, Lee Field supposed to help him

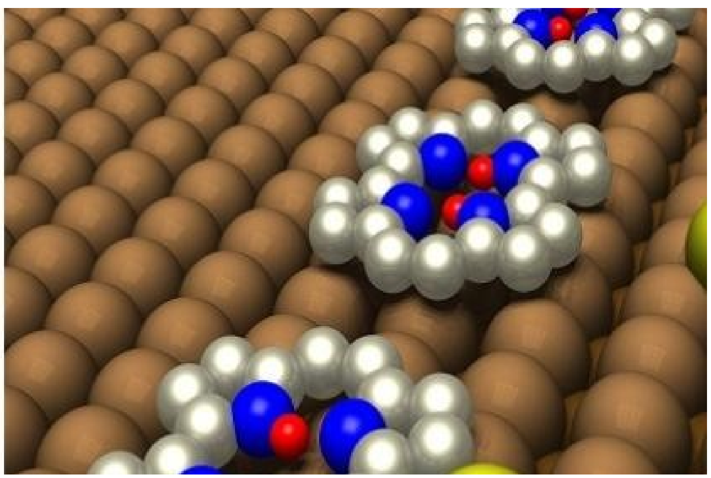


The porphycene molecule

"We were pretty surprised to find that after depositing the molecules on the copper substrate, hydrogen ions in the porphycene molecule formed a configuration that had never before been observed, despite many years of research on this compound," says Waluk. "Instead of being located in opposite corners of the tetragon formed by nitrogen atoms, the hydrogen atoms took positions next to each other."

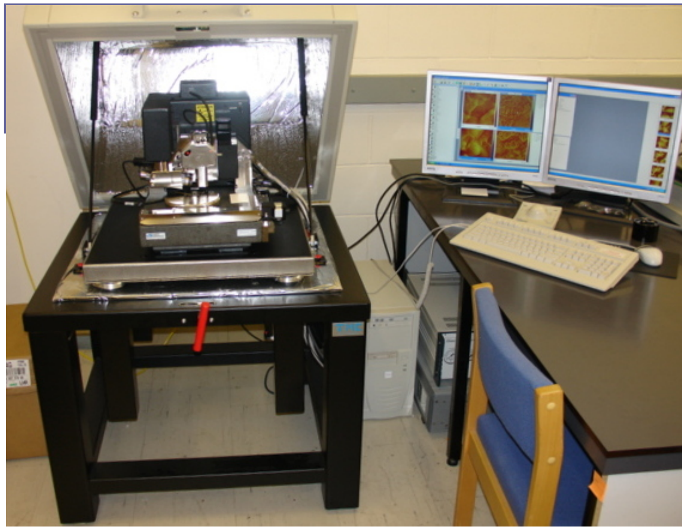
The researchers then used the tungsten tip of the STM to place single copper atoms around the porphycene molecule, observing how the positions of the copper atoms affected tautomerization.

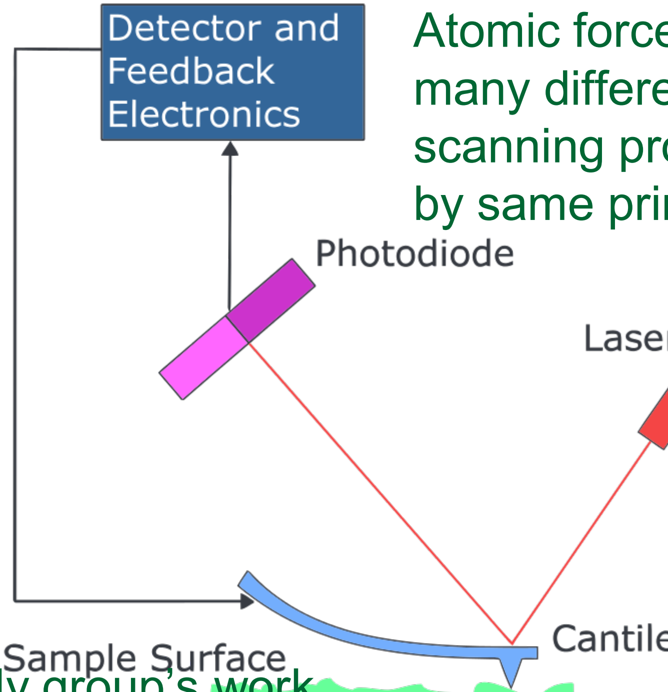
http://www.nature.com/nchem/journal/v6/n1/full/nchem.1804.html



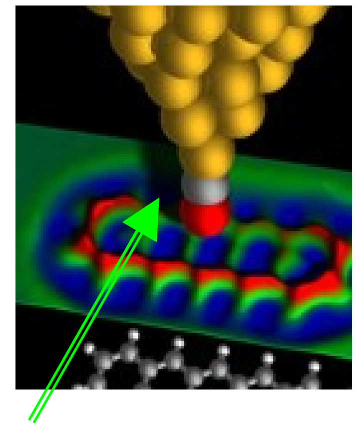
Two protons (red) in a porphycene molecule deposited onto the surface of a perfect copper crystal (brown) can change their positions at nitrogen atoms (blue) depending on the position of a single copper atom (yellow).

Waluk. *Nature Chemistry*, 2014

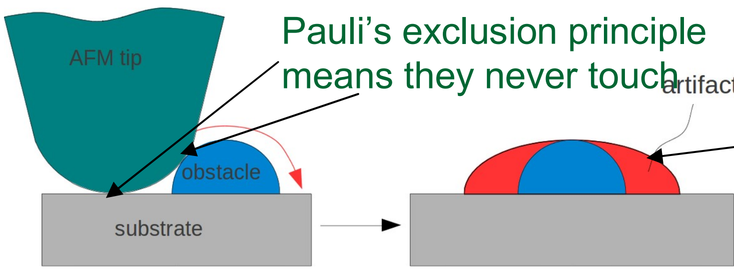




Atomic force microscopy, many different kinds of scanning probe microscopes by same principle



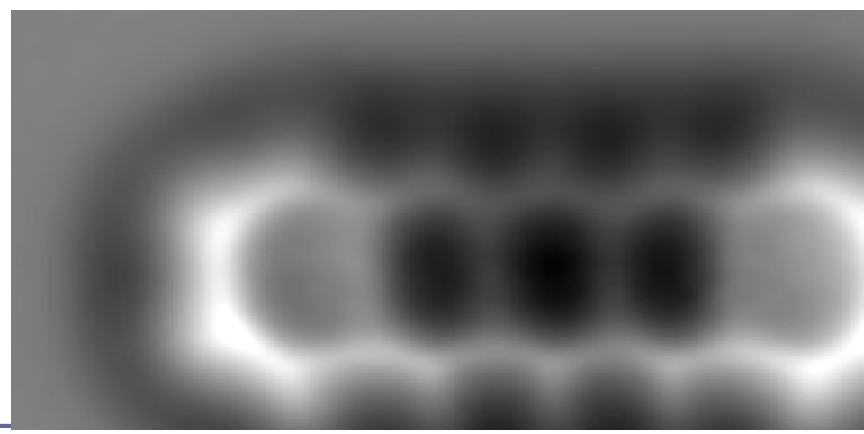
Special functionalization



Pauli's exclusion principle means they never touch

My group's work minimizes this effect

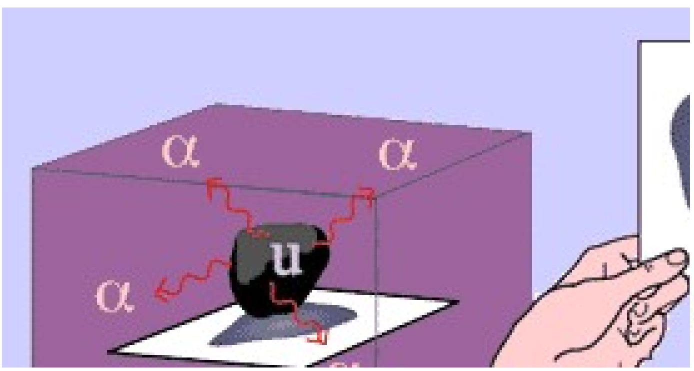
AFM image of a pentacene molecule. The five hexagonal carbon rings are resolved clearly and even the carbon-hydrogen bonds are imaged.

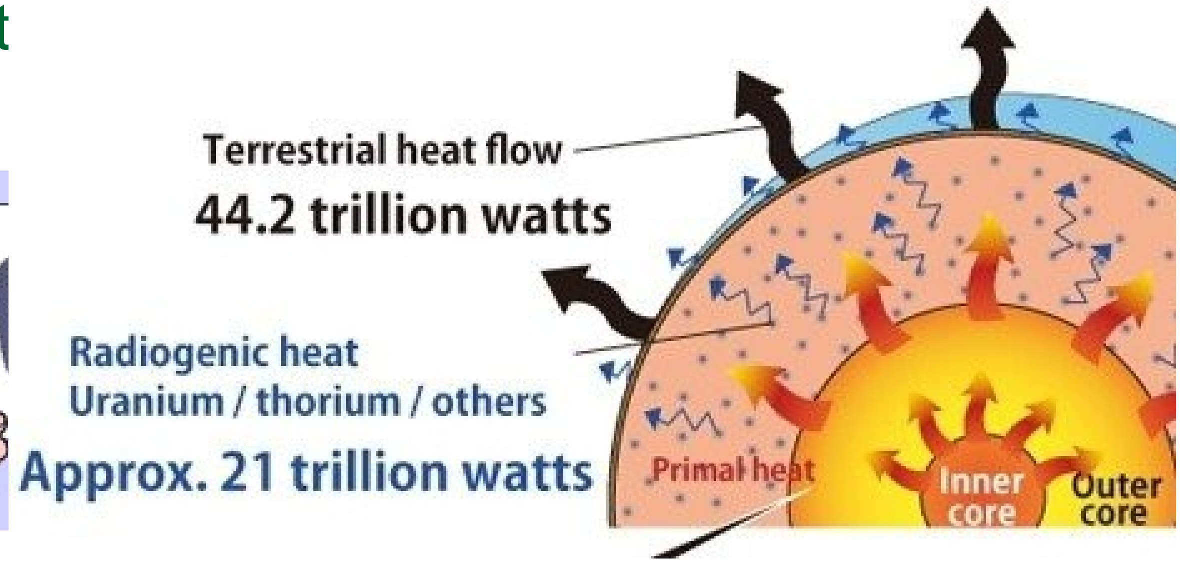


Could be further improved by enforcing point symmetry 2mm …

http://www.zurich.ibm.com/st/atomic_manipulation/pentacene.html

There is also radioactivity (from 1896 onwards): electrons and other particles, e.g. alpha particles, (nuclei of He, two proton + two neutrons) come out of the atoms of cert radioactive elements





end of this course, nuclear physics

Alpha-Particle Decay

- All α particles emitted from any one source have nearly the same energy and, for all known emitters, emerge with kinetic energies in the same narrow range, from about 4 to 9 MeV.
- In contrast to the uniformity of energies, the half-life of the emitter (time taken for half of the emitting substance to decay) varies over an enormous range—more than 20 orders of magnitude!—according to the emitting element (Table 7.1).

Table 7.1 Characteristics of Some Common α Emitters

Element	α Energy	Half-Life*
$^{212}_{84}Po$	8.95 MeV	2.98×10^{-7} s
$^{240}_{96}Cm$	6.40 MeV	27 days
$^{226}_{88}Ra$	4.90 MeV	1.60×10^{3} yr
$^{232}_{90}Th$	4.05 MeV	1.41×10^{10} yr

*Note that half-lives range over 24 orders of magnitude when α energy changes by a factor of 2.

$$t_{1/2} = \frac{\ln 2}{\lambda} = \frac{0.693}{\lambda}$$

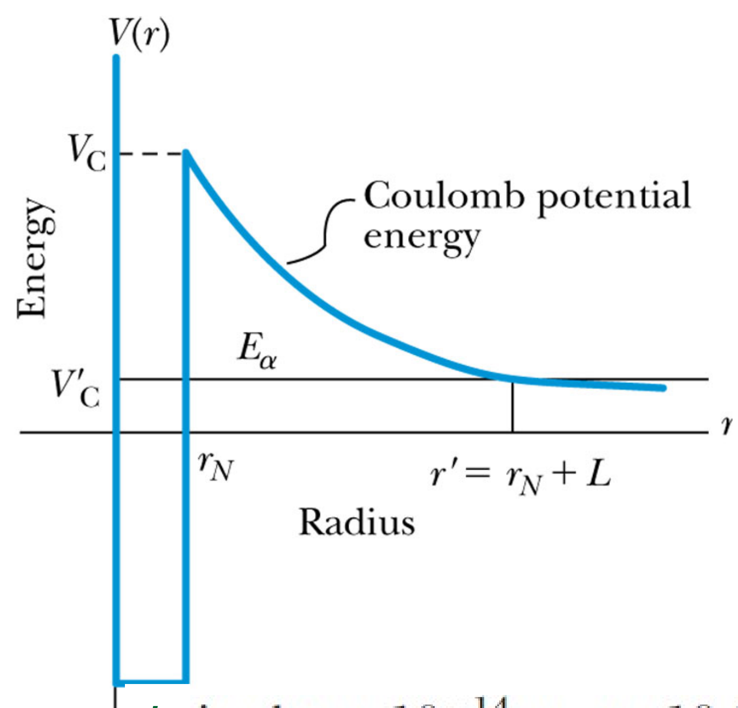
decay rate λ

the probability of α emission per unit time

Key idea: there must be an exponential relationship as obtained in tunneling

Alpha-Particle Decay

- The phenomenon of tunneling explains the alpha-particle decay of heavy, radioactive nuclei.
- Inside the nucleus, an alpha particle feels the very strong, but short-range attractive nuclear force as well as the repulsive Coulomb force.
- The nuclear force dominates inside the nuclear radius where the potential is approximately a square well.
- The Coulomb force dominates outside the nuclear radius.
- The potential barrier at the nuclear radius is several times greater than the energy of an alpha particle.
- quantum mechanics predicts that the alpha particle will tunnel through the barrier.



© 2006 Brooks/Cole - Thomson

L is about 10^{-14} m, or 10 fm

We have seen earlier that tunneling can often be approximated by exponential functions, e.g.

$$T = 16\frac{E}{V_0}\left(1-\frac{E}{V_0}\right)e^{-2\kappa L}$$ where $\kappa = \frac{\sqrt{2m(V_0-E)}}{\hbar}$

$$R \propto e^{\frac{Z-2}{\sqrt{KE}}}$$

R: decay rate, Geiger-Nuttal relation

The radioactive decay process also can be understood in terms of the time evolution of a nonstationary state, in this case one representing the α particle initially confined to the parent nucleus. Solving the Schrödinger equation for the time-dependent waveform in this instance is complicated, making numerical studies the option of choice here. The interested reader is referred to our companion Web site for further details and a fully quantum-mechanical simulation of α decay from an unstable nucleus. Go to http://info.brookscole.com/mp3e, select QMTools Simulations → Leaky Wells (Tutorial) and follow the on-site instructions.

$$T(E) = \exp\left\{-4\pi Z\sqrt{\frac{E_0}{E}} + 8\sqrt{\frac{ZR}{r_0}}\right\} \qquad (7.13)$$

Transmission coefficient for α particles of an unstable nucleus

In this expression, $a_0 = \hbar^2/m_\alpha ke^2$ is a kind of "Bohr" radius for the α particle. The mass of the α particle is $m_\alpha = 7295 m_e$, so r_0 has the value $a_0/7295 = 7.25 \times 10^{-5}$ Å, or 7.25 fm. The length r_0, in turn, defines a convenient energy unit E_0 analogous to the Rydberg in atomic physics:

$$E_0 = \frac{ke^2}{2r_0} = \left(\frac{ke^2}{2a_0}\right)\left(\frac{a_0}{r_0}\right) = (13.6\text{ eV})(7295) = 0.0993\text{ MeV}$$

To obtain decay rates, $T(E)$ must be multiplied by the number of collisions per second that an α particle makes with the nuclear barrier. This collision frequency f is the reciprocal of the transit time for the α particle crossing the nucleus, or $f = v/2R$, where v is the speed of the α particle inside the nucleus. In most cases, f is about 10^{21} collisions per second (see Problem 17). The decay rate λ (the probability of α emission per unit time) is then

$$\lambda = fT(E) \approx 10^{21}\exp\{-4\pi Z\sqrt{E_0/E} + 8\sqrt{Z(R/r_0)}\}$$

R size of the nucleus, E is total *classical* kinetic energy of the alpha particle (about 3,730 times smaller than rest energy), so we get away with non-relativistic treatment

k is Coulomb's constant here

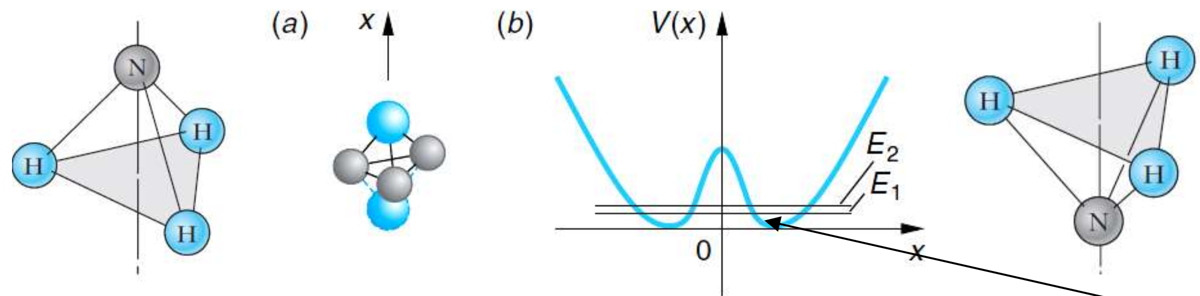
EXPLORING
NH_3 Atomic Clock

There is no mechanism for tunneling, as fast as the uncertainty principle allows, some theorist say it takes no time at all

Barrier penetration also takes place in the case of the periodic *inversion* of the ammonia molecule. The NH_3 molecule has two equilibrium configurations, as illustrated in Figure 6-31*a*. The three hydrogen atoms are arranged in a plane. The nitrogen atom oscillates between two equilibrium positions equidistant from each of the H atoms above and below the plane. The potential energy function $V(x)$ acting on the N atom has two minima located symmetrically about the center of the plane, as shown in Figure 6-31*b*. The N atom is bound to the molecule, so the energy is quantized and the lower states lie well below the central maximum of the potential. The central maximum presents a barrier to the N atoms in the lower states through which they ~~slowly~~ tunnel back and forth.[17] The oscillation frequency $f = 2.3786 \times 10^{10}$ Hz when the atom is in the state characterized by the energy E_1 in Figure 6-31*b*. This frequency is quite low compared with the frequencies of most molecular vibrations, a fact that allowed the N atom tunneling frequency in NH_3 to be used as the standard in the first *atomic clocks*, devices that now provide the world's standard for precision timekeeping.

Only slowly with respect to molecular vibrations in general, but with a well defined (predictable) tunneling coefficient

All states are symmetric about x = 0, E_1 and E_2 are the same in both troughs by symmetry



Approximately two Hooke potentials, harmonic oscillation

Figure 6-31 (*a*) The NH_3 molecule oscillates between the two equilibrium positions shown. The H atoms form a plane; the N atom is colored. (*b*) The potential energy of the N atom, where *x* is the distance above and below the plane of the H atoms. Several of the allowed energies, including the two lowest shown, lie below the top of the central barrier through which the N atom tunnels.

Time independent, one space dimension	$$\frac{-\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} + V(x)\psi(x) = E\psi(x)$$	**6-18**
Normalization condition	$$\int_{-\infty}^{+\infty} \Psi^*(x,t)\Psi(x,t)\,dx = 1$$	**6-9**
	and	
	$$\int_{-\infty}^{+\infty} \psi^*(x)\psi(x)\,dx = 1$$	**6-20**
Acceptability conditions	1. $\psi(x)$ must exist and satisfy the Schrödinger equation. 2. $\psi(x)$ and $d\psi/dx$ must be continuous. 3. $\psi(x)$ and $d\psi/dx$ must be finite. 4. $\psi(x)$ and $d\psi/dx$ must be single valued. 5. $\psi(x) \longrightarrow 0$ fast enough as $x \longrightarrow \pm\infty$ so that the normalization integral, Equation 6-20, remains bounded.	

2. Infinite square well

Allowed energies	$$E_n = n^2\frac{\pi^2\hbar^2}{2mL^2} = n^2E_1 \qquad n = 1, 2, 3, \ldots$$	**6-24**
Wave functions	$$\psi_n(x) = \sqrt{\frac{2}{L}}\sin\frac{n\pi x}{L} \qquad n = 1, 2, 3, \ldots$$	**6-32**

3. Finite square well	For a finite well of width L the allowed energies E_n in the well are lower than the corresponding levels for an infinite well. There is always at least one allowed energy (bound state) in a finite well.	
4. Expectation values and operators only three operators are fundamental	The expectation or average value of a physical quantity represented by an operator, such as the momentum operator p_{op}, is given by $\langle p \rangle = \int_{-\infty}^{+\infty} \psi^* p_{op} \psi \, dx = \int_{-\infty}^{+\infty} \psi^* \left(\frac{\hbar}{i} \frac{\partial}{\partial x} \right) \psi \, dx$	**6-48**
5. Simple harmonic oscillator Allowed energies	$E_n = \left(n + \frac{1}{2} \right) \hbar\omega \qquad n = 0, 1, 2, \ldots$ or on the same order of magnitude	**6-56**
6. Reflection and transmission	energy function When the potential changes abruptly in a distance small compared to the de Broglie wavelength, a particle ~~may~~ be reflected even though $E > V(x)$. A particle ~~may~~ also penetrate into a region where $E < V(x)$.	

Plane wave representation for a free particle

$$\Psi_k(x, t) = Ae^{i(kx - \omega t)} = A\{\cos(kx - \omega t) + i \sin(kx - \omega t)\}$$

$$\frac{d^2\psi}{dx^2} = \frac{2m}{\hbar^2} [U(x) - E] \psi(x) \qquad i\hbar \frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m} \left(\frac{\partial^2 \Psi}{\partial x^2} + \frac{\partial^2 \Psi}{\partial y^2} + \frac{\partial^2 \Psi}{\partial z^2} \right) + V\Psi(x, y, z, t)$$

$$R(E) + T(E) = 1 \qquad T(E) \approx \exp\left(-\frac{2}{\hbar} \sqrt{2m} \int \sqrt{U(x) - E} \, dx \right)$$

If not a square barrier or ditch

https://phet.colorado.edu/sims/cheerpj/quantum-tunneling/latest/quantum-tunneling.html?simulation=quantum-tunneling

- https://www.youtube.com/watch?v=Hmy-N4AFNDM

- To pronounce Albert Einstein correctly and then some …

EXAMPLE 6.9 Energy of a Finite Well: Exact Treatment

Impose matching conditions on the interior and exterior wavefunctions and show how these lead to energy quantization for the finite square well.

Solution The exterior wavefunctions are the decaying exponential functions given by Equation 6.20 with decay constant $\alpha = [2m(U-E)/\hbar^2]^{1/2}$. The interior wave is an oscillation with wavenumber $k = (2mE/\hbar^2)^{1/2}$ having the same form as that for the infinite well, Equation 6.15; here we write it as

$$\psi(x) = C \sin kx + D \cos kx \qquad \text{for } 0 < x < L$$

To join this smoothly onto the exterior wave, we insist that the wavefunction and its slope be continuous at the well edges $x = 0$ and $x = L$. At $x = 0$ the conditions for smooth joining require

four equations for four unknown

$$\psi(x)^* = A^* \sin kx + B^* \cos kx \qquad \text{for } 0 < x < L \qquad (6.15)$$

$$\psi(0)^* = B^* = 0 \qquad \text{(continuity at } x = 0)$$
$$\psi(L)^* = A^* \sin kL^* = 0 \qquad \text{(continuity at } x = L) \qquad (6.16)$$

* Infinitely deep

The last condition requires that $kL = n\pi$, where n is any positive integer.[9]

$$\psi(x) = Ae^{+\alpha x} \qquad \text{for } x < 0$$
$$\psi(x) = Be^{-\alpha x} \qquad \text{for } x > L \qquad (6.20)$$

For finite square well,

B* → C ≠ 0

ψ(L) = A sin kL* → D ≠ 0

[9]For $n = 0$ ($E = 0$), Schrödinger's equation requires $d^2\psi/dx^2 = 0$, whose solution is given by $\psi(x) = Ax + B$ for some choice of constants A and B. For this wavefunction to vanish at $x = 0$ and $x = L$, both A and B must be zero, leaving $\psi(x) = 0$ everywhere. In such a case the particle is nowhere to be found; that is, no description is possible when $E = 0$. Also, the inclusion of negative integers $n < 0$ produces no new states, because changing the sign of n merely changes the sign of the wavefunction, leading to the same probabilities as for positive integers.

$$A = D \qquad \text{(continuity of } \psi\text{)}$$

$$\alpha A = kC \qquad \left(\text{continuity of } \frac{d\psi}{dx}\right)$$

Dividing the second equation by the first eliminates A, leaving

$$\frac{C}{D} = \frac{\alpha}{k}$$

In the same way, smooth joining at $x = L$ requires

$$C \sin kL + D \cos kL = Be^{-\alpha L} \qquad \text{(continuity of } \psi\text{)}$$

$$kC \cos kL - kD \sin kL = -\alpha Be^{-\alpha L} \qquad \left(\text{continuity of } \frac{d\psi}{dx}\right)$$

Again dividing the second equation by the first eliminates B. Then replacing C/D with α/k gives

$$\frac{(\alpha/k)\cos kL - \sin kL}{(\alpha/k)\sin kL + \cos kL} = -\frac{\alpha}{k}$$

For a specified well height U and width L, this last relation can only be satisfied for special values of E (E is contained in both k and α). For any other energies, the waveform will not match smoothly at the well edges, leaving a wavefunction that is physically inadmissable. (Note that the equation cannot be solved explicitly for E; rather, solutions must be obtained using numerical or graphical methods.)

From classical physics we have for the harmonic oscillator

P. Sanghera, Quantum physics … Wiley 2011

$$\frac{d^2x(t)}{d^2}+\frac{\kappa}{m}x(t)=0 \qquad x = Ae^{i\sqrt{\kappa/m}\,t} \quad \text{or} \quad x(t) = A\sin\omega t$$

Where A is amplitude, i.e. maximal x, and κ is spring constant, it can be shown that

$$\frac{dP}{dx}=A\pi\sqrt{1-(x/A)}$$

Compare that to the harmonic quantum oscillator

$$\frac{dP}{dx}=\frac{1}{\pi}\sqrt{\frac{\alpha}{2n+1}}\{\sqrt{1-\frac{\alpha x^2}{2n+1}}\}^{-1}$$

We can "relate" A to *α* by setting these two equations equal and obtain

$$A_{taken\_as\_\lim\_where\_quantum\_osc.\_behave\_classical}=\sqrt{\frac{2n+1}{\alpha}}$$

Since α is constant

$$\alpha=\frac{\sqrt{m\kappa}}{\hbar}$$

The higher the quantum number, the less the quantum oscillator overshoots its classical limit (and the less tunneling), Bohr's correspondence principle