II. Schrödinger Theory

Now we'll look at Schrödinger theory, where quantum theory came together, with Schrödinger's 1926 development of a wave equation that describes particles. It's nonrelativistic* but otherwise general – it accounts for all kinds of particle interactions if we specify the potential.

Shrödinger did not derive his equation from first principles; rather, he developed it based on some features he thought it should have from some of the results we discussed above. We'll do something similar – that is, give a plausibility argument. When Schrödinger's equation gave the correct results (i.e. they agreed w/ expt), he knew he was on the right track. In particular, it also provided the explanation for atomic spectra, and the stationary states came right out, as we'll see below.

Wave function Ψ

As discussed in the intro, it became clear that particles have wavelike properties, so we need a way to describe them mathematically. We know how to do this in general; a wave w/a wavelength λ

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* Dirac came up with the relativistic version in 1928.

and frequency $\underline{\nu}$ can be described by a sin or cos:

$$A \sin 2\pi\left(\frac{x}{\lambda} - \nu t\right) \qquad (\text{or } \cos)$$

Let's <u>change</u> to a more common <u>notation</u>

$$k = \frac{2\pi}{\lambda} \equiv \text{wave number}$$

$$\omega = 2\pi\nu \equiv \text{angular frequency}$$

Also, let's call the function above ψ. So

$$\psi \sim A \sin(kx - \omega t) \quad \text{or} \quad \cos(kx - \omega t)$$

Broglie tells us the <u>connection</u> between the wave properties (λ, ν or equivalently k, ω) and the <u>momentum</u> and <u>energy</u> of the corresponding particle – a free particle with momentum p:

$$p = \frac{h}{\lambda} \qquad \text{or} \qquad \boxed{\begin{matrix} p = \hbar k \\ E = \hbar\omega \end{matrix}} \qquad \text{where } \hbar \equiv \frac{h}{2\pi}$$

$$E = h\nu$$

"h-bar"

Furthermore, we know that for a <u>free</u> particle,

$$E = KE = \frac{1}{2}mv^2 = \frac{p^2}{2m}$$

Translating this in terms of k & ω,

$$\hbar\omega = \frac{\hbar^2 k^2}{2m} \quad \text{or} \quad \boxed{\omega = \frac{\hbar k^2}{2m}}$$

So we can write our wave as

$$\psi \sim A \sin\left(kx - \hbar k^2 t/2m\right) \qquad \text{(or cos)}$$

So we have this function, ψ, that describes a de Broglie wave. What do we do with it – what does it mean physically?

<u>Physical interp. of ψ: Born</u>

Born gave the answer, but first recall that the reason we need waves is because electrons display interference + diffraction. So remember how it works for E-M waves

<u>Recall for EM waves</u>: The relevant function is the electric field $\vec{E}$, + it satisfies

– superposition : $\vec{E}_{tot} = \vec{E}_1 + \vec{E}_2$

If $\vec{E}_1$ is sol'n to Maxwell's, + $\vec{E}_2$ is sol'n, so is $a\vec{E}_1 + b\vec{E}_2$

from which you get interference, because

–intensity $I \propto |\vec{E}|^2$

$$\Rightarrow I_{tot} \propto |\vec{E}_{tot}|^2 = |\vec{E}_1|^2 + |\vec{E}_2|^2 + 2\vec{E}_1 \cdot \vec{E}_2$$

interference

and the <u>intensity</u> is proportional to the <u>energy/unit volume</u>, which is also proportional to the average <u>number</u> of <u>photons</u>, or equivalently, to the <u>probability</u> of a photon crossing some area/unit time.

Born suggested an analogy for particles. The crucial point is that you get interference when you have superposition of a function & the relevant intensity/probability goes like the square. So Born postulated that

$|\psi(x,t)|^2$ measures the probability/unit volume for finding the particle at a particular place (x) and time (t)

and superposition applies to the wave function ψ itself. (So you can no longer specify the exact location of a particle from the equations of motion; you can only work with probabilit

This interpretation gives rise to the correct wave-like behavior. Now we just need an equation for ψ that we can apply in various physical situations.

Comment: The absolute value signs above are used not because ψ is a vector — it's not — but because in general it is complex. So

$$|\psi|^2 = \psi^*\psi$$

Note that because it is the absolute square, the probability is guaranteed to be real and nonnegativ

Complex Numbers: Quick Review

See also
Appendix F

There is no real number sol'n to the eq'n $x^2+1=0$.

So invent a new, imaginary number i that solves it:
$$i = \sqrt{-1}$$

You can multiply i by a real number to get another imaginary number, and you can add a real and an imaginary to get a complex number

$$z = a + ib$$

a and b are real numbers. a is called the real part of z ($\mathrm{Re}\, z = a$) and b is the imaginary part ($\mathrm{Im}\, z = b$).

Algebra is a natural extension of real algebra:

1. Addition: $(a+bi)+(c+di) = a+c + (b+d)i$
2. Subtraction: $a+bi-(c+di) = a-c+(b-d)i$
3. Multiplication: $(a+bi)(c+di) = a(c+di) + bi(c+di)$
$$= ac + adi + bci + bd(\underbrace{i^2}_{-1})$$
$$= ac - bd + i(ad+bc)$$
4. Division: see below

Complex conjugate: $z^* \equiv a - bi$. This implies

$$zz^* = z^*z = (a+bi)(a-bi) = a^2 + abi - abi - i^2b^2$$
$$= a^2 + b^2$$

This is called the absolute value squared;

$$|z|^2 = zz^* = z^*z$$

and it is always real and nonnegative.

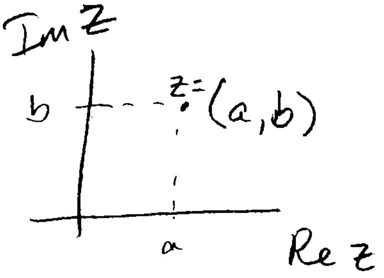
Also, $z + z^* = 2a = 2\,\mathrm{Re}\,z$

$$z - z^* = 2bi = 2i\,\mathrm{Im}\,z$$

Now we can define

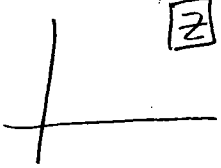
4. Division: $\dfrac{a+bi}{c+di} = \dfrac{a+bi}{c+di}\left(\dfrac{c-di}{c-di}\right) = \dfrac{ac+bd+i(bc-ad)}{c^2+d^2}$

Graphical representation: We can plot the real and imaginary parts of z on independent axes; z becomes a 2-dim vector:



Note that the dist. from the origin to z is just the magnitude of z.

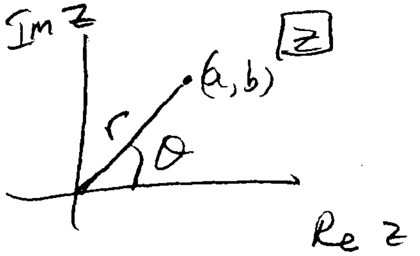
This is called the complex plane, + is sometimes identified as



(complex no. review, cont.)

2.4.3

Just as we can identify a point in an ordinary plane using polar coordinates, so we can in the complex plane:



$r = |z|$; $r^2 = a^2 + b^2$

$a = r\cos\theta$

$b = r\sin\theta$

$\Rightarrow \boxed{z = r(\cos\theta + i\sin\theta)}$

Euler's formula: Recall $e^x = 1 + x + \frac{x^2}{2!} + \dots$

Let $x = e^{i\theta}$. Then we get

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

where we've used the expansions for sin + cos also

That means we can write

$$z = \boxed{r(\cos\theta + i\sin\theta) = re^{i\theta}} \quad \text{Euler's formula}$$

and when we're taking powers, this is a useful form, e.g.

$$z^{1/2} = (re^{i\theta})^{1/2} = r^{1/2}e^{i\theta/2}$$

And it's useful for deriving trig identities, e.g.

$$\cos(\alpha+\beta) = \operatorname{Re} e^{i(\alpha+\beta)} = \operatorname{Re}(e^{i\alpha}e^{i\beta})$$

$$= \operatorname{Re}[(\cos\alpha + i\sin\alpha)(\cos\beta + i\sin\beta)] = (\cos\alpha\cos\beta - \sin\alpha\sin\beta)$$

Now we'll use Euler's equation to write the *free particle wave fn* in a slightly different form. Instead of writing $\psi \sim \sin(kx-\omega t)$ or cos, use

$$\psi(x,t) = A\left[\cos(kx-\omega t) + i\sin(kx-\omega t)\right]$$
$$= Ae^{i(kx-\omega t)} \qquad \text{"plane wave"}$$

[Note we can always get sin + cos back by taking combinations of ψ + ψ^*, cf. pp. 2.4.2–2.4.3]

This is a standard way to write free part. w.f.'s + will be the appropriate form for obtaining the Schrödinger eq'n.

Argument for the Schrödinger Eq'n

This is a little different from the argument in the book, and a little closer to Schrödinger's.

We want an equation that tells us *how* the wave function *ψ depends on space (x) + time (t).* Typically we look for how ψ changes with changes in x and t, i.e. we look for a *differential* equation.

~~Comments:~~ Note that it will be a *partial* diff. eq'n, because x + t vary independently, so it'll involve $\frac{\partial}{\partial x}$ + $\frac{\partial}{\partial t}$. Recall "$\frac{\partial}{\partial x}$" means "take derivative with respect to x, holding t const."

— Note also that in principle we could have an integral equation, but physicists are better at differential eq'ns. (Would an integral eq'n still satisfy superposition?

Conditions the Schr. Eq'n should satisfy:

① It's *linear* and *homogeneous*.

This is so we can have *superposition*,* which we need for the wave properties. It means we can have terms proportional to Ψ and its derivatives, but nothing else, e.g. not Ψ^2 or $\Psi \frac{\partial \Psi}{\partial x}$ or $f(x,t)$ where f doesn't have anything to do with Ψ.

Exercise: Show that terms like those don't satisfy superposition, but linear ones do.

② It satisfies the *energy relation*

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

③ It has the *plane wave solution* for a free particle,

④ *DeBroglie* + *Einstein* are right:

$$p = \hbar k \quad \text{and} \quad E = \hbar\omega$$

(in general, not just for free particles)

*I.e., if Ψ_1 + Ψ_2 are sol'ns, $a\Psi_1 + b\Psi_2$ is also a sol'n.

Let's work with the plane wave + try to get momentum + energy out of it in differential form. We have

$$\Psi = A e^{i(kx-\omega t)} \quad + \quad p = \hbar k, \quad E = \hbar\omega$$

To get p out of ψ, we have to bring down a factor of k. Taking a derivative with respect to x does the trick:

$$\frac{\partial \Psi}{\partial x} = ikAe^{i(kx-\omega t)} = ik\Psi$$

Since $p = \hbar k$, multiply by $-i\hbar$:

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

So that operating on Ψ with $-i\hbar\frac{\partial}{\partial x}$ gives the momentum, so

$$\boxed{-i\hbar\frac{\partial}{\partial x} \text{ is the momentum operator}}$$

Similarly, from $\Psi = Ae^{i(kx-\omega t)}$ we get E by bringing down a factor of ω, by taking $\frac{\partial}{\partial t}$. Specifically,

$$i\hbar\frac{\partial}{\partial t}\Psi = \hbar\omega\Psi = E\Psi$$

So

$$\boxed{i\hbar \frac{\partial}{\partial t} \text{ is the energy operator}}$$

Now, back to the conditions for the Schr. Eq'n. For a free particle, $E = \frac{p^2}{2m}$. If we turn this into an operator equation, we have

$$i\hbar \frac{\partial}{\partial t} = \frac{-\hbar^2}{2m}\frac{\partial^2}{\partial x^2} \iff E^2 = \frac{p^2}{2m}$$

Now we just have it act on Ψ:

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

This satisfies all the conditions o
a free particle.

same w.f.
as E+M,
diff. eqn
⟺ diff $k \leftrightarrow \omega$

[**Aside**: Dirac used a relativistic ver
this to develop his relativistic eq'n, the Dirac eqn, which reduces to the Schr. Eq'n in the nonrelativistic limit.]

What if there's a potential, V(x)? Then

$$\frac{p^3}{2m} + V = E$$

and if we turn this into an operator eq'n acting on Ψ, V will just multiply Ψ. This is strictly true if V is const., in which case the solution is still a plane wave (why?), but $\frac{\hbar^2 k^2}{2m} + V = \hbar\omega$ now. Then we can argue that if V is slowly varying, then in a small region it's as if V is constant, so V(x) still multiplies Ψ. Finally, if V varies pretty rapidly, we simply postulate that we still multiply V + Ψ. And we find it works!

So we get the 1-D Schr. Eq'n in all* its glory:

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

1-D Schrödinger Eq'n

Now let's repeat the interpretation of the wave function:

same t

$$\boxed{\Psi^*(x,t)\,\Psi(x,t)\,dx = |\Psi(x,t)|^2 dx \text{ is the probability of finding the particle in the region between } x + x+dx}$$

i.e. $|\Psi|^2$ is the probability density.

Normalization: Note that the S.E., being linear and homogeneous in Ψ, doesn't care about normalization. We can multiply Ψ by any constant and it still satisfies the S.E. It's the probability condition that sets the normalization, because . . .

The probability of the particle being somewhere is equal to 1, i.e.,

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

Now what if we apply this to a plane wave:

$$\Psi^*\Psi = |A|^2 e^{-i(kx-\omega t)}\, e^{+i(kx-\omega t)} = |A|^2,\ \text{indep. of } x$$

And $\int_{-\infty}^{\infty} |A|^2\,dx \to \infty$ Yikes! This doesn't seem to work, because the integral is infinite.

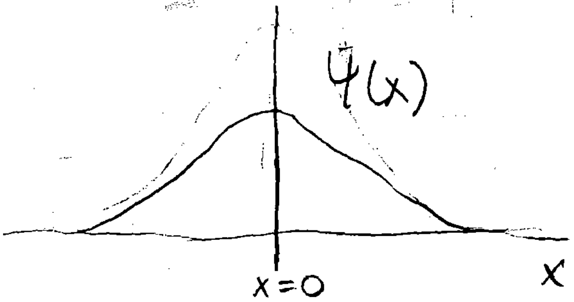
Turns out a plane wave is a very special case, and it isn't meaningful to talk about it in all space, so we consider it to be confined to a finite region. This is usually called "box normalization." In real life a plane wave tends to be too much of an idealization, and a better description is obtained from a more complicated but better behaved entity called a wave packet.

Fortunately the other wave functions we'll deal with are much better behaved and we can define a reasonable normalization.

Next: What kind of info about the particle can we get from the wave function?

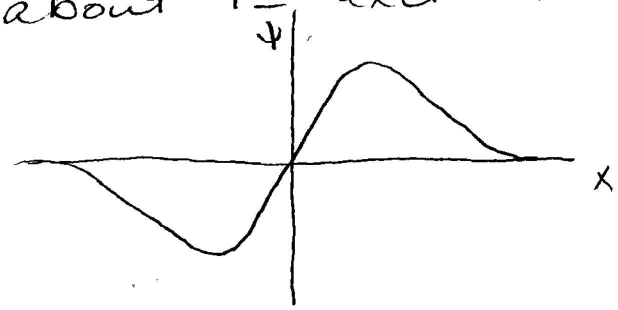
Ex A better behaved wave function is a Gaussian, which happens to be the ground state of the simple harmonic oscillator.

$\Psi \sim e^{-(\,)x^2}$



Particle most likely to be found, i.e. prob. is highest, near center. And $P(x) \to 0$ as $x \to \infty$, and integral is finite.

What about 1st excited state? It has w.f.



antisymm abt $x=0$.

Q1: What is prob density at $x=0$?

A1: 0

Q2: Can particle have $x<0$? Is prob. also anti symm abt 0?

A2: Yes can have $x<0$. $P=|\psi|^2$ is symm abt $x=0$

Q3: Particle has small but finite prob for x very large. What about classical s.h.o.?

A3: It has fixed limits, + prob. is highest near them.

Expectation Values

Now we want to extract info. about the particle from the w.f. The first thing that comes to mind is position x. It's obvious since we're dealing with a probability amplitude in x that we won't be able to predict the exact position of particles (we kinda knew that from the uncertainty principle).

What we can do: average over a large number of measurements on identical systems, also known as the

expectation value of x

$$\bar{X} = \int_{-\infty}^{\infty} x\, P(x,t)\, dx$$

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

same time

[Note: The order here is foreshadowing. You can think of $x\,\Psi(x,t)$ as the operator x mutiplying Ψ. We'll need this idea below.]

Now suppose we want to know the expectation value of x^2? It's

$$\overline{x^2} = \int_{-\infty}^{\infty} \Psi^*(x,t)\, x^2\, \Psi(x,t)\, dx$$

... and any function of x works the same way:

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

[Notation: expectation values are often written $\langle f \rangle$, with brackets instead of bars.]

We can define expectation values of other dynamical quantities too, like p + E, but it's subtle.

~~Expectation value of p~~: Generically it's

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

i.e., knowing x + t tells you p

Now, in classical mechanics we can write p as a function of x + t, but not so in QM, since we can't know p + x exactly at the same time. But we need to express p in terms of x + t, even if it's not exactly a function. Our result for the free particle wave fn solves the problem: recall the

Momentum operator $\boxed{-i\hbar \frac{\partial}{\partial x}}$

That's exactly what we need to use here.

So

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

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

Similarly, recalling that the energy operator is

<u>energy operator</u> $\boxed{i\hbar\frac{\partial}{\partial t}}$

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we get for the expectation value of the energy

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

An <u>equivalent</u> expression comes from the energy equation $E = \frac{p^2}{2m} + V(x,t)$, taking everything as an operator (which is how we got the Schrödinger eq'n): $E \rightarrow \frac{\left(-i\hbar\frac{\partial}{\partial x}\right)^2}{2m} + V(x,t)$

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

or

$$\boxed{\bar{E} = \int_{-\infty}^{\infty} \Psi^*(x,t)\left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x,t)\right)\Psi(x,t)\,dx}$$

So you can generalize to any dynamical quantity that's not only a function of $x + t$ but also possibly p; to get the expectation value, turn it into an operator by replacing p w/ $-i\hbar\frac{\partial}{\partial x}$:

$$\boxed{\overline{f(x,p,t)} = \int_{-\infty}^{\infty} \Psi^*(x,t)\, f_{op}\left(x, \frac{\hbar}{i}\frac{\partial}{\partial x}, t\right) \Psi(x,t)\,dx}$$

where I've used $-i = \frac{1}{i}$.

Fluctuations: variance + root mean-squared deviation.

We can get not only expectation values of things like x from the wave functions, we can also get an indication of the size of their fluctuations. The standard measure for this in statistics is the root-mean-squared (rms) deviation, or standard deviation.

The deviation refers to deviation from the mean.

Why not just deviation, then? Why rms? Because th

** average deviation from the mean is 0. **

If you think about it, that's really what we mean by the mean in the first place. We can show it's true; and take x for definiteness.

$$\text{avg. dev} = \int (x - \bar{x})\, P(x)\, dx$$

i.e., for each x we subtract the mean, weight it by the prob. density, + integrate over all x. We get

$$\int (x-\bar{x})P(x)dx = \underbrace{\int x\, P(x)dx}_{=\,\bar{x}} - \bar{x}\underbrace{\int P(x)dx}_{=\,1}$$

where we too $\bar{x}$ outside because it's a numb

$$= \bar{x} - \bar{x} = 0$$

That's because x has just as much probability to greater than the mean as to be less than the mean. So that doesn't tell us anything. We need a measure of the average distance from the mean that doesn't distinguish between positive + negative.

We can do this by squaring the deviation in, and averaging that. That gives us the

mean-squared deviation = variance

$$= \overline{(x-\bar{x})^2} = \int (x-\bar{x})^2\, P(x)dx$$

$$= \underbrace{\int x^2 P(x)dx}_{\overline{x^2}} - 2\bar{x}\underbrace{\int x\, P(x)dx}_{\bar{x}} + \bar{x}^2\underbrace{\int P(x)dx}_{1}$$

$$= \overline{x^2} - 2\bar{x}\bar{x} + \bar{x}^2 = \boxed{\overline{x^2} - \bar{x}^2 = \text{Variance}}$$

Now just take the square root, and we get the ⓶.17

root-mean-squared deviation = standard deviation

$$= \sqrt{\overline{x^2} - \bar{x}^2}$$

Comment: We could have found the expression for the variance without writing the integrals explicitly. With the convention $\bar{f} \equiv \int f P(x)dx$ where f is a generic function of x, we have

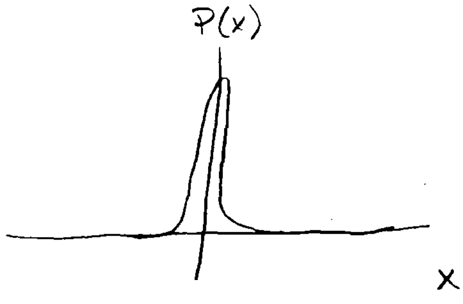
$$\overline{(x-\bar{x})^2} = \overline{x^2 - 2x\bar{x} - \bar{x}^2}$$

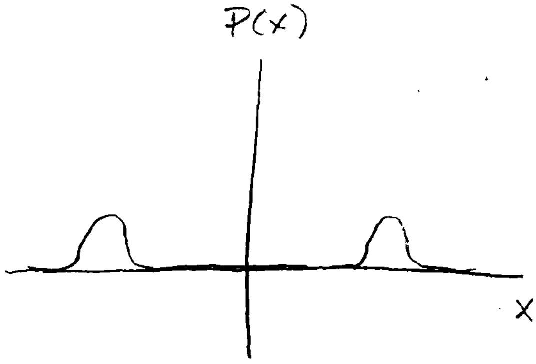
$$= \overline{x^2} - 2\bar{x}\bar{x} - \bar{x}^2$$

$$= \overline{x^2} - \bar{x}^2$$

because the avg of a const is a const, + $\bar{x}$ is a const

Note that distributions can have the same mean but very different standard deviations, because the s.d. measures the spread about the average, e.g.





Example Particle in 1D box

Consider a particle, mass m, that's free but constrained to stay between $x = \pm a/2$ by completely impenetrable walls. When we solve the S.E we'll find that the ground state is

$$\Psi(x,t) = \begin{cases} A\cos\frac{\pi x}{a}\, e^{-iEt/\hbar} & -\frac{a}{2} < x < \frac{a}{2} \\ 0 & x \le -\frac{a}{2} \text{ or } x \ge +\frac{a}{2} \end{cases}$$

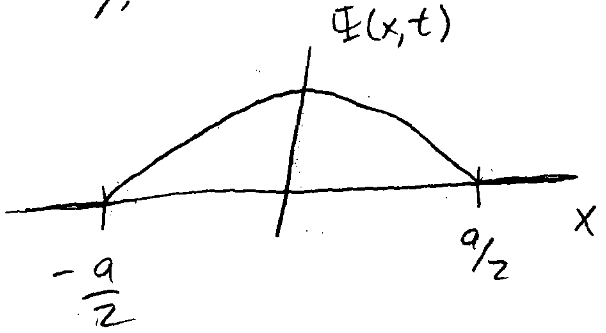
Q1: What does Ψ look like as a fn of x? Is it continuous?

A1: It's certainly continuous for $|x| < \frac{a}{2}$. What about $x = \pm\frac{a}{2}$?

$$\Psi\left(\pm\frac{a}{2}, t\right) = A\cos\left(\pm\frac{\pi}{2}\frac{a}{a}\right)e^{-iEt/\hbar} = A\cos\left(\pm\frac{\pi}{2}\right)e^{-iEt/\hbar}$$

$$= 0 \quad \text{ok}$$

Graphically, it looks like



+ we've assumed t is fixed (and, strictly speaking, taken the real or imaginary part).

Q2 Show Ψ satisfies the S.E.

A2 S.E. is $$-\frac{\hbar^2}{2m}\frac{\partial^2\Psi}{\partial x^2} + V\Psi = i\hbar\frac{\partial\Psi}{\partial t}$$

The particle is free, so V is constant, and we can take it to be 0. Now we need derivatives:

$$\frac{\partial\Psi}{\partial x} = -A\frac{\pi}{a}\sin\frac{\pi x}{a}e^{-iEt/\hbar}$$

$$\frac{\partial^2\Psi}{\partial x^2} = -A\frac{\pi^2}{a^2}\cos\frac{\pi x}{a}e^{-iEt/\hbar} = -\frac{\pi^2}{a^2}\Psi$$

$$\frac{\partial\Psi}{\partial t} = \frac{-iE}{\hbar}A\cos\frac{\pi x}{a}e^{-iEt/\hbar} = -\frac{iE}{\hbar}\Psi$$

(+ these are all 0 for $|x| \geq \frac{a}{2}$)

Combining,

LHS: $$-\frac{\hbar^2}{2m}\frac{\partial^2\Psi}{\partial x^2} = \frac{\hbar^2}{2m}\frac{\pi^2}{a^2}\Psi$$

RHS: $$i\hbar\frac{\partial\Psi}{\partial t} = E\Psi$$

LHS = RHS $\Rightarrow$ $$E = \frac{\hbar^2\pi^2}{2ma^2}$$

So the S.E. is satisfied if $E = \frac{\hbar^2\pi^2}{2ma^2}$. The S.E. told us what E has to be!

Q3 Is $\frac{\partial\Psi}{\partial x}$ continuous?

Skip

A3 $$\frac{\partial\Psi}{\partial x} = -A\frac{\pi}{a}\sin\frac{\pi x}{a}e^{-iEt/\hbar}$$

Again, look at $x = \pm\frac{a}{2}$ (It's definitely continuous elsewhere.)

$$\left.\frac{\partial\Psi}{\partial x}\right|_{x=\pm\frac{a}{2}} = -A\frac{\pi}{a}\sin\pm\frac{\pi}{2}e^{-iEt/\hbar} = \mp\frac{A\pi}{a}e^{-iEt/\hbar}$$

but it's 0 outside

$\Rightarrow$ not continuous. This is because of the special nature of the impenetrable barrier.

Example Particle in a box, again

Find the expectation values of a) x, b) p, c) x^2, + d) p^2 e) E f) E^2 for the particle in the box. Also find standard deviations in x + p.

First note that x + p don't depend on t. That means that when we write

$$\overline{(\,)} = \int \Psi^* \, (\,) \, \Psi \, dx$$

Ψ^* will contain $e^{+iEt/\hbar}$ and Ψ will contain $e^{-iEt/\hbar}$ and there will be no other t dependence. These multiply to give 1:

$$e^{+iEt/\hbar} e^{-iEt/\hbar} = e^0 = 1$$

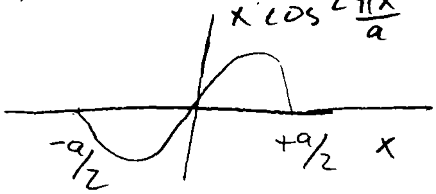
So let's ignore the time dependence for the rest of the example.

a) First, find $\bar{x}$:

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

$$= A^2 \int_{-a/2}^{a/2} x \cos^2 \frac{\pi x}{a} \, dx$$

Now notice that this integrand is an odd function of x:



and when we integrate from $-a/2$ to $a/2$ we get 0, as we do for any odd function.

<u>Aside</u>: The integral of an odd function over a region symmetric about 0 is 0.

Odd means $f(-x) = -f(x)$

Let $I = \int_{-x_0}^{+x_0} f(x)\,dx$

$$= \int_{-x_0}^{0} f(x)\,dx + \int_{0}^{x_0} f(x)\,dx$$

$$= -\int_{0}^{x_0} f(x)\,dx + \int_{0}^{x_0} f(x)\,dx$$

$$= 0$$

Where the 1st term came from:

In $\int_{-x_0}^{0} f(x)\,dx$

let $x' = -x$ then

$f(x) = f(-x') = -f(x')$

$dx = -dx'$

& $x = 0 \Leftrightarrow x' = 0$

$x = -x_0 \Rightarrow x' = x_0$

Int becomes

$+\int_{x_0}^{0} f(x')\,dx' = -\int_{0}^{x_0} f(x')\,dx'$

So $\bar{x} = 0$. Physically, makes sense. Box is symmetric so particle equally likely to have $x > 0$ & $x < 0$

b) Similarly, $\bar{P} = 0$:

2.23

$$\bar{P} = \int_{-\infty}^{\infty} \Psi^*(x,t)\left(-i\hbar\frac{\partial}{\partial x}\right)\Psi(x,t)$$

$$\frac{\partial \Psi}{\partial x} = \frac{-\pi}{a} A \sin\frac{\pi x}{a} e^{-iEt/\hbar}$$

$$= i\hbar\,\frac{\pi}{a} A^2 \int_{-a/2}^{a/2} \cos\frac{\pi x}{a}\sin\frac{\pi x}{a}\,dx$$

$= 0$ since odd integrand.

Good thing, too, because that $-i$ in front would give an imaginary result, which is no good for a physical quantity.

Does this make sense physically? Yes; particle is bouncing around + changing sign of momenta. Positive and negative momenta are equally likely.

c) Now for $\overline{x^2}$:

$$\overline{x^2} = \int_{-\infty}^{\infty} \Psi^* x^2 \Psi\,dx$$

$$= A^2 \int_{-a/2}^{+a/2} x^2\cos^2\left(\frac{\pi x}{a}\right)dx \quad = 2A^2\int_{0}^{a/2} x^2\cos^2\left(\frac{\pi x}{a}\right)dx$$

(even integrand)

Before trying to evaluate this (actually we're going to look it up) it's useful to change variables so the argument of the cosine matches the integration variable.

So let $u = \frac{\pi x}{a}$ $\Rightarrow$ $x^2 = \frac{a^2}{\pi^2}u^2$ & $dx = \frac{a}{\pi}du$

& $x=0 \Rightarrow u=0$ & $x=\frac{a}{2} \Rightarrow u=\frac{\pi}{2}$

& note that u is dimensionless

So

$$\overline{x^2} = 2A^2\left(\frac{a}{\pi}\right)^3 \underbrace{\int_0^{\pi/2} u^2 \cos^2 u \, du}_{\text{pure number}}$$

Note: Without even evaluating the integral, we've done something useful, i.e., we can get some informati out of this. That's because the integral is just a pure number, so all the dimensionful quantities appear in the overall factor. That means, for example, we can find out how $\overline{x^2}$ depends on **a**, the length of the box.

Except we can't, quite, without knowing A. We get it from the normalization condition:

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

$$= A^2 \int_{-a/2}^{a/2} \cos^2 \frac{\pi x}{a} \, dx$$ & making the same change of variable $u = \frac{\pi x}{a}$

$$= 2A^2 \frac{a}{\pi} \underbrace{\int_0^{\pi/2} \cos^2 u \, du}_{\pi/4} = A^2 \frac{a}{2} = 1 \Rightarrow \boxed{A = \sqrt{\frac{2}{a}}}$$

Does this make sense? What dimensions does A have to have? Well, since $\int \Psi^* \Psi dx = 1$, then $A^2 \int \cos^2 \frac{\pi x}{a} dx$ should be dimensionless.

The integral has dimensions of length, so

$$[A^2] \text{ Length} = 1 \Rightarrow [A] = \text{length}^{-1/2} \quad \text{OK.}$$

Now back to $\overline{x^2}$:

$$\overline{x^2} = 2 A^2 \left(\frac{a}{\pi}\right)^3 * \underbrace{\text{number}}_{= \int_0^{\pi/2} u^2 \cos^2 u \, du}$$

$$= 2 * \frac{2}{a} \frac{a^3}{\pi^3} * \text{number}$$

$$= \frac{4a^2}{\pi^3} * \text{number}$$

So $\overline{x^2}$ is proportional to a^2, the square of the length of the box. Makes sense; the bigger the box, the bigger $\overline{x^2}$ can be. In fact we had to get this result, because there's nothing else in the problem with dimensions of length.

[Or is there? The particle has a mass. Could we get a length, or a dimensionless const by combining mass + $\hbar$? Nope; $[\hbar]$ = joule-sec = $\text{kg} \frac{\overset{\text{meters}}{m^2}}{\text{sec}}$ No way to get meters by combining with kilograms.]

Now we just evaluate the integral near the top of p. 2.24 to find the number; it's

$$\int_0^{\pi/2} u^2 \cos^2 u \, du = \frac{\pi}{8}\left(\frac{\pi^2}{6} - 1\right)$$

So $$\overline{x^2} = 2A^2\left(\frac{a}{\pi}\right)^3 \frac{\pi}{8}\left(\frac{\pi^2}{6}-1\right) \quad \& \; A^2 = \frac{2}{a}$$

$$= \frac{a^2}{2\pi^2}\left(\frac{\pi^2}{6} - 1\right) = 0.033\,a^2$$

We'll use this below for the variance.
Note that even though $\overline{x} = 0$, $\overline{x^2}$ is not; x varies!

d) Now find $\overline{p^2}$:

$$\overline{p^2} = \int_{-\infty}^{\infty} \Psi^* \underbrace{(-i\hbar)^2 \frac{\partial^2 \Psi}{\partial x^2}}_{= \frac{\hbar^2 \pi^2}{a^2}\Psi \text{ fr/ p. 2.14}} dx$$

$$= \frac{\hbar^2 \pi^2}{a^2} \underbrace{\int_{-a/2}^{a/2} \Psi^* \Psi \, dx}_{=1}$$

so $$\overline{p^2} = \left(\frac{\hbar \pi}{a}\right)^2$$ Units? $$[p] = \frac{\text{kg}\,\text{m}^2}{\text{sec}}\frac{1}{\text{m}} = \frac{\text{kg}\,\text{m}}{\text{sec}}$$ okay

Again, $\overline{p^2} \neq 0$ even though $\overline{p} = 0$.
We'll look at variance below.

e) Find $\bar{E}$:

$$\bar{E} = \int_{-\infty}^{\infty} \Psi^* \, i\hbar \frac{\partial \Psi}{\partial t} \, dx$$

+ we're putting back in the time dependence because it's easier this way.

Now, $i\hbar \frac{\partial}{\partial t}\Psi = E\Psi$,

+ from p. 2.20, $E = \frac{\hbar^2 \pi^2}{2ma^2}$

$$= \int_{-a/2}^{a/2} \Psi^* \frac{\hbar^2 \pi^2}{2ma^2} \Psi \, dx$$

$$= \frac{\hbar^2 \pi^2}{2ma^2} \underbrace{\int_{-a/2}^{a/2} \Psi^* \Psi \, dx}_{=1}$$

So the expectation of E is the fixed value we got abov

~~f) Now~~ try $\overline{E^2}$. It's obvious from (e) that when we take $\left(i\hbar\frac{\partial}{\partial t}\right)^2$ we're just going to bring down a second factor of $\frac{\hbar^2\pi^2}{2ma^2}$, so

$$\overline{E^2} = \left(\frac{\hbar^2 \pi^2}{2ma^2}\right)^2 = \bar{E}^2$$

We'll come back to this.

g) Now find the variances + standard deviations of x, p, + E (2.28)

$\boxed{x:}$ $\text{var}(x) = \overline{x^2} - \overline{x}^2 = \frac{a^2}{2\pi^2}\left(\frac{\pi^2}{6} - 1\right) - 0 = 0.033a^2$

$\text{std. dev.}(x) = \sqrt{\text{var}(x)} = 0.18a$

So the average position is at the center and the size of fluctuations is about 20% of the length of the box. (Recall that this is for the ground state.)

$\boxed{p:}$ $\text{var}(p) = \overline{p^2} - \overline{p}^2 = \left(\frac{\hbar\pi}{a}\right)^2 - 0 = \frac{\hbar^2\pi^2}{a^2}$

$\text{std. dev.}(p) = \sqrt{\text{var}} = \frac{\hbar\pi}{a} = \sqrt{2mE}$; this is because we measure either $p = +\sqrt{2mE}$ or $-\sqrt{2mE}$

Now let's identify the size of fluctuations with the uncertainties in these quantities*

Then $\Delta x \, \Delta p = 0.18a \frac{\hbar\pi}{a} = 0.57\hbar$

Recall that the uncertainty principle says that $\Delta x \, \Delta p \geq \frac{\hbar}{2}$. This is pretty near the lower limit

*We'll do this a lot

$\boxed{E:}$ $\mathrm{var}(E) = \overline{E^2} - \overline{E}^2 = \left(\frac{\hbar^2\pi^2}{2ma^2}\right)^2 - \left(\frac{\hbar^2\pi^2}{2ma^2}\right)^2 = 0$!!

The energy has zero variance! Does that mean it always has the same value? Yes! Recall the def of variance:

$$\mathrm{var}(E) = \int \Psi^* (E-\overline{E})^2 \Psi \, dx$$

If E were ever different from the mean value, it would give a positive contribution to the integral and the variance would be non zero.

So E has a definite value, and this wave function is said to be in an eigenstate of energy. If you measure the energy, you will get $\frac{\hbar^2\pi^2}{2ma^2}$ every time. (Units okay?)

Separation of the Schrödinger Equation

We want to solve the Schr. Eq'n for particular potentials. The eq'n is

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

It's a partial diff eq'n. depending on 2 var's, & in general not so easy to solve. Our best hope is separation of variables – writing Ψ as a product of separate functions that depend on x and t, and finding equations for each. So write

$$\underset{\nearrow\ \text{upper case}}{\Psi}(x,t) = \underset{\nwarrow\ \text{lower case}}{\psi}(x)\,\varphi(t)$$

+ subst into S.E. :

$$-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\left[\psi(x)\,\varphi(t)\right] + V(x,t)\,\psi(x)\,\varphi(t) = i\hbar\frac{\partial}{\partial t}\left[\psi(x)\,\varphi(t)\right]$$

becomes

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

and dividing by $\psi(x)\,\varphi(t)$, (Note total derivatives now.)

$$\frac{1}{\psi(x)}\left[-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\psi(x) + V(x,t)\,\psi(x)\right] = \left[i\hbar\frac{d\varphi(t)}{dt}\right]\frac{1}{\varphi(t)}$$

Now let's assume $V = V(x)$ only. Otherwise we're in trouble. With that assumption, then notice that

- LHS = function of x only
- RHS = function of t only

But these must be equal for any $x + t$, so they must both be equal to a constant – the <u>same</u> constant. Call it C. So

$$i\hbar\frac{d\varphi(t)}{dt} = C\,\varphi(t)$$

and

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

Time indep. Schr. eq'n.

The equation for φ is straightforward to solve. Rearranging,

$$\frac{d\varphi(t)}{\varphi(t)} = \frac{C}{i\hbar}\,dt$$

Integrating from 0 to t, $\ln\left(\frac{\varphi(t)}{\varphi(0)}\right) = \frac{C}{i\hbar}t$

→

or
$$\varphi(t) = \varphi(0)\, e^{-iCt/\hbar}$$

Comments on $\varphi(t)$

- We have some freedom to pick $\varphi(0)$. Remember that we have to normalize $\Psi(x,t) = \psi(x)\,\varphi(t)$ s.t.

$$\int \Psi^* \Psi \, dx = 1$$

for all t. To keep things simple, we'll put all the normalization stuff into $\psi(x)$, and just take $\varphi(0)=1$ so that $\varphi^*\varphi = 1$ always. That means
$$\int \Psi^* \Psi \, dx = \int \psi^* \psi \, dx = 1$$

- The constant C can be determined by recalling the plane wave sol'n $e^{i(kx-\omega t)} = e^{ikx}\, e^{-iEt/\hbar}$

Identifying the time-dependent part with the sol'n for $\varphi(t)$ above, we find $C = E$; the constant is the energy of the particle. No surprise, as we already identified $i\hbar\frac{\partial}{\partial t}$ as the energy operator. So
$$\boxed{\varphi(t) = e^{-iEt/\hbar}}$$

- so $\varphi(t)$ always has the same form, indep of V, but the actual values E can take on depend on the potential.

Back to the time-indep eq'n

$$\boxed{-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2}+V(x)\psi(x)=E\psi(x)}$$ Time indep. Schr. Eq'n

This is an example of an eigenvalue eq'n, i.e. an eq'n of the form

$$(\text{Operator})\,\psi = \text{const}\,\psi$$

Tψ is called an eigen function and the constant (in this case E) is called the eigenvalue.

This all means that by separating the time and space dependence of the S.E., we get wave functions that describe states w/ definite energy. Is this too much of a restriction? Not really, because we can always make superpositions of states w/ different energies.

Comments about wave functions + quantization of energy

To solve for an actual wave function ψ, we need to know the potential $V(x)$. But we can figure out some generic properties of wave functions just by looking at the equation itself.

First some conditions the wave function must satisfy:

ψ and $\frac{d\psi}{dx}$ must be
- continuous
- finite
- single valued

This mostly follows from the fact that experimentally measurable quantities, which can be obtained from ψ, must be well-behaved, i.e. physically meaningful.

Aside: Note a couple of these are redundant, e.g.

finite $\frac{d\psi}{dx} \leftrightarrow$ continuous ψ

Now let's look at the wave function. We can learn a lot by looking at the S.E. geometrically. Write it as

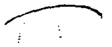
$$\frac{d^2\psi}{dx^2} = \frac{2m}{\hbar^2}\left[V(x) - E\right]\psi$$

It's an equation for the curvature of ψ.

Now recall that $\frac{d^2\psi}{dx^2} > 0$ means concave upward

; slope increases, becoming more positive and/or less negative

$\frac{d^2\psi}{dx^2} < 0$ means concave downward



; slope decreases, becoming more negative (or less positive)

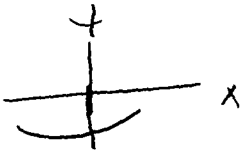
Now, the sign of the curvature is determined by the signs of [V−E] and ψ. [Note: we'll often use the case of constant potential to illustrate.] Recall that E is fixed (though we don't know at what value) so we'll try to figure out how ψ behaves in terms of V & E.

$\boxed{V(x) - E < 0}$: This says the total energy is larger than the potential. This is the classically allowed region

a. $\psi > 0 \Rightarrow \frac{d^2\psi}{dx^2} < 0$

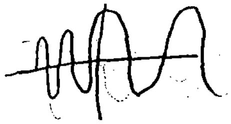
ψ above axis, concave downwar

b. $\psi < 0 \Rightarrow \frac{d^2\psi}{dx^2} > 0$

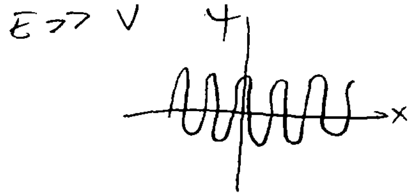


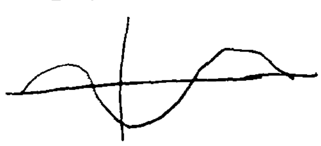
ψ below axis, concave upwa

($V-E<0$, continued)

In both cases, ψ curves back towards the axis, i.e. its behavior is oscillatory. In general, you could have  etc.

Ex: For const. V, this oscillatory behavior is sinusoidal: $V=\text{const} \Rightarrow \psi \sim e^{\pm i\sqrt{2m(E-V)}\,x/\hbar}$, i.e. sines + cosines. Note also that the bigger is E compared to V, the faster the wiggles are.

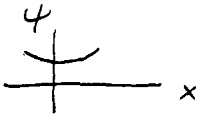




Note that if V varies slowly, you still get something close to sinusoidal, but if it varies fast, though ψ still wiggles, it's not sinusoidal.

$\boxed{V(x)-E>0}$: Now total energy is less than the potential energy. Classically, this isn't even allowed: $E=V+K$, + $K>0 \Rightarrow E>V$. But quantum-mechanical it can happen.

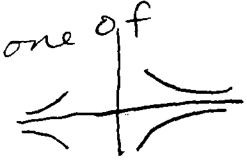
a. $\psi>0 \Rightarrow \frac{d^2\psi}{dx^2}>0 \Rightarrow \psi$ above axis, concave upward

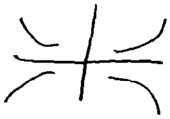


b. $\psi<0 \Rightarrow \frac{d^2\psi}{dx^2}<0 \Rightarrow \psi$ below axis, concave downward

(V−E > 0, continued).

Now in both cases, ψ <u>curves away from</u> the axis. It can't oscillate, because it can never get back to the axis. This time it's approx. <u>exponential</u>. You can have one of



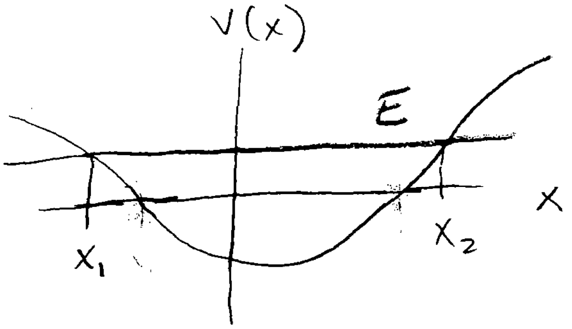
or  . But be careful with the latter, because remember ψ has to be finite. If the region where E<V extends to ∞, you can't have these.

Ex: For const V, ψ is exactly exponential; V = const ⇒ $\psi \sim e^{\pm\sqrt{2m(V-E)}\,x/\hbar}$ and the sign in the exponent depends on whether $x > 0$ (take − sign) or $x < 0$ (+) in the region that has $x \to \infty$

<u>Energy quantization + bound states</u>. When we put this together, we find that when E < V as $x \to \pm\infty$, the energy is quantized and you get bound states.

Aside: Note that we have to have E > V <u>somewhere</u> or else ψ curves away fr/ the axis everywhere + we get no solution w/ finite ψ.

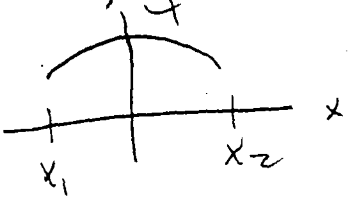
How does this happen?



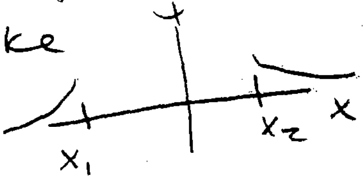
Well, ψ has to go to 0 as $x \to +\infty$ <u>and</u> as $x \to -\infty$, and that requirement + continuity of ψ + its derivative means you can't find a solution for just any ψ.

Take the potential given above.

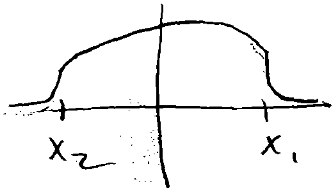
$x_1 \le x \le x_2 \Rightarrow \psi$ curves toward axis; let's say a solution is



$x < x_1$ and $x > x_2 \Rightarrow \psi$ curves away fr/ axis, but it has to be finite so it's something like



Now we can slap these together + adjust the normalization to make ψ continuous, like



but the derivative of ψ isn't continuous. The S.E. says that x_1 + x_2 are inflection points because $E=V$ there (so $\frac{d^2\psi}{dx^2}=0$), so the slope $\frac{d\psi}{dx}$ cannot change. And $\frac{d\psi}{dx}$ has to be continuous since $\frac{d^2\psi}{dx^2}$ is finite.

The crucial point is that the steepness of the slope depends on the energy (think of the exponentials + plane waves). So only certain energies give continuous derivatives at both points, i.e. only certain energies are allowed!

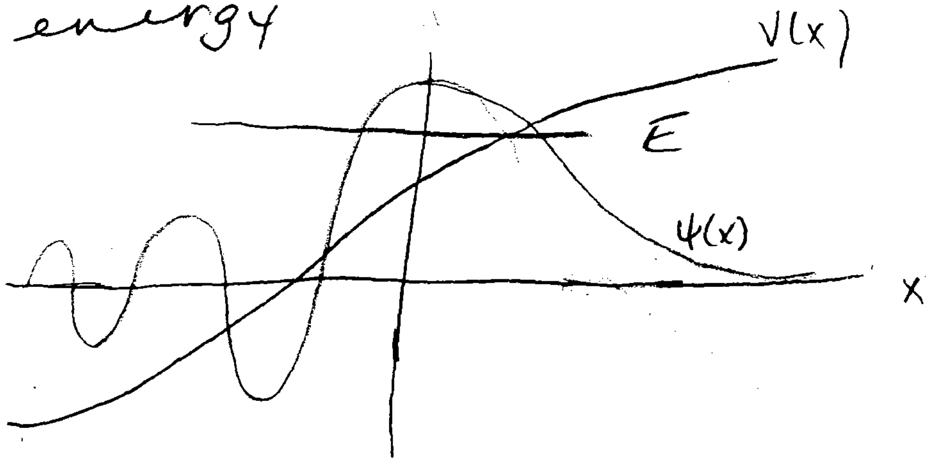
$\Rightarrow$ Energy is quantized

These states are called **bound states** because $\psi \to 0$ as $x \to \pm\infty$; the particle can't escape.

If $E > V$ as $x \to +\infty$ or $x \to -\infty$, then we don't have quantization; any E above V is allowed and we have oscillatory solutions. The size of V just determines the frequency of the wiggles. These are called unbound or scattering states.

So, generically, if we have a potential ⓶.40

and energy



Then the wave function looks something like ↑ & notice that as V gets closer to E, the magnitude of ψ gets bigger. Classically that would mean the kinetic energy is small, so the particle is going slow and hanging around in that region more. In terms of the S.E., remember

$$\frac{d^2\psi}{dx^2} \sim (V-E)*\psi$$

& if V−E is small, ψ has to be big for $\frac{d^2\psi}{dx^2}$ to be big enough to get the wave fn. to turn over.

3-D Schrödinger Equation

In general we'll want to work in three space dimensions, not just one, so we need the three-dimensional version of the Schr. Eq'n.

The extension to 3D is completely straightforward, and we can get it by realizing that the momentum is now a 3-component vector. We can then repeat the development of the S.E. as we did in 1D. Only the space parts change. Now the plane wave sol'n is

$$\Psi(\vec{r},t) = A\, e^{i(\vec{p}\cdot\vec{r} - Et)/\hbar} \qquad \text{where } \vec{r} = (x,y,z)$$

Now the momentum operator has to bring down $\vec{p}$, so it's the natural vector version of $-i\hbar\frac{\partial}{\partial x}$:

$$\boxed{-i\hbar\vec{\nabla} \longleftrightarrow \text{momentum operator}}$$

and $\frac{p^2}{2m}$ $\vec{p}\cdot\vec{p}/2m$ becomes $-\frac{\hbar^2}{2m}\nabla^2$, where $\vec{\nabla} = \left(\hat{x}\frac{\partial}{\partial x} + \hat{y}\frac{\partial}{\partial y} + \hat{z}\frac{\partial}{\partial z}\right)$

and $\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$ so the Schrödinger eq'n in 3-D is

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

separation of the eq'n to get the time indep. version also works the same way as in 1D. We have

$$\Psi(\vec{r},t) = \psi(\vec{r})\,\varphi(t)$$

and everything for $\varphi(t)$ is exactly the same, so we still have

$$i\hbar \frac{d\varphi(t)}{dt} = E\varphi(t)$$

and so

$$\varphi(t) = e^{-iEt/\hbar}$$

The time-indep. equation becomes

$$\boxed{-\frac{\hbar^2}{2m}\nabla^2\psi(\vec{r}) + V(\vec{r})\,\psi(\vec{r}) = E\,\psi(\vec{r})}$$

We'll solve this later, when we do the hydrogen atom. In the meantime, some comments about probability conservation.

Probability and conservation

In 3-D, the probability density is still $\Psi^*\Psi$:

$\Psi^*(\vec{r},t)\,\Psi(\vec{r},t)\,d^3x$ = prob that particle is found btwn $\vec{r}$ & $\vec{r}+d\vec{r}$

where $d\vec{r} = \hat{x}dx + \hat{y}dy + \hat{z}dz$

and $d^3x = dx\,dy\,dz$

Now the normalization condition is still that the total probability of finding the particle anywhere is 1, but the integration is over all space:

$$\int_{\substack{\text{all}\\ \text{space}}} \Psi^*(\vec{r},t)\,\Psi(\vec{r},t)\,d^3x = 1$$

same t

Now we can ask: is probability conserved, i.e. if Ψ is normalized at one time, is it still normalized later?

To answer this, look at the behavior of the probability density $\rho(\vec{r},t)$

$$\rho(\vec{r},t) = |\Psi(\vec{r},t)|^2$$

[Aside, we called this P before]

Consider how ρ changes with time:

$$\frac{\partial\rho}{\partial t} = \frac{\partial}{\partial t}\left[\Psi^*\Psi\right] = \left(\frac{\partial\Psi^*}{\partial t}\right)\Psi + \Psi^*\left(\frac{\partial\Psi}{\partial t}\right)$$

The Schrödinger eq'n tells us

$$\frac{\partial\Psi}{\partial t} = \frac{1}{i\hbar}\left[\frac{-\hbar^2}{2m}\nabla^2\Psi + V\Psi\right]$$

+ the complex conjugate gives us $\partial\Psi^*/\partial t$

So substituting, we find

$$\frac{\partial \rho}{\partial t} = \frac{-\hbar}{2mi}\left[\Psi^*(\nabla^2\Psi) - (\nabla^2\Psi^*)\Psi\right] + \frac{1}{i\hbar}\underbrace{\left[\Psi^*(V\Psi) - (V^*\Psi^*)\Psi\right]}_{\substack{=0 \text{ if } V \text{ real,} \\ \text{i.e. if } V^* = V}}$$

+ we can write what's left of the right-hand-side as

$$-\vec{\nabla}\cdot\underbrace{\frac{\hbar}{2mi}\left[\Psi^*\vec{\nabla}\Psi - (\vec{\nabla}\Psi^*)\Psi\right]}_{\equiv \vec{J} = \text{curr}}$$

i.e., prob can't change w/o particles going somewhere

This thing $\vec{J}$ is called the
and we have the <u>contin</u>

$$\boxed{\frac{\partial \rho}{\partial t} + \vec{\nabla}\cdot\vec{J} = 0}$$

Now, ρ has dimensions of particles/unit volume (or prob)
(since $\int \rho \, d^3x = 1$ particle)

and $\vec{J}$ has dimensions particles/unit area/unit time (or prob)
(since $\vec{\nabla}\cdot\vec{J}$ has same units as $\frac{\partial \rho}{\partial t}$)

This says that the probability density can only change with time if there's a corresponding flux of probability current into or out of the region, i.e. <u>probability</u> is conserved.

This is the same continuity equation you saw in electricity + magnetism (in fact if you multiply the probability density and current density by charge you get the quantum versions of charge and current density) and it applies to anything that flows.

Comment: Notice that $\vec{J}$ is nonzero only if Ψ is complex! If Ψ is real, then $\frac{\partial \rho}{\partial t}$ is zero and we can only describe static probability distributions.

or just Ψ

can use the continuity equation to show that probability is conserved, i.e. that if Ψ is normalized at one time, it's normalized forever. To do that we have to show that $\frac{d}{dt}\int \rho \, d^3x = 0$.

$$\frac{d}{dt}\int \Psi^* \Psi \, d^3x = \frac{d}{dt}\int \rho \, d^3x$$

$$= \int \frac{\partial \rho}{\partial t} d^3x$$

partial deriv. because $\rho = \rho(\vec{r}, t)$

$$= -\int \vec{\nabla} \cdot \vec{J} \, d^3x \quad \text{from continuity eq'n}$$

Now recall Gauss's divergence thm fr/ vector calculus:

$$\int_{\text{volume}} \vec{\nabla}\cdot\vec{A}\,dV = \int_{\substack{\text{surface}\\ \text{enclosing volume}}} \vec{A}\cdot d\vec{s}$$

Applying this to the $\vec{\nabla}\cdot\vec{J}$ integral, we get

$$\frac{d}{dt}\int_{\substack{\text{all}\\ \text{space}}} \Psi^*\Psi\,d^3x = -\int_{\substack{\text{surface}\\ \text{enclosing}\\ \text{all space}}} \vec{J}\cdot d\vec{s}$$

Now, in any reasonable situation, the wave function goes to 0 at ∞, which means $\vec{J}=0$ there. Therefore

$$\boxed{\frac{d}{dt}\int \Psi^*\Psi\,d^3x = 0}$$

and probability is conserved.

Aside: This gives us a hint about why the S.E. only has a first time derivative. If it had a $\frac{\partial^2\Psi}{\partial t^2}$, then as an initial condition we could specify $\frac{\partial\Psi}{\partial t}$. But that gives us the freedom to make $\frac{\partial\rho}{\partial t}$ at $t=0$ be anything we want, and we could violate conservation of probability, which would be a bad thing.

Comment. Let's go back to our separation of the Schrödinger eq'n, + consider an energy eigenstate $\Psi(\vec{r},t) = \psi(\vec{r})\, e^{-iEt/\hbar}$.

Its probability density is

$$\rho = |\psi(\vec{r})|^2$$

and $\frac{\partial \rho}{\partial t} = 0$ ("stationary state") so $\vec{\nabla}\cdot\vec{J} = 0$; the current density has no divergence.