Review:

A free particle (i.e. w/ no external forces)
with momentum p and energy E satisfies

$$E = \frac{p^2}{2m} \quad \text{(nonrelativistic)}$$

A matter wave corresponding to a free particle has
wavenumber $k = \frac{p}{\hbar}$ (de Broglie) and angular frequency $\omega = \frac{E}{\hbar}$ (Einstein)

We showed that a travelling matter wave of the form

$$\psi = A\left[\cos\left(\frac{p}{\hbar}x - \frac{E}{\hbar}t\right) + i\sin\left(\frac{p}{\hbar}x - \frac{E}{\hbar}t\right)\right]$$

obeys the t.d. S.e. for a free particle

$$i\hbar\frac{\partial\psi}{\partial t} = -\frac{\hbar^2}{2m}\frac{\partial^2\psi}{\partial x^2}$$

Let's verify this by rewriting the travelling wave as

$$\psi = A\,e^{i\left(\frac{px}{\hbar} - \frac{Et}{\hbar}\right)}$$

$$= A\,e^{\frac{ipx}{\hbar}}\,e^{-\frac{iEt}{\hbar}}$$

$$i\hbar\frac{\partial\psi}{\partial t} = i\hbar\left(-\frac{iE}{\hbar}\right)A e^{\frac{ipx}{\hbar}}e^{-\frac{iEt}{\hbar}} = E\psi$$

$$-\frac{\hbar^2}{2m}\frac{\partial^2\psi}{\partial x^2} = -\frac{\hbar^2}{2m}\left(\frac{ip}{\hbar}\right)^2 A e^{\frac{ipx}{\hbar}}e^{-\frac{iEt}{\hbar}} = \frac{p^2}{2m}\psi$$

Since $E = \frac{p^2}{2m}$, t.d.Se is satisfied.

Matter wave of momentum p in $+x$ direction

$$\psi_p = A e^{\frac{ipx}{\hbar}} e^{-\frac{iEt}{\hbar}}$$

A matter wave of momentum p in $-x$-direction is

$$\psi_{-p} = A e^{-\frac{ipx}{\hbar}} e^{-\frac{iEt}{\hbar}}$$

ψ_p and ψ_{-p} correspond to particle of same energy because $\frac{(-p)^2}{2m} = \frac{p^2}{2m}$

Two (or more) solutions of same energy are called "degenerate"

Degeneracy = # of (linearly independent) solutions of t.d. S.e having the same energy

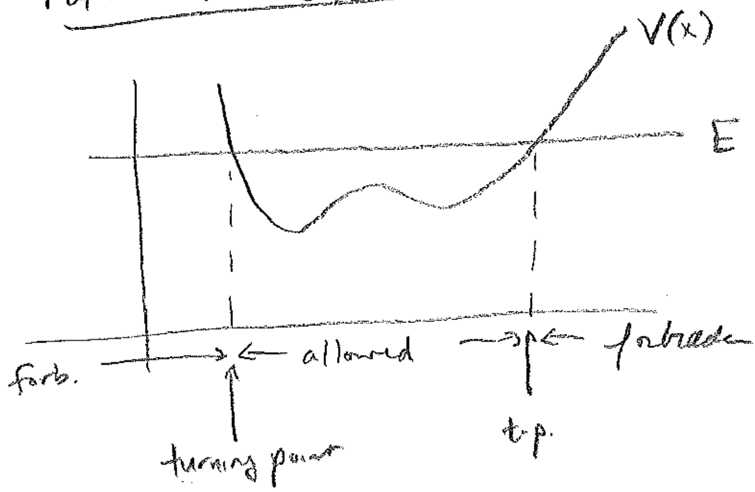
in this case, degeneracy = 2

if degeneracy = 1, called "nondegenerate"

A particle experiencing a conservative force has energy

$$E = \frac{p^2}{2m} + V(x) \qquad \text{where } V(x) = \text{potential energy}$$

Potential energy diagram



If allowed region is finite, particle is in a bound state

Total energy is conserved, but momentum is changing in time

A free particle (no forces) with a well-defined energy E and well-defined momentum and is described by

$$\psi(x,t) = A\, e^{\frac{ipx}{\hbar}}\, e^{-\frac{iEt}{\hbar}}$$

This suggests that a particle in a potential with well-defined energy E (but not momentum) is described by

$$\psi(x,t) = u(x)\, e^{-\frac{iEt}{\hbar}}$$

[Let's see if this works]

(t.d.S.E.) $$i\hbar \frac{\partial \psi}{\partial t} = -\frac{\hbar^2}{2m}\frac{\partial^2 \psi}{\partial x^2} + V(x)\,\psi$$ (PDE)

$$i\hbar \frac{\partial \psi}{\partial t} = i\hbar\left(-\frac{iE}{\hbar}\right)u(x)\,e^{-\frac{iEt}{\hbar}} = E\,u(x)\,e^{-\frac{iEt}{\hbar}}$$

$$\frac{\partial^2 \psi}{\partial x^2} = \frac{d^2 u}{dx^2}\,e^{-\frac{iEt}{\hbar}}$$

$$\Rightarrow \boxed{-\frac{\hbar^2}{2m}\frac{d^2 u}{dx^2} + V(x)\,u = E\,u}$$ (O.DE)

time-independent Schrodinger eqn
(t.i.S.e)

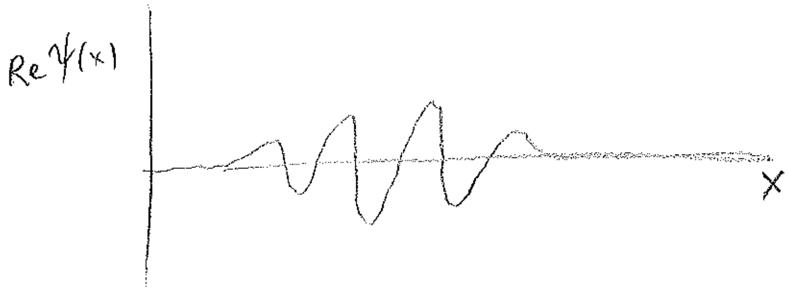
our proposal $\psi(x,t) = u(x)\,e^{-\frac{iEt}{\hbar}}$
works provided $u(x)$ obeys t.i.S.e

Erwin with his ψ can do
Calculations quite a few.
But one thing has not been seen:
Just what does ψ really mean?

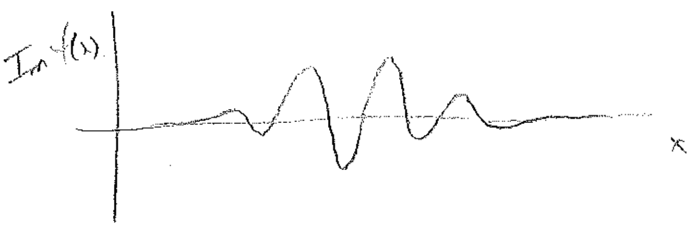
–English translation by Felix Bloch of a poem by Erich Hückel.

(not Walter)

What is the physical meaning of the wavefunction ψ?
In general it is a <u>complex</u> function
[in general, it is complex; not directly physical]



[where is the particle?
where $\mathrm{Re}\,\psi(x)$ is nonzero?
where $\mathrm{Im}\,\psi(x)$ is nonzero?
more likely to be where these are large?]



<u>Probability interpretation</u> (Max Born, 1926)

Probability of finding the particle at a point x is proportional to

$$(\mathrm{Re}\,\psi)^2 + (\mathrm{Im}\,\psi)^2 = |\psi|^2 = \psi^*\psi$$

[squared so that it is nonnegative]

$$|\psi(x,t)|^2 = \text{probability density}$$

$$\psi(x,t) = \text{probability amplitude}$$

Exercise in mean values

(a) if die is fair, what is mean value of # thrown?

$$\frac{1+2+3+4+5+6}{6} = \boxed{3.5}$$

(b) if 1, 2, 3 twice as likely as 4, 5, 6,

$$\frac{2}{9}(1+2+3) + \frac{1}{9}(4+5+6) = \boxed{3}$$

(c) if 2 is twice as likely etc..

$$\frac{1^2+2^2+3^2+4^2+5^2+6^2}{1+2+3+4+5+6} = \frac{91}{21} = \boxed{4\frac{1}{3}}$$

Lesson: $\langle A \rangle = \sum p_n a_n$

$$\sum p_n = 1$$

A particle with well-defined energy E is described by a wavefunction

$$\psi_E(x,t) = u(x)\, e^{-\frac{iEt}{\hbar}}$$

where $u(x)$ obeys the t.i.S.e..

Probability density of such a particle is

$$|\psi_E(x,t)|^2 = \psi_E^*(x,t)\,\psi_E(x,t)$$
$$= u^*(x)\, e^{\frac{iEt}{\hbar}}\, u(x)\, e^{-\frac{iEt}{\hbar}}$$
$$= u^*(x)\, u(x)\, e^{0}$$
$$= |u(x)|^2$$

Constant in time! If the energy is well defined, then the likelihood of finding particle at a particular location is always the same

$\Rightarrow \psi_E(x,t)$ is a "stationary state."

[But things change in time! Particles move!]

Puzzle: how can we describe systems that change in time using stationary states $\psi_E(t)$?

Answer: By using linear combinations of stationary states

[exercise 25]

example 2.1 G 2e

6)

Let $\psi(x,t)$ be a *linear combination* of stationary states

$$c_1 u_1(x) e^{-iE_1 t/\hbar} + c_2 u_2(x) e^{-iE_2 t/\hbar}$$

where c_1 and c_2 are arbitrary constants.

(a) Show that $\psi(x,t)$ is a solution of the time-dependent Schrödinger equation, provided that

$$-\frac{\hbar^2}{2m}\frac{d^2u_1}{dx^2} + V(x)u_1 = E_1 u_1 \qquad \text{and} \qquad -\frac{\hbar^2}{2m}\frac{d^2u_2}{dx^2} + V(x)u_2 = E_2 u_2.$$

(b) Calculate the probability density for $\psi(x,t)$ and express it in an explicitly real form. (For this part of the exercise, you may assume that c_1 and c_2 are real constants, and $u_1(x)$ and $u_2(x)$ are real functions.) As you can see, a linear combination of stationary states is *not* necessarily stationary (i.e., does not have a time-independent probability density).

b) $$\psi^*\psi = \left(c_1 u_1 e^{iE_1 t/\hbar} + c_2 u_2 e^{iE_2 t/\hbar}\right)\left(c_1 u_1 e^{-iE_1 t/\hbar} + c_2 u_2 e^{-iE_2 t/\hbar}\right)$$

$$= c_1^2 u_1^2 + c_2^2 u_2^2 + c_1 c_2 u_1 u_2 \left(e^{\frac{i(E_1-E_2)t}{\hbar}} + e^{-i\left(\frac{E_1-E_2}{\hbar}\right)t}\right)$$

$$= c_1^2 u_1^2 + c_2^2 u_2^2 + 2c_1 c_2 u_1 u_2 \cos\left(\frac{E_1-E_2}{\hbar}t\right)$$

- not stationary because cross term has time dependence
- stationary if $E_1 = E_2$!

[If c_n, u_n not real $\Rightarrow$ $$c_1 c_2^* u_1 u_2^* e^{-\frac{i(E_1-E_2)t}{\hbar}} + c_2 c_1^* u_2 u_1^* e^{+\frac{i(E_1-E_2)t}{\hbar}}$$

$$= z + z^* = \text{real}$$

We will discover that the t.i.S.e has infinitely many solutions $u_n(x)$ of different energies E_n (where n labels the solutions)

Since $u_n(x) e^{-\frac{iE_n t}{\hbar}}$ obeys the t.d.s.e for each n, and since the t.d.S.e is a linear differential equation any linear combination

$$\sum c_n u_n(x) e^{-\frac{iE_n t}{\hbar}}$$ (where c_n = arbitrary complex const)

also obeys the t.d.S.e.

[assign exercise 25]

These linear combinations are <u>not</u> stationary states & ∴ can describe changing systems

[can more this later]

Define the Hamiltonian operator (or energy operator)

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

[use hat to denote an operator.
operator acts on object to give another object of same type.
E.g. matrix: col. vector → col. vector]

$\hat{H}$ acts on a function to give another function.

The t.d.S.e can be written

$$i\hbar \frac{\partial \Psi}{\partial t} = \hat{H}\Psi$$

The t.i.S.e can be written (recall $\Psi(x,t) = u_n(x)\, e^{-\frac{iE_n t}{\hbar}}$)

$$\hat{H}\, u_n(x) = E_n\, u_n(x)$$

This type of eqn is called an eigenvalue eqn.
$u_n(x)$ is called an eigenfunction of $\hat{H}$
E_n (a constant) is called its eigenvalue

Thus $u_n(x)$ can be described as
- solution of t.i.S.e
- state of well-defined energy
- stationary state
- eigenfunction of $\hat{H}$ (or energy eigenfunction)

[Exercise: u_1, u_2 eigfens of $\hat{H}$. When is $c_1u_1 + c_2u_2$ an eigfen?]

Let $u_1(x)$ and $u_2(x)$ be eigenfunctions of $\hat{H}$ with eigenvalues E_1 and E_2 respectively. Under what conditions is the linear combination $c_1u_1(x) + c_2u_2(x)$ an eigenfunction of $\hat{H}$?

$$\hat{H} u_1 = E u_1$$
$$\hat{H} u_2 = E u_2$$

$$\hat{H}\,(c_1 u_1 + c_2 u_2)$$

$$= \left(-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V(x)\right)[c_1 u_1 + c_2 u_2]$$

$$= c_1\left[-\frac{\hbar^2}{2m}\frac{d^2 u_1}{dx^2} + V(x)u_1\right] + c_2\left[-\frac{\hbar^2}{2m}\frac{d^2 u_2}{dx^2} + V(x)u_2\right]$$

$$= c_1 E_1 u_1 + c_2 E_2 u_2$$

$$= E\,(c_1 u_1 + c_2 u_2) \quad \text{iff} \quad \underline{E_1 = E_2}$$

Hence a linear comb of degenerate eigenfns is an eigenfn
but a lin. comb of non degen efs is not

[After exercise 25 about linear combinations has been presented]

$$\psi(x,t) = \sum c_n u_n(x)\, e^{-\frac{iE_n t}{\hbar}} \qquad (c_n = \text{arbitrary complex constants})$$

is a solution of the t.d.S.e
but does not have a well-defined energy
and is not stationary.
To see this, calculate the probability density

$$|\psi(x,t)|^2 = \psi^* \psi = \Big(\sum_n c_n^* u_n^*(x)\, e^{\frac{iE_n t}{\hbar}}\Big)\Big(\sum_m c_m u_m(x)\, e^{-\frac{iE_m t}{\hbar}}\Big)$$

independent sums

$$= \underbrace{\sum_n |c_n|^2 |u_n(x)|^2}_{\substack{\text{"diagonal" terms} \\ \text{(time-independent)}}} + \underbrace{\sum_n \sum_{\substack{m \\ (m \neq n)}} c_n^* c_m u_n^*(x) u_m(x)\, e^{\frac{i(E_n - E_m)t}{\hbar}}}_{\substack{\text{"off diagonal terms"} \\ \text{depend on time}}}$$

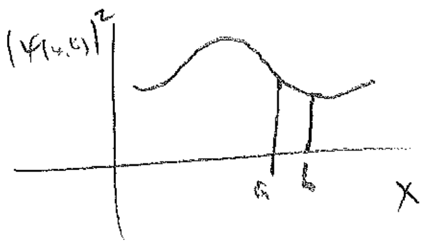
---

e.g.
$$\begin{aligned}(a_1 + a_2 + a_3)(b_1 + b_2 + b_3) = \; & a_1 b_1 + a_1 b_2 + a_1 b_3 \\ & + a_2 b_1 + a_2 b_2 + a_2 b_3 \\ & + a_3 b_1 + a_3 b_2 + a_3 b_3 \end{aligned}$$

← "diagonal"

$$\Big(\sum a_n\Big)\Big(\sum b_m\Big) = \underbrace{\sum_n a_n b_n}_{\text{diagonal}} + \underbrace{\sum_n \sum_{\substack{m \\ (n \neq m)}} a_n b_m}_{\text{off-diagonal}}$$

$|\Psi(x,t)|^2 =$ probability density $= \dfrac{\text{probability}}{\text{length}}$



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

$$\int_a^b |\Psi(x,t)|^2\, dx$$

Probability of finding the particle anywhere is 100%

$$\int_{-\infty}^{\infty} |\Psi(x,t)|^2\, dx = 1 \quad \longleftarrow \text{"normalization condition"}$$

We will assume that our stationary state solutions $u_n(x)e^{-iE_n t/\hbar}$ are normalized

$$\Rightarrow \int_{-\infty}^{\infty} |u_n(x)|^2\, dx = 1$$

Also, I will later prove that stationary states corresponding to different energies ($E_n \neq E_m$) are "orthogonal" which means

$$\int_{-\infty}^{\infty} u_n^*(x)\, u_m(x)\, dx = 0 \quad (\text{if } E_n \neq E_m)$$

We now require that arbitrary linear combination is also normalized

$$1 = \int |\Psi(x,t)|^2 dx = \sum_n |c_n|^2 \underbrace{\int |u_n(x)|^2 dx}_{1} + \sum_n \sum_{\substack{m \\ (n\neq m)}} c_n^* c_m e^{\frac{i(E_n - E_m)t}{\hbar}} \underbrace{\int_{-\infty}^{\infty} u_n^*(x)\, u_m(x)\, dx}_{0}$$

$$= \sum_n |c_n|^2$$

The arbitrary coefficients c_n must satisfy $\sum |c_n|^2 = 1$

This suggests $|c_n|^2$ should be interpreted as probabilities

Consider a particle described by the wavefunction

$$\psi(x,t) = \sum_n c_n u_n(x) e^{-\frac{iE_n t}{\hbar}}$$

If one measures the energy of this particle, one may obtain any of the eigenvalues E_n appearing in the sum (provided the corresponding coefficient $c_n \neq 0$), with probability $|c_n|^2$.

The sum of probabilities is $\sum |c_n|^2 = 1$.

If there is only one term in the sum, eg $u_m(x) e^{-\frac{iE_m t}{\hbar}}$ one is guaranteed to obtain the result E_m

ie energy eigenfunctions give a definite value for the energy

---

If one has many identical copies of a particle, all described by $\psi = \sum c_n u_n e^{-\frac{iE_n t}{\hbar}}$

and measures the energy of each of them, obtaining many different results,

the mean value of the results (a.k.a. the expectation value of the energy) is

$$\langle E \rangle = \sum |c_n|^2 E_n$$

The expectation value of energy may be calculated directly from $\Psi(x,t)$ using

$$\langle E \rangle = \int_{-\infty}^{\infty} dx \quad \Psi^*(x,t) \ \hat{H} \ \Psi(x,t)$$

- exercise: show that if $\Psi = \sum c_n u_n(x) e^{-iE_n t/\hbar}$ then this formula yields $\langle E \rangle = \sum E_n |c_n|^2$ agreeing with the previous definition

EXERCISE 27: Let a particle be described by a linear combination of stationary states

$$\psi(x,t) = \sum_n c_n u_n(x) e^{-iE_n t/\hbar}$$

where c_n are complex constants. Compute $\langle E \rangle$ for this particle using the expression above.

$$\langle E \rangle = \int_{-\infty}^{\infty} dx \; \psi^* \hat{H} \psi$$

$$\hat{H}\psi = \sum c_n (\hat{H} u_n) e^{-\frac{iE_n t}{\hbar}}$$

$$= \sum c_n E_n u_n e^{-\frac{iE_n t}{\hbar}}$$

$$\langle E \rangle = \int_{-\infty}^{\infty} dx \left(\sum_n c_n^* u_n e^{\frac{iE_n t}{\hbar}} \right) \left(\sum_m c_m E_m u_m e^{-\frac{iE_m t}{\hbar}} \right)$$

$$= \int_{-\infty}^{\infty} dx \left[\sum_n |c_n|^2 E_n u_n^2 + \sum_{n \neq m} c_n^* c_m E_m e^{\frac{i(E_n - E_m)t}{\hbar}} u_n(x) u_m(x) \right]$$

$$= \sum_n |c_n|^2 E_n \left[\underbrace{\int_{-\infty}^{\infty} dx \; u_n^2(x)}_{1} \right] + \sum_{n \neq m} c_n^* c_m E_m e^{\frac{i(E_n - E_m)t}{\hbar}} \underbrace{\int_{-\infty}^{\infty} u_n u_m \, dx}_{0}$$

$$\boxed{\langle E \rangle = \sum E_n |c_n|^2}$$