The Schrödinger equation

Announcements:

- Next homework (#7) assignment is due tomorrow at 1pm.
- If anyone is interested, I brought forms to join the American Physical Society. Can return them to me!
- As always have homework to return – homework (#6)

Erwin Schrödinger
(1887 – 1961)

We begin working with the Schrödinger equation. Today will be free particle and Friday will be the infinite square well (particle in a box).

Getting to Schrödinger's wave equation

$$\boxed{\frac{\partial^2 E}{\partial x^2} = \frac{1}{c^2}\frac{\partial^2 E}{\partial t^2}}$$

Works for light (photons), why doesn't it work for electrons?

We found that solutions to this equation are

$$y = A\cos(kx)\sin(\omega t) + B\sin(kx)\cos(\omega t)$$

or $y = C\sin(kx - \omega t) + D\sin(kx + \omega t)$

with the constraint $k = \dfrac{\omega}{c}$ which can be written $\omega = kc$

Multiplying by ħ we get $\hbar\omega = \hbar kc$ which is just $E = pc$

But we know that *E=pc* only works for massless particles so this equation can't work for electrons.

Getting to Schrödinger's wave equation

$$\frac{\partial^2 E}{\partial x^2} = \frac{1}{c^2}\frac{\partial^2 E}{\partial t^2}$$ doesn't work for electrons. What does?

$$y = A\cos(kx)\sin(\omega t) + B\sin(kx)\cos(\omega t)$$

or $$y = C\sin(kx - \omega t) + D\sin(kx + \omega t)$$

Note that each derivative of *x* gives us a *k* (momentum) while each derivative of *t* gives us an ω (energy).

Equal numbers of derivatives result in $E = pc$

For massive particles we need $K = \dfrac{p^2}{2m}$

So we need two derivatives of *x* for p^2 but only one derivative of t for *K*.

If we add in potential energy as well we get the Schrödinger equation…, but first operators and expectation values.

Expectation Values

To relate a quantum mechanical calculation to something you can observe in the laboratory, the "expectation value" of the measurable parameter is calculated. For the position x, the expectation value is defined as

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

Can be interpreted as the average value of x that we expect to obtain from a large number of measurements. Alternatively, average value of position for many particles which are described by the same wavefunction.

Expectation Value cont.

The expectation value of position has the appearance of an average of the function, but the expectation value of momentum involves the representation of momentum as a quantum mechanical operator

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

where

$$p_{operator} = \frac{\hbar}{i} \frac{\partial}{\partial x}$$

is the operator for the x component of momentum.

Expectation Values cont.

Since the energy of a free particle is given by

$$E = \frac{p^2}{2m} \quad then \quad \langle E \rangle = \frac{\langle p^2 \rangle}{2m}$$

and the expectation value for energy becomes

$$\langle E \rangle_{free\ particle} = \int_{-\infty}^{\infty} \psi^* \frac{(-\hbar^2)}{2m} \frac{\partial^2}{\partial x^2} \psi dx$$

for a particle in 1 dimension. In general, the expectation value for any observable quantity is found by putting the quantum mechanical operator for that observable in the integral of the wavefunction over space:

$$\langle Q \rangle = \int_{-\infty}^{\infty} \psi^* Q_{operator} \psi dV$$

integral over all space

Expectation Values cont.

The energy operator is given by $\hat{E} = i\hbar\frac{\partial}{\partial t}$

$$\psi(x,t) = C\sin(kx - \omega t) + D\sin(kx + \omega t)$$

$$\psi(x,t) = Ee^{i(kx-\omega t)} + Fe^{-i(kx+\omega t)}$$

Traveling to right

Traveling to left

$$\hat{E}\psi(x,t) = i\hbar\frac{\partial}{\partial t}\psi(x,t) = -i^2\hbar\omega\,\psi(x,t) = \hbar\omega\,\psi(x,t)$$

Expectation Value cont.

$$p_{operator} = \frac{\hbar}{i}\frac{\partial}{\partial x}$$

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

$$\frac{\hat{p}^2}{2m} = \left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\right)$$

$$\frac{\hat{p}^2}{2m}\psi(x,t) = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\psi(x,t)$$

$$\psi(x,t) = Ee^{i(kx-\omega t)} + Fe^{-i(kx+\omega t)}$$

$$\frac{\hat{p}^2}{2m}\psi(x,t) = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\psi(x,t) = \frac{\hbar^2 k^2}{2m}\psi(x,t)$$

The Schrödinger equation

The Schrodinger equation for a matter wave in one dimension Ψ(x,t):

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

Kinetic energy + Potential energy = Total energy

This is the *time dependent* Schrödinger equation (TDSE) (discussed in 7.11) and is also the most general form.

Note, we now use *V* instead of *U* for the potential energy.

This potential energy is a function of *x* and *t*. It gives the potential energy of the particle for any *x* and *t*. It is not intrinsic to the particles but something from the problem at hand.

Deriving time independent Schrödinger equation

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

In most physics situations (like hydrogen atom) the potential function *V* does not change in time so can write *V(x,t) = V(x)*.

In this case, we can separate Ψ(x,t) into ψ(x)ϕ(t): $\Psi(x,t) = \psi(x)\phi(t)$

Can prove that ϕ(t) is always the same: $\phi(t) = e^{-iEt/\hbar}$

Text uses $\phi(t) = e^{-i\omega t}$ which is exactly the same since $E = \hbar\omega$

Putting $\Psi(x,t) = \psi(x)\phi(t)$ with $\phi(t) = e^{-iEt/\hbar}$, into the TDSE gives the time independent Schrödinger equation (TISE):

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

HW problem 8 takes you through these steps in detail.

Solving quantum mechanics problems

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

1. Determine *V(x)* for the problem.
2. Guess (or lookup) the functional form of the solution
3. Plug in solutions to check that solution is correct and find any constraints on constants
4. Figure out boundary conditions and apply them to the general solution to get more constraints
5. Use the normalization constraint $\int_{-\infty}^{\infty}|\psi(x)|^2 dx = 1$ to normalize the spatial wave function.
6. Multiply by time dependence for full solution: $\Psi(x,t)=\psi(x)e^{-iEt/\hbar}$
7. Use solution to obtain information like graphs of ψ(x) and $|\psi(x)|^2$, energy levels, probabilities on positions, etc.

Clicker question 1 — Set frequency to AD

Given a potential energy function V(x), where would a particle naturally want to be?

A. Where V(x) is highest
B. Where V(x) is lowest
C. Where V(x) < kinetic energy
D. Where V(x) > kinetic energy
E. Does not depend on V(x)

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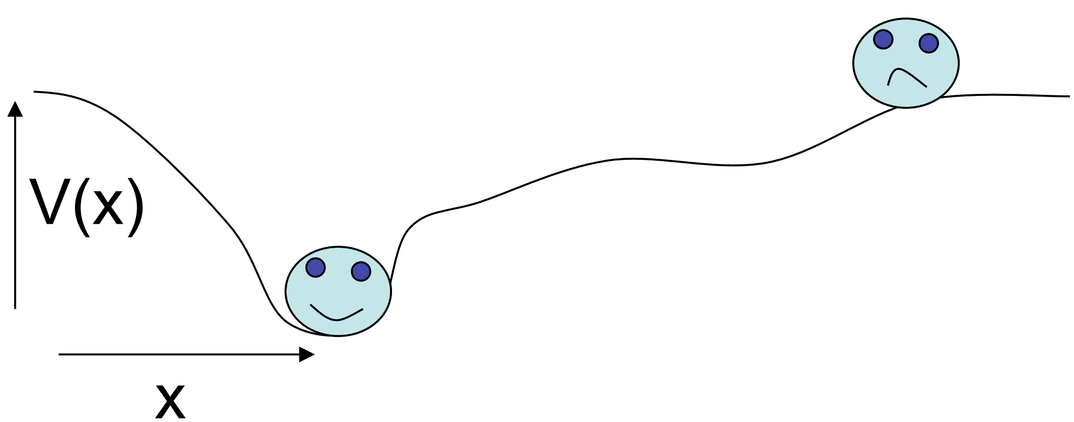
Particles want to go to position of lowest potential energy, like a ball going downhill.



Mathematically we know this because $\vec{F} = -\vec{\nabla} U$

Free particle

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

Start with simplest case of a free particle (no forces acting on it).

What is V(x) for a free particle?

Constant. Smart (easy) choice is V(x)=0.

What are the boundary conditions for a free particle?

None.

So we need to find what functions satisfy $-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2}=E\psi(x)$

but we don't need to apply boundary conditions.

Clicker question 2 | Set frequency to AD

Which of the following are possible solutions to $-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} = E\psi(x)$

A. $A\cos(kx)$

B. Ae^{-kx}

C. $A\sin(kx)$

D. A and C

E. None of A,B,C

Clicker question 2

Set frequency to AD

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Try answer B: $\frac{d^2\psi(x)}{dx^2} = A(-k)(-k)e^{-kx} = k^2\psi(x)$

This gives us $-\frac{\hbar^2 k^2}{2m}\psi(x) = E\psi(x)$

This works as long as $k^2 = -\frac{2mE}{\hbar^2}$

But *k* is a real measurable quantity so it cannot be complex and therefore k^2 is positive.

Since the only energy we have is kinetic, it must also be positive so the quantity $2mE/\hbar^2$ must be positive.

So answer B does not work. Answers A and C both work.

For A: $\frac{d^2\psi(x)}{dx^2} = -Ak^2\cos(kx) = -k^2\psi(x)$ which gives $\frac{\hbar^2 k^2}{2m}\psi(x) = E\psi(x)$

Clicker question 3

Set frequency to DA

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

Putting either ψ(x)=Acos(kx) or ψ(x)=Asin(kx) into the TISE we end up with $\frac{\hbar^2 k^2}{2m}\psi(x) = E\psi(x)$

This works as long as $\frac{\hbar^2 k^2}{2m} = E$ Since $p=\hbar k$ this just means the total energy is the kinetic energy

Based on this, what can we say about the free particle energy?

A. Quantized as $E_n = E_0 n^2$
B. Quantized as $E_n = E_0 n$
C. Quantized as $E_n = E_0/n^2$
D. Quantized in some other way
E. Not quantized

Clicker question 3 Set frequency to DA

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C. Quantized as $E_n = E_0/n^2$
D. Quantized in some other way
E. Not quantized

The only requirement is $E=p^2/2m$. There is no quantization.

The energy of a free particle is <u>not</u> quantized!