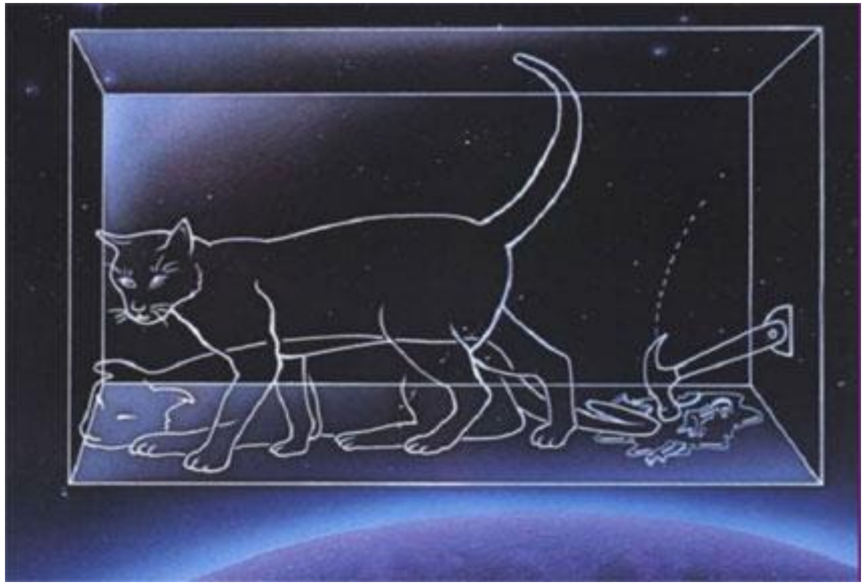
SS406 - L2



"Is the state of the cat to be created only when a physicist investigates the situation at some definite time? Nobody really doubts that the presence or absence of a dead cat is something independent of observation.."

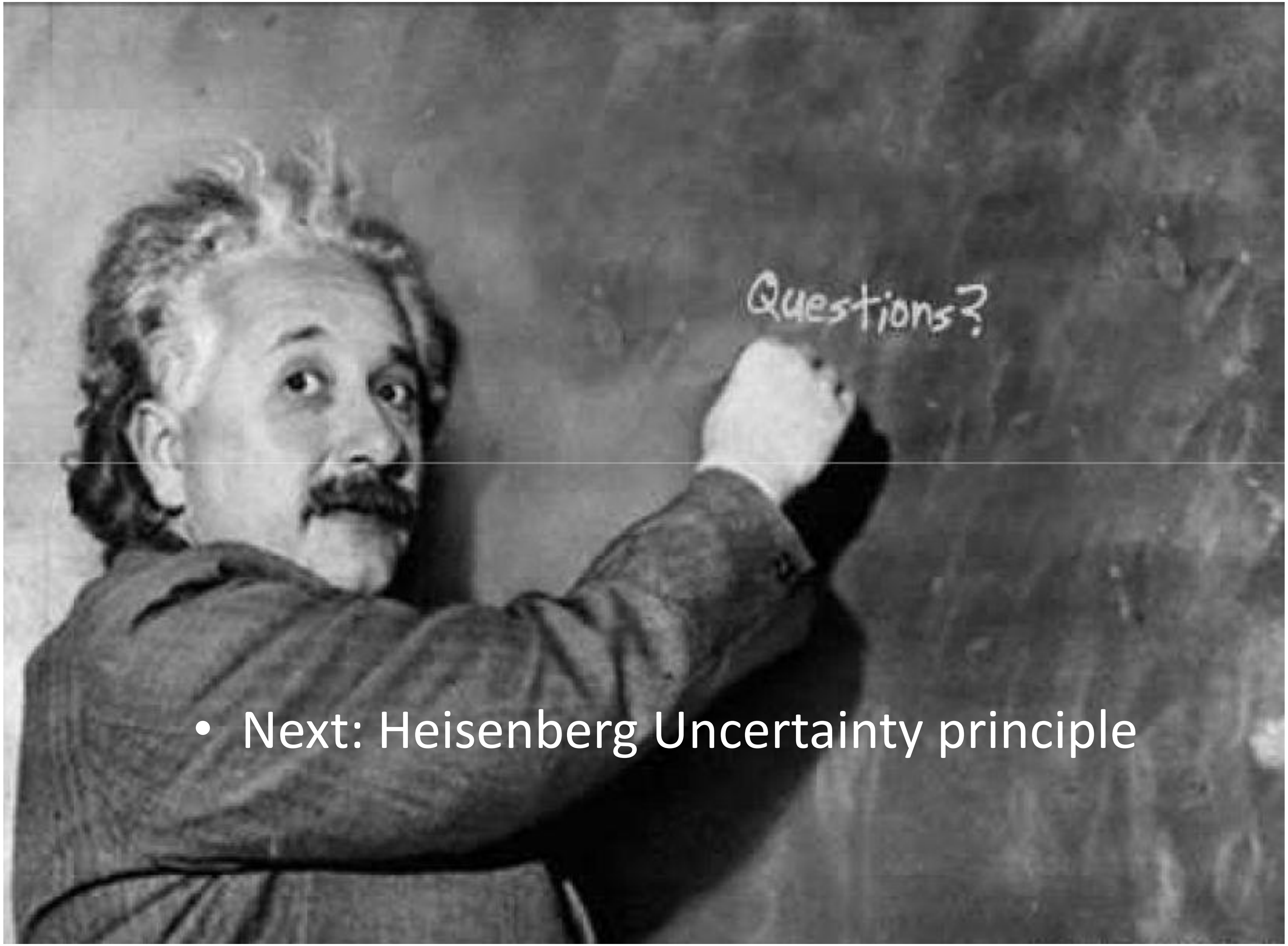
– **Albert Einstein**

Last time:

- some math
- Particles wave duality
- Wave Uncertainty principle
- Quantum mechanics

Today:

- Heisenberg Uncertainty principle
- Quantum mechanics problems we can solve:
  - Potential well, Harmonic oscillator, Hydrogen atom
- Operators, eigenfunctions, and eigenvalues
- Momentum operator
- Energy operator



- Next: Heisenberg Uncertainty principle

Plane Waves

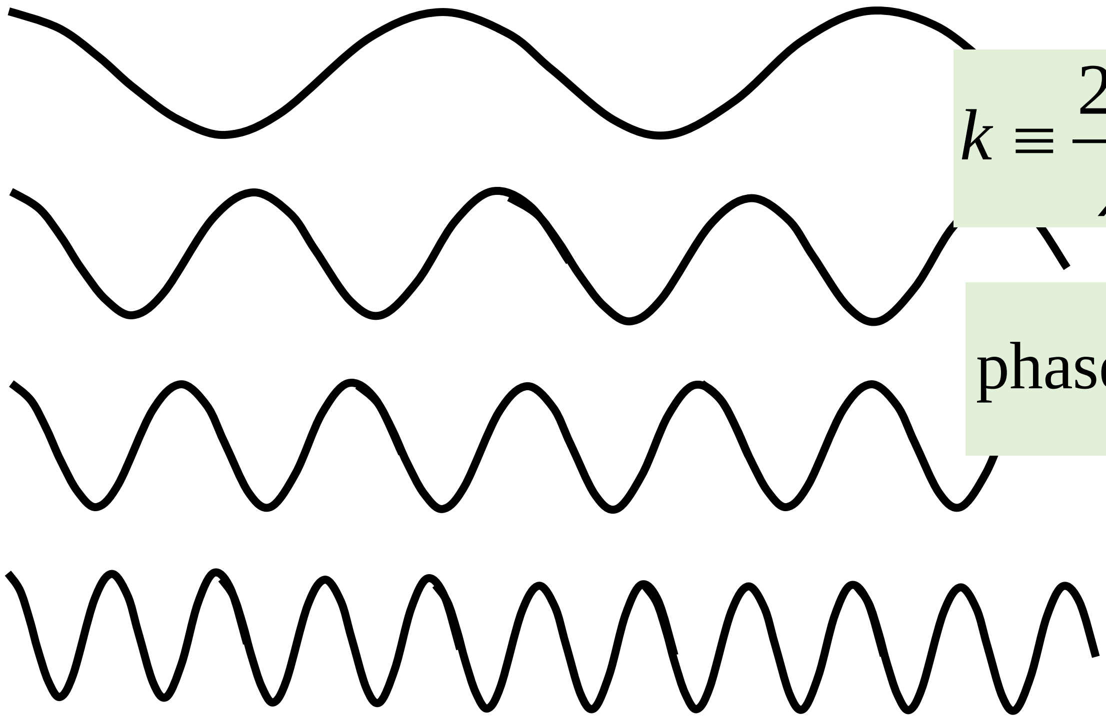
Plane waves (sines, cosines, complex exponentials) extend forever in space:

$$\Psi_1(x,t) = \exp\left[i\left(k_1 x - \omega_1 t\right)\right]$$

$$\Psi_2(x,t) = \exp\left[i\left(k_2 x - \omega_2 t\right)\right]$$

$$\Psi_3(x,t) = \exp\left[i\left(k_3 x - \omega_3 t\right)\right]$$

$$\Psi_4(x,t) = \exp\left[i\left(k_4 x - \omega_4 t\right)\right]$$



$$k \equiv \frac{2\pi}{\lambda} \quad \text{and} \quad \omega = \frac{2\pi}{T}$$

$$\text{phase velocity } \mathrm{v}_{\text{phase}} = \frac{\omega}{k}$$

Different *k*'s correspond to different momenta $p = \hbar k$

Different ω's correspond to different energies $E = \hbar\omega$

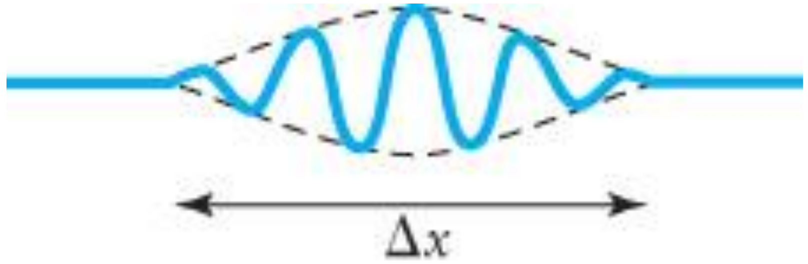
Heisenberg Uncertainty Principle

Mathematical property of waves: $\Delta k \cdot \Delta x \geq 1$

:

- A definite wavelength must extend forever.

- Finite wave packet:
  A wave packet requires a spread Δk of wavelengths.



We need a spread of wavelengths in order to get destructive interference.

Using $p = h/\lambda = \hbar k$, we have:

$\hbar\,(\Delta k \cdot \Delta x \geq 1) \Rightarrow (\hbar \Delta k) \cdot \Delta x \geq \hbar \Rightarrow \boxed{\Delta p \cdot \Delta x \geq \hbar}$

The Heisenberg Uncertainty Principle limits the accuracy with which we can know the position and momentum of objects.

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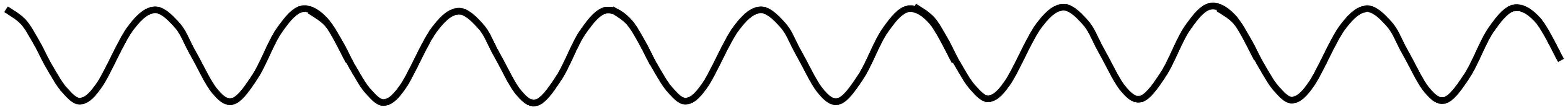
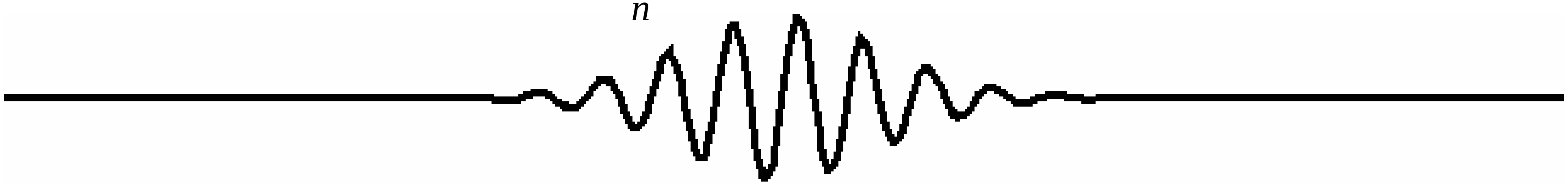
Plane Waves vs. Wave Packets

$$\Psi(x,t) = A\exp\left[i\left(kx - \omega t\right)\right]$$



$$\Psi(x,t) = \sum_n A_n \exp\left[i\left(k_n x - \omega_n t\right)\right]$$

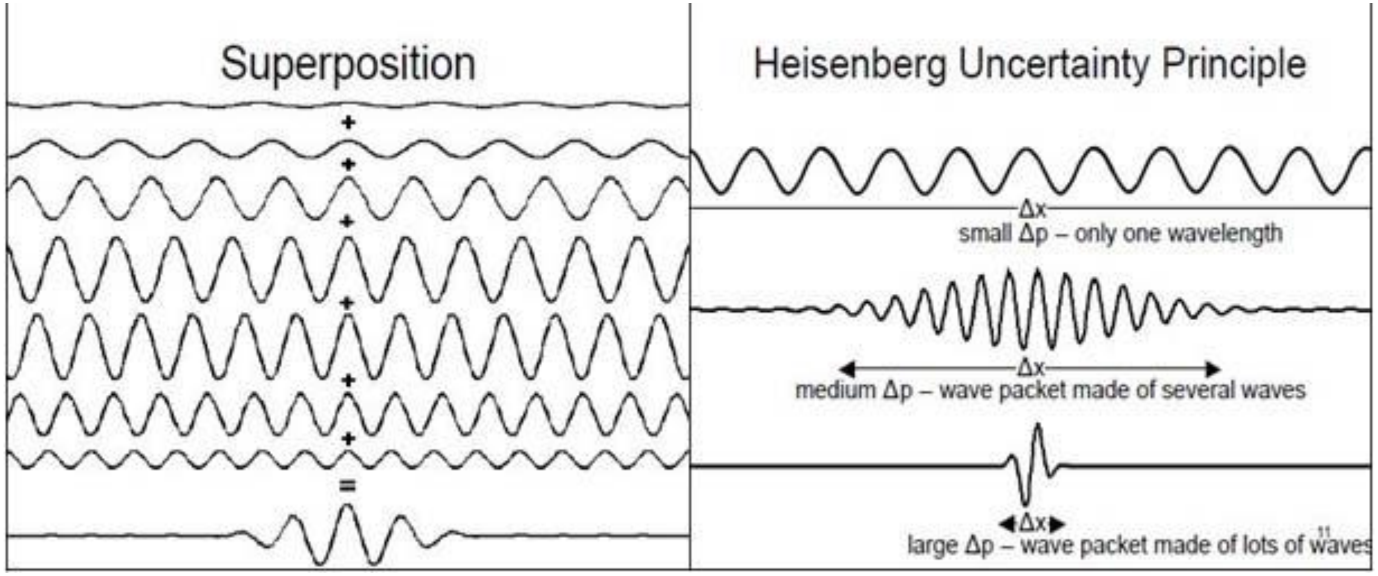


For which type of wave are the position (x) and momentum (p) most well-defined?

A) x most well-defined for plane wave, p most well-defined for wave packet.
B) p most well-defined for plane wave, x most well-defined for wave packet.
C) p most well-defined for plane wave, x equally well-defined for both.
D) x most well-defined for wave packet, p equally well-defined for both.
E) p and x are equally well-defined for both.

Uncertainty Principle

A Wave Interpretation:



- Wave packets are constructed from a series of plane waves.
- The more spatially localized the wave packet, the less uncertainty in position.
- With less uncertainty in position comes a greater uncertainty in momentum.

Energy-Time Uncertainty Principle

If we are to make a wave packet in time– ie a pulse that last for a time Δt (instead of over an infinite time as for a single wave), we must include the frequencies of many waves to have them cancel everywhere but over the time interval Δt

$$\Psi(x,t)=\sum_n A_n \exp\left[i\left(k_n x-\omega_n t\right)\right]$$

$$\Delta\omega\Delta t \geq 1/2$$

combined with the energy frequency relation

$$E = hf = \hbar\omega \Rightarrow \Delta E = \hbar\Delta\omega$$

Heisenberg uncertainty principle for energy and time

$$\Rightarrow \quad \Delta E \cdot \Delta t \geq \frac{\hbar}{2}$$

The energy and lifetime of a particle cannot **both** be determined with complete precision.

Implication of uncertainty principle

Consider a particle for which the location is known within a width of $\Delta\ell$ along the axis. We then know the position of the particle to within a distance

$$\Delta x \leq l / 2$$

The uncertainty principle specifies that Δp is limited by

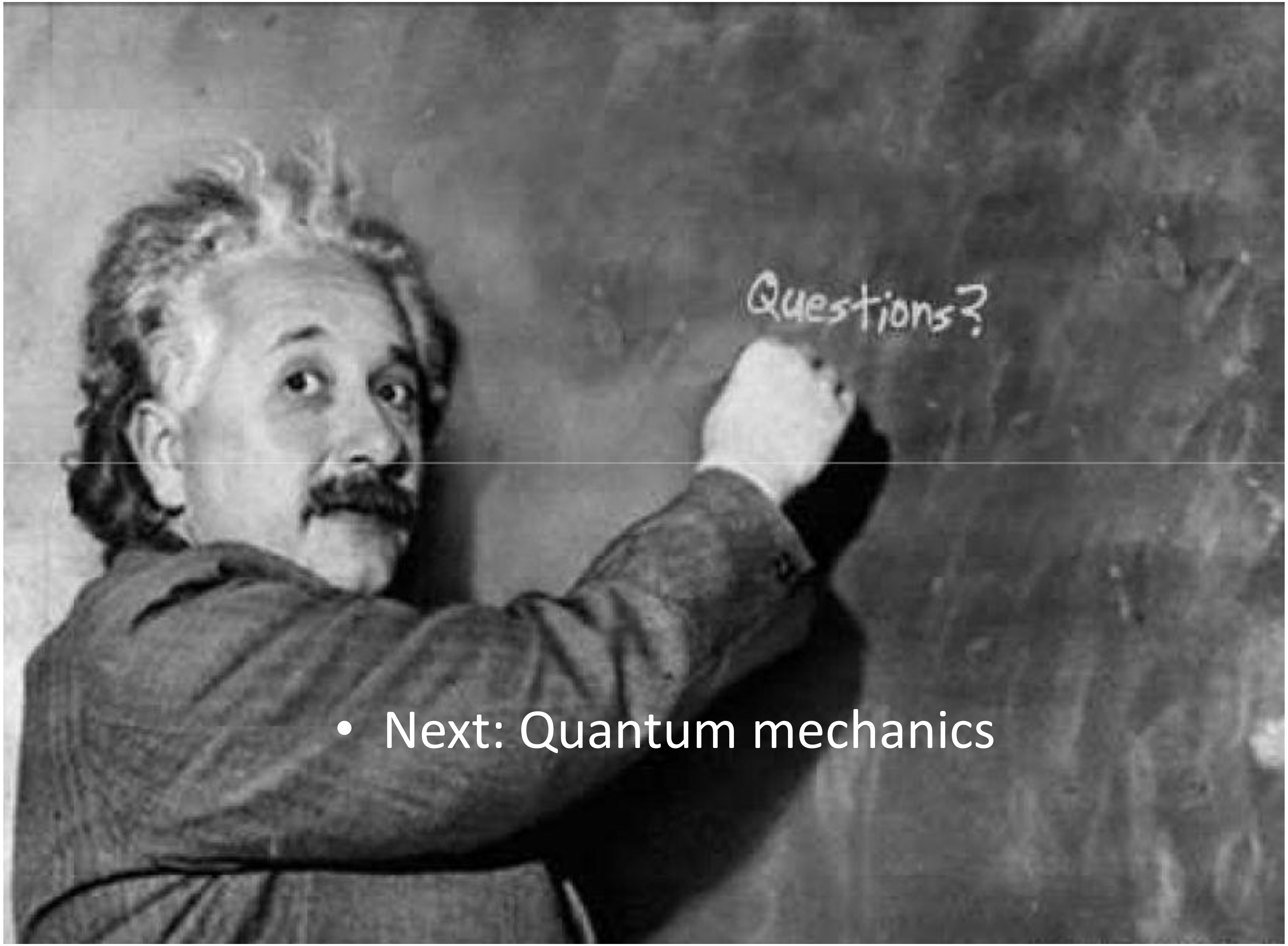
$$\Delta p \geq \frac{\hbar}{2\Delta x} \geq \frac{\hbar}{l}$$

The kinetic energy (non-relativistic)

$$K_{\text{min}} = \frac{p_{\text{min}}^2}{2m} \geq \frac{(\Delta p)^2}{2m} \geq \frac{\hbar^2}{2m\ell^2}$$

Zero point energy

$\mapsto$ if a particle is confined to a region of finite size, the particle's kinetic energy must be non-zero!!!



- Next: Quantum mechanics

Quantum Mechanics: Law 1

Law 1. The state of a quantum mechanical system is completely specified by a wave function $\Psi(r, t)$ that depends on the coordinates of the particle(s) and on time.

$$\psi(\mathbf{r},t) \quad \textit{Wave function}$$

$$|\psi(\mathrm{r},t)|^2 = \psi(\mathrm{r},t)^* \cdot \psi(\mathrm{r},t)$$

Probability to find particle at position r at time t.

$$\int_{-\infty}^{+\infty} |\psi(\mathbf{r},t)|^2 dr = 1$$

Normalization.

Schrödinger equation in 1D

Schrodinger – If particles are associated with a wave function there must be a wave equation describing their dynamics!

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

Of course for any real system, need 3 dimensions,
just add partial derivatives of y and z, and V(x,y,z) etc.

Schrödinger wrote it down, solved for hydrogen,
got solutions that gave exactly the same electron energy levels as Bohr.

Superposition principle

$$\text{if } \psi_1 \text{ and } \psi_2 \text{ are states then:}$$

$$c_1\psi_1 + c_2\psi_2 \equiv \psi_3 \text{ is also a state}$$

Time independent Schrödinger equation in 1D

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

Most physical situations, like H atom, no time dependence in V!

Simplification #1:V = V(x) only.

(Important, will use in all Shrödinger equation problems!!)

Ψ(x,t) separates into position dependent part ψ(x)
and time dependent part φ(t) =exp(-iEt/ħ). Ψ(x,t)= ψ(x)φ(t)

Plug in, get equation for ψ(x)

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

"time independent Schrodinger equation"

Plug in, get equation for ϕ(x)

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

Stationary states

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

- the wave function can be written as:

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

$$\text{with} : \omega = E/\hbar$$

- The probability density becomes:

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

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

- If V is time independent, then, the probability distributions are constant in time!
- This is a standing wave phenomenon that is called the stationary state.

Properties of Valid Wave Functions

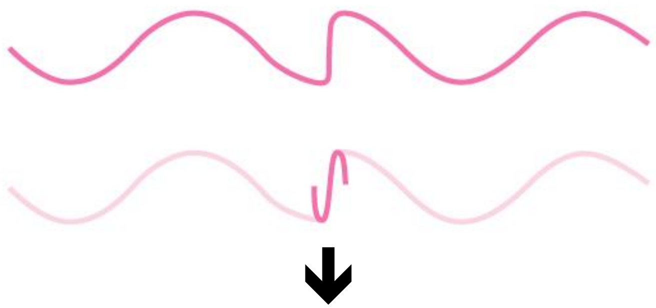
1) To avoid infinite probabilities, the wave function must be finite everywhere.

2) to avoid multiple values of the probability, the wave function must be single valued.

3) to normalize the wave functions, they must be finite everywhere and approach zero as x approaches infinity.

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

4) 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 infinite.)



Acts like a 0 wavelength
→ ∞ Momentum and KE

If the Ψ had a discontinuity, its first derivative would be infinite at the point of discontinuity→ non physical!

Solving the Schrödinger equation for electron wave in 1-D:

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

1. Figure out what V(x) is, for situation given.
2. Guess or look up functional form of solution.
3. Plug in to check if ψ's and all x's drop out, leaving an equation involving only a bunch of constants.
4. Figure out what boundary conditions must be to make sense physically.
5. Figure out values of constants to meet boundary conditions and normalization:

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

6. Multiply by time dependence $\varphi(t) = \exp(-iEt/\hbar)$ to have full solution if needed.

Quantum Mechanics

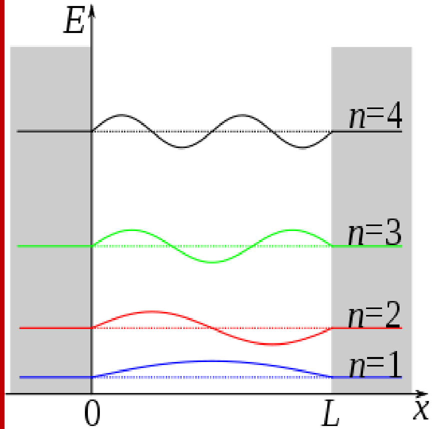
Only 4 exactly Solved Problems!

Free Particle

$$V(x) = 0$$

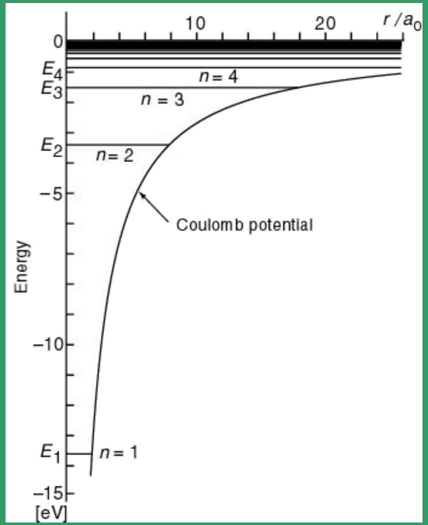
Particle in a box

$$V(x) = \begin{cases} 0 & 0 < x < L \\ \infty & x < 0; x > L \end{cases}$$



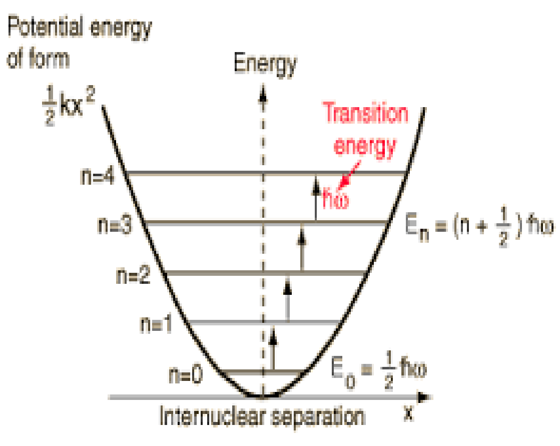
Hydrogen atom

$$V(r) = \frac{1}{4\pi\varepsilon_0}\frac{q}{r}$$



Harmonic oscillator

$$V(r) = \frac{1}{2}m\omega^2 x^2$$



Solving Schrodinger Equation for free particle

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

Electron in free space, no electric fields or gravity around.

1. Where does it want to be?
2. What is V(x)?
3. What are boundary conditions on ψ(x)?

1. No preference- all x the same.
2. Constant.
3. None, could be anywhere.

Smart choice of constant, V(x) = 0!

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

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

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

The total energy of the electron is:

A. Quantized according to E_n = (constant) x n^2, n= 1,2, 3,…
B. Quantized according to E_n = const. x (n)
C. Quantized according to E_n = const. x ($1/n^2$)
D. Quantized according to some other condition but don't know what it is.
E. Not quantized, energy can take on any value.

Ans: E - No boundary, energy can take on any value.

$$\psi(x) = A\cos kx \quad \frac{\hbar^2 k^2}{2m} = E \quad p = \hbar k$$

k (and therefore E) can take on any value.

Almost have a solution, but remember we still have to include time dependence:

$$\Psi(x,t) = \psi(x)\phi(t) \quad \boxed{\phi(t) = e^{-iEt/\hbar}}$$

…bit of algebra, using identity: $e^{ix} = \cos(x) + i\sin(x)$ and wave propagating in the positive x direction

$$\Psi(x,t) = A\cos(kx - \omega t) + i\,A\sin(kx - \omega t)$$

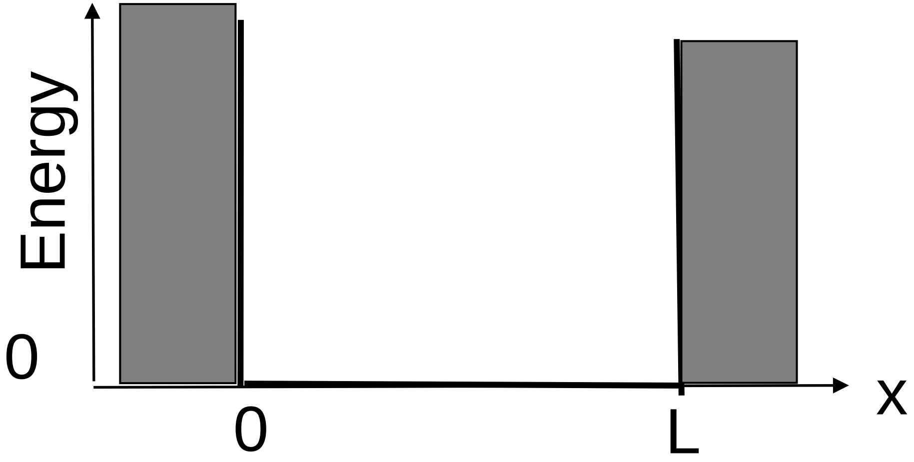
The wave function is not restricted to being real.
Only the physically measurable quantities must be real: probability, momentum and energy.

Infinite Square-Well Potential

- 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

x<0, V(x) ~ infinite
x> L, V(x) ~ infinite
0<x<L, V(x) =0



Clever approach means just have to solve:

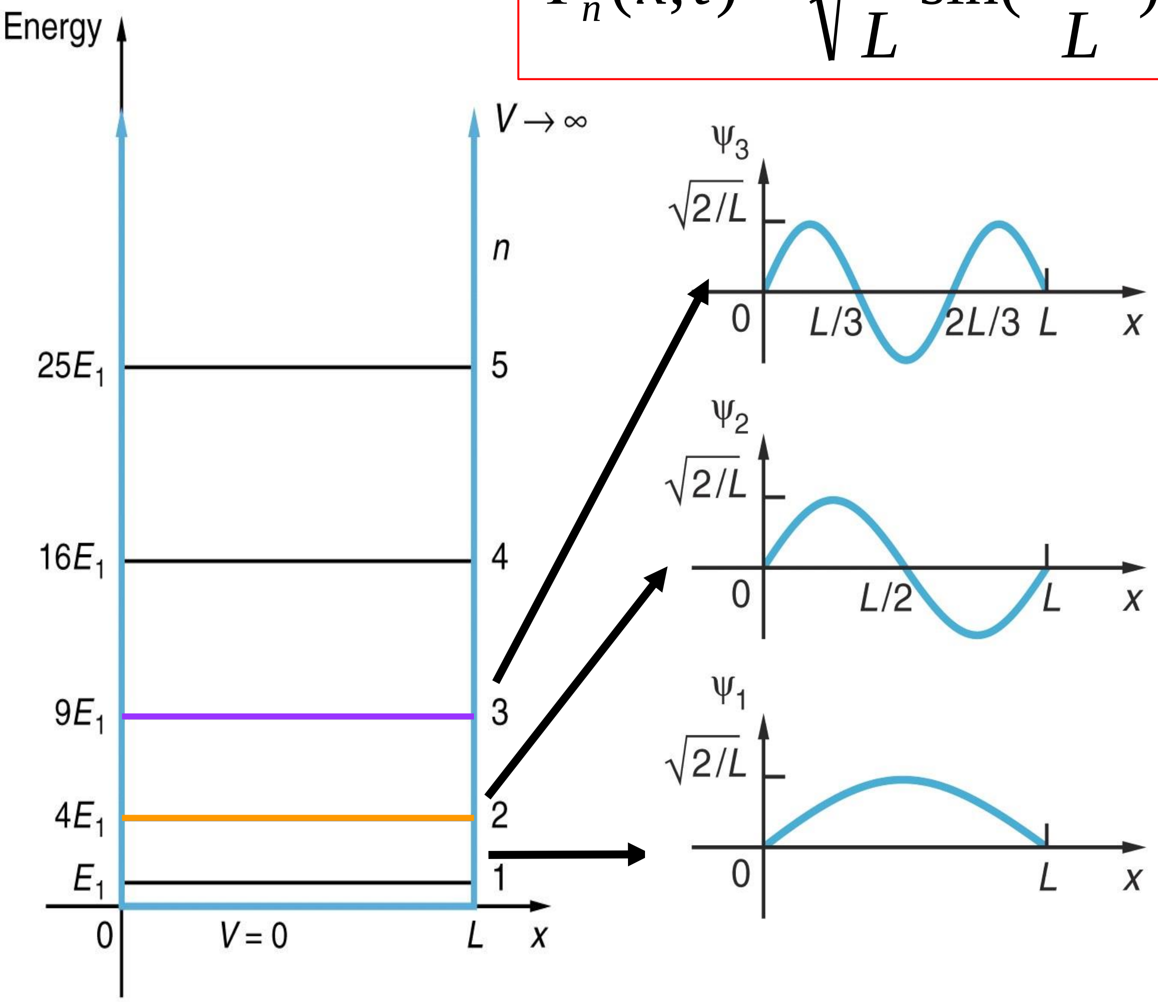
$$-\frac{\hbar^2}{2m}\frac{\partial^2\psi(x)}{\partial x^2} = E\psi(x)$$

with boundary conditions,
$\psi(0)=\psi(L)=0$

Solution a lot like microwave & guitar string

Infinite Square-Well Potential- wave functions

$$\Psi_n(x,t)=\sqrt{\frac{2}{L}}\sin\left(\frac{n\pi x}{L}\right)e^{-iEt/\hbar}$$



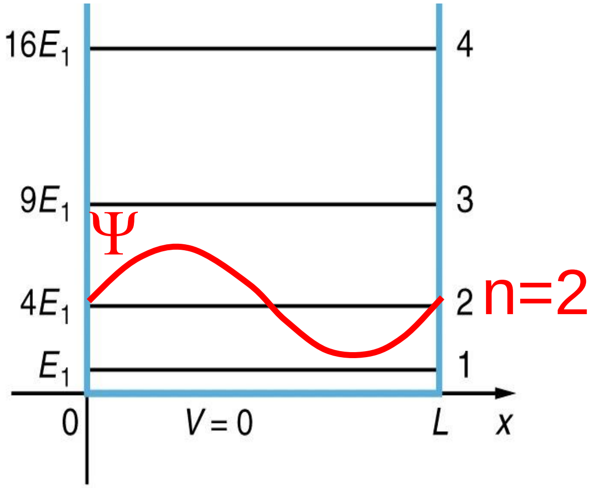
Quantized:

$$k_n=n\frac{\pi}{L}$$

$$E_n=n^2\frac{\pi^2\hbar^2}{2mL^2}=n^2\frac{h^2}{8mL^2}=n^2E_1$$

The larger the curvature of the wave function the higher the energy!

Not surprising: $$-\frac{\hbar^2}{2m}\frac{\partial^2\psi(x)}{\partial x^2}=E\psi(x)$$



$$\Psi(x,t) = \sqrt{\frac{2}{L}}\sin(\frac{n\pi x}{L})e^{-iEt/\hbar}$$

Quantized: k=nπ/L

Quantized: $E_n = n^2 \frac{\pi^2\hbar^2}{2mL^2} = n^2 E_1$

<u>What you expect classically:</u>	<u>What you get quantum mechanically:</u>
Electron can have any energy	Electron can only have specific energies. (quantized)
Electron is localized	Electron is delocalized … spread out between 0 and L

Electron is not a localized particle bouncing back and forth!

Infinite Square-Well Potential

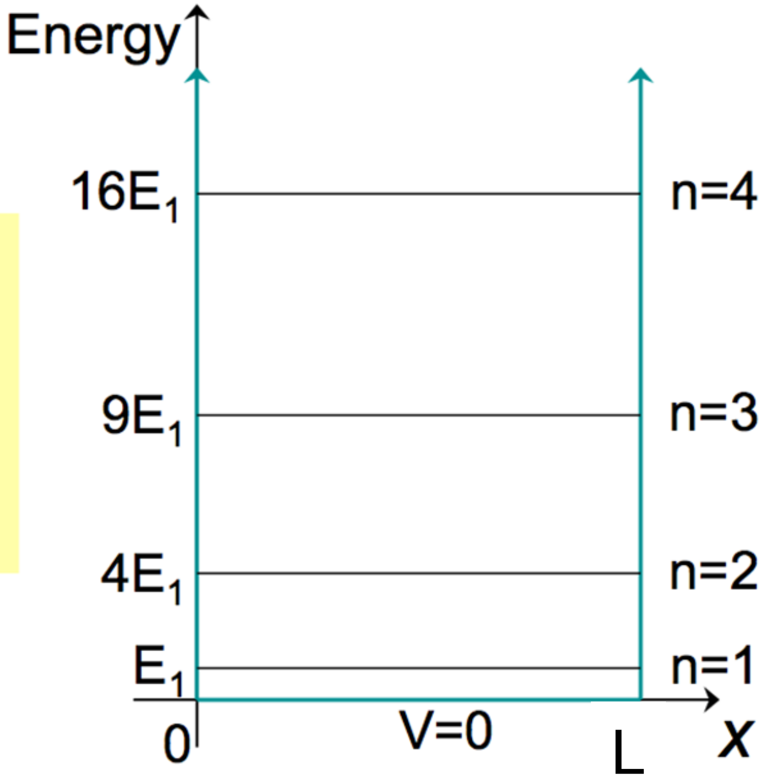
<u>Things to notice:</u>

Energies are quantized.

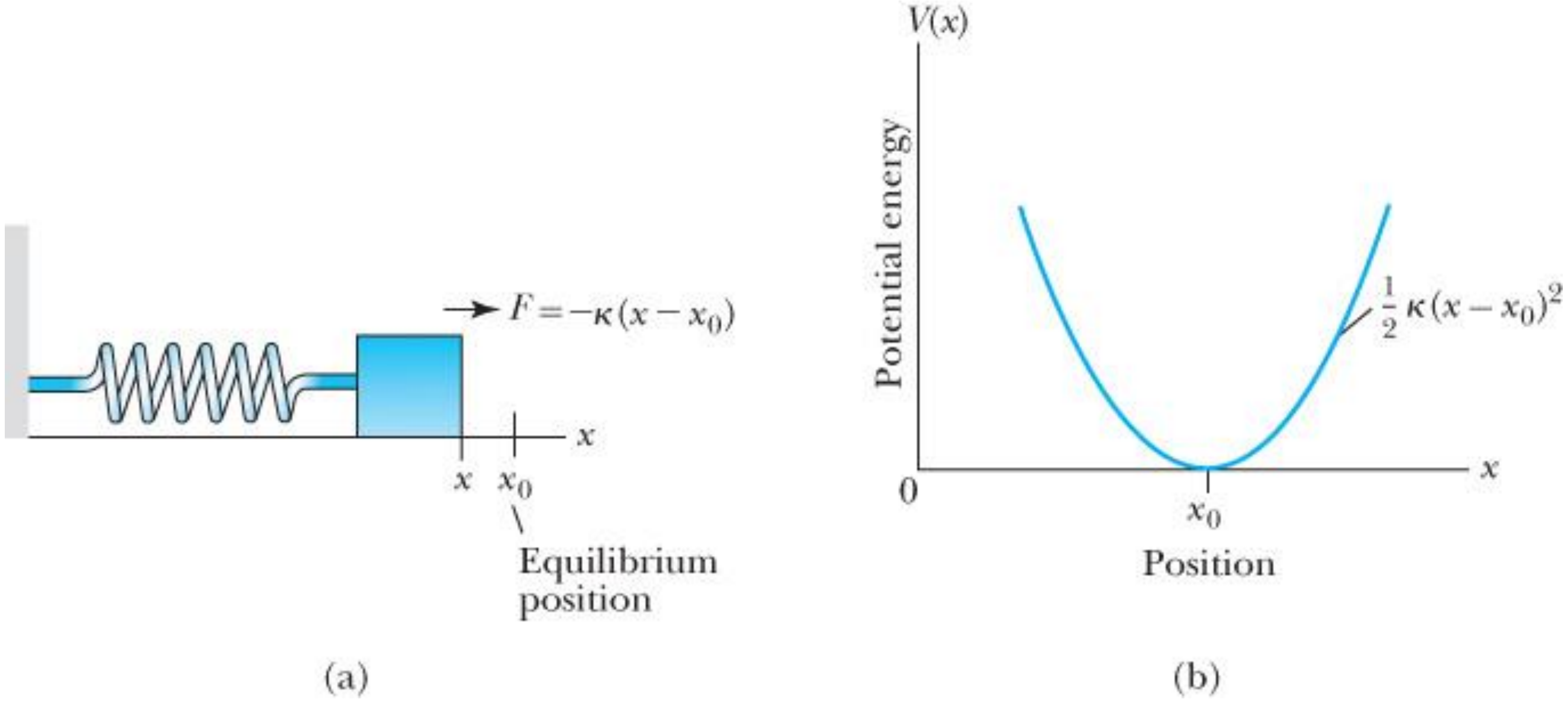
Minimum energy E_1 is **not** zero.

Consistent with uncertainty principle. x is between 0 and a so Δx~a/2. Since $\Delta x \Delta p \geq \hbar/2$, must be uncertainty in p. But if E=0 then p=0 so Δp=0, violating the uncertainty principle.

When L is large, energy levels get closer so energy becomes more like continuum (like classical result).



1D Harmonic oscillator



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

$$V(x) = \frac{1}{2}\kappa x^2$$

Assume $x_0=0$

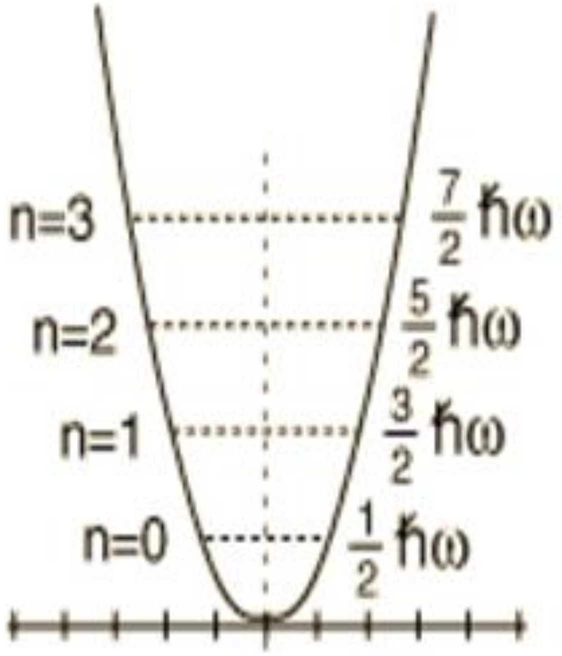
1D Harmonic oscillator

$$-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2}+\frac{1}{2}\kappa x^2\psi(x)=E\psi(x)$$

- The energy levels are given by

$$E_n=\left(n+\frac{1}{2}\right)\hbar\omega \quad \text{n=0,1,2...}$$

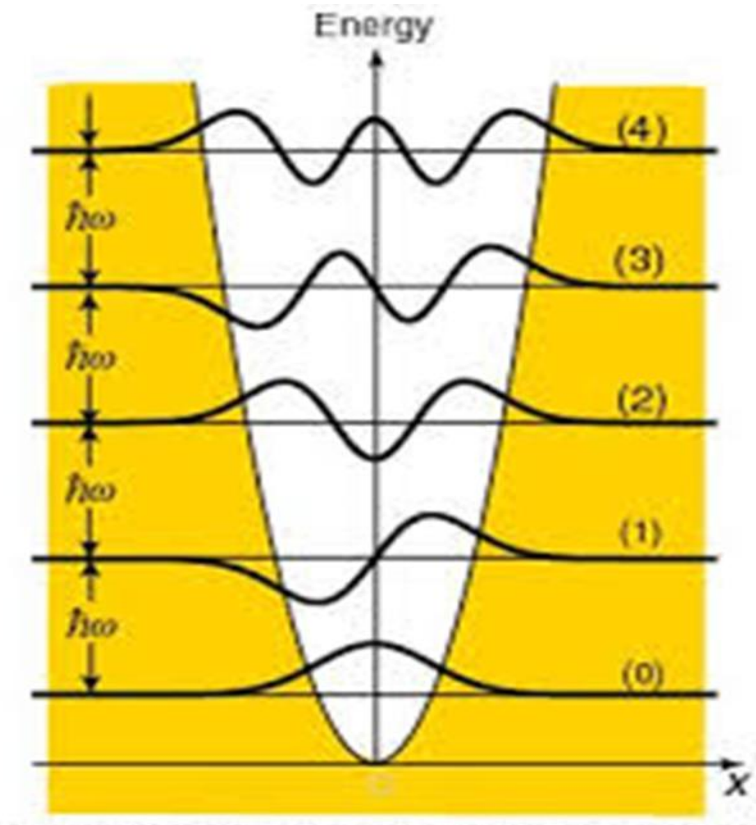
$$\omega=\sqrt{\frac{\kappa}{m}}$$



- The zero point energy is called the Heisenberg limit:

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

1D Harmonic oscillator



The thick solid curves are the wave functions.
(0) : the ground state
(1) (2) (3) . . . : the excited states

The wave function solutions are

$$\psi_n(x) = \frac{1}{\sqrt{2^n n! \sqrt{\pi}}} H_n(x) e^{-\frac{x^2}{2a^2}}; \quad a^2 = \frac{\hbar}{m\omega}$$

$H_n(x)$ are Hermite polynomials of order n

- 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*.

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How many possible energy levels are there in a Harmonic oscillator?

A. $N_{\text{possible}} = 2\left(\frac{E_n}{\Delta E_n} + 1\right)$

B. $N_{\text{possible}} = \frac{E_n}{\Delta E_n}$

C. $N_{\text{possible}} = \infty$

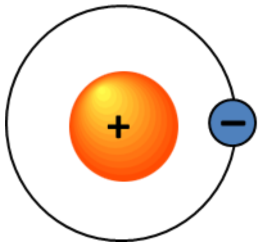
D. $N_{\text{possible}} = \frac{E_n}{\Delta E_n}(2n + 1)$

$$E_n = \left(n + \frac{1}{2}\right)\hbar\omega$$ n=0,1,2…

$$\Delta E_n = \hbar\omega$$ Equally spaced!

ΔE_n is the energy difference between the nth and n+1 HO states.

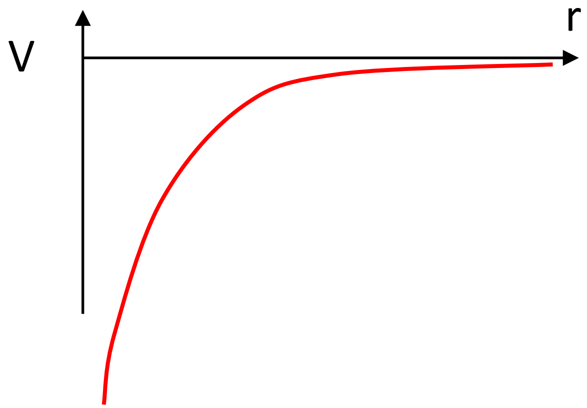
Hydrogen atom



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

where:

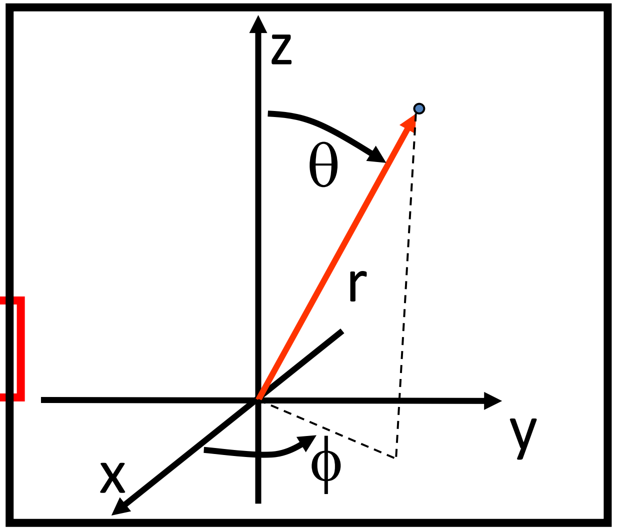
$$V(r)=-\frac{Zke^2}{r}=-\frac{Zke^2}{(x^2+y^2+z^2)^{1/2}}$$



$$E_n=-\frac{mZ^2k^2e^4}{2\hbar^2n^2}=-Ryd\,\frac{1}{n^2}=-\frac{13.6}{n^2}eV,\quad n=1,2,\ldots$$

Hydrogen wavefunctions

$$\psi_{nlm}(r,\theta,\phi) = R_{nl}(r)Y_{lm}(\theta,\phi)$$



Shape of ψ depends on n, l ,m. Each (nlm) gives unique ψ

2p

n=2

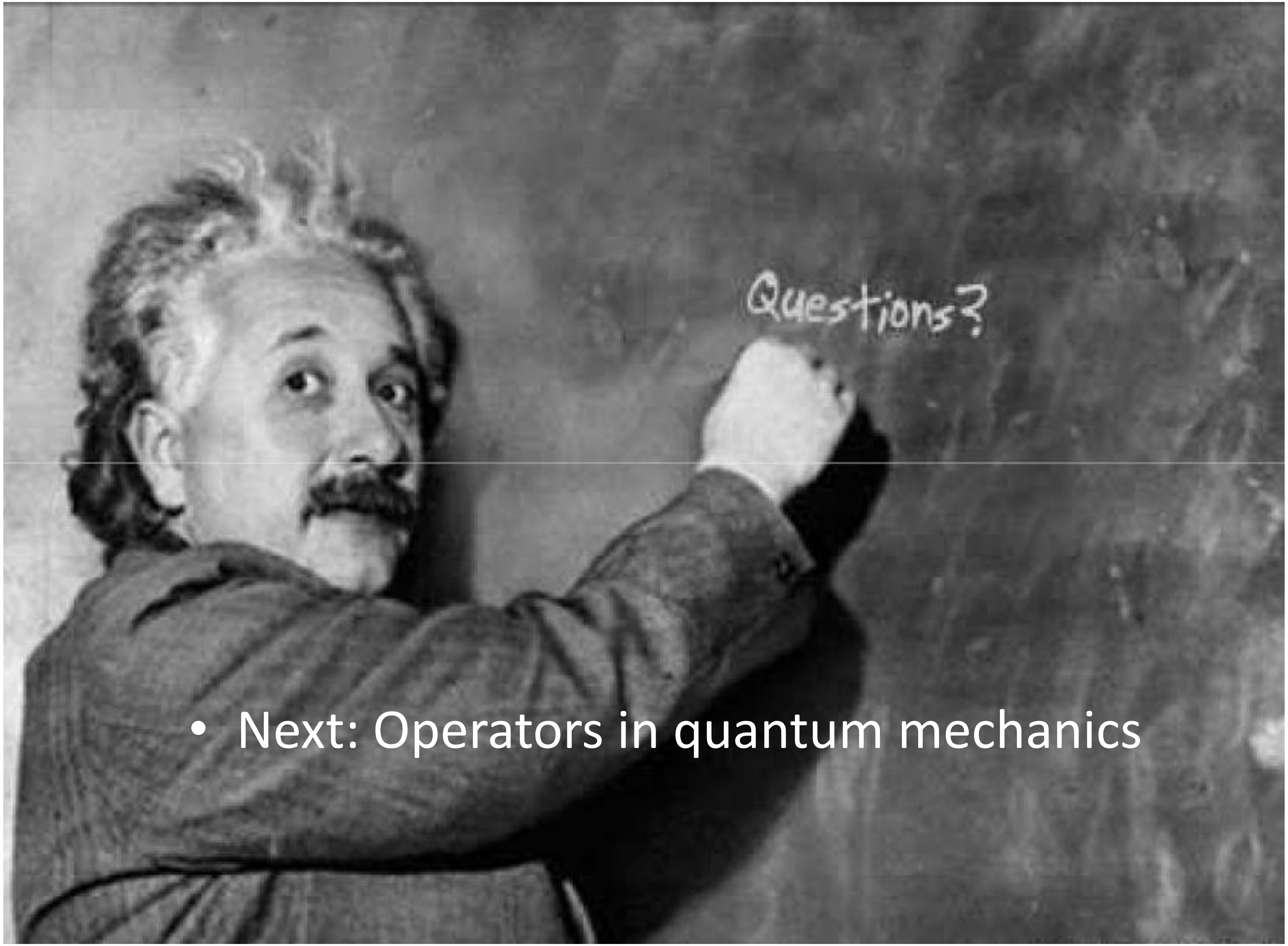
l=1

m=-1,0,1

n=1, 2, 3 … = Principal Quantum Number

l=0, 1, 2, 3 …= Angular Momentum Quantum Number
=s, p, d, f (restricted to 0, 1, 2 … n-1)

m = … -1, 0, 1.. = z-component of Angular Momentum
(restricted to –l to l)



- Next: Operators in quantum mechanics

Quantum Mechanics: Notation

Law1. The state of a quantum mechanical system is completely specified by a function $\Psi(r, t)$.

- Dirac notation

$$\psi(x) \Rightarrow |\psi\rangle \quad ket$$

$$\psi^*(x) \Rightarrow \langle\psi| \quad bra$$

- Principle of superposition. If Ψ_1 and Ψ_2 are possible states of a system then any linear superposition. Ψ is also an allowed state.

$$|\psi\rangle = a_1|\psi_1\rangle + a_2|\psi\rangle_2$$

- Inner product

$$\langle\phi|\psi\rangle = \int \phi^*(r)\psi(r)d\mathbf{r}$$

$\psi(x)$ $|\psi\rangle$ $\hat{x}$

$\psi(p)$ $|\psi\rangle$ p

Quantum Mechanics: Law 2

Law 2. To every observable in classical mechanics there corresponds an operator which is used to obtain physical information about the observable from the wave function

Observable	Classical	Quantum operator
Canonical momentum	$\boldsymbol{p}$	$-i\hbar\nabla = -i\hbar(\frac{\partial}{\partial x}\hat{x} + \frac{\partial}{\partial y}\hat{y} + \frac{\partial}{\partial z}\hat{z})$
Mechanical momentum	$\vec{\boldsymbol{p}} + q\vec{A}(\boldsymbol{r},\boldsymbol{t})$	$-i\hbar\nabla + \hat{A}(\hat{r},t)$
Kinetic energy (KE)	$\frac{p^2}{2m}$	$-\frac{\hbar^2}{2m}\nabla^2 = -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right)$
Total energy KE+U	$\frac{p^2}{2m} + U(\vec{r})$	$\hat{H} \equiv -\frac{\hbar^2}{2m}\nabla^2 + U(\hat{r})$

Quantum Mechanics: Law 2 (cont)

- Operators acting on the state of the system produce another allowed state.
$$\hat{O}|\psi\rangle = |\psi'\rangle$$

- Every operator has set of states that are not changed by the action of the operator, except for being multiplied by a constant.
- These are the eigenstates and the numbers are the eigenvalues of the operator.
$$\hat{O}|\psi_a\rangle = a|\psi_a\rangle$$

Example: the momentum operator

- Solve for the Eigenstates and eigenvalues of the momentum operator

$$\hat{p}|\psi_p\rangle = p|\psi_p\rangle$$

$$\Rightarrow -i\hbar\nabla\psi_p = p\psi_p$$

$$1\text{D}: \quad -i\hbar\frac{\partial\psi_p}{\partial x} = p\psi_p$$

1. Which of these wavefunctions represents an eigenstate with momentum p?

(a) $\psi_p = Ce^{-kx}$

(b) $\psi_p = C\sin kx$

(c) $\psi_p = Ce^{ik\cdot x}$

(d) $\psi_p = Cx^2$

2. What is the value of k

(a) $k = \frac{p}{\hbar}$

(b) $k = p$

(c) $k = p^2$

(d) $k = \hbar p$

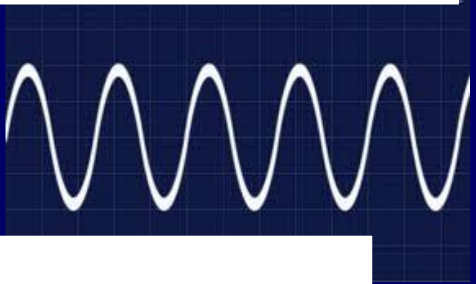
E.Y. Andrei

Solution: the momentum operator

- Solve for the Eigenstates and eigenvalues of the momentum operator

$$\hat{p}|\psi_p\rangle = p|\psi_p\rangle$$
$$\Rightarrow -i\hbar\nabla\psi_p = p\psi_p$$
$$1D: \quad -i\hbar\frac{\partial\psi_p}{\partial x} = p\psi_p$$

PLANE WAVE



$$\Rightarrow \psi_p = Ce^{i\frac{p}{\hbar}\cdot x} = Ce^{ik\cdot x}; \quad p = \hbar k$$

1. Which of these wavefunctions represents an eigenstate with momentum p?

(a) $\psi_p = Ce^{-kx}$

(b) $\psi_p = C\sin kx$

(c) $\psi_p = Ce^{ik\cdot x}$

(d) $\psi_p = Cx^2$

2. What is the value of k

(a) $k = \frac{p}{\hbar}$

(b) $k = p$

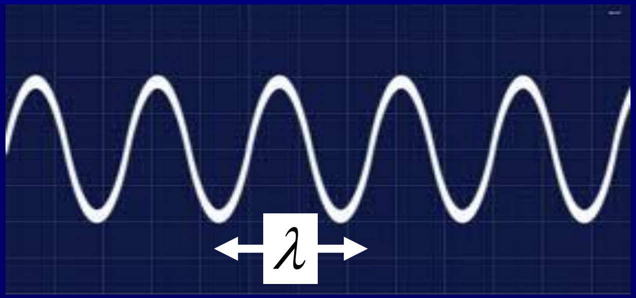
(c) $k = p^2$

(d) $k = \hbar p$

The momentum operator

- The Eigenstates of the momentum operator are PLANE WAVES

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



$$\Rightarrow \psi_p = Ce^{ik\cdot x}; \quad where\ k = \frac{p}{\hbar}$$

$$\lambda = \frac{2\pi}{k} = \frac{h}{p}$$ de Broglie wavelength!

- The Eigenvalues of the momentum operator p = all real numbers
- Plane waves have a well defined momentum p with no uncertainty $\Delta p=0$
- Plane waves are infinite in space they have no well defined position $\Delta x=00$ consistent with the uncertainty principle!

$$\Delta p\cdot\Delta x \geq \hbar$$

Quantum Mechanics: Law 3

Law 3. The only possible result of the measurement of an observable A is one of the eigenvalues of the corresponding operator.

- The eigenvalues of operators corresponding to observables are real. (we measure only real numbers)
- Operators with real eigenvalues are called *hermitian*.

- Eigenstates of hermitian operators form a basis that spans the set of allowed states :
- Orthogonal

$$\langle a_j | a_k \rangle = \int \psi^*_{a_j}(r)\psi_{a_k}(r)d\mathbf{r} = \delta_{jk} \equiv \begin{cases} 1 & j = k \\ 0 & j \neq k \end{cases}$$

- Complete. This means than an arbitrary state can be expanded as a linear combination of the eigenstates.

$$|\psi\rangle = \sum_n c_n |a_n\rangle \quad c_n = \langle a_n | \psi \rangle$$

The energy operator: Hamiltonian

When the total energy is conserved, the system is best described by the eigenvalues of the total energy operator, the Hamiltonian:

The Eigenstates and eigenvalues of the total energy operator, the Hamiltonian:

$$\hat{H}|\psi_E\rangle = \left[\frac{\hat{p}^2}{2m} + V(x)\right]|\psi_E\rangle = E|\psi_E\rangle$$

$$\hat{p} = -i\hbar\nabla \Rightarrow \hat{p}^2 = -\hbar^2\nabla^2$$

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

the Hamiltonian

$$\hat{H} \equiv -\frac{\hbar^2}{2m}\nabla^2 + V(\vec{r})$$

This is just the time-independent Schroedinger equation!!

The time-independent Schrödinger Equation

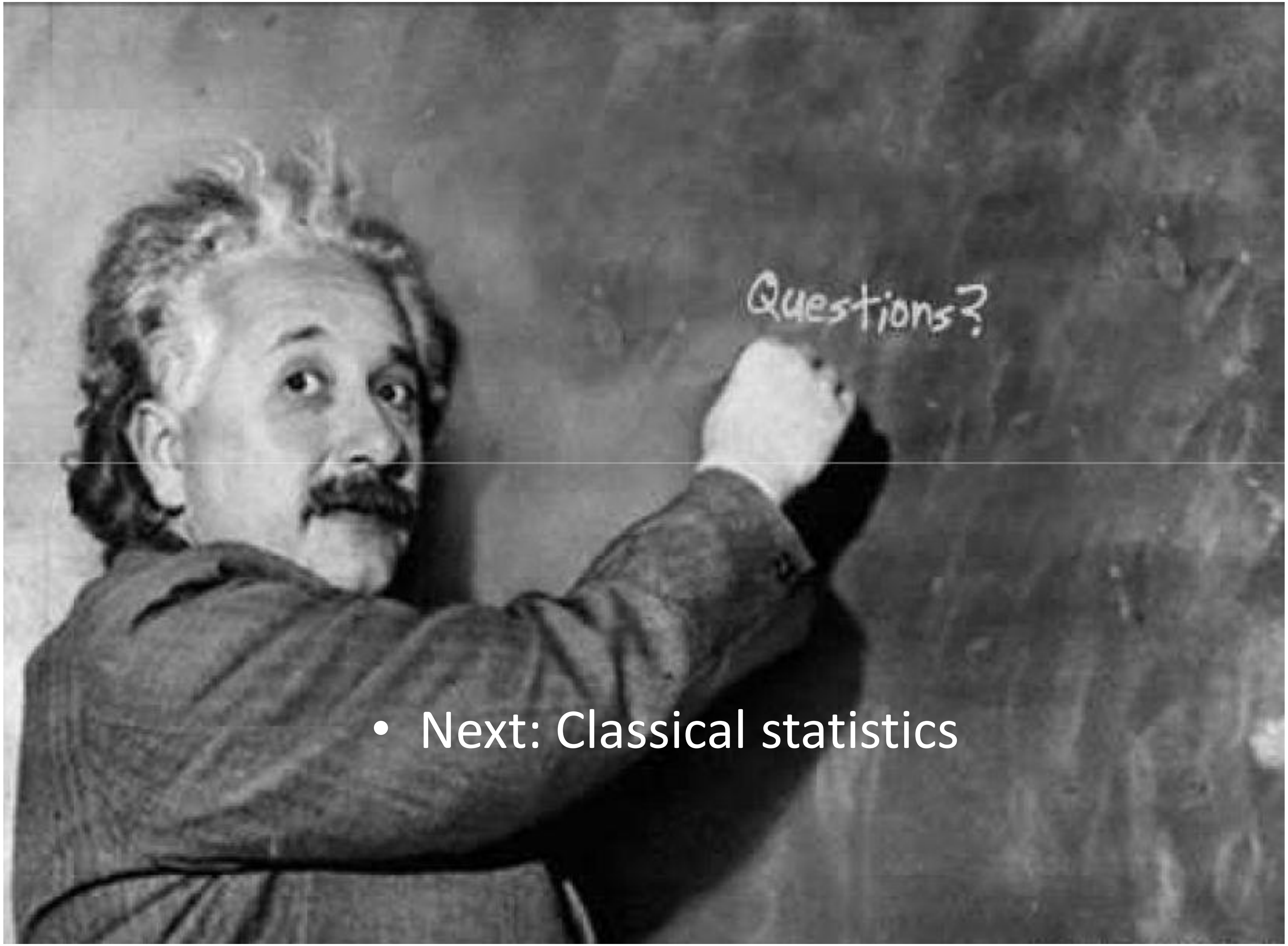
The wave function $\Psi(r, t)$ for a state with a well defined total energy E is a solution of the Schrödinger Equation

$$\text{in 1D}: \quad \hat{p} = -i\hbar \frac{\partial}{\partial x} \Rightarrow \hat{p}^2 = -\hbar^2 \frac{\partial^2}{\partial x^2}$$

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

$$\hbar = \frac{h}{2\pi}$$

Note that the KE of the particle depends on the curvature ($d^2\psi/dx^2$) of the wave function. This is sometimes useful when analyzing a problem


Questions?
• Next: Classical statistics

Summary of L2

- Heisenberg Uncertainty principle
- Quantum mechanics problems we can solve:
  - Potential well, Harmonic oscillator, Hydrogen atom
- Operators, eigenfunctions, and eigenvalues
- Momentum operator
- Energy operator

Next time

- Statistics: Maxwell Boltzmann
- Equipartition theorem
- Specific heat of solids

Reading assignment

- Simon Ch 2

Homework

Posted