

Lecture #3

Quantum Mechanics: Introduction

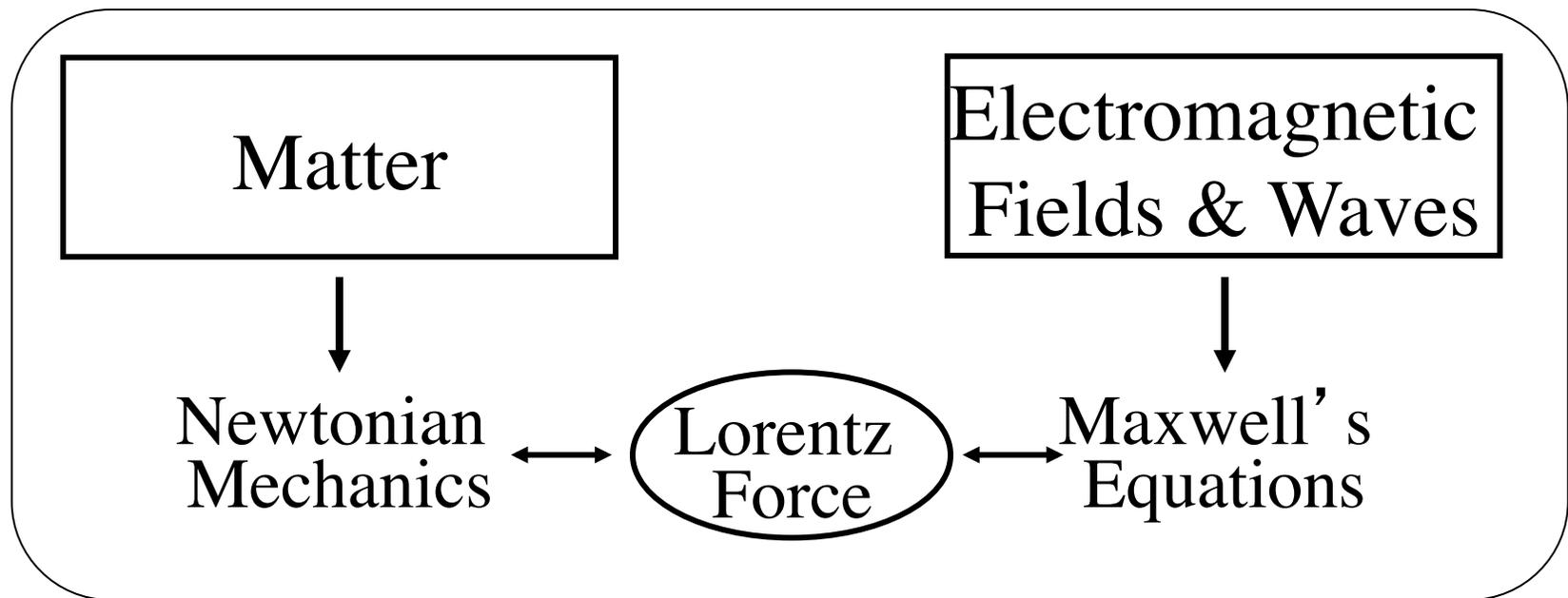
- Topics
 - Why QM for magnetic resonance?
 - Historical developments
 - Wavefunctions
- Handouts and Reading assignments
 - Levitt, Chapter 6 (optional)
 - Miller, Chapter 1-3 (optional).

Classical versus Quantum NMR

- QM is only theory that correctly predicts behavior of matter on the atomic scale, and QM effects are seen in vivo.
- Systems of isolated nuclei can be described with the intuitive picture of a classical magnetization vector rotating in 3D space (Bloch equations).
- Systems of interacting nuclei, in particular spin-spin coupling, require a more complete QM description (density matrix theory).
- We will develop a QM analysis of MR, based on density matrix theory, but retaining the intuitive concepts of classical vector models (product operator formalism).

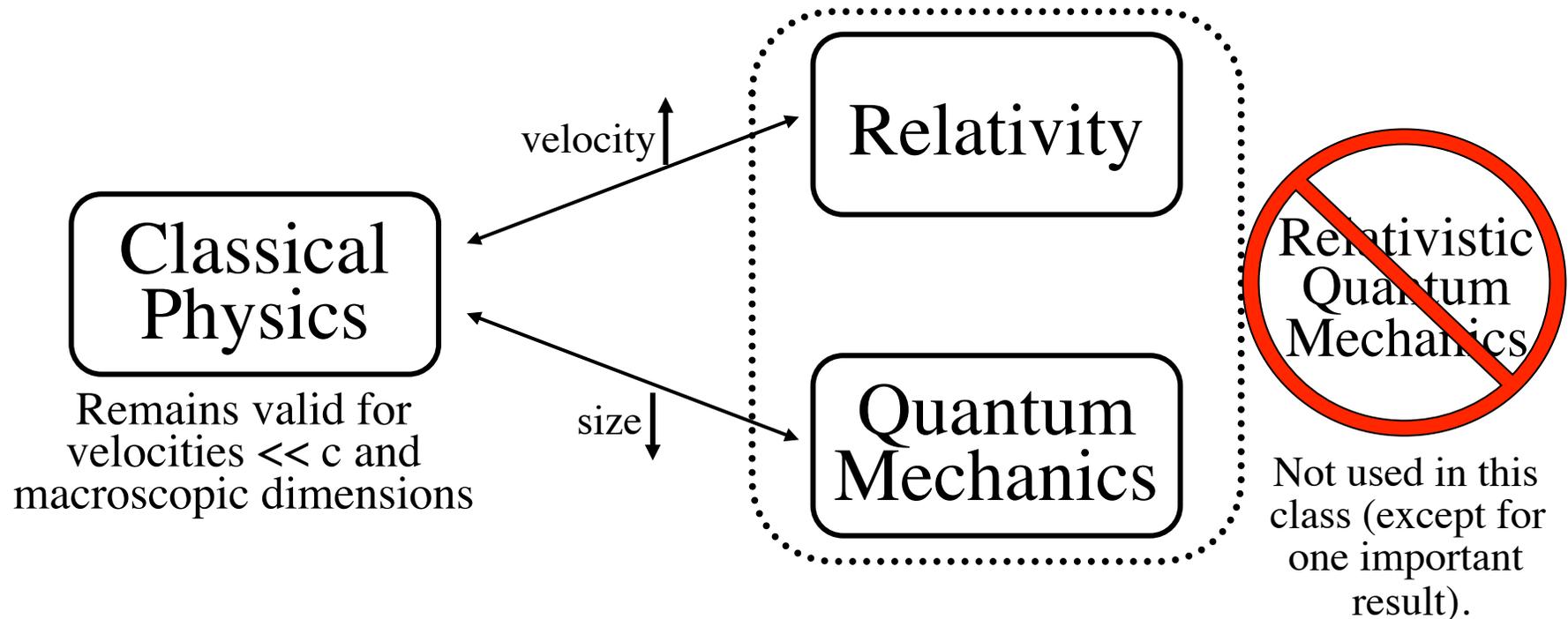
19th Century Physics

- At the end of the 19th century, physicists divided the world into two entities:



Classical Physics

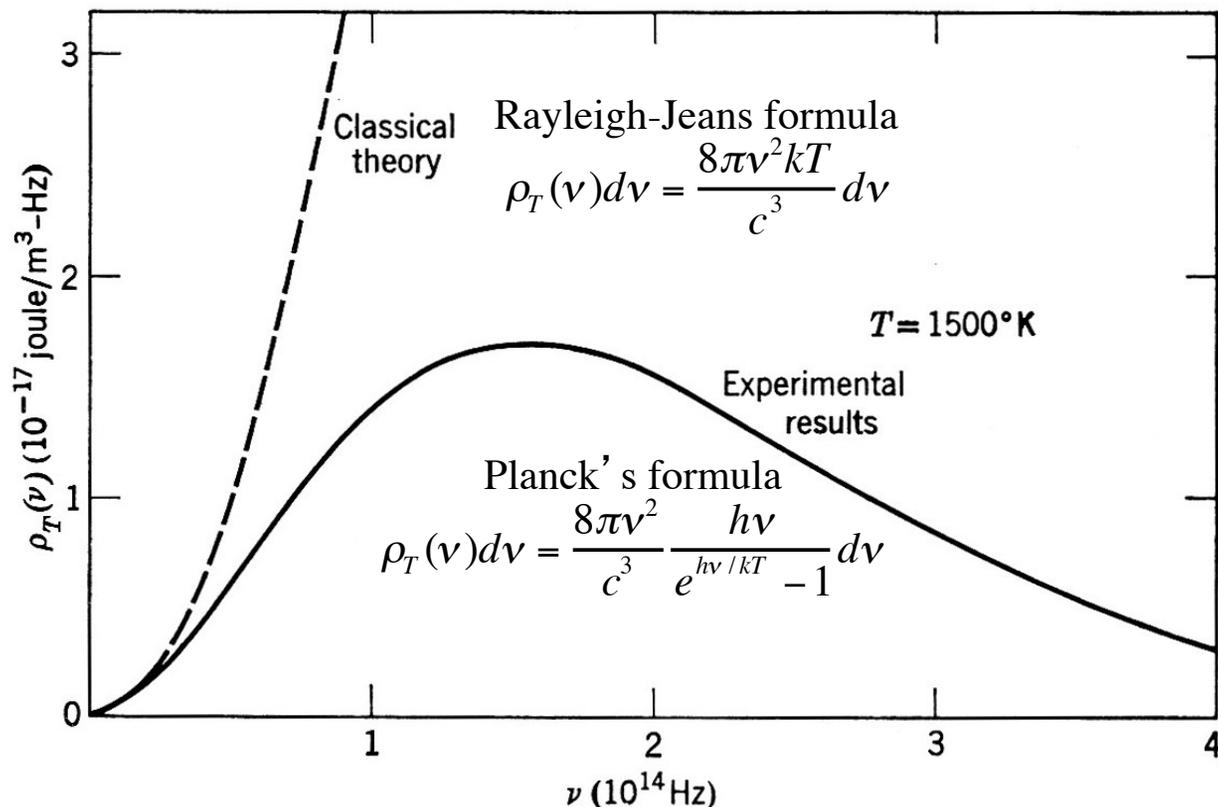
Early 20th Century Physics



Analogy: geometric optics versus inclusion of diffraction effects

Blackbody Radiation

- A blackbody is an object that absorbs all incident thermal radiation.



- Classical theory leads to the “ultraviolet catastrophe”

- Max Planck solved problem by assuming energy is quantized such that

$$E = nh\nu$$

where $n = \text{integer}$ and
 $h = 6.63 \times 10^{-34} \text{ j}\cdot\text{s}$.

Planck's Theory of Cavity Radiation (1900) => energy quantization

Photons

- Einstein generalized Planck's results
 - Proposed a return to the particle theory of light. i.e. light = photons each with energy $h\nu$.
 - Photons explain the photoelectric effect (1905).
 - Note: photons not experimentally shown to exist until the Compton effect (1924).
- EM waves (radiation) exhibit both wave and particle features with parameters linked by

$$\begin{aligned} E &= h\nu = \hbar\omega \\ \vec{p} &= \hbar\vec{k} \end{aligned}$$

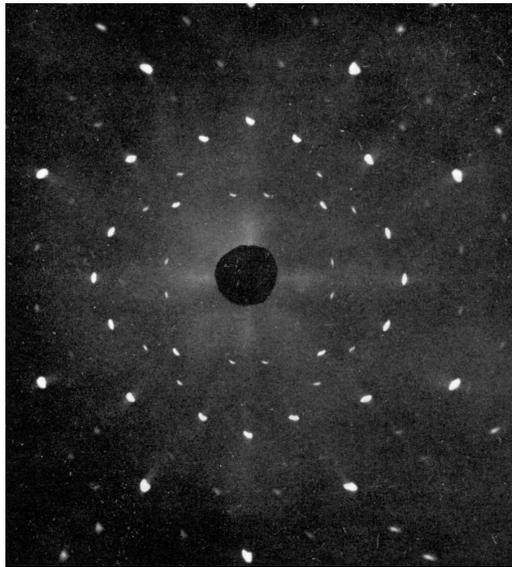
where

$$\begin{aligned} |\vec{k}| &= 2\pi / \lambda \quad \leftarrow \text{wavelength} \\ \hbar &= h / 2\pi \end{aligned}$$

Planck-Einstein relations

Matter Wave-Particle Duality

- de Broglie (1923) hypothesis: material particles (e.g. electrons, protons, etc), just like photons, can have wavelike aspects.
- Wave properties of matter later demonstrated via interference patterns obtained in diffraction experiments.



x-ray diffraction by
single NaCl crystal



neutron diffraction by
single NaCl crystal

Matter Wave-Particle Duality

- With each particle we associate:

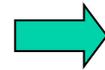
energy E

momentum \vec{p}

angular frequency $\omega = 2\pi\nu$

wave number \vec{k}

(later we'll add spin)



$$E = h\nu = \hbar\omega$$

$$\vec{p} = \hbar\vec{k}$$

$$\lambda = \frac{2\pi}{|\vec{k}|} = \frac{h}{|\vec{p}|} \quad \text{de Broglie wavelength}$$

(remember h is **very** small)

- Example 1: baseball moving at $v = 10$ m/s (assume $m = 0.1$ kg)

de Broglie wavelength $\lambda = \frac{h}{p} = \frac{h}{mv} = 6.6 \times 10^{-34} \text{ m} = 6.6 \times 10^{-24} \text{ \AA}$

- Example 2: dust speck with $m = 10^{-15}$ kg and $v = 10^{-3}$ m/s

de Broglie wavelength $\lambda = \frac{h}{p} = \frac{h}{mv} = 6.6 \times 10^{-16} \text{ m} = 6.6 \times 10^{-6} \text{ \AA}$

Conclusion: living in a macroscopic world, we have little intuition regarding the behavior of matter on the atomic scale.

Quantum vs Classical Physics

- QM does not deal directly with observable physical quantities (e.g. position, momentum, M_x , M_y , M_z).
- QM deals with the state of the system, as described by a wavefunction $\psi(t)$ or the density operator $\rho(t)$, independent of the observable to be detected.
- Probability is fundamental.

Classical physics: “If we know the present exactly,
we can predict the future.”

Quantum mechanics: “We *cannot* know the present exactly,
as a matter of principle.”

Wave Functions

- For the classical concept of a trajectory (succession in time of the state of a classical particle), we substitute the concept of the quantum state of a particle characterized by a *wave function*, $\psi(\vec{r}, t)$.
- $\psi(\vec{r}, t)$
 - contains all info possible to obtain about the particle
 - interpreted as a probability amplitude of the particle's presence with the probability density given by:

$$dP(\vec{r}, t) = C |\psi(\vec{r}, t)|^2 d^3\vec{r}, \quad C \text{ constant.}$$

$$\int dP(\vec{r}, t) = 1 \implies \frac{1}{C} = \int |\psi(\vec{r}, t)|^2 d^3\vec{r} \ll \infty$$

← square-integrable!

- wave functions typically normalized, i.e. $\int |\psi(\vec{r}, t)|^2 d^3\vec{r} = 1$

Schrödinger's Equation

- How does $\psi(\vec{r}, t)$ change with time?
- Time evolution given by the Schrödinger's equation:

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

Laplacian: $\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$

- Often written: $\frac{\partial}{\partial t} \psi(\vec{r}, t) = -\frac{i}{\hbar} H \psi(\vec{r}, t)$

where $H = -\frac{\hbar^2}{2m} \nabla^2 + V(\vec{r}, t)$

(H operator for total energy called the *Hamiltonian*)

kinetic energy \nearrow \searrow potential energy

Note, classically $H = \frac{p^2}{2m} + V \quad \longrightarrow \quad p = -i\hbar \frac{\partial}{\partial \vec{r}}$

In QM, physical quantities are expressed as operators.

Quantum Description of a Free Particle

- For a particle subject to no external forces:

$$V(\vec{r}, t) = 0 \quad \Rightarrow \quad i\hbar \frac{\partial}{\partial t} \psi(\vec{r}, t) = -\frac{\hbar^2}{2m} \nabla^2 \psi(\vec{r}, t)$$

- Easy to show that this equation is satisfied by:

$$\psi(\vec{r}, t) = A e^{i(\vec{k} \cdot \vec{r} - \omega t)} \quad \text{where} \quad \omega = \frac{\hbar \vec{k}^2}{2m}$$

plane wave with wave number $\vec{k} = \vec{p}/\hbar$

- Since, $|\psi(\vec{r}, t)|^2 = |A|^2$, the probability of finding the particle is uniform throughout space.

Note, strictly speaking, $\psi(\vec{r}, t)$ is not square integrable, but as engineers we won't worry too much about this (comparable to dealing with $\delta(x)$ in Fourier theory).

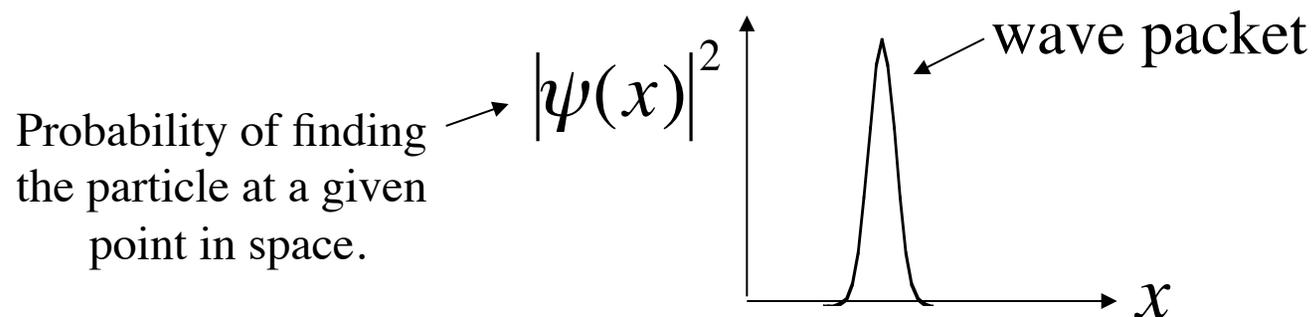
Quantum Description of a Free Particle (cont.)

- Linearity of Schrodinger's equation implies superposition holds, i.e. general linear combination of plane waves is also a solution.

$$\psi(\vec{r}, t) = \frac{1}{(2\pi)^{3/2}} \int g(\vec{k}) e^{i(\vec{k} \cdot \vec{r} - \omega(\vec{k})t)} d^3 \vec{k}$$

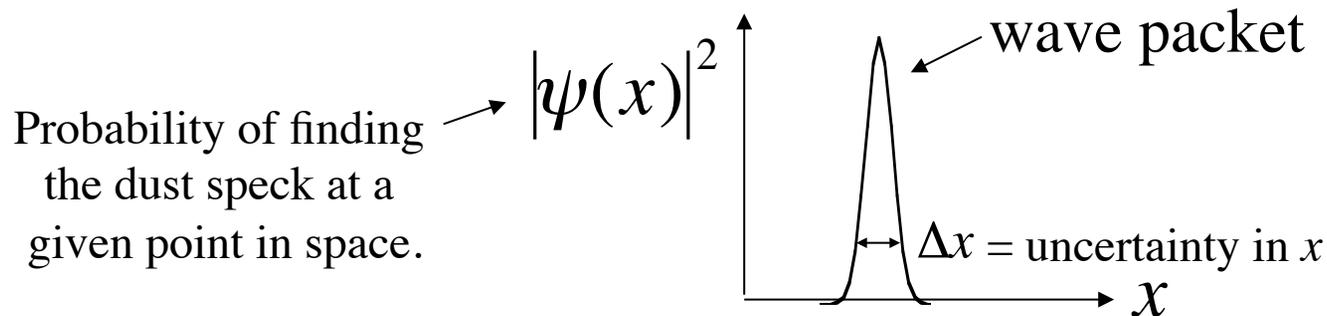
- Consider 1D case evaluated at a fixed time, say t=0:

$$\psi(x, 0) = \frac{1}{\sqrt{2\pi}} \int g(k) e^{ikx} dk$$



Wave Packets

- Example: dust speck with $m = 10^{-15}$ kg and $v = 10^{-3}$ m/s
de Broglie wavelength $\lambda = \frac{h}{p} = \frac{h}{mv} = 6.6 \times 10^{-16}$ m = 6.6×10^{-6} Å



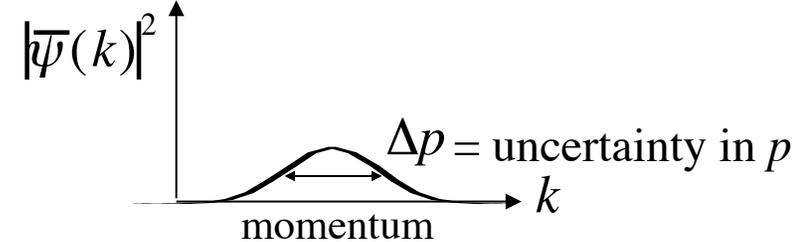
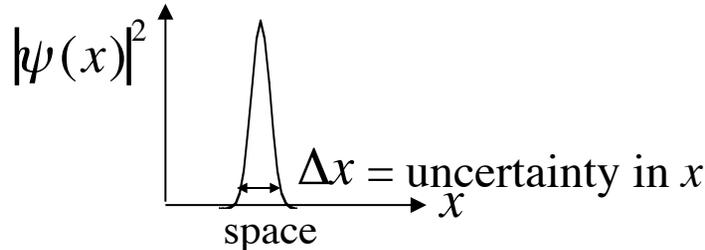
- In quantum terms, the dust speck is described by a wave packet:
 - group velocity $v = 10^{-3}$ m/s
 - average momentum $p = 10^{-18}$ kg m/s
 - maximum represents the “position”

How accurately can we measure the dust speck’s position?

Wave Packets

remember: $p = \hbar k$

$$\bullet \quad \psi(x,0) = \frac{1}{\sqrt{2\pi}} \int g(k) e^{ikx} dk \quad \Rightarrow \quad \psi(x) = \frac{1}{\sqrt{2\pi}} \int \bar{\psi}(k) e^{ikx} dk$$



Fourier theory of equivalent widths immediately yields most common form of the uncertainty principle $\Rightarrow \Delta x \cdot \Delta p \geq \hbar / 2$

- Example: dust speck with $m = 10^{-15}$ kg and $v = 10^{-3}$ m/s. If the position is measured to an accuracy of $\Delta x = 0.01 \mu$, then

$$\Rightarrow \Delta p \cong \frac{\hbar}{\Delta x} = 10^{-26} \text{ kg} \cdot \text{m/s} \Rightarrow$$

Since no momentum measuring device can achieve this level of accuracy, both Δx and Δp are negligible. Hence the we can treat the dust speck as a classical particle.

- At the atomic level, Δx and Δp are *not* negligible.
- For NMR, we' ll not be dealing with x and p , but rather another intrinsic property of matter known as spin.

Summary: Wave Functions

- Replaces the classical concept of a trajectory.
- $\psi(\vec{r}, t)$ contains all information possible to obtain about a particle.
- Probability of finding particle in differential volume $d^3\vec{r}$ is given by

$$dP(\vec{r}, t) = C |\psi(\vec{r}, t)|^2 d^3\vec{r}$$

↙ normalization
constant

- Time evolution given by the Schrödinger's equation:

$$\frac{\partial}{\partial t} \psi(\vec{r}, t) = -\frac{i}{\hbar} H \psi(\vec{r}, t)$$

Next Lecture: Mathematics of QM

Appendix I

Plausibility of Schrodinger's Eqn.

Given...

Newton: $F = \frac{d}{dt} p$

↑ force ↓ momentum

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

↑ energy ↓ kinetic ↓ potential

de Broglie-Einstein: $k = \frac{2\pi}{\lambda} = \frac{p}{\hbar}$

↑ wavenumber

$$E = \omega \hbar$$

↑ frequency

Reasonable to look for a QM wave of the form:

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

(1 d case)

Sinusoidal traveling wave with constant wavenumber and frequency (momentum and energy). For example, this satisfies Newton and de Broglie-Einstein for $V = \text{constant}$.

Plausibility of Schrodinger's Eqn.

Consider:

$$\frac{\partial}{\partial x} \psi(x,t) = i \frac{p}{\hbar} e^{i(kx-\omega t)} \longrightarrow -i\hbar \frac{\partial}{\partial x} \psi(x,t) = p\psi(x,t)$$

$$\text{operator form: } \hat{p} = -i\hbar \frac{\partial}{\partial x}$$

$$\frac{\partial}{\partial t} \psi(x,t) = -i \frac{E}{\hbar} e^{i(kx-\omega t)} \longrightarrow i\hbar \frac{\partial}{\partial t} \psi(x,t) = E\psi(x,t)$$

$$\text{operator form: } \hat{E} = i\hbar \frac{\partial}{\partial t}$$

Substituting into operator form of energy equation:

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

Note: equation linear in ψ , hence waves can add yielding interference effects, etc.