Lecture #3
Quantum Mechanics: Introduction

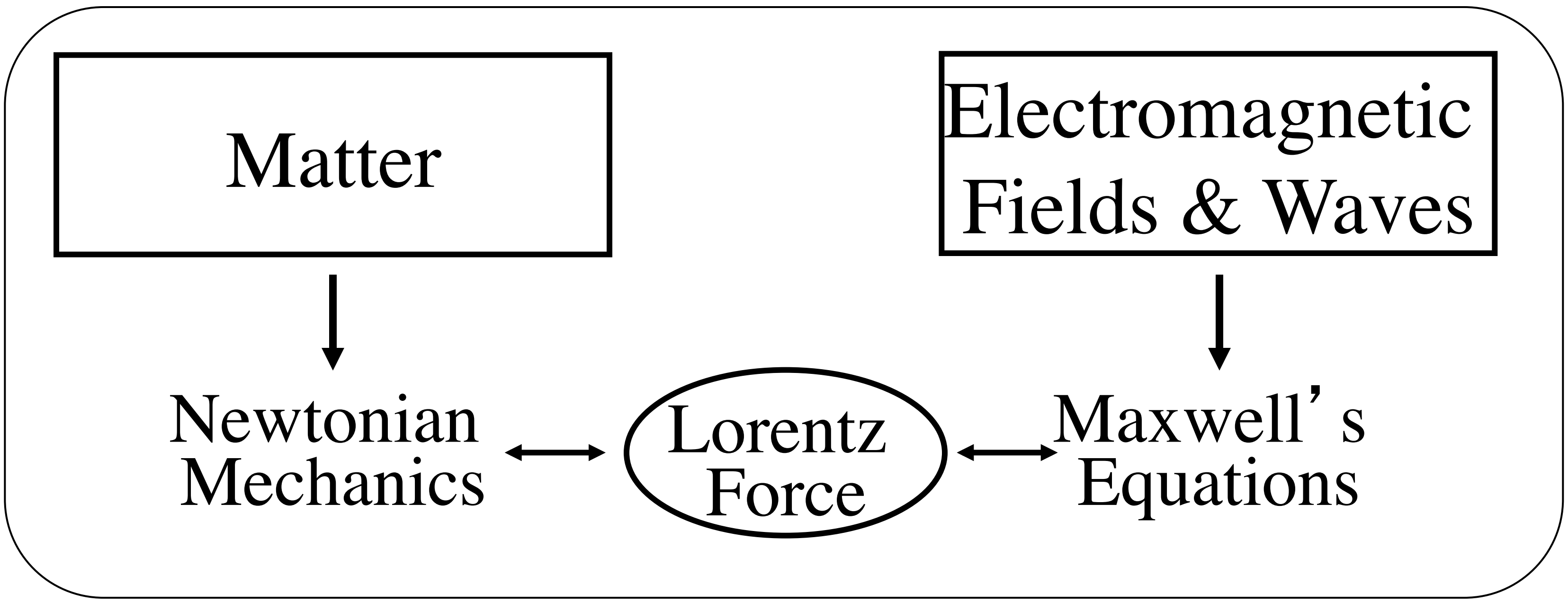
- Topics
  - Why QM for magnetic resonance?
  - Historical developments
  - Wavefunctions
- Handouts and Reading assignments
  - Levitt, Chapter 6 (optional)
  - Miller, Chapter 1-3 (optional).

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).

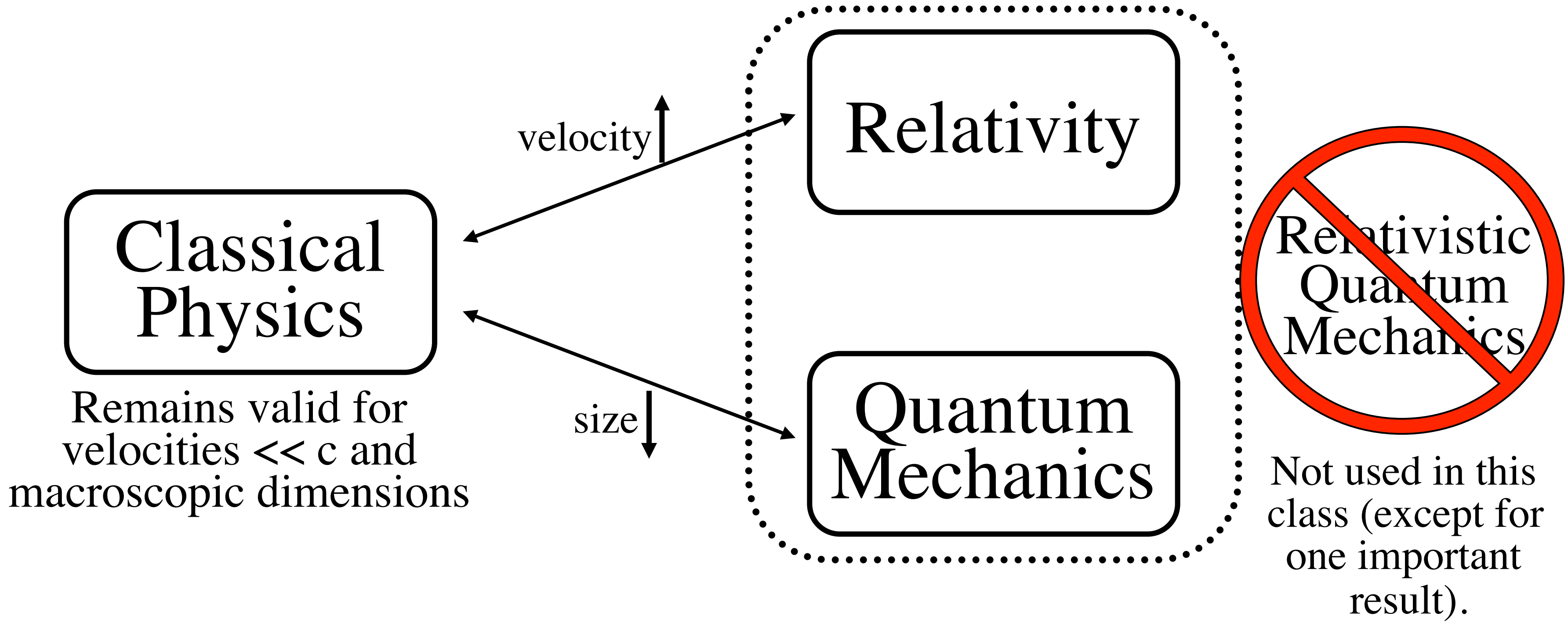
19th Century Physics

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



Classical Physics

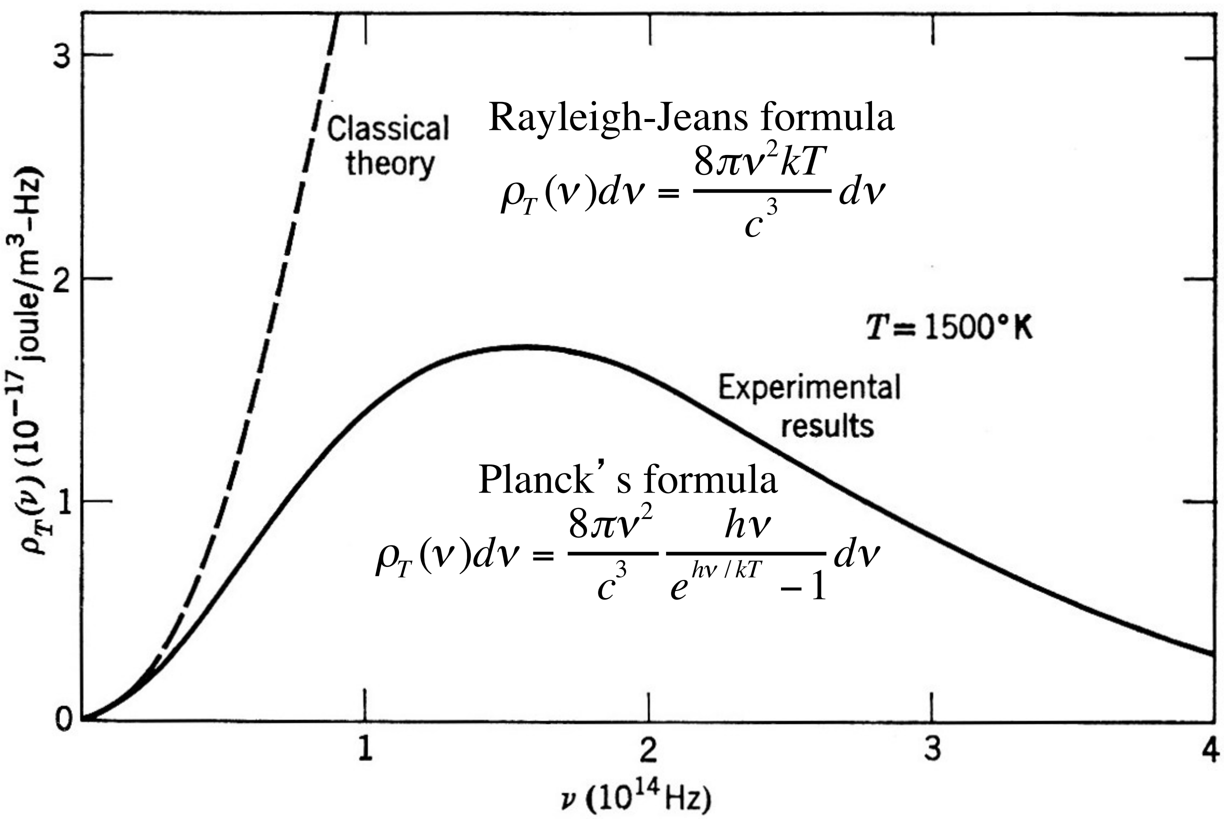
Early 20th Century Physics



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=integer and

$$h=6.63\times10^{-34}\ \text{j·s}.$$

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

ref: Eisberg and Resnick, Quantum Physics, pp 3-24.

Photons

- Einstein generalized Planck's results
  - Proposed a return to the particle theory of light. i.e. light = photons each with energy hν.
  - 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

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

where

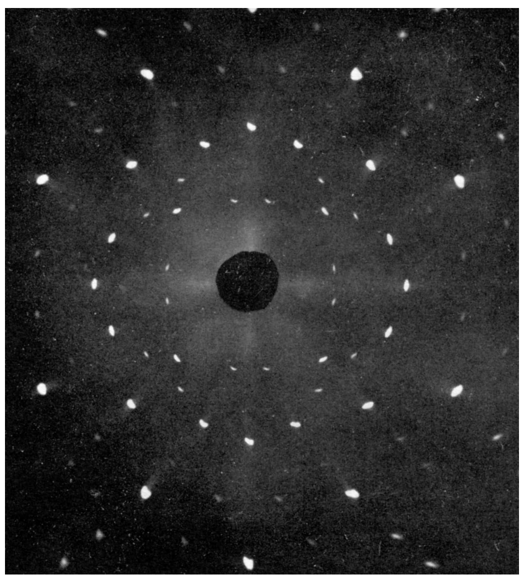
$$\left|\vec{k}\right| = 2\pi/\lambda \quad \text{wavelength}$$

$$\hbar = h/2\pi$$

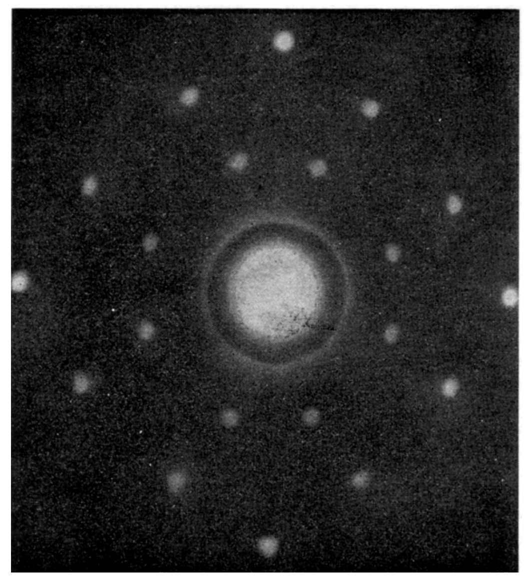
Planck-Einstein relations

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)

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

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

$$\lambda = \frac{2\pi}{\left|\vec{k}\right|} = \frac{h}{\left|\vec{p}\right|}$$

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 $\lambda = \frac{h}{p} = \frac{h}{mv} = 6.6\times10^{-34}\text{ m} = 6.6\times10^{-24}\text{ Å}$

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

de Broglie wavelength $\lambda = \frac{h}{p} = \frac{h}{mv} = 6.6\times10^{-16}\text{ m} = 6.6\times10^{-6}\text{ Å}$

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:

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

$$\int dP(\vec{r},t) = 1 \Longrightarrow \frac{1}{C} = \int \left|\psi(\vec{r},t)\right|^2 d^3\vec{r} \quad << \infty$$

square-integrable!

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

Schrödinger's Equation

- How does $\psi(\vec{r},t)$ change with time?

- Time evolution given by the Schrödinger's equation:

potential energy

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

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

potential energy

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

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:

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

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 δ(x) in Fourier theory).

Quantum Description of a Free Particle (cont.)

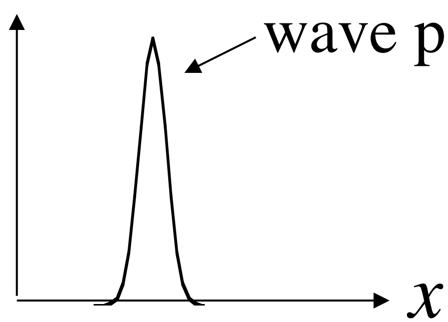
- Linearity of Schrodinger's equation implies superposition holds, i.e. general linear combination of plane waves is also a solution.

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

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

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

Probability of finding the particle at a given point in space. → $|\psi(x)|^2$

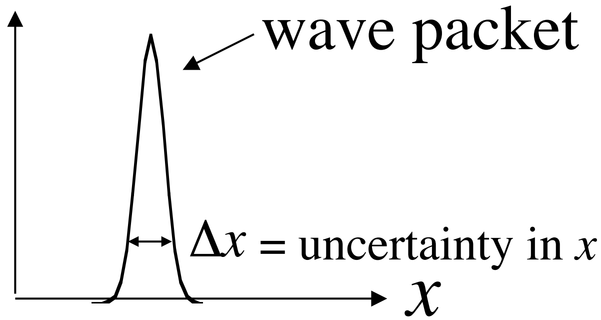


Wave Packets

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

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

Probability of finding the dust speck at a given point in space. $|\psi(x)|^2$



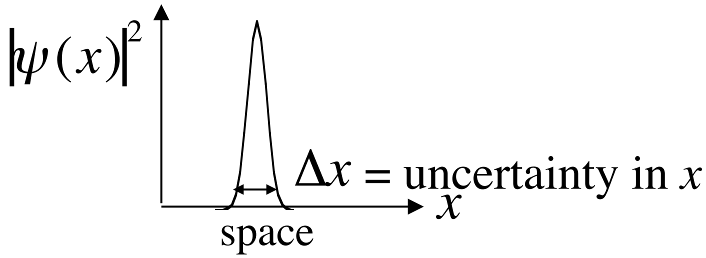
- In quantum terms, the dust speck is described by a wave packet:
  - group velocity $v = 10^{-3}$ m/s
  - average momentum $p = 10^{-18}$ kg m/s
  - maximum represents the "position"

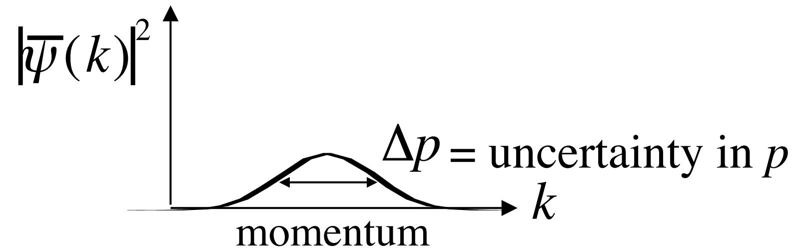
How accurately can we measure the dust speck's position?

Wave Packets

remember: $p = \hbar k$

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





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

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

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

normalization constant

- Time evolution given by the Schrödinger's equation:

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

Next Lecture: Mathematics of QM

Appendix I
Plausibility of Schrodinger's Eqn.

Given…

Newton: $F = \frac{d}{dt} p$ $\qquad E = \frac{p^2}{2m} + V$

force momentum energy kinetic potential

de Broglie-Einstein: $k = 2\pi/\lambda = p/\hbar$ $\qquad E = \omega\hbar$

wavenumber 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=constant.

Plausibility of Schrodinger's Eqn.

Consider:

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

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

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

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

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.