"Complementi di Fisica"
Lectures 5, 6

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Course Outline - Reminder

- **Quantum Mechanics: an introduction**
  - Reminder on waves
  - Waves as particles and particles as waves (the crisis of classical physics); atoms and the Bohr model
  - The Schrӧdinger equation and its interpretation
  - (1-d) Wave packets, uncertainty relations; barriers and wells
  - (3-d) Hydrogen atom, angular momentum, spin
  - Systems with many particles
- **Introduction to the physics of semiconductors**

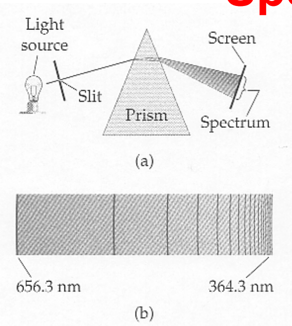
Lectures 10-11 - outline

- A first attempt at "explaining" the experimental observations on atoms and e.m. radiation
  - Spectroscopy
  - The Bohr model of the hydrogen atom
  - Attempts to extend it; the Correspondence Principle
- "Wave mechanics" of a single particle (i.e. an electron) subject to external forces, represented by potential energy
  - Guidelines for the development of a theory
  - Basic postulates and the Schrödinger equation
  - Time-Independent Schrödinger equation
  - Some 1-d examples (wavefunction, free particle, confined particle)
- The Big Picture: more complicated systems? Photon absorption and emission? Many particles systems, creation/annihilation?
  - Not for this course! Just some hints…
  - General postulates of "Quantum Mechanics"
  - "Second Quantization" ⇒ quantum field theory

Bohr model

Spectroscopy
Hydrogen atom
Extensions?

Spectroscopy



• **Figure 5–1** (a) The principle of a spectrometer: Here, a prism is used to spread the spectrum of light from a source composed of a variety of different wavelengths onto a screen. In practice, reflection gratings are used. (b) The series of spectral lines known as the Balmer lines in the spectrum of hydrogen.

Empirical fit of observed lines of the hydrogen spectrum:

(several series of approaching lines, see for example the "Balmer series" in the figure)

$$\frac{1}{\lambda} = Ry\left(\frac{1}{n^2} - \frac{1}{m^2}\right)$$

n, m positive integers $(m > n)$

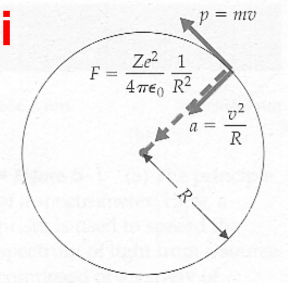
$Ry = 1.09737 \times 10^7\ \mathrm{m}^{-1}$

"Balmer series": $n = 2, m > 2$

Hydrogen atom: Bohr model

- **Assumptions:**
  - **Atoms can only exist in certain "allowed" states, characterized by a well defined energy; any transition in the system, including emission and absorption of radiation, takes place as transitions between these allowed states**
  - **The radiation absorbed or emitted during the transition between two allowed states (energies *E'* and *E"*) has a frequency *f* given by:** $hf = E' - E''$ **(*h* : Planck's constant)**
  - **Some of the allowed states (those corresponding to classical circular orbits) have energies determined by the condition that their angular momentum is quantized as an integral multiple of Planck's constant $\hbar = h/2\pi$, that is:** $L = n\hbar,\ n = 1, 2, \dots$ **(*n* is called a "quantum number" characterizing the system)**
- **These postulates determine the radii and energies of the "allowed circular orbits"**

Hydrogen atom: Bohr radii



• Figure 5–4 Force and acceleration for a circular orbit of radius R in a hydrogenlike atom.

Classical mechanics:

$F = ma$ Newton, II principle

$F = F_{Coul} = \dfrac{q^2}{4\pi\varepsilon_0 r^2}$ from e.m.

$a = \dfrac{v^2}{r}$ from kinematics

$$\Rightarrow \frac{q^2}{4\pi\varepsilon_0 r^2} = \frac{mv^2}{r}$$

Bohr postulate:

$L_n = mvr_n = n\hbar \quad n = 1, 2, 3, \ldots$

Bohr radius:

$$\frac{q^2}{4\pi\varepsilon_0 r_n^2} = \frac{mv^2}{r_n} \qquad v = \frac{n\hbar}{mr_n}$$

$$\Rightarrow r_n = \frac{4\pi\varepsilon_0}{mq^2}(n\hbar)^2$$

$$a_0 \equiv r_1 = \ldots = 0.53\times10^{-10}\ \text{m}$$

Hydrogen atom: Bohr energy levels

Total energy: kinetic + potential

$$K = \frac{1}{2}mv^2 = \frac{1}{2}\left(\frac{q^2}{4\pi\varepsilon_0 r_n}\right)$$

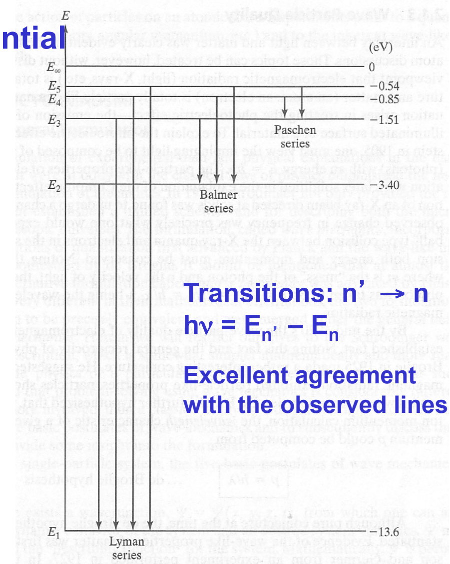
$$V = -\frac{q^2}{4\pi\varepsilon_0 r_n}$$

$$E_n = K + V = -\frac{1}{2}\left(\frac{q^2}{4\pi\varepsilon_0 r_n}\right)$$

$$\left(r_n = \frac{4\pi\varepsilon_0}{mq^2}(n\hbar)^2\right)$$

Quantized energy levels

$$E_n = -\frac{1}{2}\frac{mq^4}{(4\pi\varepsilon_0 n\hbar)^2} = -\frac{13.6}{n^2}\ \text{eV}$$



Transitions: n' → n

$h\nu = E_{n'} - E_n$

Excellent agreement with the observed lines

Extensions?

- Try to apply the same ideas (quantization of angular momentum) to other simple system, for instance:
  - Rotations of diatomic molecules and corresponding spectrum
    - Energy level spacings about 10000 times smaller: OK!
  - Harmonic oscillator
    - Expect levels equally spaced (by $\hbar\omega$): OK!
- Some help from the "Correspondence Principle"
  - The theory should agree with classical physics, in the limit in which quantum effects become unimportant ($h \rightarrow 0$)
  - This helps establishing selection rules for allowed or favored transitions, but…
- Pretty successful, but: more complicated systems and interactions, interference, etc.? Need deeper insight!
  - Quantum mechanics!

Wave mechanics (1 particle)

Guidelines
Basic postulates, Schrödinger equation
Time-Independent Schrödinger equation

Guidelines

- Starting point: experimental observation of wave-like behavior for particles (electrons etc):
  - interference patterns for the probability of observing them after their interactions with crystals, slits etc.
- To describe and explain this behavior, one needs to *postulate*
  - A (complex!) "wave function" associated with each particle
  - Some sort of interpretation linking the wave function (the square of its absolute value) to the probability of observing the particle and its kinematical properties
  - A linear differential equation determining the space-time evolution of the wave function
- No way to *derive* these *postulates* !
  - they are ***assumed*** after some educated guesswork based on analogies (i.e. optics: "physical (wave)" vs "geometrical (ray)" approach);
  - From them one can derive predictions that can be tested experimentally

Wave Mechanics: postulates - 1

"Statics"

(1) There exists a wave-function $\Psi = \Psi(x, y, z, t)$ from which one can obtain the dynamic behavior of the system and all desired system variables

(1) Ψ is a complex quantity, and will be, in general, a function of the space coordinates (x, y, z) and time t

(3) Ψ and [illegible] Ψ must be finite, continuous, and single-valued for all values of x, y, z and t .

(4) If Ψ^* is the complex conjugate of Ψ, then $\Psi^* \Psi dV = |\Psi|^2 dV$ is to be identified with the probability that the particle will be found in the spatial volume element dV .

This implies the normalization condition (integration over all space):

$$\int_V \Psi^* \Psi dV = 1$$

Wave Mechanics: postulates - 2

(5) One can associate a unique mathematical operator α_{op} with each dynamical variable α such as position or momentum; the expectation value $\langle \alpha \rangle$ is computed from:

$$\langle \alpha \rangle = \int_V \Psi^* \alpha_{op} \Psi dV$$

The unique mathematical operator corresponding to a given dynamical variable is established by the Correspondence Principle, requiring the expectation value to approach the corresponding value, obtained from classical mechanics, in the large-mass/high-energy limit. Some examples in the table:

Table 2.1 Dynamic Variable/Operator Correspondence

Dynamic Variable (α)		Mathematical Operator (α_{op})		Expectation Value—$\langle \alpha \rangle$
x, y, z	$\leftrightarrow$	x, y, z	$\cdots$	$\langle x \rangle = \int_{\mathcal{V}} \Psi^* x \Psi d\mathcal{V}$
$f(x, y, z)$	$\leftrightarrow$	$f(x, y, z)$		
p_x, p_y, p_z	$\leftrightarrow$	$\frac{\hbar}{i}\frac{\partial}{\partial x}, \frac{\hbar}{i}\frac{\partial}{\partial y}, \frac{\hbar}{i}\frac{\partial}{\partial z}$	$\cdots$	$\langle p_x \rangle = \int_{\mathcal{V}} \Psi^* \frac{\hbar}{i} \frac{\partial \Psi}{\partial x} d\mathcal{V}$
E	$\leftrightarrow$	$-\frac{\hbar}{i}\frac{\partial}{\partial t}$		

Wave Mechanics: postulates - 3

"dynamics"

(2) The wave-function Ψ for a given system and specified system constraints is determined by solving the "time-dependent Schrödinger equation" or "wave equation":

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

Where *m* is the mass of the particle, *U* the potential energy, and *i* = *√(-1)* the imaginary unit;

Remember also the definition of the *Laplacian operator*:

$$\nabla^2 \equiv \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

Schrödinger equation – comments - 1

Motivations (not proof !) for the complex wave function and for the Schrödinger equation (postulates…)

From experiment: particles ⇔ waves; DeBroglie relations between particles' dynamic variables and wave properties

particle properties — wave properties

$$p = \frac{h}{\lambda} = \frac{h}{2\pi}\frac{2\pi}{\lambda} = \hbar k$$

$$E = h\nu = \frac{h}{2\pi}2\pi\nu = \hbar\omega$$

examples of possible wavefunctions

$(1)\ \cos(kx-\omega t)$

$(2)\ \sin(kx-\omega t)$ — **sinusoidal**

$(3)\ e^{i(kx-\omega t)}$

$(4)\ e^{-i(kx-\omega t)}$ — **exponential**

"good" wavefunctions = ?
"appropriate" differential wave equation = ?

Schrödinger equation – comments - 2

"good" wavefunctions = ?
"appropriate" differential wave equation = ?

Standard wave equation (mechanical, e.m. waves) ?

$$\frac{\partial^2\psi}{\partial t^2} = \gamma\frac{\partial^2\psi}{\partial x^2} \qquad \gamma = v^2 \qquad v:\ \text{propagation velocity}$$

By substitution: wave functions (1), (2), (3), (4) are solutions if:

$$\gamma = \frac{\omega^2}{k^2} = \frac{E^2}{p^2} = \frac{p^2}{4m^2}$$

γ is an explicit function of the dynamical *variables* E, p: *not OK !*

Hint for a different equation: look at the effect of derivatives on w.f. (3) and at the classical energy-momentum relation for a free particle

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

$$\frac{\partial}{\partial t}e^{i(kx-\omega t)} = -i\omega\,e^{i(kx-\omega t)}$$

$$E = \frac{p^2}{2m} \quad \leftrightarrow \quad \hbar\omega = \frac{\hbar^2 k^2}{2m}$$

Suggests a diff. eq. with these derivatives: $\frac{\partial}{\partial t}$ $\frac{\partial^2}{\partial x^2}$

Schrödinger equation – comments - 3

Try this equation: $\frac{\partial \psi}{\partial t} = \gamma \frac{\partial^2 \psi}{\partial x^2}$ **wave functions (1), (2)** ***are not*** **solutions**

wave functions (3) or (4) ***are*** **solutions for an appropriate constant** γ
(but they are not compatible with the same γ **!)**
In particular, wave function (3) is a solution if

$$\gamma = \frac{i\omega}{k^2} = \frac{i\hbar E}{p^2} = \frac{i\hbar}{2m}$$

OK! γ **only contains constants…**

From this choice: Schrödinger equation

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

Schrödinger equation – comments - 4

Generalization to 3-d (free particle):

$$i\hbar \frac{\partial \psi}{\partial t} = -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right)\psi = -\frac{\hbar^2}{2m}\nabla^2 \psi$$

corresponding to: **with:**

$$E = \frac{\vec{p}^2}{2m} \qquad E \rightarrow i\hbar \frac{\partial}{\partial t} \qquad \vec{p} \rightarrow -i\hbar \vec{\nabla}$$

Generalization to an interacting particle:

Classical:

$$E = \frac{\vec{p}^2}{2m} + U(\vec{r},t)$$

Schrödinger:

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

Wave Mechanics postulates - comments

- **General method for solving specific problems**
  - Given a specific potential energy *U(x,y,z)* and boundary conditions, solve Schrödinger's equation (P.2) and find the system wavefunction Ψ compatible with constraints from (P.3) and (P.4)
  - Obtain information on experimental observables using Ψ and prescriptions from (P.5)
  - Only in a few cases a closed form solution for Ψ is possible; a variety of approximate or partial methods have been developed to obtain information in these cases

- **Fundamental differences with respect to classical mechanics**
  - The time evolution of the wavefunction *is* still *deterministic*, but:
  - One can only predict the *probability* of the outcome of measurements on dynamical variables (position, momentum, …), and their *expectation values* ; the classical properties are recovered in the large mass limit.
  - Different dynamical variables are coupled in a way that limits their simultaneous knowledge (for instance, position and momentum…)

Time-independent Schrödinger equation - 1

- **When the particle is subject to a *time-independent* potential energy *U(x,y,z)* , the Schrödinger equation can be solved by "separation of variables", yielding two separate equations and solutions for the space- and time-dependent parts**
  - For simplicity, let's use just one space coordinate x:

$$\boxed{i\hbar\frac{\partial\Psi}{\partial t} = -\frac{\hbar^2}{2m}\nabla^2\Psi + U(x)\Psi \qquad \text{Schrodinger eq.}}$$

$$\Psi(x,t) = \psi(x)T(t) = ?$$

$$i\hbar\psi(x)\frac{\partial T(t)}{\partial t} = T(t)\left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\psi(x) + U(x)\psi(x)\right); \qquad \text{dividing by } \Psi:$$

$$i\hbar\frac{1}{T(t)}\frac{\partial T(t)}{\partial t} = \frac{1}{\psi(x)}\left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\psi(x) + U(x)\psi(x)\right)$$

only possible solution for all values of t and x :

both members separately equal to the same constant E

Time-independent Schrödinger equation - 2

$$i\hbar\frac{1}{T(t)}\frac{\partial T(t)}{\partial t}=E. \quad\Rightarrow\quad i\hbar\frac{\partial T(t)}{\partial t}=ET(t)$$

$$\frac{1}{\psi(x)}\left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\psi(x)+U(x)\psi(x)\right)=E. \quad\Rightarrow\quad \boxed{-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\psi(x)+U(x)\psi(x)=E\psi(x)}$$

"Hamiltonian" operator $\hat{H}\equiv-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}+U(x)$
↔ classical dynamic variable
total energy *K + U*

$T(t)=e^{-iEt/\hbar}$ solution of : $i\hbar\frac{\partial T(t)}{\partial t}=ET(t)$

$\psi(x)=\psi_E(x)$ solution of : $\boxed{\hat{H}\psi_E(x)=E\psi_E(x)}$

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

Prototype of "eigenvalue equation"
***E*: "eigenvalue" ψ_E : "eigenfunction"**

Time-independent Schrödinger equation - 3

What is so interesting about "separable" solutions?
After all, most solutions *do not* take the form $\Psi(x,t)=\psi(x)T(t)$

1. They are *stationary states*

$$|\Psi(x,t)|^2=|\psi(x)|^2$$

The probability density is time-independent!

2. They are states of *definite total energy*

$$\hat{H}\psi_E(x)=E\psi_E(x) \quad\Rightarrow\quad \langle H\rangle=\int\psi_E^*\hat{H}\psi_E dx=\ldots=E$$

$$\sigma_H^2=\langle H^2\rangle-\langle H\rangle^2=0 \quad\Leftarrow\quad \langle H^2\rangle=\int\psi_E^*\hat{H}^2\psi_E dx=\ldots=E^2$$

3. *Every* solution is a *linear combination of separable solutions*

$$\Psi(x,t)=\sum_{n=1}^{\infty}c_n\psi_n(x)e^{-iE_nt/\hbar}$$

Some 1-d examples

Wave-function normalization

Expectation values and "uncertainties"

Free particle?

Confined particle?

Example 2: "particle in a box" – separable solutions

Particle in a 1-d "non-leaking" box (from $x = 0$ to $x = a$): potential energy $U(x)=0$ inside, ∞ outside ⇒ boundary conditions for $\psi(x)$

$$U(x) = 0 \quad 0 < x < a \qquad \boxed{\psi(0) = \psi(a) = 0}$$

$$-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\psi(x) = E\psi(x) \Rightarrow \frac{\partial^2}{\partial x^2}\psi(x) + \frac{2mE}{\hbar^2}\psi(x) = 0$$

$$\Rightarrow \boxed{\frac{d^2\psi}{dx^2} + k^2\psi = 0} \quad \text{with} \quad \boxed{k \equiv \sqrt{2mE/\hbar^2}} \qquad E = \frac{\hbar^2 k^2}{2m}$$

general (separable) solution:

$$\boxed{\psi_n(x) = A\sin(k_n x)} = A\left(e^{ik_n x} - e^{-ik_n x}\right)/2i \qquad \boxed{k_n = n\pi/a \quad E_n = \frac{\hbar^2 k_n^2}{2m}}$$

$$\Psi(x,t) = \psi_n(x)T(t) = \psi_n(x)e^{-iE_n t/\hbar} = A\sin(n\pi x/a)e^{-iE_n t/\hbar}$$

“particle in a box” - comments

- **The solution looks like a “standing wave”:**
  - **superposition of two opposite-going plane waves of equal amplitude**

$$\psi_n(x) = A\sin(k_n x) = A\left(e^{ik_n x} - e^{-ik_n x}\right)/2i \qquad k_n = n\pi/a \quad E_n = \frac{\hbar^2 k_n^2}{2m}$$

$$\Psi(x,t) = \psi_n(x)T(t) = \psi_n(x)e^{-iE_n t/\hbar} = A\sin(n\pi x/a)e^{-iE_n t/\hbar}$$

  - **The boundary conditions force the wave number *k* and energy *E* to only assume discrete values k_n and E_n: they are “quantized”! The minimum kinetic energy E_1 is not zero!**
  - **The magnitude A is determined by the normalization condition (simple exercise…)**

$$\int_0^a |\psi_n(x)|^2\, dx = \int_0^a |A|^2 \sin^2(k_n x)dx = |A|^2 \frac{a}{2} = 1 \quad \Rightarrow \quad |A|^2 = \frac{2}{a}$$

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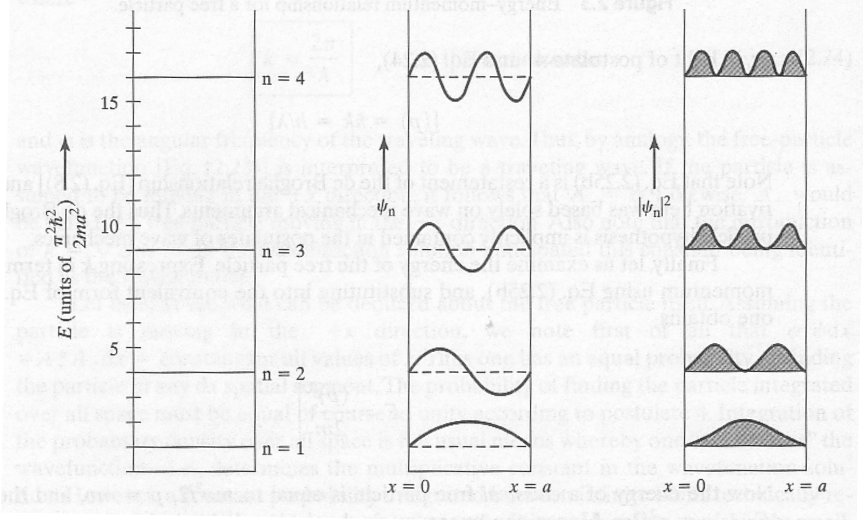
“particle in a box”: energy quantization

Energy “eigenvalues” | Wavefunctions (eigenfunctions) | Corresponding probability distributions



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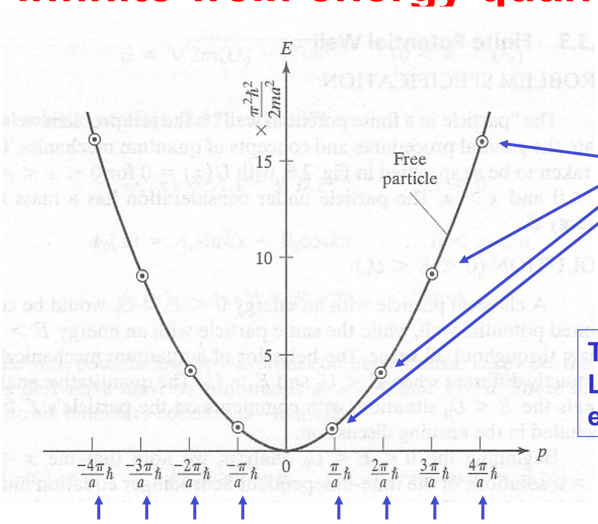
Infinite well: energy quantization



Energy "eigenvalues"

$$E_n = \frac{\pi^2 \hbar^2}{2ma^2} n^2$$

To understand better, Let's compute some expectation values !

$$p_n = \hbar k_n = \pm \hbar n \frac{\pi}{a} \quad (n = 1, 2, 3, \ldots)$$

? What are these exactly ?

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Expectation values and uncertainties - 1

- We found the energy "eigenfunctions" and "eigenvalues": what happens if the particle state is described by such an eigenfunction?

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

$$\psi_n(x) = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi}{a}x\right) \qquad E_n = \frac{\pi^2 \hbar^2}{2ma^2} n^2$$

- Rather easy to compute: energy "expectation values" and "uncertainty"

$$\langle \hat{H} \rangle = \int_0^a \Psi_n^* \left(\hat{H} \Psi_n \right) dx = \int_0^a \Psi_n^* \left(E_n \Psi_n \right) dx = E_n$$

$$\langle \hat{H}^2 \rangle = \int_0^a \Psi_n^* \left(\hat{H} \left(\hat{H} \Psi_n \right) \right) dx = \int_0^a \Psi_n^* \left(E_n^2 \Psi_n \right) dx = E_n^2$$

- No uncertainty! E_n is "certain"

$$\sigma_H^2 = \langle \hat{H}^2 \rangle - \langle \hat{H} \rangle^2 = E_n^2 - E_n^2 = 0$$

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Expectation values and uncertainties - 2

- What about momentum, in the same state? compute similarly the momentum "expectation values" and "uncertainty"
- Result: the uncertainty on p_x is not zero!
- We should have expected it: superposition of two plane wave states, with opposite momenta: a measurement can give one of two opposite values for p_x

$$\langle \hat{p}_x \rangle = \int_0^a \Psi_n^* \left(\hat{p}_x \Psi_n \right) dx = \int_0^a \Psi_n^* \left(-i\hbar \frac{\partial}{\partial x} \Psi_n \right) dx =$$
$$= \frac{2}{a} \left(-i\hbar \frac{n\pi}{a} \right) \int_0^a \sin\left(\frac{n\pi}{a} x \right) \cos\left(\frac{n\pi}{a} x \right) dx =$$
$$= 0$$

$$\langle \hat{p}_x^2 \rangle = \int_0^a \Psi_n^* \left(\hat{p}_x \left(\hat{p}_x \Psi_n \right) \right) dx = \ldots$$
$$= \frac{\pi^2 \hbar^2 n^2}{a^2} = 2mE_n = 2m \langle \hat{H} \rangle \neq 0$$
$$\sigma_{p_x}^2 = \langle \hat{p}_x^2 \rangle - \langle \hat{p}_x \rangle^2 = \frac{\pi^2 \hbar^2 n^2}{a^2} \neq 0$$

"Standing wave" and other solutions - 1

- For a given *n*, the corresponding standing wave solution Ψ_n
  - Corresponds to a "certain", well defined value of energy E_n, since it is an eigenfunction of the energy operator
  - Has also a well defined
    - absolute value of momentum $| p_x |$
    - square of momentum p_x^2
  - But the momentum p_x is "uncertain": we understand this! This happens because the "standing waves" are not eigenfunctions of the operator corresponding to p_x, but rather superpositions of two plane waves with opposite values of p_x
- Can the particle be in other states, described by different wave functions? What happens of energy in these cases? Can one generalize?

"Standing wave" and other solutions - 1

- **Can the particle be in other (non-standing wave) states, described by different wave functions? Yes!**
  - Any normalized linear combination of solutions is still a solution of the time-dependent Schrödinger equation,
  - even if it will no longer be a solution of the time-independent equation… For instance, a specific case:

Two standing waves (*n* = *1* (ground state), and *n* = *2*)

$$\psi_1(x)=\sqrt{\frac{2}{a}}\sin\left(\frac{\pi}{a}x\right)\qquad \psi_2(x)=\sqrt{\frac{2}{a}}\sin\left(\frac{2\pi}{a}x\right)$$

Superposition (coefficients c_1 = c_2 = *1/sqrt(2)*)

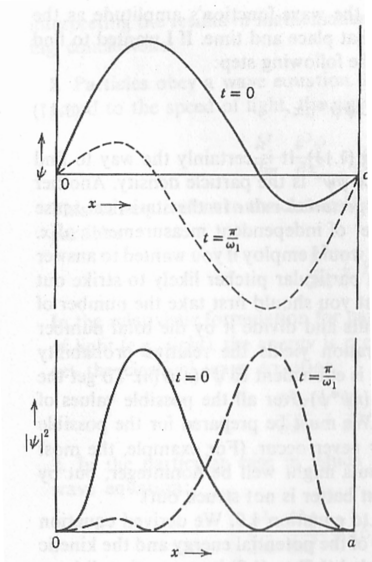
$$\Psi(x,t)=\sqrt{\frac{1}{a}}\sin\left(\frac{\pi}{a}x\right)e^{-i\left(\pi^2\hbar/2ma^2\right)t}+\sqrt{\frac{1}{a}}\sin\left(\frac{2\pi}{a}x\right)e^{-i\left(4\pi^2\hbar/2ma^2\right)t}$$

ω_1 $\qquad$ $\omega_2 = 4\omega_1$

"Standing wave" and other solutions - 2

Playing with these "combined" solutions, one can see that:

- Energy is no longer "certain"
- The expectation values and "uncertainties" in position and momentum change
- One can build solutions "bouncing back and forth between the two walls", etc.
- See here the wave function defined in the previous page and its square at two different times
- We can compute expectation values at different times and follow their evolution…



"particle in a box" - comments

- **Some interesting properties of the separable solutions:**
  1. **Alternative even and odd with respect to the center of the box**
  2. **Going up in energy, every successive wave function has one more "node" (zero crossing) inside the box**
  3. **They are mutually *"orthogonal"***

$$\int \psi_m(x)^* \psi_n(x)dx = 0 \quad \text{for} \quad m \neq n$$

  4. **They are *"complete"* (Fourier series, Dirichlet's theorem)**

$$f(x) = \sum_{n=1}^{\infty} c_n \psi_n(x) = \sqrt{\frac{2}{a}} \sum_{n=1}^{\infty} c_n \sin\left(\frac{n\pi}{a}x\right)$$

$$c_n = \int \psi_n(x)^* f(x)dx$$

"particle in a box" - comments

- **Trick to compute the time evolution of an arbitrary wave function in the box, known at time *t = 0*:**
  - **Compute expansion coefficients c_n at *t=0***
  - **Express the evolved wave function at later time, as superposition of stationary states (separable solutions) with the above computed coefficients and the appropriate time factors**

$$\Psi(x,0) \quad \Rightarrow \quad c_n = \sqrt{\frac{2}{a}} \int_0^a \sin\left(\frac{n\pi}{a}x\right) \Psi(x,0)dx$$

$$\Psi(x,t) = \sum_{n=1}^{\infty} c_n \psi_n(x) e^{-iE_n t/\hbar} = \sum_{n=1}^{\infty} c_n \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi}{a}x\right) e^{-i\left(n^2\pi^2\hbar/2ma^2\right)t}$$

Wave mechanics: outlook - 1

- One can progress a lot using this formulation of wave mechanics, for instance:
  - Give rational explanation and predictions for "self-interference" effects (diffraction etc) and for Uncertainty Relations (see wave packets etc)
  - Solve interesting problems with a single electron subject to 1- or 3-dimensional potentials V(x,y,z) (for instance: 1-d potential barriers; hydrogen atom, using an electrostatic Coulomb potential)
  - Extend the study of dynamical variables to angular momentum!
  - Introduce approximate methods (perturbation theory); with spin and magnetic moment, understand fine and hyperfine spectroscopy including interactions with magnetic fields
  - Extend the treatment to multi-particle systems (multi-electron atoms, molecules, etc.)
  - Etc…
- We will explore some of these applications, but…

Wave mechanics: outlook - 2

- Great success, but still many unanswered questions:
  - We started from photons: what about them? What is their "wavefunction": the e.m. field? What is their "Schrödinger's equation": is it somehow derived from Maxwell's equations?
  - Full theory of photoelectric effect, Compton, electron-positron pair creation, etc?
  - Photons are intrinsically relativistic, Schrödinger's equation is not!
  - Photons can be created (emitted) and destroyed (absorbed): even in its multi-particle version, the wave function we introduced describes a fixed number of particles
  - Spin can be included in Schrödinger's equation, that however remains intrinsically non-relativistic: it cannot described effects observed at high speed and energies: experimentally we know that also particles like the electron can be "created" or "destroyed"! How can we account for this?

The Big Picture (just a hint!)

What is missing?
Quantum Mechanics, General Postulates
Second Quantization

What is missing?

- A more *general formulation* of quantum mechanics helps understanding the roles of wave-functions and observables, and tackling complicated problems, even in the non-relativistic domain
- *Special relativity* must be included: this brings to a deep re-formulation ("second quantization") in which the *e.m. field* (for photons) and *wave-functions* (for the other particles), *obeying* appropriate *"field-equations"* are re-interpreted in terms of operators that can create or destroy quanta of the relevant fields, similarly to what happens in the quantum mechanical treatment of the harmonic oscillator.

Quantum Mechanics: general postulates

- (See for instance D.J.Griffiths, chapter 3, or Schaum's Outline, chapters 2 and 4, or A.Sudbery, chapters 2 and 3);
- Main ingredients:
  - "statics":
    - From "wavefunctions" to "state vectors" (abstract "state space")
    - Measurable physical quantities correspond to "hermitian operators", and possible measurements to their "eigenvalues"
    - Prescriptions for the probability of observing an "eigenvalue", and for the effect of measurements, forcing state vectors into "eigenvectors"
    - (representations of state vectors and operators; uncertainty relations for non-commuting operators)
  - "dynamics":
    - Time evolution of state vectors (Schrödinger's equation), governed by the Hamiltonian operator
    - Equivalence of "Schrödinger" and "Heisenberg" pictures of time evolution
- Need Perturbation Theory or other approximate methods to extract useful answers!

Quantum Field Theory (2nd quantization)

- Relativistic field equations
  - photons: Maxwell's equations (4-potential formulation, explicitly relativistic); other particles: equations corresponding to classical relations involving relativistic energy; all particles are "quanta" of their fields
  - Interactions between different fields (particles): from "symmetry principles"
- Quantization prescriptions, fields become operators
  - "canonical quantization", commutation relations involving field operators
  - "path integrals": an alternative equivalent formulation
- Fields: annihilation and creation operators
  - Acting on "state vectors" of a generalized "state space", admitting a variable number of particles
- Perturbation theory to make quantitative predictions
  - QED: interactions of electrons, positrons and photons…
  - "Standard Model" includes strong and weak interactions
- Too much for an introductory course...

Lectures 10-11 - summary

- **We discussed the postulates of Wave Mechanics for a single particle, and the limitations of this theory**
- **We will stick to it, investigating mainly 1-d problems and then moving on to the study of the behavior of electrons in crystals (approximated by static periodic potentials)**
- **Next lectures:**
  - **Realistic free particle, partially localized in space: wave packet, uncertainty relations**
  - **Effect of potential wells and barriers; tunneling**
  - **Eigenvalues and eigenfunctions of dynamical observables**

Lectures 10-11 - exercises

- **Exercise 10.1:** The attractive gravitational force between an electron and a proton is Gm_pm_e/r^2, where $m_e=0.9\text{x}10^{-30}$ kg, $m_p=1.67\text{x}10\text{-}27$ kg, and $G=6.67\text{x}10^{-11}$ m^3/kg.s^2. What is the lowest Bohr gravitational radius?
- **Exercise 10.2:** Suppose that an hydrogen atom in its ground state absorbs a photon whose wavelength is 15 nm. Will the atom be ionized? If so, what will be the kinetic energy of the electron when it gets far away from its atom of origin?
- **Exercise 10.3:** The muon, with mass $m_\mu=209m_e$, acts as a heavy electron, and can bind to a proton forming a “muonic atom”. Calculate the ionization energy of this atom in its ground state, ignoring reduced-mass effects.
- **Exercise 10.4:** Consider the time-independent wave-function $C\exp(-x^2/2a^2)$. Determine the normalization constant C. Calculate the expectation values $\langle x\rangle$, $\langle x^2\rangle$, $\langle p\rangle$,$\langle p^2\rangle$ for this wave-function, evaluate the corresponding “uncertainties” (uncertainty^2 ≡ variance)

Back-up slides

Expectation values, examples
Uncertainties
Free particle?

Wavefunction normalization: an example

- Normalization of a given wavefunction (P.4):

Example 6–2 Consider the pulselike wave function $\psi(x) = A\exp(-x^2/2a^2)$, where a is a constant with the dimensions of length. What value of A is needed to normalize this wave function?

Solution The constant A is determined by the requirement that

$$1 = \int_{-\infty}^{+\infty} |\psi(x)|^2\, dx = A^2 \int_{-\infty}^{+\infty} \exp\left(\frac{-x^2}{a^2}\right) dx.$$

The integral is a standard integral found in Appendix B.2:

$$\int_{-\infty}^{+\infty} \exp\left(\frac{-x^2}{a^2}\right) dx = a\sqrt{\pi}.$$

With this result, our first equation reads

$$1 = A^2 a(\pi)^{1/2},$$

an equation easily solved for A:

$$A = (a)^{-1/2}(\pi)^{-1/4}.$$

normalized Gaussian
centered at x = 0
standard deviation
σ = a
independent of time

Expectation value, an example: $\langle p_x \rangle$

- **Expectation value for a dynamical variable (P.5):**

Example 6–3 Calculate $\langle p \rangle$, $\langle p^2 \rangle$, and $\langle p^3 \rangle$ for the normalized wave function of Example 6–2. (Such quantities are the legitimate aim of experimental measurement, because a full set of expectation values for a physical system contains all the information about the system.)

Solution Let us start with $\langle p \rangle$, which for this wave function is given by

$$\langle p \rangle = A^2 \int_{-\infty}^{+\infty} \exp\left(\frac{-x^2}{2a^2}\right)\left(-i\hbar\frac{\partial}{\partial x}\right)\exp\left(\frac{-x^2}{2a^2}\right) dx$$

$$= \left(\frac{i\hbar A^2}{a^2}\right)\int_{-\infty}^{\infty} \exp\left(\frac{-x^2}{2a^2}\right) x \exp\left(\frac{-x^2}{2a^2}\right) dx$$

$$= \left(\frac{i\hbar A^2}{a^2}\right)\int_{-\infty}^{\infty} x \exp\left(\frac{-x^2}{a^2}\right) dx.$$

$< p_x > = 0$

This formula looks like it might give a complex number. In general, that would be very troublesome, since we expect the average value of the momentum to be real. The momentum is an observable quantity, and its expectation value should be a real number.

Expectation value, another example: $\langle p_x^2 \rangle$

But we are saved from this embarrassment by the nature of the integrand. Taken as a whole, the integrand, say $f(x)$, has the property that it is odd about the origin—that is, that $f(-x) = -f(x)$. This means that, as we are integrating from minus infinity to infinity, the total integral will be zero: The integration from minus infinity to zero will cancel against the integration from zero to infinity, and $\langle p \rangle = 0$. Exactly the same argument will work for $\langle p^3 \rangle$.

For $\langle p^2 \rangle$, we must take two powers of the quantity in Eq. (6–28), and the result is real. Using

$$\frac{\partial^2}{\partial x^2}\exp\left(\frac{-x^2}{2a^2}\right) = \left(\frac{x^2}{a^4} - \frac{1}{a^2}\right)\exp\left(\frac{-x^2}{2a^2}\right),$$

we see that we have an integrand, which we may call $g(x)$, that is even; that is, $g(x) = +g(-x)$. Thus we can integrate from zero to infinity and simply double the answer:

$$\langle p^2 \rangle = 2(-i\hbar)^2 A^2 \int_0^{\infty}\left(\frac{x^2}{a^4} - \frac{1}{a^2}\right)\exp\left(\frac{-x^2}{a^2}\right) dx.$$

We reduce the integral in this equation to a standard integral by the substitution $y = x/a$, so that

$$\langle p^2 \rangle = 2\hbar^2 A^2 \frac{1}{a}\int_0^{\infty}(1 - y^2)\exp(-y^2)\, dy = \frac{\hbar^2}{2a^2}.$$

$< p_x^2 > = \hbar^2/2a^2$

In the last step, we used Appendix B.2 for the standard integrals and also substituted for A^2, the quantity we calculated in Example 6–2.

Note that since a is the only length in the problem, we would expect, on purely dimensional grounds, that the magnitude of p^2 is proportional to $(\hbar/a)^2$.

Intrinsic "uncertainties" of x and p_x?

- "dispersion" or "uncertainty" of a variable α, characterized by a probability distribution?
  - From statistics: the "uncertainty" can be described computing the variance (square of "standard deviation"), defined as:

$$\sigma_\alpha^2 \equiv \left\langle \left(\alpha - \langle\alpha\rangle\right)^2 \right\rangle = \langle\alpha^2\rangle - \langle\alpha\rangle^2$$

- In our previous example, starting from the given wave-function:

$$\sigma_x \equiv \sqrt{\langle x^2\rangle - \langle x\rangle^2} = a$$

$$\sigma_{p_x} \equiv \sqrt{\langle p_x^2\rangle - \langle p_x\rangle^2} = \sqrt{\frac{\hbar^2}{2a^2} - 0} = \frac{\hbar}{\sqrt{2}a}$$

  - The expected "dispersions" of results in measurements of x and p_x are correlated and inversely proportional, through $\hbar$!

Example 1: "free particle" – general solution

Free particle (constant potential energy $U(x) = 0$): the simplest possible case? Not really! Surprisingly subtle and tricky…
(see also: R.F.Pierret, Advanced Semiconductor Fundamentals, section 2.3.1, p. 33-35; J.Bernstein et al., Modern Physics, section 7.1, p.177-179; D.Griffiths, Introduction to QM, section 2.4)

$$\text{free particle: constant potential} \quad V(x) = 0. \quad \Rightarrow$$

$$-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\psi(x) = E\psi(x) \quad \Rightarrow \quad \frac{\partial^2}{\partial x^2}\psi(x) + \frac{2mE}{\hbar^2}\psi(x) = 0$$

$$\Rightarrow \boxed{\frac{d^2\psi}{dx^2} + k^2\psi = 0} \quad \text{with} \quad \boxed{k \equiv \sqrt{2mE/\hbar^2}} \qquad E = \frac{\hbar^2 k^2}{2m}$$

$$\text{general (separable) solution:}$$

$$\boxed{\psi(x) = A_+ e^{ikx} + A_- e^{-ikx}}$$

$$\Psi(x,t) = \psi(x)T(t) = \psi(x)e^{-iEt/\hbar} = A_+ e^{i(kx - Et/\hbar)} + A_- e^{-i(kx + Et/\hbar)}$$

Example 1: "free particle" – plane wave ?

- The general solution looks like a superposition of two "plane waves" propagating in opposite directions; all energy values *E* are allowed!

general (separable) solution:

$$\Psi(x,t) = \psi(x)T(t) = \psi(x)e^{-iEt/\hbar} = A_+e^{i(kx-Et/\hbar)} + A_-e^{-i(kx+Et/\hbar)}$$

- In the next lecture:
  - Normalization ?
  - Interpretation: wave number, angular frequency, phase velocity?
  - Momentum expectation value?
  - Energy expectation value?
  - Is it really a satisfactory "free particle" state? Wave packets!

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