

ECE 162A
Mat 162A

Lecture #4: Schroedinger Theory of
Quantum Mechanics
Read Chapter 5 of Eisberg, Resnick

Principle of Complementarity

- Neils Bohr: The wave and particle models are complementary; if a measurement proves the wave character of radiation or matter, then it is impossible to prove the particle character in the same experiment.
- Which model is used (wave or particle) is determined by the experiment.

Particle/Wave Duality

- All material objects show both particle and wave aspects.
 - $E=h\nu$
 - $P=h/\lambda$
- The uncertainty principle means that an experiment to determine particle aspects (for example position) means that momentum is unknown (i.e. wavelength is unknown) and vice versa.

Rutherford Scattering

- Rutherford, a former student of Thompson, tested this theory by scattering experiments of alpha particles (He^{++}) on thin foils of metal.
- **Most alpha particles showed small angle scattering. A few showed large angle scattering.**
- An alpha particle is 10,000 times heavier than an electron.
- This is analogous to firing a “15 inch shell at a piece of tissue paper and it came back and hit you.” –Rutherford.

How is this possible?

Think about pool.

There must be particles of similar mass to He^{++}

Rutherford Model

- Rutherford proposed that all of the positive charge and essentially all of the mass were concentrated on a small region in the center called the nucleus.
- Most scattering is electron-alpha scattering (small angle).
- Occasionally, an alpha particle scatters off a nucleus giving a large angle (pool ball like) scattering.

Solution: Niels Bohr

- Bohr Postulates:
- Electrons move in a circular orbit obeying the laws of classical mechanics: $F=ma$ or

$$1/(4\pi\epsilon_0) Ze^2/r^2 = m v^2/r$$

- The only orbits allowed are the ones where its orbital angular momentum L is an integral multiple of \hbar :

$$mrv = n\hbar$$

- An electron in an allowed orbit does not radiate.
- An electron can absorb or emit photons with energy $E=h\nu$ and energy is conserved $E_i - E_f = h\nu$
- Result: $E = E_0/n^2$
- So $k = 1/\lambda = \nu/c = (E_i - E_f)/(hc) = R_H/(hc) (1/p^2 - 1/n^2)$ where p is the number of the initial state and n is the number of the final state.

Fine structure splitting

When the spectral lines of the hydrogen spectrum are examined at very high resolution, they are found to be closely-spaced doublets. This splitting is called fine structure (and was one of the first experimental evidences for electron spin).

How to explain with Bohr theory?

Sommerfeld's model:
Attempt to explain using elliptical orbits. . Treat relativistically.

However, dashed lines don't appear experimentally. Why?
Selection rules....

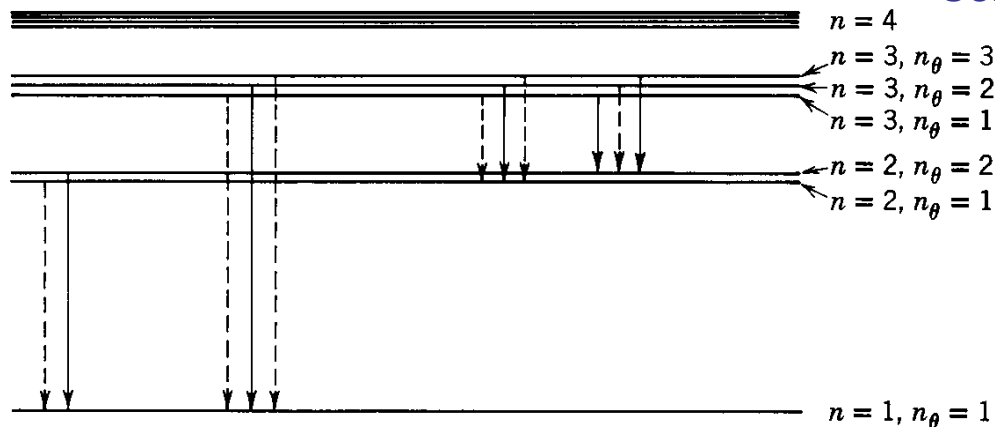
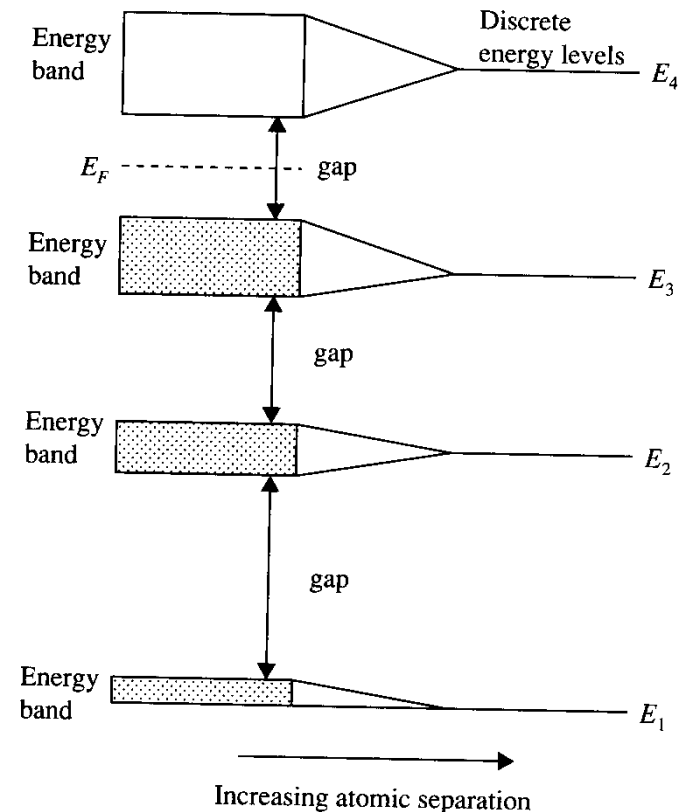


Figure 4-19 The fine-structure splitting of some energy levels of the hydrogen atom. The splitting is greatly exaggerated. Transitions which produce observed lines of the hydrogen spectrum are indicated by solid arrows.

Origin of Semiconductor Bandgap

- The discrete energy states of electrons in an atom are broadened from the individual atom states into energy bands as the atoms are brought closer together to form a crystal.
- When the bandgap energy is on the order of 2eV, room temperature thermal energy can break covalent bonds and accelerate ionized electrons into empty states in the crystal where they can conduct electrically -> Semiconductors



Old (Bohr Model)

Quantum Theory Problems

- It only works for one electron systems:
 - Hydrogen, alkali elements
 - It fails for He, and most other elements.
 - It allows the calculation of energies, but not of rates of transition.
- It is intellectually unsatisfying; why is momentum quantized? Why don't electrons radiate?

Schroedinger's Equation (1926)

$$-\frac{\hbar^2}{2m} \frac{\partial^2 \psi(x,t)}{\partial x^2} + \underbrace{V(x,t)}_{\text{Potential environment that particle or wave is traveling in}} \psi(x,t) = i\hbar \underbrace{\frac{\partial \psi(x,t)}{\partial t}}_{\text{Rate of change of time development along spatial path for particle or wave}}$$

Equivalent to gradient of particle in spatial dimension
Time development and spatial path for particle or wave

- Plausible?
- Classical equation of motion:
 - Kinetic energy + Potential energy = Total energy
 - Kinetic energy:

$$\frac{1}{2} mv^2 = p^2/2m = h^2/(2m \lambda^2) = \hbar^2 k^2 / (2m)$$

Free particle

($V=0$: No landscape change)

- Schroedinger's equation:

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

- Possible Solutions?

- Sin or cosine alone do not work:

$$\psi(x,t) = A \exp(i(kx - \omega t))$$

- Exponential does work:

$$\frac{\hbar^2 k^2}{2m} = \hbar \omega$$

$$\frac{\hbar^2 k^2}{2m} = E$$

Schroedinger's equation is linear

- No terms in ψ^2 (except in voltage term)
- Hence, if ψ_1 and ψ_2 are solutions, then
- $\psi = a\psi_1 + b\psi_2$ is a solution (Linear principle of differential equations)

Schroedinger's equation is in the nonrelativistic limit.

- Instead of

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

Use (following Dirac) to suggest the form of the equation:

$$E = \sqrt{c^2 p^2 + (m_0 c^2)^2}$$

Probability of finding a particle at a location x at time t

- If, at instant t , a measurement is made to locate the particle associated with the wave function $\psi(x,t)$, then the probability that the particle will be found at a coordinate between x and $x+dx$ is

$$\psi(x,t) \psi^*(x,t)dx$$

Where * means complex conjugate.

- It does not tell us that a particle in a given energy state will be found in a ***precise location at a certain time***, but only the ***relative probabilities that the particle will be found in various locations at that time***.
- ***The prediction is statistical!***

Classical Problem Solution

- Solve a differential equation (wave equation, heat equation, etc.). Determine eigenfunctions (valid solutions): $\psi_i(x, t, \dots)$
- Apply boundary conditions (determined by the landscape V and physics of wavefunction) and determine solutions (eigenvalues): E_i
- The complete solution is the sum of all wave functions (solutions) weighted by their probability of occurrence (A)

$$\psi(x, t) = \sum_i A_i \psi_i(x, t)$$

- Apply initial condition to determine the coefficients. A_i
- Then SE tells us how the particle/wave will behave exactly for ***all time!***

Quantum Mechanical Problem Solution

- Solve Schroedinger's equation. Determine eigenfunctions. $\psi_i(x,t,\dots)$. Normalize eigenfunctions.
 - Why do we normalize? Because the probability of the particle/wave being somewhere must be 1!
- Apply boundary conditions and determine solutions (eigenvalues): E_i
- The complete solution is

$$\psi(x,t) = \sum A_i \psi_i(x,t)$$

- Apply initial condition to determine the coefficients. A_i
- The instantaneous **state** of the system is exactly known for all time, but **particle positions** are only determined by measurement and the average of **many** measurements is given by (Note this average is the same as the interference pattern)

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

The probability is real and positive:

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

$\psi(x, t) = R(x, t) + iI(x, t)$ where R and I are real

so

$$|\psi(x, t)|^2 = (R + iI)(R - iI) = R^2 + I^2 \geq 0$$

Normalize eigenfunctions

$$\int_{-\infty}^{\infty} P dx = 1$$

$$\int_{-\infty}^{\infty} \Psi^* \Psi dx = 1$$

$$\Psi = \sum_i A_i \psi_i$$

Normalize

$$\int_{-\infty}^{\infty} \psi_i^* \psi_i dx = 1$$

The solutions are orthogonal
(Orthonormal)

$$\int_{-\infty}^{\infty} \psi_i^* \psi_j dx = 0 \quad \text{if } i \neq j$$

If the wavefunctions are normalized

$$\int_{-\infty}^{\infty} \psi_i^* \psi_j dx = \delta_{ij}$$

where

$$\delta_{ij} = 1 \quad \text{if } i = j$$

$$0 \quad \text{if } i \neq j$$

Why Orthonormal Eigenfunctions ? Because the probability weights A_i are unique for each wave function and not cross coupled only for orthonormal functions

Expectation Values

- We may not know the position without making a measurement, but we can calculate the **average value** for the position (the expectation value).

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

$$\bar{x} = \int_{-\infty}^{\infty} \Psi^*(x, t)x\Psi dx$$

- This is true for **any variable: e.g. energy, momentum, ...**
- The order doesn't matter here, but will later when we calculate the expectation value of operators.

Operators

- Use operators to represent mathematical operations. For example:

- Momentum and Energy $p \leftrightarrow -i\hbar \frac{\partial}{\partial x}$

$$E \leftrightarrow i\hbar \frac{\partial}{\partial t}$$

- Note that $p^2 \leftrightarrow -\hbar^2 \frac{\partial^2}{\partial x^2}$

- So Schroedinger's equation becomes in operator form

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

Momentum Expectation Value

$$\overline{p} = \int \Psi^* p \Psi dx$$

The expectation value for the dynamic quantity $f(x,p,t)$ is

$$\overline{f(x,p,t)} = \int_{-\infty}^{\infty} dx \Psi^* f\left(x, -i\hbar \frac{\partial}{\partial x}, t\right) \Psi$$

Note: The wave function contains information not just on the probability density versus time, but also the momentum, energy, or $f(x,p,t)$

Solve Time Dependent Schroedinger Equation when $V(x)$ is a function of x only

Try separation of variables: LHS is a function of x only and RHS is a function of t only, so both sides must equal a constant.

$$\Psi(x, t) = \psi(x)\varphi(t)$$

$$-\frac{\hbar^2 \varphi(t)}{2m} \frac{d^2 \psi(x)}{dx^2} + V(x)\psi(x)\varphi(t) = -i\hbar \psi(x) \frac{d\varphi(t)}{dt}$$

$$-\frac{\hbar^2}{2m\psi} \frac{d^2 \psi(x)}{dx^2} + V(x) = \frac{-i\hbar}{\varphi(t)} \frac{d\varphi(t)}{dt}$$

Time
Independent
Schroedinger
Equation

$$\left\{ \begin{array}{l} -\frac{\hbar^2}{2m\psi} \frac{d^2 \psi(x)}{dx^2} + V(x) = \frac{-i\hbar}{\varphi(t)} \frac{d\varphi(t)}{dt} = E \\ -\frac{\hbar^2}{2m} \frac{d^2 \psi(x)}{dx^2} + V(x)\psi(x) = E\psi(x) \end{array} \right.$$

Time Independent Schroedinger Equation

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

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

Requirements on Solution

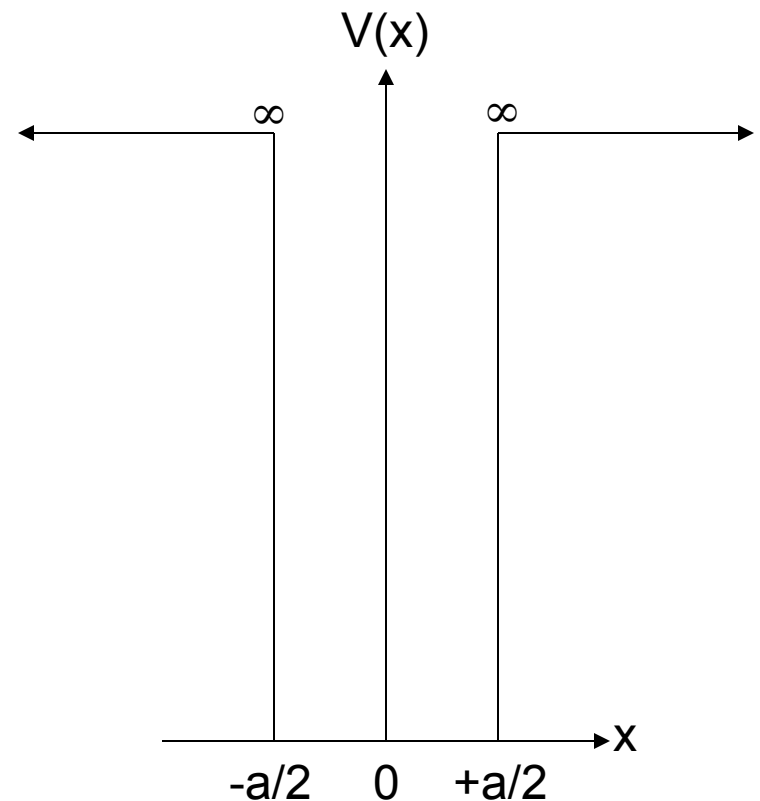
- $\psi(\mathbf{x})$, $\psi(\mathbf{x})'$ must be finite.
- $\psi(\mathbf{x})$, $\psi(\mathbf{x})'$ must be single valued.
- $\psi(\mathbf{x})$, $\psi(\mathbf{x})'$ must be continuous.

Problem

- Consider a particle in an infinite box

$$V = 0 \text{ for } |x| < a/2$$

$$V = \infty \text{ for } |x| > a/2$$



Summary

- Define: orthogonal, orthonormal, eigenvalue, eigenfunction, operator, expectation value
- Describe separation of variables,
- Describe uncertainty principle, principle of complementarity.
- Show that $|\psi(x, t)|^2$ is real and positive
- $|\psi(x, t)|^2 dx$ is the probability of finding a particle between x and $x+dx$.

- Homework #2 due next Tuesday