

# Notes for Physics 137A: Quantum Mechanics

## UC Berkeley Fall 2019

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**Physics 137A: Quantum Mechanics****Fall 2019****Lecture 1: Introduction***Lecturer: Irfan Siddiqi**29 August**Aditya Sengupta*

**Note:** *LaTeX* format adapted from template for lecture notes from CS 267, Applications of Parallel Computing, UC Berkeley EECS department.

## 1.1 Small Stuff is Hard to Figure Out

Quantum mechanics came about because classical mechanics stopped working. Around 1900, physicists were super happy because electricity and magnetism were unified; mechanics seemed to make sense; and statistical mechanics existed as a nice theory to explain thermodynamics. However, there were some unresolved problems.

In 1792, Wedgwood discovered that the emitted colour of a heated substance depends only on the temperature to which it is heated. Based on this, Kirchoff came up with a theory of blackbody radiation, which gave us a theoretical infinite energy density which didn't make sense. Blackbody radiation from a solid is continuous, whereas atomic emission from a gas yielded discrete line spectra.

This led to some problems with the classical model of an atom, in which an electron orbited a nucleus; if an oscillating electron creates light, then it also carries away energy which has to come from the orbital energy of the electron. This would cause the orbit of an electron to decay and crash into the nucleus. Quantum mechanics arose from wanting to resolve this.

## 1.2 Blackbodies

Consider a blackbody held at a certain temperature. This blackbody emits light. The energy for this emission comes from thermal energy. In the early 1900s, scientists figured out how to characterize the light in terms of emitted power per unit area,  $R(\lambda, T)$ .  $R$  over  $\lambda$  is usually an askew bell curve (add in tikzpicture). The area under that curve represents the total power, which we intuitively see is finite. Experimentally, astronomers found that this energy goes as  $T^4$ ,

$$R(T) = \int_0^{\infty} R(\lambda, T) d\lambda = \sigma T^4 \quad (1.1)$$

where  $\sigma = 5.67 \times 10^{-8} \frac{\text{W}}{\text{m}^2 \text{K}^4}$ .

We also see from the graph that there is a wavelength at which the energy peaks, which gives us Wien's law,

$$\lambda_{\max} T = 2.898 \times 10^{-3} \text{m} \cdot \text{K} \quad (1.2)$$

and the slope of the curve in the high- $\lambda$  region gives us the classical formulation in Rayleigh-Jeans' law,

$$R(\lambda, T) = \frac{8\pi k_B T}{\lambda^4} \quad (1.3)$$

This theory caused an unbounded amount of energy at low wavelengths, which was considered unphysical. To resolve this, we turn to (what else) harmonic oscillators. Consider a cube containing a network of harmonic oscillators and a slit for light to come out. The blackbody approximation states that this system is at equilibrium, for all frequencies.

The total power scales as the number of oscillation modes multiplied by the energy of each of the modes.

### 1.3 Standing Waves

All the oscillation modes are solutions to the wave equation. The classical wave equation is

$$\nabla^2 \psi(\vec{r}, t) = \frac{1}{c^2} \frac{\partial^2}{\partial t^2} \psi(\vec{r}, t) \quad (1.4)$$

$\psi$  is the thing that oscillates, that's the technical term. Solving this differential equation requires boundary conditions. Suppose the blackbody is a cube with side  $L$ ; then, the boundary conditions are

$$\psi(x=0, y, z, t) = \psi(x=L, y, z, t) = 0 \quad (1.5)$$

and the same along  $y$  and  $z$ . One possible solution to this is a sine wave,

$$\psi(\vec{r}, t) = A(t) \sin(k_1 x) \sin(k_2 y) \sin(k_3 z) \quad (1.6)$$

where  $k_i = \frac{n_i \pi}{L}$ . This is an ansatz, from which we can get further constraints on the coefficients by substituting into the wave equation.

$$-(n_1^2 + n_2^2 + n_3^2) \frac{\pi^2}{L^2} A(t) B(x, y, z) = \frac{1}{c^2} B(x, y, z) \frac{\partial^2}{\partial t^2} A(t) \quad (1.7)$$

As another ansatz, set  $A(t) = A_0 \cos(\omega t) + \varphi$ . Then, we get

$$\omega^2 = \frac{c^2 \pi^2}{L^2} (n_1^2 + n_2^2 + n_3^2) \quad (1.8)$$

To count the number of modes, we integrate over a density function (number of modes per frequency)  $g$ ,

$$N(\omega) = \int_0^\omega g(\omega') d\omega' \quad (1.9)$$

Intuitively, we want to find all the  $n_1, n_2, n_3$  that satisfy

$$n_1^2 + n_2^2 + n_3^2 \leq \frac{\omega^2 L^2}{c^2 \pi^2} \quad (1.10)$$

which is a phase-space sphere. Therefore, the solution corresponds to the volume of a sphere,

$$N(\omega) = \frac{1}{8} \left( \frac{4}{3} \pi \frac{\omega^3 L^3}{c^3 \pi^3} \right) = \frac{\omega^3 V}{6c^3 \pi^2} \quad (1.11)$$

Then, by the fundamental theorem of calculus, we can recover  $g$ ,

$$g(f) = \frac{dN(f)}{df} = \frac{4\pi f^2 V}{c^3} \quad (1.12)$$

Also, there are two polarization directions, which gives us

$$g(f) = \frac{8\pi f^2}{c^3} V \quad (1.13)$$

Classically, each of these modes has energy  $k_B T$ , therefore we get

$$\rho(f) = \frac{8\pi}{c^3} f^2 k_B T \quad (1.14)$$

and  $f = \frac{c}{\lambda} \implies df = -c \frac{d\lambda}{\lambda^2}$

Therefore, we get

$$\rho(f) = \frac{8\pi k_B T}{\lambda^4} \quad (1.15)$$

which is Rayleigh-Jeans' law from before. This is a problem (some would say a *catastrophe*) because not every mode can have energy  $k_B T$ .

**Physics 137A: Quantum Mechanics**

**Fall 2019**

Lecture 2: Basics of quantum theories (using the word “ansatz” a lot)

Lecturer: *Irfan Siddiqi*

3 September

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## 2.1 Planck’s quantum postulate

Planck postulated that an oscillator could not take all values of energy. Instead, he supposed that energy was quantized in steps  $E \sim nhf$ . The average energy can then be given by the sum of all the energies multiplied by the probability of each one, which is a normalized weighting factor:

$$\bar{E} = \sum_{n=0}^{\infty} nhf \frac{e^{-nhf/k_B T}}{\sum_{n=0}^{\infty} e^{-nhf/k_B T}} \quad (2.1)$$

To solve this, let  $x = e^{-hf/k_B T}$ . Then

$$\bar{E} = hf \sum_{n=0}^{\infty} n \frac{x^n}{\sum_{n=0}^{\infty} x^n} = hf \frac{x}{1-x} = hf \frac{e^{-hf/k_B T}}{1 - e^{-hf/k_B T}} \quad (2.2)$$

This gives us an overall  $\rho$ ,

$$\rho(f, T) = \frac{g(f)}{V} \bar{E}_n = \frac{8\pi hf^3}{c^3} \frac{1}{e^{hf/k_B T} - 1} \quad (2.3)$$

## 2.2 Bohr’s atomic model

In parallel, Bohr found a problem with a purely electromagnetic-orbital model of an atom; if every orbital were allowed, the electron would spiral into the nucleus. Therefore, he proposed that not all orbits were stable or allowed. Instead, only radii  $r_n$  were allowed. Each orbital has an associated energy, so if an electron transitioned between levels, it would absorb or emit light.

Each orbital has an associated angular momentum, and quantizing the radius quantizes the angular momentum:

$$\vec{L} = \vec{r} \times \vec{p} \implies L_n = mvr_n = n\hbar \quad (2.4)$$

## 2.3 de Broglie wavelengths

Based on the discovery of the wave nature of light, de Broglie suggested that everything could have wave properties.



$$\lambda_{matter} = \frac{h}{p} \quad (2.5)$$

$$f = \frac{E}{h} \quad (2.6)$$

## 2.4 Discrete-Orbitals Model of the Atom

In a simplified version of an atom in which the electron and nucleus are equally and oppositely charged, there is a Coulomb force  $\frac{ke^2}{r^2}$  balancing a centripetal force  $\frac{mv^2}{r}$ . The total energy is the sum of the kinetic and potential energies, which gives us

$$E = T + V = \frac{ke^2}{2r} + \left(-\frac{ke^2}{r}\right) = -\frac{ke^2}{2r} \quad (2.7)$$

Solving for the discrete radii, we get

$$r_n = \frac{n\hbar}{m_e v} = \frac{n^2 \hbar^2}{m k e^2} \quad (2.8)$$

This reduces to just a proportionality constant on  $n^2$ ,

$$r_n = n^2 a_0 = n^2 \cdot 0.529 \text{Å} \quad (2.9)$$

and the discrete energies are given by

$$E_n = -\frac{ke^2}{2a_0} \frac{1}{n^2} = \frac{-13.6 \text{ eV}}{n^2} \quad (2.10)$$

## 2.5 Shortcomings of Bohr’s atom

- fails to predict the intensity of emitted light
- limited success with multi-electron atoms
- fails to produce time dynamics

Overall, it did not produce a general scheme for quantization. More fundamentally, quantum theory needs to be able to produce equations of motion to be useful.

## 2.6 Wave Mechanics

Waves have characteristic amplitudes and wavelengths. They can interfere and superpose with one another. If matter is inherently waves, as postulated by de Broglie, these wave properties should be present for regular matter.

Quantum mechanics supposes that everything can be described in terms of a wavefunction,  $\psi(x, t)$ . It is not possible to directly measure the wavefunction, but we can measure  $|\psi(x, t)|^2$ . In theory, any property  $\hat{A}\psi(x, t)$  can be measured.

**Physics 137A: Quantum Mechanics**

**Fall 2019**

**Lecture 3: Quantum Information**

*Lecturer: Irfan Siddiqi*

*5 September*

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(guest lecture)

Physics 137A: Quantum Mechanics

Fall 2019

## Lecture 4: Wave description of matter

Lecturer: Irfan Siddiqi

10 September

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### 4.1 Goal

We want to come up with a mathematical construction of how to describe matter as waves. Specifically, we will try and construct a wavefunction  $\psi$  that contains all the information about matter in terms of wave properties. We cannot directly measure the wavefunction, but we can interact with it through operators.

### 4.2 Classical waves

Classically, the equation for a plane wave encodes the direction of propagation and its variations in space. The direction of propagation is encoded in a vector  $k$ , whose magnitude is the spatial frequency of the wave. The distance over which a part of the wave repeats is called the wavelength  $\lambda$ . Temporal variations are also encoded in the period  $T$  and angular frequency  $\omega$ .

All of this is encoded in a field equation of the form  $\vec{E}(\vec{r}, t)$ :

$$\vec{E} = \vec{E}_0 e^{i(\vec{k} \cdot \vec{r} - \omega t + \varphi)} \quad (4.1)$$

The  $\vec{k} \cdot \vec{r}$  component represents the spatial behaviour of the wave, and the  $\omega t$  component represents its temporal behaviour.  $\varphi$  represents the starting condition.

Consider a one-dimensional wave propagating in the  $\hat{x}$  direction. It can be represented by

$$E = E_{0x} e^{i(kx - \omega t + \varphi)} \quad (4.2)$$

We can superpose waves to create effects such as interference (cf. Young's double-slit experiment).

$$|\vec{E}|^2 = \vec{E} \cdot \vec{E}^* = (E_{01} e^{i\delta_1} + E_{02} e^{i\delta_2}) \quad (4.3)$$

The phase difference creates the interference term. Note that only a phase difference shows up; the absolute phase is not physically significant.

The takeaway from this is that to carry out superposition, we add their wavefunctions even though these wavefunctions are not directly measurable.

Max Born in 1926 considered identical copies of a system in which a measurement of  $\vec{r}$  within volume  $d\vec{r}$  is made. This gave us Born's rule, relating a probability density to a wavefunction,

$$P(\vec{r}, t)d\vec{r} = |\psi(\vec{r}, t)|^2 d\vec{r} \quad (4.4)$$

This gives us that  $P(\vec{r}, t) = \psi^*(\vec{r}, t)\psi(\vec{r}, t)$ . If we integrate the wavefunction magnitude over all space, we expect to get 1, because it is a probability.

$$\int_{\text{all space}} |\psi(\vec{r}, t)|^2 d\vec{r} = 1 \quad (4.5)$$

### 4.3 Particle Wavefunction: Single Plane Wave

Consider a free particle of mass  $m$  moving in the  $\hat{x}$  direction. It has an energy and a momentum that are related by

$$E = \frac{p_x^2}{2m} \quad (4.6)$$

We want to describe this using plane waves, i.e. using the form

$$\psi(x, t) = Ae^{i(k_x x - \omega(k)t)} \quad (4.7)$$

If we take the squared magnitude of this, we just get  $|\psi(x, t)|^2 = |A|^2$ . Integrating this over all space causes the integral to go to infinity, not 1 as is physically required.

The plane wave approximation is still useful, as long as we normalize the wavefunction properly. Specifically, the wavefunction of a free particle can be written as

$$\psi(x, t) = Ae^{i(p_x x - E(p_x)t/\hbar)} \quad (4.8)$$

By taking a derivative, we can get

$$i\hbar \frac{\partial \psi}{\partial t} = E\psi \quad (4.9)$$

$$-i\hbar \frac{\partial \psi}{\partial x} = p_x \psi \quad (4.10)$$

This is a preliminary to the Schrodinger equation.

### 4.4 Particle Wavefunction: Sum of Plane Waves

$$\psi(x, t) = \int_{-\infty}^{\infty} e^{i[p_x x - E(p_x)t]/\hbar} \phi(p_x) dp(x) \quad (4.11)$$

Physics 137A: Quantum Mechanics

Fall 2019

## Lecture 5: Wavefunctions, Fourier Transforms

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12 September

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### 5.1 Recap

Recall that we introduced the idea of a wavefunction, which is a function  $\psi(x, t)$  whose amplitude squared is a pdf, and on which operators can extract energy and momentum:

$$\hat{E} = i\hbar \frac{\partial}{\partial t} \quad (5.1)$$

$$\hat{p} = -i\hbar \vec{\nabla} \quad (5.2)$$

This gives us the eigenvalue equations

$$\hat{E}\psi = E\psi \quad (5.3)$$

$$\hat{p}\psi = p\psi \quad (5.4)$$

### 5.2 Free particle model

Last time, we saw that a plane wave representation of a particle would cause the wavefunction amplitude squared to go to infinity. The intuitive issue with this is it constrained  $x$  completely, meaning no information about  $k$  and therefore about  $p$  could be derived (Heisenberg uncertainty.) To resolve this, we consider a wavepacket model, where a particle is the sum of a number of plane waves of differing  $k$ . Allowing some spread in  $x$  makes the spread in  $p$  more calculable.

Mathematically, we consider

$$\psi(x, t) = \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} e^{i[p_x x - E(p_x)t]/\hbar} \phi(p_x) dp_x \quad (5.5)$$

This depends on a weighting function  $\phi(p_x)$ . We will consider two different  $\phi$ s; a narrow peak function (in a limit this will become the Dirac delta) and a Gaussian-like spread function that goes as  $e^{-p^2}$ .

### 5.3 The Peak Function

Suppose we have a  $\phi(p_x)$  centered at some  $p_0$  with a full-width at half-maximum of  $2\Delta p_x$ . For notational convenience, let  $\beta(p_x) = p_x x - E(p_x)t$ .

$$\psi(x, t) = \frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} e^{i\beta(p_x)/\hbar} \phi(p_x) dp_x \quad (5.6)$$

Far away from  $p_0$ , we get  $\psi \rightarrow 0$  because  $\phi \rightarrow 0$ . Also, we consider that  $\beta$  varies very little, otherwise it would be like an integral over a sine which would average out to zero.

We also apply the so-called stationary phase condition,

$$\left. \frac{d\beta(p_x)}{dp_x} \right|_{p_x=p_0} = 0 \quad (5.7)$$

If we apply this to the given  $\beta$ , we get

$$x - \left( \frac{dE(p_x)}{dp_x} \right) t = 0 \quad (5.8)$$

This allows us to solve for something with the dimensions of velocity, which turns out to be the group velocity:

$$v_g = \left. \frac{dE(p_x)}{dp_x} \right|_{p_x=p_0} \quad (5.9)$$

Each component in the wavepacket moves at  $v_{phase} = \frac{x}{t} = \frac{E(p_0)}{p_0}$ .

Going back to the free particle, we want the group velocity to match the actual velocity of the particle:

$$v_g = v = \frac{p_0}{m} \implies \frac{dE(p_x)}{dp_x} = \frac{p_x}{m} \implies E(p_x) = \frac{p_x^2}{2m} \quad (5.10)$$

We know that at  $p_x = p_0$ , the energy is given by  $E(p_0) = \frac{p_0^2}{2m}$ . For points in momentum-space around that, we write a Taylor expansion:

$$E(p_x) = \frac{p_0^2}{2m} + \frac{p_0}{m}(p_x - p_0) + \frac{(p_x - p_0)^2}{2m} + \dots \quad (5.11)$$

$$= E(p_0) + v_g(p_x - p_0) + \frac{(p_x - p_0)^2}{2m} + \dots \quad (5.12)$$

We drop the second-order term and integrate to get the wavefunction,

$$\psi(x, t) = \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} e^{i[p_x x - E(p_0)t - v_g t p_x + v_g t p_0]/\hbar} \psi(p_x) dp_x \quad (5.13)$$

We pull out the part that is independent of  $p_x$ , and we get

$$\psi(x, t) = \frac{1}{\sqrt{2\pi\hbar}} e^{i[p_0 x - E(p_0)t]/\hbar} \int_{-\infty}^{\infty} e^{i(p_x - p_0)(x - v_g t)/\hbar} \phi(p_x) dp_x \quad (5.14)$$

The exponential term is a single plane wave moving at the group velocity, so a weighted integral over a number of them represents an envelope. For convenience, we refer to the integral component as  $F(x, t)$ . With appropriate normalization on  $\phi(p_x)$ , we can absorb the  $\frac{1}{2\pi\hbar}$  constant factor and say that  $|\psi|^2 = |F(x, t)|^2$ .

## 5.4 Fourier Transforms

The Fourier transform provides a general way to derive the coefficients of sines and cosines that make up any function.

Consider  $f : \mathbb{R} \rightarrow \mathbb{R}$  that is  $2\pi$  periodic, i.e. it has the property that  $f(x + 2\pi) = f(x) \forall x \in \mathbb{R}$ . This means we only have to specify the values that  $f(x)$  takes on over an interval  $[-\pi, \pi]$  to fully specify it.

Since sines and cosines with argument  $nx$  are periodic with period  $2\pi$  (or  $\frac{2\pi}{n}$ , but for integral  $n$  that implies periodicity over  $2\pi$ ), we suppose there exist coefficients  $A_i, B_i$  such that

$$f(x) = \frac{1}{2} A_0 + \sum_{n=1}^{\infty} (A_n \cos(nx) + B_n \sin(nx)) \quad (5.15)$$

To find these, we use the property of orthogonality of sines and cosines, i.e. that  $\int_{-\pi}^{\pi} \cos(mx) \cos(nx) dx = 0$  if  $m \neq n$ , and the same for sines or for one sine one cosine. Therefore, we can derive the coefficients by integrating the whole function with the corresponding sine or cosine,

$$A_m = \frac{2}{\pi} \int_{-\pi}^{\pi} f(x) \cos(mx) \quad (5.16)$$

(check against the textbook for this, I missed the exact expression and i'm too lazy to normalize anything myself)

and similarly for  $B_m$  with the corresponding sine.

We could also use complex exponentials,

$$f(x) = \frac{1}{\sqrt{2\pi}} \sum_{n=-\infty}^{\infty} c_n e^{inx} \quad (5.17)$$

$$C_m = \frac{1}{\sqrt{2\pi}} \int_{-\pi}^{\pi} f(x) e^{-imx} dx \quad (5.18)$$

The Fourier transform is a natural way to represent a wavepacket, because fundamentally the FT carries out a sum of complex exponentials weighted by some function. In general, we have



$$f(x) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} g(k) e^{ikx} dk \leftrightarrow g(k) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} f(x) e^{-ikx} dx \quad (5.19)$$

This gives us  $\phi(p_x)$  in terms of  $\psi$ .

## 5.5 The Dirac Delta

The Dirac delta is the function whose FT is a single complex exponential:

$$\delta(x - x') = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{ik(x-x')} dk \quad (5.20)$$

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## Lecture 6: Wavepacket Fourier Analysis

Lecturer: *Irfan Siddiqi*

17 September

*Aditya Sengupta*

### 6.1 Position-Momentum Spread

Previously, we discussed the idea of a wavepacket, which has a representation  $\sum e^{i(kx-\omega t)}$ . Wavepackets in space can be formally written as

$$\psi(x, t) = \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} e^{i[p_x x - E(p_x)t]/\hbar} \phi(p_x) dp_x \quad (6.1)$$

and particle and wave properties are related by  $E = \hbar\omega, p = \hbar k$ . Now, we try to apply Fourier transform properties; from combining the expressions for the Fourier transform and the inverse Fourier transform, we can write

$$f(x) = \frac{1}{2\pi} \int_{-\infty}^{\infty} \left( f(x') e^{-ikx'} dx' \right) e^{ikx} dk \quad (6.2)$$

$$= \int_{-\infty}^{\infty} f(x') \delta(x - x') dx' \quad (6.3)$$

where the Dirac delta is formally defined as the Fourier transform of a single notch,

$$\delta(x - x') = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{ik(x-x')} dk \quad (6.4)$$

Some spread  $\Delta k$  in  $\phi(p_x)$  causes an envelope around a wavepacket, with a width that we can call  $\Delta x$ . If we restrict  $\Delta x$  to be small, that causes increased spread in  $\Delta k$ ; if  $x$  is a Dirac delta,  $\phi(p_x)$  becomes a completely sine-like wave. This is intuitively why Heisenberg uncertainty has to be true.

### 6.2 Gaussian Wavepackets

Consider a Gaussian  $\phi$ ,

$$\phi(p_x) = C e^{\frac{-(p_x - p_0)}{2(\Delta p_x)^2}}. \quad (6.5)$$

Suppose we want to find  $\phi(x, t = 0)$  ( $t$  is a constant term relative to  $\phi$  so this doesn't matter anyway but for convenience we'll say  $t = 0$ .) We can just substitute into the Fourier transform:

$$\phi(x) = \frac{1}{\sqrt{2\pi\hbar}} \cdot C \int e^{\frac{ip_x x}{\hbar}} e^{-\frac{(p_x - p_0)^2}{2(\Delta p_x)^2}} dp_x \quad (6.6)$$

Using the result

$$\int e^{-\alpha u^2} e^{-\beta u} du = \sqrt{\frac{\pi}{\alpha}} e^{\beta^2/4\alpha} \quad (6.7)$$

we can evaluate this wavefunction to get

$$\phi(x) = \frac{\pi^{-1/4}}{\sqrt{\hbar}} (\Delta p_x)^{1/2} e^{ip_0 x/\hbar} e^{-\frac{(\Delta p_x)^2 x^2}{2\hbar^2}} \quad (6.8)$$

Hey look that's a Gaussian. Match the negative-real-exponential part of this to a Gaussian in  $x$ :

$$-\frac{(\Delta p_x)^2 x^2}{2\hbar^2} = -\frac{x^2}{2\Delta x^2} \implies \Delta x \Delta p = \hbar \quad (6.9)$$

Heisenberg's uncertainty principle (which we'll get to later) states that this is the minimal value of  $\Delta x \Delta p$ . This makes Gaussian wavepackets a good approximation to classical physics.

### 6.3 Time Dependence

If we propagate the Gaussian wavepacket forward in time, it starts to spread. We can evaluate this, starting from the general wavepacket  $\psi$ :

$$\psi(x, t) = \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} e^{\frac{i[p_x x - E(p_x)t]}{\hbar}} e^{-\frac{(p_x - p_0)^2}{2(\Delta p_x)^2}} dp_x \quad (6.10)$$

We consider the case of a free particle,  $E = \frac{p_x^2}{2m}$ , and evaluate the integral:

$$\psi(x, t) = \pi^{-1/4} \left[ \frac{\Delta p_x/\hbar}{1 + i(\Delta p_x)^2 t/m\hbar} \right] \exp \left[ \frac{ip_0 x/\hbar - \left(\frac{\Delta p_x}{\hbar}\right)^2 \frac{x^2}{2} - ip_0^2 t/2m\hbar}{1 + i(\Delta p_x)^2 t/m\hbar} \right] \quad (6.11)$$

To verify this, we can set  $t = 0$  and confirm we get the previous expression.

Now, we can find modulus  $\psi$  squared:

$$|\psi(x, t)|^2 = \frac{1}{\sqrt{\pi}} \frac{\Delta p_x / \hbar}{\left[1 + \frac{(\Delta p_x)^4 t^2}{m^2 \hbar^2}\right]^{1/2}} \exp \left[ \frac{-(\Delta p_x / \hbar)^2 (x - v_g t)^2}{1 + (\Delta p_x)^4 t^2 / m^2 \hbar^2} \right] \quad (6.12)$$

We match the exponential to a Gaussian to get

$$\Delta x(t) = \frac{\hbar}{\Delta p_x} \left[ 1 + \frac{(\Delta p_x)^4}{m^2 \hbar^2} t^2 \right]^{1/2} \quad (6.13)$$

Consider  $t_1 = \frac{m\hbar}{(\Delta p_x)^2}$ . For an electron, we have an allowed  $\Delta x \sim 10^{-10}$  m. This gives us a  $\Delta p_x = \frac{\hbar}{\Delta x} \sim 10^{-24}$ .

Consider a 1g mass localized to within  $\Delta x \approx 10^{-6}$  m. The corresponding  $t_1 \sim 10^{19}$ s. This suggests that on human timescales, quantum mechanics is equally well suited to describe macroscopic objects and microscopic.

## 6.4 Interpreting the Conjugate Wavefunction

The function  $\phi(p_x, t)$  can be interpreted as its own wavefunction:

$$\phi(p_x, t) = \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} e^{-ip_x x / \hbar} \psi(x, t) dx \quad (6.14)$$

## 6.5 Uncertainty in Experiments

Recall the double-slit experiment, in which there are two slits with a distance  $d$  between them and a length  $L$  to a screen. If we fire an electron through one of the slits, we will get a sine-like interference pattern. But if we look through one of the slits and either detect an electron or don't, we change the outcome of the experiment and don't see the interference pattern. The slits are resolved if  $\lambda < d$ .

The momentum spread of the electron is

$$\Delta p_e \approx \frac{h}{\lambda} > \frac{h}{d} \quad (6.15)$$

and therefore  $d\Delta p_e > h$ . Through geometry, we get

$$\Delta\theta \approx \frac{\Delta p}{p} = \frac{h}{pd} = \frac{\lambda_e}{d} \quad (6.16)$$

Therefore, we get  $L\Delta\theta = \lambda_e \frac{L}{d}$ . This gives us a description of the uncertainty in the experiment.

Similarly,  $\Delta E \Delta t \gtrsim \hbar$ . In time, the size of a wavepacket should be approximately the lifetime of a particle. If we consider a wavepacket with  $\Delta t \sim$  some  $\tau_b$ , we can say the energy spread is known only to within  $\Delta E_b = \frac{\hbar}{\tau_b}$ .

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## Lecture 7: Deriving the Schrödinger equation

Lecturer: Irfan Siddiqi

19 September

Aditya Sengupta

### 7.1 Motivation

Previously, we saw that a Gaussian wavepacket had an uncertainty  $\Delta x \Delta p_x = \Delta E \Delta t = \hbar$ . It is generally true that  $\Delta x \Delta p_x \gtrsim \hbar$ . But we still don't know how to actually find  $\psi$ ; all we've got is some solutions that work (the plane wave and the Gaussian wavepacket).

We want some way to determine  $\psi$  such that it is linear, it agrees with classical physics in limiting cases, and such that we can determine time-evolution once we know  $\psi(x, t_0)$ . This means we should only have one derivative in time,  $\frac{\partial \psi}{\partial t}$ .

### 7.2 “Ansatz” is my favourite word

Consider a 1D nonrelativistic particle of mass  $m$  and momentum  $\vec{p} = p_x \hat{x}$ . We previously saw that the corresponding wavefunction is

$$\psi(x, t) = Ae^{i(p_x x - E(p_x)t)/\hbar} \quad (7.1)$$

We're allowed one derivative in time:

$$\frac{\partial}{\partial t} \psi(x, t) = \frac{-iE}{\hbar} \psi(x, t) \quad (7.2)$$

To match the  $E$  term, which we know is equal to  $p_x^2/2m$ , we take two derivatives in space:

$$\frac{\partial^2}{\partial x^2} \psi(x, t) = \frac{-p_x^2}{\hbar^2} \psi \quad (7.3)$$

Therefore, a plane wave satisfies

$$i\hbar \frac{\partial}{\partial t} \psi(x, t) = \frac{-\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \psi(x, t) \quad (7.4)$$

This is the time-dependent Schrödinger equation for a free particle.

We can simplify the notation a bit by introducing the notion of operators,

$$\hat{E} = i\hbar \frac{\partial}{\partial t}; \hat{p}_x = -i\hbar \frac{\partial}{\partial x} \quad (7.5)$$

### 7.3 Behaviour of Free Particles

Consider a force  $\vec{F}(\vec{r}, t)$  acting on a free particle. Suppose this force is conservative, i.e. there exists some scalar function  $V(\vec{r}, t)$  such that

$$\vec{F}(\vec{r}, t) = -\vec{\nabla}V(\vec{r}, t) \quad (7.6)$$

Let's introduce a potential energy operator  $\hat{V}(\vec{r}, t)\psi(\vec{r}, t) = V(\vec{r}, t)\psi(\vec{r}, t)$ . This is an eigenvalue equation with eigenvalue  $V(\vec{r}, t)$  and eigenfunction  $\psi(\vec{r}, t)$ . To agree with classical physics, we're going to require that the eigenvalue is real. Therefore, we have to consider Hermitian operators, i.e. operators such that  $\hat{H} = \hat{H}^*$ .

Thus,

$$\hat{E}\psi(\vec{r}, t) = \left[ \frac{\hat{p}^2}{2m} + \hat{V}(\vec{r}, t) \right] \psi(\vec{r}, t) \quad (7.7)$$

Replacing  $\hat{E}$  and  $\hat{p}$  with the operators,

$$i\hbar \frac{\partial}{\partial t} \psi(\vec{r}, t) = \left[ \frac{-\hbar^2}{2m} \nabla^2 + \hat{V}(\vec{r}, t) \right] \psi(\vec{r}, t) \quad (7.8)$$

This is ~~the equation for life~~ a generalized energy-balance equation that we can solve for specific cases. If we tried to solve this for actual matter, we wouldn't be able to, because we have no idea what  $\hat{V}$  is.

We're going to specify  $\hat{V}$  and solve for  $\psi$  based on that. First, we look at standing wave solutions that are variable-separable,  $\psi(\vec{r}, t) = \psi(\vec{r})A(t)$ . These are stable solutions that correspond to measurements.

Next, we exploit the fact that the norm-squared of the wavefunction is a probability density:

$$\int_{\text{all space}} |\psi(\vec{r}, t)|^2 d\vec{r} = 1 \quad (7.9)$$

$$\frac{\partial}{\partial t} \int |\psi(\vec{r}, t)|^2 d\vec{r} = 0 \quad (7.10)$$

$$\int_V \left[ \psi^* \left( \frac{\partial \psi}{\partial t} + \left( \frac{\partial \psi^*}{\partial t} \right) \psi \right) \right] d\vec{r} \quad (7.11)$$

Rewriting this, we get

$$0 = \frac{i\hbar}{2m} \int_V \vec{\nabla} \cdot [\psi^*(\nabla\psi) - (\nabla\psi^*)\psi] d\vec{r} \quad (7.12)$$

Call everything in the square brackets  $\vec{j}$ . Then we have an integral over a volume of a divergence, so we can rewrite this as a surface integral:

$$-\int \vec{j} \cdot d\vec{s} = \frac{\partial}{\partial t} \int_V |\psi(\vec{r}, t)|^2 d\vec{r} \quad (7.13)$$

where

$$j = \frac{\hbar}{2mi} [\psi^*(\nabla\psi) - (\nabla\psi^*)\psi] \quad (7.14)$$

is the probability current.

I missed something, but we got the equation

$$0 = \frac{1}{i\hbar} \int [\psi^*(\hat{H}\psi) - (\hat{H}\psi)^*\psi] d\vec{r} \quad (7.15)$$

Therefore, the inside of the integral must be zero. We get that  $\hat{H} = \hat{H}^*$ , meaning that  $\hat{H}$  is Hermitian.

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## Lecture 8: Measurements, Operators

Lecturer: Irfan Siddiqi

24 September

Aditya Sengupta

### 8.1 Recap

So far, we have described reality using the wavefunction  $\psi$ , and more directly through a probability density  $|\psi|^2$  or through operators applied to the wavefunction. For example,  $i\hbar\frac{\partial}{\partial t}$  gives the energy, and  $-i\hbar\vec{\nabla}$  gives the momentum vector of the system. We also derived the Schrödinger equation, which we can encode in an operator:

$$i\hbar\frac{\partial\psi}{\partial t} = \left[ \frac{-\hbar^2}{2m}\nabla^2 + \hat{V}(\vec{r}, t) \right] \psi = \hat{H}\psi \quad (8.1)$$

### 8.2 Measurements and Eigenvalues

Making a measurement can be considered to be applying an operator  $\hat{M}$ , from which we recover its eigenvalues,

$$\hat{M}\psi_m = m\psi_m \quad (8.2)$$

This collapses the wavefunction to  $\psi_m$ , and you measure “ $m$ ”. This suggests that  $m$  takes on discrete values, although it is sometimes continuous. Specifically,  $m$  is continuous if we do not have boundary conditions, i.e. in the limit of large length scales.

### 8.3 Expectations

It can be useful to consider the expected value of a certain measurement, so that we get some idea of what  $m$  is likely to be. This can be found by integrating all the possible outcomes over its probability:

$$\langle \vec{r} \rangle = \int \vec{r}P(\vec{r}, t)d\vec{r} = \int \psi^*(\vec{r}, t)\vec{r}\psi(\vec{r}, t)d\vec{r} \quad (8.3)$$

The  $\vec{r}\psi(\vec{r}, t)$  in this is an eigenvalue equation, so we can say

$$\langle f(\vec{r}, t) \rangle = \int \psi^* \hat{f}(\vec{r}, t)\psi(\vec{r}, t)d\vec{r} \quad (8.4)$$



Similarly, in momentum space, we can say

$$g(\vec{p}, t) = \int \psi^*(\vec{r}, t) \hat{g}(-i\hbar\vec{\nabla}, t) \psi(\vec{r}, t) d\vec{r} \quad (8.5)$$

For a concrete example, take

$$\langle xp_x \rangle = \int \psi^*(\vec{r}, t) \hat{x} \hat{p}_x \psi(\vec{r}, t) d\vec{r} \quad (8.6)$$

$$= \int \psi^*(x, t) x \left( -i\hbar \frac{\partial}{\partial x} \right) \psi(x, t) dx \quad (8.7)$$

Then, by integration by parts where we let  $u = \psi^* x$  and  $v = \psi$ , we get

$$\langle xp_x \rangle = -i\hbar x \psi^*(x, t) \psi(x, t) \Big|_{-\infty}^{\infty} + i\hbar \int \psi \left[ \frac{\partial}{\partial x} (x \psi^*(x, t)) \right] dx \quad (8.8)$$

$$= i\hbar \int \psi(x, t) x \frac{\partial \psi^*(x, t)}{\partial x} dx + i\hbar \int \psi^* \psi dx \quad (8.9)$$

$$= \langle xp_x \rangle^* + i\hbar \quad (8.10)$$

Through a similar process, we get  $\langle p_x x \rangle = \langle p_x x \rangle^* - i\hbar$ .

## 8.4 Commutators

We just saw that  $p_x$  does not commute with  $x$ . In more generality, we can say that two operators commute if its commutator is identically zero, where the commutator is defined by

$$[\hat{A}, \hat{B}] = \hat{A}\hat{B} - \hat{B}\hat{A} \quad (8.11)$$

If this is zero, then the two operators commute, meaning that they share eigenfunctions and can be measured simultaneously. If this is nonzero, they do not commute, meaning there are no common eigenfunctions and that they are related by an uncertainty relation.

Let's compute the commutator of  $\hat{x}$  and  $\hat{p}$ :

$$[\hat{x}, \hat{p}_x] = [\hat{x}\hat{p}_x - \hat{p}_x\hat{x}] = x \left( -i\hbar \frac{\partial}{\partial x} \right) + i\hbar \left( \frac{\partial}{\partial x} \right) x \quad (8.12)$$

To make this clearer, we apply this commutator to a dummy  $\hat{\psi}$ :

$$[x, p_x] \hat{\psi} = \left( -i\hbar x \frac{\partial \hat{\psi}}{\partial x} + i\hbar \left[ \hat{\psi} + x \frac{\partial \hat{\psi}}{\partial x} \right] \right) = i\hbar \hat{\psi} \quad (8.13)$$

Therefore  $[x, p_x] = i\hbar$ . This tells us that  $x$  and  $p_x$  do not commute and do not have common eigenfunctions.

## 8.5 Time-Independent Schrödinger Equation

To get time independence, we want to find separable solutions:

$$\psi(\vec{r}, t) = \psi(\vec{r})f(t) \quad (8.14)$$

From this, we can eventually construct the general solution as a linear combination of these separable solutions. We substitute this separated form into the time-dependent Schrödinger equation:

$$i\hbar \frac{\partial \psi(\vec{r}, t)}{\partial t} = \left[ \frac{-\hbar^2}{2m} \nabla^2 + \hat{V}(\vec{r}, t) \right] \psi(\vec{r}, t) \quad (8.15)$$

$$i\hbar \psi(\vec{r}) \frac{df(t)}{dt} = \left[ \frac{-\hbar^2}{2m} \nabla^2 \psi(\vec{r}) + \hat{V}(\vec{r}) \psi(\vec{r}) \right] f(t) \quad (8.16)$$

Divide by  $\psi(\vec{r})f(t)$  to get

$$i\hbar \frac{1}{f(t)} \frac{df(t)}{dt} = \frac{1}{\psi(\vec{r})} \left[ \frac{-\hbar^2}{2m} \nabla^2 \psi(\vec{r}) + V(\vec{r}) \psi(\vec{r}) \right] \quad (8.17)$$

These both have to equal a constant (cf. separation of variables), say  $E$ , so we get

$$i\hbar \frac{df(t)}{dt} = E f(t) \implies f(t) = C e^{-iEt/\hbar} \quad (8.18)$$

Therefore, we get

$$\left[ \frac{-\hbar^2}{2m} \nabla^2 + \hat{V}(\vec{r}) \right] \psi(\vec{r}) = E \psi(\vec{r}) \quad (8.19)$$

We can write this compactly as  $\hat{H}\psi = E\psi$ , which is very visibly an eigenvalue equation whose eigenvalues are the allowed energies (eigenenergies) and whose eigenfunctions are the allowed associated wavefunctions.

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## Lecture 9: Seeing the Eigenvalue Schrödinger Equation

Lecturer: Irfan Siddiqi

26 September

Aditya Sengupta

### 9.1 Graphically Solving the Schrödinger Equation

We've seen the Schrödinger equation a few times now and we know it can be expressed as an eigenvalue equation where the eigenvalues are the allowed energies. To construct a basis of solutions, we use a spatial representation,  $\psi = \psi(\vec{r}, t)$ . The  $\hat{x}$  operator is just multiplication by  $x$ , and the  $\hat{p}_x$  operator is  $-i\hbar\frac{\partial}{\partial x}$ .

Suppose  $V(x)$  is such that it has asymptotes at  $V_{\pm}$  (finite values) at  $\pm\infty$ , and it has a minimum at  $x_0$ . We want to solve the Schrödinger equation for this case.

$$\left[ \frac{-\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x) \right] \psi(x) = E\psi(x) \quad (9.1)$$

Rearranging gives us

$$\frac{d^2\psi(x)}{dx^2} = \frac{2m}{\hbar^2} [V(x) - E] \psi(x) \quad (9.2)$$

#### 9.1.1 Classical

We split this into four regions:  $E < V_{min}$ ,  $V_{min} < E < V_-$ ,  $V_- < E < V_+$ ,  $E > V_+$ . Classically, we expect no solutions at  $E < V_{min}$ . For  $V_{min} < E < V_-$ , the classical solution is confined between the  $x$  values with total energy less than or equal to  $E$ . The same logic applies for  $V_- < E < V_+$ , with the exception that the solution is not bounded to the left because the energy never exceeds  $E$  to the left of the intersection with  $V_+$  or any energy  $V_- < E < V_+$ . Finally, if  $E > V_+$ , there are solutions everywhere.

#### 9.1.2 Quantum

Quantum mechanically, we want  $\psi(x)$  to be finite and continuous, and  $\psi'(x)$  to be continuous. In the region  $E < V_{min}$ , the second derivative of  $\psi$  curves up because  $\frac{\partial^2\psi}{\partial x^2}$  has the same sign as  $x$ ; in the region  $E > V_+$ , the second derivative curves down; in the intermediate regions, the second derivative alternates its curvature (crosses 0). We see that quantum mechanically as well as classically, no solution exists.

In the second region,  $\psi''$  and  $\psi$  only have opposing signs within the classical solution region, i.e. the intersections  $x_1, x_2$  where  $V(x) = E$ . Within this allowed region, the solutions are sinusoidal. However, for the continuity of the wavefunction and its derivative, we have to allow the wavefunction to decay outside the classical region to zero, meaning that there is some region of nonzero probability that would not be classically allowed. This is exponential decay, so in the limit of physically macroscopic distances, this probability looks like a step directly to zero, but it does this continuously but very fast.

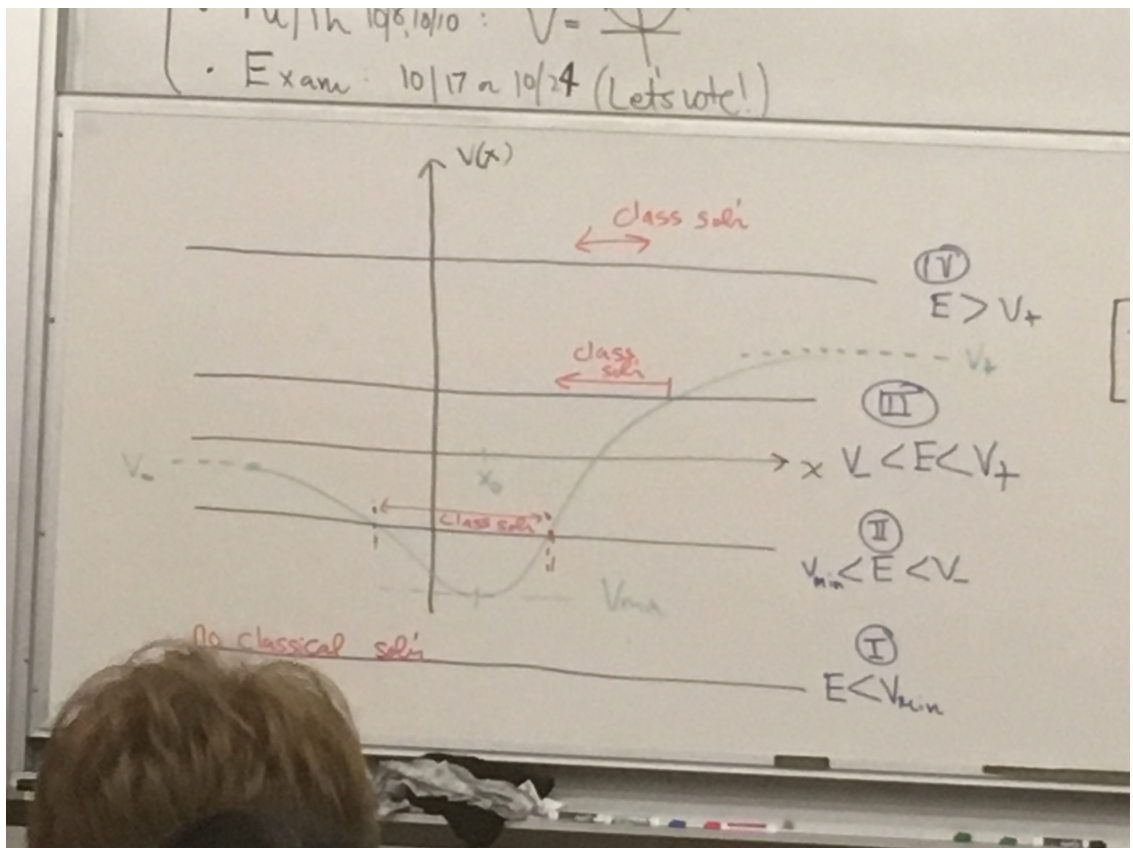


Figure 9.1: Quantum and classical solutions to the Schrödinger equation for an interesting potential

As  $V(x) \rightarrow \infty$ , we want this to decay even faster. We will later see that the decay constant is proportional to the energy difference between  $V(x)$  and  $E$ .

## 9.2 Eigenfunctions and the general solution

If two eigenfunctions  $\psi_E, \psi_{E'}$  have  $E \neq E'$ , they are orthogonal.

$$\int \psi_{E'}^*(\vec{r})\psi_E(\vec{r})d\vec{r} = \delta_{EE'} \quad (9.3)$$

We can show this using the eigenvalue property.

$$\hat{H}\psi_E = E\psi_E \quad (9.4)$$

$$\psi_{E'}^*(\hat{H}\psi_E) = E\psi_{E'}^*\psi_E \quad (9.5)$$

$$(\hat{H}\psi_{E'})^* = E'\psi_{E'}^* \quad (9.6)$$

$$(\hat{H}\psi_{E'})^*\psi_E = E'\psi_{E'}^*\psi_E \quad (9.7)$$

$$(9.8)$$

By algebra on the above things (I'm too lazy to do labels) we get

$$(E - E') \int \psi_{E'}^*\psi_E d\vec{r} = \int \psi_{E'}^*(\hat{H}\psi_E) - (\hat{H}\psi_{E'})^*\psi_E d\vec{r} \quad (9.9)$$

$$\int \psi_{E'}^*H\psi_E - \psi_{E'}^*H^*\psi_E = 0 \quad (9.10)$$

$$\therefore (E - E') \int \psi_{E'}^*\psi_E d\vec{r} = (E - E') \int \psi_{E'}^*(\vec{r})\psi_E(\vec{r})d\vec{r} = \delta_{EE'} \quad (9.11)$$

We postulate that  $\{\psi_E\}$  represent all possible energy states and span the space of wavefunctions. Then, any valid wavefunction should be of the form

$$\psi(\vec{r}, t) = \sum_E C_E(t)\psi_E(\vec{r}) \quad (9.12)$$

To find these coefficients, we use the Fourier trick from, like, everything:

$$\int \psi_{E'}^*(\vec{r})\psi(\vec{r}, t)d\vec{r} = \sum_E C_E(t) \int \psi_{E'}^*(\vec{r})\psi(\vec{r})d\vec{r} = C_{E'}(t) \quad (9.13)$$

We also know that all time dependence is rotations clockwise on the wavefunction. Therefore, the general solution is

$$\psi(\vec{r}, t) = \sum_E C_E(t_0) e^{iE(t-t_0)} \psi_E(\vec{r}) \quad (9.14)$$

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## Lecture 10: Solving Schrödinger's equation for 1D problems

Lecturer: Irfan Siddiqi

1 October

Aditya Sengupta

### 10.1 Zero Potential

For the simplest case of a 1D free particle,  $V(x) = 0$ , so the differential equation that we get is just a regular second-order equation.

$$-\frac{\hbar^2}{2m} \frac{\partial^2 \psi(x)}{\partial x^2} = E\psi(x) \implies k = \frac{\sqrt{2mE}}{\hbar} \quad (10.1)$$

The general solution to this is  $\phi(x) = Ae^{ikx} + Be^{-ikx}$ . Further, we require that  $k$  is real. We can observe that

1.  $E = \frac{\hbar^2 k^2}{2m} \geq 0$  and  $p = \hbar k$ .
2.  $E$  can be considered continuous; we don't need to bring in quantization yet.
3.  $E$  is doubly degenerate, because both  $e^{ikx}$  and  $e^{-ikx}$  are present.
4.  $e^{\pm ikx}$  are also eigenfunctions of the momentum operator:  $\hat{p} = -i\hbar \frac{\partial}{\partial x}$ , and  $\hat{p}(e^{ikx}) = \hbar k(e^{ikx})$ .

We know what the general time-dependence of a solution to the Schrodinger equation looks like, so we can set up the general time-dependent solution based on this:

$$\phi(x, t) = (Ae^{ikx} + Be^{-ikx})e^{-iEt/\hbar} = Ae^{i(kx-\omega t)} + Be^{-i(kx-\omega t)} \quad (10.2)$$

This is a sum of plane waves. To proceed, set  $B = 0$  and we get  $\phi(x, t) = Ae^{i(kx-\omega t)}$ . The intuition behind this is a particle moving to the right with  $p = \hbar k = \frac{2\pi\hbar}{\lambda}$ . The velocity of this particle is  $\frac{\partial \omega}{\partial k} = \frac{\hbar k}{m}$ .

Note that the probability of finding the particle anywhere is  $|\phi(x, t)|^2 = |A|^2$ , which is independent of  $x, t$ . This is because this is an idealized solution for a particle of momentum  $\hbar k$ . To check this, we require that the probability current density obey the classical relation  $j = Pv$ .

$$j = \frac{\hbar}{2mi} \left[ \psi^* \frac{\partial \psi}{\partial x} - \psi \frac{\partial \psi^*}{\partial x} \right] = \frac{\hbar}{2mi} [A^*(Aik) - A(A^*(-ik))] \quad (10.3)$$

$$j = \frac{\hbar}{2m} |A|^2 = Pv \quad (10.4)$$

If we consider  $A = 0$  instead, this is the same as the opposite case but with the particle moving in the  $-x$  direction.

Next, consider the case  $A = B$ . We get

$$\phi(x, t) = A(e^{ikx} + e^{-ikx})e^{-i\omega t} = 2A \cos(kx)e^{i\omega t} \quad (10.5)$$

This is a standing wave with modes  $x_n = \frac{\pm(\frac{\pi}{2} + n\pi)}{k}$ .

Then, it's natural to consider  $A = -B$ , which gives us  $\phi(x, t) = 2iA \sin kxe^{-i\omega t}$ . This gives us modes  $x_n = \frac{\pm n\pi}{k}$ . And so on.

## 10.2 Nontrivial Potentials

Consider the step function,  $V(x) = V_0 u(x)$ . Classically, if  $E < V_0$  the particle should bounce off the wall, and under quantum mechanics, there is some finite probability of finding the particle in  $x > 0$ , which is called tunnelling. We can construct solutions in the  $V = 0$  and  $V = V_0$  regions, and stitch them together by requiring the continuity of the wavefunction and its derivative.

$$Ae^{ikx} + Be^{-ikx} = De^{-\kappa x} \implies A + B = D \quad (10.6)$$

$$-ik(A - B) = -\kappa D \implies A = \frac{1 + i\kappa/k}{2}D, B = \frac{1 - i\kappa/k}{2}D \quad (10.7)$$



Physics 137A: Quantum Mechanics

Fall 2019

## Lecture 11: Solving the Schrödinger equation more

Lecturer: Irfan Siddiqi

3 October

Aditya Sengupta

### 11.1 Potential Step

Consider the potential step function,

$$V(x) = \begin{cases} 0 & x < 0 \\ V_0 & x \geq 0 \end{cases} \quad (11.1)$$

There are no solutions of Schrödinger's equation for  $E < 0$ , so we can split this up into just two cases.

#### 11.1.1 $E < V_0$

Let's first consider the case  $0 < E < V_0$ ; then we get

$$\begin{aligned} \frac{d^2\psi(x)}{dx^2} + k^2\psi(x) &= 0, x < 0 \\ \frac{d^2\psi(x)}{dx^2} - \kappa^2\psi(x) &= 0 \end{aligned}$$

for  $k = \frac{\sqrt{2mE}}{\hbar}$ , and  $[\frac{2m}{\hbar^2}(V_0 - E)]^{1/2}$ . The solutions to these are  $\psi(x) = Ae^{ikx} + Be^{-ikx}$  for  $x < 0$ , and  $\psi(x) = Ce^{\kappa x} + De^{-\kappa x}$ . To satisfy the wavefunction dying out as  $x \rightarrow \infty$ , we set  $C = 0$ , then we require that the wavefunction and its derivative are continuous at  $x = 0$ . This gives us

$$A + B = D \quad (11.2)$$

$$ik(A - B) = -\kappa D \quad (11.3)$$

We can use this to solve for  $\frac{B}{A}$  and  $\frac{D}{A}$  so that we only have one amplitude factor. This gives us

$$\psi(x) = \begin{cases} 2Ae^{i\alpha/2} \cos(kx - \alpha/2) & x < 0 \\ 2Ae^{i\alpha/2} \cos(\frac{\alpha}{2}) e^{-\kappa x} & x \geq 0 \end{cases} \quad (11.4)$$

where  $\alpha = 2 \tan^{-1} \left[ -\left(\frac{V_0}{E} - 1\right)^{1/2} \right]$ . We're interested in the probabilities that the particle shows up in the left or right. We get this by calculating  $|\psi|^2$ :

$$P(x) = \begin{cases} 4|A|^2 \cos^2(kx - \alpha/2) & x < 0 \\ |D|^2 e^{-2kx} & x \geq 0 \end{cases} \quad (11.5)$$

It's interesting that the  $x < 0$  case has oscillatory behaviour. This physically shows up due to an interference pattern of a plane wave with its reflection off the barrier. To the particle under the barrier,  $\Delta x \approx \frac{1}{\kappa}$  and therefore

$$\Delta p_x \gtrsim \frac{\hbar}{\delta x} \approx \hbar \kappa = [2m(V_0 - E)]^{1/2} \quad (11.6)$$

Therefore the uncertainty in the energy is

$$\Delta E = \frac{(\Delta p_x)^2}{2m} \gtrsim V_0 - E \quad (11.7)$$

i.e. we can't find the particle there.

### 11.1.2 $E > V_0$

This is similar, but now the solution is oscillatory in both regions.

$$\psi(x) = \begin{cases} Ae^{ikx} + Be^{-ikx} & x < 0 \\ Ce^{ik'x} + De^{-ik'x} & x > 0 \end{cases} \quad (11.8)$$

We can discard  $D$  without loss of generality (assume the particle is left-incident) and we essentially end up with the Fresnel equations:

$$\begin{aligned} A + B &= C \\ k(A - B) &= k'C \\ \frac{B}{A} &= \frac{k - k'}{k + k'}, \quad \frac{C}{A} = \frac{2k}{k + k'} \\ R &= \frac{|B|^2}{|A|^2} = \frac{\left[1 - \left(1 - \frac{V_0}{E}\right)^2\right]^2}{\left[1 + \left(1 - \frac{V_0}{E}\right)^2\right]^2} \end{aligned}$$

$R$  drops off gradually with  $E/V_0$  after  $E/V_0 > 1$  (which is the case we're assuming). Further, we get the transmission coefficient,

$$T = \frac{v'|C|^2}{v|A|^2} = \frac{4\left(1 - \frac{V_0}{E}\right)^2}{\left(1 + \left(1 - \frac{V_0}{E}\right)^{1/2}\right)^2} \quad (11.9)$$

## 11.2 The Potential Barrier

Consider

$$V(x) = \begin{cases} V_0 & 0 < x < a \\ 0 & \text{otherwise} \end{cases} \quad (11.10)$$

(he didn't center it about 0 I'm disgusted)

The process here is similar to above, except now we have three places to enforce boundary conditions:  $x = 0, x = a, x \rightarrow \infty$ .

Here, we get

$$\psi(x) = Fe^{\kappa x} + Ge^{-\kappa x} \text{ for } x \in [0, a], \kappa = \left( \frac{2m}{\hbar^2}(V_0 - E) \right)^{1/2} \quad (11.11)$$

To the left we have the usual oscillating sum, and to the right we have one oscillating component (there's no reflection causing an  $e^{-ikx}$  component on the right.)

$$\begin{aligned} A + B &= F + G \\ ik(A - B) &= \kappa(F - G) \end{aligned}$$

algebra!

$$\frac{B}{A} = \frac{(k^2 + \kappa^2)(e^{2\kappa a} - 1)}{e^{2\kappa a}(k + i\kappa)^2 - (k - i\kappa)^2} \quad (11.12)$$

$$\frac{C}{A} = \frac{4ik\kappa e^{-ika} e^{\kappa a}}{e^{2\kappa a}(k + i\kappa)^2 - (k - i\kappa)^2} \quad (11.13)$$

$$R = \left( 1 + \frac{4E(V_0 - E)}{V_0^2 \sinh^2(\kappa a)} \right)^{-1} \quad (11.14)$$

$$T = \left( 1 + \frac{V_0^2 \sinh^2(\kappa a)}{4E(V_0 - E)} \right)^{-1} \quad (11.15)$$

This is where quantum tunnelling comes from: we see that  $|\psi|^2$  is nonzero in the high-potential region as is required for continuity. This is a totally non-classical effect.

$T \rightarrow 1$  only when  $k'a = n\pi$ ; these are Fresnel resonances.

WHATDOESSPECLARELATIVITY'LOOK'LIKE?

Physics 137A: Quantum Mechanics

Fall 2019

## Lecture 12: Harmonic Oscillator

Lecturer: *Irfan Siddiqi*

8 October

*Aditya Sengupta*

### 12.1 Infinite Square Well

Consider the potential  $V(x) = \begin{cases} 0 & |x| \leq a \\ \infty & |x| > a \end{cases}$ . We can solve the Schrödinger equation in this region by enforcing the continuity of  $\psi$ . We can't enforce continuity of  $\psi'$  because of the infinite potential. Within the potential well, we have  $\psi(x) = Ae^{ikx} + Be^{-ikx}$  where  $k = \frac{\sqrt{2mE}}{\hbar}$ . For continuity of  $\psi$ , we want  $A \cos(ka) = 0$  and  $B \sin(ka) = 0$ .

If  $B = 0$  then  $\cos(ka) = 0$ , so  $k_n = \frac{n\pi}{2a} = \frac{n\pi}{L}$ . Normalization gives us  $A = 1/\sqrt{a}$ , so we can write the even solution,

$$\psi_n(x) = \frac{1}{\sqrt{a}} \cos\left(\frac{n\pi x}{2a}\right) \quad (12.1)$$

for  $n = 1, 3, 5, \dots$

If  $A = 0$  then  $\sin(ka) = 0$ , which similarly gives us the odd solutions,

$$\psi_n = \frac{1}{\sqrt{a}} \sin\left(\frac{n\pi x}{2a}\right) \quad (12.2)$$

The general solution is just a sum of these. The energy of each of these states is

$$E_n = \frac{\hbar^2 k_n^2}{2m} = \frac{\hbar^2 \pi^2 n^2}{2mL^2} \quad (12.3)$$

For a 1D even potential, we always have definite parity eigenstates.

### 12.2 Finite Square Well

Suppose

$$V(x) = \begin{cases} -V_0 & |x| \leq a \\ 0 & |x| > a \end{cases} \quad (12.4)$$

Solutions with  $E > 0$  are the scattering states, and  $E < 0$  are the bound states. For  $-V_0 < E < 0$ , we get

$$\frac{d^2\psi(x)}{dx^2} + \alpha^2\psi(x) = 0, \alpha = \left[ \frac{2m}{\hbar^2}(V_0 + E) \right]^{1/2} \quad (12.5)$$

for  $|x| < a$ , and

$$\frac{d^2\psi(x)}{dx^2} - \beta^2\psi(x) = 0, \beta = \left( -\frac{2mE}{\hbar^2} \right)^{1/2} \quad (12.6)$$

for  $|x| > a$ . Therefore, the even solutions are  $\psi(x) = A \cos(\alpha x), x \in [0, a]$  and  $C e^{-\beta x}, x > a$ . Similarly, the odd solutions, are  $\psi(x) = B \sin(\alpha x), x \in [0, a]$  and  $C e^{-\beta x}, x > a$ . We apply boundary conditions on both at  $x = a$ . For the even solution, we get  $\alpha \tan(\alpha a) = \beta$ , and for the odd one, we get  $\alpha \cot(\alpha a) = -\beta$ .

We can't solve this analytically, but we can do it graphically. Let  $\xi = \alpha a, \eta = \beta a$ . Then the equations become  $\xi \tan \xi = \eta, \xi \cot \xi = -\eta$  and  $\xi^2 + \eta^2 = \gamma^2$ , where  $\gamma = \left( \frac{2mV_0 a^2}{\hbar^2} \right)^{1/2}$ . In  $\xi - \eta$  phase space, this represents intersections of tangent/cotangent curves with lines of constant radius (arcs of circles), so we can find these points graphically.

Within the well, only discrete energies exist, and above it, energies can be said to exist in a continuous spectrum.

## 12.3 Harmonic Oscillator

Recall that a normal harmonic oscillator is characterized by  $F = -Kx$  and  $V(x) = \frac{1}{2}Kx^2$ . We can consider the wavefunction of a particle in this potential. We claim that  $\psi_n \sim e^{-x^2} H_n(x)$ , where  $H_n(x)$  is the  $n$ th Hermite polynomial.

Let  $\hat{H} = \frac{\hbar^2}{2m} \frac{d^2}{dx^2} + \frac{1}{2}Kx^2$ . Further, we define dimensionless constants  $\lambda = \frac{2E}{\hbar\omega}$ ,  $\xi = \alpha x$ , and  $\alpha = \left( \frac{m\omega}{\hbar} \right)^{1/2}$ . Then, we want to solve

$$\frac{d^2\psi(\xi)}{d\xi^2} + (\lambda - \xi^2)\psi(\xi) = 0 \quad (12.7)$$

As  $|\xi| \rightarrow \infty$ , the asymptotic solution is  $\left( \frac{d^2}{d\xi^2} - \xi^2 \right) \psi(\xi) = 0 \implies \psi(\xi) = e^{\pm \xi^2/2}$ . Since the Gaussian decays fast enough, we can say that this multiplied by any polynomial is also a solution asymptotically.

$$\psi(\xi) = H(\xi)e^{-\xi^2/2} \quad (12.8)$$

If we substitute this into the original equation, we can get some constraints on what the polynomial  $H(\xi)$  has to be.

$$\frac{d^2 H}{d\xi^2} - 2\xi \frac{dH}{d\xi} + (\lambda - 1)H = 0 \quad (12.9)$$

This is the Hermite equation. To solve it, we'll first look for even solutions, of the form  $H(\xi) = \sum_{l=0}^{\infty} c_l \xi^{2l}$ , where  $c_0 \neq 0$ . Substitute this into the Hermite equation, and we get

$$\sum_{l=0}^{\infty} \left[ 2l(2l-1)c_l \xi^{2(l-1)} + (\lambda - 1 - 4l)c_l \xi^{2l} \right] = 0 \quad (12.10)$$

We can rewrite this to have only  $\xi^{2l}$  terms together, and require that each of those is 0. We get

$$c_{l+1} = \frac{4l + 1 - \lambda}{2(l+1)(2l+1)} c_l \quad (12.11)$$

If you keep all the terms, you get an unphysical wavefunction, so we'll need to terminate the series. Next time, we'll see how that works.

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**Lecture 13: Harmonic Oscillator Solutions**

*Lecturer: Irfan Siddiqi*

*15 October*

*Aditya Sengupta*

Previously, we got a recurrence relation for the coefficients of the solution to the Hermite equation:

$$c_{l+1} = \frac{4l + 1 - \lambda}{2(l+1)(2l+1)} c_l \quad (13.1)$$

For large  $l$ ,  $c_{l+1}c_l \sim \frac{1}{l}$ , so  $c_l$  is approximately geometric or exponential. Consider

$$\xi^{2p} e^{\xi^2} = \xi^{2p} \left( \sum_l \frac{(\xi^2)^l}{l!} \right) \quad (13.2)$$

Further, consider  $\psi \sim e^{-\xi^2/2} H \sim \xi^{2p} e^{+\xi^2/2}$ . This blows up, so we can't take this.

Suppose we want the series to terminate at some  $N$ , i.e. we are requiring that  $c_N \neq 0, c_{N+1} = 0$ . Therefore the numerator in the recurrence relation has to be zero, i.e.

$$\lambda = 4N + 1 \quad (13.3)$$

Since  $\lambda$  was a ratio of energies, we've required that the energy is quantized.

Similarly for the odd solutions, we get

$$H(\xi) = \sum_{l=0}^{\infty} d_l \xi^{2l+1}, d_0 \neq 0 \quad (13.4)$$

$$d_{l+1} = \frac{4l + 3 - \lambda}{2(l+1)(2l+3)} d_l \lambda = 4N + 3 \quad (13.5)$$

Recall that  $\lambda = \frac{2E}{\hbar\omega}$ , so solving for all the energies allowed, we get

$$E_n = \left( n + \frac{1}{2} \right) \hbar\omega \quad (13.6)$$

“If you become a journalist, you should remember this result; if you become a physicist, you should live by this result.”

The  $\frac{1}{2}\hbar\omega$  term means we never have zero energy, as this would result in simultaneously knowing the exact position and momentum of the particle.

### 13.1 General solutions to the Hermite equation

We previously saw that general solutions to the Hermite equations have the form

$$\psi_n(\xi) = e^{-\frac{\xi^2}{2}} H_n(\xi) \quad (13.7)$$

The  $n$ th polynomial is given by the expression

$$H_n(\xi) = (-1)^n e^{\xi^2} \frac{d^n}{d\xi^n} e^{-\xi^2} = e^{\frac{\xi^2}{2}} \left( \xi - \frac{d}{d\xi} \right)^n e^{-\frac{\xi^2}{2}} \quad (13.8)$$

The first few Hermite polynomials are

$$\begin{aligned} H_0(\xi) &= 1 \\ H_1(\xi) &= 2\xi \\ H_2(\xi) &= 4\xi^2 - 2 \\ H_3(\xi) &= 8\xi^3 - 12\xi \end{aligned}$$

Combining this with requiring that solutions are normalized in the sense that  $\int \psi_n^*(x)\psi_n(x)dx = 1$ , we get

$$\psi_n(x) = \left( \frac{\alpha}{\sqrt{\pi} 2^n n!} \right)^{1/2} e^{-\alpha^2 x^2 / 2} H_n(\alpha x) \quad (13.9)$$

where  $\alpha = \left( \frac{m\omega}{\hbar} \right)^{1/2}$ .

This is the time-independent solution; now, we'll look at the time-dependent case. We're interested in creating solutions of the form  $\psi(\vec{r}, t) = \sum_E c_E(t) \psi_E(\vec{r})$ , where  $\psi_E$  is an eigensolution; that is,  $\hat{H}\psi_E = E\psi_E$ .

$$\begin{aligned} i\hbar \frac{\partial}{\partial t} \psi(\vec{r}, t) &= i\hbar \frac{\partial}{\partial t} \sum_E c_E(t) \psi_E(\vec{r}) = \hat{H} \sum_E c_E(t) \psi_E(\vec{r}) \\ &= \sum_E c_E(t) \hat{H} \psi_E(\vec{r}) \\ &= \sum_E c_E(t) E \psi_E(\vec{r}) \end{aligned}$$

We multiply by  $\psi_{E'}^*(\vec{r})$  and use orthogonality to get

$$i\hbar \frac{\partial}{\partial t} \sum_E c_E(t) \int \psi_{E'}^*(\vec{r}) \psi_E(\vec{r}) d\vec{r} = \sum_E c_E(t) E \int \psi_{E'}^*(\vec{r}) \psi_E(\vec{r}) d\vec{r} \quad (13.10)$$

$$i\hbar \frac{d}{dt} c_E(t) = E c_E(t) \quad (13.11)$$



i.e. we get

$$c_E(t) = c_E(t_0)e^{iE(t-t_0)/\hbar} \quad (13.12)$$

and so

$$\psi(\vec{r}, t) = \sum_E c_E(t_0)e^{-iE(t-t_0)/\hbar} \quad (13.13)$$

$$= \sum_E \left( \int \psi_E^*(\vec{r}')\psi(\vec{r}', t_0)d\vec{r}' \right) e^{iE(t-t_0)/\hbar} \quad (13.14)$$

Taking the complex conjugate of this, we get

$$\psi^*(\vec{r}, t) = \sum_{E'} c_{E'}(t_0)\psi_{E'}^*(\vec{r})e^{iE'(t-t_0)/\hbar} \quad (13.15)$$

Then, we let  $c_E = c_E(t_0)e^{iE(t-t_0)/\hbar}$  and require that  $\psi$  integrates to 1, to get

$$1 = \sum_E \sum_{E'} c_{E'}^* c_E e^{-i(E-E')t/\hbar} \int \psi_{E'}^*(\vec{r})\psi_E(\vec{r})d\vec{r} \quad (13.16)$$

$$= \sum_E \sum_{E'} c_{E'}^* c_E e^{-i(E-E')t/\hbar} \delta_{E'E} \quad (13.17)$$

$$1 = \sum_E |c_E|^2 \quad (13.18)$$

The sum of eigenstates has a non-trivial time dependence.

For example, let's try and find the expectation of the Hamiltonian operator for a general state.

$$\langle H \rangle_\psi = \int \psi^*(\vec{r}, t)\hat{H}\psi(\vec{r}, t)d\vec{r} \quad (13.19)$$

$$= \sum_E \sum_{E'} c_{E'}^* c_E e^{-i(E-E')t/\hbar} \int \psi_{E'}^*(\vec{r})\hat{H}\psi_E(\vec{r})d\vec{r} \quad (13.20)$$

$$= \sum_E |c_E|^2 E \quad (13.21)$$

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## Lecture 14: Dirac Notation

*Lecturer: Irfan Siddiqi*

*17 October*

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### 14.1 Motivation

So far, it seems like waves are essential to quantum mechanics, so we'd like a more compact representation of a wavefunction so that we don't have to keep writing out integrals and the definitions of operators. This will allow us to carry out more complicated operations; for example, the expectation value of  $x$  in the 48th state of the harmonic oscillator.

$$\langle x \rangle = \int \psi^* \hat{x} \psi dx, \psi \sim e^{-x^2/2} H_{49}(x) \quad (14.1)$$

A more abstract representation would be helpful here. To do this, we use Dirac notation, or bra-ket notation. This enables us to use matrix methods in quantum mechanics as well as carry out algebraic manipulations more easily. We write down a wavefunction as a ket  $|\psi\rangle$ , and we'll see how to apply operators to it later. For now, we introduce some postulates, based on which we'll build up to a full theory:

- Postulate 1. An ensemble of physical systems can be expressed by a wavefunction containing all the knowable information. If we have a system of  $N$  particles, then a wavefunction  $\psi(r_1, \dots, r_n, t)$  completely expresses the system;  $\psi^* \psi$  gives the probability of particle 1 at  $r_1$ , 2 at  $r_2$ , and so on.
- Postulate 2. Superposition: we want our new formalism to reflect the fact that if  $\psi_1, \psi_2$  are solutions to the Schrödinger equation, then so is  $\psi = c_1 \psi_1 + c_2 \psi_2$ .

### 14.2 The Notation

Dirac notation is a way of denoting an inner product between an adjoint/"bra" on the left of the bracket, and a vector/"ket" on the right.

$$\langle \psi_1 | \psi_2 \rangle = \int \psi_1^*(\vec{r}) \psi_2(\vec{r}) d\vec{r} \quad (14.2)$$

Dirac brackets have the following properties:

1. Conjugate-symmetry:

$$\langle \psi_2 | \psi_1 \rangle^* = \langle \psi_1 | \psi_2 \rangle \quad (14.3)$$

2. Vector scaling:

$$\langle \psi_1 | c\psi_2 \rangle = c \langle \psi_1 | \psi_2 \rangle \quad (14.4)$$

3. Conjugate-adjoint scaling:

$$\langle c\psi_1|\psi_2\rangle = c^* \langle\psi_1|\psi_2\rangle \quad (14.5)$$

4. Superposition of vectors:

$$\langle\psi_3|\psi_1 + \psi_2\rangle = \langle\psi_3|\psi_1\rangle + \langle\psi_3|\psi_2\rangle \quad (14.6)$$

5. Orthonormality of  $\psi$ s: if  $\psi_i, \psi_j$  are orthonormal (e.g. the first and second eigenstates of a harmonic oscillator), then  $\langle\psi_i|\psi_j\rangle = \delta_{ij}$ .

6. Momentum space normalization:  $\langle\Phi|\Phi\rangle = 1$ .

Further, we can introduce Hermitian operators in Dirac notation, and say that they correspond to real eigenvalues. We add the following postulates relating to operators:

Postulate 3. Dynamical variables correspond to linear operators, whose eigenvalues are the observable values.

Postulate 4. A precise measurement of some dynamical variable whose linear operator is  $\hat{A}$  corresponds to one eigenvalue  $a_n$ , and  $\psi$  corresponds to some eigenstate  $\psi_n$ , i.e.  $\hat{A}\psi_n = a_n\psi_n$ .

Postulate 5. A series of measurements on an identical ensemble should give identical results.

In general,

$$\langle x|\hat{A}\psi\rangle = \langle\hat{A}x|\psi\rangle = \langle x|\hat{A}|\psi\rangle \quad (14.7)$$

If  $\psi$  is an eigenfunction, then this allows us to say

$$\langle\psi_n|\hat{A}|\psi_n\rangle = a_n \langle\psi_n|\psi_n\rangle \quad (14.8)$$

Postulate 5 can be simply written as  $\langle\hat{A}\rangle = \frac{\langle\psi|\hat{A}|\psi\rangle}{\langle\psi|\psi\rangle}$ .

Suppose we have some eigenstuff (that's the technical term)  $\hat{A} : \psi_n, a_n$ , and  $\hat{B} : \phi_n, b_n$ : if we measure  $\hat{A}$  or  $\hat{B}$ , we get an eigenstate of that operator. If  $\hat{A}$  and  $\hat{B}$  commute, then they share eigenstates. That is, if you operate  $\hat{A}$  then  $\hat{B}$  on a state and you get the same result as if you'd operated  $\hat{B}$  then  $\hat{A}$ , the eigenstate they're operating on has to be the same.

## 14.3 Adjoint Operators

We define the adjoint operator to an operator as follows:

$$|\phi\rangle = \hat{A}|x\rangle \iff \langle\phi| = \langle x|\hat{A}^\dagger \quad (14.9)$$

This is equivalent to a dual space transformation. In general,  $A^* \neq A^\dagger$ . The rules for taking the adjoint are

1. Conjugate scaling:  $(c\hat{A})^\dagger = c^* \hat{A}^\dagger$ .
2. Superposition:  $(\hat{A} + \hat{B})^\dagger = \hat{A}^\dagger + \hat{B}^\dagger$ .
3. Anticommutativity:  $(\hat{A}\hat{B})^\dagger = \hat{B}^\dagger \hat{A}^\dagger$ .
4. Applying functions:  $[f(\hat{A})]^\dagger = f^*(\hat{A}^\dagger)$ .

## 14.4 Types and Examples of Operators

**Identity operator** Also called the unit operator, it satisfies  $\hat{I}|\psi\rangle = |\psi\rangle$ .

**Inverse operators** Given  $\hat{A}, \hat{B}$ ,  $\hat{B}$  is the inverse of  $\hat{A}$  iff  $\hat{B}\hat{A} = \hat{A}\hat{B} = \hat{I}$ .

**Unitary operators** A linear operator is unitary if  $\hat{U}^{-1} = \hat{U}^\dagger$ . A unitary operator can be written in the form  $\hat{U} = e^{i\hat{A}}$  where  $\hat{A}$  is Hermitian.

**Projection operators** A projection operator has the property that  $\hat{\Lambda}^2 = \hat{\Lambda}$ , i.e. if we project a state twice, it's the same as projecting it once. All projection operators are idempotent.

## 14.5 Applying Operators

To make it easier to act operators on states, we add another postulate:

Postulate 6. In the non-degenerate case, a general wavefunction can be expressed as a sum of eigenfunctions:

$$|\psi\rangle = \sum_n c_n |\psi_n\rangle \quad (14.10)$$

Further, by orthonormality, we can separate the action of the operator into its action on each eigenstate.

Recall the following:

$$\psi(\vec{r}, t) = \sum_n \left( \int \psi_n^*(\vec{r}') \psi(\vec{r}', t) d\vec{r}' \right) \psi_n(\vec{r}) \quad (14.11)$$

$$= \int \left( \sum_n \psi_n^*(\vec{r}') \psi_n(\vec{r}) \right) \psi(\vec{r}', t) d\vec{r}' \quad (14.12)$$

$$\therefore \sum_n \psi_n^*(\vec{r}') \psi_n(\vec{r}) = \delta(\vec{r} - \vec{r}') \quad (14.13)$$

This is called the closure relation. We can use this to write out the application of an operator more easily:

$$\langle x|\psi\rangle = \int x^*(\vec{r}, t)\psi(\vec{r}, t)d\vec{r} \quad (14.14)$$

$$= \int \int x^*(\vec{r}, t)\delta(\vec{r} - \vec{r}')\psi(\vec{r}', t)d\vec{r}d\vec{r}' \quad (14.15)$$

$$= \sum_n \int x^*(\vec{r}, t)\psi_n(\vec{r})d\vec{r} \int \psi_n^*(\vec{r}')\psi(\vec{r}', t)d\vec{r}' \quad (14.16)$$

$$= \sum_n \langle x|\psi_n\rangle \langle \psi_n|\psi\rangle \quad (14.17)$$

This gives us the relation

$$\sum_n |\psi_n\rangle \langle \psi_n| = \hat{I}. \quad (14.18)$$

This is referred to as the outer product of  $\psi_n$  with itself.

## 14.6 Probability Amplitudes

Start with an operator, and have it act on  $\psi$  to the left and right (to find the expectation value):

$$\langle \hat{A} \rangle = \langle \psi | \hat{A} | \psi \rangle \quad (14.19)$$

We can express the right  $\psi$  as a linear combination of eigenfunctions of  $\hat{A}$ , and similarly on the left but with a different index and with a dagger:

$$\langle \hat{A} \rangle = \left( \sum_m c_m |\psi_m\rangle \right)^\dagger \hat{A} \left( \sum_n c_n |\psi_n\rangle \right) \quad (14.20)$$

$$= \left( \sum_m c_m |\psi_m\rangle \right)^\dagger \left( \sum_n c_n a_n |\psi_n\rangle \right) \quad (14.21)$$

Now, we apply orthonormality,

$$\langle \hat{A} \rangle = \sum_m \sum_n c_m^* c_n a_n \langle \psi_m | \psi_n \rangle = \sum_n |c_n|^2 a_n \quad (14.22)$$

i.e. the expectation of an operator is the probabilistic weighted sum of all its eigenvalues (attainable values).

Physics 137A: Quantum Mechanics

Fall 2019

## Lecture 15: Dirac Notation contd.

Lecturer: *Irfan Siddiqi*

22 October

*Aditya Sengupta*

### 15.1 Degenerate States

Recall that if we expand an operator in its eigenbasis, we get

$$\langle \hat{A} \rangle = \langle \psi | \hat{A} | \psi \rangle = \sum_{m,n} c_m^* c_n \langle \psi_m | \hat{A} | \psi_n \rangle \quad (15.1)$$

$$= \sum_n |c_n|^2 a_n \quad (15.2)$$

for  $\hat{A} |\psi_n\rangle = a_n |\psi_n\rangle$ .

If we observe a non-degenerate eigenvalue, then the state collapses into the corresponding eigenstate, but if we have a degenerate eigenvalue, the state is a superposition of the degenerate states. For example, suppose  $a_n$  is repeated  $\alpha$  times for  $\psi_{n_r}, r = 1, \dots, \alpha$ . Then

$$p_n = \sum_{r=1}^{\alpha} |c_{n_r}|^2 \quad (15.3)$$

and the state is

$$\psi = \frac{1}{p_n} \sum_{r=1}^{\alpha} c_{n_r} \psi_{n_r}. \quad (15.4)$$

This generalizes to continuous systems or mixed discrete/continuous systems, i.e.

$$\langle \hat{A} \rangle = \sum_n |c_n|^2 a_n + \int |c(x)|^2 a_x dx \quad (15.5)$$

for eigenvalues  $a_x$  of a continuous variable  $x$ .

### 15.2 Commuting Observables

The headline: if two observables commute, they share eigenfunctions, and vice versa.

Let  $[\hat{A}, \hat{B}] = \hat{A}\hat{B} - \hat{B}\hat{A}$ . The two operators commute if and only if  $[\hat{A}, \hat{B}] = 0$ . Suppose both are observable, and there exists a complete set of functions that are simultaneously eigenfunctions of both  $\hat{A}$  and  $\hat{B}$ . Then for each  $|\psi_n\rangle$ ,

$$\hat{A}|\psi_n\rangle = a_n|\psi_n\rangle, \hat{B}|\psi_n\rangle = b_n|\psi_n\rangle \quad (15.6)$$

so we can easily see the commutator will be  $a_nb_n - b_na_n = 0$ . The converse is also true but is harder to prove.

### 15.3 Uncertainty Relations

Define  $\sigma_A = \left(\langle(\hat{A} - \langle\hat{A}\rangle)^2\rangle\right)^{1/2}$  and  $\sigma_B$  similarly. Then the lower limit on the product of uncertainties is given by

$$\sigma_A\sigma_B \geq \frac{1}{2} \left| \langle[\hat{A}, \hat{B}]\rangle \right|^2 \quad (15.7)$$

If  $\hat{A} = \hat{x}$  and  $\hat{B} = \hat{p}$ , this gives us the Heisenberg uncertainty relation:  $\Delta x \Delta p \geq \frac{\hbar}{2}$ .

### 15.4 Unitary Operators

Unitary operators are the generators of symmetries. They must leave a physical system unchanged. That is, if  $\hat{A}|\psi\rangle = |x\rangle$ , and  $|\psi'\rangle = \hat{U}|\psi\rangle$ ,  $|x'\rangle = \hat{U}|x\rangle$ , then we have  $\hat{A}'|\psi'\rangle = |x'\rangle$ . More explicitly, this is

$$\hat{A}'\hat{U}|\psi\rangle = \hat{U}|x\rangle = \hat{U}\hat{A}|\psi\rangle. \quad (15.8)$$

If  $\hat{U}$  is unitary,  $\hat{U}\hat{U}^\dagger = \hat{U}^\dagger\hat{U} = \hat{1}$ , so

$$\hat{A}' = \hat{U}\hat{A}\hat{U}^\dagger. \quad (15.9)$$

Under a unitary transformation, Hermitian operators remains Hermitian. Operator equations are unchanged, and the operator has the same eigenvalues before and after the transformation. Matrix elements are also unchanged:

$$\langle x|\hat{A}\psi\rangle = \langle x'|\hat{A}'\psi'\rangle \quad (15.10)$$

## 15.5 Infinitesimal unitary transforms

Consider an infinitesimal unitary transformation,  $\hat{U} = \hat{1} + i\epsilon\hat{F}$  for a small  $\epsilon$  and a Hermitian  $\hat{F}$ . This is called the generator of  $\hat{U}$ . A state under this transformation is

$$|\psi'\rangle = |\psi\rangle + |\delta\psi\rangle = |\psi\rangle + i\epsilon\hat{F}|\psi\rangle, \quad (15.11)$$

and an operator is

$$\hat{A}' = \hat{A} + \delta\hat{A} = (\hat{1} + i\epsilon\hat{F})\hat{A}(\hat{1} - i\epsilon\hat{F}) = \hat{A} + i\epsilon[\hat{F}, \hat{A}] + O(\epsilon^2), \quad (15.12)$$

so

$$\delta\hat{A} = i\epsilon[\hat{F}, \hat{A}]. \quad (15.13)$$

## 15.6 Matrix representations

Choose an eigenbasis  $\{|\psi_n\rangle\}$ . Then

$$|\psi\rangle = \sum_n c_n |\psi_n\rangle, c_n = \langle\psi_n|\psi\rangle. \quad (15.14)$$

Also,

$$|x\rangle = \sum_m d_m |\psi_m\rangle, d_m = \langle\psi_m|x\rangle. \quad (15.15)$$

Then  $|x\rangle = \hat{A}|\psi\rangle$ , so we can derive a relation between the  $d_m$ s and  $c_n$ s:

$$d_m = \langle\psi_m|\hat{A}\psi\rangle = \sum_n \langle\psi_m|\hat{A}\psi_n\rangle c_n \quad (15.16)$$

Define  $A_{mn} = \langle\psi_m|\hat{A}\psi_n\rangle$ , so we have the matrix representations we expect:

$$|x\rangle = \begin{bmatrix} d_1 \\ d_2 \\ \vdots \end{bmatrix}_{\{|\psi_n\rangle\}} = \begin{bmatrix} a_{11} & a_{12} & \dots \\ a_{21} & a_{22} & \dots \\ & & \ddots \end{bmatrix} \begin{bmatrix} c_1 \\ c_2 \\ \vdots \end{bmatrix}_{\{|\psi_n\rangle\}} \quad (15.17)$$



We denote this matrix representation by  $[\hat{A}]$ . The operator being Hermitian implies

$$[\hat{A}^{-1}] = [\hat{A}]^{-1}, [\hat{A}]^\dagger = ([\hat{A}]^*)^\top. \quad (15.18)$$

## 15.7 Time evolution of a system

Time evolution is unitary, so it is generated by some Hermitian operator.

$$|\psi(t)\rangle = \hat{U}(t, t_0) |\psi(t_0)\rangle. \quad (15.19)$$

We decompose  $\hat{U}$  into the composition of tiny time translations:

$$\hat{U}(t, t_0) = \hat{U}(t, t_n) \hat{U}(t_n, t_{n-1}) \dots \hat{U}(t_1, t_0). \quad (15.20)$$

Also,  $\hat{U}(t_0, t) = \hat{U}(t, t_0)^{-1}$ . Substituting this into the time-dependent Schrödinger equation, we get

$$\hat{U}(t - t_0) = \hat{1} - \frac{i}{\hbar} \int_{t_0}^t \hat{H} \hat{U}(t', t_0) dt' \quad (15.21)$$

Expanding derivatives, we get  $\hat{U}(t_0 + \delta t, t_0) = \hat{1} - \left(\frac{i}{\hbar} \hat{H}\right) \delta t$ . So the Hamiltonian generates time translation!

Lecture 16: Time dependence

Lecturer: *Irfan Siddiqi*

29 October

*Aditya Sengupta*

A complete basis of functions (such as eigenfunctions of an operator) is all we need to express any state. Every state is some combination of steady states for a system. Dynamics are governed by the TDSE,

$$i\hbar \frac{\partial \psi}{\partial t} = \hat{H}\psi, \tag{16.1}$$

the solution to which gives us time translation as the exponential of a Hermitian operator, the Hamiltonian:

$$\psi(t) = e^{(-i/\hbar)\hat{H}(t-t_0)}\psi(0), \tag{16.2}$$

which can be expanded in a series as

$$\hat{U}(t, t_0) = \sum_{n=0}^{\infty} \frac{1}{n!} \left(\frac{-i}{\hbar}\right)^n \hat{H}^n (t - t_0)^n \tag{16.3}$$

Consider the time dependence of an expectation value:

$$\frac{d}{dt}\langle \hat{A} \rangle = \frac{d}{dt} \langle \psi | \hat{A} \psi \rangle \tag{16.4}$$

$$= \frac{\partial}{\partial t} \langle \psi | \hat{A} \psi \rangle + \left\langle \psi \left| \frac{\partial}{\partial t} \hat{A} \psi \right. \right\rangle + \left\langle \psi \left| \hat{A} \frac{\partial}{\partial t} \psi \right. \right\rangle \tag{16.5}$$

$$= \frac{d}{dt} \langle \hat{A} \rangle = \frac{1}{i\hbar} \langle [\hat{A}, \hat{H}] \rangle + \left\langle \frac{\partial}{\partial t} \hat{A} \right\rangle \tag{16.6}$$

If  $\langle \frac{\partial}{\partial t} \hat{A} \rangle = 0$ , then  $\hat{A}$  commutes with  $\hat{H}$  and  $\hat{A}$  is conserved.

We can use operators to re-solve the harmonic oscillator! See Problem Set 9 for that.

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## Lecture 17: Spooky

Lecturer: *Irfan Siddiqi*

31 October

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### 17.1 Spooky angular momentum

Suppose we've measured  $x$  in a quantum system. Then, we can measure simultaneously with arbitrary precision any quantity whose commutator with  $\hat{x}$  is zero. For example,  $[\hat{x}, \hat{y}] = 0$ , and although  $[\hat{x}, \hat{p}_x] \neq 0$ , we can measure the  $y$  momentum as  $[\hat{x}, \hat{p}_y] = 0$ .

Consider angular momentum,  $\vec{L} = \vec{r} \times \vec{p}$ . We can calculate the components according to

$$\begin{aligned} L_x &= yP_z - zP_y \\ L_y &= zP_x - xP_z \\ L_z &= xP_y - yP_x \end{aligned}$$

We can't measure multiple components of angular momentum at once, because they don't commute.  $L^2$  does commute with all the components of angular momentum, but it can't be measured classically.

Based on the above definitions, we can explicitly write out each component of angular momentum,

$$\hat{L}_x = -i\hbar \left( y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y} \right) \quad (17.1)$$

and similarly by cyclically permuting  $x, y, z$  we can write out the other two.

$$[L_x, L_y] = [(yP_z - zP_y), (zP_x - xP_z)] = [yP_z, zP_x] + [zP_y, xP_z] - [yP_z, xP_z] - [zP_y, zP_x] \quad (17.2)$$

We rewrite the first term as  $yP_z zP_x - zP_x yP_z = yP_x [P_z z - zP_z] = -i\hbar y P_x$ . Proceed similarly for the other terms, and we get

$$[L_x, L_y] = i\hbar(xP_y - yP_x) = i\hbar L_z \quad (17.3)$$

Based on this, we can show that  $L^2$  commutes, like we claimed above:

$$[L^2, L_x] = [L_x^2 + L_y^2 + L_z^2, L_x] = [L_y^2 + L_z^2, L_x] = [L_y^2, L_x] + [L_z^2, L_x] \quad (17.4)$$

We can pull out one of the squared factors like this:

$$[L_y^2, L_x] = L_y[L_y, L_x] + [L_y, L_x]L_y \quad (17.5)$$

Therefore

$$[L^2, L_x] = L_y[L_y, L_x] + [L_y, L_x]L_y + L_z[L_z, L_x] + [L_z, L_x]L_z = \text{algebra} = 0 \quad (17.6)$$

## 17.2 Spooky spherical coordinates

This one actually is spooky because he says mathematicians use the wrong coordinate system.  $\theta$  is the polar angle and  $\varphi$  is the azimuthal angle. We can rewrite the component-wise angular momentum as follows:

$$L_x = -i\hbar \left( \sin \varphi \frac{\partial}{\partial \theta} - \cot \theta \cos \varphi \frac{\partial}{\partial \varphi} \right) \quad (17.7)$$

$$L_y = -i\hbar \left( \cos \varphi \frac{\partial}{\partial \theta} + \cot \theta \sin \varphi \frac{\partial}{\partial \varphi} \right) \quad (17.8)$$

$$L_z = -i\hbar \frac{\partial}{\partial \varphi} \quad (17.9)$$

and their squared sum:

$$L^2 = -\hbar^2 \left[ \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \varphi^2} \right] \quad (17.10)$$

Note that  $r$  is absent from these expressions: this lets us write  $[L_x, f(r)] = 0$  and also  $[L^2, f(r)] = 0$ .

## 17.3 Eigenvalues and eigenfunctions of angular momentum

Consider the eigenfunctions of  $\hat{L}_z$ . Let's say the eigenfunction with eigenvalue  $m\hbar$  is  $\Phi_m(\varphi)$ . To check this ansatz, we operate  $\hat{L}_z$  on it:

$$\hat{L}_z \Phi_m(\varphi) = m\hbar \Phi_m(\varphi) \quad (17.11)$$

$$-i \frac{\partial}{\partial \varphi} \Phi_m(\varphi) = m \Phi_m(\varphi) \quad (17.12)$$

$$\therefore \Phi_m(\varphi) = \frac{1}{\sqrt{2\pi}} e^{im\varphi} \quad (17.13)$$

Further, we can require that  $\Phi_m(2\pi) = \Phi_m(0)$  which tells us that  $m$  can only take on  $2\pi$ -integer values. Therefore  $m$  is quantized - which agrees with the Bohr model of the atom!

The  $\Phi_m$ s are a complete orthonormal set, i.e.

$$\int_0^{2\pi} \Phi_{m'}^*(\varphi)\Phi_m(\varphi)d\varphi = \delta_{m'm} \quad (17.14)$$

Therefore if we say  $f(\varphi) = \sum_{m=-\infty}^{\infty} a_m \Phi_m(\varphi)$  then  $a_m = \int_0^{2\pi} \Phi_m^*(\varphi)f(\varphi)d\varphi$ .

Further, since  $\hat{L}_z$  commutes  $\hat{L}^2$ , they share eigenfunctions. As an ansatz, let's say the general eigenfunction shared by both is  $Y_{l,m}(\theta, \varphi)$  and the  $\hat{L}^2$  eigenvalue is  $l(l+1)\hbar^2$ . Then

$$L^2 Y_{l,m}(\theta, \varphi) = l(l+1)\hbar^2 Y_{l,m}(\theta, \varphi) \quad (17.15)$$

$$L_z Y_{l,m}(\theta, \varphi) = m\hbar Y_{l,m}(\theta, \varphi) \quad (17.16)$$

Let's look for a separable solution, of the form  $Y_{l,m}(\theta, \varphi) = \Theta_{l,m}(\theta)\Phi_m(\varphi)$ . Act  $L^2$  on this, and we get

$$\left[ \frac{1}{\sin \theta} \frac{d}{d\theta} \left( \sin \theta \frac{d}{d\theta} \right) + \left( l(l+1) - \frac{m^2}{\sin^2 \theta} \right) \right] \Theta_{l,m}(\theta) = 0 \quad (17.17)$$

Let  $\omega = \cos \theta$ . Then this equation becomes

$$\left[ (1-\omega^2) \frac{d^2}{d\omega^2} - 2\omega \frac{d}{d\omega} + l(l+1) - \frac{m^2}{1-\omega^2} \right] F_{lm}(\omega) = 0 \quad (17.18)$$

If we set  $m = 0$ , this is the Legendre equation. We follow the same process that we used to find the Hermite polynomials, to get the Legendre polynomials:

$$P_l(\omega) = 2^{-l} (l!)^{-1} \frac{d^l}{d\omega^l} (\omega^2 - 1)^l \quad (17.19)$$

Based on this, we can write out the full solution:

$$Y_{l,m}(\theta, \varphi) = (-1)^m \left( \frac{(2l+1)(l-m)!}{4\pi(l+m)!} \right)^{1/2} P_l^m(\cos \theta) e^{im\varphi}$$

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## Lecture 18: More on angular momentum

Lecturer: Irfan Siddiqi

5 November

Aditya Sengupta

### 18.1 Raising and lowering angular momentum

To recap,  $\vec{L} = \vec{r} \times \vec{p}$ , and using known commutators, namely  $[\hat{p}_i, \hat{p}_j] = 0$ ,  $[\hat{r}_i, \hat{r}_j] = 0$ , and  $[\hat{r}_i, \hat{p}_j] = i\hbar\delta_{ij}$ , we can write down a commutation relation for angular momentum:

$$[\hat{L}_i, \hat{L}_j] = i\hbar\hat{L}_k, \quad (18.1)$$

and  $[\hat{L}^2, \hat{L}_z] = 0$ , so we get simultaneous eigenfunctions  $Y_{lm}(\theta, \phi)$ , the spherical harmonics. These have eigenvalues  $l(l+1)\hbar^2$  for  $\hat{L}^2$  and  $m\hbar$  for  $\hat{L}_z$ , where  $l \in \mathbb{N}$  and  $m \in [-l, l] \cap \mathbb{N}$ . We can expand any state in this eigenbasis:

$$\psi(\theta, \varphi) = \sum_{l=0}^{\infty} \sum_{m=-l}^l a_{lm} Y_{lm}(\theta, \varphi), \quad (18.2)$$

and by Fourier analysis, we can extract these coefficients,

$$a_{lm} = \int Y_{lm}^* \psi d\Omega. \quad (18.3)$$

This connects to chemistry:  $l = 0$  are  $s$  orbitals,  $l = 1$  are  $p$  orbitals,  $l = 2$  are  $d$  orbitals, and so on.

Since we've enumerated the states with a constant  $l$  by an index  $m$ , it's natural to think we can construct them by iterating up and down  $m$ , and we can! Angular momentum states can be constructed using raising and lowering operators. To construct these, consider

$$\hat{L}_{\pm} = \hat{L}_x \pm i\hat{L}_y. \quad (18.4)$$

These are conjugate pairs:  $\hat{L}_{\pm}^{\dagger} = \hat{L}_{\mp}$ . Also, their commutator with  $\hat{L}^2$  is 0. However, they do not commute with each other, as can be seen by taking a product:

$$\hat{L}_{\pm}\hat{L}_{\mp} = \hat{L}^2 - \hat{L}_z^2 \pm \hbar\hat{L}_z \implies [\hat{L}_+, \hat{L}_-] = 2\hbar\hat{L}_z. \quad (18.5)$$

Also,

$$[\hat{L}_z, \hat{L}_\pm] = \pm \hbar \hat{L}_\pm. \quad (18.6)$$

Consider acting these operators on elements of the eigenbasis  $Y_{lm}(\theta, \varphi) = \langle \theta, \varphi | lm \rangle$ :

$$\hat{L}_\pm \hat{L}_z |lm\rangle = \hat{L}_\pm (m\hbar) |lm\rangle. \quad (18.7)$$

Also, from the commutator,

$$\hat{L}_\pm \hat{L}_z |lm\rangle = (\hat{L}_z \hat{L}_\pm \mp \hbar \hat{L}_\pm) |lm\rangle, \quad (18.8)$$

so,

$$\hat{L}_z \hat{L}_\pm |lm\rangle = (m \pm 1)\hbar \hat{L}_\pm |lm\rangle \quad (18.9)$$

The  $\hat{L}_\pm$  operators have changed the  $z$  component of  $\vec{L}$  by  $\hbar$ .

You can do a similar process with  $\hat{L}^2$ , but we would find no change: the operators can only change  $l$ , not  $m$ .

## 18.2 Other components of angular momentum

Consider the state  $|lm\rangle$ .

$$\langle \hat{L}_x \rangle = \langle lm | \hat{L}_x | lm \rangle = \frac{1}{2} \langle lm | (\hat{L}_x + \hat{L}_-) | lm \rangle = 0. \quad (18.10)$$

Similarly,  $\langle \hat{L}_y \rangle = 0$ . We can get the specific relation between a state and its raised or lowered counterpart, as well:

$$\hat{L}_\pm |lm\rangle = \hbar (l(l+1) - m(m \pm 1))^{1/2} |l, m \pm 1\rangle. \quad (18.11)$$

The expectation values of the components-squared can be found as follows:

$$\langle \hat{L}_x^2 \rangle = \langle \hat{L}_y^2 \rangle = \frac{1}{2} \langle \hat{L}^2 - \hat{L}_z^2 \rangle = \frac{1}{2} (l(l+1) - m^2) \hbar^2. \quad (18.12)$$

The  $l(l+1)$  part adds some uncertainty. Suppose  $l = 2, m = 0$ . Then, we measure  $|\hat{L}^2| = \sqrt{6}\hbar > 2\hbar$ , so there must be some nonzero  $x$  and  $y$  components.

For example, a particle on a sphere of radius  $a$  has a Hamiltonian of  $\frac{\hat{L}^2}{2I}$ , where  $I$  is the moment of inertia. The Hamiltonian is

$$\hat{H} = \frac{\hat{L}^2}{2I} + \hat{V}(\theta, \varphi). \quad (18.13)$$

If  $\hat{V} = 0$ , then the Hamiltonian is just a scaled version of the angular momentum, so we know we have energies of  $\frac{l(l+1)\hbar^2}{2I}$ !



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## Lecture 19: Generalized Angular Momentum

Lecturer: Irfan Siddiqi

7 November

Aditya Sengupta

The kinetic energy operator in spherical coordinates is

$$\hat{T} = \frac{\hat{p}^2}{2m} = -\frac{\hbar^2}{2m} \left( \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2}{\partial \varphi^2} \right) \quad (19.1)$$

$$= -\frac{\hbar^2}{2m} \left( \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right) - \frac{\hat{L}^2}{\hbar^2 r^2} \right) \quad (19.2)$$

If we consider a free particle on a surface (a good model for diatomic molecules), we can say  $V = 0$  and  $r$  is constant.

Let's look at generalized angular momentum  $\vec{J}$  (I'm not sure of the physical relevance of this, I'd have to go back to the last lecture), satisfying the relation  $[\hat{J}_x, \hat{J}_y] = i\hbar \hat{J}_z$  (and the other two that we get by cyclically permuting this one). Further, we construct  $\hat{J}^2 = \hat{J}_x^2 + \hat{J}_y^2 + \hat{J}_z^2$ . Like we saw with the usual angular momentum,  $[\hat{J}^2, \hat{J}_x] = 0$ : the overall angular momentum squared commutes with each of its components. This means that  $\hat{J}^2$  and, say,  $\hat{J}_z$  share eigenfunctions. Let's say the quantum number associated with  $\hat{J}^2$  is  $j$ , and that associated with  $\hat{J}_z$  is  $m$ . Then, we can place these in a ket  $|jm\rangle$ , satisfying

$$\hat{J}^2 |jm\rangle = j(j+1)\hbar^2 |jm\rangle \quad (19.3)$$

$$\hat{J}_z |jm\rangle = m\hbar |jm\rangle \quad (19.4)$$

We can then define and use the raising and lowering operators:

$$\hat{J}_+ = \hat{J}_x + i\hat{J}_y \quad (19.5)$$

$$\hat{J}_- = \hat{J}_x - i\hat{J}_y \quad (19.6)$$

Applying these to the ket we defined above gives us

$$\hat{J}_+ |jm\rangle = [j(j+1) - m(m+1)]^{1/2} \hbar |j, m+1\rangle \quad (19.7)$$

$$\hat{J}_- |jm\rangle = [j(j+1) - m(m-1)]^{1/2} \hbar |j, m-1\rangle \quad (19.8)$$

We can verify that  $\hat{J}^2$  commutes with  $\hat{J}_\pm$ . Also, we can calculate the commutator between the two:

$$\hat{J}_\pm \hat{J}_\mp = \hat{J}^2 - \hat{J}_z \pm \hbar \hat{J}_z \quad (19.9)$$

$$[\hat{J}_+, \hat{J}_-] = 2\hbar \hat{J}_z \quad (19.10)$$

$$[\hat{J}_z, \hat{J}_\pm] = \pm \hbar \hat{J}_\pm \quad (19.11)$$

There is some maximum and some minimum value for  $m$ : say they're  $m_T$  and  $m_B$  respectively. We don't know what these are, but we know that  $m_T - m_B$  has to be some nonnegative integer  $n$ .

$$\hat{J}_+ \quad (19.12)$$

$$\text{ket}jm_T = 0 \quad (19.13)$$

$$\hat{J}_-(\hat{J}_+ |jm_T\rangle) = (J^2 - J_z^2 - \hbar J_z) |jm_T\rangle \quad (19.14)$$

$$= (j(j+1) - m_T^2 - m_T)\hbar^2 |jm_T\rangle = 0 \quad (19.15)$$

Therefore  $j(j+1) = m_T^2 + m_T$ . Analogously, we can say that

$$\hat{J}_+\hat{J}_- |jm_B\rangle = [j(j+1) - m_B^2 + m_B]\hbar^2 |jm_B\rangle = 0 \quad (19.16)$$

Therefore  $j(j+1) = m_B^2 - m_B$ . Setting these two equal, we get that either  $m_T = m_B - 1$  (rejected as we can't have the highest state lower than the lowest state) or  $m_T = -m_B$ . This tells us that  $m_T = j$  and  $m_B = -j$ . Therefore  $m_T - m_B = 2j$ , which can take on any positive integer values. This gives us that the allowed values of  $j$  are  $0, \frac{1}{2}, 1, \frac{3}{2}, \dots$ . This structure is how we describe spin.

If we take the inner product of any state  $jm$  with any other state, we get  $\langle j'm' | jm \rangle = \delta_{j'j} \delta_{m'm}$  by orthogonality. I lost track of the motivation to look at the following quantity, but

$$[\hat{J}^2]_{j'm'} = \langle j'm' | \hat{J}^2 | jm \rangle = j(j+1)\hbar^2 \langle j'm' | jm \rangle = j(j+1)\hbar^2 \delta_{j'j} \delta_{m'm} \quad (19.17)$$

This gives us the structure of a diagonal matrix.

Similarly,  $[\hat{J}_z] = m\hbar \delta_{j'j} \delta_{m'm}$ , and so

$$[J_+] = [j(j+1) - m(m+1)]^{1/2} \hbar \delta_{j'j} \delta_{m', m+1} \quad (19.18)$$

and from this we can construct the other components of generalized angular momentum:  $\hat{J}_x = \frac{1}{2}(\hat{J}_+ + \hat{J}_-)$ , and  $\hat{J}_y = \frac{1}{2i}(\hat{J}_+ - \hat{J}_-)$ .

We can calculate some components by fixing  $j$  and  $m$ : if  $j = 0, m = 0$ , then  $J_x = J^2 = J_z = J_y = 0$ . This isn't too interesting.

If  $j = \frac{1}{2}$ , then  $m = -\frac{1}{2}, \frac{1}{2}$ , and we get

$$J^2 = \frac{3}{4}\hbar^2 \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}, J_x = \frac{\hbar}{2} \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}$$

$$J_z = \frac{\hbar}{2} \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}, J_y = \frac{\hbar}{2} \begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix}$$

Therefore, in general, we can write  $J$  as the combination of Jordan blocks: down the diagonal, we first have the matrix for  $j = 0$ , then the matrix for  $j = \frac{1}{2}$ , then the matrix for  $j = 1$ , and so on.

Let's replay all of the above while specifying that the generalized angular momentum we're interested in is spin. Elementary particles have an internal degree of freedom called spin, described as an angular momentum. Call this  $\hat{s}$ . We know from the theory of generalized angular momentum that we built up that

$$[\hat{s}_x, \hat{s}_y] = i\hbar\hat{s}_z \quad (19.19)$$

and that we can find simultaneous eigenfunctions of  $\hat{s}^2$  and  $\hat{s}_z$ :

$$\hat{s}^2 |sm_s\rangle = s(s+1)\hbar^2 |sm_s\rangle \quad (19.20)$$

$$\hat{s}_z |sm_s\rangle = m_s\hbar |sm_s\rangle \quad (19.21)$$

The eigenvalue  $s$  can take on values  $0, \frac{1}{2}, 1, \frac{3}{2}$  and  $m_s$  has  $2s+1$  values:  $-s, -s+1, -s+2, \dots, s$ . Particles with integer  $s$  are called bosons, and half-integer  $s$  are called fermions. We can write out the spin-one matrices:

$$s_z = \hbar \begin{bmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{bmatrix} \quad (19.22)$$

$$s^2 = 2\hbar^2 \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \quad (19.23)$$

$$s_x = \frac{\hbar}{\sqrt{2}} \begin{bmatrix} 0 & 1 & 0 \\ 1 & 0 & 1 \\ 0 & 1 & 0 \end{bmatrix} \quad (19.24)$$

$$s_y = \frac{\hbar}{\sqrt{2}} \begin{bmatrix} 0 & -i & 0 \\ i & 0 & -i \\ 0 & i & 0 \end{bmatrix} \quad (19.25)$$

The eigenvectors corresponding to each value of  $m_s$  are

$$m_s = \hbar : \chi_{1,1} = \begin{bmatrix} 1 \\ 0 \\ 0 \end{bmatrix} \quad (19.26)$$

$$m_s = 0 : \chi_{1,0} = \begin{bmatrix} 0 \\ 1 \\ 0 \end{bmatrix} \quad (19.27)$$

$$m_s = -\hbar : \chi_{1,-1} = \begin{bmatrix} 0 \\ 0 \\ 1 \end{bmatrix} \quad (19.28)$$

We can write down a wavefunction indicating the (uncertainty of the spin state?)

$$\psi(\vec{r}, t, \sigma) = \sum_{m_s=-s}^{m_s=+s} \psi_{m_s}(\vec{r}, t) \chi_{s, m_s} \quad (19.29)$$

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## Lecture 20: Spin one-half systems

*Lecturer: Irfan Siddiqi*

*12 November*

*Aditya Sengupta*

We can interpret the wavefunction we got in the previous lecture as follows:  $|\psi_{m_s}(\vec{r}, t)|^2 d^3\vec{r}$  is the probability of finding the particle at  $\vec{r}$  within  $d^3\vec{r}$ , with  $m_s$  spin in the  $z$  direction. This is a joint discrete-continuous distribution: if we want position independent of spin at  $\vec{r}$ , we can write the probability as a sum,

$$P = \sum_{m_s=-s}^s |\psi_{m_s}(\vec{r}, t)|^2 d^3\vec{r}, \quad (20.1)$$

and if we want spin independent of position, we can write it as an integral,

$$P = \int |\psi_{m_s}(\vec{r}, t)|^2 d^3\vec{r}. \quad (20.2)$$

### 20.1 Spin one-half systems

We'll consider spin  $\frac{1}{2}$  particles in detail. This is a model that is accurate to electrons and protons, among others. They are particles with  $s = \frac{1}{2}$  and  $m_s \in \{-\frac{1}{2}, \frac{1}{2}\}$ , meaning a state is a combination of  $\chi_{1/2, -1/2}$  and  $\chi_{1/2, 1/2}$ .

The action of each of the spin operators is as follows:

$$\hat{S}^2 |\uparrow\rangle = \frac{3}{4}\hbar^2 |\uparrow\rangle \quad (20.3)$$

$$\hat{S}^2 |\downarrow\rangle = \frac{3}{4}\hbar^2 |\downarrow\rangle \quad (20.4)$$

$$\hat{S}_z |\uparrow\rangle = \frac{\hbar}{2} |\uparrow\rangle \quad (20.5)$$

$$\hat{S}_z |\downarrow\rangle = \frac{-\hbar}{2} |\downarrow\rangle \quad (20.6)$$

These are eigenequations, but the ones for  $\hat{S}_x$  and  $\hat{S}_y$  are not. We can get them from the raising and lowering operators:

$$\hat{S}_+ |\uparrow\rangle = 0 \quad (20.7)$$

$$\hat{S}_+ |\downarrow\rangle = \hbar |\uparrow\rangle \quad (20.8)$$

$$\hat{S}_- |\uparrow\rangle = \hbar |\downarrow\rangle \quad (20.9)$$

$$\hat{S}_- |\downarrow\rangle = 0, \quad (20.10)$$

and from there, we get  $\hat{S}_x = \frac{S_+ + S_-}{2}$  and  $\hat{S}_y = \frac{S_+ - S_-}{2i}$ . They act on the spin  $\frac{1}{2}$  basis as follows:

$$\hat{S}_x |\uparrow\rangle = \frac{\hbar}{2} |\downarrow\rangle \quad (20.11)$$

$$\hat{S}_x |\downarrow\rangle = \frac{\hbar}{2} |\uparrow\rangle \quad (20.12)$$

$$\hat{S}_y |\uparrow\rangle = \frac{i\hbar}{2} |\downarrow\rangle \quad (20.13)$$

$$\hat{S}_y |\downarrow\rangle = \frac{-i\hbar}{2} |\uparrow\rangle \quad (20.14)$$

In matrices, we choose a basis  $\{|\uparrow\rangle, |\downarrow\rangle\}$ . With this choice, we can construct the Pauli spin matrices:

$$[\hat{S}_z] = \frac{\hbar}{2} \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} \quad (20.15)$$

$$[\hat{S}_y] = \frac{\hbar}{2} \begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix} \quad (20.16)$$

$$[\hat{S}_x] = \frac{\hbar}{2} \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} \quad (20.17)$$

$$[\hat{S}^2] = \frac{3}{4}\hbar^2 \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} \quad (20.18)$$

The relationship between these matrices can be explicitly found to be  $\hat{S}_i \hat{S}_j = \frac{i\hbar \epsilon_{ijk}}{2} \hat{S}_k$ . The higher-dimensional generalizations of these are called the Gell-Mann matrices. The spin matrices  $\sigma_{x,y,z} = \frac{[\hat{S}_{x,y,z}]}{\hbar/2}$  all have a zero trace, a negative-unit determinant, and form a basis of SU(2) together with the identity.

## 20.2 Sum of angular momenta

We'll now work with  $\vec{J} = \vec{L} + \vec{S}$ , the sum of orbital and spin angular momenta.  $\vec{J}$  generates rotations:

$$\hat{U}_n(\alpha) = e^{-i/\hbar(\alpha \hat{n} \cdot \vec{J})} \quad (20.19)$$

where  $\alpha$  is the angle and  $\hat{n}$  is the axis.

We can combine the two angular momenta we're interested in into a single ket  $|j_1 j_2 m_1 m_2\rangle$ . We can put further restrictions on this. In particular, since we're taking  $\hat{J}^2$  and  $\hat{J}_z$  as our canonical observables, we can describe a state either by a sum and lengths  $|j_T, m_T, j_1, j_2\rangle$  or by a sum and  $z$  projection  $|j_T, m_T, m_1, m_2\rangle$ .

We could take  $\vec{J}_T^2$  as an observable, but we'll see that doesn't commute with  $\hat{J}_{1z}, \hat{J}_{2z}$ , so that isn't a good choice of basis.

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## Lecture 21: Spin systems, 3D problems

Lecturer: Irfan Siddiqi

14 November

Aditya Sengupta

### 21.1 Adding angular momenta

Suppose we have two particles with momenta  $\vec{J}_1, \vec{J}_2$ . We can describe their state in a ket  $|j_1 j_2 m_1 m_2\rangle$ . Their momenta commute because they're from different particles, so we can write the total angular momentum:

$$\vec{J} = \vec{J}_1 + \vec{J}_2 \quad (21.1)$$

$$(21.2)$$

This allows us to write down  $\vec{J}^2$  and  $\vec{J}_z$ :

$$\vec{J}^2 = (\vec{J}_1 + \vec{J}_2)^2 = \vec{J}_1^2 + \vec{J}_2^2 + 2\vec{J}_1 \cdot \vec{J}_2 \quad (21.3)$$

$$\vec{J}_z = \vec{J}_{1z} + \vec{J}_{2z} \quad (21.4)$$

These two should commute. We can get the eigenvalue for  $\vec{J}_z$ :

$$\vec{J}_z |j_1 j_2 m_1 m_2\rangle = (\vec{J}_{1z} + \vec{J}_{2z}) |j_1 j_2 m_1 m_2\rangle = (m_1 + m_2)\hbar |j_1 j_2 m_1 m_2\rangle \quad (21.5)$$

However, when you write out the componentwise representation of  $\vec{J}^2$ , we get cross terms which don't commute with  $\vec{J}_z$ . Therefore, we can't measure  $\vec{J}^2, \vec{J}_z, \vec{J}_{1z}, \vec{J}_{2z}$  all at once. But we can measure  $\vec{J}^2, \vec{J}_z, \vec{J}_1^2, \vec{J}_2^2$ .

In  $\vec{J}_1$  we have  $2j_1 + 1$  states, and in  $\vec{J}_2$  we have  $2j_2 + 1$  states. Therefore, the total system has  $(2j_1 + 1)(2j_2 + 1)$  states. The associated wavefunctions are denoted  $\psi_{j_1 j_2 m_1 m_2}(1, 2)$ . We can explicitly find the state by:

$$|j_1 j_2 j m\rangle = \sum_{m_1 m_2} \langle j_1 j_2 m_1 m_2 | j m\rangle |j_1 j_2 m_1 m_2\rangle \quad (21.6)$$

The operator we're adjoining is given by the Clebsch-Gordon coefficients, which can be looked up.

**Example 21.1.** Consider the case  $j_1 = 1, j_2 = \frac{3}{2}$ . The allowed values of  $m_1$  are  $1, 0, -1$  and the allowed values of  $m_2$  are  $\frac{3}{2}, \frac{1}{2}, -\frac{1}{2}, -\frac{3}{2}$ . This lets us build a table of all the allowed states:

$m_1$	$m_2$	$m$	$j$
1	3/2	5/2	5/2
0	3/2	3/2	5/2, 3/2
1	1/2		
-1	3/2	1/2	5/2, 3/2, 1/2
0	1/2		
1	-1/2		
-1	-1/2	-1/2	5/2, 3/2, 1/2
0	-1/2		
1	-3/2		
-1	-1/2	-3/2	5/2, 3/2
-1	-3/2	-5/2	5/2

□

Let's look at the case of a single particle, where we're interested in its spin and angular momentum.

$$\psi_{lm_lsm_s} = Y_{lm_l}(\theta, \varphi)\chi_{s,m_s} \quad (21.7)$$

Suppose we take  $\vec{L} + \vec{S} = \vec{J}$ . Then  $j = |l - s|, |l - s| + 1, \dots, l + s$ . Then we can measure  $J^2, J_z, L^2, S^2$  and we get

$$\mathcal{Y}_{ls}^{jm_j} = \sum_{m_l m_s} \langle lsm_l m_s | jm_j \rangle \psi_{lsm_l m_s} \quad (21.8)$$

For example, for spin one-half, we get

$$\mathcal{Y}_{l,1/2}^{l+1/2,m_j} = \quad (21.9)$$

For two spin one-half particles, we start from just the addition of spins:

$$\vec{S} = \vec{S}_1 + \vec{S}_2 \quad (21.10)$$

$$(21.11)$$

We say the combined eigenfunctions for particles  $i = 1, 2$  are denoted by  $\chi_{1/2, \pm 1/2}(i)$ . Therefore, we can take products of these, and they denote spin states:

$$\uparrow\uparrow \chi_{1/2,1/2}(1)\chi_{1/2,1/2}(2), M_s = 1 \quad (21.12)$$

$$\uparrow\downarrow \chi_{1/2,1/2}(1)\chi_{1/2,-1/2}(2), M_s = 0 \quad (21.13)$$

$$\downarrow\uparrow \chi_{1/2,-1/2}(1)\chi_{1/2,1/2}(2), M_s = 0 \quad (21.14)$$

$$\downarrow\downarrow \chi_{1/2,-1/2}(1)\chi_{1/2,-1/2}(2), M_s = -1 \quad (21.15)$$

For  $s = 0$ , we make a superposition of the two states having  $M_s = 0$ :



$$\chi_{0,0} = \frac{1}{\sqrt{2}}[|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle] \quad (21.16)$$

This is antisymmetric with respect to particle exchange.

For  $s = 1$ , we have three possibilities:

$$\chi_{1,1} = |\uparrow\uparrow\rangle \quad (21.17)$$

$$\chi_{1,0} = \frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle) \quad (21.18)$$

$$\chi_{1,-1} = |\downarrow\downarrow\rangle \quad (21.19)$$

This is a spin triplet.

## 21.2 3D Problems

Consider two particles of masses  $m_1, m_2$ . The Schrödinger equation for this system is

$$i\hbar \frac{\partial}{\partial t} \Psi(\vec{r}_1, \vec{r}_2, t) = \left[ \frac{-\hbar^2}{2m_1} \nabla_{r_1}^2 - \frac{\hbar^2}{2m_2} \nabla_{r_2}^2 + \hat{V}(\vec{r}_1 - \vec{r}_2) \right] \Psi(\vec{r}_1, \vec{r}_2, t) \quad (21.20)$$

This is a seventh-order partial differential equation, so you should remember how to solve those from kindergarten.

We introduce relative coordinates  $\vec{r} = \vec{r}_1 - \vec{r}_2$  and  $\vec{R} = \frac{m_1\vec{r}_1 + m_2\vec{r}_2}{m_1 + m_2}$ , and masses  $M = m_1 + m_2, \mu = \frac{m_1 m_2}{m_1 + m_2}$ . Then the Schrödinger equation becomes

$$i\hbar \frac{\partial}{\partial t} \Psi(\vec{R}, \vec{r}, t) = \left[ -\frac{\hbar^2}{2M} \nabla_R^2 - \frac{\hbar^2}{2\mu} \nabla_r^2 + V(\vec{r}) \right] \Psi(\vec{R}, \vec{r}, t) \quad (21.21)$$

As an ansatz, we say that  $\psi$  is separable:

$$\Psi(\vec{R}, \vec{r}, t) = \Phi(\vec{R})\psi(\vec{r}) \exp[-i(E_{CM} + E)t/\hbar] \quad (21.22)$$

This allows us to split the two-dimensional problem into two one-dimensional problems:

$$-\frac{\hbar^2}{2M} \nabla_R^2 \Phi(\vec{R}) \quad (21.23)$$

$$\left[ -\frac{\hbar^2}{2\mu} \nabla_r^2 + V(\vec{r}) \right] \psi(\vec{r}) = E\psi(\vec{r}) \quad (21.24)$$

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## Lecture 22: Solving Schrödinger's Equation for 3D Situations

Lecturer: *Irfan Siddiqi*

19 November

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### 22.1 General Setup

To find a 3D wavefunction, we solve Schrödinger's equation in 3D, with separation:

$$\Psi(\vec{r}, t) = \psi(\vec{r})f(t), \quad (22.1)$$

where  $f(t) = e^{-i\frac{E}{\hbar}t}$  gives steady state eigenvalues.

For 3D problems, the general Hamiltonian is

$$\hat{H} = -\frac{\hbar^2}{2m}\vec{\nabla}^2 + \hat{V}(\vec{r}). \quad (22.2)$$

### 22.2 Free Particle

$\vec{V} = 0$  and  $r = a$  is a known case (motion on a sphere), but now we'll do  $V = 0$  not on a sphere - a free particle. The solution to this is 3D plane waves in spherical coordinates.

In Cartesian coordinates, separation of variables is sometimes possible. If  $(\vec{r}) = V_1(x) + V_2(y) + V_3(z)$ , then we can write  $\psi(x, y, z) = X(x)Y(y)Z(z)$ , solve each one separately according to a 1D problem, and combine all their solutions with  $E = E_x + E_y + E_z$ .

For a free particle,  $\psi(x) = Ae^{ikx} + Be^{-ikx}$ , and to account for 3D, we move to

$$\psi_{\vec{k}} = Ce^{i\vec{k}\cdot\vec{r}} + De^{-i\vec{k}\cdot\vec{r}}, \quad (22.3)$$

with  $E = \frac{\hbar^2}{2m}|\vec{k}|^2$  and  $\vec{p} = \hbar\vec{k}$ .

### 22.3 Infinite Square Well

Next, we consider a 3D infinite square well: again, we can separate this, and we get

$$\psi_{n_x, n_y, n_z} = \sqrt{\frac{8}{L_1 L_2 L_3}} \sin\left(\frac{n_x \pi x}{L_1}\right) \sin\left(\frac{n_y \pi y}{L_2}\right) \sin\left(\frac{n_z \pi z}{L_3}\right), \quad (22.4)$$

with energy  $E = \frac{\hbar^2 \pi^2}{2m} \left( \frac{n_x^2}{L_1^2} + \frac{n_y^2}{L_2^2} + \frac{n_z^2}{L_3^2} \right)$ .

When two or three of the lengths are equal, we get some degeneracy. For example, the lowest mode, (1, 1, 1) has no degeneracy, but (2, 1, 1) and (2, 2, 1) are both triply degenerate.

## 22.4 3D SHO

The solution to this is given by

$$\psi_{n_x n_y n_z} = \left( \prod_{i=1}^3 \left( \frac{\alpha_i}{\sqrt{\pi} 2^{n_i} n_i!} \right)^{1/2} H_{n_i}(\alpha_i x_i) \right) e^{-\frac{1}{2} \sum_{i=1}^3 \alpha_i^2 r_i^2} \quad (22.5)$$

with energy

$$E = \sum_{i=1}^3 \hbar \omega_i \left( n_i + \frac{1}{2} \right). \quad (22.6)$$

If all the  $k_i$ s are equal, this simplifies to the isotropic oscillator. The ground state energy is  $\frac{3}{2} \hbar \omega$  from (0, 0, 0), after which we get the triply degenerate  $\frac{5}{2} \hbar \omega$  from (1, 0, 0). After that, we get  $\frac{7}{2} \hbar \omega$  from both (1, 1, 0) and (2, 0, 0) so its degeneracy is 6.

## 22.5 Spherically Symmetric Potentials

This is the first step towards solving hydrogen! Consider a potential  $V(\vec{r}) = V(r)$ .

$$\hat{H} = -\frac{\hbar^2}{2m} \left( \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2}{\partial \varphi^2} \right) + \hat{V}(r). \quad (22.7)$$

This can be more simply written as

$$\hat{H} = -\frac{\hbar^2}{2m} \left( \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right) - \frac{\hat{L}^2}{\hbar^2 r^2} \right) + V(r). \quad (22.8)$$

We know that  $[\hat{L}_i, \hat{L}^2] = 0$  and  $Y_{lm}(\theta, \phi)$  are their common eigenfunctions. We also have that  $[\hat{V}(r), \hat{L}_i] = 0$  since there is no angular dependence in  $V$ , and the potential commutes with  $\hat{L}^2$  for the same reason. Therefore, we get

$$[\hat{H}, \hat{L}_i] = [\hat{H}, \hat{L}^2] = 0 \quad (22.9)$$

So we'll use three quantities, and describe a state in a ket  $|Elm\rangle$ . Therefore, we're looking for solutions of the form

$$\Psi_{Elm} = R_{Elm}(r)Y_{lm}(\theta, \varphi) \quad (22.10)$$

Substituting into the Schrödinger equation, we get

$$\hat{H}\psi_{Elm} = \left( -\frac{\hbar^2}{2m} \left( \frac{d^2}{dr^2} + \frac{2}{r} \frac{d}{dr} + \frac{l(l+1)\hbar^2}{2mr^2} + \hat{V}(r) \right) + \hat{V}(r) \right) R_{Elm}(r) = ER_{Elm}(r). \quad (22.11)$$

If we define  $U(r) = rR(r)$ , this becomes a 1D problem:

$$-\frac{\hbar^2}{2m} \frac{d^2}{dr^2} U_{Elm}(r) + V_{eff}(r)U_{Elm}(r) \quad (22.12)$$

where  $V_{eff}(r) = V(r) + \frac{l(l+1)\hbar^2}{2mr^2}$ .

Now, let's consider the free particle case again. In Cartesian coordinates we still have  $e^{\pm i\vec{k}\cdot\vec{r}}$  with  $\vec{k}^2 = \frac{2mE}{\hbar^2}$  like we would expect, but the radial equation is now

$$\left( \frac{d^2}{dr^2} + \frac{2}{r} \frac{d}{dr} - \frac{l(l+1)}{r^2} + \vec{k}^2 \right) R_{Elm}(r) = 0 \quad (22.13)$$

Again, let  $U = rR$ , so

$$\left( \frac{d^2}{dr^2} - \frac{l(l+1)}{r^2} + k^2 \right) U = 0, \quad (22.14)$$

and we can further require that  $R$  is finite at  $r = 0$ , so that  $U \rightarrow 0$  as  $r \rightarrow 0$ , so  $l = 0$  has  $U(r) \sim \sin(kr)$ . This means  $R(r)$  is a Bessel function!

If  $l \neq 0$ , let  $\rho = kr$ ; then the differential equation is

$$\left( \frac{d^2}{d\rho^2} + \frac{2}{\rho} \frac{d}{d\rho} \left( 1 - \frac{l(l+1)}{\rho^2} \right) \right) R_l(\rho) = 0. \quad (22.15)$$

The solutions to these are the spherical Bessel solutions,  $j_l(\rho) = \left( \frac{\pi}{2\rho} \right)^{1/2} J_{l+\frac{1}{2}}(\rho)$  where the  $J_{\dots}$  terms are ordinary Bessel functions. Another set of solutions are the spherical Neumann functions:

$$n_l(\rho) = (-1)^{l+1} \left( \frac{\pi}{2\rho} \right)^{1/2} J_{-l-\frac{1}{2}}(\rho), \quad (22.16)$$

but this does not meet the boundary conditions.

We can augment these radial solutions with the spherical harmonics to get a decomposition of a plane wave into spherical coordinates:

$$e^{i\vec{k}\cdot\vec{r}} = \sum_{l=0}^{\infty} \sum_{m=-l}^l c_{lm} j_l(kr) Y_{lm}(\theta, \phi). \quad (22.17)$$

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## Lecture 23: Schrödinger's Equation in 3D, continued

Lecturer: Irfan Siddiqi

21 November

Aditya Sengupta

### 23.1 Recap

Previously, we saw that using a central potential, we could reduce three-dimensional problems to one dimension:

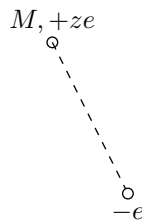
$$\hat{H} = -\frac{\hbar^2}{2m} \left( \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right) - \frac{\hat{L}^2}{\hbar^2 r^2} \right) + \hat{V}(r) \quad (23.1)$$

If we take  $\psi_{Elm}(\vec{r}) = R_{Elm}(r)\mathcal{Y}_{lm}(\theta, \varphi)$ , and further let  $U(r) = rR(r)$ , this reduces to a one-dimensional problem:

$$\left( -\frac{\hbar^2}{2m} \frac{d^2}{dr^2} + V_{eff}(r) \right) U(r) = EU(r) \quad (23.2)$$

For example, if  $V(r) = 0$ , then  $\psi_{Elm}(r) = Cj_l(kr)\mathcal{Y}_{lm}(\theta, \varphi)$  (where  $p = \hbar k$ ).

### 23.2 Hydrogenic Atoms



The potential associated with this atom is  $V(r) = \frac{-ze^2}{(4\pi\epsilon_0)r}$ . In center-of-mass coordinates, we can just solve the 1D Schrödinger equation.

$$\hat{H} = \frac{p^2}{2\mu} - \frac{ze^2}{(4\pi\epsilon_0)r}, \mu = \frac{mM}{m+M} \quad (23.3)$$

By Taylor expansion, we can show that  $R(r)$  approaches some finite value as  $r \rightarrow 0$ , i.e.  $R \sim r^l$ . Therefore,  $U(r) \sim r^{l+1}$  as  $r \rightarrow 0$ .

The Schrödinger equation is

$$\frac{d^2}{dr^2}U(r) + \frac{2\mu}{\hbar^2}(E - V_{eff}(r))U(r) = 0 \quad (23.4)$$

where

$$V_{eff}(r) = \frac{-ze^2}{(4\pi\epsilon_0)r} + \frac{l(l+1)\hbar^2}{2\mu r^2} \quad (23.5)$$

Let  $\rho = \left(\frac{-8\mu E}{\hbar^2}\right)^{1/2} r$ . Further, we can define

$$\lambda = \frac{ze^2}{(4\pi\epsilon_0)\hbar} \left(\frac{-\mu}{2E}\right)^{1/2} = z\alpha \left(\frac{-\mu c^2}{2E}\right)^{1/2} \quad (23.6)$$

where  $\alpha = \frac{e^2}{4\pi\epsilon_0\hbar c} \approx \frac{1}{137}$ . This is the fine structure constant.

Using these definitions, we can rewrite the Schrödinger equation as follows:

$$\left(\frac{d^2}{d\rho^2} - \frac{l(l+1)}{\rho^2} + \frac{\lambda}{\rho} - \frac{1}{4}\right)U(\rho) = 0 \quad (23.7)$$

In the asymptotic limit  $\rho \rightarrow \infty$ , the two  $\frac{1}{\rho^l}$  terms drop out and we're left with an exponential solution:

$$U(\rho) \sim e^{-\rho/2} \implies U(\rho) = e^{-\rho/2}f(\rho) \quad (23.8)$$

where  $f(\rho)$  is something that grows slower than  $e^{-\rho/2}$  as  $\rho \rightarrow \infty$ . Substitute back, and we get

$$\left(\frac{d^2}{d\rho^2} - \frac{d}{d\rho} - \frac{l(l+1)}{\rho^2} + \frac{\lambda}{\rho}\right)f(\rho) = 0 \quad (23.9)$$

In the limit  $\rho \rightarrow 0$ , we've seen that  $U \sim \rho^{l+1}$ , so  $f(\rho) = \rho^{l+1}g(\rho)$ . Now, all we know about  $g(\rho)$  is that it fills in the gaps between these asymptotic limits. We expand it in a power series:

$$g(\rho) = \sum_{k=0}^{\infty} c_k \rho^k; c_0 \neq 0 \quad (23.10)$$

$$\left(\rho \frac{d^2}{d\rho^2} + (2l+2-\rho) \frac{d}{d\rho} + (\lambda-l-1)\right)g(\rho) = 0 \quad (23.11)$$

$$\sum_{k=0}^{\infty} (k(k-1)c_k \rho^{k-1} (2l+2-\rho)k c_k \rho^{k-1} + (\lambda-l-1)c_k \rho^k) = 0 \quad (23.12)$$

Collecting terms, we get

$$\sum_{k=0}^{\infty} ([k(k+1) + (2l+2)(k+1)]c_{k+1} + (\lambda - l - 1 - k)c_k) \rho^k = 0 \quad (23.13)$$

Requiring that each of these is 0 gives us a recurrence relation:

$$c_{k+1} = \frac{k+l+1-\lambda}{(k+1)(k+2l+2)} c_k \quad (23.14)$$

For large  $k$ ,  $\frac{c_{k+1}}{c_k} \sim \frac{1}{k}$ . This is the same as the limiting behaviour for an exponential of the form  $\rho^p e^\rho$ , but we can show that this isn't its behaviour everywhere. Recall that  $U \sim \rho^{l+1} e^{-\rho/2} g(\rho)$ . Since for the chosen form of  $g(\rho)$  this diverges as  $\rho \rightarrow \infty$ , it must terminate at some point.  $g(\rho)$  must be a polynomial in  $\rho$  with highest power  $n_r$ . Therefore  $C_{n_r+1} = 0$ , meaning  $0 = k+l+1-\lambda$ . Write  $n_r$  instead of  $k$ ; then we get  $\lambda = n_r + l + 1$ .  $\lambda$  can take on values  $1, 2, 3, \dots$ . We refer to this as the principal quantum number. If we redimension  $\lambda$ , we get

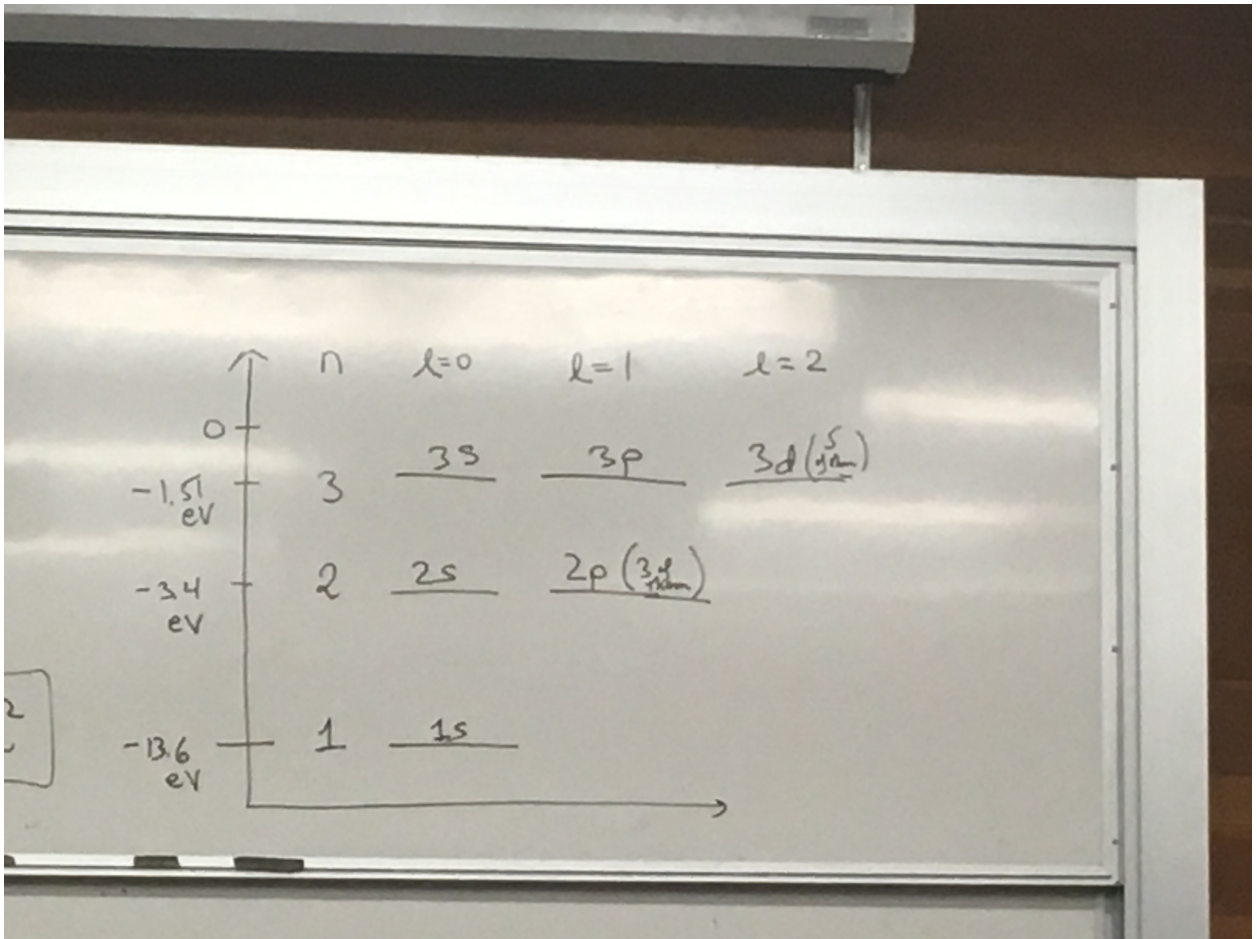
$$E_n = \frac{-\mu}{2\hbar^2} \left( \frac{ze^2}{4\pi\epsilon_0} \right) \frac{1}{n^2} \stackrel{z=1}{=} \frac{-13.6\text{eV}}{n^2} \quad (23.15)$$

This reproduces the result we know from Bohr's model! These are the eigenvalues of the Hamiltonian, and we can also find the eigenfunctions.

For each energy  $E_n$ ,  $l$  can take on the values  $0, 1, \dots, n-1$ . Further, there are  $2l+1$  values of  $m$ . Therefore the total degeneracy is

$$\sum_{l=0}^{n-1} (2l+1) = n^2 \quad (23.16)$$





### 23.3 Eigenfunctions of bound states

We match the differential equation in  $g$ , given by 23.11, to the standard form of the Kumer-Laplace equation,

$$z \frac{d^2 w}{dz^2} + (c - z) \frac{dw}{dz} - aw = 0 \quad (23.17)$$

with  $z = \rho$ ,  $w = g$ ,  $a = l + 1 - \lambda$ ,  $c = 2l + 2$ . The solutions are confluent hypergeometric functions.

$${}_1F_1(a, c, z) = \frac{\Gamma(c)}{\Gamma(a)} e^z z^{a-c} \quad (23.18)$$

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## Lecture 24: The Hydrogen Atom

Lecturer: *Irfan Siddiqi*

26 November

*Aditya Sengupta*

### 24.1 Laguerre Polynomials

Previously, we saw that we could model the hydrogen atom using a separable wavefunction:

$$\psi(\vec{r}, \theta, \varphi) = R(r)\mathcal{Y}_{lm}(\theta, \varphi) \quad (24.1)$$

This gave us a single-variable version of the Schrödinger equation, using  $U(r) = rR(r)$ :

$$\left( -\frac{\hbar^2}{2m} \left( \frac{d^2}{dr^2} + \frac{2}{r} \frac{d}{dr} \right) + \frac{l(l+1)\hbar^2}{2mr^2} + V(r) \right) R(r) = ER(r) \quad (24.2)$$

If we put in the  $\frac{1}{r}$  potential, we saw last time that if we used  $\rho = \left( \frac{-8\mu E}{\hbar^2} \right)^{1/2} r$  then we could get confluent hypergeometric functions solving this equation.

Note that  ${}_1F_1$  tends to an exponential, i.e.  $U \rightarrow \infty$  as  $rr \rightarrow \infty$ . Therefore, in general, we keep a finite set of terms, we get quantized energies, and associated Laguerre polynomials  $L_p^q$ :

$$L_{n+l}^{2l+1}(\rho) = \frac{-[(n+l)]^2}{(n-l-1)!(2l+1)!} {}_1F_1(l+1-n, 2l+2, \rho) \quad (24.3)$$

This can be more simply expressed in terms of a generating function:

$$L_q(\rho) = e^\rho \frac{d^q}{d\rho^q} (\rho^q e^{-\rho}) \quad (24.4)$$

To get the associated Laguerre polynomial, we take an arbitrary-degree derivative of this:

$$L_q^p(\rho) = \frac{d^p}{d\rho^p} L_q(\rho) \quad (24.5)$$

This gives us all of the radial solutions,

$$R_{nl}(r) = N e^{-\rho/2} r h \rho^l L_{n+l}^{2l+1}(\rho) \quad (24.6)$$

$$(24.7)$$

where  $N = - \left( \left( \frac{2z}{na_\mu} \right)^3 \frac{(n-l-1)!}{2n((n+l)!)^3} \right)^{1/2}$

The first solution to this is  $n = 1, l = 0$ :

$$R_{10}(r) = 2 \left( \frac{z}{a_\mu} \right)^{3/2} e^{-(zr/a_\mu)} \quad (24.8)$$

and after that,  $n = 2, l = 0$  gives us

$$R_{20}(r) = 2 \left( \frac{z}{2a_\mu} \right)^{3/2} \left( 1 - \frac{zr}{2a_\mu} \right) e^{-zr/2a_\mu} \quad (24.9)$$

For  $n = 2, l = 1$ , we get

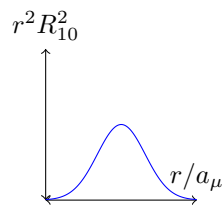
$$R_{21}(r) = \frac{1}{\sqrt{3}} \left( \frac{z}{2a_\mu} \right)^{3/2} \left( \frac{zr}{a_\mu} \right) e^{-zr/2a_\mu} \quad (24.10)$$

## 24.2 Probability Densities

The probability density is proportional to  $|R(r)|^2$ .

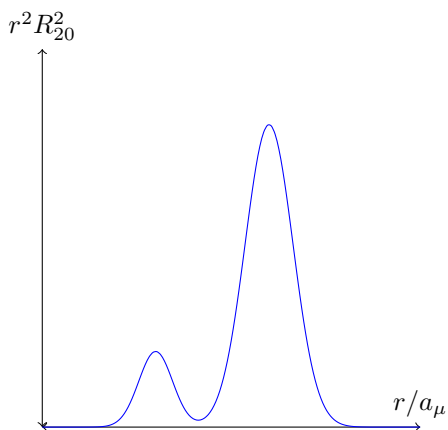
$$|\psi_{nlm}(r, \theta, \varphi)|^2 = |R(r)|^2 \cdot |\mathcal{Y}_{lm}(\theta, \varphi)|^2 \quad (24.11)$$

Integrating the probability over  $4\pi r^2$ , we get that the pdf is proportional to  $r^2 R(r)^2$ . We can compute this pdf for some specific cases

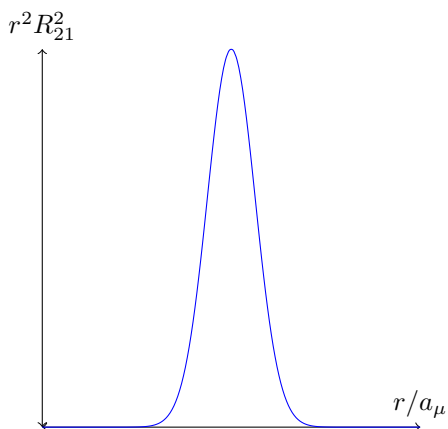


This is a normal distribution around the Bohr radius.

With  $R_{20}$ , we get a bimodal distribution with a small peak around 1 and a larger peak between 2 and 10:



With  $R_{21}$ , we go back to the normal distribution, but now centered around 5.



## 24.3 Shells

We can connect this with the chemical view of energy levels and shells of electrons!

Shell	Quantum Numbers (n, l, m)	Spectral Notation	$\psi(r, \theta, \varphi)$
K	1, 0, 0	1s	$1/\sqrt{\pi}(z/a_\mu)^{3/2}e^{-zr/a_\mu}$
L	2, 0, 0	2s	$2/\sqrt{\pi}(z/a_\mu)^{3/2}\left(1 - \frac{zr}{2a_\mu}\right)e^{-zr/2a_\mu}$
L	2, 1, 0	2p <sub>0</sub>	$\frac{1}{4\sqrt{2\pi}}(z/a_\mu)^{3/2}(zr/a_\mu)e^{-zr/2a_\mu}$
L	2, 1, $\pm 1$	2p <sub><math>\pm 1</math></sub>	$\mp \frac{1}{8\sqrt{\pi}}(z/a_\mu)^{3/2}(zr/a_\mu)e^{-zr/2a_\mu} \sin \theta e^{\pm i\varphi}$

## 24.4 Observations

- The  $s$  states, with  $l = 0$ , have spherical symmetry:  $\mathcal{Y}_{l=0,m=0} = \frac{1}{\sqrt{4\pi}}$ . Thus

$$|\psi_{n00}(0)|^2 = \frac{1}{4\pi}|R_{n0}(0)|^2 = \frac{z^3}{\pi a_\mu^3 n^3} \quad (24.12)$$

2.  $R_{nl}(r) \propto r^l$  as  $r \rightarrow 0$ .
3.  $r^2|R(r)|^2$  has  $n - l$  maxima.

For the largest  $l$ , we only have one maximum. We can find this by taking a derivative of  $r^2|R|^2$ .

$$R_{n,n-1}(r) \sim r^{n-1}e^{-zr/na_\mu} \quad (24.13)$$

Taking the derivative and setting it to zero, we get

$$\left(2nr^{2n-1} - \frac{2zr^{2n}}{na_\mu}\right)e^{-2zr/na_\mu} \quad (24.14)$$

Solving for  $n$ , we get  $r = \frac{n^2 a_\mu}{z}$ . For  $z = 1$ , this matches the Bohr radii!

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## Lecture 25: Fine Structure of Hydrogen

Lecturer: Irfan Siddiqi

3 December

Aditya Sengupta

### 25.1 First Order Perturbation Correction

Consider a time-independent Hamiltonian  $\hat{H} = \hat{H}_0 + \lambda \hat{H}^{(1)}$ , where  $\hat{H}_0$  is a standard solvable problem that is being perturbed to first order by some  $\hat{H}^{(1)}$ , scaled by  $\lambda \ll 1$ . We know that

$$\hat{H}_0 \psi_n^{(0)} = E_n^{(0)} \psi_n^{(0)} \quad (25.1)$$

and we're looking for solutions of the form  $\hat{H} \psi_n = E_n \psi_n$ . We assume this is non-degenerate and that the perturbation is small enough that  $E_n$  is closest to  $E_n^{(0)}$ .

$$E_n = \sum_{j=0}^{\infty} \lambda^j E_n^{(j)} \quad (25.2)$$

and the corresponding wavefunction,

$$\psi_n = \sum_{j=0}^{\infty} \lambda^j \psi_n^{(j)} \quad (25.3)$$

We substitute these into the usual eigenvalue equation:

$$(\hat{H}_0 + \lambda \hat{H}^{(1)}) (\psi_n^{(0)} + \lambda \psi_n^{(1)} + \lambda^2 \psi_n^{(2)} + \dots) = (E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \dots) (\psi_n^{(0)} + \lambda \psi_n^{(1)} + \lambda^2 \psi_n^{(2)} + \dots) \quad (25.4)$$

If we isolate all the terms that are constant in  $\lambda$ , we just get  $\hat{H}_0 \psi_n^{(0)} = E_n^{(0)} \psi_n^{(0)}$ , and if we isolate all the terms that are linear in  $\lambda$ , we get

$$\hat{H}_0 \psi_n^{(1)} + \hat{H}^{(1)} \psi_n^{(0)} = E_n^{(0)} \psi_n^{(1)} + E_n^{(1)} \psi_n^{(0)} \quad (25.5)$$

We take an inner product of this with  $\psi_n^{(0)}$  to isolate  $E_n^{(1)}$ .

$$\langle \psi_n^{(0)} | H_0 - E_n^{(0)} | \psi_n^{(1)} \rangle + \langle \psi_n^{(0)} | H^{(1)} - E_n^{(1)} | \psi_n^{(0)} \rangle = 0 \quad (25.6)$$

We split up the operator  $H_0 - E_n^{(0)}$ : we get

$$\langle \psi_n^{(0)} | H_0 - E_n^{(0)} | \psi_n^{(1)} \rangle = \langle \psi_n^{(1)} | H_0 | \psi_n^{(0)} \rangle^* - E_0 \langle \psi_n^{(1)} | \psi_n^{(0)} \rangle^* = 0 \quad (25.7)$$

Therefore, we're left with

$$\langle \psi_n^{(0)} | H^{(1)} | \psi_n^{(0)} \rangle = E_n^{(1)} \quad (25.8)$$

We can find the wavefunction by

$$\psi_n^{(1)} = \sum_{l \neq n} \frac{\langle \psi_l^{(0)} | H^{(1)} | \psi_n^{(0)} \rangle}{E_n^{(0)} - E_l^{(0)}} \psi_l^{(0)} \quad (25.9)$$

## 25.2 Applying the perturbation model to hydrogen

Let's start with the Bohr model of the hydrogen atom, and start adding correction terms.

$$\hat{H}_0 = \frac{p^2}{2m} - \frac{ze^2}{(4\pi\epsilon_0)r} \quad (25.10)$$

To this, we add corrections  $H' = H'_1 + H'_2 + H'_3$ , due to special relativity, the spin orbit, and the spread of the nucleus.

For  $H_1$ , the total relativistic energy of a particle is  $\sqrt{p^2c^2 + m^2c^4}$ . The kinetic energy is this minus  $mc^2$ , and if we Taylor expand this, we get the correction

$$H'_1 = -\frac{p^4}{8m^3c^2} \quad (25.11)$$

The spin orbit correction is

$$H'_2 = \frac{1}{2m^2c^2} \frac{1}{r} \frac{dV}{dr} \vec{L} \cdot \vec{s} \quad (25.12)$$

The electron feels the  $\vec{E}$  field from the nucleus, with magnitude  $\vec{E} = \frac{e\vec{r}}{4\pi\epsilon_0 r^3}$ , and there's an associated magnetic field due to motion, given by  $\vec{B} = (1/c^2)(-\vec{v} \times \vec{E})$ . Therefore we get this perturbation from dotting this  $\vec{B}$  with the magnetic moment of the electron.

The third part is

$$H'_3 = \frac{\pi\hbar^2}{2m^2c^2} \left( \frac{ze^2}{4\pi\epsilon_0} \right) \delta(\vec{r}) \quad (25.13)$$

Therefore, using the result we derived before for first-order corrections, we get

$$\Delta E_1 = \left\langle \psi_{nlm_l m_s}^{(0)} \left| \frac{-p^2}{8m^3c^2} \right| \psi_{nlm_l m_s}^{(0)} \right\rangle \quad (25.14)$$

and similarly for the other two. Calculating things, we get

$$\Delta E_1 = -E_n^{(0)} \frac{(z\alpha)^2}{n^2} \left( \frac{3}{4} - \frac{n}{l + \frac{1}{2}} \right) \quad (25.15)$$

$$\Delta E_2 = -E_n^{(0)} \frac{(z\alpha)^2}{2nl(l+1/2)(l+1)} \cdot \begin{cases} l & j = l + \frac{1}{2} \\ l-1 & j = l - 1/2 \end{cases} \quad (25.16)$$

$$\Delta E_3 = -E_n^{(0)} \frac{(z\alpha)^2}{n} \text{ for } l = 0 \quad (25.17)$$

Therefore,

$$E_n = E_n^{(0)} \left( 1 + \frac{(z\alpha)^2}{n^2} \left( \frac{n}{j+1/2} - \frac{3}{4} \right) \right) \quad (25.18)$$



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## Lecture 26: Overlapping Wavefunctions, Entanglement

Lecturer: Irfan Siddiqi

5 December

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### 26.1 Multiparticle Systems

Suppose we have a system of  $N$  particles, in which the  $i$ th particle is described by  $\vec{r}_i, \vec{p}_i, \vec{s}_i$ . Denote these by  $q_i$ , representing a complete set of commuting observables. Denote the wavefunction of the ensemble by  $\psi(q_1, q_2, \dots, q_N)$ . This obeys the Schrödinger equation:

$$i\hbar \frac{\partial}{\partial t} \psi(q_1, q_2, \dots, q_N) = \hat{H} \psi(q_1, q_2, \dots, q_N) \quad (26.1)$$

and for some time-independent potential  $\hat{V}$ , we can say that  $\hat{H} = \hat{T} + \hat{V}$ . There exist some eigenvalues:

$$\hat{H} \psi_E = E \psi_E \quad (26.2)$$

$\hat{H}$  must be symmetric with respect to the exchange of two particles  $i$  and  $j$ . Let the operator  $\hat{p}_{ij}$  do this. Then

$$[\hat{p}_{ij}, \hat{H}] = 0 \quad (26.3)$$

In general, an exact eigenfunction  $\psi(q_1, q_2, \dots, q_N)$  has no particular symmetry with respect to exchange of  $i$  and  $j$ . Therefore, if  $\psi(q_1, \dots, q_N)$  is an eigenfunction of  $\hat{H}$  with  $E$ , then so is  $\hat{p}_{ij} \psi$ . Therefore

$$\hat{p}_{ij} \psi(q_1, \dots, q_N) = \epsilon \psi(q_1, \dots, q_N) \quad (26.4)$$

Further, we know that  $\hat{p}_{ij}^2 = I$ , so  $\epsilon = \pm 1$ : the exchange is either symmetric or antisymmetric. There are  $N!$  permutations of  $q_1, \dots, q_N$ . If we want to define an arbitrary state caused by some rearrangement, we can define the permutation operator  $\hat{P}$  through successive applications of  $\hat{p}_{ij}$ . Since each of these commute with  $\hat{H}$ , we can say that  $[\hat{P}, \hat{H}] = 0$ .

Note that not all  $N!$  permutations  $\hat{P}$  commute with themselves, i.e.  $\psi(q_1, \dots, q_N)$  is not an eigenfunction of all  $N!$  permutations  $\hat{P}$ . However, there are two states where this is the case: either when the permutation is totally symmetric, i.e.  $\hat{P} \psi_S = \psi_S$ , or when the permutation is totally anti-symmetric, i.e.  $\hat{P} \psi_A = \psi_A$  with an even number of swaps and  $\hat{P} \psi_A = -\psi_A$  with an odd number of swaps.

$\psi_S$  and  $\psi_A$  are sufficient to describe all particles. The symmetric wavefunction describes a boson, which has zero or integer spin. This covers all mesons, photons, and vector bosons, as well as the Higgs boson. The anti-symmetric wavefunction describes a fermion, which has half-odd integer spin. This covers all leptons and baryons.

For two identical particles given by  $\psi(q_1, q_2)$ , we can write

$$\psi_S(q_1, q_2) = \frac{1}{\sqrt{2}} (\psi(q_1, q_2) + \psi(q_2, q_1)) \quad (26.5)$$

$$\psi_A(q_1, q_2) = \frac{1}{\sqrt{2}} (\psi(q_1, q_2) - \psi(q_2, q_1)) \quad (26.6)$$

Consider the case of no interactions. There are local Hamiltonians  $\hat{h}_i$ , where

$$\hat{h}_i u_\lambda(q_i) = E_\lambda u_\lambda(q_i) \quad (26.7)$$

The solution is a product state:

$$\psi(q_1, q_2, \dots, q_N) = U_\alpha(q_1) U_\beta(q_2) \dots U_\nu(q_N) \quad (26.8)$$

$$E = E_\alpha + E_\beta + \dots + E_\nu \quad (26.9)$$

With  $N = 2$ , we can say

$$\psi_S(q_1, q_2) = \frac{1}{\sqrt{2}} (U_\alpha(q_1) U_\beta(q_2) + U_\alpha(q_2) U_\beta(q_1)) \quad (26.10)$$

$$\psi_A(q_1, q_2) = \frac{1}{\sqrt{2}} (U_\alpha(q_1) U_\beta(q_2) - U_\alpha(q_2) U_\beta(q_1)) \quad (26.11)$$

The particles are entangled, due to the states that are not product states,  $U_\alpha(q_2)$  and  $U_\beta(q_1)$ . Neither particle is in an energy eigenstate.

## 26.2 Pauli Exclusion Principle

For  $N$  particles that are totally antisymmetric, we write the wavefunction as a so-called Slater determinant:

$$\psi(q_1, \dots, q_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} U_\alpha(q_1) & U_\beta(q_1) & \dots & U_\nu(q_1) \\ U_\alpha(q_2) & U_\beta(q_2) & & U_\nu(q_2) \\ \vdots & & \ddots & \vdots \\ U_\alpha(q_N) & U_\beta(q_N) & \dots & U_\nu(q_N) \end{vmatrix} \quad (26.12)$$

If two or more sets of quantum numbers  $\alpha, \beta$  are identical, then  $\psi$  vanishes. Therefore, only one fermion is allowed per single quantum state. This is the Pauli exclusion principle.