Quantum Mechanics in Three Dimensions

Lecture 21

Physics 342
Quantum Mechanics I

Monday, March 22nd, 2010

We are used to the temporal separation that gives, for example, the time-independent Schrödinger equation. In three dimensions, even this time-independent form leads to a PDE, and so we consider spatial separation, familiar from E&M.

21.1   Three Copies

Our one-dimensional replacement: $p_x \longrightarrow \frac{\hbar}{i} \frac{\partial}{\partial x}$ can be generalized to three dimensions in the obvious way. Cartesian coordinates have no preferential directions, so we expect the three-dimensional replacement:

$$\mathbf{p} \longrightarrow \frac{\hbar}{i} \nabla \tag{21.1}$$

applied to the Hamiltonian. In addition, our wavefunctions become functions of all three coordinates: $\Psi(x, y, z, t)$ or any other equivalent set (spherical, cylindrical, prolate spheroidal, what have you).

We can work out the commutation relations for the three obvious copies of our one-dimensional: $[x, p_x] = i\,\hbar$, but what about the new players: $[x, y]$ and $[x, p_y]$ (and obvious extensions involving z and p_z)?

The coordinate operators clearly commute, $[x, y] = 0$, and the momentum operators will as well, by cross-derivative equality:

$$[p_x, p_y] = -\hbar^2 \left(\frac{\partial^2}{\partial x \partial y} - \frac{\partial^2}{\partial y \partial x} \right) = 0. \tag{21.2}$$

Finally, mixtures of coordinates and momenta that are not related, like $[x, p_y]$ will commute since $\frac{\partial x}{\partial y} = 0$ – throwing in a test function to make the

situation clear, we have

$$[x, p_y] f(x, y) = \frac{\hbar}{i} \left(x \frac{\partial f}{\partial y} - \frac{\partial}{\partial y} (x f(x, y)) \right) = \frac{\hbar}{i} \left(x \frac{\partial f}{\partial y} - x \frac{\partial f}{\partial y} \right) = 0.$$
(21.3)

Tabulating our results, the three-dimensional commutation relations read (letting r_i be $r_1 = x$, $r_2 = y$, $r_3 = z$ for $i = 1, 2, 3$)

$$[r_i, p_j] = i \, \hbar \, \delta_{ij} \quad [r_i, r_j] = [p_i, p_j] = 0.$$
(21.4)

The wavefunction itself must now be interpreted as a full three-dimensional density, with $|\Psi(\mathbf{r}, t)|^2 \, d\tau$ the "probability per unit volume" of finding a particle in the vicinity of $\mathbf{r}$ at time t. The normalization condition becomes a volume integral, as do all expectation values:

$$1 = \int |\Psi|^2 \, d\tau$$

$$\langle \mathbf{r} \rangle = \int \Psi^* \, \mathbf{r} \, \Psi \, d\tau$$
(21.5)

$$\langle \mathbf{p} \rangle = \int \Psi^* \left(\frac{\hbar}{i} \nabla \right) \Psi \, d\tau.$$

where the integration is over all space, and $d\tau$ is the volume element. In Cartesian coordinates, $d\tau = dx \, dy \, dz$, but it takes different forms depending on how we've parametrized (in cylindrical coordinates, for example, $d\tau = s \, ds \, d\phi \, dz$).

For a finite volume, we have the obvious interpretation

$$\int_\Omega |\Psi|^2 \, d\tau$$
(21.6)

is the probability of finding the particle in the volume defined by Ω.

To find the probability flowing into and out of this volume, we can use the probability conservation statement in three dimensions. Let $\rho = |\Psi(\mathbf{r}, t)|^2$, then we had $\mathbf{J} = -\frac{i\,\hbar}{2\,m} [\Psi^* \nabla \Psi - \Psi \nabla \Psi^*]$, and

$$\frac{\partial \rho}{\partial t} = -\nabla \cdot \mathbf{J} \longrightarrow \frac{d}{dt} \int_\Omega \rho \, d\tau = - \oint_{d\Omega} \mathbf{J} \cdot d\mathbf{a}$$
(21.7)

where the left-hand side is the rate of change of probability inside the volume Ω, and the right-hand side is the amount of probability flowing out through the boundary of the volume $d\Omega$, reminiscent of the electromagnetic charge conservation equation (which has identical form).

21.1.1   Two Dimensional Example

Suppose we retreat to two dimensions and take the simplest possible potential (other than the free particle case) – an infinite square "well". Our two-dimensional potential can be specified via:

$$V(x, y) = \begin{cases} 0 & 0 < x < a \text{ and } 0 < y < a \\ \infty & \text{otherwise} \end{cases} \tag{21.8}$$

We must solve Schrödinger's equation, with boundary conditions. In this dimensionally expanded setting, the boundary conditions for $\psi(x, y)$ are:

$$\psi(0, y) = \psi(a, y) = \psi(x, 0) = \psi(x, a) = 0, \tag{21.9}$$

and the time-independent Schrödinger's equation on the interior of the boundary reads

$$-\frac{\hbar^2}{2\,m} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} \right) \psi(x, y) = E\,\psi(x, y). \tag{21.10}$$

The temporal separation has already occurred here, we had the usual: $\hat{H}\,\Psi(x, y, t) = i\,\hbar\,\frac{\partial \Psi(x,y,t)}{\partial t}$, and took $\Psi(x, y, t) = \psi(x, y)\,\phi(t)$. Then we can separate with constant E, leading to (21.10) and $\phi(t) = e^{-i\frac{E}{\hbar}t}$.

If we use multiplicative separation in (21.10): $\psi(x, y) = X(x)\,Y(y)$, then we can write the above as

$$\left(\frac{X''(x)}{X(x)} + \frac{Y''(y)}{Y(y)} \right) = -\frac{2\,m\,E}{\hbar^2}. \tag{21.11}$$

The usual separation argument holds, on the left, we have two functions, one only depending on x, one only on y, and together, these must equal the constant on the right. Then each term must individually be equal to a constant, and a solution to (21.11) follows from a solution to the set of three equation:

$$\begin{aligned} X''(x) &= -k^2\,X(x) \\ Y''(y) &= -\ell^2\,Y(y) \\ -k^2 - \ell^2 &= -\frac{2\,m\,E}{\hbar^2}. \end{aligned} \tag{21.12}$$

The ODEs in X and Y imply sinusoidal dependence on x and y – so we have

$$X(x) = A \cos(k\,x) + B \sin(k\,x) \quad Y(y) = F \cos(\ell\,y) + G \sin(\ell\,y),$$
$$(21.13)$$

together with our side constraint on the sum of k^2 and ℓ^2. It's time to impose the boundary conditions: The wave function reads:

$$\psi(x,y) = (A \cos(k\,x) + B \sin(k\,x))\,(F \cos(\ell\,y) + G \sin(\ell\,y)). \quad (21.14)$$

Take $x = 0$, our boundary condition requires that $\psi(0,y) = 0$, and this immediately tells us that $A = 0$. Similarly, for $y = 0$, we learn that $F = 0$. After imposing these, our wave function looks like

$$\psi(x,y) = B\,G \sin(k\,x)\,\sin(\ell\,y). \quad (21.15)$$

We absorb the product $B\,G$ into a single constant: $P = B\,G$, and we are ready to set the boundary at a. In order to satisfy

$$\psi(a,y) = P \sin(k\,a) \sin(\ell\,y) = 0 \quad (21.16)$$

for all y, we must have $k\,a = m\,\pi$ for integer m. On the y-side, we want

$$\psi(x,a) = P \sin(k\,x) \sin(\ell\,a) = 0, \quad (21.17)$$

and this gives $\ell\,a = n\,\pi$ for integer n. The wave function, satisfying Schrödinger's equation and all boundary conditions, is:

$$\boxed{\begin{aligned}\psi_{mn}(x,y) &= P \sin\left(\frac{m\,\pi\,x}{a}\right) \sin\left(\frac{n\,\pi\,y}{a}\right) \qquad \text{for } m,\,n \in \mathbb{Z}^+ \\ E_{mn} &= \frac{\hbar^2}{2\,M}\left(\left(\frac{m\,\pi}{a}\right)^2 + \left(\frac{n\,\pi}{a}\right)^2\right)\end{aligned}} \quad (21.18)$$

(I have denoted mass with M in the above) with P left for overall normalization.

As always, we can normalize the individual wavefunctions. In this case, we have, with probability one, a particle of mass M localized to the region $(x,y) \in [0,a] \times [0,a]$. Then

$$1 = \int_0^a \int_0^a P^2 \sin^2\left(\frac{m\,\pi\,x}{a}\right) \sin^2\left(\frac{n\,\pi\,y}{a}\right) dx\,dy \; = \left(\frac{a}{2}\right)^2 P^2 \quad (21.19)$$

so that $P = \frac{2}{a}$. Check the units, we now have $\psi_{mn}^*(x,y)\,\psi_{mn}(x,y)$ a probability density in two dimensions.

As always, the general solution is a linear combination of the particular solutions:

$$\Psi(x,y,t) = \sum_{m=1}^{\infty} \sum_{n=1}^{\infty} c_{mn}\psi_{mn}(x,y)\, e^{-i\,\frac{E_{mn}\,t}{\hbar}} \qquad (21.20)$$

and the set $\{c_{mn}\}$ are just waiting for an initial $\bar{\psi}(x,y)$ to be provided, at which point they can be set.

There are a couple of important differences between the one dimensional infinite square well and this two-dimensional form. The most noticeable is the *degeneracy* associated with energy. In one dimension, the energies were related to an integer n via: $E_n = \frac{n^2\,\pi^2\,\hbar^2}{2\,m\,a^2}$, so for each n, there was an energy. In the two-dimensional case, the independent (and orthonormal) wave functions $\psi_{21}(x,y)$ and $\psi_{12}(x,y)$ both have the same energy. It is interesting to think about what a measurement of energy does in this context. Suppose we measure the energy $E = 5 \times \frac{\pi^2\,\hbar^2}{2\,m\,a^2}$, then we know that the wave function collapses to the associated eigenstate – but *which* associated eigenstate – $\psi_{12}(x,y)$ or $\psi_{21}(x,y)$?

In addition, there is the question – do we have one particle in two dimensions, or two particles in one dimension? How could we tell? And what, really, is the distinction?

21.2 Orbital Motion and Classical Mechanics

Consider the classical mechanics form of the Lagrangian governing, for example, orbital motion in a spherically symmetric gravitational field:

$$L = \frac{1}{2}\,m\,(\dot{r}^2 + r^2\,\dot{\theta}^2 + r^2\,\sin^2\theta\,\dot{\phi}^2) - U(r) \quad U(r) = -\frac{G\,M\,m}{r}. \qquad (21.21)$$

We have written the Lagrangian in terms of spherical coordinates, related to the Cartesian ones in the usual way:

$$x = r\,\sin\theta\,\cos\phi \quad y = r\,\sin\theta\,\sin\phi \quad z = r\,\cos\theta. \qquad (21.22)$$

We can form the Hamiltonian as usual, the canonical momenta are:

$$p_r = \frac{\partial L}{\partial \dot{r}} = m\,\dot{r}$$
$$p_\theta = \frac{\partial L}{\partial \dot{\theta}} = m\,r^2\,\dot{\theta} \tag{21.23}$$
$$p_\phi = \frac{\partial L}{\partial \dot{\phi}} = m\,r^2\,\sin^2\theta\,\dot{\phi},$$

and then the Hamiltonian is just the Legendre transform of L

$$H = \left(\dot{r}\,p_r + \dot{\theta}\,p_\theta + \dot{\phi}\,p_\phi - L \right)\Bigg|_{(p_r,p_\theta,p_\phi)}, \tag{21.24}$$

where the "evaluated at" sign reminds us to evaluate the Hamiltonian in terms of the momenta (which we can do by inverting (21.23)) rather than the time derivatives of the coordinates. Written out, we have

$$H = \frac{1}{2\,m}\left(p_r^2 + \frac{p_\theta^2}{r^2} + \frac{p_\phi^2}{r^2\,\sin^2\theta} \right) + U(r). \tag{21.25}$$

The first term, is of course, $\mathbf{p} \cdot \mathbf{p}$ in spherical coordinates. Regardless, our usual observation is that we can set motion into the $x - y$ plane by requiring $\dot{\theta} = 0$ and $\theta = \frac{\pi}{2}$, then the Hamiltonian simplifies:

$$H = \frac{1}{2\,m}\left(p_r^2 + \frac{p_\phi^2}{r^2} \right) + U(r), \tag{21.26}$$

and finally, we know from the equations of motion[1] that $\frac{\partial H}{\partial \phi} = -\dot{p}_\phi = 0$ so that p_ϕ is a constant. The problem of orbital motion reduces to a one-dimensional Hamiltonian – the radial coordinate is the only "interesting" equation of motion, and it is governed by an "effective potential". If we write:

$$H = \frac{p_r^2}{2\,m} + \left(U(r) + \frac{p_\phi^2}{2\,m\,r^2} \right) \tag{21.27}$$

then we may as well be considering the one-dimensional problem: Find the motion $r(t)$ given a Hamiltonian that is a function only of p_r and r (p_ϕ,

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[1]This is also an example of Noether's theorem – the lack of dependence on ϕ means that ϕ itself is "ignorable", and we can add a constant to ϕ without changing the Lagrangian at all – that symmetry implies conservation, in this case, of the z-component of angular momentum.

as we have just established is a constant). We mention all of this because the same basic breakup occurs when we consider the quantum mechanical analogue of the above, wavefunctions governed by a spherically symmetric potential. That we should be interested in such a restrictive form for the potential is dictated by the ultimate problem we wish to solve over the next few days: the Hydrogen atom, with its Coulombic potential.

Note that the above use of p_r, p_θ and p_ϕ induces the question: What are the quantum mechanical operators associated with these classical momenta? We will sidestep the issue for now, but be on the lookout for a return later on.

21.3   QM in Spherical Coordinates

Without going through the explicit transformations to spherical coordinates, we note that Schrödinger's equation still reads:

$$H\,\Psi(\mathbf{r},t) = i\,\hbar\,\frac{\partial \Psi(\mathbf{r},t)}{\partial t}, \tag{21.28}$$

and now the Hamiltonian is

$$H = \frac{\mathbf{p}\cdot\mathbf{p}}{2\,m} + U(r) \longrightarrow \hat{H} = -\frac{\hbar^2}{2\,m}\,\nabla^2 + U(r) \tag{21.29}$$

using the usual replacement, and assuming that the potential $U(\mathbf{r})$ depends only on the distance to the origin (i.e. $U(\mathbf{r}) = U(r)$ is spherically symmetric). Now, we already know the Laplacian in spherical coordinates:

$$\nabla^2\,\Psi(r,\theta,\phi,t) = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial \Psi}{\partial r}\right) + \frac{1}{r^2\,\sin\theta}\frac{\partial}{\partial \theta}\left(\sin\theta\,\frac{\partial \Psi}{\partial \theta}\right) + \frac{1}{r^2\,\sin^2\theta}\left(\frac{\partial^2 \Psi}{\partial \phi^2}\right). \tag{21.30}$$

Assuming that the potential $U(r)$ is time-independent, we can once again separate the temporal and spatial portions of the wavefunction, $\Psi(\mathbf{r},t) = \psi(\mathbf{r})\,\phi(t)$ and recover the time-independent Schrödinger equation

$$\hat{H}\,\psi = E\,\psi \quad \phi(t) = e^{-i\,\frac{E}{\hbar}\,t}, \tag{21.31}$$

allowing us to focus on the spatial portion $\psi(\mathbf{r})$.

We can separate further: Let $\psi(r, \theta, \phi) = R(r)\,\Theta(\theta)\,\Phi(\phi)$, then the Hamiltonian operator can be written as

$$\left(\frac{1}{R}\frac{d}{dr}\left(r^2 \frac{dR}{dr}\right) + \underbrace{\frac{1}{\sin^2\theta}\left(\frac{\sin\theta}{\Theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right) + \frac{1}{\Phi}\frac{d^2\Phi}{d\phi^2}\right)}_{(\theta,\phi)} \right) - \frac{2\,m\,r^2}{\hbar^2}U(r)$$
$$= -\frac{2\,m\,r^2}{\hbar^2}E.$$

$$(21.32)$$

The angular and radial portions are now separated – we will call the separation constant $\ell\,(\ell+1)$ (for reasons which should be familiar from, for example, electrodynamics).

21.3.1   The Angular Equations

Set the angular terms equal to the negative of the separation constant:

$$\frac{1}{\sin^2\theta}\left(\frac{\sin\theta}{\Theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right) + \frac{1}{\Phi}\frac{d^2\Phi}{d\phi^2}\right) = -\ell\,(\ell+1). \qquad (21.33)$$

Now, one of the terms depends only on Φ, so we will set it equal to a constant, call it m^2:

$$\frac{1}{\Phi}\frac{d^2\Phi}{d\phi^2} = -m^2 \longrightarrow \Phi(\phi) = A\,e^{i\,m\,\phi} + B\,e^{-i\,m\,\phi}, \qquad (21.34)$$

and by allowing m to be positive or negative, we can recover either solution, so we will just set:

$$\Phi(\phi) = e^{i\,m\,\phi} \qquad (21.35)$$

where we float the normalization – since this is multiplicative separation, we know there will be an overall constant that we can set at the end. At this point, we see that the particulars of this form for $\Phi(\phi)$ will not play a role in the probability density, since $|\Psi|^2$ will have $\Phi^*\Phi = 1$ built in. Still it is "usual" in terms of E&M in particular, to require that $\Phi(\phi) = \Phi(\phi + 2\,\pi)$, which implies that m is an integer, although this will also be forced on us from the rest of the angular separation.

For the $\Theta(\theta)$ portion, we have:

$$\sin\theta\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right) + (\ell\,(\ell+1)\,\sin^2\theta - m^2)\,\Theta = 0. \qquad (21.36)$$

To bring this into more familiar form, let $z = \cos\theta$, then $\frac{d}{d\theta} = \frac{dz}{d\theta}\frac{d}{dz} = -\sqrt{1-z^2}\frac{d}{dz}$, and the above becomes (thinking of Θ as a function of z, now)

$$-(1-z^2)\frac{d}{dz}\left(-(1-z^2)\frac{d\Theta(z)}{dz}\right) + (\ell(\ell+1)(1-z^2)-m^2)\,\Theta(z) = 0, \quad (21.37)$$

or

$$\frac{d}{dz}\left((1-z^2)\frac{d\Theta(z)}{dz}\right) + \left(\ell(\ell+1) - \frac{m^2}{1-z^2}\right)\Theta(z) = 0 \qquad (21.38)$$

which is the standard form for the "associated Legendre equation"[2]. Its solutions are known as "associated Legendre Polynomials", and are defined in terms of the Legendre polynomials via

$$P_\ell^m(z) = (1-z^2)^{|m|/2}\frac{d^{|m|}}{dz^{|m|}}P_\ell(z). \qquad (21.39)$$

Since this is a second order differential equation, there is, of course, another solution (associated Legendre "Q" functions), but these blow up at $z = \pm 1$. As a further restriction, these functions are only defined for integer $m \in [-\ell, \ell]$ for a given ℓ (which must then also be an integer).

We have, finally, the form for the angular solution (at least, separable solution) for Schrödinger's equation with spherically symmetric potential:

$$\Theta(\theta)\,\Phi(\phi) \sim e^{i\,m\,\phi}\,P_\ell^m(\cos\theta). \qquad (21.40)$$

Looking ahead to the full normalization for the probability density, we have (introducing a factor A in front of the angular terms):

$$1 = \int |\Psi|^2\,d\tau = \int_0^\infty \int_0^\pi \int_0^{2\pi} |A|^2\,R^*\,r\,R\,\Theta^*\,\Theta\,\Phi^*\,\Phi\,r^2\,\sin\theta\,d\phi\,d\theta\,dr$$

$$= \int_0^\infty R^*\,R\,r^2\,dr\left(\int_0^\pi 2\,\pi\,|A|^2\,(P_\ell^m(\cos\theta))^*\,P_\ell^m(\cos\theta)\,\sin\theta\right).$$

$$(21.41)$$

We can normalize the angular part by itself[3], by setting A such that

$$\left(\int_0^\pi 2\,\pi\,|A|^2\,(P_\ell^m(\cos\theta))^*\,P_\ell^m(\cos\theta)\sin\theta\right) = 1. \qquad (21.42)$$

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[2]See, for example, Riley, Hobson & Bence p. 666. Notice that the $m = 0$ case gives back Legendre's equation.

[3]Keep in mind that this will mean we need to separately normalize the radial part, $\int_0^\infty R^*\,R\,r^2\,dr = 1$.

It turns out that the value of A is,

$$A = \epsilon \sqrt{\frac{(2\,\ell+1)}{4\,\pi}\frac{(1-|m|)!}{(1+|m|)!}} \quad \epsilon \equiv \begin{cases} (-1)^m & m \leq 0 \\ 1 & m > 0 \end{cases} \tag{21.43}$$

With this normalization, the angular solutions are called "spherical harmonics", denoted $Y_\ell^m(\theta,\phi)$ (spherical since they are in spherical coordinates, harmonic because they are associated with solutions of Laplace's equation: $\nabla^2 F = 0$). Written out:

$$Y_\ell^m(\theta,\phi) = \epsilon \sqrt{\frac{(2\,\ell+1)}{4\,\pi}\frac{(1-|m|)!}{(1+|m|)!}}\, e^{i\,m\,\phi}\, P_\ell^m(\cos\theta) \tag{21.44}$$

These are orthonormal in the sense that

$$\int Y_\ell^m(\theta,\phi)^* \, Y_{\ell'}^{m'}(\theta,\phi)\, d\Omega = \int_0^{2\pi}\int_0^\pi Y_\ell^m(\theta,\phi)^* \, Y_{\ell'}^{m'}(\theta,\phi)\, \sin\theta\, d\theta\, d\phi$$

$$= \delta_{\ell\ell'}\,\delta_{mm'}. \tag{21.45}$$

Homework

Reading: Griffiths, pp. 131–139.

Problem 21.1

Griffiths 4.1. Here, you will work out the relevant, Cartesian, commutators for position and momentum. Feel free to use indexed notation, and in particular, the relation: $\frac{\partial x_i}{\partial x_j} = \delta_{ij}$ (think of $\frac{\partial x}{\partial x} = 1$, and $\frac{\partial x}{\partial y} = 0$).

Problem 21.2

Griffiths 4.2. Finding the stationary states of a three-dimensional infinite "well".

Problem 21.3

The ordinary differential equation:

$$\dot{z}(t) + \alpha\, z(t) = 0 \tag{21.46}$$

is solved by $z(t) = z_0\, e^{-\alpha\, t}$ for initial value $z(0) = z_0$. In this problem, we will develop the series solution (Frobenius method) in preparation for our work to come.

a. Start by setting $z(t) = t^p \sum_{j=0}^{\infty} c_j\, t^j$ (for unknown p). Take the derivative of this function (as a series) with respect to t.

b. Insert $z(t)$ and your expression for $\dot{z}(t)$ in (21.46), collecting all like powers of t into a single expression, i.e. fill in the ...s in: $t^p \left[(\ldots)\, t^{-1} + \sum_{j=0}^{\infty}(\ldots)\, t^j \right] = 0$.

c. You should have a lone t^{-1} term, use this to set $p = 0$, and, from the independence of powers of t^j, develop the recursion relation between the coefficients c_{j+1} and c_j. Solve the recursion, starting with $c_0 = z_0$, and compare with the Taylor series expansion of $z_0\, e^{-\alpha\, t}$.