Robertson-Schrödinger Uncertainty Relation

$$\sigma_A^2 \sigma_B^2 = \langle f|f\rangle\langle g|g\rangle \geq |\langle f|g\rangle|^2 = [\mathrm{Re}(z)]^2 + [\mathrm{Im}(z)]^2$$

$$\sigma_A^2 \sigma_B^2 \geq \left| \frac{1}{2}\langle\{\hat{A},\hat{B}\}\rangle_\psi - \langle\hat{A}\rangle_\psi\langle\hat{B}\rangle_\psi \right|^2 + \left(\frac{\langle[\hat{A},\hat{B}]\rangle_\psi}{2i}\right)^2$$

covariance

Three dimensions

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

2nd-order, linear in Ψ, homogeneous, Partial D.E

Laplacian $\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$ in Cartesian coords

$[\hat{r}_i, \hat{p}_j] = i\hbar\delta_{ij}$ e.g. $[\hat{y}, \hat{p}_x] = 0$ // $[\hat{r}_i, \hat{r}_j] = 0 = [\hat{p}_i, \hat{p}_j]$

$\Rightarrow \sigma_x\sigma_{p_x} \geq \frac{\hbar}{2}$, $\sigma_y\sigma_{p_y} \geq \frac{\hbar}{2}$, but $\sigma_x\sigma_{p_y}$ is unrestricted

We saw previously the 3-dim infinite square well, 3-dim quantum harmonic oscillator, both in Cartesian

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Now spherical Polar Coordinates $\{r, \theta, \varphi\}$

$r = |\vec{r}|$ = distance from origin, θ is polar angle

$\theta = 0^\circ$ = North pole, $\theta = 90^\circ$ = equator, $\theta = 180^\circ = \pi$ = South Pole

φ is azimuthal angle $[0, 2\pi]$ (physics convention)

Laplacian

$$\nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}$$

Separation of Variables $\psi(\vec{r}) = R(r)\,Y(\theta,\varphi)$

Assume $V(\vec{r}) = V(r)$ central potential

12-2 #4

TISE:

$$-\frac{\hbar^2}{2m}\left[\frac{Y}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)+\frac{R}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right)+\frac{R}{r^2\sin^2\theta}\frac{\partial^2 Y}{\partial\varphi^2}\right]$$

$$+V\underbrace{RY}_{\psi}=E\underbrace{RY}_{\psi}$$

Divide by $R(r)\,Y(\theta,\varphi)$ muliply by $\frac{-2mr^2}{\hbar^2}$

$\forall r,\theta,\varphi$

$$0=\underbrace{\left\{\frac{1}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)-\frac{2mr^2}{\hbar^2}\left[V(r)-E\right]\right\}}_{\text{only a function of } r}+\underbrace{\frac{1}{Y}\left\{\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2 Y}{\partial\varphi^2}\right\}}_{\text{function of } \theta,\varphi}$$

$$0=f(r)+g(\theta,\varphi)\quad\forall r,\theta,\varphi \implies \begin{array}{l} f(r)=\text{constant} \\ g(\theta,\varphi)=-\text{constant}\end{array}$$

We could call this first separation constant C, but in fact we will call it: $\ell(\ell+1)$ ← ℓ could be complex at this point.

Angular Equation: $\sin\theta\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right)+\frac{\partial^2 Y}{\partial\varphi^2}=-\ell(\ell+1)\sin^2\theta\, Y$

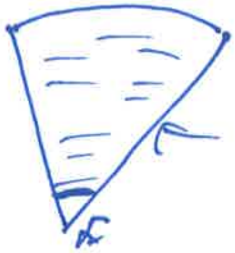
Separation of Variables again: $Y(\theta,\varphi)=T(\theta)F(\varphi)$

$$\underbrace{\left\{\frac{1}{T}\left[\sin\theta\frac{d}{d\theta}\left(\sin\theta\frac{dT}{d\theta}\right)\right]+\ell(\ell+1)\sin^2\theta\right\}}_{\text{function of } \theta}+\underbrace{\frac{1}{F}\frac{d^2F}{d\varphi^2}}_{\text{function of } \varphi}=0$$

Need a second separation constant: m^2 — *m could be complex at this point.*

Azimuthal Equation: $\frac{1}{F(\varphi)} F''(\varphi) = -m^2 \Rightarrow F''(\varphi) + m^2 F(\varphi) = 0$

$F(\varphi) = A e^{im\varphi} + B e^{-im\varphi}$ or <u>sine</u> and <u>cosine</u>



solve the S.E. in a pie wedge
$\Rightarrow$ boundary conditions determine possible values of <u>m</u>.

Usually have the full $[0, 2\pi]$ range of φ.

Later, when we introduce raising and lowering operators for angular momentum, we will see that
$\ell = 0, \frac{1}{2}, 1, \frac{3}{2}, 2, \frac{5}{2}, \ldots$ and $m = \{-\ell, -\ell+1, \ldots +\ell\}$.

Right now, I want to argue that for <u>orbital</u> (not spin) angular momentum, <u>m</u> must be integer, not half integer.

If e.g. $m = \frac{1}{2}$, then ψ as a function of angle φ looks like  twice around before repeating, but then ψ is not single-valued, so which ψ do I use to compute probabilities?

Also ψ cannot have a jump discontinuity 
because $\hat{L}_z = \frac{\hbar}{i}\frac{\partial}{\partial\varphi}$ would be ∞ at the jump but
$L_z|\psi\rangle = m|\psi\rangle$ with <u>m</u> $= \frac{1}{2}$ e.g. $\neq \infty$.

Griffiths' Quantum Mechanics

You may have encountered this equation already—it occurs in the solution to Laplace's equation in classical electrodynamics. As always, we try separation of variables:

$$Y(\theta, \phi) = \Theta(\theta)\Phi(\phi). \tag{4.19}$$

Plugging this in, and dividing by $\Theta\Phi$, we find

$$\left\{\frac{1}{\Theta}\left[\sin\theta\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right)\right] + l(l+1)\sin^2\theta\right\} + \frac{1}{\Phi}\frac{d^2\Phi}{d\phi^2} = 0.$$

The first term is a function only of θ, and the second is a function only of ϕ, so each must be a constant. This time I'll call the separation constant m^2:[4]

$$\frac{1}{\Theta}\left[\sin\theta\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right)\right] + l(l+1)\sin^2\theta = m^2; \tag{4.20}$$

$$\frac{1}{\Phi}\frac{d^2\Phi}{d\phi^2} = -m^2. \tag{4.21}$$

The ϕ equation is easy:

$$\frac{d^2\Phi}{d\phi^2} = -m^2\Phi \Rightarrow \Phi(\phi) = e^{im\phi}. \tag{4.22}$$

/ $Ae^{im\varphi} + Be^{-im\varphi}$ two solutions because 2nd order differential equation.

[Actually, there are *two* solutions: $\exp(im\phi)$ and $\exp(-im\phi)$, but we'll cover the latter by allowing m to run negative. There could also be a constant factor in front, but we might as well absorb that into Θ. Incidentally, in electrodynamics we would write the azimuthal function (Φ) in terms of sines and cosines, instead of exponentials, because electric potentials must be *real*. In quantum mechanics there is no such constraint, and the exponentials are a lot easier to work with.] Now, when ϕ advances by 2π, we return to the same point in space (see Figure 4.1), so it is natural to require that[5]

$$\boxed{\Phi(\phi + 2\pi) = \Phi(\phi).} \tag{4.23}$$

In other words, $\exp[im(\phi + 2\pi)] = \exp(im\phi)$, or $\exp(2\pi im) = 1$. From this it follows that m must be an *integer*:

$$m = 0, \pm 1, \pm 2, \ldots. \tag{4.24}$$

In E+M: $\nabla^2 V(\vec{r}) = 0$ Laplace's Equation for electric potential = voltage. $V(\varphi+2\pi) = V(\varphi)$ because $V(\vec{r})$ is measurable with a voltmeter, but wavefunction ψ is not measurable.

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[4] Again, there is no loss of generality here since at this stage m could be any complex number; in a moment, though, we will discover that m must in fact be an *integer*. *Beware:* The letter m is now doing double duty, as *mass* and as the so-called **magnetic quantum number**. There is no graceful way to avoid this since both uses are standard. Some authors now switch to M or μ for mass, but I hate to change notation in midstream, and I don't think confusion will arise as long as you are aware of the problem.

[5] This is a more subtle point than it looks. After all, the *probability* density ($|\Phi|^2$) is single valued *regardless* of m. In Section 4.3 we'll obtain the condition on m by an entirely different—and more compelling—argument.

Polar Equation

$$\sin\theta \frac{d}{d\theta}\left[\sin\theta \frac{dT(\theta)}{d\theta}\right] + \left[\ell(\ell+1)\sin^2\theta - m^2\right]T(\theta) = 0$$

Associated Legendre Differential Equation

2nd order: $T(\theta) = C\, P_\ell^m(\cos\theta) + D\, Q_\ell^m(\cos\theta)$

first second

associated Legendre functions of the ___ type

The P_ℓ^m are complete and orthogonal by themselves — span the Hilbert space; Q_ℓ^m not necessary.

Q_ℓ^m functions $\to \infty$ at North & South Poles.

Radial Equation

$$\frac{1}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) - \frac{2mr^2}{\hbar^2}\left[V(r) - E\right] = \ell(\ell+1)$$

Define: $u(r) = r\,R(r)$

$$-\frac{\hbar^2}{2m}\frac{d^2 u(r)}{dr^2} + \left[V(r) + \frac{\hbar^2}{2m}\frac{\ell(\ell+1)}{r^2}\right]u(r) = E\,u(r)$$

ψ ψ ψ

Looks like 1-dim Schrödinger Eq. with $u(r) = \psi(r)$

and $V_{eff}(r) = V(r) + \frac{\hbar^2}{2m}\frac{\ell(\ell+1)}{r^2}$ centrifugal term (repulsive)

Table 4.2: The first few spherical harmonics, $Y_l^m(\theta, \phi)$.

$Y_0^0 = \left(\frac{1}{4\pi}\right)^{1/2}$	$Y_2^{\pm 2} = \left(\frac{15}{32\pi}\right)^{1/2} \sin^2\theta e^{\pm 2i\phi}$
$Y_1^0 = \left(\frac{3}{4\pi}\right)^{1/2} \cos\theta$	$Y_3^0 = \left(\frac{7}{16\pi}\right)^{1/2} (5\cos^3\theta - 3\cos\theta)$
$Y_1^{\pm 1} = \mp\left(\frac{3}{8\pi}\right)^{1/2} \sin\theta e^{\pm i\phi}$	$Y_3^{\pm 1} = \mp\left(\frac{21}{64\pi}\right)^{1/2} \sin\theta(5\cos^2\theta - 1)e^{\pm i\phi}$
$Y_2^0 = \left(\frac{5}{16\pi}\right)^{1/2} (3\cos^2\theta - 1)$	$Y_3^{\pm 2} = \left(\frac{105}{32\pi}\right)^{1/2} \sin^2\theta\cos\theta e^{\pm 2i\phi}$
$Y_2^{\pm 1} = \mp\left(\frac{15}{8\pi}\right)^{1/2} \sin\theta\cos\theta e^{\pm i\phi}$	$Y_3^{\pm 3} = \mp\left(\frac{35}{64\pi}\right)^{1/2} \sin^3\theta e^{\pm 3i\phi}$

$$\boxed{Y_l^m(\theta, \phi) = \epsilon\sqrt{\frac{(2l+1)}{4\pi}\frac{(l-|m|)!}{(l+|m|)!}}\, e^{im\phi} P_l^m(\cos\theta),} \tag{4.32}$$

where $\epsilon = (-1)^m$ for $m \geq 0$ and $\epsilon = 1$ for $m \leq 0$. As we shall prove later on, they are automatically orthogonal, so

Griffiths' QM again

$$\int_0^{2\pi}\int_0^{\pi} [Y_l^m(\theta, \phi)]^*[Y_{l'}^{m'}(\theta, \phi)] \sin\theta\, d\theta\, d\phi = \delta_{ll'}\delta_{mm'}. \tag{4.33}$$

In Table 4.2 I have listed the first few spherical harmonics.

$*$**Problem 4.3** Use Equations 4.27, 4.28, and 4.32 to construct Y_0^0 and Y_2^1. Check that they are normalized and orthogonal.

Problem 4.4 Show that

$$\Theta(\theta) = A\ln[\tan(\theta/2)] \quad \propto Q_0^0(\cos\theta)$$

satisfies the θ equation (Equation 4.25) for $l = m = 0$. This is the unacceptable "second solution"—what's *wrong* with it? nothing; it is normalizable,

The answer he had in mind is that $\Theta(\theta)$ blows up at $\theta = 0, \pi$ North and South poles, but wavefunction ψ is not measurable.

$*$**Problem 4.5** Using Equation 4.32, find $Y_l^l(\theta, \phi)$ and $Y_3^2(\theta, \phi)$. Check that they satisfy the angular equation (Equation 4.18), for the appropriate values of the parameters l and m.

$**$**Problem 4.6** Starting from the Rodrigues formula, derive the orthonormality condition for Legendre polynomials:

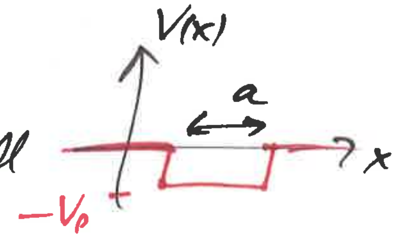
$$\int_{-1}^{1} P_l(x)P_{l'}(x)\,dx = \left(\frac{2}{2l+1}\right)\delta_{ll'}. \tag{4.34}$$

Hint: Use integration by parts.

Finite Spherical Square Well

step function
Heaviside function

$$V(r) = \begin{cases} -V_0, & r \le a \\ 0, & r > a \end{cases} = -V_0\,\theta(a-r)$$



Remember for 1-dim finite square well

always has at least one bound solution, no matter how shallow or narrow the well.

Future homework: Show that in 3 dimensions, there is not always a bound state.

For $\ell = 0$: $u(r) = A\sin(kr) + B\cos(kr)$

$$R(r) = \frac{u(r)}{r} \qquad \lim_{r\to 0} \frac{\sin(kr)}{r} \to k\,, \quad \lim_{r\to 0} \frac{\cos(kr)}{r} \to \frac{1}{r}$$

$\frac{1}{r}$ is integrable when multiplied by the measure: $r^2 \sin\theta \, dr\, d\theta\, d\varphi$ for spherical polar coordinates

but if $\psi(r) \propto \frac{1}{r}$, then $\nabla^2\left(\frac{1}{r}\right) \propto \delta(r)$ and there is no Dirac delta function in the potential $V(r)$.

where

Griffiths QM

$$k \equiv \frac{\sqrt{2mE}}{\hbar}, \tag{4.42}$$

as usual. Our problem is to solve this equation, subject to the boundary condition $u(a) = 0$. The case $l = 0$ is easy:

$$\frac{d^2u}{dr^2} = -k^2u \quad \Rightarrow \quad u(r) = A\sin(kr) + B\cos(kr).$$

So what? this is not the real problem.

But remember, the actual radial wave function is $R(r) = u(r)/r$, and $[\cos(kr)]/r$ blows up as $r \to 0$. So[10] we must choose $B = 0$. The boundary condition then requires $\sin(ka) = 0$, and hence $ka = n\pi$, for some integer n. The allowed energies are evidently

$$E_{n0} = \frac{n^2\pi^2\hbar^2}{2ma^2}, \quad (n = 1, 2, 3, \ldots), \tag{4.43}$$

the same as for the one-dimensional infinite square well (Equation 2.23). Normalizing $u(r)$ yields $A = \sqrt{2/a}$; inclusion of the angular part (constant, in this instance, since $Y_0^0(\theta, \phi) = 1/\sqrt{4\pi}$), we conclude that

$$\psi_{n00} = \frac{1}{\sqrt{2\pi a}} \frac{\sin(n\pi r/a)}{r}. \tag{4.44}$$

[Notice that the stationary states are labeled by *three* **quantum numbers**, n, l, and m: $\psi_{nlm}(r, \theta, \phi)$. The *energy*, however, depends only on n and l: E_{nl}.]

The general solution to Equation 4.41 (for an arbitrary integer l) is not so familiar:

$$u(r) = Arj_l(kr) + Brn_l(kr), \tag{4.45}$$

where $j_l(x)$ is the **spherical Bessel function** of order l, and $n_l(x)$ is the **spherical Neumann function** of order l. They are defined as follows:

$$j_l(x) \equiv (-x)^l \left(\frac{1}{x}\frac{d}{dx}\right)^l \frac{\sin x}{x}; \quad n_l(x) \equiv -(-x)^l \left(\frac{1}{x}\frac{d}{dx}\right)^l \frac{\cos x}{x}. \tag{4.46}$$

For example,

$$j_0(x) = \frac{\sin x}{x}; \quad n_0(x) = -\frac{\cos x}{x};$$

$$j_1(x) = (-x)\frac{1}{x}\frac{d}{dx}\left(\frac{\sin x}{x}\right) = \frac{\sin x}{x^2} - \frac{\cos x}{x};$$

---

[10] Actually, all we require is that the wave function be *normalizable*, not that it be *finite*: $R(r) \sim 1/r$ at the origin *would* be normalizable (because of the r^2 in Equation 4.31). For a more compelling proof that $B = 0$, see R. Shankar, *Principles of Quantum Mechanics* (New York: Plenum, 1980), p. 351. 342

Shanker QM

If c is nonzero, then

$$R \sim \frac{U}{r} \sim \frac{c}{r}$$

diverges at the origin. This in itself is not a disqualification, for R is still s
integrable. The problem with $c \neq 0$ is that the corresponding total wave functi

$$\psi \sim \frac{c}{r} Y_0^0$$

does not satisfy Schrödinger's equation at the origin. This is because of the re

$$\nabla^2(1/r) = -4\pi\delta^3(\mathbf{r}) \qquad (1$$

the proof of which is taken up in Exercise 12.6.4. Thus unless $V(r)$ contains a
function at the origin (which we assume it does not) the choice $c \neq 0$ is unten
Thus we deduce that

$$U_{El} \xrightarrow[r \to 0]{} 0 \qquad (12.$$

*Exercise 12.6.4.** (1) Show that

$$\delta^3(\mathbf{r}-\mathbf{r}') \equiv \delta(x-x')\delta(y-y')\delta(z-z') = \frac{1}{r^2 \sin\theta}\,\delta(r-r')\delta(\theta-\theta')\delta(\phi-\phi')$$

(consider a test function).

(2) Show that

$$\nabla^2(1/r) = -4\pi\delta^3(\mathbf{r})$$

(Hint: First show that $\nabla^2(1/r)=0$ if $r \neq 0$. To see what happens at $r=0$, consider a
sphere centered at the origin and use Gauss's law and the identity $\nabla^2\phi = \nabla\cdot\nabla\phi$).§

General Properties of U_{El}

We have already discussed some of the properties of U_{El} as $r \to 0$ or ∞. We
try to extract further information on U_{El} by analyzing the equation governing
these limits, without making detailed assumptions about $V(r)$. Consider first the l
$r \to 0$. Assuming $V(r)$ is less singular than r^{-2}, the equation is dominated by

‡ As we will see in a moment, $l \neq 0$ is incompatible with the requirement that $\psi(\mathbf{r}) \to r^{-1}$ as $r \to 0$.
the angular part of ψ has to be $Y_0^0 = (4\pi)^{-1/2}$.

§ Or compare this equation to Poisson's equation in electrostatics $\nabla^2\phi = -4\pi\rho$. Here $\rho = \delta^3(\mathbf{r})$,
represents a unit point charge at the origin. In this case we know from Coulomb's law that $\phi = 1/$