Robertson-Schrödinger Uncertainty Relation

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

$\sigma_A^2 \sigma_B^2 \geq \left| \frac{1}{2} \left( \langle \mathbf{A}, \mathbf{B} \rangle - \langle \mathbf{A} \rangle \langle \mathbf{B} \rangle \right) \right|^2 + \left( \frac{\langle \mathbf{C}, \mathbf{D} \rangle}{2i} \right)^2$

Covariance
Three dimensions

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

and-order, linear in \( \Psi \), 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

\[ [\hat{r}_i, \hat{p}_j] = i\hbar \delta_{ij}, \quad \text{e.g.} \quad [\hat{y}, \hat{p}_y] = 0, \quad [\hat{r}_i, \hat{r}_j] = 0 \]

\( \Rightarrow \nabla \cdot \vec{\rho} \geq \frac{\hbar}{\lambda}, \quad \nabla \times \vec{\rho} \geq \frac{\hbar}{\lambda}, \quad \text{but} \ \nabla \cdot \vec{\rho} \ \text{is unrestricted} \)

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

Now spherical polar coordinates \( \{ r, \theta, \phi \} \)

\( r = |\vec{r}| = \text{distance from origin}, \ \theta \ \text{is polar angle} \)
\( \theta = 0^\circ = \text{North pole}, \ \theta = 90^\circ = \text{equator}, \ \theta = 180^\circ = \pi = \text{South pole} \)
\( \phi \ \text{is azimuthal angle} \ [0, 2\pi] \) \ (physics convention)

\[
\begin{align*}
\text{Laplacian} & \quad \nabla^2 = \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2}{\partial \phi^2}
\end{align*}
\]

Separation of Variables \( \Psi(\vec{r}) = R(r) Y(\theta, \phi) \)

Assume \( V(\vec{r}) = V(r) \) \ (central potential)
\[ TISE: \]
\[-\frac{h^2}{2m} \left[ \frac{1}{r^2} \frac{d}{dr} \left( r^2 \frac{dR}{dr} \right) + \frac{R}{r^2 \sin \theta} \left( \sin \theta \frac{\partial V}{\partial \theta} \right) + \frac{R}{r^2 \sin^2 \theta} \frac{\partial^2 V}{\partial \phi^2} \right] \]
\[ + V R \psi = \frac{E \psi}{2} \]

Divide by \( R(r) \) \( \psi(\theta, \phi) \) multiply by \( \frac{-2m \hbar^2}{h^2} \)

\[ 0 = \sum \frac{1}{R} \frac{d}{dr} \left( r^2 \frac{dR}{dr} \right) - \frac{2m \hbar^2}{\hbar^2} \left[ V(r) - E \right] \]
\[ + \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial \psi}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2 \psi}{\partial \phi^2} \]

only a function of \( r \)

function of \( \theta, \phi \)

\[ 0 = f(r) + g(\theta, \phi) \quad \forall \theta, \phi \Rightarrow f(r) = \text{constant} \]
\[ g(\theta, \phi) = -\text{constant} \]

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

Angular Equation: \( \sin \theta \frac{d}{d\theta} \left( \sin \theta \frac{d\psi}{d\theta} \right) + \frac{\partial^2 \psi}{\partial \phi^2} = -\lambda (l+1) \sin \theta \psi \)

Separation of Variables again: \( \psi(\theta, \phi) = T(\theta) F(\phi) \)

\[ \frac{1}{F} \left[ \sin \theta \frac{d}{d\theta} \left( \sin \theta \frac{dT}{d\theta} \right) \right] + \lambda (l+1) \sin^2 \theta T + \frac{1}{F} \frac{d^2 F}{d\phi^2} = 0 \]

function of \( \theta \)

function of \( \phi \)
Need a second separation constant: \( m^2 \) could be complex at this point.

Azimuthal Equation: \( \frac{1}{F(\phi)} \frac{\partial^2 F(\phi)}{\partial \phi^2} - m^2 F(\phi) = 0 \)

\( F(\phi) = A e^{im\phi} + B e^{-im\phi} \) or sine and cosine

Solve the S.E. in a pie wedge → boundary conditions determine possible values of \( m \).

Usually have the full \([0, 2\pi]\) range of \( \phi \).

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 \( m = \ell, \ell+1, \ldots \pm \ell \).

Right now, I want to argue that for orbital (not spin) angular momentum, \( \ell \) must be integer, not half integer.

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

Also, \( \Psi \) can not have a jump discontinuity because \( \hat{z} = \frac{\hbar}{i} \frac{\partial}{\partial \phi} \) would be 0 at the jump but

\[ \hat{z} |\Psi\rangle = m |\Psi\rangle \] with \( m = \frac{1}{2} \) e.g. \( \neq 0 \).
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:

\[ Y(\theta, \phi) = \Theta(\theta)\Phi(\phi). \quad [4.19] \]

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

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

The first term is a function only of \( \theta \), and the second is a function only of \( \phi \), so each must be a constant. This time I'll call the separation constant \( m^2 \):\(^4\)

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

\[
\frac{1}{\Phi} \frac{d^2 \Phi}{d\phi^2} = -m^2. \quad [4.21]
\]

The \( \phi \) equation is easy:

\[
\frac{d^2 \Phi}{d\phi^2} = -m^2 \Phi \Rightarrow \Phi(\phi) = e^{\pm im\phi}. \quad [4.22]
\]

[Actually, there are two solutions: \( \exp(i m\phi) \) and \( \exp(-i m\phi) \), 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 \( \Theta \). Incidentally, in electrodynamics we would write the azimuthal function (\( \Phi \)) 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 \( \phi \) advances by \( 2\pi \), we return to the same point in space (see Figure 4.1), so it is natural to require that\(^5\)

\[
\Phi(\phi + 2\pi) = \Phi(\phi). \quad [4.23]
\]

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

\[
m = 0, \pm 1, \pm 2, \ldots. \quad [4.24]
\]

\(^4\)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 \( \mu \) 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

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

Associated Legendre Differential Equation

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

First \( \rightarrow \) second associated Legendre functions of the \( \ell \) type

The \( P_\ell^m \) are complete and orthogonal by themselves—span the Hilbert space; \( Q_\ell^m \) not necessary.

\( Q_\ell^m \) functions \( \rightarrow \) as at North South Poles.

Radial Equation

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

Define: \( \Phi(r) = r R(r) \)

\[
-\frac{\hbar^2}{am} \frac{d^2 \Phi(r)}{dr^2} + \left[ V(r) + \frac{\hbar^2}{am} \frac{\ell (\ell + 1)}{r^2} \right] \Phi(r) = E \Phi(r)
\]

Looks like 1-dim Schrödinger Eq. with \( \Phi(r) = \Phi(r) \)

and \( V_{\mathrm{eff}}(r) = V(r) + \frac{\hbar^2}{am} \frac{\ell (\ell + 1)}{r^2} \) centrifugal term (repulsive)
Table 4.2: The first few spherical harmonics, \( Y_l^m(\theta, \phi) \).

<table>
<thead>
<tr>
<th>( Y_l^m(\theta, \phi) )</th>
<th>( Y_l^m(\theta, \phi) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( Y_0^0 = \left( \frac{1}{4\pi} \right)^{1/2} )</td>
<td>( Y_2^0 = \left( \frac{15}{32\pi} \right)^{1/2} \sin^2 \theta e^{\pm 2i\phi} )</td>
</tr>
<tr>
<td>( Y_1^0 = \left( \frac{3}{4\pi} \right)^{1/2} \cos \theta )</td>
<td>( Y_3^0 = \left( \frac{7}{16\pi} \right)^{1/2} (5\cos^3 \theta - 3\cos \theta) )</td>
</tr>
<tr>
<td>( Y_1^\pm = \mp \left( \frac{3}{8\pi} \right)^{1/2} \sin \theta e^{\pm i\phi} )</td>
<td>( Y_3^\pm = \mp \left( \frac{21}{64\pi} \right)^{1/2} \sin \theta (5\cos^2 \theta - 1)e^{\pm i\phi} )</td>
</tr>
<tr>
<td>( Y_2^0 = \left( \frac{5}{16\pi} \right)^{1/2} (3\cos^2 \theta - 1) )</td>
<td>( Y_3^2 = \left( \frac{105}{32\pi} \right)^{1/2} \sin^2 \theta \cos \theta e^{\pm 2i\phi} )</td>
</tr>
<tr>
<td>( Y_2^\pm = \mp \left( \frac{15}{8\pi} \right)^{1/2} \sin \theta \cos \theta e^{\pm i\phi} )</td>
<td>( Y_3^3 = \mp \left( \frac{35}{64\pi} \right)^{1/2} \sin^3 \theta e^{\pm 3i\phi} )</td>
</tr>
</tbody>
</table>

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

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

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

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

\[
\Theta(\theta) = A \ln[\tan(\theta/2)] \propto \Theta_0 \cos \theta
\]

satisfies the \( \theta \) equation (Equation 4.25) for \( l = m = 0 \). This is the unacceptable "second solution"—what’s wrong with it? **Nothing; it is normalizable.**

*Problem 4.5* Using Equation 4.32, find \( Y_1^0(\theta, \phi) \) 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:

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

**Hint:** Use integration by parts.
**Finite Spherical Square Well**

\[ V(r) = \begin{cases} -V_0, & r \leq a \\ 0, & r > a \end{cases} = -V_0 \Theta(a-r) \]

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 \( L = 0 \): \( U(r) = A \sin(kr) + B \cos(kr) \)

\[ R(r) = \frac{U(r)}{r} \underset{r \to 0}{\longrightarrow} \frac{\sin(kr)}{kr} \to k \quad \underset{r \to 0}{\longrightarrow} \frac{\cos(kr)}{kr} \to \frac{1}{k} \]

\( k \) is integrable when multiplied by the measure: \( r^2 \sin \theta \, d \theta \, d \phi \) for spherical polar coordinates but if \( f(r) \propto \frac{1}{r} \), then \( \nabla^2 f \propto f(r) \) and there is no Dirac delta function in the potential \( V(r) \).
where
\[ k \equiv \frac{\sqrt{2mE}}{\hbar}, \quad [4.42] \]
as usual. Our problem is to solve this equation, subject to the boundary condition \( u(a) = 0 \). The case \( l = 0 \) is easy:

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

But remember, the actual radial wave function is \( R(r) = \frac{u(r)}{r}, \) 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

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

\[ \psi_{n00} = \frac{1}{\sqrt{2\pi a}} \frac{\sin(n\pi r/a)}{r}. \quad [4.44] \]
[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:

\[ u(r) = Arj_l(kr) + Brn_l(kr), \quad [4.45] \]
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:

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

For example,

\[ j_0(x) = \frac{\sin x}{x}; \quad n_0(x) = -\frac{\cos x}{x}; \]
\[ j_1(x) = (-x)^{-1} \frac{d}{dx} \left( \frac{\sin x}{x} \right) = \frac{\sin x}{x^2} - \frac{\cos x}{x}; \]

\(^{10}\) 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. \[4.42\]
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 \( r \)-integrable. The problem with \( c \neq 0 \) is that the corresponding total wave function

\[
\psi \sim \frac{c}{r} Y_0^0
\]

does not satisfy Schrödinger's equation at the origin. This is because of the right-hand side of (12.3.17),

\[
\nabla^2 (1/r) = -4\pi \delta^3 (r)
\]

the proof of which is taken up in Exercise 12.6.4. Thus unless \( V(r) \) contains a term 

\[
U_{El} \xrightarrow{r \to 0} 0
\]

Thus we deduce that

Exercise 12.6.4. *(1) Show that

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

(consider a test function).

(2) Show that

\[
\nabla^2 (1/r) = -4\pi \delta^3 (r)
\]

(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 \( \infty \). 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 case \( r \to 0 \). Assuming \( V(r) \) is less singular than \( r^{-2} \), the equation is dominated by

\[\dagger \]

As we will see in a moment, \( l \neq 0 \) is incompatible with the requirement that \( \psi (r) \to r^{-1} \) as \( r \to 0 \).

\[\ddagger \]

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