Quantum Mechanics

Notes from the reading of the book by Griffiths

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Contents

Chapter 4

Quantum Mechanics in Three Dimensions

Schrödinger's Equation is still

$$i\hbar\frac{\partial \Psi}{\partial t} = \widehat{H}\Psi$$

where the Hamiltonian is now

$$\frac{1}{2m}\left(p_x^2 + p_y^2 + p_z^2\right) + V$$

Consequently, we have

$$\widehat{H} = -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right) + V$$

and thus,

$$i\hbar\frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m}\nabla^2\Psi + V\Psi$$

where ∇^2 is the Laplacian. Also, the wave is now normalized as

$$\iiint_{\mathbb{R}^3} |\Psi(\mathbf{r}, t)|^2 \; d^3\mathbf{r} = 1$$

If the potential function is independent of time, there will be a complete set of stationary states,

$$\Psi_n(\mathbf{r}, t) = \psi_n(\mathbf{r})e^{-iE_n t/\hbar}$$

where the spatial wave function ψ_n satisfies the *Time Independent Schrödinger Equation*,

$$-\frac{\hbar^2}{2m}\nabla^2\psi + V\psi = E\psi$$

and thus, the general solution to the time-dependent Schrödinger equation is

$$\Psi(\mathbf{r}, t) = \sum_n c_n\psi_n(\mathbf{r})e^{-iE_nt/\hbar}$$

as before.

4.1 Separation of Variables

We shall solve the Time Independent Schrödinger Equation in spherical coordinates, $(\mathbf{r}, \theta, \phi)$. The Laplacian takes the following form

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

We look for solutions of a separable form and hope that they form a basis,

$$\psi(r, \theta, \phi) = R(r)Y(\theta, \phi)$$

Substituting the above and simplifying, we obtain

$$\left\{\frac{1}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) - \frac{2mr^2}{\hbar^2}(V(r) - E)\right\} + \frac{1}{Y}\left\{\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2 Y}{\partial\phi^2}\right\} = 0$$

Notice that the first term is a function of only r while the second is a function of only θ and ϕ, thus both must be constants. Let us denote this constant by $l(l+1)$, where $l \in \mathbb{C}$. We are now left with:

$$\frac{1}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) - \frac{2mr^2}{\hbar^2}(V(r) - E) = l(l+1)$$
$$\frac{1}{Y}\left\{\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2 Y}{\partial\phi^2}\right\} = -l(l+1)$$

4.1.1 Angular Equation

Multiply out $Y\sin^2\theta$ to obtain

$$\sin\theta\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right)+\frac{\partial^2 Y}{\partial\phi^2}=-l(l+1)Y\sin^2\theta$$

We attempt to separate variables again, this time, let

$$Y(\theta,\phi)=\Theta(\theta)\Phi(\phi)$$

Substituting the above and dividing by $\Theta\Phi$, we obtain

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

Again, the first term is a function of only θ and the second is a function of only ϕ and therefore must be constants. We shall denote this constant by m^2, where $m\in\mathbb{C}$. This gives us

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

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

The second differential equation is trivially solvable and obtain $\Phi(\phi)=e^{im\phi}$. A trivial boundary condition on Φ is given by

$$\Phi(\phi+2\pi)=\Phi(\phi)$$

from which it follows that $m\in\mathbb{Z}$. Next, solving the equation in θ,

$$\sin\theta\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right)+(l(l+1)\sin^2\theta-m^2)\Theta=0$$

This does not have simple solution. The most general solution is given by

$$\Theta(\theta)=AP_l^m(\cos\theta)$$

where P_l^m is the *associated Legendre Function*, defined by

$$P_l^m(x)=(1-x^2)^{|m|/2}\frac{d^{|m|}}{dx^{|m|}}P_l(x)$$

where $P_l(x)$ is the l-th *Legendre Polynomial*, defined by

$$P_l(x) = \frac{1}{2^l l!} \frac{d^l}{dx^l} (x^2 - 1)^l$$

It is important to note here that the equation for θ is a Second Order Differential Equation and therefore, must have two linearly independent solutions. We only consider one of them because the other blows up at $\theta \in \{0, \pi\}$.

Legendre Polynomials

This is a digression, in attempt to elucidate a few properties of Legendre Polynomials. I present first, three equivalent definitions

$$\frac{1}{\sqrt{1 - 2xt + t^2}} = \sum_{n=0}^{\infty} P_n(x) t^n$$

$$(n+1) P_{n+1}(x) = (2n+1) x P_n(x) - n P_{n-1}(x)$$

with the base cases $P_0(x) = 1$ and $P_1(x) = x$.

$$(1 - x^2) P_n''(x) - 2x P_n'(x) + n(n+1) P_n(x) = 0$$

which leads us to the Rodrigues' Formula:

$$P_n(x) = \frac{1}{2^n n!} \frac{d^n}{dx^n} (x^2 - 1)^n$$

The Legendre Polynomials are known to be *orthogonal* in the vector space of polynomials equipped with the integral inner product. That is,

$$\int_{-1}^{1} P_m(x) P_n(x) \, dx = \frac{2}{m+n+1} \delta_{mn}$$

where δ_{mn} is the Kronecker-Delta, which can be proved using the Principle of Mathematical Induction.

Coming back, we normalize the angular and radial wave functions separately and obtain:

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

where

$$\varepsilon_m = \begin{cases} (-1)^m & m \geq 0 \\ 1 & m \leq 0 \end{cases}$$

This gives an added condition:

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

which implies orthogonality.

4.1.2 Radial Equation

Note that the angular part of the wave function $Y(\theta, \phi)$ is the same for all spherically symmetric potentials. The potential function $V(\mathbf{r})$ affects only the *radial* part of the wave function,

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

Performing the substitution $u = rR$, we obtain

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

This is identical in form to the one-dimensional Schrödinger equation with the *effective potential*

$$V_{\text{eff}} = V + \frac{\hbar^2}{2m}\frac{l(l+1)}{r^2}$$

the extra term in the above equation is known as the *centrifugal term*. The normalization condition is given by

$$\int_0^{\infty} |u|^2 \, dr = 1$$

4.2 The Hydrogen Atom

In this case, we know $V(r)$ explicitly:

$$V(r) = -\frac{e^2}{4\pi\varepsilon_0}\frac{1}{r}$$

and the radial equation becomes:

$$-\frac{\hbar^2}{2m}\frac{d^2u}{dr^2} + \left[-\frac{e^2}{4\pi\varepsilon_0}\frac{1}{r} + \frac{\hbar^2}{2m}\frac{l(l+1)}{r^2}\right]u = Eu$$

Let now,

$$\kappa = \frac{\sqrt{-2mE}}{\hbar}$$

and

$$\rho = \kappa r \qquad \text{and} \qquad \rho_0 = \frac{me^2}{2\pi\varepsilon_0\hbar^2\kappa}$$

so that

$$\frac{d^2u}{d\rho^2} = \left[1 - \frac{\rho_0}{\rho} + \frac{l(l+1)}{\rho^2}\right]u$$

We shall attempt to look for solutions of the form:

$$u(\rho) = \rho^{l+1}e^{-\rho}v(\rho)$$

The process after this requires us to expand $v(\rho)$ as a formal series:

$$v(\rho) = \sum_{j=0}^{\infty} c_j\rho^j$$

and we would like to determine the coefficients $\langle c_0, c_1, \ldots\rangle$. Substituting this into the differential equation, we obtain:

$$c_{j+1} = \left\{\frac{2(j+l+1)-\rho_0}{(j+1)(j+2l+2)}\right\}c_j$$

Let us examine the above recursion for $j >> 1$:

$$c_{j+1} \asymp$$

4.3 Angular Momentum

It is well known that

$$\mathbf{L} = \mathbf{r} \times \mathbf{p}$$

In cartesian coordinates, this looks like

$$L_x = yp_z - zp_x \qquad L_y = zp_x - xp_z \qquad L_z = xp_y - yp_x$$

and the corresponding quantum operators can be obtained by performing the usual substitution $p_x \mapsto -i\hbar\partial/\partial x$ and so on. Then, one can obtain:

$$[L_x, L_y] = i\hbar L_z \qquad [L_y, L_z] = i\hbar L_x \qquad [L_z, L_x] = i\hbar L_y$$

Now, since L_x, L_y and L_z are *incompatible observables*, according to the generalized uncertainty principle,

$$\sigma_{L_x}\sigma_{L_y} \geq \frac{\hbar}{2}|\langle L_z\rangle|$$

It is therefore futile to look for states that are simultaneously eigenfunctions of L_x and L_y. Consider the operator $L^2 \equiv L_x^2 + L_y^2 + L_z^2$, the square of the total angular momentum. The commutator

$$\begin{aligned}
[L^2, L_x] &= [L_x^2, L_x] + [L_y^2, L_x] + [L_z^2, L_x] \\
&= L_y[L_y, L_x] + [L_y, L_x]L_y + L_z[L_z, L_x] + [L_z, L_x]L_z \\
&= i\hbar(-L_yL_z - L_zL_y + L_zL_y + L_yL_z) \\
&= 0
\end{aligned}$$

And thus, L^2 commutes with L_x, L_y and L_z, and consequently,

$$[L^2, \mathbf{L}] = 0$$

Therefore, L^2 is compatible with each component of $\mathbf{L}$ and we can hope to find simultaneous eigenstates of L^2 and L_z:

$$L^2 f = \lambda f \qquad \text{and} \qquad L_z f = \mu f$$