PHYS 621 – Quantum Mechanics Study Notes

Richard Whitehill

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Contents

CHAPTER 1

The Failure of Classical Physics

The following is a quick summary of some of the phenomena which classical mechanics and electromagnetic theory could not properly model and explain.

1.1 Black-body radiation

The primary quantity of interest here is the energy density of some box which is kept at temperature T, denoted as $u(\nu, T)$. The total energy that strikes an area A of the wall of the box in time t is

$$\int_0^{2\pi} \mathrm{d}\phi \int_0^{\pi/2} \mathrm{d}\theta \sin\theta \int_0^{ct} r^2 \frac{A\cos\theta}{4\pi r^2} u(\nu, T)\,\mathrm{d}\nu = \frac{ctA}{4} u(\nu, T)\,\mathrm{d}\nu\,. \tag{1.1}$$

If the box absorbs some fraction $f(\nu, T)$ of this energy, then the total energy absorbed by the box at temperature T from light at frequency ν is

$$E(\nu, T) = \frac{c}{4} f(\nu, T) u(\nu, T). \tag{1.2}$$

A body is called "black" if $f \equiv 1$, meaning that all light is perfectly absorbed.

1.1.1 Classical treatment

We can solve Maxwell's equations (no sources!) inside the box with periodic boundary conditions, which gives

$$\frac{\partial^2 \tilde{\mathbf{E}}}{\partial t^2} + c^2 k^2 \tilde{\mathbf{E}} = 0, \tag{1.3}$$

where $\tilde{\mathbf{E}}(\mathbf{k})$ are the Fourier expansion coefficients of the electric field such that

$$\vec{\boldsymbol{E}} = \sum_k e^{i\vec{\boldsymbol{k}}\cdot\vec{\boldsymbol{r}}} \tilde{\mathbf{E}}(\mathbf{k}). \tag{1.4}$$

A similar equation holds for the magnetic field. We can thus model the electromagnetic (EM) radiation by an infinite set of uncoupled harmonic oscillators.

Next, we find the number of modes in a small volume of the reciprocal space to be

$$\rho(\vec{\boldsymbol{k}})\,\mathrm{d}^3\vec{\boldsymbol{k}} = 2\frac{V}{(2\pi)^3}\,\mathrm{d}\vec{\boldsymbol{k}}\,. \tag{1.5}$$

The factor of two comes from the fact that there are two independent components in $\tilde{E}$ (in solving MEs, there is a condition that $\vec{\boldsymbol{E}}$ be perpendicular to $\vec{\boldsymbol{k}}$), and the second factor comes from the volume per mode in the reciprocal space.

Using the equipartition theorem (which states that $U = \frac{1}{2}k_BT$ is the energy contribution from each quadratic degree of freedom in the Hamiltonian – of which there are two for a given harmonic oscillator), the relation $\mathrm{d}^3\vec{\boldsymbol{k}} = 4\pi k^2\,\mathrm{d}k$ (assuming angular symmetry), and the dispersion relation $c = \nu\lambda$ ($k = 2\pi/\lambda$), we recover the Rayleigh-Jeans law for the energy density of a blackbody:

$$\boxed{\frac{(k_BT/2)\rho(k)\,\mathrm{d}k}{V} = \underbrace{8\pi\frac{k_BT}{c^3}\nu^2\,\mathrm{d}\nu}_{u(\nu,T)}}\,, \tag{1.6}$$

Clearly the energy density diverges to ∞ for more energetic light (which is where the term "ultraviolet catastrophe" originates).

1.1.2 Quantum treatment

The quantum nature comes from using Einstein's formula for the energy of a photon of light at frequency ν: $E = nh\nu$ ($n = 0, 1, 2, \ldots$). We can use the partition function to derive the fact that the average energy of a harmonic oscillator is

$$\langle E\rangle = \frac{h\nu}{e^{\beta h\nu} - 1}, \tag{1.7}$$

where $\beta = 1/k_BT$. Using this fact instead of the equipartition theorem, we find

$$\boxed{u(\nu, T) = \frac{8\pi h}{c^3}\frac{\nu^3}{e^{\beta h\nu} - 1}}\,. \tag{1.8}$$

Notice that this resolves the ultraviolet catastrophe since the energy density now is bounded at all frequencies of light, peaking at some ν_0 (is there a well-known formula for this?).

1.2 Photo-electric effect

The photo-electric effect is the phenomenon that if light is shined on a metal and set up a potential difference between the metal and some other metallic plate, say, that there is a current between the plates (in some circumstances).

1.2.1 Classical Treatment

We can treat an electron at the surface of the metal, which absorbs the light, to be a harmonic oscillator driven by the light (i.e. the force that the electric field of the light wave exerts on the electron). That is,

$$m\ddot{x}(t) + kx(t) = -e\mathcal{E}_0 \cos(\omega t). \tag{1.9}$$

Solving gives,

$$x(t) = x_0 \cos(\omega_0 t + \phi_0) - \frac{e\mathcal{E}_0}{m} \frac{\cos(\omega t)}{\omega_0^2 - \omega^2}, \tag{1.10}$$

where $\omega_0^2 = k/m$, which depends on the metal in consideration. The first term is just the homogeneous solution of the equation with x_0 and ϕ_0 determined by initial conditions. Notice that the energy of the electron is (considering only the contribution associated with the transient term – i.e. that from the driving force)

$$E(t) = \frac{1}{2}m\dot{x}^2 + \frac{k}{2}x \approx \frac{e^2\mathcal{E}_0^2}{2m} \frac{1}{(\omega_0^2 - \omega^2)^2} [\omega^2 \sin^2(\omega t) + \omega_0^2 \cos^2(\omega t)]. \tag{1.11}$$

The average energy over one period of oscillation $T = 2\pi/\omega$ is just

$$\langle E \rangle = \frac{e^2\mathcal{E}_0^2}{4m} \frac{\omega_0^2 + \omega^2}{(\omega_0^2 - \omega^2)^2}. \tag{1.12}$$

Recall that the intensity of light is proportional to $\mathcal{E}_0^2$, so the average energy of the electron is predicted to be proportional to the intensity of the light shone on the metal. Above some threshold energy, we should observe a current, and by increasing the intensity of the light, we would expect classically that the current is proportional in some way (would have to work out the proportionality) to the intensity. In fact, for any color of light, we could observe a current if we have intense enough light.

1.2.2 Quantum Treatment

The classical treatment is inconsistent with experimental observations. In reality, it is found that no matter how intense we make the light, some wavelengths are simply incapable of generating any current. Again, in this case, we quantize the energy of a photon as $E = h\nu$. For a metal with work function $W = h\nu_0$, where ν_0 is a convenient parameter with which to compare the frequency of the light, the kinetic energy of an electron which is freed from the metal by this photon is

$$K = E - W = h(\nu - \nu_0). \tag{1.13}$$

Clearly then, we have to have $\nu > \nu_0$ at the very least to observe a current. If we satisfy this condition, then increasing the intensity of light – which corresponds to increasing the number of photons – does in fact lead to larger observed currents.

1.3 Compton scattering

In classical mechanics, treating light as a wave, if we shine light on a charged particle, say an electron, we would find that the electron is excited by the light similar to the above argument. In quantum mechanics, however, treating the photon as a particle, the light has momentum proportional to $p = h/\lambda = h\nu/c$, and the photon interacts "concretely" with the electron by exchanging momentum and scattering at some angle θ relative to the axis of the incoming light. Quantitatively, we have the Compton relation

$$\Delta\lambda = \frac{h}{mc}(1 - \cos\theta). \tag{1.14}$$

Note that h/mc is known as the Compton wavelength of the electron.

We can derive this relation as follows. First, let us work in the rest frame of the electron, and the photon approach the electron with momentum $\vec{\boldsymbol{p}}_\gamma = h/\lambda\hat{\boldsymbol{x}}$. After the collision, the photon has momentum $\vec{\boldsymbol{p}}'_\gamma = \frac{h}{\lambda'}\left[\sin\theta\hat{\boldsymbol{x}} + \cos\theta\hat{\boldsymbol{y}}\right]$ while the electron has momentum $\vec{\boldsymbol{p}}'_e$. Note that energy conservation gives

$$p_\gamma c + mc^2 = p'_\gamma c + \sqrt{m^2c^4 + p'^2_e c^2}. \tag{1.15}$$

If we subtract $p'_\gamma c$ from both sides and square, we have

$$\begin{gathered}
[(p_\gamma - p'_\gamma)c + mc^2]^2 = m^2c^4 + |\vec{\boldsymbol{p}}'_\gamma - \vec{\boldsymbol{p}}_\gamma|^2c^2 \\
(p'_\gamma - p_\gamma)^2 + 2(p_\gamma - p'_\gamma)mc = p'^2_\gamma + p^2_\gamma - 2p'_\gamma p_\gamma\cos\theta \\
\frac{1}{p'_\gamma} - \frac{1}{p_\gamma} = \frac{1 - \cos\theta}{mc} \\
\lambda' - \lambda = \Delta\lambda = \frac{h}{mc}(1 - \cos\theta).
\end{gathered} \tag{1.16}$$

1.4 Atom stability and spectral lines

In the homework, we completed a problem showing that based on classical mechanics an electron should collapses into the nucleus of an atom very quickly (because of the EM radiation from its acceleration). Clearly this is in contrast with the stability of the universe in general, and can be broached with the introduction of a few different models, although the Schrödinger equation is the most correct treatment and is the subject of much of the topic of non-relativistic QM.

There is also the issue of the spectral lines from atoms, which are distinct wavelengths of light emitted and absorbed by atoms. Note that the emission and absorption spectra are identical (corresponding to the energy levels of an atom). This observation is in stark contradiction to the classical expectation, which is that the spectra are continuous. For emission, the electron radiates light of all frequencies within a certain range, given by its acceleration at any time. On the other hand, there is no classical restriction on which frequencies an electron is permitted to interact with, so it absorbs any light happily.

CHAPTER 2

Wave-Particle Duality and Wave Mechanics

In the previous chapter, we have observed that light can be treated as both a particle in some instances and a wave in others. It is natural then to extend this to matter particles such as electrons, which have in some instances as wave-like properties. De Broglie introduced the wavelength of a particle as $\lambda = h/p$, and from this formula, we can reproduce the different observations which corroborate this wave-particle duality of matter. For instance, a couple well known results are the two-slit experiment and Bragg reflection, both of which give interference patterns that can only be attributed to the wave nature of particles.

2.1 Wave packets

A particle's wave-function can be written

$$\Psi(\vec{\boldsymbol{r}}, t) = \int \frac{\mathrm{d}^3\vec{\boldsymbol{k}}'}{(2\pi)^{3/2}} g(\vec{\boldsymbol{k}}') e^{i[\vec{\boldsymbol{k}}'\cdot\vec{\boldsymbol{r}} - \omega(\vec{\boldsymbol{k}}')t]}, \tag{2.1}$$

where g is some complex profile function whose magnitude $|g|$ is strongly localized around $\vec{\boldsymbol{k}}$. This is a superposition of plane waves corresponding to different momenta (we will see later that we cannot consider a particle with definite momentum $\vec{\boldsymbol{p}} = \hbar\vec{\boldsymbol{k}}$) with time dependence given by a phase with $\omega = E/\hbar = \hbar k'^2/2m$.

We can analyze this wave-packet using the method of stationary phase. Defining $\phi(\vec{\boldsymbol{k}}') = \vec{\boldsymbol{k}}' \cdot \vec{\boldsymbol{r}} - \omega t$, we expand around the peak of $|g|$, which gives

$$\phi(\vec{\boldsymbol{k}}') \approx \phi(\vec{\boldsymbol{k}}) + (\vec{\boldsymbol{k}}' - \vec{\boldsymbol{k}}) \cdot \vec{\boldsymbol{\nabla}}_{\vec{\boldsymbol{k}}'} \phi(\vec{\boldsymbol{k}}')|_{\vec{\boldsymbol{k}}'=\vec{\boldsymbol{k}}} + \ldots. \tag{2.2}$$

Putting this into Eq. (2.1), we have

$$\Psi(\vec{\boldsymbol{r}}, t) \approx e^{i[\vec{\boldsymbol{k}}\cdot\vec{\boldsymbol{r}} - \omega(\vec{\boldsymbol{k}})t]} \int \frac{\mathrm{d}^3\vec{\boldsymbol{k}}'}{(2\pi)^{3/2}} g(\vec{\boldsymbol{k}}') e^{i[\vec{\boldsymbol{r}} - \frac{\hbar\vec{\boldsymbol{k}}}{m}t]\cdot[\vec{\boldsymbol{k}}' - \vec{\boldsymbol{k}}]}. \tag{2.3}$$

Notice that the first factor is just a phase factor, and the line of constant phase $\phi = \phi_0$ is given by

$$x_i = \frac{\phi_0}{k_i} + \frac{\omega(\vec{\boldsymbol{k}})}{k_i} t. \tag{2.4}$$

The coefficient in front of the second term is called the phase velocity.

Now, turning to the phase factor inside the integral, we have some argument that depends on the distance between $\vec{\boldsymbol{r}}$ and $\vec{\boldsymbol{r}}_0 = (\hbar\vec{\boldsymbol{k}}/m)t$. We can identify $\vec{\boldsymbol{r}}_0$ with the "center" of the wave-packet since for $\vec{\boldsymbol{r}}$ far from $\vec{\boldsymbol{r}}_0$, the exponential is very oscillatory and hence damps the amplitude of Ψ, but for $\vec{\boldsymbol{r}} \approx \vec{\boldsymbol{r}}_0$, there are no such cancellations and a peak at $\vec{\boldsymbol{r}} = \vec{\boldsymbol{r}}0$. It is clear then that the wave-packet moves globally with this center at the group velocity $\vec{\boldsymbol{v}}_{\text{group}} = \hbar\vec{\boldsymbol{k}}/m$.

2.2 Mathematical Digression: δ-Function Definition and Properties

In the hand-wavey approach, we can regard delta-functions as the limit of a sequence of functions $\delta(x) = \lim_{n\to\infty} f_n(x)$ such that $\delta(x) = 0$ for all $x \neq 0$ and

$$\int_{-\infty}^{\infty} \phi(x)\delta(x)\,\mathrm{d}x = \phi(0). \tag{2.5}$$

A few examples (certainly not exhaustive) of (f_n) include

- $f_n(x) = \begin{cases} n & |x| < 1/2n \\ 0 & |x| > 1/2n \end{cases}$
- $f_n(x) = \dfrac{n}{2} e^{-n|x|}$
- $f_n(x) = \dfrac{n}{\pi} \dfrac{1}{(nx)^2 + 1}$
- $f_n(x) = \dfrac{n}{\sqrt{\pi}} e^{-(nx)^2}$
- $f_n(x) = \dfrac{1}{\pi} \dfrac{\sin(nx)}{x}$
- $f_n(x) = \dfrac{1}{n\pi} \dfrac{\sin^2(nx)}{x^2}$

There are a couple of properties of δ-functions that should be enumerated[1]

1. The δ-function is even: $\delta(x) = \delta(-x)$, which can be easily shown by a substitution $x \to -x$.
2. $\delta(cx) = \delta(x)/|c|$ for $c \in \mathbb{R}$ (substitute $u = cx$ and consider $c > 0$ and $c < 0$ separately).

[1] Note that by equality of two dirac functions D_1 and D_2, we really mean that $\int \mathrm{d}x\, \phi(x) D_1(x) = \int \mathrm{d}x\, \phi(x) D_2(x)$.

3. For a function $f(x)$ with simple roots $\{x_i \ : \ f(x_i) = 0\}$, $\delta(f(x)) = \sum_i \delta(x - x_i)/|f'(x_i)|$ (Break the integral into small pieces around each x_i and Taylor expand $f(x)$ about x_i.).

Generalizing to n dimensions, we can define $\delta^{(n)}(\vec{\boldsymbol{x}}) = 0$ for all $\vec{\boldsymbol{x}} \neq 0$ and

$$\int_{\mathcal{D}} \phi(\vec{\boldsymbol{x}})\delta(\vec{\boldsymbol{x}} - \vec{\boldsymbol{x}}_0)\,\mathrm{d}x = \begin{cases} \phi(\vec{\boldsymbol{x}}_0) & \vec{\boldsymbol{x}}_0 \in \mathcal{D} \\ 0 & \vec{\boldsymbol{x}}_0 \notin \mathcal{D} \end{cases}. \tag{2.6}$$

Focusing on three dimensions, we have

$$\delta^{(3)}(\vec{\boldsymbol{r}}) = \delta(x)\delta(y)\delta(z). \tag{2.7}$$

If we want to change to curvilinear coordinates (u, v, w), then

$$\delta^{(3)}(\vec{\boldsymbol{r}}) = |\mathrm{Jac}[(x, y, z) \to (u, v, w)]|\ \delta(u)\delta(v)\delta(w). \tag{2.8}$$

For example, changing from Cartesian to spherical, we have

$$\delta^{(3)}(\vec{\boldsymbol{r}} - \vec{\boldsymbol{r}}_0) = \frac{1}{r^2}\delta(r - r_0)\delta(\cos\theta - \cos\theta_0)\delta(\phi - \phi_0). \tag{2.9}$$

2.3 Mathematical Digression: Fourier Transform Definition and Properties

Generically, an integral transform is of the form

$$\tilde{f}(y) = \int_a^b \mathrm{d}x\, K(x, y)f(x). \tag{2.10}$$

The function K is called the kernel of the transform.

The Fourier transform is defined with $K(x, y) = e^{-iyx}/\sqrt{2\pi}$ such that

$$\tilde{f}(y) = \int_{-\infty}^{\infty} \frac{\mathrm{d}x}{\sqrt{2\pi}} e^{-iyx} f(x). \tag{2.11}$$

Note that only functions f which are square integrable[2] have a fourier transform.

If we know the transform of f, we can invert the Fourier transform as follows to obtain

$$f(x) = \int_{-\infty}^{\infty} \frac{\mathrm{d}x}{\sqrt{2\pi}} e^{iyx} \tilde{f}(y). \tag{2.12}$$

There are a few properties that are useful to enumerate:

1. Parseval's identity: $\displaystyle\int_{-\infty}^{\infty} |f(x)|^2\,\mathrm{d}x = \int_{-\infty}^{\infty} |\tilde{f}(y)|^2\,\mathrm{d}y$
2. $\mathcal{F}\left\{\dfrac{\mathrm{d}^n f}{\mathrm{d}x^n}\right\}(y) = (iy)^n \tilde{f}(y)$.

[2] $\int_{-\infty}^{\infty} |f(x)|^2\,\mathrm{d}x \in \mathbb{R}$

3. The Fourier transform of $h(x) = \int_{-\infty}^{\infty} \mathrm{d}x'\, f(x-x')g(x')$ (called a convolution) is just the product of the transforms of f and g separately: $\tilde{h}(y) = \sqrt{2\pi}\tilde{f}(y)\tilde{g}(y)$.

One more useful result to have in our back pocket is the Fourier transform of the δ-function[3]:

$$\tilde{\delta}(y) = \int_{-\infty}^{\infty} \frac{\mathrm{d}x}{\sqrt{2\pi}} e^{-iyx}\delta(x-x_0) = \frac{e^{-ix_0 y}}{\sqrt{2\pi}}. \tag{2.13}$$

From this we can also derive the integral representation of the δ-function by taking the inverse Fourier transform of Eq. (2.13)

$$\delta(x-x_0) = \int_{-\infty}^{\infty} \frac{\mathrm{d}y}{\sqrt{2\pi}} e^{iyx}\tilde{\delta}(y) = \int_{-\infty}^{\infty} \frac{e^{-i(x-x_0)y}}{2\pi}\,\mathrm{d}x\,. \tag{2.14}$$

Finally, we can extend the notion of this one-dimensional Fourier transform to three dimensions by taking successive Fourier transforms in each coordinate direction:

$$\tilde{f}(\vec{\boldsymbol{k}}) = \int \frac{\mathrm{d}^3\vec{\boldsymbol{r}}}{(2\pi)^{3/2}} e^{-i\vec{\boldsymbol{k}}\cdot\vec{\boldsymbol{r}}} f(\vec{\boldsymbol{r}}). \tag{2.15}$$

2.4 Wave mechanics

Recall that a wave packet is defined by

$$\Psi(\vec{\boldsymbol{r}},t) = \int \frac{\mathrm{d}^3\vec{\boldsymbol{k'}}}{(2\pi)^{3/2}} g(k') e^{i[\vec{\boldsymbol{k}}'\cdot\vec{\boldsymbol{r}}-\omega(\vec{\boldsymbol{k}}')t]}. \tag{2.16}$$

Notice that this wave-function satisfies what we will call the free-particle Schrödinger equation (S.E.):

$$i\hbar\frac{\partial\Psi(\vec{\boldsymbol{r}},t)}{\partial t} = -\frac{\hbar^2}{2m}\nabla^2\Psi(\vec{\boldsymbol{r}},t). \tag{2.17}$$

Acting on the wave-packet explicitly reproduces the dispersion relation $E = \hbar\omega = \hbar^2k^2/2m$.

At this point, we introduce the Born interpretation of the wave function, which is that $\rho(\vec{\boldsymbol{r}},t) = |\Psi(\vec{\boldsymbol{r}},t)|^2$ is the spatial probability density for the particle which is describes. Note that these wave-functions must be normalized in the sense that

$$\int_{-\infty}^{\infty} \rho(\vec{\boldsymbol{r}},t)\,\mathrm{d}^3\vec{\boldsymbol{r}} = 1 \tag{2.18}$$

since measurement of the particle's position is certain to return some value.

Observe that this normalization is independent of time:

$$\frac{\mathrm{d}}{\mathrm{d}t}\int_{-\infty}^{\infty} |\Psi|^2\,\mathrm{d}^3\vec{\boldsymbol{r}} = 0, \tag{2.19}$$

[3] We will skirt the problem of the existence of such a Fourier transform which requires that the δ-function is square integrable but is not well defined at this point

This implies that

$$\int \mathrm{d}^3\vec{\boldsymbol{r}}\left[\Psi^*\frac{\partial\Psi}{\partial t}+\text{c.c.}\right]=\int \mathrm{d}^3\vec{\boldsymbol{r}}\left[\Psi^*\Big(-\frac{\hbar}{2mi}\nabla^2\Psi\Big)+\text{c.c.}\right]=0$$
$$-\int \mathrm{d}^3\vec{\boldsymbol{r}}\,\frac{\hbar}{2mi}\Big[\Psi^*\nabla^2\Psi-\Psi\nabla^2\Psi^*\Big]=-\int \mathrm{d}^3\vec{\boldsymbol{r}}\,\vec{\boldsymbol{\nabla}}\cdot\frac{\hbar}{2mi}\Big[\Psi^*\vec{\boldsymbol{\nabla}}\Psi-\Psi\vec{\boldsymbol{\nabla}}\Psi^*\Big]=0$$
$$-\int \mathrm{d}S_\infty\underbrace{\frac{\hbar}{2mi}\Big[\Psi^*\vec{\boldsymbol{\nabla}}\Psi-\Psi\vec{\boldsymbol{\nabla}}\Psi^*\Big]}_{\vec{\boldsymbol{j}}(\vec{\boldsymbol{r}},t)}=0, \tag{2.20}$$

where $\vec{\boldsymbol{j}}$ is interpreted the probability current density. It should be clear that $\vec{\boldsymbol{j}}(\vec{\boldsymbol{r}},t)|_{S_\infty}=0$ since $\Psi\to 0$ as $|\vec{\boldsymbol{r}}|\to\infty$. Here we have proven a continuity equation

$$\frac{\partial\rho}{\partial t}+\vec{\boldsymbol{\nabla}}\cdot\vec{\boldsymbol{j}}=0, \tag{2.21}$$

which is a local probability conservation result.

Once we have the wave-function, we can calculate the average of a function $f(\vec{\boldsymbol{r}})$ is

$$\langle f(\vec{\boldsymbol{r}})\rangle(t)=\int \mathrm{d}^3\vec{\boldsymbol{r}}\,f(\vec{\boldsymbol{r}})\rho(\vec{\boldsymbol{r}},t). \tag{2.22}$$

In particular, the average position of a particle is

$$\langle\vec{\boldsymbol{r}}(t)\rangle=\int \mathrm{d}^3\vec{\boldsymbol{r}}\;\vec{\boldsymbol{r}}|\Psi(\vec{\boldsymbol{r}},t)|^2. \tag{2.23}$$

Now, we turn our attention to the calculation of the average momentum. We can define a momentum space wave-function by taking the Fourier transform of the coordinate wave-function:

$$\begin{aligned}\tilde{\Psi}(\vec{\boldsymbol{p}},t)&=\int\frac{\mathrm{d}^3\vec{\boldsymbol{r}}}{(2\pi)^{3/2}}e^{-i\vec{\boldsymbol{k}}\cdot\vec{\boldsymbol{r}}}\Psi(\vec{\boldsymbol{r}},t)\\&=\int\frac{\mathrm{d}^3\vec{\boldsymbol{r}}}{(2\pi\hbar)^{3/2}}e^{-i\vec{\boldsymbol{p}}\cdot\vec{\boldsymbol{r}}/\hbar}\left[\int\frac{\mathrm{d}^3\vec{\boldsymbol{p}'}}{(2\pi\hbar)^{3/2}}g(\vec{\boldsymbol{p}}'/\hbar)e^{-i}e^{i[\vec{\boldsymbol{p}}'\cdot\vec{\boldsymbol{r}}-Et]/\hbar}\right]\\&=e^{-iEt/\hbar}g(\vec{\boldsymbol{p}}).\end{aligned} \tag{2.24}$$

From this, it is trivial to see that the average momentum is

$$\langle\vec{\boldsymbol{p}}(t)\rangle=\int \mathrm{d}^3\vec{\boldsymbol{p}}\;\vec{\boldsymbol{p}}|\tilde{\Psi}(\vec{\boldsymbol{p}},t)|^2. \tag{2.25}$$

Less trivially, in terms of the coordinate space wave-function:

$$\begin{aligned}
\langle \vec{\boldsymbol{p}}(t) \rangle &= \int \frac{\mathrm{d}^3 \vec{\boldsymbol{p}}}{(2\pi\hbar)^{3/2}} \vec{\boldsymbol{p}} \tilde{\Psi}^*(\vec{\boldsymbol{p}}, t) \tilde{\Psi}(\vec{\boldsymbol{p}}, t) \\
&= \int \frac{\mathrm{d}^3 \vec{\boldsymbol{p}}}{(2\pi\hbar)^{3/2}} \vec{\boldsymbol{p}} \left[\int \frac{\mathrm{d}^3 \vec{\boldsymbol{r}}'}{(2\pi\hbar)^{3/2}} e^{-i\vec{\boldsymbol{p}}\cdot\vec{\boldsymbol{r}}'/\hbar} \Psi^*(\vec{\boldsymbol{r}}', t) \right] \left[\int \frac{\mathrm{d}^3 \vec{\boldsymbol{r}}}{(2\pi\hbar)^{3/2}} e^{i\vec{\boldsymbol{p}}\cdot\vec{\boldsymbol{r}}/\hbar} \Psi(\vec{\boldsymbol{r}}, t) \right] \\
&= \int \frac{\mathrm{d}^3 \vec{\boldsymbol{p}}}{(2\pi\hbar)^{3/2}} \left[\int \frac{\mathrm{d}^3 \vec{\boldsymbol{r}}'}{(2\pi\hbar)^{3/2}} e^{-i\vec{\boldsymbol{p}}\cdot\vec{\boldsymbol{r}}'/\hbar} \Psi^*(\vec{\boldsymbol{r}}', t) \right] \left[\int \frac{\mathrm{d}^3 \vec{\boldsymbol{r}}}{(2\pi\hbar)^{3/2}} \Big(i\hbar\vec{\boldsymbol{\nabla}} e^{i\vec{\boldsymbol{p}}\cdot\vec{\boldsymbol{r}}/\hbar} \Big) \Psi(\vec{\boldsymbol{r}}, t) \right] \\
&= \int \frac{\mathrm{d}^3 \vec{\boldsymbol{p}}}{(2\pi\hbar)^{3/2}} \left[\int \frac{\mathrm{d}^3 \vec{\boldsymbol{r}}'}{(2\pi\hbar)^{3/2}} e^{-i\vec{\boldsymbol{p}}\cdot\vec{\boldsymbol{r}}'/\hbar} \Psi^*(\vec{\boldsymbol{r}}', t) \right] \left[\int \frac{\mathrm{d}^3 \vec{\boldsymbol{r}}}{(2\pi\hbar)^{3/2}} e^{i\vec{\boldsymbol{p}}\cdot\vec{\boldsymbol{r}}/\hbar} \Big(- i\hbar\vec{\boldsymbol{\nabla}} \Psi(\vec{\boldsymbol{r}}, t) \Big) \right] \\
&= \int \frac{\mathrm{d}^3 \vec{\boldsymbol{r}}}{(2\pi\hbar)^{3/2}} \Psi^*(\vec{\boldsymbol{r}}, t) \Big(- i\hbar\vec{\boldsymbol{\nabla}} \Big) \Psi(\vec{\boldsymbol{r}}, t).
\end{aligned} \tag{2.26}$$

From this, we may define the coordinate space momentum operator $\vec{\boldsymbol{p}} = -i\hbar\vec{\boldsymbol{\nabla}}$.

We could actually reverse the argument for $\langle \vec{\boldsymbol{r}}(t) \rangle$, which would give

$$\langle \vec{\boldsymbol{r}}(t) \rangle = \int \frac{\mathrm{d}^3 \vec{\boldsymbol{p}}}{(2\pi\hbar)^{3/2}} \tilde{\Psi}^*(\vec{\boldsymbol{p}}, t) \Big(i\hbar\vec{\boldsymbol{\nabla}}_p \Big) \tilde{\Psi}(\vec{\boldsymbol{p}}, t). \tag{2.27}$$

From this, the momentum space position operator is given as $\vec{\boldsymbol{r}} = i\hbar\vec{\boldsymbol{\nabla}}_p$, which is quite similar to the momentum operator. This is one of the first hints of the intimate connection between position and momentum.

CHAPTER 3

Schrödinger Equation; Uncertainty Relations

3.1 Time-dependent Schrödinger Equation

In the last section, we derived the governing equation for the wave-function of a free particle

$$i\hbar\frac{\partial\Psi(\vec{\boldsymbol{r}},t)}{\partial t} = -\frac{\hbar^2}{2m}\nabla^2\Psi(\vec{\boldsymbol{r}},t). \tag{3.1}$$

We can add in interactions through the potential $V(\vec{\boldsymbol{r}})$ as

$$i\hbar\frac{\partial\Psi(\vec{\boldsymbol{r}},t)}{\partial t} = \Big[-\frac{\hbar^2}{2m}\nabla^2 + V(\vec{\boldsymbol{r}})\Big]\Psi(\vec{\boldsymbol{r}},t) = H\Psi, \tag{3.2}$$

where we define the Hamiltonian operator $H = \vec{\boldsymbol{p}}^2/2m + V(\vec{\boldsymbol{r}})$.

Note that we still retain the Born interpretation of the wave-function, which is that $\rho(\vec{\boldsymbol{r}},t) = |\Psi(\vec{\boldsymbol{r}},t)|^2$ is the spatial probability density, and furthermore, we could repeat the manipulations to derive the probability density current and arrive at the exact same answer (worked out in a homework problem):

$$\vec{\boldsymbol{j}}(\vec{\boldsymbol{r}},t) = \frac{\hbar}{2mi}\Big[\Psi^*\vec{\boldsymbol{\nabla}}\Psi - \Psi\vec{\boldsymbol{\nabla}}\Psi^*\Big]. \tag{3.3}$$

Furthermore, we still have the local continuity equation

$$\frac{\partial\rho}{\partial t} + \vec{\boldsymbol{\nabla}}\cdot\vec{\boldsymbol{j}} = 0, \tag{3.4}$$

which follows from the normalization of the wave-function

$$\int_{-\infty}^{\infty}|\Psi(\vec{\boldsymbol{r}},t)|^2 = 1. \tag{3.5}$$

Working toward a solution, we use separation of variables and write $\Psi(\vec{\boldsymbol{r}},t) = f(t)\psi(\vec{\boldsymbol{r}})$ and obtain

$$\frac{1}{f(t)}\Big(i\hbar\frac{\mathrm{d}f}{\mathrm{d}t}\Big) = \frac{1}{\psi(\vec{\boldsymbol{r}})}\Big[-\frac{\hbar^2}{2m}\nabla^2\psi(\vec{\boldsymbol{r}}) + V(\vec{\boldsymbol{r}})\psi(\vec{\boldsymbol{r}})\Big] = E. \tag{3.6}$$

Thus, we have two separate equations for the time and spatial dependence. The time-dependence has a trivial solution

$$f(t) = e^{-iEt/\hbar}. \tag{3.7}$$

3.2 Time-independent Schrödinger Equation

Continuing with our separable solution, we see the spatial differential equation does not quite have such a trivial solution

$$\Big[-\frac{\hbar^2}{2m}\nabla^2 + V(\vec{\boldsymbol{r}})\Big]\psi(\vec{\boldsymbol{r}}) = H\psi(\vec{\boldsymbol{r}}) = E\psi(\vec{\boldsymbol{r}}). \tag{3.8}$$

This is called the time-independent S.E. typically. It is also an energy eigenvalue equation, where E and ψ are the energy eigenvalue and eigenfunction, respectively, of the Hamiltonian operator. Generally, we can only say a few things about E and ψ without an explicit form for the potential.

- For a separable wave-function: $\langle H\rangle = \int \mathrm{d}^3\vec{\boldsymbol{r}}\, e^{iEt/\hbar}\psi^*(\vec{\boldsymbol{r}})He^{-iEt/\hbar}\psi(\vec{\boldsymbol{r}}) = E$
- The energy spectrum is strictly real: H is a hermitian operator[1], so $\langle H\rangle = E = \int \mathrm{d}^3\vec{\boldsymbol{r}}\,[H\psi(\vec{\boldsymbol{r}})]^*\psi(\vec{\boldsymbol{r}}) = E^*$
- The set of energy eigenfunctions is orthogonal: Notice that $\int \mathrm{d}^3\vec{\boldsymbol{r}}\,\psi_m^* H\psi_n = E_n\int \mathrm{d}^3\vec{\boldsymbol{r}}\,\psi_m^*\psi_n = E_m\int \mathrm{d}^3\vec{\boldsymbol{r}}\,\psi_m^*\psi_n$ exploiting the hermiticity of H. Subtracting the two equations, we have $(E_n - E_m)\int \mathrm{d}^3\vec{\boldsymbol{r}}\,\psi_m^*\psi_n = 0$, and since $E_n - E_m \neq 0$, ψ_m and ψ_n must be orthogonal.
- The eigenfunctions of H form a complete basis such that any square-integrable function $\phi(\vec{\boldsymbol{r}}) = \sum_n c_n\psi_n(\vec{\boldsymbol{r}})$ with $c_n = \int \mathrm{d}^3\vec{\boldsymbol{r}}\,\psi_n^*(\vec{\boldsymbol{r}})\phi(\vec{\boldsymbol{r}})$.

3.3 General Solution of the Time-dependent Schrödinger Equation

We worked with separable solutions above, but in general, a solution $\Psi(\vec{\boldsymbol{r}},t)$ of the S.E. need not be separable. However, any solution can be expanded in the basis of energy eigenfunctions as in the bullet point of the last bullet point:

$$\Psi(\vec{\boldsymbol{r}},t) = \sum_n c_n\psi_n(\vec{\boldsymbol{r}})e^{-iE_nt/\hbar}. \tag{3.9}$$

Note that $\Psi(\vec{\boldsymbol{r}},t)$ must satisfy the relevant boundary conditions (BCs)[2]. Additionally, for bound states, Ψ must be normalizable as well.

[1] $\int \mathrm{d}^3\vec{\boldsymbol{r}}\, f^*(\vec{\boldsymbol{r}})Hg(\vec{\boldsymbol{r}}) = \int \mathrm{d}^3\vec{\boldsymbol{r}}\,[Hf(\vec{\boldsymbol{r}})]^*g(\vec{\boldsymbol{r}})$

[2] ψ and $\vec{\boldsymbol{\nabla}}\psi$ must be continuous – except perhaps in the case where $V(\vec{\boldsymbol{r}})$ contains a δ-function

3.4 Heisenberg's uncertainty relations

The commutator of two operators A and B is $[A, B] = AB - BA$. For the position and momentum operators

$$[x,p]f(x) = -i\hbar[x, \frac{\partial}{\partial x}]f(x) = -i\hbar\Big[x\frac{\partial f}{\partial x} - \frac{\partial}{\partial x}xf(x)\Big] = i\hbar f(x) \tag{3.10}$$

$$\Rightarrow [x,p] = i\hbar. \tag{3.11}$$

Generally, $[x_i, p_j] = i\hbar\delta_{ij}$.

Let us also define the uncertainty in the observable A corresponding to the operator A as

$$\Delta A^2 = \big\langle (A - \langle A\rangle)^2\big\rangle = \big\langle A^2\big\rangle - \langle A\rangle^2 . \tag{3.12}$$

Note that ΔA is not some measurement error. It is an intrinsic uncertainty in the quantity A imposed by the fact that the wave-function is not necessarily an eigenstate of A. We can derive a lower bound on $\Delta A \Delta B$ that depends on the commutator $[A, B]$.

For any square-integrable functions f and g we have the Cauchy-Schwarz inequality (derived in the appendix)

$$\left(\int \mathrm{d}^3\vec{\boldsymbol{r}}\,|f(\vec{\boldsymbol{r}})|^2\right)\left(\int \mathrm{d}^3\vec{\boldsymbol{r}}\,|g(\vec{\boldsymbol{r}})|^2\right) \geq \left|\int \mathrm{d}^3\vec{\boldsymbol{r}}\,g^*(\vec{\boldsymbol{r}})f(\vec{\boldsymbol{r}})\right|^2 . \tag{3.13}$$

Note that the roles of f and g are interchangeable, so we can also write

$$\begin{aligned}\left(\int \mathrm{d}^3\vec{\boldsymbol{r}}\,|f(\vec{\boldsymbol{r}})|^2\right)\left(\int \mathrm{d}^3\vec{\boldsymbol{r}}\,|g(\vec{\boldsymbol{r}})|^2\right) &\geq \frac{1}{2}\left[\left|\int \mathrm{d}^3\vec{\boldsymbol{r}}\,g^*(\vec{\boldsymbol{r}})f(\vec{\boldsymbol{r}})\right|^2 + \left|\int \mathrm{d}^3\vec{\boldsymbol{r}}\,f^*(\vec{\boldsymbol{r}})g(\vec{\boldsymbol{r}})\right|^2\right] \\ &\geq \frac{1}{4}\Big|\int \mathrm{d}^3\vec{\boldsymbol{r}}\,\big[g^*(\vec{\boldsymbol{r}})f(\vec{\boldsymbol{r}}) - f^*(\vec{\boldsymbol{r}})g(\vec{\boldsymbol{r}})\big]\Big|^2 .\end{aligned} \tag{3.14}$$

Note that we used the following inequality to go from the first to the second line:

$$|a-b|^2 \leq |a+b|^2 + |a-b|^2 = 2\big(|a|^2 + |b|^2\big) \tag{3.15}$$

with $a = \int \mathrm{d}^3\vec{\boldsymbol{r}}\,g^* f$ and $b = \int \mathrm{d}^3\vec{\boldsymbol{r}}\,g^* f$.

Observe

$$\Delta A^2 \Delta B^2 = \left(\int \mathrm{d}^3\vec{\boldsymbol{r}}\,\Psi^*(A - \langle A\rangle)^2\Psi\right)\left(\int \mathrm{d}^3\vec{\boldsymbol{r}}\,(B - \langle B\rangle)^2\right). \tag{3.16}$$

Since we are interested in observables A and B, we assume that A and B are hermitian such that if we define $f = (A - \langle A\rangle)\Psi$ and $g = (B - \langle B\rangle)\Psi$ then

$$\begin{aligned}\Delta A^2 \Delta B^2 &= \Big(\int \mathrm{d}^3\vec{\boldsymbol{r}}\,|f(\vec{\boldsymbol{r}})|^2\Big)\Big(\int \mathrm{d}^3\vec{\boldsymbol{r}}\,|g(\vec{\boldsymbol{r}})|^2\Big) \\ &\geq \frac{1}{4}\Big|\int \mathrm{d}^3\vec{\boldsymbol{r}}\,\Psi^*\big[(B - \langle B\rangle)(A - \langle A\rangle) - (A - \langle A\rangle)(B - \langle B\rangle)\big]\Psi\Big|^2 \\ &= \frac{1}{4}|\,\langle [A,B]\rangle\,|^2 .\end{aligned} \tag{3.17}$$

From this, we can write down the famous Heisenberg uncertainty relation

$$\Delta x \Delta p \geq \frac{\hbar}{2}. \tag{3.18}$$

CHAPTER 4

The One-Dimensional Schrödinger Equation

In one-dimension, the S.E. reduces to

$$-\frac{\hbar^2}{2m}\frac{\partial\psi(x)}{\partial x} + V(x)\psi(x) = E\psi(x). \tag{4.1}$$

We will simplify this a bit by introducing $v(x) = 2mV(x)/\hbar^2$ and $\epsilon = 2mE/\hbar^2$, which gives

$$\psi''(x) = [v(x) - \epsilon]\psi(x). \tag{4.2}$$

Essentially, we have just introduced dimensionless constants/functions to make accounting for units a bit simpler and to avoid carrying around a lot of factors.

4.1 Nature of the Energy Spectrum and General Properties of the Eigenfunctions

Consider an arbitrary potential $v(x)$ such that $v_\pm = v(x \to \pm\infty)$ and with global minimum v_0. We can consider the general behavior of ψ in certain regions of the energy spectrum relative to these values $v_\pm$. Without loss of generality assume $v_- > v_+$.

1. Consider $\epsilon < v_0$. The S.E. becomes $\psi''(x) = [v(x) - \epsilon]\psi(x)$. Note that this factor on the r.h.s. is positive for all x since $v(x) - \epsilon \geq v_0 - \epsilon > 0$. Thus, the concavity always has the same sign as that of the wave-function. In the first case, if $\psi(x) > 0$, then $\psi''(x) > 0$, meaning that ψ grows unbounded as $x \to \infty$. If, however, $\psi(x) < 0$, the wave function grows unbounded toward $-\infty$ as $x \to -\infty$. These singular behaviors are not physical since we require a wave-function (or superposition of them) to be normalizable.

2. Consider $v_0 < \epsilon < v_-$. In this case, we have $\psi''(x) = [v_\pm - \epsilon]\psi(x)$ in the extreme regions. This accomodates decaying exponential solutions (throwing out increasing exponentials to ensure normalizability). Clearly then,

we have two solutions in two regions, and matching (of ψ and ψ') along with normalization will determine the two constants. Our problem is then overdetermined, meaning that a solution may only exist if the matching conditions are redundant. It can be proven that the eigenfunctions in this case are non-degenerate (i.e. there do not exist linearly independent ψ_1 and ψ_2 with the same corresponding energy ϵ). Additionally, one can also prove via a couple different arguments (a rigorous one based on the Sturm-Liouville equation and a more intuitive one from Feynman) that the ground state wave function has no nodes (i.e. there is no x such that $\psi(x) = 0$), and by induction, the n^{th} ground state has n nodes.

3. Consider $v_+ < \epsilon < v_-$. In this case our energy is bounded as $x \to -\infty$, meaning we still have our decaying exponential here (1 constant), but as $x \to \infty$ the energy is unbounded. Hence, our solutions are imaginary exponentials in the extreme positive region (2 constants). Notice that these solutions are not normalizable. Hence, we only have the matching conditions on these energy eigenstates, leaving one undetermined constant overall, which is determined by normalizing a wave-packet. In this region then we have a single solution at each energy.

4. Finally, consider $v_- < \epsilon$. In this case, we have imaginary exponentials in both extreme regions (4 constants), and we still only have two matching conditions constraining these values. Hence, there are two undetermined constants and, furthermore, two linearly independent solutions at each energy.

4.2 Infinite Deep Potential Well

Consider

$$v(x) = \begin{cases} 0 & |x| < a/2 \\ \infty & |x| > a/2. \end{cases} \tag{4.3}$$

Notice that the wave-function is identically zero in the region $|x| > a/2$. Consider a well of finite depth v_0 ($\epsilon < v_0$). In the region $|x| > a/2$ the wave function reads

$$\psi(x) = e^{-\sqrt{v_0 - \epsilon}|x|}. \tag{4.4}$$

If we take $v_0 \to \infty$ then $\psi \equiv 0$ for $|x| > a/2$.

For the interesting region $|x| < a/2$, the S.E. reads

$$\psi''(x) = -\epsilon\psi(x), \tag{4.5}$$

and has solution

$$\psi(x) = A\cos kx + B\sin kx, \tag{4.6}$$

where $k = \sqrt{\epsilon}$. Continuity of the wave-function at $x = \pm a/2$ gives the following conditions:

$$A\cos(ka/2) - B\sin(ka/2) = 0 \tag{4.7}$$

$$A\cos(ka/2) + B\sin(ka/2) = 0. \tag{4.8}$$

From our discussion above, observe that we have these two matching conditions and normalization. Generally, these are not consistent equations, but for some energy values, these matching conditions are linearly dependent, given by

$$\det \begin{pmatrix} \cos(ka/2) & -\sin(ka/2) \\ \cos(ka/2) & \sin(ka/2) \end{pmatrix} = 2\sin(ka/2)\cos(ka/2) = \sin ka = 0. \tag{4.9}$$

This has solution when $ka = n\pi$ for integer n. We restrict $n \geq 1$, though since the negative integers are linearly dependent on the positive ones and are hence not distinct, and furthermore, the $n = 0$ solution gives the trivial wave function $\psi \equiv 0$, which is certainly a valid mathematical solution but not physically interesting from the perspective of the Born interpretation. Putting this back into the second matching condition, we find

$$A\cos(n\pi/2) + B\sin(n\pi/2) = 0. \tag{4.10}$$

Clearly, if n is even, then $A = 0$, but if n is odd, then $B = 0$.

The bound state solutions (which are the only ones permitted here) are given by

$$\psi_n(x) = \sqrt{\frac{2}{a}} \begin{cases} \cos(n\pi x/a) & n = 1, 3, \dots \\ \sin(n\pi x/a) & n = 2, 4, \dots, \end{cases} \tag{4.11}$$

and the corresponding energies

$$E_n = \frac{\hbar^2}{2m}\epsilon_n = \frac{n^2\pi^2\hbar^2}{2ma^2}. \tag{4.12}$$

4.3 Attractive δ-Function Potential

The attractive δ-potential can be written $v(x) = -v_0\delta(x)$[1]. The S.E. gives (for a bound state with $\epsilon < 0$)

$$\psi(x) = \begin{cases} Ae^{\kappa x} & x < 0 \\ Be^{-\kappa x} & x > 0, \end{cases} \tag{4.13}$$

where $\kappa = \sqrt{|\epsilon|}$.

The solution itself is not very interesting, but the matching condition for ψ' is. The S.E. reads

$$\psi''(x) = -[v_0\delta(x) + \epsilon]\psi(x). \tag{4.14}$$

Integrating around $x = 0$ in an interval of size 2η, we find

$$\psi'(0^+) - \psi(0^-) = -v_0. \tag{4.15}$$

Integrating a second time, though, in this small region around $x = 0$ shows that this discontinuity is washed out such that $\psi(0^-) = \psi(0^+)$, meaning the

[1] In the course notes, the δ-function is centered at $x = a$, which can be obtained by shifting to $x \to x - a$.

wave-function still is continuous there. Imposing these boundary conditions, we have

$$A = B \tag{4.16}$$
$$\kappa(-B - A) = -v_0 A. \tag{4.17}$$

Thus,

$$\kappa = \frac{v_0}{2} \Rightarrow \epsilon = -\frac{v_0^2}{4} \Rightarrow E = -\frac{mV_0}{2\hbar^2}, \tag{4.18}$$

and

$$\psi(x) = \sqrt{\kappa} e^{-\kappa|x|}. \tag{4.19}$$

4.4 Parity

The parity operator $\mathcal{P}$ performs the spatial inversion $\mathcal{P}f(x) = f(-x)$. If $V(x)$ is even (i.e. $\mathcal{P}V(x) = V(-x) = V(x)$), there are a number of interesting properties that the bound states satisfy regardless of the shape or form of V. First, if $\psi(x)$ solves the S.E., then $\psi(-x)$ also solves the S.E. That is, $\mathcal{P}\psi(x)$ solves the S.E.

For bound states, observe $\psi(-x) = c\psi(x)$ since these two solutions correspond to the same energy and must be therefore linearly dependent since these states are non-degenerate. Acting with the parity operator on this relation, we obtain $\psi(x) = c\psi(-x)$, and multiplying the two relations together, we have that $c^2 = 1$ or $c = \pm 1$. Hence, $\psi(x)$ must be either an even or odd function.

We can go a little further and deduce that the ground state is an even function since it has no nodes. If it were odd, there would necessarily have to be a node at $x = 0$. Inductively, then, the states alternate between even and odd functions.

For scattering states, our energy spectrum is doubly degenerate, so $\psi(-x)$ may be distinct from $\psi(x)$, and any general solution may be formed as a linear combination of two linearly independent solutions.

CHAPTER 5

Scattering in One Dimension

5.1 Scattering in a δ-function potential

Consider a repulsive δ-function potential of the form $v(x) = v_0\delta(x)$. We are concerned here with the so-called scattering states, which exist for $\epsilon > 0$. Recall that we have two linearly independent solutions for such an energy regime since the energy is unbounded for $x \to \pm\infty$. We can write them as follows

$$\psi_k^{(1)}(x) = \begin{cases} e^{ikx} + A^{(1)}e^{-ikx} & x < 0 \\ B^{(1)}e^{ikx} & x > 0 \end{cases} \text{ and } \psi_k^{(2)}(x) = \begin{cases} B^{(2)}e^{-ikx} & x < 0 \\ e^{-ikx} + A^{(2)}e^{ikx} & x > 0. \end{cases} \tag{5.1}$$

A general solution is obtained by taking a linear combination $\psi_k(x) = \alpha_k\psi_k^{(1)}(x) + \beta_k\psi_k^{(2)}(x)$, but for our purposes we will stick to analyzing the first since this corresponds to particles coming in from the left at $x = -\infty$, interacting with the δ-function potential at $x = 0$ and either reflecting back to $x = -\infty$ or being transmitted and continuing to $x = \infty$. Note that this is quite distinct from the classical expectation, where the potential here acts as essentially a very hard wall and sends the particle back elastically without fail.

The BCs at $x = 0$ give (dropping the superscript for brevity)

$$1 + A = B \tag{5.2}$$

$$ik[B - (1 - A)] = v_0 B. \tag{5.3}$$

Solving gives

$$A = \frac{v_0}{-v_0 + 2ik} \tag{5.4}$$

$$B = \frac{2ik}{-v_0 + 2ik}. \tag{5.5}$$

At this point, we motivate how to compute the reflection and transmission

probabilities by considering a wave-packet of the form[1]

$$\Psi(x,t) = \int \mathrm{d}k\, g(k)\psi_k(x)e^{-i\omega t} = \begin{cases} \int \mathrm{d}k\, g(k)e^{i(kx-\omega t)} + \int \mathrm{d}k\, g(k)A(k)e^{-i(kx+\omega t)} & x<0 \\ \int \mathrm{d}k\, g(k)B(k)e^{i(kx-\omega t)} & x>0 \end{cases}$$
$$= \begin{cases} \Psi_I(x,t) + \Psi_R(x,t) & x<0 \\ \Psi_T(x,t) & x>0, \end{cases} \tag{5.6}$$

where $\Psi_{I,R,T}$ are the incident, reflected, and transmitted wave-packets, $\omega = \hbar k^2/2m$, and as usual $g(k)$ is strongly localized around some $k = k_0$. Using the stationary phase method of the second chapter, the incident wave packet

$$\Psi_I(x,t) \approx e^{i(k_0 x - \omega_0 t)} \int \mathrm{d}k\, g(k) e^{i[x - x_I(t)][k-k_0]}, \tag{5.7}$$

where $\frac{\mathrm{d}}{\mathrm{d}k}[kx - \omega t]_{x=x_I(t)} = 0$ or $x_I(t) = (\hbar k/m)t$. Observe from this that the incident wave packet's center reaches the potential at $t = 0$, and for $t \gg 0$, $x_I(t) \gg 0$ and the exponential is strongly oscillatory, implying that $|\Psi_I(x,t)| \approx |\Psi(x - x_I(t), 0)| \approx 0$.

Next, we analyze the reflected wave packet:

$$\Psi_R(x,t) = \int \mathrm{d}k\, g(k)|A(k)|e^{i(kx+\omega t+\alpha(k))}. \tag{5.8}$$

We have written

$$A(k) = |A(k)|e^{i\alpha(k)}, \tag{5.9}$$

where

$$|A(k)| = \frac{v_0}{\sqrt{v_0^2 + 4k^2}} \text{ and } \alpha(k) = \arctan\left(\frac{2k}{v_0}\right). \tag{5.10}$$

Thus, the stationary phase method gives

$$\Psi_R(x,t) \approx |A(k_0)|e^{i(k_0 x + \omega_0 t - \alpha(k_0))} \int \mathrm{d}k\, g(k) e^{i(k-k_0)(x - x_R(t))}, \tag{5.11}$$

where

$$x_R(t) = -\frac{\hbar k_0}{m}[t - \tau] \tag{5.12}$$

with

$$\tau = \frac{m}{\hbar k_0}\alpha'(k_0) = \frac{m}{\hbar k_0}\frac{2v_0}{v_0^2 + 4k^2}. \tag{5.13}$$

This is interpreted as the time-delay between the interaction with the potential and reflection.

[1] Usually there is a factor $1/\sqrt{2\pi}$ because of the wave-packet's connection to the Fourier transform, but we absorb it into $g(k)$ because it would only be brought along for the ride and has no bearing on the physics.

Finally, we analyze the transmitted wave packet:

$$\Psi_T(x,t) \approx |B(k_0)| e^{i(k_0 x - \omega_0 + \beta(k))} \int \mathrm{d}k\, g(k) e^{i(k-k_0)(x - x_T(t))}, \tag{5.14}$$

where $|B(k_0)| = 4k^2/\sqrt{v_0^2 + 4k^2}$ and $\beta(k) = \arctan\left(\frac{v_0}{2k}\right)$, which gives

$$x_T(t) = \frac{\hbar k_0}{m}[t - \tau] \tag{5.15}$$

with

$$\tau = \frac{m}{\hbar k_0} \frac{2v_0}{v_0^2 + 4k^2}, \tag{5.16}$$

which is the same as for the reflected packet.

Let us define

$$G(x) = \int g(k) e^{i(k-k_0)x}. \tag{5.17}$$

This allows us to write the wave-packet as

$$\Psi(x,t) \approx \begin{cases} e^{i(k_0 x - \omega_0 t)} G(x - x_I(t)) + A(k_0) e^{-i(k_0 x + \omega_0 t)} G(x - x_R(t)) & x < 0 \\ B(k_0) e^{i(kx - \omega_0 t)} G(x - x_T(t)) & x > 0. \end{cases} \tag{5.18}$$

Observe that for $|x| \gg 0$, $G(x) \approx 0$. For times much before the interaction $t \to -\infty$, $\Psi(x,t) \approx \Psi_I(x,t)\theta(-x)$, and for times much after the interaction $t \to \infty$, $\Psi(x,t) \approx \Psi_R(x,t)\theta(-x) + \Psi_T(x,t)\theta(x)$. The conservation of proability gives

$$\int_{-\infty}^{0} |\Psi_I(x, t \to -\infty)|\, \mathrm{d}x = \int_{-\infty}^{0} |\Psi_R(x, t \to \infty)|^2 + \int_0^{\infty} |\Psi_T(x, t \to \infty)|^2 \tag{5.19}$$

and inserting the definitions

$$1 = |A(k_0)|^2 + |B(k_0)|^2. \tag{5.20}$$

We thus call the reflection and transmission coefficients

$$R = |A(k_0)|^2 \quad T = |B(k_0)|^2. \tag{5.21}$$

5.2 Scattering: An Alternative Treatment

Generally, the wave-packet treatment is the most rigorous, but the algebra for more complicated potentials can become unwieldy, but we can avoid this mess to obtain the reflection and transmission coefficients. In the previous section, we had

$$\psi_k(x) = \begin{cases} e^{ikx} + A(k) e^{-ikx} & x < 0 \\ B(k) e^{ikx} & x > 0. \end{cases} \tag{5.22}$$

The probability current density of this is

$$j(x) = \frac{\hbar k}{m}\begin{cases} 1-|A(k)|^2 & x<0 \\ |B(k)|^2 \end{cases} = \begin{cases} j_I + j_R & x<0 \\ j_T \end{cases}. \tag{5.23}$$

The reflection and transmission probabilities then are just ratios of the reflected and transmitted probability currents to the incident probability current:

$$R = \left|\frac{j_R}{j_I}\right| = |A(k)|^2 \quad T = \left|\frac{j_T}{j_I}\right| = |B(k)|^2. \tag{5.24}$$

5.3 Scattering in a parity-invariant potential: phase shift method

Let us consider the repulsive δ-potential. The even and odd scattering states are

$$\psi_k^e(x) = \begin{cases} Ae^{ikx} + Be^{-ikx} & x<0 \\ Be^{ikx} + Ae^{-ikx} & x>0 \end{cases} \quad \psi_k^o(x) = \begin{cases} Ce^{ikx} + De^{-ikx} & x<0 \\ -De^{ikx} - Ce^{-ikx} & x>0. \end{cases} \tag{5.25}$$

Imposing BCs on the even solutions gives

$$\frac{B}{A} = \frac{2ik - v_0}{2ik + v_0}. \tag{5.26}$$

For the odd solutions, the BCs give $C = -D$. We can write

$$\frac{2ik - v_0}{2ik + v_0} = e^{2i\delta(k)} \text{ with } \delta(k) = \frac{1}{2}\arctan\left(\frac{4kv_0}{4k^2 - v_0}\right). \tag{5.27}$$

Thus, the even and odd wave-functions can be expressed as

$$\psi_k^e(x) = Ae^{i\delta}\begin{cases} e^{i(kx-\delta)} + e^{-i(kx+\delta)} & x<0 \\ e^{i(kx+\delta)} + e^{-i(kx-\delta)} & x<0 \end{cases} = 2Ae^{i\delta}\cos[k|x| - \delta(k)] \tag{5.28}$$

and

$$\psi_k^0(x) = C\begin{cases} e^{ikx} - e^{-ikx} & x<0 \\ e^{ikx} - e^{-ikx} & x>0 \end{cases} = 2iC\sin(kx). \tag{5.29}$$

The reflection and transmission coefficients are (can do the derivation later)

$$R(k) = \sin^2\delta(k) \quad T(k) = \cos^2\delta(k). \tag{5.30}$$

5.4 Reflection and Transmission in a Generic Potential: General Considerations

Pressed for time so only the gist is given here

The asymptotic regions are considered with both solutions

$$\psi_k(x) = \begin{cases} Ae^{ik_- x} + Be^{-ik_- x} & x \to -\infty \\ Ce^{ik_+ x} + De^{ik_+ x} & x \to \infty. \end{cases} \tag{5.31}$$

The probaility current is then

$$j(x) = \begin{cases} \frac{\hbar k_-}{m}(|A|^2 - |B|^2) & x < 0 \\ \frac{\hbar k_+}{m}(|C^2| - |D|^2) & x > 0 \end{cases}. \tag{5.32}$$

Defining $A' = \sqrt{k_-}A$, $B' = \sqrt{k_-}B$, $C' = \sqrt{k_+}C$, and $D' = \sqrt{k_+}D$, so that

$$Eq.\ (\mathbf{??})|A'|^2 + |B'|^2 = |C'|^2 + |D'|^2. \tag{5.33}$$

The matching conditions generally give

$$B' = S_{11}A' + S_{12}C' \tag{5.34}$$
$$D' = S_{21}A' + S_{22}C', \tag{5.35}$$

which can be written in matrix form as

$$\begin{pmatrix} B' \\ D' \end{pmatrix} = \underbrace{\begin{pmatrix} S_{11} & S_{12} \\ S_{21} & S_{22} \end{pmatrix}}_{S} \begin{pmatrix} A' & D' \end{pmatrix}. \tag{5.36}$$

This S is the so-called scattering matrix. Notice it is unitary because of Eq. (**??**). From this, we can read off the reflection and transmission coefficients

$$R^{(1)} = |S_{11}|^2 \quad T^{(1)} = |S_{12}|^2 \tag{5.37}$$
$$R^{(2)} = |S_{21}|^2 \quad T^{(2)} = |S_{22}|^2. \tag{5.38}$$

Note that S is also symmetric (i.e. $S^{\mathrm{T}} = S$).

CHAPTER 6

Mathematical Formulation of Quantum Mechanics

In the past chapters, we've solved for the wave function primarily in coordinate space. It was seen that knowledge of the wave function is knowledge of all the dynamics of a system. Indeed, though, there is nothing unique about the representation of the wave-function $\psi(\vec{\boldsymbol{r}})$. We can take the fourier transform of $\psi(\vec{\boldsymbol{r}})$ and obtain the momentum-space wave-function $\tilde{\psi}(\vec{\boldsymbol{r}})$, which satisfies an equivalent momentum-space Schrödinger equation and satisfies analogous properties to the coordinate space wave-function. In this chapter, we will see how to define an abstract quantity that describes the "state" of a quantum system that satisfies Schrödinger's equation and is equivalent to the wave-function. On the way, we will build up the mathematical framework of Hilbert spaces, which is where our states will live, and operators which act on those spaces with particular attention on operators representing observables.

6.1 Hilbert space $L^2(\mathbb{R}^3)$ of square-integrable functions

In our discussion of the coordinate wave-function $\psi(\vec{\boldsymbol{r}})$ which satisfy the Schrödinger equation, we only imposed that they be normalizable in order to satisfy the Born interpretation:

$$\int_{-\infty}^{\infty} |\psi(\vec{\boldsymbol{r}})|^2 \, \mathrm{d}^3\vec{\boldsymbol{r}} < \infty. \tag{6.1}$$

This property actually defines a normed vector space of square integrable functions $L^2(\mathbb{R}^3)$. It turns out that a linear combination of two square integrable functions $\lambda_1\psi_1 + \lambda_2\psi_2$ is also square-integrable, meaning $\lambda_1\psi_1 + \lambda_2\psi_2 \in L^2(\mathbb{R}^3)$. It is an inner product space because we can define a bilinear operation

$$(\psi, \phi) = \int \mathrm{d}^3\vec{\boldsymbol{r}} \, \psi^*(\vec{\boldsymbol{r}})\phi(\vec{\boldsymbol{r}}), \tag{6.2}$$

which satisfies the following properties:

1. $(\psi, \phi) = (\phi, \psi)^*$
2. $(\phi, \lambda_1\psi_1 + \lambda_2\psi_2) = \lambda_1(\phi, \psi_1) + \lambda_2(\phi, \psi_2)$
3. $(\psi, \psi) \geq 0$ for all $\psi \in L^2(\mathbb{R}^3)$
4. $(\psi, \psi) = 0 \Leftrightarrow \psi = 0$

From this, a norm of a vector in the space $L^2(\mathbb{R}^3)$ can be defined simply as $||\psi|| = \sqrt{(\psi, \psi)}$, and it can be shown that it satisfies all the following properties quite easily:

1. $||\psi|| \geq 0$ for all $\psi \in L^2(\mathbb{R}^3)$
2. $||\psi|| = 0 \Leftrightarrow \psi = 0$
3. $||\lambda\psi|| = |\lambda|||\psi||$
4. $||\psi + \phi|| \leq ||\psi|| + ||\phi||$

6.2 Operators in $L^2(\mathbb{R}^3)$

Generically, we define a unary operator as a mapping from a Hilbert space to itself[1]. That is, if A is an operator on $L^2(\mathbb{R}^3)$, then $A : L^2(\mathbb{R}^3) \to L^2(\mathbb{R}^3)$ and $A : \psi(\vec{\boldsymbol{r}}) \mapsto \psi'(\vec{\boldsymbol{r}}) = A\psi(\vec{\boldsymbol{r}})$. Typically, in quantum mechanics, we are interested in linear operators where $A(\lambda_1\psi_1 + \lambda_2\psi_2) = \lambda_1 A\psi_1 + \lambda_2 A\psi_2$. We can define the composition of operators A and B as AB, where $(AB)\psi = A(B\psi)$. Notice that the composition is not generally commutative: $AB \neq BA$.

Next, we define the important notion of an adjoint operator. The adjoint of an operator A is denoted $A^\dagger$ and defined such that $(A^\dagger\phi, \psi) = (\phi, A\psi)$. From this, a few properties immediately follow:

1. $(A^\dagger)^\dagger = A$
2. $(\lambda A)^\dagger = \lambda^* A^\dagger$
3. $(A + B)^\dagger = A^\dagger + B^\dagger$
4. $(AB)^\dagger = B^\dagger A^\dagger$

Furthermore, there is are two important classes of operators: (1) self-adjoint or hermitian, meaning that $A^\dagger = A$ and (2) unitary, meaning that $A^\dagger = A^{-1}$.

6.3 Discrete and continuous bases

In the previous chapters, when we solved the Schrödinger equation, we claimed that the energy eigenstates formed a complete basis for a generic solution. Here we formally define a basis as a collection of linearly independent vectors which span a vector space. Recall that linear independence of a set of vectors $\{\phi_i\}$

[1] an endomorphism

implies that

$$\sum_i c_i \phi_i = 0 \tag{6.3}$$

if and only if $c_i = 0$. Additionally, a set of vectors $\{\phi_i\}$spans a vector space if any vector

$$\psi = \sum_i c_i \phi_i \tag{6.4}$$

for some combination of coefficients c_i. We define the dimension of a vector space as the cardinality of its basis[2]

It is generally convenient to work with orthogonal bases. If our vector space has an inner product $(\cdot, \cdot)$, two vectors ϕ and ψ are orthogonal if $(\phi, \psi) = 0$. Notice that a generic basis is not necessarily orthogonal. Take as an example the simple case of vectors in $\mathbb{R}^2$. We can use the basis $\{\hat{\boldsymbol{x}}, \hat{\boldsymbol{y}}\}$, or equivalently, we can use $\{\hat{\boldsymbol{x}}, \hat{\boldsymbol{x}} + \hat{\boldsymbol{y}}\}$. It is clear that these are both linearly dependent sets from which we can derive any vector $a\hat{\boldsymbol{x}} + b\hat{\boldsymbol{y}}$, but if we define the inner product to be the dot product, it is clear that by definition the first set is orthogonal but not the second. We can, however, obtain an orthogonal (and even better normalized) basis from the second via the Gram-Schmidt procedure.

With this, we can define completeness through the definition of our basis. Let ψ be a vector. First, if our basis is denumerable with dimension n (possibly infinite), then

$$\lim_{p \to n} \left|\left| \psi - \sum_{m=1}^{p} \lambda_m \phi_m \right|\right| = 0. \tag{6.5}$$

In this limit, we can find the coefficients $\lambda_m = (\phi_m, \psi)$ if our basis is orthonormal. Next, if our basis is infinite but continuous (with the orthogonality condition $(\phi_\alpha, \phi_\beta) = \delta(\alpha - \beta)$), then a space is complete in the sense that any vector

$$\psi(\vec{\boldsymbol{r}}) = \int \mathrm{d}\alpha \, c(\alpha) \phi_\alpha(\vec{\boldsymbol{r}}), \tag{6.6}$$

where $c_\alpha = (\phi_\alpha, \psi)$.

6.4 Abstract Hilbert space

We can define an abstract vector space which holds objects that represent states of a quantum system in a generic sense, independent of any particular representation or coordinates. Following the work of Dirac, we define the ket space as a Hilbert space $\mathcal{S}$ holding vectors $|\psi\rangle$, which are called state vectors. Next, we

[2] One may question the uniqueness of this definition since there is not necessarily only one basis of a vector space. It can be proven that the cardinality of any basis of a vector space is the same. Essentially, the proof proceeds via contradiction. One assumes that two bases have different cardinality. It is proven that the set with larger cardinality is linearly dependent since we can expand these vectors in the other basis exactly.

define the bra space $\mathcal{S}^*$, which is the dual vector space to the ket space. The correspondence between the ket and bra space is such that for each vector $|\psi\rangle$ there is a corresponding bra vector $\langle\psi|$ (denoted $|\psi\rangle \rightleftharpoons \langle\psi|$) such that the inner product on the space $\mathcal{S}$ is $\langle\psi|\psi\rangle \in \mathbb{R}$. The inner product between two distinct vectors $|\psi\rangle$ and $|\phi\rangle$ is $\langle\phi|\psi\rangle = \langle\psi|\phi\rangle^*$ and satisfies all the necessary properties. The norm of a vector is then defined as $||\psi|| = \sqrt{\langle\psi|\psi\rangle}$.

6.5 Operators

The definition of an operator generalizes directly from our previous discussion on the space of square-integrable functions to $\mathcal{S}$. That is, an operator $\hat{A} : \mathcal{S} \to \mathcal{S}$. As stated previously, in general, the operators we deal with are linear: $\hat{A}(\lambda_1 |\psi_1\rangle + \lambda_2 |\psi_2\rangle) = \lambda_1 \hat{A} |\psi_1\rangle + \lambda_2 \hat{A} |\psi_2\rangle$. Addition of operators is both commutative and associative, but while multiplication is associative, it is not necessarily commutative, meaning that $[\hat{A}, \hat{B}] = \hat{A}\hat{B} - \hat{B}\hat{A} \neq 0$ in general. Note that we can also define the action of an operator on the dual space $\mathcal{S}^*$, where $\hat{A}$ acts from the right on a bra vector: $A : \langle\psi| \mapsto \langle\psi| \hat{A}$. Observe, however that the vector $\langle\psi| \hat{A} \neq \hat{A} |\psi\rangle$. We can see this easily by defining an operator $\hat{A} = |\psi\rangle \langle\phi|$. If we act as $\hat{A} |\chi\rangle = \langle\phi|\chi\rangle |\psi\rangle \rightleftharpoons \langle\chi|\phi\rangle \langle\psi| = \langle\chi| (|\phi\rangle \langle\psi|) = \langle\chi| A^\dagger$. Clearly the operator in parentheses is not equal to A, and in fact it is by definition the adjoint of A.

This correspondence is actually more general. We define the adjoint $\hat{A}^\dagger$ of A such that the correspondence $\hat{A} |\psi\rangle \rightleftharpoons \langle\psi| \hat{A}^\dagger$ is satisfied. Alternatively, we can write $\langle\phi| \hat{A} |\psi\rangle = \langle\psi| \hat{A}^\dagger |\phi\rangle^*$. Using this, we can prove a number of facts about adjoint operators, which are identical to those outlined in the section on operators acting on $L^2(\mathbb{R}^3)$. Again, a hermitian operator is one such that $\hat{A}^\dagger = \hat{A}$, and a unitary operator is one such that $\hat{A}^\dagger \hat{A} = \mathbb{1}$, where $\mathbb{1}$ is the identity operator.

Let us examine another operator that will be useful: $\hat{P}_\psi = |\psi\rangle \langle\psi|$. This is a projection operator in the sense that $\hat{P}_\psi |\phi\rangle = |\psi\rangle \langle\psi|\phi\rangle$ is a scalar multiple of $|\psi\rangle$ for any $|\phi\rangle$. It should be clear that $\hat{P}_\psi$ is a linear, hermitian operator. Additionally, we can observe that $\hat{P}_\psi$ is idempotent, meaning that $\hat{P}_\psi = \hat{P}_\psi$. We can extend this notion of a projection operator onto a single state to a projection operator onto a subspace $\{|\psi_n\rangle\}$ by defining

$$\hat{P}_{\{\psi\}} = \sum_n |\psi_n\rangle \langle\psi_n| . \tag{6.7}$$

Additionally, we can define a function of an operator through the power series of a function as

$$f(\hat{A}) = \sum_{n=0}^{\infty} \frac{f^{(n)}(0)}{n!} \hat{A}^n. \tag{6.8}$$

As an example, consider

$$e^{i\hat{A}} = \sum_{n=0}^{\infty} \frac{1}{n!} \left(i\hat{A}\right)^n. \tag{6.9}$$

Suppose that A is a Hermitian operator, then it follows that this exponential is a unitary operator, and furthermore, its adjoint $(e^{i\hat{A}})^\dagger = e^{-i\hat{A}}$. It may be tempting to conclude from this that the exponential with operator "powers" inherits those properties with real number powers such as $e^a e^b = e^{a+b}$, but this is not true. In fact, it is only true if $[A, B] = 0$. If they do not commute, then the product $e^{\hat{A}} e^{\hat{B}}$ is given by the Baker-Campbell-Hausdorff formula.

6.6 Representations

Choosing a representation means choosing a basis in the state space. Let us suppose that our basis is orthonormal and complete. For now, let us also assume that our basis is denumerable. Once we choose a respresentation, we can use the completeness property to expand any state as

$$|\psi\rangle = \sum_n c_n |\phi_n\rangle , \tag{6.10}$$

where $c_n = \langle\phi_n|\psi\rangle$. Note that this gives an alternate statement of completeness for an orthonormal basis $\sum_n |\phi_n\rangle \langle\psi_n| = \sum_n \hat{P}_n = \mathbb{1}$. From this, there exists a unique isomorphism between the Hilbert space $\mathcal{S}$ and $\mathbb{R}^N$, where N is the dimension of the Hilbert space. It follows then that

$$|\psi\rangle \mapsto \psi = \begin{pmatrix} c_1 \\ c_2 \\ \vdots \end{pmatrix} , \tag{6.11}$$

and additionally, there is an isomorphism between operators and $\mathbb{R}^{N\times N}$:

$$A \mapsto A = \begin{pmatrix} A_{11} & A_{12} & \dots \\ A_{21} & A_{22} & \dots \\ \vdots & \vdots & \ddots \end{pmatrix} , \tag{6.12}$$

where the matrix elements $A_{nm} = \langle\psi_n| \hat{A} |\psi_m\rangle$.

6.7 Change of representation

As we discussed previously, there is not a unique basis of a vector space. Suppose that for $\mathcal{S}$, we have two distinct bases $\{\phi_n\}$ and $\{|\chi_n\rangle\}$. Our goal here is to understand how the components of our abstract vectors and operators under the isomorphism change when we change representations/bases. The components of $|\psi\rangle$ in the χ-basis as

$$c_n^{(\chi)} = \langle\chi_n|\psi\rangle . \tag{6.13}$$

If we insert the completeness relation for the ϕ-basis, then

$$c_n^{(\chi)} = \sum_m \langle\chi_n|\phi_m\rangle \langle\phi_m|\psi\rangle = \sum_m T^*_{nm} c_m^{(\phi)} = \sum_m T^\dagger_{mn} c_m^{(\phi)} . \tag{6.14}$$

Observe that we have defined a matrix T with elements $T_{nm} = \langle \phi_n | \chi_m \rangle$ wich performs the change of basis. By inverting the transformation, we can write

$$c_n^{(\phi)} = \sum_m T_{nm} c_m^{(\chi)}, \tag{6.15}$$

and furthermore, we find

$$c_n^{(\phi)} = \sum_m \Big(\sum_l T_{lm}^\dagger T_{nm} \Big) c_l^{(\phi)}. \tag{6.16}$$

In order to ensure that the left and right-hand-sides are in fact equal, we find that $T^\dagger T = \mathbb{1}$, meaning that our change of basis/coordinates is unitary.

Next, we address the matrix elements under the change of basis. Observe that

$$\begin{aligned} A_{nm}^{(\chi)} &= \langle \chi_n | \hat{A} | \chi_m \rangle = \sum_{p,q} \langle \chi_n | \phi_p \rangle \langle \phi_p | \hat{A} | \phi_q \rangle \langle \phi_q | \chi_m \rangle \\ &= \sum_{p,q} T_{pn}^* A_{pq}^{(\phi)} T_{qm} = \sum_{p,q} T_{np}^\dagger A_{pq}^{(\phi)} T_{qm}. \end{aligned} \tag{6.17}$$

Thus, $A^{(\chi)} = T^\dagger A^{(\phi)} T$, or exploiting the unitarity of T, we have $A^{(\phi)} = T A^{(\chi)} T^\dagger$.

6.8 Eigenvalues and eigenvectors of a hermitian operator

In linear algebra, we were introduced to the eigenvalue problem. We have the same kind of problem with abstract operators. Suppose that $\hat{A}$ has an eigenvalue, eigenvector pair $\lambda, |\psi\rangle$ such that $\hat{A} |\psi\rangle = \lambda |\psi\rangle$. For this section, suppose that $\hat{A}$ is a hermitian operator. It follows that $\lambda \in \mathbb{R}$. Notice that the dual of this equation is $\langle \psi | \hat{A}^\dagger = \langle \psi | \hat{A} = \lambda^* \langle \psi |$, so

$$\langle \psi | \hat{A} | \psi \rangle = \lambda = \lambda^*. \tag{6.18}$$

Thinking about the matrix representation of A, it may be that a given eigenvalue λ is degenerate. That is, for each eigenvalue λ_i there may be a set of corresponding, distinct eigenvectors $\{\psi_i^j\}$, where $j = 1, \ldots, g_i$ is the degeneracy label for the eigenvalue λ_i.

We can prove that eigenvectors corresponding to distinct eigenvectors are orthogonal. Suppose that we have the eigenvalue, eigenvector pairs $\lambda, |\psi_\lambda\rangle$ and $\mu, |\psi_\mu\rangle$, where $\lambda \neq \mu$, then

$$\langle \psi_\mu | \hat{A} | \psi_\lambda \rangle = \mu \langle \psi_\mu | \psi_\lambda \rangle = \lambda \langle \psi_\mu | \psi_\lambda \rangle \Rightarrow \lambda = \mu. \tag{6.19}$$

Notice that this proof hinged on the fact that $\lambda - \mu \neq 0$. Therefore, there is no such proof here that the degenerate eigenvectors are automatically orthogonal, but we can perform a procedure such as Gram-Schmidt orthogonalization to construct an orthonormal set of degenerate eigenvectors.

6.9 Changing to the basis of eigenvectors

In this section, we describe how to construct the change of basis between an arbitrary representation of our Hilbert space and the eigenrepresentation. For this, notice that the matrix representation of $\hat{A}$ in the eigenbasis is diagonal, assuming that we have already made any degenerate eigenvectors orthogonal. Our goal here is to construct the matrix T_{nm} which performs the change of basis. Let us denote $|\phi_n\rangle$ and $|\psi_n\rangle$ as the basis vectors in an arbitrary and the eigenvector representations. Recall that $T_{nm} = \langle\phi_n|\psi_m\rangle$. If we expand our eigenvectors in the ϕ-basis, we have

$$T_{nm} = \sum_p \langle\phi_n|\phi_p\rangle \langle\phi_p|\psi_m\rangle = \sum_p \delta_{np} c_p^{(m)} = c_n^{(m)}, \tag{6.20}$$

where $c_n^{(m)}$ is the n^{th} component of the m eigenvector of $\hat{A}$ in the ϕ-representation. Thus, if our space has dimension N, we can write

$$T = \begin{pmatrix} c_1^{(1)} & c_1^{(2)} & \dots & c_1^{(N)} \\ c_2^{(1)} & c_2^{(2)} & \dots & c_2^{(N)} \\ \vdots & \vdots & \ddots & \vdots \\ c_N^{(1)} & c_N^{(2)} & \dots & c_N^{(N)} \end{pmatrix}. \tag{6.21}$$

6.10 Observables

We define an operator $\hat{A}$ to be an observable if it is hermitian and its eigenstates form a basis of $\mathcal{S}$:

$$\hat{A}\left|\psi_i^{(j)}\right\rangle = \lambda_i \left|\psi_i^{(j)}\right\rangle, \quad \sum_{i,j} \left|\psi_i^{(j)}\right\rangle \left\langle\psi_i^{(j)}\right| = \mathbb{1}, \tag{6.22}$$

where i labels the eigenvalue of $\hat{A}$ and j labels the degeneracy of a given eigenvalue. Based on our discussion above, it may be tempting to think that any hermitian operator admits a complete basis of the Hilbert space of interest, but this is not necessarily true. It is generally tricky to prove completeness. Here we only postulate that observables are operators which do have a complete spectrum.

Observe the following results that hold for observables:

1. If $\hat{A}$ and $\hat{B}$ commute and $|\psi\rangle$ is an eigenstate of $\hat{A}$, then $\hat{B}|\psi\rangle$ is also an eigenstate of $\hat{A}$ corresponding to the same eigenvalue a of $\hat{A}$. If a is non-degenerate, it must follow that $\hat{B}|\psi\rangle = b|\psi\rangle$, meaning that $|\psi\rangle$ is also an eigenstate of $\hat{B}$. However, if a is degenerate, then all we can say is that $B|\psi\rangle$ is a vector in the subspace spanned by the eigenstates of $\hat{A}$ corresponding to eigenvalue a: $\hat{B}\left|\psi^{(j)}\right\rangle = \sum_i c_i^{(j)} \left|\psi^i\right\rangle$ or $c_i^{(j)} = \left\langle\psi^{(i)}\right| \hat{B} \left|\psi^{(j)}\right\rangle$.

2. If $\hat{A}$ and $\hat{B}$ commute and $|\psi_1\rangle$ and $|\psi_2\rangle$ are eigenstates of $\hat{A}$ corresponding to eigenvalues $a_1 \neq a_2$ of $\hat{A}$, respectively, then $\langle\psi_1|\hat{B}|\psi_2\rangle = 0$.

3. If $\hat{A}$ and $\hat{B}$ commute, then there exists a basis of common eigenstates of $\hat{A}$ and $\hat{B}$. This is immediate when the spectrum of $\hat{A}$ is non-degenerate. If the spectrum of $\hat{A}$ is degenerate, then we can only guarantee the $\hat{B}$ is block-diagonal in its matrix representation with respect to the eigenbasis of $\hat{A}$. We can, however, diagonalize these sub-blocks. This amounts to constructing the eigenstates of $\hat{B}$ by taking linear combinations of degenerate eigenstates of $\hat{A}$. Since we are solely taking linear combinations of the degenerate eigenvectors of $\hat{A}$, the result is still an eigenstate of $\hat{A}$ but also is an eigenstate of $\hat{B}$. We thus have a basis where both $\hat{A}$ and $\hat{B}$ are diagonal in their matrix representations.

In our last point, we outlined a sketch of how to construct a basis of $\mathcal{S}$ where both $\hat{A}$ and $\hat{B}$ are diagonal. Note, however, that this does not prove that this common eigenbasis is non-degenerate. If we are lucky enough to find that there is no degeneracy, we have managed to find a complete set of commuting observables. Essentially, specifying the eigenvalues of both $\hat{A}$ and $\hat{B}$ uniquely specify the corresponding common eigenstate. Alternatively, if the common spectrum is degenerate, then we must find other observables which commute with $\hat{A}$ and $\hat{B}$ and further if necessary such that the total spectrum is non-degenerate.

In our study of bound states of one-dimensional potentials, we found that the energy eigenvalues were all non-degenerate, meaning that $\hat{H}$ forms a complete set of commuting observables trivially. However, in our study of scattering, we found that each energy is doubly degenerate. For example, though, the Hamiltonian and parity operators uniquely specify the scattering states from a one-dimensional repulsive delta-function potential at the origin.

6.11 The r-representation

In this section, we will see how wave mechanics arises from the more abstract framework of quantum mechanics in terms of Hilbert spaces and operators. Consider a position operator $\hat{x}$, which is an observable and has continuous eigenvalues such that $\hat{x}\left|\phi_x\right\rangle = x\left|\phi_x\right\rangle$, where $-\infty < x < \infty$. By assumption, the states of $\hat{x}$ are orthogonal and complete in the sense that

$$\langle\phi_x|\phi_{x'}\rangle = \delta(x-x'), \quad \int_{-\infty}^{\infty} \mathrm{d}x\left|\phi_x\right\rangle\left\langle\phi_x\right| = \mathbb{1}. \tag{6.23}$$

We can then expand our state $|\psi\rangle$ in position eigenstates as

$$|psi\rangle = \int_{-\infty}^{\infty} \mathrm{d}x\left|\phi_x\right\rangle\left\langle\phi_x|\psi\right\rangle = \int_{-\infty}^{\infty} \mathrm{d}x\,\psi(x)\left|\phi_x\right\rangle, \tag{6.24}$$

where we have the wave-function $\psi(x) = \langle\phi_x|\psi\rangle$ as the component of $|\psi\rangle$ corresponding to position x.

It follows then that operators which are functions of position such as the poten-

tial energy operator have position matrix elements

$$\langle \phi_x | \hat{V}(\hat{x}) | \phi_{x'} \rangle = \langle \phi_x | \sum_{n=0}^{\infty} \frac{V^{(n)}(0)}{n!} \hat{x}^n | \phi_{x'} \rangle = \sum_{n=0}^{\infty} \frac{V^{(n)}(0)}{n!} x^n \langle \phi_x | \phi_{x'} \rangle$$
$$= V(x)\delta(x - x'). \tag{6.25}$$

If we consider, however, the momentum operator, the matrix elements are

$$\langle \phi_x | \hat{p} | \phi_{x'} \rangle = -i\hbar \frac{\mathrm{d}}{\mathrm{d}x} \delta(x - x'). \tag{6.26}$$

This follows from the commutation relation $[\hat{x}, \hat{p}] = i\hbar \mathbb{1}$ and considering the operator $\hat{T} = \mathbb{1} - i\eta\hat{p}/\hbar$, where η is a very small parameter. We can generalize to $\langle \phi_x | \hat{p}^n | \phi_{x'} \rangle = (-i\hbar)^n \frac{\mathrm{d}^n}{\mathrm{d}x^n} \delta(x - x')$ by inserting completeness between each factor of $\hat{p}$.

6.11.1 Eigenvalue problems in the r-representation

Consider an observable $\hat{A}$ with eigenvalue problem $\hat{A} | \psi \rangle = a | \psi \rangle$, which we would like to solve in the r-representation. We can project onto the eigenstate $| \phi_x \rangle$ and insert completeness to find that

$$\int_{-\infty}^{\infty} \mathrm{d}x' \, A(x, x') \psi(x') = a\psi(x), \tag{6.27}$$

where $A(x, x') = \langle \phi_x | \hat{A} | \phi_{x'} \rangle$.

As an example, consider the momentum operator. We have

$$\int_{-\infty}^{\infty} \mathrm{d}x' - i\hbar \frac{\mathrm{d}}{\mathrm{d}x} \delta(x - x') \psi(x') = -i\hbar \frac{\mathrm{d}\psi}{\mathrm{d}x} = p\psi. \tag{6.28}$$

This is a differential equation for the eigenstates of $\hat{p}$ in the r-representation and has solution $\psi_p(x) = e^{ipx/\hbar}/\sqrt{2\pi\hbar}$, where the factor $1/\sqrt{2\pi\hbar}$ is introduced to respect the normalization of momentum eigenstates.

Next, consider the Hamiltonian operator, which is an observable since it corresponds to the total energy of a system, $\hat{H} = \frac{\hat{p}^2}{2m} + \hat{V}(\hat{x})$. If we project onto the position states as above, we find

$$\int_{-\infty}^{\infty} H(x, x') \psi(x') = \int_{-\infty}^{\infty} \mathrm{d}x' \Big[-\frac{\hbar^2}{2m} \frac{\mathrm{d}^2}{\mathrm{d}x^2} + V(x) \Big] \delta(x - x') \psi(x')$$
$$= \Big[-\frac{\hbar^2}{2m} \frac{\mathrm{d}^2}{\mathrm{d}x^2} + V(x) \Big] \psi(x) = E\psi(x), \tag{6.29}$$

which is the time-independent Schödinger equation in position space.

6.12 The p-representation

As we have seen, quantum mechanics is equally valid in the p-representation as in the r-representation. The momentum operator is an observable, meaning its eigenstates are orthonormal and complete. As in the r-representation

$\langle\psi_p|\,\hat{F}(\hat{p})\,|\psi_{p'}\rangle = F(p)\delta(p-p')$ and

$$\langle\psi_p|\,\hat{x}\,|\psi_{p'}\rangle = i\hbar\frac{\partial}{\partial p}\delta(p-p'). \tag{6.30}$$

We can insert the completeness of position states on both sides of $\hat{x}$ and use the results of the previous section to derive this result. It follows in the same way as above that an abstract eigenvalue problem reduces to

$$\int_{-\infty}^{\infty}\mathrm{d}p'\,A(p,p')\tilde{\psi}(p') = a\tilde{\psi}(p'), \tag{6.31}$$

where $A(p,p') = \langle\psi_p|\,\hat{A}\,|\psi_{p'}\rangle$. We also can quickly derive the relationship between the r and p-space wave-functions:

$$\tilde{\psi}(\vec{\boldsymbol{p}}) = \langle\psi_p|\psi\rangle = \int_{-\infty}^{\infty}\frac{\mathrm{d}x}{\sqrt{2\pi\hbar}}e^{-ipx/\hbar}\psi(x), \tag{6.32}$$

where

$$\psi(x) = \int_{-\infty}^{\infty}\frac{\mathrm{d}p}{\sqrt{2\pi\hbar}}e^{ipx/\hbar}\tilde{\psi}(p). \tag{6.33}$$

Additionally, we can write the momentum-space Schrödinger equation as

$$\Big(E-\frac{p^2}{2m}\Big)\tilde{\psi}(p) = \frac{1}{\sqrt{2\pi\hbar}}\int_{-\infty}^{\infty}\mathrm{d}p'\,\tilde{V}(p-p')\tilde{\psi}(p'). \tag{6.34}$$

6.13 Tensor products

In the past two sections, we considered states constrained only to one-dimensional position and momentum. Generally, though, our particles live in three dimensions. Thus, the Hilbert space of position states is really $\mathcal{S}_{\vec{\boldsymbol{r}}}$ with states $|\phi_{\vec{\boldsymbol{r}}}\rangle$. We can however construct this space using the tensor product:

$$\mathcal{S}_{\vec{\boldsymbol{r}}} = \mathcal{S}_x\otimes\mathcal{S}_y\otimes\mathcal{S}_z, \tag{6.35}$$

where the state $|\phi_{\vec{\boldsymbol{r}}}\rangle = |\phi_x\rangle\otimes|\phi_y\rangle\otimes|\phi_z\rangle$. Note that the relative ordering of the basis states is irrelevant. These are separate one-dimensional Hilbert spaces which do not interact with each other directly and only are composed together to construct the three-dimensional Hilbert space. Thus, we can write a three-dimensional state

$$|\psi\rangle = \int\mathrm{d}x\int\mathrm{d}y\int\mathrm{d}z\,\psi(x,y,z)\,|\phi_x\rangle\otimes|\phi_y\rangle\otimes|\phi_z\rangle = \int\mathrm{d}^3\vec{\boldsymbol{r}}\,\psi(\vec{\boldsymbol{r}})\,|\phi_{\vec{\boldsymbol{r}}}\rangle\,. \tag{6.36}$$

Additionally, we can promote an operator acting in a one-dimensional Hilbert space to the three-dimensional Hilbert space by taking a tensor product of the operator with the identity operator in the other Hilbert spaces. For example, $\hat{A}_x \to \hat{A}_x\otimes\mathbb{1}_y\otimes\mathbb{1}_z$, and therefore

$$\hat{A}_x\times\mathbb{1}_y\otimes\mathbb{1}_z\,|\psi\rangle = \int\mathrm{d}x\int\mathrm{d}y\int\mathrm{d}z\,\psi(x,y,z)\,\hat{A}_x\,|\phi_x\rangle\otimes|\phi_y\rangle\otimes|\phi_z\rangle\,. \tag{6.37}$$

As a final note, there is nothing special about the position eigenstates. If we have a complete set of commuting observables, then we can compose our Hilbert space as a tensor product of the Hilbert spaces of the commuting observables. For example, we could substitute any of these position states with momentum and obtain a valid expansion. Certainly, the details will look slightly different, but the result will be just as valid and different problems may require different choices for our decompositions.

CHAPTER 7

Physical Interpretation

Now that we have a mathematical framework to work in for quantum mechanics, we need to discuss how to use it to do real-world physics. For this, we establish a few postulates with which we interpret the mathematical framework and connect it to phenomenology.

First, the state of a system at fixed time t_0 is represented by a ket belonging to the state space $\mathcal{S}$, a Hilbert space. This implies the superposition principle: a linear vector of state vectors is a state vector.

Second, measurable physical quantities (observables) are represented by hermitian operators acting in $\mathcal{S}$. If $\hat{A}$ is an observable, then there exists a basis of eigenstates of $\hat{A}$ in $\mathcal{S}$.

Third, the only possible result of a measurement of an observable $\hat{A}$ is one of its eigenvalues. If the spectrum of $\hat{A}$ is discrete, the results obtained by measuring $\hat{A}$ are quantized.

Fourth, when the observable $\hat{A}$ is measured on a system in state $|\psi\rangle$, the probability of obtaining the discrete eigenvalue a_i is

$$p(a_i) = \sum_{j=1}^{g_i} |\left\langle \phi_i^{(j)} \middle| \psi \right\rangle|^2, \tag{7.1}$$

where we assume that $||\psi|| = 1$, $\left|\phi_i^{(j)}\right\rangle$ are the normalized eigenstates of $\hat{A}$ with eigenvalue a_i with degeneracy g_i. This probability can also be expressed as the expectation value in the state $|\psi\rangle$ of the projector on the subspace spanned by the eigenstates $\left|\phi_i^{(j)}\right\rangle$ belonging to the eigenvalue a_i:

$$p(a_i) = \sum_{j=1}^{g_i} \left\langle \psi \middle| \phi_i^{(j)} \right\rangle \left\langle \phi_i^{(j)} \middle| \psi \right\rangle = \langle \psi | \sum_{j=1}^{g_i} \left|\phi_i^{(j)}\right\rangle \left\langle \phi_i^{(j)} \middle| \psi \right\rangle = \langle \psi | \hat{P}_i | \psi \rangle . \tag{7.2}$$

Clearly then, the probabilty of measuring an element from the spectrum of $\hat{A}$

is unity:

$$\sum_i p(a_i) = \langle\psi| \sum_i \hat{P}_i |\psi\rangle = \langle\psi| \mathbb{1} |\psi\rangle = 1. \tag{7.3}$$

One point should be noted. When a given a_i is degenerate, there is an infinite number of possible choices for the set of eigenstates with eigenvalue a_i. That is, there are an infinite number of bases in the subspace of $\mathcal{S}$ corresponding to the eigenvalue a_i. The probability $p(a_i)$, however, certainly does not depend on this choice of basis. This claim can be proven as follows. Consider two distinct bases $\{\left|\phi_i^{(j)}\right\rangle\}$ and $\{\left|\chi_i^{(j)}\right\rangle\}$ which span the subspace of vectors in $\mathcal{S}$ corresponding to eigenvalue a_i of $\hat{A}$. We know from the previous chapter that there exists a unitary operator which transforms between these bases:

$$\left|\phi_i^{(j)}\right\rangle = \sum_{n=1}^{g_i} S_{nj}^\dagger \left|\chi_i^{(n)}\right\rangle, \quad \left\langle\phi_i^{(j)}\right| = \sum_{n=1}^{g_i} S_{jn} \left\langle\chi_i^{(n)}\right|. \tag{7.4}$$

Thus, the projector onto the subspace of interest in the ϕ-basis

$$\begin{aligned}\sum_{j=1}^{g_i} \left|\phi_i^{(j)}\right\rangle \left\langle\phi_i^{(j)}\right| &= \sum_{j,l,m=1}^{g_i} S_{lj}^\dagger S_{jm} \left|\chi_i^{(l)}\right\rangle \left\langle\chi_i^{(m)}\right| \\ &= \sum_{l,m=1}^{g_i} \delta_{lm} \left|\chi_i^{(l)}\right\rangle \left\langle\chi_i^{(m)}\right| = \sum_{m=1}^{g_i} \left|\chi_i^{(m)}\right\rangle \left\langle\chi_i^{(m)}\right|\end{aligned} \tag{7.5}$$

is equal to the projector onto the subspace of interest in the χ-basis.

If the observable $\hat{A}$ has a continuous spectrum, then we have probability densities $p(\alpha)$, where the probabilty to measure the eigenvalue in an interval centered on α of width $\mathrm{d}\alpha$] is

$$p(\alpha)\,\mathrm{d}\alpha = \langle\psi| \hat{P}_\alpha |\psi\rangle\,\mathrm{d}\alpha = \left[\sum_{j=1}^{g_\alpha} \left|\left\langle\phi_\alpha^{(j)}\middle|\psi\right\rangle\right|^2\right] \mathrm{d}\alpha\,. \tag{7.6}$$

We can therefore integrate over this probability density $p(\alpha)$ to obtain the probability of measuring α within some interval.

The expectation value of an observable is given in the usual way as

$$\begin{aligned}\left\langle\hat{A}\right\rangle &= \sum_i a_i p(a_i) = \sum_{i,j} a_i \left\langle\psi\middle|\phi_i^{(j)}\right\rangle \left\langle\phi_i^{(j)}\middle|\psi\right\rangle \\ &= \langle\psi| \hat{A} \left[\sum_{i,j} \left|\phi_i^{(j)}\right\rangle \left\langle\phi_i^{(j)}\right|\right] |\psi\rangle = \langle\psi| \hat{A} |\psi\rangle\,.\end{aligned} \tag{7.7}$$

Fifth, upon measurement of $\hat{A}$, the system collapses to the subspace spanned by the eigenvalue measured. That is, if a_i is measured, then the normalized state of the system is

$$|\psi'\rangle = \frac{\hat{P}_i |\psi\rangle}{\sqrt{\langle\psi| \hat{P}_i |\psi\rangle}}, \tag{7.8}$$

where as usual

$$\hat{P}_i = \sum_{j=1}^{g_i} \left|\phi_i^{(j)}\right\rangle \left\langle\phi_i^{(j)}\right| \tag{7.9}$$

if $\hat{A}$ has a discrete spectrum If $\hat{A}$ has a continuous spectrum, its measurement on a system yields $\alpha_0 \pm \Delta\alpha$ with probability

$$\int_{\alpha_0-\Delta\alpha/2}^{\alpha_0+\Delta\alpha/2} \mathrm{d}\alpha \sum_{j=1}^{g_\alpha} \left| \left\langle \phi_\alpha^{(j)} \middle| \psi \right\rangle \right|^2, \tag{7.10}$$

and right after the measurement, the system will be in state

$$|\psi'\rangle = \frac{\hat{P}_{\Delta\alpha}(\alpha_0)\,|\psi\rangle}{\langle\psi|\,\hat{P}_{\Delta\alpha}(\alpha_0)\,|\psi\rangle}, \tag{7.11}$$

where

$$P_{\Delta\alpha}(\alpha_0) = \int_{\alpha_0-\Delta\alpha/2}^{\alpha_0+\Delta\alpha/2} \mathrm{d}\alpha \sum_{j=1}^{g_\alpha} \left|\phi_\alpha^{(j)}\right\rangle \left\langle\phi_\alpha^{(j)}\right|. \tag{7.12}$$

Finally, the time evolution of the state vector $|\psi(t)\rangle$ is governed by the Schrödinger equation

$$i\hbar \frac{\mathrm{d}\,|\psi\rangle}{\mathrm{d}t} = \hat{H}(t)\,|\psi(t)\rangle\,, \tag{7.13}$$

where $\hat{H}$ is the Hamiltonian of the system and is the observable corresponding to the total energy of the system. Notice that the evolution of the state of a system is entirely deterministic. Knowing the result of the state at some time t_0, we can determine the system's state at some arbitrary future time t by evolving it according to the S.E.

7.1 Time evolution operator

We can define a unitary operator $\hat{U}(t, t_0)$ such that given a state $|\psi(t_0)\rangle$ at some initial time t_0, its action produces the state $|\psi(t)\rangle$ at time $t > t_0$ via

$$|\psi(t)\rangle = \hat{U}(t, t_0)\,|\psi(t_0)\rangle\,. \tag{7.14}$$

Here now is why the time evolution operator is unitary. The normalization of the state must be independent of time

$$\langle\psi(t)|\psi(t)\rangle = \langle\psi(t_0)|\,\hat{U}^\dagger(t,t_0)\hat{U}(t,t_0)\,|\psi(t_0)\rangle = \langle\psi(t_0)|\psi(t_0)\rangle\,. \tag{7.15}$$

Thus, $\hat{U}^\dagger(t,t_0)\hat{U}(t,t_0) = \mathbb{1}$.

Appendices

Cauchy-Schwarz Inequality

The Cauchy-Schwarz inequality comes from the following. Observe that

$$\int \mathrm{d}^3\vec{\boldsymbol{r}}\, |f(\vec{\boldsymbol{r}}) - \lambda g(\vec{\boldsymbol{r}})|^2 \geq 0 \tag{16}$$

for any $\lambda \in \mathbb{C}$. Expanding, we have

$$\int \mathrm{d}^3\vec{\boldsymbol{r}}\, |f|^2 + |\lambda|^2 \int \mathrm{d}^3\vec{\boldsymbol{r}}\, |g|^2 - \lambda \int \mathrm{d}^3\vec{\boldsymbol{r}}\, f^* g - \lambda^* \int \mathrm{d}^3\vec{\boldsymbol{r}}\, f g^* \geq 0. \tag{17}$$

In particular, if we make the choice $\lambda = \int \mathrm{d}^3\vec{\boldsymbol{r}}\, g^* f / \int \mathrm{d}^3 r\, |g|^2$, then we recover the inequality

$$\int \mathrm{d}^3\vec{\boldsymbol{r}}\, |f|^2 + \frac{|\int \mathrm{d}^3\vec{\boldsymbol{r}}\, g^* f|^2}{\int \mathrm{d}^3\vec{\boldsymbol{r}}\, |g|^2} - \frac{\Big(\int \mathrm{d}^3\vec{\boldsymbol{r}}\, g^* f\Big)\Big(\int \mathrm{d}^3\vec{\boldsymbol{r}}\, f^* g\Big)}{\int \mathrm{d}^3\vec{\boldsymbol{r}}\, |g|^2} - \frac{\Big(\int \mathrm{d}^3\vec{\boldsymbol{r}}\, g f^*\Big)\Big(\int \mathrm{d}^3\vec{\boldsymbol{r}}\, g^* f\Big)}{\int \mathrm{d}^3\vec{\boldsymbol{r}}\, |g|^2} \geq 0 \tag{18}$$

$$\Big(\int \mathrm{d}^3\vec{\boldsymbol{r}}\, |f|^2\Big)\Big(\int \mathrm{d}^3\vec{\boldsymbol{r}}\, |g|^2\Big) \geq \Big|\int \mathrm{d}^3\vec{\boldsymbol{r}}\, g^* f\Big|^2. \tag{19}$$