Chapter 6
The Quantum Wave Function

Let's just get to the point: Quantum mechanics represents a particle as a wavefunction: $\psi(\vec{r},t)$. What does a wavefunction mean physically? It means that the probability that a particle is located in a volume dV is $|\psi(\vec{r},t)|^2 dV$.

To understand this, let's go back to classical electromagnetic radiation. EM waves have oscillating electric fields $\mathcal{E}(\vec{r},t)$. The energy E in a volume dV is

$$E = \varepsilon_0 \left[\mathcal{E}(\vec{r},t)\right]^2 dV \tag{1}$$

where ε_0 is the permittivity of the vacuum. We'll just drop these constants and use proportionality signs:

$$E \propto \left[\mathcal{E}(\vec{r},t)\right]^2 dV \tag{2}$$

In quantum mechanics, energy is carried by photons in packets with energy hf. So the number of photons in dV at $\vec{r}$ is

$$N = \frac{E}{hf} \propto \frac{\left[\mathcal{E}(\vec{r},t)\right]^2 dV}{hf} \propto \left[\mathcal{E}(\vec{r},t)\right]^2 dV \tag{3}$$

Since the square of a wave is called the *intensity*, we can say that the number of photons in a small volume dV is proportional to the intensity of the light $\left[\mathcal{E}(\vec{r},t)\right]^2$ in dV. There is a slight problem with Eq. (3). Namely, there can be a fraction on the right hand side and there is an integer on the left hand side. No such thing as half a photon. So it would be better to interpret this by saying that if we took a lot of measurements, then the average number $\langle N\rangle$ of photons, or the most probable number of photons, is proportional to the intensity:

$$\langle N\rangle = \frac{E}{hf} \propto \frac{\left[\mathcal{E}(\vec{r},t)\right]^2 dV}{hf} \propto \left[\mathcal{E}(\vec{r},t)\right]^2 dV \tag{4}$$

So we are associating intensity (square of the wavefunction) with a probability of finding a particle in a small volume. So if an electron is represented by a wavefunction $\psi(\vec{r},t)$, then the probable number of electrons in a small volume dV at $\vec{r}$ is proportional to $[\psi(\vec{r},t)]^2 dV$.

One slight complication is that in quantum mechanics, wavefunctions are complex numbers:

$$\psi = \psi_{real} + i\psi_{imag} \tag{5}$$

where $i = \sqrt{-1}$. So we need to modify the probable number of electrons to $|\psi(\vec{r},t)|^2 dV$ where

$$|\psi|^2 = \psi^*\psi = \psi_{real}^2 + \psi_{imag}^2 \tag{6}$$

and

$$\psi^* = \psi_{real} - i\psi_{imag} \tag{7}$$

is the complex conjugate of ψ. We will refer to $|\psi|^2$ as the intensity of the wavefunction. It is a positive real number as is the probability of finding an electron in a particular volume element. We choose the proportionality constant to be 1 so that we can write

$$|\psi(\vec{r},t)|^2 dV = \text{Probability of finding particle in dV at } \vec{\mathrm{r}} \tag{8}$$

We can divide both sides of the equation by dV and interpret $|\psi|^2$ as the probability density:

$$|\psi(\vec{r},t)|^2 = \text{Probability per unit volume of finding particle at } \vec{\mathrm{r}} \tag{9}$$

In quantum mechanics we cannot say definitively where an electron is until, or unless, we make a measurement (collapse the wavefunction). We can only talk about the probability of a particle being somewhere. In classical mechanics we give the probability of a flipped coin being heads or tails because we don't have enough information about the forces, etc. on the coin. But if we had that info, we could determine how the coin would land. We say that classical mechanics is deterministic. Quantum mechanics is inherently probabilistic, not because of a lack of information.

Which Slit Does the Electron Go Through?

When an electron goes through a 2-slit apparatus, its wavefunction passes through both slits like a light wave and then hits the screen in front. The dark bands on the screen correspond to where the electron waves interfere constructively according to the condition

$$d\sin\theta = n\lambda \qquad n = 0, \pm 1, \pm 2, ... \tag{10}$$

where d is the slit separation and λ the electron wavelength. This is the same equation that we use to describe the interference of a light wave going through 2 slits.

But if we think of an electron as a particle, we'd like to know which slit it went through. We can try to look and see which slit it goes through, but this doesn't work. In trying to observe or measure the electron, we perturb it so much that we mess up the wavefunction. The measurement destroys the state we are trying to observe. Usually, when you measure something, you don't want to affect the thing you are trying to observe. In quantum mechanics, you can't do that.

To see this, suppose we use light to observe which slit the electron goes through. To observe interference on the screen beyond the 2 slits, the wavelength of the electron must be of order the slit separation d:

$$\lambda_{el} \approx d \tag{11}$$

So the momentum of the electron is

$$p_{el} = \frac{h}{\lambda_{el}} \approx \frac{h}{d} \tag{12}$$

In order to see which slit the electron goes through, we need the wavelength of the light used to observe the electron to be less than or of order d:

$$\lambda_\gamma \lesssim d \tag{13}$$

So the momentum of the photon is

$$p_\gamma = \frac{h}{\lambda_\gamma} \gtrsim \frac{h}{d} \approx p_{el} \tag{14}$$

In other words the momentum of the photon is larger than the momentum of the electron. So the photon will completely change the momentum of the electron. Recall the Compton effect. If we do this to a lot of the electrons traversing the 2-slit apparatus, we will destroy the interference pattern.

Basically, quantum mechanics describes particles in terms of wavefunctions. These wavefunctions work great until they hit something or until something hits them. Then quantum mechanics doesn't work so well.

Sinusoidal Waves

The de Broglie relations say that if a particle has definite values of energy ($E = hf$) and momentum ($p = h/\lambda$), then its wavefunction has definite values of frequency and wavelength. A wave with definite frequency and wavelength is a harmonic or sinusoidal wave. So let's talk about sinusoidal waves. These are basically sine or cosine waves.

A wave traveling on a taut string has the form

$$y(x,t) = A \sin 2\pi \left(\frac{x}{\lambda} - \frac{t}{T} \right) \tag{15}$$

where x is position, t is time, A is the amplitude, λ is the wavelength, and T is the period (time to repeat the cycle). This equation describes a wave traveling to the right (see Fig. 6.8 in your book). If we want a wave traveling to the left, we just change the minus sign to a plus sign:

$$y(x,t) = A \sin 2\pi \left(\frac{x}{\lambda} + \frac{t}{T} \right) \tag{16}$$

The amplitude A is the maximum displacement of the string in the vertical direction, measured from its mean position. For a fixed time t, the wavelength λ is the distance one must go before the wave repeats. For a fixed position x on the string, the period T is the time we must wait for the wave to repeat itself. The frequency f is the number of cycles or oscillations per unit time at one fixed position:

$$f = \frac{1}{T} \tag{17}$$

The units of frequency is s^{-1} or hertz where 1 hertz = 1 Hz = 1 s^{-1}. If we define wavenumber

$$k = \frac{2\pi}{\lambda} \tag{18}$$

and angular frequency

$$\omega = 2\pi f = \frac{2\pi}{T} \tag{19}$$

then we can write the wave function as

$$y(x,t) = A\sin(kx - \omega t) \tag{20}$$

The wave speed is given by dividing the distance (λ) the wave moves in a given time (T):

$$v = \frac{\lambda}{T} = \lambda f = \frac{\omega}{k} \tag{21}$$

ω and k are used a lot in quantum mechanics so become familiar with them. In terms of ω and k, the de Broglie relations become

$$E = hf = \hbar\omega \tag{22}$$

and

$$p = \frac{h}{\lambda} = \hbar k \tag{23}$$

Wave Packets and Fourier Analysis

In reality, waves never have just one wavelength and frequency. They are usually a mixture of wavelengths and frequencies. Even though we refer to monochromatic light as having one well-defined frequency, in fact, there is always a small spread of frequencies.

True sinusoidal waves go on forever, but if we want to describe particles as waves, we want the particles to be localized in space, not spread out everywhere in the universe with equal probability. So we refer to a **wave packet** or **wave pulse** as a wave function that is localized in some region of space. Localized wave packets can be written mathematically as the sum or superposition of many different sinusoidal waves, i.e., of many different cosine and sine functions. The study of the decomposition of wave packets into sine and cosine waves is called **Fourier analysis**. There are 2 broad types of functions: (1) periodic functions that repeat at regular intervals, and (2) nonperiodic, nonrepeating functions like localized wave packets.

Fourier Series

Periodic functions can be decomposed into Fourier series which are a sum of sines and cosines. Examples of periodic functions are a square wave and a triangular wave. Let's consider an even function, i.e., $f(x) = f(-x)$. This will be a sum of cosines since cosine is even, i.e., invariant if $x \to -x$. So we can write

$$f(x) = \sum_{n=0}^{\infty} A_n \cos\left(\frac{2\pi n}{\lambda} x\right) = \sum_{n=0}^{\infty} A_n \cos\left(k_n x\right) \tag{24}$$

where A_n are constants called **Fourier coefficients**. The particular values that they take depend on the function $f(x)$. Eq. (24) is called a **Fourier sum** or **Fourier series**. Notice that the different terms correspond to different wavelengths. The $n = 0$ term is just a constant. The succeeding terms have wavelengths

$$\lambda, \frac{\lambda}{2}, \frac{\lambda}{3}, ..., \frac{\lambda}{n}, ... \tag{25}$$

The longest wavelength term is $n = 1$ which is called the fundamental. The other terms are called *higher harmonics*. Corresponding to these wavelengths are the wavenumbers

$$k_1 = \frac{2\pi}{\lambda},\ k_2 = 2 \cdot \frac{2\pi}{\lambda},\ k_3 = 3 \cdot \frac{2\pi}{\lambda}, ..., k_n = n \cdot \frac{2\pi}{\lambda}, ... \tag{26}$$

There is a straightforward way to calculate the coefficients A_n for a given function $f(x)$, but we won't go into that here. It turns out that for a square wave, the coefficients are

$$A_n = \frac{2}{\pi n} \sin\left(\frac{\pi a n}{\lambda}\right) \tag{27}$$

where a is the width of a square bump. Even though the series has an infinite number of terms, the first several terms are enough to approximate the function remarkably well as shown in Figure 6.11 in the book.

Fourier Integrals

Nonperiodic functions can be regarded as a periodic function in the limit of an infinite repeat distance. If we set the wavelength to infinity, then the spacing of the wavenumbers $\Delta k = 2\pi/\lambda$ is zero. So rather than a sum over discrete values of k, we need to do an integral over k because there is a continuous distribution of k's. So we can write the **Fourier integral** as

$$f(x) = \int A(k) \cos(kx)\, dk \tag{28}$$

The function $A(k)$ is called the **Fourier transform** of $f(x)$. It gives the weighting of the cosine functions with different values of k, i.e., with different wavelengths. In other words, $A(k)$ gives the distribution of wave numbers k that make up the wave packet.

Preview: Heisenberg's Uncertainty Principle We're going to use all this to motivate Heisenberg's Uncertainty Principle which says that

$$\Delta x \Delta p \gtrsim \frac{\hbar}{2} \tag{29}$$

This says that you cannot precisely know the position and momentum of a particle simultaneously. Δx is the uncertainty in position and Δp is the uncertainty in momentum. Since de Broglie tells us that

$$p = \frac{h}{\lambda} = \hbar k \tag{30}$$

the uncertainty (range of values that might come from a measurement of the momentum of a particle) in the momentum is

$$\Delta p = \hbar \Delta k \tag{31}$$

Here Δk is the spread in k values in a wave packet that represents a particle. (Here Δk is not the spacing between k values in a Fourier sum.) So in terms of Δk, the uncertainty principle is

$$\Delta x \Delta k \geq \frac{1}{2} \tag{32}$$

To see where this comes from, consider a wave packet of size Δx made up of a range of wave numbers Δk. It turns out that $\Delta x \Delta k$ is a number of order 1. Your book writes

$$\Delta x \Delta k \approx 1 \tag{33}$$

This means that to make a wave packet that is very wide in real space, we would use a small range of k's, i.e., small Δk. Conversely, a narrow wave packet would require large Δk. This inverse relationship between Δk and Δx comes from the fact that $k \sim 1/\lambda$ where λ is the wavelength in real space. The extreme case would be a pure sinusoidal wave like $A\sin(kx - \omega t)$. There is no uncertainty in k, so $\Delta k = 0$. This wave extends throughout all space, i.e., it never ends or diminishes, so $\Delta x = \infty$.

To establish Eq. (32), consider an even function of x made up only of cosines with wavelengths in the range from $\lambda \pm \Delta\lambda$. We focus attention on the 2 terms at the extremes: the cosine terms with $\lambda - \Delta\lambda$ and $\lambda + \Delta\lambda$. So the difference in wavelength is $2\Delta\lambda$. The spread $\Delta\lambda$ corresponds to a spread Δk in wave numbers that goes as follows. Since $k = 2\pi/\lambda$, we have

$$\Delta k = \left|\frac{dk}{d\lambda}\right| \Delta\lambda = \frac{2\pi}{\lambda^2}\Delta\lambda \tag{34}$$

We put an absolute value sign since the derivative is negative but Δk and $\Delta\lambda$ are positive by definition.

Now we need to find $\Delta\lambda$ in terms of Δx. To do this, look at Figure 6.15 which shows the 2 cosine functions. Near $x = 0$, the 2 cosines are in phase and they add. But as we go away from $x = 0$, the phase difference gets progressively larger because of the wavelength difference. After one cycle, the peaks of the 2 cosines are a distance $2\Delta\lambda$ apart. N cycles away, i.e., at $x \approx N\lambda$, the peaks of the 2 functions are $2N\Delta\lambda$ apart. When the 2 cosines are 180^o out of phase, i.e., when $2N\Delta\lambda = \lambda/2$, the 2 waves cancel. This destructive interference occurs N wavelengths from the origin, approximately at position $x = N\lambda$ where $2N\Delta\lambda = \lambda/2$. This sets N. Thus the half-width of the wave packet Δx is $N\lambda$ because $x = N\lambda$ is where the wave packet goes to 0. So we have

$$\begin{aligned} 2N\Delta\lambda &= \frac{\lambda}{2} \\ \Delta x &\approx N\lambda \end{aligned} \tag{35}$$

We can combine these equations eliminate N to get

$$\Delta x \approx \frac{\lambda^2}{4\Delta\lambda} \tag{36}$$

We can plug in Eq. (34) to eliminate $\lambda^2/\Delta\lambda$ to get

$$\Delta x \approx \frac{1}{4}\frac{2\pi}{\Delta k} \tag{37}$$

or

$$\Delta x \Delta k \approx \frac{\pi}{2} \tag{38}$$

So the larger the spread in wavelengths, the more rapidly the waves dephase as one moves away from the center of the wave packet, and the more rapidly the packet decays to zero due to destructive interference: Bigger Δk means smaller Δx and vice versa.

The right hand side Eq. (38) is of order 1 and that's what we set out to show. A more precise definition of uncertainty is given by the root-mean-square, or rms, uncertainty:

$$\Delta x = \sqrt{\langle (x - x_o)^2 \rangle} \tag{39}$$

where the brackets $\langle ... \rangle$ indicates an average over all values of x, and x_o denotes the center of the wave packet. The rms uncertainty is a bit smaller than the half-width uncertainty, and if we use this definition of Δx and a similar definition of Δk, then the uncertainty relation becomes

$$\Delta x \Delta k \geq \frac{1}{2} \tag{40}$$

This is the version that your book uses. Some books write

$$\Delta x \Delta k \gtrsim 1 \tag{41}$$

which is fine for giving rough estimates of the uncertainty in x and k.

So far we have been talking about the spread in positions of a wave function at a fixed time t. We could equally well consider the spread in times of a wave function at a particular position x. So we can talk about a wave pulse as a superposition of $\cos\omega t$ and $\sin\omega t$ for various values of angular frequency $\omega = 2\pi f = 2\pi/T$. So we can go through the same argument as above with $\cos\omega t$ replacing $\cos kx$, and $\sin\omega t$ replacing $\sin kx$. We just replace x with t and k with ω. Then we get the uncertainty principle

$$\Delta t \Delta \omega \geq \frac{1}{2} \tag{42}$$

This says that the shorter a wave lasts in time, the larger the spread in constituent frequencies that make up the wave, and vice-versa. If a wave has only a narrow band of frequencies, i.e., if the wave has a narrow bandwidth, then it lasts a long time.

Heisenberg Uncertainty Relation

As we said before, since

$$p = \frac{h}{\lambda} = \hbar k \tag{43}$$

the uncertainty (range of values that might come from a measurement of the momentum of a particle) in the momentum is

$$\Delta p = \hbar \Delta k \tag{44}$$

So Eq. (40)

$$\Delta x \Delta k \geq \frac{1}{2} \tag{45}$$

yields the Heisenberg uncertainty relation

$$\Delta x \Delta p \geq \frac{\hbar}{2} \tag{46}$$

which says we can't know the exact position and momentum of a particle simultaneously. The smaller the extent of the particle in space, the larger the spread in momentum values, and vice-versa. This is intrinsic to the wave function that represents the particle. It's not the result of experimental uncertainty.

Example: An electron is known to be somewhere in an interval of total width $a \approx 0.1$ nm (size of an atom). What is the minimum uncertainty in its velocity, consistent with this knowledge?

Since Δx is the spread of the wave packet from the central value out to either side,

$$\Delta x \leq \frac{a}{2} \tag{47}$$

According to the uncertainty relation, this implies that

$$\Delta p \geq \frac{\hbar}{2\Delta x} \geq \frac{\hbar}{a} \tag{48}$$

So

$$\Delta v = \frac{\Delta p}{m} \gtrsim \frac{\hbar}{am} = \frac{\hbar c^2}{amc^2} = \frac{200 \text{ eV} - \text{nm}}{(0.1 \text{ nm})(0.5 \times 10^6 \text{ eV})} c = \frac{c}{250} \approx 10^6 \text{ m/s} \tag{49}$$

where we multiplied the numerator and denominator by c^2 to take advantage of the useful combinations $\hbar c$ and mc^2. This is a huge uncertainty in velocity.

What about the uncertainty in the velocity in a large macroscopic object?

Example: The position x of a 0.01 g pellet is known to within ± 0.5 μm. So

$$\Delta x \leq 0.5 \ \mu\text{m} \tag{50}$$

According to the uncertainty principle,

$$\Delta p \geq \frac{\hbar}{2\Delta x} \geq \frac{10^{-34} \text{ J} - \text{s}}{10^{-6} \text{ m}} = 10^{-28} \text{ kg} - \text{m/s} \tag{51}$$

So

$$\Delta v = \frac{\Delta p}{m} \geq \frac{10^{-28} \text{ kg} - \text{m/s}}{10^{-5} \text{ kg}} = 10^{-23} \text{ m/s} \tag{52}$$

So the uncertainty in velocity is totally negligible. If something were moving at 10^{-23} m/s, it would take a million years to cross an atomic diameter.

Perhaps the most dramatic consequence of the uncertainty principle is that a particle confined to a small region cannot be at rest, i.e., cannot stop moving, even at $T = 0$ K. This is called zero point energy. If a particle is localized to a small region, then Δx is small, and Δp is large. So momentum is not precisely zero. Hence the particle must have some kinetic energy since

$$K = \frac{1}{2}mv^2 = \frac{p^2}{2m} \tag{53}$$

We can estimate the minimum kinetic energy as follows. Suppose the particle is confined to a region of size a. Then $\Delta x = a/2$, and

$$\Delta p \geq \frac{\hbar}{a} \tag{54}$$

The momentum p must be of this order, so

$$\langle K \rangle = \langle \frac{p^2}{2m} \rangle \sim \frac{(\Delta p)^2}{2m} \tag{55}$$

or

$$\langle K \rangle \gtrsim \frac{\hbar^2}{2ma^2} \tag{56}$$

As we said, this is called the **zero point energy**. It is the minimum possible kinetic energy for a quantum particle confined inside a region of size a. The kinetic energy can be larger, but not smaller.

Example: What is the minimum kinetic energy of an electron confined to a region of width $a \approx 0.1$ nm, the size of an atom?

$$\langle K \rangle \gtrsim \frac{\hbar^2}{2ma^2} = \frac{(\hbar c)^2}{(2mc^2)a^2} = \frac{(200 \text{ eV} - \text{nm})^2}{(10^6 \text{ eV})(0.1 \text{ nm})^2} = 4 \text{ eV} \tag{57}$$

This is consistent with the known kinetic energy of 13.6 eV for the ground state of a hydrogen atom.

We have just been assuming that the particle moves in one dimension. We can get better agreement if we take into account that there are 3 dimensions. The uncertainty relations in 3D are

$$\Delta x \Delta p_x \geq \frac{\hbar}{2} \qquad \Delta y \Delta p_y \geq \frac{\hbar}{2} \qquad \Delta z \Delta p_z \geq \frac{\hbar}{2} \tag{58}$$

where x, y, z are the particles 3 coordinates and p_x, p_y, and p_z are the particles 3 components of momentum.

So going back to our example of the minimum kinetic energy, if we are in 3D, then

$$\langle K \rangle \gtrsim \frac{(\Delta p_x)^2}{2m} + \frac{(\Delta p_y)^2}{2m} + \frac{(\Delta p_z)^2}{2m} \approx \frac{3(\Delta p_x)^2}{2m} = 12 \text{ eV} \tag{59}$$

When we talked about making a hydrogen atom out of an electron and a proton, we said that Coulomb's law implies that the 2 should attract each other and they should collapse to a point according to classical electrodynamics. That would make Δx very small and hence Δp would be very large. Since

$$\langle K \rangle \gtrsim \frac{(\Delta p)^2}{2m} \tag{60}$$

the kinetic energy of the electron would be very large. So the electron can lower its energy by having a wave function with a finite extent. Since $\langle K \rangle \sim 1/m$, the more massive proton will have a smaller kinetic energy even though it is confined to a smaller space and has a larger uncertainty in the momentum.

Uncertainty Relation in Time and Energy

We also found in Eq. (42) an uncertainty relation between the duration Δt and the frequency range $\Delta\omega$:

$$\Delta t \Delta\omega \geq \frac{1}{2} \tag{61}$$

If we multiply through by $\hbar$ and use $E = \hbar\omega$, then we have the Heisenberg uncertainty relation for time and energy:

$$\Delta t \Delta E \geq \frac{\hbar}{2} \tag{62}$$

Here ΔE represents the uncertainty in the particle's energy. Δt is the time spent by a wave pulse or a particle in the vicinity of a position x. If the particle only spends a short amount of time in one spot, then the energy uncertainty is large, and vice-versa. On the other hand, if $\Delta E = 0$, then $\Delta t = \infty$ which means the particle lives forever in that spot, or more precisely, in that state. These are called stationary states, and are the analog of Bohr's stationary orbits.

If a particle does not remain in the same state forever, then Δt is finite and nonzero. This means that ΔE is finite and the energy is uncertain. For example, a radioactive particle could decay after an average time Δt, and emit some other particle. The energy uncertainty of the unstable particle has a minimum uncertainty of

$$\Delta E \approx \frac{\hbar}{2\Delta t} \tag{63}$$

The emitted particle would also have energy uncertainty. Sometimes researchers measure the number of emitted particles as a function of their energy. They see a peak called a resonance. The peak has a width that is due to the uncertainty in the energy. The uncertainty in energy gives the decay rate and is approximately the inverse of the lifetime.

Example:

An excited atom is unstable and decays by emission of a photon in a time of order $\Delta t \approx 10^{-8}$ s. What is the minimum uncertainty in the energy of such an atomic state?

According to the uncertainty principle,

$$\Delta E \approx \frac{\hbar c}{2c\Delta t} \approx \frac{200 \text{ eV} - \text{nm}}{2(3 \times 10^{17} \text{ nm/s})(10^{-8} \text{ s})} \approx 3 \times 10^{-8} \text{ eV} \tag{64}$$

This is much smaller than the typical energy spacing between atomic levels.