

Phys 200: Supplementary Notes on Quantum Mechanics

These notes are intended to supplement the textbook.

For the more mathematically minded students, and those with linear algebra background, I have included some comments written *in italics*. These present a different way to look at the material and are not essential.

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1 Quantum states, eigenstates, superpositions, wavefunctions and probabilities

1.1 Quantum states

A QUANTUM STATE is a complete description of a quantum particle's state at a given time.

In classical mechanics, if we wanted a complete description of the state of the particle, we would specify its position and its velocity. From this data, knowing the forces the particle is subject to, we could compute the position and the velocity at any time in the future. Since position and velocity at some time are sufficient to compute the entire future history of the particle, they give the complete state at that time. The history of the particle is its position and velocity at all times.

In quantum mechanics, the history of the particle is given by its quantum state at all times. The quantum state changes (evolves) with time, just like particle's position and velocity changed with time. The quantum state is usually described by the wavefunction, or a superposition of some eigenstates.

The quantum state is a vector and an element of a complex vector space called the Hilbert space. The Hilbert space is the space of all possible states the particle can have. Time evolution is given by a path in the Hilbert space.

1.2 Eigenstates

An EIGENSTATE is a special quantum state. To talk about eigenstates, we first need to specify a measurement. We will be particularly interested in three different measurements: position, momentum and energy. We will therefore have three kinds of eigenstates: position eigenstates, momentum eigenstates and energy eigenstates.

A POSITION EIGENSTATE is a quantum state in which the position of the particle is well-defined. If you are certain that the particle is at some position x , you can say that it is in the eigenstate $|x\rangle$. x here is a particular position; for example, if an electron is at $x = 0.3\text{nm}$, you can say that it is in a quantum state given by $|0.3\text{nm}\rangle$.

A MOMENTUM EIGENSTATE is a quantum state in which the momentum of a particle is well defined. It is denoted by $|p\rangle$, where p is the momentum of the particle.

An ENERGY EIGENSTATE is a quantum state in which the energy of the particle is well defined. While the position and momentum eigenstates are the same in all physical situations, the energy eigenstates depend on the potential the particle is moving in, or the forces acting on it. More on this later.

For every measurement, there exists a linear operator on the Hilbert space. The eigenstates corresponding to the measurement are the eigenvectors of that operator, and the measurement outcomes are the eigenvalues. For example, the position operator \hat{x} has an eigenvector for every real number, corresponding to positions in the x -direction.

A general quantum state can be written as a superposition of different eigenstates of the same measurement. For example, a delocalized particle might be in a state of a superposition of several different position eigenstates:

$$\frac{1}{3}|0\text{nm}\rangle + \frac{2i}{3}|1\text{nm}\rangle + \frac{1 + \sqrt{3}i}{3}|2\text{nm}\rangle$$

As you can see above, the coefficients in the superposition might be complex.

Each set of eigenstates is a complete basis of the Hilbert space; therefore any vector in the Hilbert space (i.e., any quantum state) can be written as a linear combination of eigenstates.

1.3 Measurements and Probabilities

To find out the possible outcomes of a measurement made on a particle in a general quantum state, you must first write the quantum state as a superposition of eigenstates of that measurement. The probability of obtaining a certain outcome from the measurement is equal to the SQUARE of the MAGNITUDE of the coefficient of the corresponding eigenstate in the superposition. For example, the probability of finding a particle in the state above at $x = 0\text{nm}$ is equal to $1/9$. The probability of finding it at $x = 1\text{nm}$ is $|2i/3|^2 = 4/9$ and the probability of finding it at $x = 2\text{nm}$ is $|(1 + i\sqrt{3})/3|^2 = (1/3)^2 + (\sqrt{3}/3)^2 = 4/9$.

1.4 Position wavefunctions

A general quantum state can be written as a superposition of position eigenstates. Since there is an infinity of position eigenstates, one for each possible value of the x-coordinate, it makes sense to write the quantum state as an integral over all the position eigenstates:

$$\int \Psi(x)|x\rangle dx \tag{1}$$

The set of coefficients $\Psi(x)$ is called the WAVEFUNCTION. Perhaps the most important property of the (position) wavefunction is that the square of its magnitude gives the probability density for the particle's position measurement:

$$P(x) = |\Psi(x)|^2 \tag{2}$$

The textbook has a good discussion about the probabilistic interpretation of the wavefunction. One thing you need to pay attention to, though, is that the textbook does not consider complex wavefunctions, so it's missing the magnitude from its probability formula.

1.5 Momentum wavefunctions and matter waves

The momentum wavefunction is defined similarly to the position wavefunction. We can write our quantum state as a superposition of states with well-defined momentum (momentum eigenstates)

$$\int \tilde{\Psi}(p)|p\rangle dx \tag{3}$$

and the coefficients $\tilde{\Psi}(p)$ are the momentum wavefunction. The momentum wavefunction has a probabilistic interpretation which parallels that of the position wavefunction: the probability density for measuring the particle to have momentum p is the square of the magnitude of the momentum wavefunction,

$$P(p) = |\tilde{\Psi}(p)|^2 \quad (4)$$

To understand the connection between the position and momentum eigenstates, we need to review de Broglie's matter waves.

De Broglie postulated that a particle with momentum p corresponds to what he called a 'matter wave' with wavelength $\lambda = h/p$. We will interpret the de Broglie matter waves to be simply the wavefunctions for the particle, and will use complex plane waves to describe them. The position wavefunction for a particle with momentum p is then

$$e^{i\frac{2\pi}{\lambda}x} = e^{ipx/\hbar} \quad (5)$$

where we have used the relationship between wavelength and momentum to write the wave in terms of momentum instead of wavelength.

Now, consider a particle in a superposition of momentum eigenstates with different momenta. Similarly to equation (3), the wavefunction for such a superposition is given by

$$\Psi(x) = \frac{1}{\sqrt{h}} \int \tilde{\Psi}(p) e^{ipx/\hbar} dx \quad (6)$$

We have simply replaced the momentum eigenstate $|p\rangle$ in equation (3) with its wavefunction given in equation (5). The factor of \sqrt{h} is there to make the units work. The above formula allows us to compute the position wavefunction if we know the momentum wavefunction.

Conversely, if you want to compute the momentum wavefunction from the position wavefunction, you can use the following formula:

$$\tilde{\Psi}(p) = \frac{1}{\sqrt{h}} \int \Psi(x) e^{-ipx/\hbar} dp \quad (7)$$

Equivalence of equations (6) and (7) is established by a branch of mathematics called Fourier Theory.

The position and momentum wavefunctions contain exactly the same information about the particle: they are equivalent descriptions the quantum state. Which one you want to use will depend on what you need to calculate. If you want to know the probability of measuring the particle at a certain place, or Δx , you need to use the position wavefunction. If you want to know the probability of measuring a certain momentum, or Δp , you need to use the momentum wavefunction.

1.6 Energy eigenstates

Energy eigenstates are special states whose position wavefunction $\Psi_E(x)$ satisfies the time-independent Schrödinger equation (more about this later). A general wavefunction can be

written as a superposition of energy eigenstates. Since energies are typically discrete (for particles in a bound state), we don't need an integral over the energies, just a sum. A wavefunction can be written as

$$\sum_E c(E) \Psi_E(x) \tag{8}$$

where $c(E)$ are some coefficients. For example, if the two lowest energy levels in a finite square well are $1eV$ and $3eV$, we can write down the following superposition of the two lowest states:

$$\frac{1}{2}\Psi_{1eV}(x) + \frac{1+i\sqrt{2}}{2}\Psi_{3eV}(x)$$

where $\Psi_{1eV}(x)$ and $\Psi_{3eV}(x)$ are solutions to the time-independent Schrödinger equation with energies $E = 1eV$ and $3eV$ respectively.

In other words, if we know the coefficients in front of the different energy eigenstates in our superposition, it's easy to figure out the wavefunction. It's a little harder to go the other way, from the wavefunction to the coefficients, and we will not cover that here.

Since position, momentum and energy eigenstates are different complete sets of basis vectors for the Hilbert space, every quantum state can be written as a linear combination of either position, momentum or energy eigenstates. The wavefunction is simply the coefficients in the linear combination. Converting from the position wavefunction to the momentum wavefunction, for example, is nothing more but a change of basis.

1.7 Normalization of wavefunctions

Since we want to interpret the square of the magnitude of the wavefunction as a probability density, we must make sure that the probabilities add up to 1. This implies that, for a wavefunction to be properly normalized, we must have

$$\int |\Psi(x)|^2 dx = 1$$

and

$$\int |\Psi(p)|^2 dp = 1$$

In fact, if you start with a properly normalized position wavefunction, and use formula (7) to compute the momentum wavefunction, the result will be normalized automatically (this is what the factor of $\sqrt{\hbar}$ ensures). Similar statement is true if you go the other way.

2 Measurement and wavefunction collapse

In the previous section we talked about measurement and probabilities, but we did not describe what happens to the quantum state when you make the measurement. It is an important tenet of Quantum Mechanics that making the measurement **CHANGES THE QUANTUM STATE**. There is no way to make a measurement without disturbing things.

Here is a general prescription of how measurements work in Quantum Mechanics:

1. For every measurement (for example, position, momentum, energy or polarization) there is a set of states for which the outcome is certain. These are called the eigenstates (see Section 1).
2. Write the quantum state which the measurement will be performed upon as a superposition of these eigenstates.
3. When the measurement is performed, the quantum state will chose to change to one of the eigenstates of this measurement. This is known as WAVEFUNCTION COLLAPSE. This change is permanent and irreversible. The original quantum state is lost.
4. The outcome of the measurement is the value which corresponds to the eigenstate the system has chosen to change to in point 3.
5. The probability (or probability density) of choosing a particular eigenstate is equal to the square of the magnitude of the coefficient of that eigenstate in the superposition in point 2.

3 Expectation values

An EXPECTATION VALUE is the average value of a measurement you will get if you multiply it very many times. It is the average of all possible outcomes weighted by the probability of each outcome. In cases where the outcomes are described by some continuous variable such as the position, x , the expectation value, denoted with $\langle x \rangle$ is given by an integral over all possible positions weighted by the probability density:

$$\langle x \rangle = \int x P(x) dx = \int x |\Psi(x)|^2 dx \quad (9)$$

This is also known as the average x , or the mean x . The expectation value tells us where the ‘middle’ of the wavepacket is; it does not tell us how wide it is spread. A measure of the width of the wavepacket is the STANDARD (or MEAN) DEVIATION, which is given by squaring the deviations of each outcome from the mean and then adding up the squares. In math, this is:

$$(\Delta x)^2 = \int (x - \langle x \rangle)^2 |\Psi(x)|^2 dx \quad (10)$$

The mean deviation, Δx , is defined as the square root of the above formula, and is positive.

We can make similar definitions for the average momentum and the mean deviation in momentum:

$$\langle p \rangle = \int p |\tilde{\Psi}(p)|^2 dx \quad (11)$$

$$(\Delta p)^2 = \int (p - \langle p \rangle)^2 |\tilde{\Psi}(p)|^2 dx \quad (12)$$

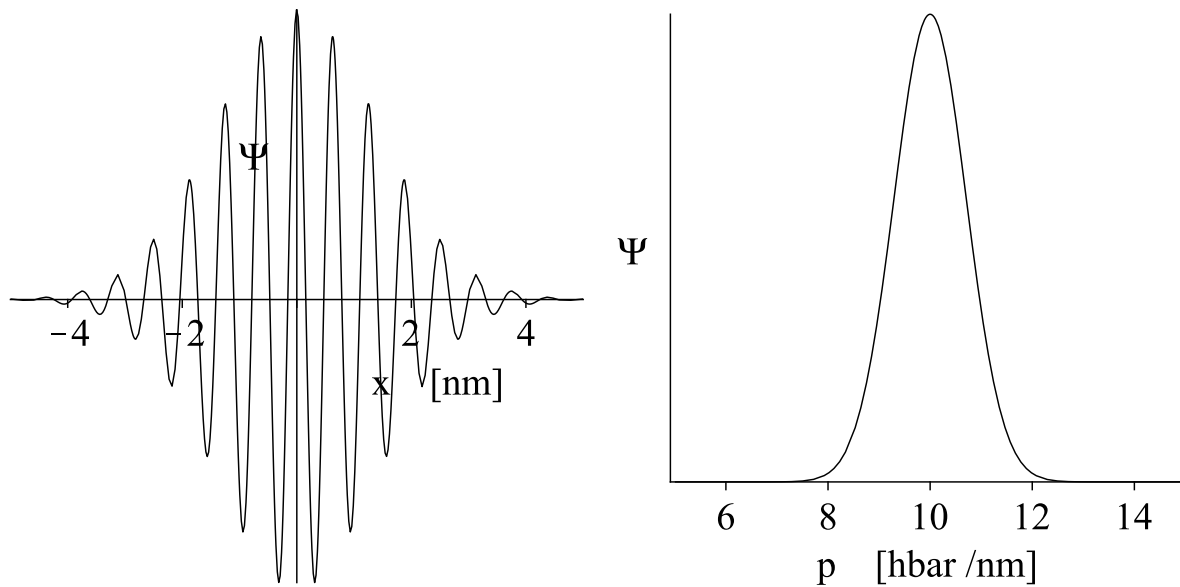


Figure 1: The real part of the position wavefunction for a wavepacket with $\langle p \rangle = 10 \hbar/\text{nm}$ and width $\Delta x = 1\text{nm}$ [left]; the momentum wavefunction of the same wavepacket [right].

One thing to pay attention to is that the wavefunctions must be properly normalized before you use any of the above formulas.

If we use this precise definition of uncertainty, we can state our Uncertainty Principle precisely, see the next section.

4 Properties of wavepackets; the uncertainty principle

4.1 The position and momentum wavefunctions of a wavepacket

The wavefunction of a momentum eigenstate, or the de Broglie wave,

$$e^{ipx/\hbar}$$

cannot be normalized properly. This is because the probability density is a constant, due to $|e^{ipx/\hbar}| = 1$ and the integral over a constant function does not converge.

In most physical situations, a particle is better approximated by a wavepacket. The basic concept of wavepackets is described in the book; here we will go into more details about the relationship between the position and the momentum wavefunction of a wavepacket.

In position space, the wavepacket might look something like the left plot in Figure 1.

How do we read information off the position wavefunction? The center of the wavepacket is clearly the approximate position of the particle. The width tells you how well localized the particle is (the narrower the wavepacket, the better the localization). Finally, the spacing of the fringes corresponds to the wavelength, which in turn corresponds to the approximate

(or average) momentum. You can see this in Figure 1: there are approximately 6.5 fringes between $x=-2\text{nm}$ and $x=2\text{nm}$, corresponding to a wavelength of $\lambda = 4\text{nm}/6.5 = 0.615\text{nm}$, or momentum $p=h/\lambda = 2\pi\hbar/\lambda = 2\pi/0.615 \hbar/\text{nm} \approx 10 \hbar/\text{nm}$, in agreement with the momentum wavefunction on the right. The more closely spaced the fringes, the smaller the wavelength and the larger the momentum.

The momentum wavefunction could be computed from the position wavefunction using formula (7). From the momentum wavefunction, it is easy to read off the mean momentum (this is the middle of the momentum wavepacket) and to estimate Δp , the width of the wavepacket.

In Figure 2, you can look at some more position and momentum wavepacket pairs. You might want to try estimating the mean momentum from the wavelength in the position wavefunction.

4.2 The Heisenberg uncertainty principle

One thing which might be apparent from Figures 1 and 2 is that if the position wavepacket gets narrower, the momentum wavepacket has to get wider and vice versa. For the (Gaussian) wavepackets plotted, the mathematical relationship is that $\Delta x \Delta p = \hbar/2$. For other shapes of wavepackets, it turns out that $\Delta x \Delta p$ is ALWAYS BIGGER than $\hbar/2$, or

$$\Delta x \Delta p \geq \hbar/2 \tag{13}$$

This is known as the HEISENBERG UNCERTAINTY PRINCIPLE. In words, it says that there is a lower limit on the product of the uncertainty in the particle's location and the uncertainty in its momentum.

Because \hbar is so small, for macroscopic objects we never notice this limitation. Even for the most precise measurements of position and momentum of a macroscopic object (such as a ball), the product of the error in the x -measurement and the error in the p -measurement is much, much greater than \hbar .

The same is obviously not true for microscopic object. If you measure the position of an electron with error Δx , you know that its momentum is uncertain by at least $\hbar/(2\Delta x)$ — and often by much more.

4.3 Time evolution of wavepackets: phase velocity, group velocity, dispersion

Wavepackets for a free particle evolve in time in a complicated way. We saw a number of different properties in the simulation (see Tutorial 10).

Wavepackets move. This is because the particle they correspond to has nonzero momentum; the more closely together the fringes are spaced, the bigger the momentum and the faster the center or peak of wavepacket moves.

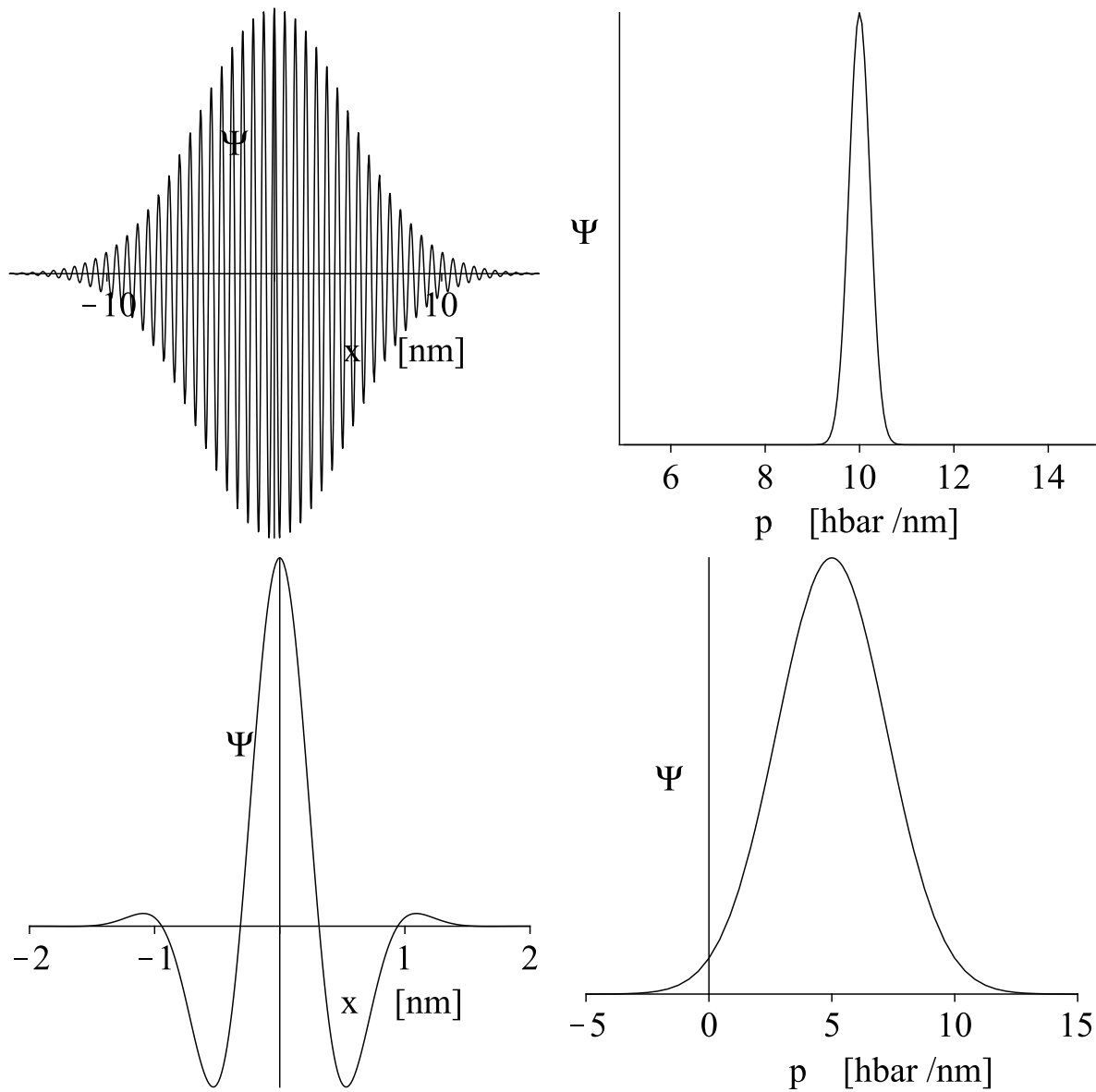


Figure 2: The real part of the position wavefunction for a wavepacket with $\langle p \rangle = 10 \hbar/\text{nm}$ and width $\Delta x = 3.16 \text{ nm}$ [top left]; the momentum wavefunction of the same wavepacket [top right]; the real part of the position wavefunction for a wavepacket with $\langle p \rangle = 5 \hbar/\text{nm}$ and width $\Delta x = 0.316 \text{ nm}$ [bottom left]; the momentum wavefunction of the same wavepacket [bottom right].

The PHASE VELOCITY (how fast the peaks and valleys of the fringes are moving) is smaller by a factor of 2 than the GROUP VELOCITY (how fast the the wavepacket is moving as a whole). The group velocity corresponds to the actual speed of the particle and is related to the momentum. For more details, including derivations, see solutions to Tutorial 10.

Wavepackets spread. This is known as DISPERSION, and is caused by the fact that the wavepacket is made up of components with many different momenta; the faster components move ahead and the slower lag behind, leading to the wavepacket spreading around. The narrower the wavepacket starts out, the faster it must spread, because a narrower wavepacket has a greater range of momenta components in it.

5 Time-dependence and the Schrödinger equation

5.1 Time-dependent Schrödinger equation

Since quantum states evolve in time to describe, for example, the trajectory of a particle, wavefunctions depend not only on position, but also on time. Their time evolution is governed by the TIME-DEPENDENT SCHRÖDINGER EQUATION, which reads:

$$i\hbar \frac{\partial}{\partial t} \Psi(x, t) = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \Psi(x, t) + V(x) \Psi(x, t) \quad (14)$$

The Schrödinger equation is a differential equation. Its solutions are functions of time and space. It constrains what kind of functions of time and space can be wavefunctions. $V(x)$ is the potential energy of the particle at point x . Solutions will depend on what potential we use. This makes sense, since the particle's motion should be affected by the forces acting on it.

The Schrödinger equation is said to govern the time evolution because if we know the wavefunction at some particular time t , we can figure out what it is at a slightly later time $t + \delta t$ as follows:

$$\begin{aligned} \Psi(t + \Delta t, x) &\approx \Psi(t, x) + \Delta t \frac{\partial}{\partial t} \Psi(t, x) = \\ &\Delta t \left(\frac{i\hbar}{2m} \frac{\partial^2}{\partial x^2} \Psi(x, t) + -\frac{i}{\hbar} V(x) \Psi(x, t) \right) \end{aligned}$$

Therefore, from the Schrödinger equation we can compute the complete future of the evolution if we know the wavefunction at just one time (but everywhere in space). This is known as the initial condition.

The second important property of the Schrödinger equation is that it is LINEAR. This means that it is compatible with the superposition principle: if you have two solutions to the Schrödinger equation, you can add them together to get a third solution.

5.2 Stationary states and the time-independent Schrödinger equation

It turns out that the time-derivative part of the Schrödinger equation is easy to deal with. If we substitute the following trial wavefunction into the equation:

$$e^{-iEt/\hbar}\psi_E(x) \tag{15}$$

we will discover that the equation now takes the form

$$-\frac{\hbar}{2m}\frac{\partial^2}{\partial x^2}\Psi(x,t) + V(x)\psi_E(x) = E\psi_E(x) \tag{16}$$

We learn several things from this simple calculation. One is that a quantum state whose time evolution is given by equation (15) can be a solution to the time-dependent Schrödinger equation. (This was not obvious a priori; we could have gotten a contradiction. Try plugging in $e^{-iEt^2/\hbar}\psi_E(x)$ and see what happens if you are confused.) Another thing we learn is that if we want a solution of the form (15), the spacial dependence, described by $\psi_E(x)$, cannot be arbitrary. $\psi_E(x)$ must satisfy equation (16), which is the TIME-INDEPENDENT SCHRÖDINGER EQUATION.

The quantum state in equation (15) is known as a STATIONARY STATE. This is because the probability density is constant in time:

$$|e^{-iEt/\hbar}\psi_E(x)|^2 = |\psi_E(x)|^2 = \text{constant}$$

The wavefunction $\psi_E(x)$ is also known as an energy eigenstate, because it satisfies the Schrödinger equation for a given energy E , meaning that the particle has a well defined energy.

As is discussed in detail in the book, for BOUND STATES (ones from which the particle cannot escape to infinity), not every energy E in the time-independent Schrödinger equation will lead to a solution which is physical (i.e., one which satisfies all boundary conditions and is normalizable). In fact, only a discrete set of energies work. The set of energies for which you can obtain a physical solution to the Schrödinger equation is called the SPECTRUM. We can say then that bound systems have discrete spectra. The number of allowed energies might be finite or infinite.

Properties of solutions to the time-independent Schrödinger equation with examples and applications are covered well in chapter 41 of the book.

5.3 General recipe for using quantum mechanics

How are quantum mechanical problems solved then? First, you need to write down the potential. This will encode all the forces acting on your particle. The potential might involve such fundamental forces as the Coulomb force. It might also come from a consideration of

the environment of the particle (for example, an electron inside and outside of a metal wire has a different energy).

Once you know the potential, you can write down the time-independent Schrödinger equation. You then need to think about the allowed boundary conditions: does the wavefunction need to vanish anywhere, for example. Once you have the differential equation and the boundary conditions, you have the mathematical problem of solving it. In this course, we have limited ourselves to substituting potential solutions into the Schrödinger equation and testing whether they work. In solving the Schrödinger equation, you will obtain the spectrum (the allowed energies) and the corresponding energy eigenstate wavefunctions $\phi_E(x)$.

Once we know the spectrum and all the energy eigenstates, we can write down the most general wavefunction possible as a superposition of the stationary states. All we need to do is take some energy eigenstates, multiply them by their appropriate $e^{iEt/\hbar}$ time-evolution factors and add them with some coefficients. The coefficients are determined by the initial condition: what do you want the wavefunction to look like at $t=0$? You saw an example of this in Tutorial 12, question 4.

Since the energy eigenstates span the Hilbert space, any quantum state at a fixed time can be written as a linear combination of the energy eigenstates. The time dependence of a stationary state, equation (15), gives you then the time evolution of any state in the Hilbert space.

5.4 What does the spectrum tell us?

The spectrum contains a lot of information about the physical system. For example, the existence of the lowest energy state implies stability of atoms (since the electron cannot lower its energy any further, and therefore does not radiate in the lowest energy state). For atoms and molecules, the spectrum determines the emission and absorption spectra. For nuclei, it determines nuclear masses and stability. For solids, it determines the conductivity properties, heat capacity, equations of state and most of thermodynamics. All of this, just from solving the time-independent Schrödinger equation.

Here is a nice example in nuclear physics: consider the fact that a proton is a bound state of three quarks. The quarks themselves are very light, but their bound state has a considerable zero-point energy. This zero-point energy makes up most of the mass of the proton. By finding the quantum spectrum for the system of three quarks, we can therefore compute the mass of the proton. If the quarks were to go into one of their excited states, they would form a different particle (not the proton anymore), with a much higher mass. The fact that the spectrum is discrete tells you that you cannot make another particle which is just like the proton, but whose mass is only a tiny bit larger.