Chapter 6

Wave Mechanics (Part A)

In the previous Chapter, we have seen how to solve a paradigmatic model (the harmonic oscillator) using an algebraic technique based (essentially) only on commutators, both for the stationary states and for the dynamics of the system. In this Chapter we explore instead more directly Schrödinger's equation in real space.

6.1 Schrödinger's wave equation

We have seen that the Hamiltonian of a particle subjected to an external potential reads

$$\hat{H} = \frac{\hat{p}^2}{2m} + V(x). \tag{6.1.1}$$

In the following we look into solutions of Schrödinger's equation in position representation, thus time-dependent amplitudes:

$$\langle x|\Psi(t)\rangle \equiv \Psi(x,t). \tag{6.1.2}$$

The amplitudes satisfy the usual equation:

$$i\hbar \frac{\partial}{\partial t} \langle x|\Psi(t)\rangle = \langle x|\hat{H}|\Psi(t)\rangle, \tag{6.1.3}$$

and recalling that

$$\hat{p}^2 = \Big(-i\hbar \frac{\partial}{\partial x}\Big)^2 = -\hbar^2 \frac{\partial^2}{\partial x^2},$$

we have the famous Schrödinger's wave equation:

$$i\hbar \frac{\partial}{\partial t} \Psi(x,t) = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \Psi(x,t) + V(x)\,\Psi(x,t). \tag{6.1.4}$$

As we have discussed in the Chapter on time evolution, the solution to this equation takes the formal solution:

$$\langle x|\Psi(t)\rangle = \langle x|\, e^{-\frac{i}{\hbar}\hat{H}\,t}\, |\Psi(0)\rangle \tag{6.1.5}$$

where we have used the fact that the Hamiltonian is time independent. Since the exponential of the Hamiltonian acts trivially on the eigenstates of the Hamiltonian $|\phi_E\rangle$:

$$e^{-\frac{i}{\hbar}\hat{H}\,t}\,|\phi_E\rangle = e^{-\frac{iE}{\hbar}\,t}\,|\phi_E\rangle, \tag{6.1.6}$$

It is very useful to solve for them explicitly, giving rise to the so-called time-independent Schrödinger equation:

$$\langle x|\hat{H}|\phi_E\rangle \;=\; E\,\langle x|\phi_E\rangle \tag{6.1.7}$$

which in functional form is equivalently written as the following differential equation:

$$-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\,\phi_E(x) \;+\; V(x)\,\phi_E(x) \;=\; E\,\phi_E(x). \tag{6.1.8}$$

The generalization of these equations to three dimensions is straightforward, as it is sufficient to recall that the kinetic energy in three dimensions is the sum of the three cartesian components; thus

$$\begin{aligned}\hat{H} &= -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} \;+\; \frac{\partial^2}{\partial y^2} \;+\; \frac{\partial^2}{\partial z^2}\right) \;+\; V(x,y,z), &(6.1.9)\\ &= -\frac{\hbar^2}{2m}\,\nabla_r^2 \;+\; V(r), &(6.1.10)\end{aligned}$$

and a three-dimensional wave function $\Psi(\mathbf{r},t)$ satisfies the corresponding Schrödinger equation with this Hamiltonian.

6.1.1 Probability flux

We have seen that a fundamental postulate of quantum mechanics is that physical wave functions are always normalized; thus:

$$\langle\Psi(t)|\Psi(t)\rangle \;=\; 1. \tag{6.1.11}$$

Similarly to the dynamics of fluids, this conservation law implies the existence of a continuity equation associated to the conservation of the integral of the probability density, $\rho(x,t) = |\Psi(x,t)|^2$. In order to find out explicitly the form of the continuity equation, we work out the time derivative of the probability density:

$$\frac{\partial}{\partial t}\,|\Psi(x,t)|^2 \;=\; \left(\frac{\partial\Psi(x,t)^*}{\partial t}\right)\Psi(x,t) \;+\; \Psi(x,t)^*\left(\frac{\partial\Psi(x,t)}{\partial t}\right), \tag{6.1.12}$$

and substituting the time derivative of the wave function with Schrödinger's equation we have

$$\begin{aligned}\frac{\partial}{\partial t}\,|\Psi(x,t)|^2 &= \frac{1}{i\hbar}\left[\frac{\hbar^2}{2m}\frac{\partial^2\Psi^*}{\partial x^2}\,\Psi \;+\; \Psi^*\Big(-\frac{\hbar^2}{2m}\frac{\partial^2\Psi}{\partial x^2}\Big)\right]\\ &= -\frac{i\hbar}{2m}\left[\left(\frac{\partial^2\Psi^*}{\partial x^2}\right)\Psi \;-\; \Psi^*\left(\frac{\partial^2\Psi}{\partial x^2}\right)\right]\\ &= -\frac{i\hbar}{2m}\frac{\partial}{\partial x}\left[\left(\frac{\partial\Psi^*}{\partial x}\right)\Psi \;-\; \Psi^*\left(\frac{\partial\Psi}{\partial x}\right)\right].\end{aligned}$$

We then have the following continuity equation

$$\frac{\partial}{\partial t}\,\rho(x,t) \;+\; \frac{\partial}{\partial x}\,J(x,t) \;=\; 0, \tag{6.1.13}$$

where we have defined the probability current

$$J(x,t) \;=\; \frac{i\hbar}{2m}\Big[\Big(\frac{\partial\Psi^*(x,t)}{\partial x}\Big)\,\Psi(x,t) \;-\; \Psi^*(x,t)\,\Big(\frac{\partial\Psi(x,t)}{\partial x}\Big)\Big]. \tag{6.1.14}$$

Eq. (6.1.13) is a continuity equation in the sense that it is similar to what is used in hydrodynamics to express the conservation of mass, whereas in this context it is derived assuming conservation of probability. The continuity equation also expresses a local conservation law for the probability. If we integrate the square modulus of the wave function in a finite interval $[a,b]$, we have

$$\frac{\partial}{\partial t}\int_a^b |\Psi(x,t)|^2\,dx \;=\; J(a,t) \;-\; J(b,t), \tag{6.1.15}$$

thus the probability in the region delimited by a and b increases or decreases as a result of the flux differences at the two extremes.

Since the probability current expresses the flow of probability density in time, we might intuitively expect that it is also related to the momentum of the particle, as much the mass current in a fluid is related to the velocity of the fluid. In his first works, Schrödinger was actually led to conjecture that each point in space one could identify this current with the actual velocity field of the particles, however this leads to complications in the theory and contradictions with the experiments. The connection between the probability flux and the momentum is only valid on average, i.e. when considering expectation values of the momentum operator. To show this, we recall that the average momentum is given by:

$$\langle p(t)\rangle \;=\; -\,i\hbar\int dx\,\Psi^*(x,t)\,\frac{\partial\Psi(x,t)}{\partial x} \tag{6.1.16}$$

$$=\; i\hbar\int dx\,\Psi(x,t)\,\frac{\partial\Psi^*(x,t)}{\partial x}, \tag{6.1.17}$$

where in the last line we have used the fact that the expectation value of the operator is always real, thus $\langle p(t)\rangle = \langle p(t)\rangle^*$. We can then conclude that

$$\int dx\,J(x,t) \;=\; \frac{\langle p(t)\rangle}{m}, \tag{6.1.18}$$

thus showing that only on average the current is equal to the particle's velocity.

6.2 General Properties of Wave Functions

We now want to establish a few general properties of the solutions of Schrödinger's wave equation. We concentrate, for simplicity, on the one-dimensional case, but all the results presented here are easily generalized to three dimensions.

6.2.1 Normalization

The first condition we have already seen, is that physically valid wave functions must be normalizable, thus

$$\int_{-\infty}^{+\infty} dx\, |\Psi(x)|^2 \;=\; 1, \tag{6.2.1}$$

which is a strict requirement due to the probabilistic interpretation of the wave-function squared. It should be remarked, however, that Schrödinger's equation generally admits both normalizable solutions and un-normalizable solutions. In fact, the only requirement we asked for eigen-kets of continuous variables is

$$\langle \xi | \xi' \rangle \;=\; \delta(\xi - \xi'), \tag{6.2.2}$$

which is the completeness requirement of the basis but does not imply the normalization condition of the eigen-kets (for discrete variables, instead, the two conditions are the same). An important consequence is that, for example, the eigen-kets of the momentum are not physically valid quantum states, since they are not normalizable! This is because they correspond to the eigen-kets of the Hamiltonian of a free particle

$$\hat{H} \;=\; \frac{\hat{p}^2}{2m}, \tag{6.2.3}$$

whose probability density of being in a certain position of space is expected to be independent on the specific position. In turn, this implies that the particle, in principle, could be anywhere in the universe with uniform probability. This is clearly an absurd requirement, and it is also the reason why the wave function is not normalizable. In general, however, free particles do not exist in Nature, since they are always confined by some external potential or by the interactions with other particles. In this sense, we can always think that there is an intrinsic scale L beyond which ($|x| > L$) it is essentially impossible to find the particle. This finite length scale makes the wave function normalizable, as we will also show in the following examples.

While some solutions of the Schrödinger equation are not normalizable, thus unphysical, they are still very much useful to analyze the dynamics of physical wave functions.

6.2.2 Continuity

On physical grounds, it is reasonable to expect that the probability density is a continuous function of x, thus $\Psi(x)$ is also expected to be continuous. From a mathematical point of view, if the potential $V(x)$ is bound and analytic, the solutions of the Schrödinger's equation must also be continuous and analytical. The situation is a bit different if the potential is singular. Roughly speaking, however, a discontinuity in the wave function can lead to a finite energy E only if it is compensated by a potential $V(x) \sim \delta'(x)$ that cancels out the singularity due to the kinetic energy at the discontinuity. For example, imagine that around $x \sim 0$ the wave function has a sign-like discontinuity $\Psi(x) = \mathrm{sign}(x)$, then around the origin:

$$-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\Psi(x) \;=\; -\frac{\hbar^2}{m}\,\delta'(x), \tag{6.2.4}$$

thus only if the potential is $V(x) = \frac{\hbar^2}{2m}\,\delta'(x)$ can cancel out this singularity and lead to a finite energy E.

6.2.3 Continuity conditions of the Derivative

In order to establish whether the first derivative $\Psi'(x)$ of the wave function is continuous or not at some point $x = a$, we integrate the Schrödinger's equation around that region with a small ϵ:

$$\int_{a-\epsilon}^{a+\epsilon} dx \left[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\Psi(x) \;+\; V(x)\,\Psi(x) \right] \;=\; E\int_{a-\epsilon}^{a+\epsilon} dx\,\Psi(x), \tag{6.2.5}$$

$$-\frac{\hbar^2}{2m}\Big[\Psi'(a+\epsilon) - \Psi'(a-\epsilon)\Big] + \int_{a-\epsilon}^{a+\epsilon} V(x)\,\Psi(x)\,dx \;=\; \mathcal{O}(\epsilon). \tag{6.2.6}$$

From this equation we see that there are, essentially, two important sub-cases.

1. $V(a)$ is finite, thus $\int_{a-\epsilon}^{a+\epsilon} V(x)\,\Psi(x)\,dx = \mathcal{O}(\epsilon)$ and we can conclude that $\Psi'(a+\epsilon) = \Psi'(a-\epsilon) + \mathcal{O}(\epsilon)$, thus the first derivative is continuous in $x = a$.
2. $V(a)$ is infinite, singular, etc. (for example, $V(x) = \delta(x-a)$), then the first derivatives is not continuous, and the discontinuity in the derivative is fixed by the equation above, thus

$$\Psi'(a+\epsilon) \;-\; \Psi'(a-\epsilon) \;=\; \frac{2m}{\hbar^2}\int_{a-\epsilon}^{a+\epsilon} V(x)\,\Psi(x)\,dx. \tag{6.2.7}$$

We have therefore seen that a discontinuity in the wave function appears if the potential, for example, $V(x) \sim \delta(x)$. Later on we will see an example application with this idealized, yet reasonable potential.

6.2.4 Minimum Allowed Energy

The energy eigenvalue E can, in general, be an arbitrary number. However, for a given potential $V(x)$ there is a minimum energy value that can be taken. Specifically, we must have

$$E \;\geq\; \min_x V(x) \tag{6.2.8}$$

$$\;=\; V_{\text{min}}. \tag{6.2.9}$$

This condition follows from the fact that the Hamiltonian contains two terms, and the first one (the kinetic energy) is positive definite. In order to see this, consider

$$|\Phi\rangle \;=\; \hat{p}\,|\Psi\rangle, \tag{6.2.10}$$

then

$$\langle\Phi|\Phi\rangle \;\geq\; 0 \tag{6.2.11}$$

$$\langle\Psi|\hat{p}^2|\Psi\rangle \;\geq\; 0. \tag{6.2.12}$$

Thus for an eigen-ket of energy E we have

$$E \;=\; \langle E|\frac{\hat{p}^2}{2m} + V(x)|E\rangle \;\geq\; \langle\Psi|V(x)|\Psi\rangle \;\geq\; V_{\text{min}}. \tag{6.2.13}$$

Another very important bound, known as variational bound, is found when considering the expectation value of the Hamiltonian over a generic state. In this case, and assuming that the Hamiltonian has a discrete spectrum ($E_0 \leq E_1 \leq E_2 \ldots$) for simplicity, we have:

$$\begin{aligned}\langle H \rangle &= \langle \Psi | \hat{H} | \Psi \rangle \\ &= E_0 \langle E_0 | \Psi \rangle^2 + E_1 \langle E_1 | \Psi \rangle^2 + \ldots \\ &\geq E_0 \langle E_0 | \Psi \rangle^2 \\ &\geq E_0.\end{aligned}$$

Therefore the expectation value of the energy on an arbitrary state cannot be lower than the ground-state energy, E_0, and it is exactly equal to E_0 only if $|\Psi\rangle = |E_0\rangle$.

6.2.5 Bound states and scattering eigenstates

The solutions of the time-independent Schroedinger equation, $|E\rangle$, can be generally classified into two kind of states, depending on the value of the energy. The main criterion is

$$\begin{cases} E < V(\pm\infty), & \text{bound state} \\ E > V(\pm\infty), & \text{scattering state} \end{cases}$$

thus the type of possible eigenstates depends on the type of potential considered. Physically speaking, bound states correspond to cases when the wave-function goes to zero in the limit $x \to \pm\infty$, thus we say that the particle is bound inside a certain finite region of space. The harmonic oscillator is a clear case where this happens, since there $V(\pm\infty) = +\infty$, and we have seen that the wave-function vanishes exponentially when approaching $x \to \pm\infty$.

Scattering states are a very different beast, since in general they do not correspond to physical states. The reason is that, since they are not required to vanish at $x \to \pm\infty$, they are not normalizable. Nonetheless, albeit not being physical states, they are still valid solutions of the time-independent Schrödinger equation and, as we will see in the following, they play an important mathematical role in solving the time-dependent Schrödinger equation.

6.2.6 Parity operator

We define the parity operator

$$\hat{\Pi} |x\rangle = |-x\rangle \tag{6.2.14}$$

which transforms coordinates into their negative values, thus acting on wave-functions as:

$$\langle x | \hat{\Pi} | \Psi \rangle = \Psi(-x). \tag{6.2.15}$$

The eigenvalues λ of the parity operator and the corresponding eigen-kets $|u_\lambda\rangle$ are found easily, since:

$$\langle x | \hat{\Pi} | u_\lambda \rangle = \lambda \langle x | u_\lambda \rangle, \tag{6.2.16}$$

$$\langle x | \hat{\Pi}\hat{\Pi} | u_\lambda \rangle = \lambda \langle x | \hat{\Pi} | u_\lambda \rangle, \tag{6.2.17}$$

$$\langle x | u_\lambda \rangle = \lambda^2 \langle x | u_\lambda \rangle, \tag{6.2.18}$$

thus $\lambda = \pm 1$, and the eigenfunctions with positive/negative eigenvalue are all the even/odd functions:

$$u_+(-x) = u_+(x), \tag{6.2.19}$$

$$u_-(-x) = -\,u_-(x). \tag{6.2.20}$$

For potential energies that are spatially symmetric, $(V(x) = V(-x))$ we can see that the Hamiltonian commutes with the parity operator. This is easily seen considering the matrix elements of the commutator in coordinate representation:

$$\begin{aligned}
\langle x|\left[\hat{H},\hat{\Pi}\right]|x'\rangle &= \langle x|\left(\frac{\hat{p}^2}{2m}\,\hat{\Pi} + V(x)\,\hat{\Pi}\right) - \left(\hat{\Pi}\,\frac{\hat{p}^2}{2m} + \hat{\Pi}\,V(x)\right)|x'\rangle \\
&= \langle x|\left(\frac{\hat{p}^2}{2m} + V(x)\right)|-x'\rangle - \langle -x|\left(\frac{\hat{p}^2}{2m} + V(x)\right)|x'\rangle \\
&= -\,\frac{\hbar^2}{2m}\,\frac{\partial^2}{\partial x^2}\delta(x+x') + V(x)\,\delta(x+x') + \\
&\quad + \frac{\hbar^2}{2m}\,\frac{\partial^2}{\partial x^2}\delta(-x-x') - V(-x)\,\delta(x+x') \\
&= \Big(V(x) - V(-x)\Big)\,\delta(x+x') \\
&= 0.
\end{aligned}$$

Thus when $V(x) = V(-x)$, we can diagonalize the Hamiltonian and the parity operator simultaneously, and the solutions of the Schroedinger's equation at some energy E must be also eigenvectors of the parity, thus they either satisfy

$$\Psi_E(x) = \Psi_E(-x), \tag{6.2.21}$$

or

$$\Psi_E(x) = -\,\Psi_E(-x). \tag{6.2.22}$$

The harmonic oscillator is one example of potential that is symmetric, and indeed we have seen that in that case the even eigenvalues $n = 0, 2, 4, \ldots$ correspond to spatially even functions, whereas the odd ones $n = 1, 3, 5, \ldots$ correspond to spatially odd functions. While we haven't used this symmetry explicitly to solve the harmonic oscillator, reflection symmetry $(V(x) = V(-x))$ is in general a very useful tool, since it allows us to solve Schrödinger's equation more easily, since we can treat even and odd functions independently, as we will see in the examples below.