Chapter 3

Time Evolution (Part A)

In the previous Chapters we have introduced the general formalism of quantum mechanics, and concentrated on the description of static quantum phenomena. Starting with this Chapter, we will introduce time dependence to quantum states and one of the fundamental tenets of non-relativistic quantum theory: Schrödinger's equation.

3.1 Transforming Quantum States in Time

In the second Chapter we have introduced the first three Axioms of quantum mechanics, essentially concerning how a quantum system is represented as a state vector, how it is manipulated through operators, and how the measurement process takes place.
How do quantum states evolve in time though? We can formalize this question by saying that we want to determine an operator $\hat{U}(t_0, t_1)$ that takes a given state at an initial time t_0, denoted $|\psi(t_0)\rangle$, and transforms it into

$$|\psi(t_1)\rangle \;=\; \hat{U}(t_0, t_1)\; |\psi(t_0)\rangle\,. \tag{3.1.1}$$

Notice that here the notation $\hat{U}(t_0, t_1)$ means that, in general, we expect the operator form to depend parametrically on both the initial (t_0) and the final time (t_1).

3.1.1 Conditions on $\hat{U}$

We can already derive several interesting properties of the operator $\hat{U}$, just by requiring some fundamental properties related to time evolution. The operator $\hat{U}$ transforms physical states into physical states, thus a first property we should expect is that it preserve the normalization of $|\psi\rangle$, since Axiom 2 requires that we have a consistent probabilistic interpretation of state vectors at each instant of time. This translates into the requirement:

$$\langle\psi(t_1)|\psi(t_1)\rangle \;=\; \langle\psi(t_0)|\; \hat{U}^\dagger(t_0, t_1)\, \hat{U}(t_0, t_1)\; |\psi(t_0)\rangle \;=\; \langle\psi(t_0)|\psi(t_0)\rangle\,. \tag{3.1.2}$$

The second property we expect from this operator is that it can be arbitrarily composed, in the sense that successive time evolutions $t_0 \to t_1 \to t_2 \to t_3, \ldots$ must be equivalent to a single time evolution of the total time. For example we must have:

$$\hat{U}(t_2, t_3)\, \hat{U}(t_1, t_2)\, \hat{U}(t_0, t_1) \;=\; \hat{U}(t_0, t_3), \tag{3.1.3}$$

where it is crucial to notice that earlier times appear on the right of the expression above, since

$$\begin{aligned} |\psi(t_3)\rangle &= \hat{U}(t_2,t_3)\ |\psi(t_2)\rangle \\ &= \hat{U}(t_2,t_3)\Big[\hat{U}(t_1,t_2)\ |\psi(t_1)\rangle\Big] \\ &= \hat{U}(t_2,t_3)\,\hat{U}(t_1,t_2)\Big[\hat{U}(t_0,t_1)\ |\psi(t_0)\rangle\Big]. \end{aligned}$$

Furthermore, if we go back in time, this operation should be equivalent to applying the inverse transformation:

$$\hat{U}(t_0,t_1) \;=\; \hat{U}^{-1}(t_1,t_0), \tag{3.1.4}$$

where $\hat{U}^{-1}$ denotes the inverse of the operator.
The last property that we can intuitively expect is that in the limit of small time evolution the operator $\hat{U}$ should strictly reduce to the identity,

$$\lim_{t_1 \to t_0} \hat{U}(t_0,t_1) \;=\; \hat{I}, \tag{3.1.5}$$

since the state is unchanged when not time evolved.

3.1.2 Time-Invariant Case

In order to determine a concrete form for the time evolution operator, we start with a simpler case, in which we imagine the system to be completely isolated from the environment, and make the assumption that the time evolution depends only on time differences and not on the absolute values of times. In other words, assuming for example that we consider equispaced time intervals $t_0 \to t_0 + \Delta t \to t_0 + 2\Delta t \ldots$, we have

$$|\psi(t_0+\Delta t)\rangle = \hat{U}(\Delta t)\ |\psi(t_0)\rangle\,, \tag{3.1.6}$$

$$|\psi(t_0+2\Delta t)\rangle = \hat{U}(\Delta t)\ |\psi(t_0+\Delta t)\rangle\,, \tag{3.1.7}$$

where it should be noticed that we are using the same operator to evolve the state of an interval Δt, regardless of the initial time. This assumption is, in practice, very well verified in the great majority of quantum systems. Later in this Chapter we will discuss how to go beyond this.
For the moment, let us show that all the conditions previously described are satisfied if we take the time evolution operator to be described by the following unitary operator

$$\hat{U}(\Delta t) \;=\; e^{-i\,\hat{\Omega}\,\Delta t}, \tag{3.1.8}$$

where $\hat{\Omega}$ is an Hermitian operator. The exponential of the operator indeed has essentially the same meaning it would have for regular numbers, and it is understood in terms of its Taylor expansion:

$$e^{-i\,\hat{\Omega}\,\Delta t} \;=\; \hat{I} \;-\; i\,\hat{\Omega}\,\Delta t \;-\; \tfrac{1}{2}\,\hat{\Omega}^2\,\Delta t^2 \;+\; \mathcal{O}\Big((\Delta t)^3\Big), \tag{3.1.9}$$

thus we can also clearly see that $\hat{\Omega}$ carries the units of a frequency. From the Taylor expansion we immediately see that (3.1.5) is verified. The unitarity assumption is also quick to verify, since it is an elementary property of exponentials of Hermitian operators that

$$\left(e^X\right)^\dagger \;=\; e^{X^\dagger},$$

thus

$$\hat{U}^\dagger(\Delta t) \;=\; e^{+i\hat{\Omega}\,\Delta t}, \qquad \hat{\Omega} \;=\; \hat{\Omega}^\dagger. \tag{3.1.10}$$

Hence

$$\hat{U}^\dagger(\Delta t)\,\hat{U}(\Delta t) \;=\; e^{+i\hat{\Omega}\,\Delta t}\,e^{-i\hat{\Omega}\,\Delta t} \;=\; \hat{I}. \tag{3.1.11}$$

The composition property is also a natural consequence of the exponential structure:

$$\hat{U}(\Delta t_1 + \Delta t_2) \;=\; \hat{U}(\Delta t_2)\,\hat{U}(\Delta t_1), \qquad e^{-i\hat{\Omega}\,(\Delta t_1+\Delta t_2)} \;=\; e^{-i\hat{\Omega}\,\Delta t_2}\,e^{-i\hat{\Omega}\,\Delta t_1}, \tag{3.1.12}$$

as well as the time-inversion property, noticing that

$$\hat{U}(-\,\Delta t) \;=\; e^{+i\hat{\Omega}\,\Delta t}, \tag{3.1.13}$$

thus we recover (3.1.4) as a direct consequence of unitarity:

$$e^{+i\hat{\Omega}\,\Delta t}\,e^{-i\hat{\Omega}\,\Delta t} \;=\; \hat{I}, \qquad \hat{U}(-\,\Delta t) \;=\; \hat{U}^{-1}(\Delta t). \tag{3.1.14}$$

The exponential form therefore satisfies all the requirements, and it is actually part of a broader mathematical result known as Stone's theorem.

3.2 The Schrödinger equation

In the previous Section we have used very general arguments to determine that the time evolution operator should take the form:

$$\hat{U}(\Delta t) \;=\; e^{-i\hat{\Omega}\,\Delta t}. \tag{3.2.1}$$

The operator $\hat{\Omega}$, which is Hermitian, is what we can immediately identify as the generator of the time evolution. In classical mechanics, the generator of the time evolution is the Hamiltonian of the system. By analogy, it is therefore natural to identify $\hat{\Omega}$ also as the Hamiltonian operator of the quantum system. $\hat{\Omega}$, as previously introduced, however has the dimensions of a frequency, whereas in classical mechanics the Hamiltonian has the units of an energy. We thus define the actual Hamiltonian operator of the system with the correct units:

$$\hat{H} \;=\; \hbar\,\hat{\Omega}, \tag{3.2.2}$$

through Planck's reduced constant $\hbar$. This units rescaling, strictly speaking, is not of fundamental importance for the development of the theory at this stage, however we will show later on that this definition allows us to consistently recover classical physics at the macroscopic scale. We stress however that the Hamiltonian operator concept is a broader concept than that found in classical mechanics, and that it is often the case that quantum Hamiltonians do not have a direct classical counterpart. In this sense, the analogy should always be taken with a grain of salt, and strictly speaking, only the definition through the operator $\hat{U}$ is always correct.

From the previous reasoning and definitions, we thus have that a quantum state evolves according to

$$|\psi(t+\Delta t)\rangle \;=\; e^{-\frac{i}{\hbar}\hat{H}\,\Delta t}\,|\psi(t)\rangle\,. \tag{3.2.3}$$

This equation is, in essence, all we need to perform the time evolution of the system. However, we can derive a more famous equation when considering an infinitesimal time step Δt. Using the Taylor series for the exponential, we get

$$|\psi(t+\Delta t)\rangle \;=\; |\psi(t)\rangle \;-\; \tfrac{i}{\hbar}\,\hat{H}\,\Delta t\,|\psi(t)\rangle \;+\; \mathcal{O}\Big((\Delta t)^2\Big), \tag{3.2.4}$$

and slightly rearranging the terms we obtain

$$i\,\hbar\,\frac{|\psi(t+\Delta t)\rangle - |\psi(t)\rangle}{\Delta t} \;=\; \hat{H}\;|\psi(t)\rangle\,. \tag{3.2.5}$$

By taking the limit $\Delta t \to 0$ in the previous expression, this leads to the famous Schrödinger equation for quantum states:

$$i\,\hbar\,\frac{\partial}{\partial t}\;|\psi(t)\rangle \;=\; \hat{H}\;|\psi(t)\rangle\,, \tag{3.2.6}$$

which fully specifies how a quantum state evolves in time, once an initial condition $|\psi(t=0)\rangle$ is given and the Hamiltonian operator is established.

3.3 Energy Eigenstates

So far, we have determined a very important differential equation governing the time evolution of a quantum state, Eq. (3.2.6). We now analyze more in detail the connection between the spectrum of $\hat{H}$ and the dynamics of the quantum system.
A first observation is that we are considering the case in which $\hat{H}$ is time independent, as a direct consequence of the time-invariance assumption we have previously made (we will see later that when this assumption is violated the Hamiltonian can be thought of changing in time). For the moment, for time-independent $\hat{H}$ we can always define time-independent eigen-kets

$$\hat{H}\;|E_k\rangle \;=\; E_k\;|E_k\rangle\,, \tag{3.3.1}$$

where, for the sake of simplicity, we assume they are labeled by an integer index k. In this case, we can always expand the time-dependent state in terms of the energy eigen-kets:

$$|\psi(t)\rangle \;=\; \sum_k\;|E_k\rangle\;\langle E_k|\psi(t)\rangle \;=\; \sum_k\;c_k(t)\;|E_k\rangle\,. \tag{3.3.2}$$

The action of Schrödinger's equation in this representation is then particularly easy to visualize:

$$i\,\hbar\,\frac{\partial}{\partial t}\sum_k\;c_k(t)\;|E_k\rangle \;=\; \sum_k\;\hat{H}\;|E_k\rangle\;c_k(t). \tag{3.3.3}$$

Hence

$$i\,\hbar\sum_k\;|E_k\rangle\;\frac{\partial}{\partial t}c_k(t) \;=\; \sum_k\;E_k\;|E_k\rangle\;c_k(t). \tag{3.3.4}$$

Further multiplying on the left by $\langle E_{k'}|$ and using orthonormality, we get that each coefficient c_k satisfies

$$i\,\hbar\,\frac{d}{dt}\,c_k(t) \;=\; E_k\,c_k(t), \tag{3.3.5}$$

which has the solution

$$c_k(t) \;=\; e^{-\frac{i}{\hbar}E_k\,t}\,c_k(0). \tag{3.3.6}$$

We therefore already see the importance of energy eigenstates: if we know the expansion coefficients of the initial state in terms of the energy eigen-kets, then we can determine the state at all times. Notice that in this basis, dynamics is just a simple phase multiplication, thus it is also clear that by construction $\sum_k \left|c_k(t)\right|^2 \;=\; \sum_k \left|c_k(0)\right|^2$, the norm conservation condition.

It is also instructive to derive the same result just using the form of the exponential operator $\hat{U}(t) = \exp\!\Big(-\frac{i}{\hbar}\,\hat{H}\,t\Big)$, and noticing that it acts trivially on the eigenstates of the Hamiltonian:

$$\begin{aligned}
\hat{U}(t)\;|\psi(0)\rangle \;&=\; e^{-\frac{i}{\hbar}\hat{H}\,t}\;|\psi(0)\rangle \\
&=\; e^{-\frac{i}{\hbar}\hat{H}\,t}\sum_k c_k(0)\;|E_k\rangle \\
&=\; \sum_k c_k(0)\,e^{-\frac{i}{\hbar}E_k\,t}\;|E_k\rangle \\
&=\; \sum_k c_k(t)\;|E_k\rangle\,.
\end{aligned}$$

3.4 Time-Dependence of Observables

Having established the fundamental equation governing the dynamics of a given quantum state, Eq. (3.2.6), we can now also determine how observables behave. To this purpose, we compute the expectation value of some observable $\hat{A}$ at time t using the standard rules:

$$\langle\hat{A}\rangle(t) \;=\; \langle\psi(t)|\;\hat{A}\;|\psi(t)\rangle\,. \tag{3.4.1}$$

Thus

$$\langle\psi(t)|\;\hat{A}\;|\psi(t)\rangle \;=\; \langle\psi(0)|\;e^{+\frac{i}{\hbar}\hat{H}\,t}\,\hat{A}\,e^{-\frac{i}{\hbar}\hat{H}\,t}\;|\psi(0)\rangle\,, \tag{3.4.2}$$

and in order to compute this explicitly, it is convenient to consider the eigenstates of the Hamiltonian and insert twice a completeness relation:

$$\begin{aligned}
\langle\psi(0)|\;e^{+\frac{i}{\hbar}\hat{H}\,t}\,\hat{A}\,e^{-\frac{i}{\hbar}\hat{H}\,t}\;|\psi(0)\rangle &= \sum_{k,k'}\langle\psi(0)|\;e^{+\frac{i}{\hbar}\hat{H}\,t}\;|E_k\rangle\;\langle E_k|\;\hat{A}\;|E_{k'}\rangle\;\langle E_{k'}|\;e^{-\frac{i}{\hbar}\hat{H}\,t}\;|\psi(0)\rangle \\
&= \sum_{k,k'}\exp\!\Big(\tfrac{i}{\hbar}\,(E_k - E_{k'})\,t\Big)\,c_k(0)^*\,A(k,k')\,c_{k'}(0),
\end{aligned} \tag{3.4.3}$$

where we have introduced the matrix elements of the operator $\hat{A}$ in the energy basis, $A(k,k') \equiv \langle E_k|\;\hat{A}\;|E_{k'}\rangle$, as well as the expansion coefficients of the initial state at $t = 0$,

$c_k(0) \equiv \langle E_k|\psi(0)\rangle$. This expression shows that the expectation value of a generic operator, in general, is a summation of characteristic oscillations in time, with frequencies depending only on the energy differences:

$$\omega_{k,k'} = \frac{E_k - E_{k'}}{\hbar}. \tag{3.4.4}$$

We will see soon that these kinds of oscillations, first predicted by Niels Bohr, can be experimentally observed and, among other things, they allow for the most precise measurements of $\hbar$ available so far.

3.4.1 Special Case: Conserved Quantities

While in general the expectation value of observables will oscillate in time (as in Eq. (3.4.2)), there is however a very important case in which measuring the same quantity at later times will yield the same average results. In other words, we can find specific observables for which $\langle\hat{A}\rangle(t) = \langle\hat{A}\rangle(0)$ at all times. These are called conserved quantities, since their expectation value is conserved as a function of time.

In general, a conserved quantity is associated to an operator $\hat{A}_c$ that commutes with the Hamiltonian, i.e.

$$\left[\hat{A}_c, \hat{H}\right] = 0, \tag{3.4.5}$$

thus implying, as seen before, that the eigenstates of $\hat{H}$ are also eigenstates of $\hat{A}_c$. In turn, this means that the matrix elements of the operator in the energy eigen-basis greatly simplify:

$$\langle E_k|\,\hat{A}_c\,|E_{k'}\rangle = \delta_{k,k'}\,a_k, \tag{3.4.6}$$

and all the Bohr frequencies vanish, resulting in

$$\langle\psi(t)|\,\hat{A}_c\,|\psi(t)\rangle = \sum_k \left|c_k(0)\right|^2 a_k, \tag{3.4.7}$$

which in turn is identical to the initial value

$$\begin{aligned}
\langle\psi(0)|\,\hat{A}_c\,|\psi(0)\rangle &= \sum_{k,k'} c_k(0)^*\,\langle E_k|\,\hat{A}_c\,|E_{k'}\rangle\,c_{k'}(0)\\
&= \sum_k \left|c_k(0)\right|^2 a_k\\
&= \langle\psi(t)|\,\hat{A}_c\,|\psi(t)\rangle\,.
\end{aligned}$$

Hence the expectation value of such an operator remains constant in time.