

7 The time-dependent Schrödinger Equation

$$i\hbar \frac{\partial}{\partial t} \psi(x, t) = H\psi(x, t) \quad (7.1)$$

where, H is called the Hamiltonian operator. It is the operator in quantum mechanics that corresponds to the energy of the system.

In quantum mechanics, every measurable quantity, has a corresponding operator. As we studied in the Stern-Gerlach experiments (and from the subsequent treatment of kets and operators), a measurement “projects” a system onto the eigenstates of the operator.

H can be written as a sum of the kinetic and potential energy:

$$H = K + V = \frac{p^2}{2m} + V \quad (7.2)$$

Now if we substitute the momentum operator in Eq. (H.7) (see [the Operators handout](#), i.e. $\hat{p} = -i\hbar \frac{\partial}{\partial x}$), we can write down the Hamiltonian operator as

$$H = \frac{p^2}{2m} + V = \frac{1}{2m} \left[-i\hbar \frac{\partial}{\partial x} \right]^2 + V = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V \quad (7.3)$$

where $-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} = \frac{1}{2m} \left[-i\hbar \frac{\partial}{\partial x} \right]^2$ is the kinetic energy operator.

In addition, note that we have used $\psi(x, t)$ in Eq. (7.1) instead of an abstract ket. So we have already chosen a representation, the position (or coordinate) representation.

A general comment: in the coordinate representation, the Schrödinger Equation is a differential equation. (In other representations, it may actually be a matrix equation. This is similar to how we noted in the previous class that an operator goes to a matrix, while a ket goes to a vector!)

The time-dependent Schrödinger Equation (7.1) can be rationalized from the wave-particle duality. We will proceed to show this below.

1. We have seen earlier in the Stern Gerlach experiments that there is this great analogy between wave-like behavior and particle-like behavior. We noted that the behavior of spin states in the presence of a magnetic field can be exactly reproduced by considering the behavior of plane-polarized light.
2. Hence, can we write $\langle x | \psi \rangle \equiv \psi(x)$ as a collection of waves? Consider the following:

$$h(x) = \int dk f(k) \exp \{ikx\} = \int dp f(p) \exp \left\{ i \frac{p}{\hbar} x \right\} \quad (7.4)$$

How does one obtain this expression?

3. Note that in Eq. (7.4), $h(x)$ is a linear combination of waves such as those in the Change of basis section.
4. Note further that waves $\exp \{ikx\}$ are eigenstates of the momentum operator. (Why is $\exp \{ikx\}$ considered to be a wave? Because, $\exp \{ikx\} = \cos \{kx\} + i \sin \{kx\}$.)
5. Note also that Eq. (7.4) is obtained from resolution of identity in terms of the momentum Eigenstates. In addition, those of you who have seen Fourier transforms before will note that the function $h(x)$ is now a Fourier transform of the function $f(k)$.
6. **Wavepackets:** Why in Eq. (7.4) do we say that $h(x)$ is a *linear combination of waves* when we write it as an integral? Because:
 - (a) $\exp \{ikx\}$ forms a continuous representation as noted earlier in Eq. (E.6) (where we have represented the eigenstates of momentum as $|k\rangle$, that is using the abstract *ket* vector).
 - (b) As noted in Eq. (E.5) for continuous representations the sum is changed to integral.
 - (c) Hence Eq. (7.4) is the *continuous multi-dimensional* analogue of Eq. (A.1) in the **vector algebra review**.
 - (d) Hence we can say that in Eq. (7.4), we have written $h(x)$ as a continuous linear combination of waves. So could we call it a "packet" of waves then? Indeed!!! In fact, $\psi(x)$ as written on the right hand side of Eq. (7.4) is called a *wavepacket* (as in "packet-of-waves").
7. $h(x)$ in Eq. (7.4) does not have a time-dependence. So, lets go ahead and multiply Eq. (7.4) by the quantity $\exp \{-i\omega t\} = \exp \left\{ -i \frac{E}{\hbar} t \right\}$ so as to maintain the same wave-form as in Eq. (2.6),

$$\psi(x, t) = \int \int dp dE f(p) g(E) \exp \left\{ i \left[\frac{p}{\hbar} x - \frac{E}{\hbar} t \right] \right\} \quad (7.5)$$

8. Note now the similarities between the integrand in Eq. (7.5) and the plane polarized light seen earlier. How does one rationalize Eq. (7.5)?
9. Let us go ahead substitute the right hand side of Eq. (7.5) into Eq. (7.1) to see what happens. (Lets forget about V for now.)
10. Differentiating Eq. (7.5) twice with respect to x we obtain:

$$\begin{aligned}
 -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \psi(x, t) &= -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \int dp dE f(p) g(E) \exp \left\{ i \left[\frac{p}{\hbar} x - \frac{E}{\hbar} t \right] \right\} \\
 &= -\frac{\hbar^2}{2m} \int \int dp dE f(p) g(E) \left[i \frac{p}{\hbar} \right]^2 \exp \left\{ i \left[\frac{p}{\hbar} x - \frac{E}{\hbar} t \right] \right\} \\
 &= \frac{1}{2m} \int \int dp dE f(p) g(E) p^2 \exp \left\{ i \left[\frac{p}{\hbar} x - \frac{E}{\hbar} t \right] \right\} \quad (7.6)
 \end{aligned}$$

11. Note further from Eq. (7.2) that in the absence of V , $E = \frac{p^2}{2m}$. Hence, Eq. (7.6) can be re-written as:

$$-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \psi(x, t) = \int \int dp dE f(p) g(E) E \exp \left\{ i \left[\frac{p}{\hbar} x - \frac{E}{\hbar} t \right] \right\} \quad (7.7)$$

12. Differentiating Eq. (7.5) with respect to t we obtain (for the right side of Eq. (7.1) we obtain:

$$\begin{aligned}
 i\hbar \frac{\partial}{\partial t} \psi(x, t) &= i\hbar \frac{\partial}{\partial t} \int \int dp dE f(p) g(E) \exp \left\{ i \left[\frac{p}{\hbar} x - \frac{E}{\hbar} t \right] \right\} \\
 &= i\hbar \int \int dp dE f(p) g(E) \left[-i \frac{E}{\hbar} \right] \exp \left\{ i \left[\frac{p}{\hbar} x - \frac{E}{\hbar} t \right] \right\} \\
 &= \int \int dp dE f(p) g(E) E \exp \left\{ i \left[\frac{p}{\hbar} x - \frac{E}{\hbar} t \right] \right\} \quad (7.8)
 \end{aligned}$$

13. Note that the right hand side of Eqs. (7.8) and Eq. (7.7) are identical. Hence the left hand sides of Eqs. (7.8) and (7.7) must be equal to each other which leads to the time-dependent Schrödinger equation.

This provides a good rationalization for the time-dependent Schrödinger Equation (TDSE) in Eq. (7.1) using the wave-particle duality and the analogy to plane-polarized light.

That is, the TDSE holds for all functions that can be written as linear combination of waves.

8 The time-independent Schrödinger Equation

1. Let us now restrict ourselves to a certain kind of solution to the TDSE, Eq. (7.1).

$$\psi(x, t) = \phi(x)f(t) \quad (8.1)$$

Eq. (8.1) assumes that space (x) and time (t) dependence of the wavefunction $\psi(x, t)$ can be separated. This is not always the case as we will see later in a homework problem.

2. Substituting Eq. (8.1) into the time-dependent Schrödinger Equation (TDSE), we obtain:

$$\begin{aligned} i\hbar \frac{\partial}{\partial t} \psi(x, t) &= H\psi(x, t) \\ i\hbar \phi(x) \frac{\partial}{\partial t} f(t) &= -\frac{\hbar^2}{2m} f(t) \frac{\partial^2 \phi(x)}{\partial x^2} + V\phi(x)f(t) \end{aligned} \quad (8.2)$$

3. Dividing both sides from the left (why is this distinction in directionality left/right important? **Homework**) by $[\phi(x)f(t)]$ yields:

$$\begin{aligned} i\hbar \frac{\phi(x)}{\phi(x)f(t)} \frac{\partial}{\partial t} f(t) &= -\frac{\hbar^2}{2m} \frac{f(t)}{\phi(x)f(t)} \frac{\partial^2 \phi(x)}{\partial x^2} + \frac{V\phi(x)f(t)}{\phi(x)f(t)} \\ i\hbar \frac{1}{f(t)} \frac{\partial}{\partial t} f(t) &= -\frac{\hbar^2}{2m} \frac{1}{\phi(x)} \frac{\partial^2 \phi(x)}{\partial x^2} + \frac{1}{\phi(x)} V\phi(x) \\ i\hbar \frac{1}{f(t)} \frac{\partial}{\partial t} f(t) &= \frac{1}{\phi(x)} H\phi(x) \end{aligned} \quad (8.3)$$

4. Note in Eq. (8.3) that the left hand side only depends on time (t) while the right hand side only depends of space (x). The only way they can each be equal to the other is if they are both equal to some constant (say, E : we dont know what that constant is yet though):

$$i\hbar \frac{1}{f(t)} \frac{\partial}{\partial t} f(t) = E = \frac{1}{\phi(x)} H\phi(x) \quad (8.4)$$

which gives two equations:

$$i\hbar \frac{1}{f(t)} \frac{\partial}{\partial t} f(t) = E \quad (8.5)$$

and

$$\frac{1}{\phi(x)} H\phi(x) = E \quad (8.6)$$

Or we could rewrite these two equations as:

$$i\hbar \frac{\partial}{\partial t} f(t) = E f(t) \quad (8.7)$$

and

$$H\phi(x) = E\phi(x) \quad (8.8)$$

5. Eq. (8.8) is called the time-independent Schrödinger Equation.
6. Eq. (8.7) is a first order differential equation in time that we can solve as follows.
- (a) First multiply both sides by dt ,

$$\begin{aligned} i\hbar \frac{\partial}{\partial t} f(t) &= E f(t) \\ i\hbar df(t) &= E f(t) dt \end{aligned} \quad (8.9)$$

- (b) Then divide both sides by $f(t)$, and

$$i\hbar \frac{df(t)}{f(t)} = E dt$$

- (c) Note now that we can integrate both sides with respect to time as shown below:

$$\begin{aligned} \int i\hbar \frac{df(t)}{f(t)} &= \int E dt \\ i\hbar \ln [f(t)] &= Et + C \end{aligned} \quad (8.10)$$

where C is a constant of integration. Exponentiating Eq. (8.10) we obtain:

$$f(t) = \exp \left[-\frac{iEt}{\hbar} \right] \exp \left[-\frac{iC}{\hbar} \right] \quad (8.11)$$

But $\exp \left[-\frac{iC}{\hbar} \right]$ is also a constant, since C is a constant. So we can write this as say A :

$$f(t) = A \exp \left[-\frac{iEt}{\hbar} \right] \quad (8.12)$$

which is the solution to Eq. (8.7).

(Some of you may be AIs for general chemistry. You may have encountered, or will encounter, a similar expression for the first order rate. But note that there is an important difference here, the complex number i which is not present for the first order rate equation.)

7. The time-independent Schrödinger Equation is Eq. (8.8):

$$\begin{aligned} H\phi(x) &= E\phi(x) \\ -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \phi(x) + V\phi(x) &= E\phi(x) \end{aligned} \quad (8.13)$$

is a second order differential equation (and eigenvalue problem!!) that depends on the potential V . We will consider a few cases in this course where the solution to this equation can be worked out analytically. *However, for the majority of cases, the time-independent Schrödinger Equation can only be solved through approximations. This is the case for all chemical systems with more than a few atoms.* We will spend a little bit of time later in this course outlining some of the methods involved in solving Eq. (8.13)

8. However, we can now write our restricted (why restricted? **Homework**) solution to the TDSE as:

$$\begin{aligned}\psi(x, t) &= \phi(x)f(t) \\ &= \phi(x) \left\{ A \exp \left[-\frac{iEt}{\hbar} \right] \right\}\end{aligned}\quad (8.14)$$

9. Equation (8.14) is called the "stationary-state-solution" to the time-dependent Schrödinger Equation and the functions $\phi(x)$ are called the *stationary state*.
10. Why is this called the stationary state? It is certainly not "stationary" since it depends on time. But, the probability density $|\psi(x, t)|^2 = \psi(x, t)^* \psi(x, t)$ is time-independent since

$$\begin{aligned}|\psi(x, t)|^2 &= \psi(x, t)^* \psi(x, t) \\ &= |\phi(x)|^2 A^* A \exp \left[-\frac{iEt}{\hbar} \right] \exp \left[\frac{iEt}{\hbar} \right] \\ &= A^* A |\phi(x)|^2\end{aligned}\quad (8.15)$$

Note that the right side does not depend on time. This is the reason why Eq. (8.14) is called a *stationary-state-solution* to the time-dependent Schrödinger Equation.

Homework: Let ψ_1 be a solution to the time-dependent Schrödinger Equation in Eq. (7.1) of the form $\psi_1(x, t) = \phi_1(x)f_1(t)$. Similarly consider a second solution to the time-dependent Schrödinger Equation in Eq. (7.1) of the form $\psi_2(x, t) = \phi_2(x)f_2(t)$.

1. Prove that $\psi_3(x, t) = c_1\psi_1(x, t) + c_2\psi_2(x, t)$ (where c_1 and c_2 are constants) is also a solution to the time-dependent Schrödinger Equation in Eq. (7.1) (**Hint** : To solve this problem, (a) substitute $\psi_1(x, t)$ in Eq. (7.1), (b) substitute $\psi_2(x, t)$ in Eq. (7.1), (c) multiply the first equation generated from the equation in (a) above by c_1 , multiply the second equation generated from the equation in (b) above by c_2 , add these to new equations and show that this becomes the time-dependent Schrödinger Equation for $\psi_3(x, t) = c_1\psi_1(x, t) + c_2\psi_2(x, t)$.)
2. Is $\psi_3(x, t)$ of the form in Eq. (8.1)? What are your conclusions?

Extra Credit Homework:

1. On the basis of the above homework you see that the form of $\psi(x, t)$ is very restricted and more general solutions are possible to the time-dependent Schrödinger Equation that do not conform to this simple form. In this homework I hope to show you how more general forms of this solution can be derived.
 - (a) Take Eq. (7.1) and multiply both sides by $\exp \{iEt/\hbar\}$.
 - (b) Integrate with respect to t between the limits $-\infty$ to $+\infty$.
 - (c) Show that the result is identical to Eq. (8.8).
 - (d) This presents an alternate approach to derive the time-independent Schrödinger Equation

2. Now something more general:
 - (a) Take Eq. (7.1) and multiply both sides by $\exp \{iEt/\hbar\}$.
 - (b) Integrate with respect to t between the limits 0 to $+\infty$.
 - (c) When you simplify this you don't get Eq. (8.8), do you?
 - (d) How do you argue this result?
 - (e) If you had integrated from t_1 to t_2 instead of 0 to $+\infty$ above, what would you have obtained? Do you see how both the time-independent Schrödinger Equation and the equation obtained above by integrating from 0 to $+\infty$ are special cases of this equation?
 - (f) The equations you have derived here are called the "time-independent wavepacket Schrödinger Equation (TIWSE)" and are a more general form than the TISE. What do you think they are useful for?