8 The time-independent Schrödinger Equation

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

   \[ \psi(x, t) = \phi(x) f(t) \]  
   \[ (8.1) \]

   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:

   \[ i\hbar \frac{\partial}{\partial t} \psi(x, t) = H \psi(x, t) \]

   \[ i\hbar \phi(x) \frac{\partial}{\partial t} f(t) = \frac{-\hbar^2}{2m} f(t) \frac{\partial^2 \phi(x)}{\partial x^2} + V\phi(x) f(t) \]  
   \[ (8.2) \]

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

   \[ i\hbar \frac{\phi(x)}{\phi(x)f(t)} \frac{\partial}{\partial t} f(t) = -\frac{\hbar^2}{2m} f(t) \frac{\partial^2 \phi(x)}{\partial x^2} + V\phi(x) f(t) \]

   \[ i\hbar \frac{1}{f(t)} \frac{\partial}{\partial t} f(t) = -\frac{\hbar^2}{2m} \frac{1}{\phi(x)} \frac{\partial^2 \phi(x)}{\partial x^2} + \frac{1}{\phi(x)} V\phi(x) \]

   \[ i\hbar \frac{1}{f(t)} \frac{\partial}{\partial t} f(t) = \frac{1}{\phi(x)} H\phi(x) \]  
   \[ (8.3) \]

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):

   \[ i\hbar \frac{1}{f(t)} \frac{\partial}{\partial t} f(t) = E \]

   \[ (8.4) \]

   which gives two equations:

   \[ i\hbar \frac{1}{f(t)} \frac{\partial}{\partial t} f(t) = E \]  
   \[ (8.5) \]

   and

   \[ \frac{1}{\phi(x)} H\phi(x) = E \]  
   \[ (8.6) \]

   Or we could rewrite these two equations as:

   \[ i\hbar \frac{\partial}{\partial t} f(t) = Ef(t) \]  
   \[ (8.7) \]

   and

   \[ H\phi(x) = E\phi(x) \]  
   \[ (8.8) \]
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 \( dt \),
   \[
   \frac{\hbar}{i} \frac{\partial f(t)}{\partial t} = Ef(t)
   \]
   \[
   \frac{\hbar df(t)}{f(t)} = E dt
   \]

   (b) Then divide both sides by \( f(t) \), and
   \[
   \frac{\hbar df(t)}{f(t)} = Et
   \]

   (c) Note now that we can integrate both sides with respect to time as shown below:
   \[
   \int \frac{\hbar df(t)}{f(t)} = \int E dt
   \]
   \[
   \hbar \ln f(t) = Et + C
   \]
   where \( C \) is a constant of integration. Exponentiating Eq. (8.10) we obtain:
   \[
   f(t) = \exp \left[ - \frac{iEt}{\hbar} \right] \exp \left[ - \frac{iC}{\hbar} \right]
   \]
   But \( \exp \left[ - \frac{iC}{\hbar} \right] \) is also a constant, since \( C \) is a constant. So we can write this as say \( A \):
   \[
   f(t) = A \exp \left[ - \frac{iEt}{\hbar} \right]
   \]
   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):
   \[
   H \phi(x) = E \phi(x)
   \]
   \[
   -\frac{\hbar^2}{2m} \frac{\partial^2 \phi(x)}{\partial x^2} + V \phi(x) = E \phi(x)
   \]
8. However, we can now write our restricted (why restricted?) solution to the TDSE as:

\[ \psi(x,t) = \phi(x)f(t) \]

\[ = \phi(x) \left\{ A \exp \left[ -\frac{iEt}{\hbar} \right] \right\} \]  \hspace{1cm} (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

\[ |\psi(x,t)|^2 = \psi(x,t)^*\psi(x,t) \]

\[ = |\phi(x)|^2 A^* A \exp \left[ -\frac{iEt}{\hbar} \right] \exp \left[ \frac{iEt}{\hbar} \right] \]

\[ = A^* A |\phi(x)|^2 \]  \hspace{1cm} (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 \( \psi_1 \) 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 that the TISE. What do you think they are useful for?