3.6: The Time-Dependent Schrodinger Equation

The time-dependent Schrödinger equation, is used to find the time dependence of the wavefunction. This equation relates the energy to the first time derivative analogous to the classical wave equation that involved the second time derivative. This equation,

$$\hat{H}(r,t)\psi(r,t) = i\hbar\frac{\partial}{\partial t}\psi(r,t) \tag{3.6.1}$$

where r represents the spatial coordinates (x, y, z), must be used when the Hamiltonian operator depends on time, e.g. when a time dependent external field causes the potential energy to change with time.

Even if the Hamiltonian does not depend on time, we can use this equation to find the time dependence $\varphi(t)$ of the eigenfunctions of $\hat{H}(r)$. First we write the wavefunction $\Psi(r,t)$ as a product of a space function ($\psi(r)$) and a time function ($\varphi(t)$) and substitute into Equation 3.6.1.

$$\Psi(r,t) = \psi(r)\varphi(t) \tag{3.6.2}$$

We use a product function because the space and time variables are separated in Equation 3.6.1 when the Hamiltonian operator does not depend on time. Since $\psi(r)$ is an eigenfunction of $\hat{H}(r)$ with eigenvalue E, this substitution leads to Equation 3.6.5

$$\hat{H}(r)\psi(r)\varphi(t) = i\hbar\frac{\partial}{\partial t}\psi(r)\varphi(t) \tag{3.6.3}$$

$$E\psi(r)\varphi(t) = i\hbar\psi(r)\frac{\partial}{\partial t}\psi(t) \tag{3.6.4}$$

which rearranges to

$$\frac{d\varphi(t)}{\varphi(t)} = \frac{-iE}{\hbar}dt \tag{3.6.5}$$

Integration gives

$$\varphi(t) = e^{-i\omega t} \tag{3.6.6}$$

by setting the integration constant to 0 and using the definition $\omega = \frac{E}{\hbar}$. Thus, we see the time dependent Schrödinger equation contains the condition $E = \hbar\omega$ proposed by Planck and Einstein.

The eigenfunctions of a time-independent Hamiltonian therefore have an oscillatory time dependence given by a complex function, i.e. a function that involves $\sqrt{-1}$.

$$\Psi(r,t) = \psi(r)e^{-i\omega t} \tag{3.6.7}$$

When molecules are described by such an eigenfunction, they are said to be in an eigenstate of the time-independent Hamiltonian operator. We will see that all observable properties of a molecule in an eigenstate are constant or independent of time because the calculation of the properties from the eigenfunction is not affected by the time dependence of the eigenfunction. A wavefunction with this oscillatory time dependence e-iωt therefore is called a stationary-state function.

When a system is not is a stationary state, the wavefunction can be represented by a sum of eigenfunctions like those above. In this situation, the oscillatory time dependence does not cancel out in calculations, but rather accounts for the time dependence of physical observables. Examples are provided in Chapter 4, Activity 2, and Chapter 5, Activity 1.

> **Example 3.6.16**
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> Complete the steps leading from Equation 3.6.1 to Equation 3.6.7.

> **Example 3.6.17**
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> Show that Equation 3.6.7 is a solution to Equation 3.6.1 when the Hamiltonian operator does not depend on time and $\psi(r)$ is an eigenfunction of the Hamiltonian operator.

This might be a good time to review complex numbers