

8 Solving the Time-dependent Schrödinger Equation: Brief introduction to the quantum mechanical propagator

1. How do we solve the TDSE? Suppose we say:

$$\psi(x, t) = \exp\left\{\frac{-iHt}{\hbar}\right\} \psi(x, t = 0) \quad (8.1)$$

2. It is possible to show that Eq. (8.1) is a solution to the TDSE:

$$\begin{aligned} i\hbar \frac{\partial}{\partial t} \psi(x, t) &= i\hbar \frac{\partial}{\partial t} \left[\exp\left\{\frac{-iHt}{\hbar}\right\} \psi(x, t = 0) \right] \\ &= i\hbar \frac{-iH}{\hbar} \exp\left\{\frac{-iHt}{\hbar}\right\} \psi(x, t = 0) \\ &= H \left[\exp\left\{\frac{-iHt}{\hbar}\right\} \psi(x, t = 0) \right] \end{aligned} \quad (8.2)$$

3. Thus Eq. (8.1) is indeed a solution to the TDSE.

4. But $\exp\left\{\frac{-iHt}{\hbar}\right\}$ is an operator. How can we see that this is in fact an operator? (Taylor's series review in class.)

5. What does this operator $\exp\left\{\frac{-iHt}{\hbar}\right\}$ do?

$$\psi(x, t) = \exp\left\{\frac{-iHt}{\hbar}\right\} \psi(x, t = 0) \quad (8.3)$$

It “propagates” (or moves in time) $\psi(x, t = 0) \rightarrow \psi(x, t)$.

6. Hence, for obvious reasons, the operator $\exp\left\{\frac{-iHt}{\hbar}\right\}$ is called the propagator.

7. Things “move” in chemical reactions (dynamics). The propagator allows us to visualize and derive new insights by “calculating” such motions.

8. How do you use the propagator, to actually propagate the initial state $\psi(x, t = 0)$. A brief discussion in class.

9. A few examples of how the propagator might be useful can be seen from the following movies:

- Click on <http://www.indiana.edu/%7Essiweb/C561/movies/SLO-Eig1evol.mpg> to see the evolution of a “quantized proton” in a biological enzyme active site. The quantum evolution has a significant effect on the experimentally observed reaction rate in this case.
- Click on <http://www.indiana.edu/%7Essiweb/C561/movies/ClHCl-3D-pov-new.gif> to view the dynamics of a “trapped proton” between two Cl atoms. (Can you see where the proton is?) Turns out to have an important effect on the experimental vibrational spectrum.
- Check this movie http://www.indiana.edu/%7Essiweb/C561/movies/w31H_coloredP.mpg which indicates that a hydrated proton is amphiphilic!!