

CHEM2024 - Week 25 Lecture 2 - Partial differential equations

Chapter 14 of Steiner, "The Chemistry Maths Book", 2nd edition.

1. Time-independent Schrödinger equation

The variable separation procedure described in the previous lecture connects the *time-dependent Schrödinger equation* that describes non-relativistic quantum dynamics

$$\frac{\partial}{\partial t} \psi(\vec{r}, t) = -i\hat{H}(\vec{r}, t)\psi(\vec{r}, t) \quad (1)$$

with the *time-independent Schrödinger equation*

$$\hat{H}(\vec{r})\varphi(\vec{r}) = E\varphi(\vec{r}) \quad (2)$$

that describes properties of stationary quantum systems, for example molecular orbitals. In the first equation, $\psi(\vec{r}, t)$ is the wavefunction, and $\hat{H}(\vec{r}, t)$ is an integro-differential and multiplicative operator called *Hamiltonian*, its observable $\langle \psi | \hat{H} | \psi \rangle$ is the energy of the system. Both the wavefunction and the Hamiltonian depend on time and on the coordinates of all particles present – those are collected into \vec{r} . Equation (1) is what Erwin Schrödinger had derived, yet somehow chemists keep using Equation (2) and calling it "Schrödinger's Equation". We will now derive the connection.

Consider a molecule at rest and in the absence of any external perturbations. Its energy is constant and therefore its Hamiltonian operator is time-independent and does not act on the time variable:

$$\frac{\partial}{\partial t} \psi(\vec{r}, t) = -i\hat{H}(\vec{r})\psi(\vec{r}, t) \quad (3)$$

This is a partial differential equation, and we can proceed to solve it using variable separation. As per the theorem discussed in the previous lecture,

$$\psi(\vec{r}, t) = \sum_{km} a_{km} \varphi_k(\vec{r}) g_m(t) \quad (4)$$

where $\{\varphi_k(\vec{r})\}$ and $\{g_m(t)\}$ are complete basis sets on the spaces of all well-behaved functions of coordinates and time respectively. After using the variable separation substitution $\varphi(\vec{r})g(t)$, we get:

$$\frac{\partial}{\partial t} \varphi(\vec{r})g(t) = -i\hat{H}(\vec{r})\varphi(\vec{r})g(t) \quad \Rightarrow \quad \frac{i}{g(t)} \frac{\partial}{\partial t} g(t) = \frac{1}{\varphi(\vec{r})} \hat{H}(\vec{r})\varphi(\vec{r}) \quad (5)$$

The two sides of this equation depend on different variables. They can only be equal if they are independently equal to a constant. Because the Hamiltonian is the energy operator, that constant is energy:

$$\left\{ \begin{array}{l} \frac{i}{g(t)} \frac{\partial}{\partial t} g(t) = E \\ \frac{1}{\varphi(\vec{r})} \hat{H}(\vec{r})\varphi(\vec{r}) = E \end{array} \right. \Rightarrow \left\{ \begin{array}{l} \frac{\partial}{\partial t} g(t) = -iEg(t) \\ \hat{H}(\vec{r})\varphi(\vec{r}) = E\varphi(\vec{r}) \end{array} \right. \Rightarrow \psi(\vec{r}, t) = \sum_k a_k \varphi_k(\vec{r}) e^{-iE_k t} \quad (6)$$

The first equation in this system is trivial. The difficult one that involves the Hamiltonian:

$$\hat{H}(\vec{r})\varphi(\vec{r}) = E\varphi(\vec{r}) \quad (7)$$

is called the *time-independent Schrödinger equation*. It is clear that this is simply an eigensystem problem for the Hamiltonian operator. In the context of molecular quantum mechanics, the eigenfunctions $\varphi_k(\vec{r})$

are molecular orbitals, and the associated eigenvalues E_k are their energies. Very few instances of such equations have analytical solutions. Modern quantum chemistry calculations run almost exclusively using matrix representations in generic (*e.g.* plane wave) basis sets.

2. Time-dependent Schrödinger equation for a particle in a box

TDSE for a particle in a box of size a looks very similar to the 1D diffusion equation considered in the previous lecture, except complex numbers are involved:

$$i \frac{\partial}{\partial t} \psi(x, t) = -\frac{1}{2m} \frac{\partial^2}{\partial x^2} \psi(x, t) \quad (8)$$

and the boundary conditions are different – the particle cannot go inside a wall:

$$\psi(0, t) = 0, \quad \psi(a, t) = 0 \quad (9)$$

The product representation for the wavefunction $\psi(x, t)$ is:

$$\psi(x, t) = \sum_{n,k} a_{nk} \varphi_n(x) g_k(t) \quad (10)$$

It would satisfy Equation (8) when it is satisfied by each $\varphi_n(x) g_k(t)$ term individually. Substituting a generic $\varphi(x) g(t)$ product into Equation (8) yields:

$$i \frac{\partial}{\partial t} [\varphi(x) g(t)] = -\frac{1}{2m} \frac{\partial^2}{\partial x^2} [\varphi(x) g(t)] \quad (11)$$

The time derivative operator does not affect functions of x and the coordinate derivative operator does not affect functions of t , therefore:

$$\varphi(x) i \frac{\partial}{\partial t} g(t) = -g(t) \frac{1}{2m} \frac{\partial^2}{\partial x^2} \varphi(x) \quad (12)$$

Dividing this equation by the product $\varphi(x) g(t)$ produces:

$$i \frac{1}{g(t)} \frac{\partial}{\partial t} g(t) = -\frac{1}{2m} \frac{1}{\varphi(x)} \frac{\partial^2}{\partial x^2} \varphi(x) \quad (13)$$

The left hand side only depends on time and the right hand side only depends on the coordinate. The two sides can only be equal for all values of x and t if they are both constant, meaning that the following two equations must simultaneously be true for some constant (in our case energy) E :

$$\begin{cases} i \frac{1}{g(t)} \frac{\partial}{\partial t} g(t) = E \\ -\frac{1}{2m} \frac{1}{\varphi(x)} \frac{\partial^2}{\partial x^2} \varphi(x) = E \end{cases} \Rightarrow \begin{cases} i \frac{\partial}{\partial t} g(t) = E g(t) \\ -\frac{1}{2m} \frac{\partial^2}{\partial x^2} \varphi(x) = E \varphi(x) \end{cases} \quad (14)$$

The first equation is a simple first-order ODE with exponentials as solutions. The second equation is only cosmetically different from the one we had already solved in a previous lecture:

$$-\frac{1}{2m} \frac{\partial^2 \varphi(x)}{\partial x^2} = E \varphi(x) \quad \Rightarrow \quad \frac{\partial^2 \varphi(x)}{\partial x^2} = -2mE \varphi(x) \quad (15)$$

Its general solution is sines and cosines:

$$\varphi(x) = \alpha \cos(\sqrt{2mEx}) + \beta \sin(\sqrt{2mEx}) \quad (16)$$

where α and β are arbitrary numbers. The solution must be zero at $x=0$, meaning that $\alpha=0$. We are therefore left with:

$$\varphi(x) = \beta \sin(\sqrt{2mEx}) \quad (17)$$

which must also be zero at $x=a$, therefore:

$$\beta \sin(\sqrt{2mEa}) = 0 \quad \Rightarrow \quad \sqrt{2mEa} = \pi n \quad \Rightarrow \quad E_n = \frac{\pi^2 n^2}{2ma^2}, \quad n = 1, 2, 3... \quad (18)$$

where the solution with $n=0$ has been discarded because it corresponds to there being no particle at all. After substituting the energy into the eigenfunction, we get:

$$\varphi_n(x) = \beta \sin\left(\frac{\pi nx}{a}\right) \quad (19)$$

Optionally, the coefficient β may be adjusted so that the functions have a unit norm:

$$\langle \varphi_n | \varphi_n \rangle = \int_0^a \beta^2 \sin^2\left(\frac{\pi nx}{a}\right) dx = 1 \quad \Rightarrow \quad \beta = \sqrt{\frac{2}{a}} \quad (20)$$

The solution to the time-independent Schrödinger equation is:

$$E_n = \frac{\pi^2 n^2}{2ma^2}, \quad \varphi_n(x) = \sqrt{\frac{2}{a}} \sin\left(\frac{\pi nx}{a}\right), \quad n = 1, 2, 3... \quad (21)$$

As expected for a differential operator, the number of eigenfunction-eigenvalue pairs is infinite. We can now use these spatial wavefunctions and their energies to construct the solution of the original time-dependent Schrödinger equation. The temporal part is different for each energy:

$$\frac{\partial}{\partial t} g(t) = -iE_n g(t) \quad \Rightarrow \quad g_n(t) = \exp(-iE_n t) \quad (22)$$

After plugging the two sets of functions into Equation (10) – note that they are numbered by the same index in this case – we obtain the general solution for the TDSE describing a quantum mechanical particle of mass m in a box of size a :

$$\psi(x, t) = \sum_n \alpha_n \sin\left(\frac{\pi nx}{a}\right) \exp\left(-i \frac{\pi^2 n^2}{2ma^2} t\right) \quad (23)$$

where the coefficients α_n are determined by the initial condition (*i.e.* the starting state of the system). It is easy to verify by direct inspection that this solution satisfies Equation (8).