# 3. Analytical Solutions for Simple Potentials

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Analytical vs. Numerical Solutions

Engineer: $\sqrt{3} = 2$
Statistician: $\sqrt{3} = 1.7$
Physicist: $\sqrt{3} = 1.73205$

Mathematician: $\sqrt{3}$ is $\sqrt{3}$
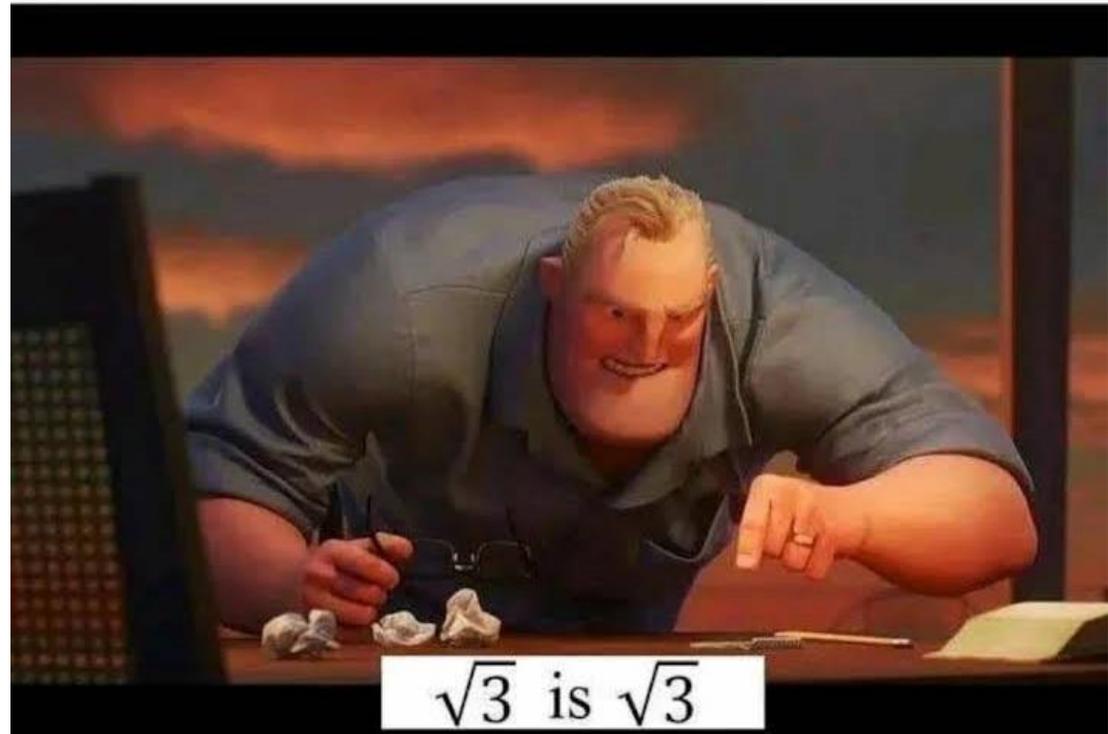
Analytical vs. Numerical Solutions

Consider a simple quadratic equation

$$x^2 = 2.$$

We all know that the two solutions of this equation is $x = \pm\sqrt{2}$.

These solutions are exact, as $\sqrt{2}$ is defined to be a number which yields 2 when squared. Such exact solutions are called analytical solutions.

On the other hand, if we try to solve this equation by using a computer or a calculator, the answer we get (for a 10-digit display) is

$$x = \pm 1.414213562,$$

which is as accurate as the machine precision and is certainly not exact. Such solutions are called numerical solutions.

Analytical vs. Numerical Solutions

Analytical solutions of an equation or a differential equation only involve exact numbers and functions.

There are (many) cases where we cannot obtain analytical solutions, but we can still calculate numerical solutions with a high precision.

ex) polynomial equations of 5th or higher order, or equations which involve transcendental functions, such as $\ln x = \sin x$.

For a given problem, we usually try to find the analytical solutions first, as they often give useful insights.

If it seems not possible to do so, we calculate the numerical solutions with enough accuracy, which can still be used for practical purposes.

Schrödinger Equation with Simple Potentials

The (time-independent) Schrödinger equation

$$\hat{H}\psi = E\psi$$

is determined by two factors:
- The dimensionality of the system
- The form of the potential energy operator $\hat{V}$ for particles in the system.

In undergraduate physical chemistry course, we study some cases that provide analytical solutions,
- Free particle / particle in a box (1-dim)
- Harmonic oscillator (1-dim)
- Rigid rotor (2-dim)
- Hydrogen atom (3-dim)

Free Particle

This is the easiest (and arguably the most boring) Schrödinger equation.

The particle does not feel any potential (hence the name "free particle"),

$$V(x) = 0.$$

Solving the Schrödinger equation

$$-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} = E\psi(x), \quad E > 0,$$

gives the solutions and eigenvalues of

$$\psi(x) = e^{\pm ikx}, \quad k = \frac{\sqrt{2mE}}{\hbar}.$$

As there is no restraint on E, all positive energies are allowed.
We therefore do not see any quantization in this case.

Particle in a Box

This is where we start seeing the effect of quantization. In this case, the particle is trapped in a finite-sized well of length L and infinite depth,

$$V(x) = \begin{cases} \infty, & x < 0, \\ 0, & 0 \leq x < L, \\ \infty, & x \geq L. \end{cases}$$

The infinite potential imposes the boundary condition

$$\psi(0) = \psi(L) = 0,$$

which allows the solutions and eigenvalues of

$$\psi_n(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right), \quad E_n = \frac{n^2 \pi^2 \hbar^2}{2mL^2},$$

with quantized energies E_n depending on the quantum number n.

$$\vdots$$

$$L$$

7
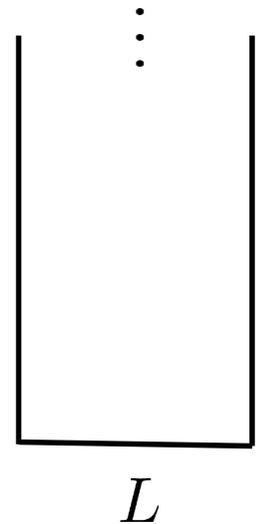
Harmonic Oscillator

This problem is motivated by a mass attached to a spring, which is also a prototypical model for molecular vibration. The potential is

$$V(x) = \frac{1}{2}m\omega^2 x^2,$$

where $\omega = 2\pi\nu$ is the angular frequency of the vibration. The first few solutions and eigenvalues are ($\alpha = m\omega/\hbar$)

$$\psi_0(x) = \left(\frac{\alpha}{\pi}\right)^{1/4} e^{-\alpha x^2/2}, \qquad\qquad E_0 = \frac{1}{2}\hbar\omega,$$

$$\psi_1(x) = \left(\frac{4\alpha^3}{\pi}\right)^{1/4} x e^{-\alpha x^2/2}, \qquad\qquad E_1 = \frac{3}{2}\hbar\omega,$$

$$\psi_2(x) = \left(\frac{\alpha}{4\pi}\right)^{1/4} (2\alpha x^2 - 1)e^{-\alpha x^2/2}, \quad E_2 = \frac{5}{2}\hbar\omega, \quad \cdots$$

8
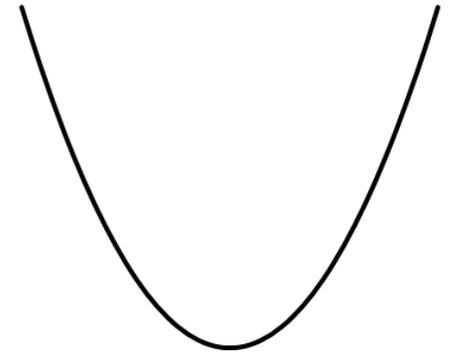
Harmonic Oscillator

ex) Show that the Schrödinger equation is satisfied for

$$\psi_1(x) = \left(\frac{4\alpha^3}{\pi}\right)^{1/4} x e^{-\alpha x^2/2},$$

with the eigenvalue $E_1 = \dfrac{3}{2}\hbar\omega$.

9

Harmonic Oscillator

The general expression for the solutions and eigenvalues are

$$H_0(x) = 1,$$
$$H_1(x) = 2x,$$
$$H_2(x) = 4x^2 - 2,$$
$$H_3(x) = 8x^3 - 12x,$$
$$H_4(x) = 16x^4 - 48x^2 + 12,$$
$$H_5(x) = 32x^5 - 160x^3 + 120x,$$
$$H_6(x) = 64x^6 - 480x^4 + 720x^2 - 120,$$
$$H_7(x) = 128x^7 - 1344x^5 + 3360x^3 - 1680x,$$
$$H_8(x) = 256x^8 - 3584x^6 + 13440x^4 - 13440x^2 + 1680,$$
$$H_9(x) = 512x^9 - 9216x^7 + 48384x^5 - 80640x^3 + 30240x,$$
$$H_{10}(x) = 1024x^{10} - 23040x^8 + 161280x^6 - 403200x^4 + 302400x^2 - 30240.$$

$$\psi_n(x) = \frac{1}{\sqrt{2^n n!}} \left(\frac{\alpha}{\pi}\right)^{1/4} H_n(\sqrt{\alpha}x)e^{-\alpha x^2/2},$$

$$E_n = \hbar\omega\left(n + \frac{1}{2}\right),$$

$$\alpha = m\omega/\hbar,$$

where $H_n(x)$ is the Hermite polynomial of order n.

The energies of the states are uniformly spaced by the amount of $\hbar\omega$.

https://en.wikipedia.org/wiki/Hermite_polynomials

Molecular Degrees of Freedom
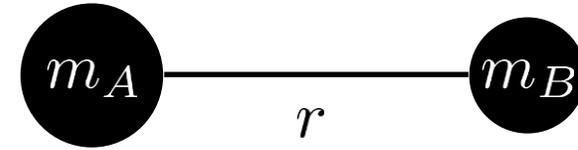
A diatomic molecule has $3 \times 2 = 6$ coordinates of movement in total (degrees of freedom, DOFs).

Among them, three DOFs are translational motions of the center of mass, whose total mass is $M = m_A + m_B$.

The remaining three DOFs of a molecule can be classified as rotational (two DOFs) and vibrational (one DOF) motions.

These motions are equivalent to the motions of a single particle connected to a fixed point by a spring. The mass of this fictitious particle is called the reduced mass,

$$\mu = \frac{m_A m_B}{m_A + m_B} \quad \left(\frac{1}{\mu} = \frac{1}{m_A} + \frac{1}{m_B} \right).$$

11
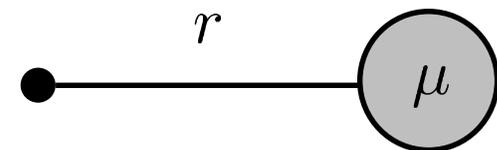
Rigid Rotor

Suppose a point mass of μ is at a fixed distance r_0 from the origin, and is allowed to freely rotate along the angular coordinates.

As this system has spherical symmetry, it is better to use spherical polar coordinates rather than Cartesian coordinates.

$$x = r \sin\theta \cos\phi$$
$$y = r \sin\theta \sin\phi$$
$$z = r \cos\theta$$

r_0

μ

fixed point (origin)

https://en.wikipedia.org/wiki/Spherical_coordinate_system
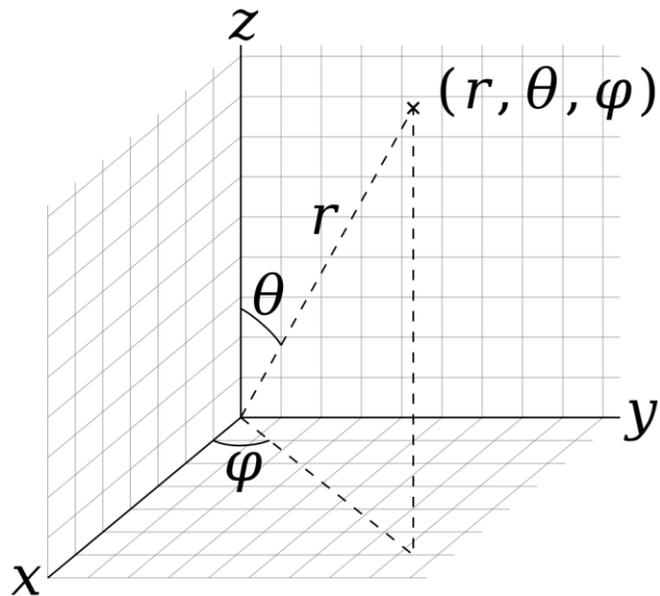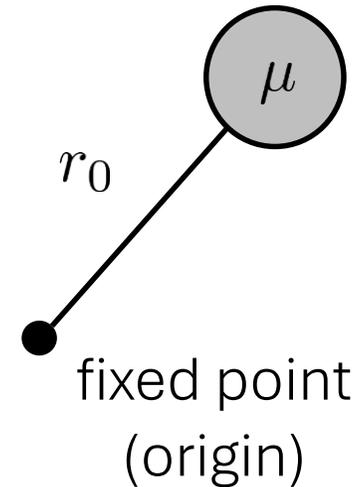
Rigid Rotor

The Hamiltonian in such system is

$$\hat{H} = \hat{K} = -\frac{\hbar^2}{2\mu r_0^2}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right], \quad \hat{V} = 0.$$

Solving the Schrödinger equation gives the solutions and eigenvalues of

$$\psi_l^m(\theta,\phi) = Y_l^m(\theta,\phi), \quad E_l = \frac{\hbar^2}{2\mu r_0^2}l(l+1).$$

where $Y_l^m(\theta,\phi)$ is called spherical harmonics, which is specified by the quantum numbers l and m.

l is a non-negative integer, and m is an integer satisfying $-l \le m \le l$. As the energies do not depend on m, there are $2l+1$ degenerate solutions for a single value of l.

13

Rigid Rotor

TABLE 5.1 $S_{l,m}(\theta)$

$l = 0$: $S_{0,0} = \frac{1}{2}\sqrt{2}$

$l = 1$: $S_{1,0} = \frac{1}{2}\sqrt{6}\cos\theta$

              $S_{1,\pm 1} = \frac{1}{2}\sqrt{3}\sin\theta$

$l = 2$: $S_{2,0} = \frac{1}{4}\sqrt{10}(3\cos^2\theta - 1)$

              $S_{2,\pm 1} = \frac{1}{2}\sqrt{15}\sin\theta\cos\theta$

              $S_{2,\pm 2} = \frac{1}{4}\sqrt{15}\sin^2\theta$

$l = 3$: $S_{3,0} = \frac{3}{4}\sqrt{14}\left(\frac{5}{3}\cos^3\theta - \cos\theta\right)$

              $S_{3,\pm 1} = \frac{1}{8}\sqrt{42}\sin\theta(5\cos^2\theta - 1)$

              $S_{3,\pm 2} = \frac{1}{4}\sqrt{105}\sin^2\theta\cos\theta$

              $S_{3,\pm 3} = \frac{1}{8}\sqrt{70}\sin^3\theta$

$$Y_l^m(\theta, \phi) = \frac{1}{\sqrt{2\pi}}S_{l,m}(\theta)e^{im\phi}$$
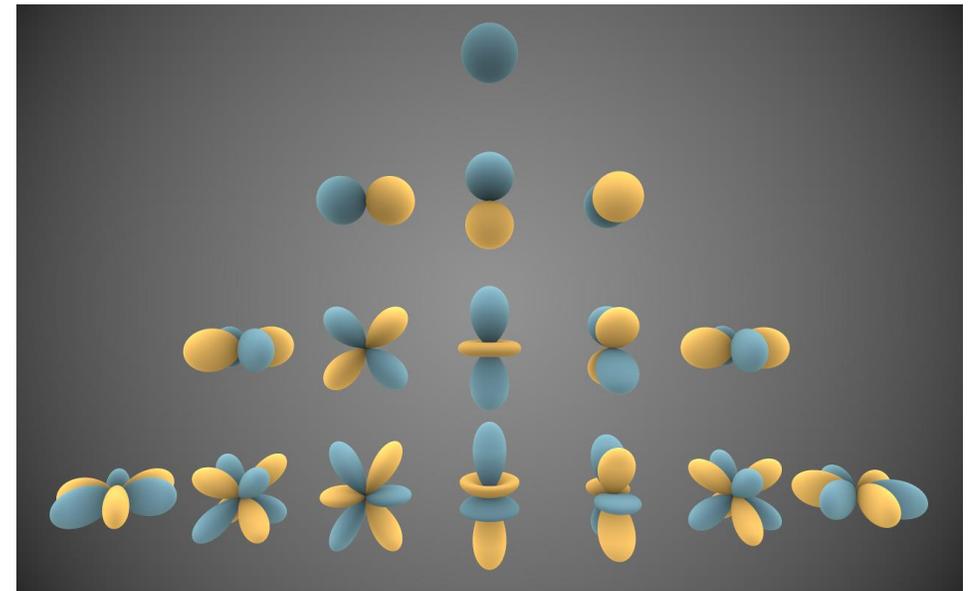
Levine, I. N. *Quantum Chemistry*, 7th ed.
https://en.wikipedia.org/wiki/Spherical_harmonics

Rigid Rotor

ex) Show that the Schrödinger equation is satisfied for

$$Y_1^1(\theta, \phi) = \frac{\sqrt{3}}{2} \sin \theta \, e^{i\phi},$$

with the eigenvalue $E_1 = \dfrac{\hbar^2}{\mu r_0^2}$.

Hydrogen-Like Atom

One electron is electronically bound to the nucleus with the charge $+Ze$.

ex) $\mathrm{H}, \ \mathrm{He}^+, \ \mathrm{Li}^{2+} \cdots$

The Hamiltonian for this system is

$$\hat{H} = \hat{K} + \hat{V}$$

$$= -\frac{\hbar^2}{2\mu}\left(\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r} + \frac{1}{r^2}\frac{\partial^2}{\partial \theta^2} + \frac{1}{r^2}\cot\theta\frac{\partial}{\partial \theta} + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial \phi^2} \right) - \frac{Ze^2}{4\pi\epsilon_0 r},$$

which can be solved by separation of variables by assuming the solution of the form

$$\psi(r,\theta,\phi) = f(r)g(\theta)h(\phi).$$

16
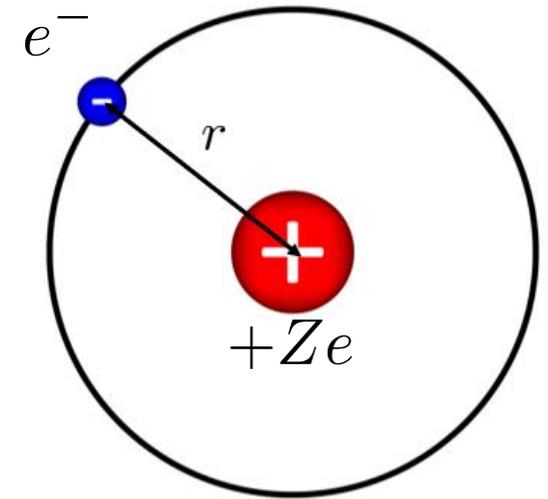
Hydrogen-Like Atom

Solving the Schrödinger equation leads to atomic orbitals, which is characterized by three quantum numbers n (principal quantum number), l (azimuthal quantum number), and m (magnetic quantum number).

n is a positive integer, l is a non-negative integer ranging from 0 to $n-1$ for a given n, and m is an integer ranging from $-l$ to l for a given n and l.

An orbital is named after its principal and azimuthal quantum numbers.

The energy of the orbital only depends on n:

$$E_{n,l,m} = -\frac{\mu e^4}{32\pi^2 \epsilon_0^2 \hbar^2} \frac{Z^2}{n^2} = (-1312.7 \text{ kJ mol}^{-1}) \frac{Z^2}{n^2}.$$

For a given n, there are n^2 degenerate orbitals.

17

Hydrogen-Like Atom

TABLE 6.2   Real Hydrogenlike Wave Functions

$$1s = \frac{1}{\pi^{1/2}}\left(\frac{Z}{a}\right)^{3/2} e^{-Zr/a}$$

$$2s = \frac{1}{4(2\pi)^{1/2}}\left(\frac{Z}{a}\right)^{3/2}\left(2 - \frac{Zr}{a}\right)e^{-Zr/2a}$$

$$2p_z = \frac{1}{4(2\pi)^{1/2}}\left(\frac{Z}{a}\right)^{5/2} re^{-Zr/2a}\cos\theta$$

$$2p_x = \frac{1}{4(2\pi)^{1/2}}\left(\frac{Z}{a}\right)^{5/2} re^{-Zr/2a}\sin\theta\,\cos\phi$$

$$2p_y = \frac{1}{4(2\pi)^{1/2}}\left(\frac{Z}{a}\right)^{5/2} re^{-Zr/2a}\sin\theta\,\sin\phi$$

$$a = \frac{4\pi\epsilon_0\hbar^2}{\mu e^2}$$

$$3s = \frac{1}{81(3\pi)^{1/2}}\left(\frac{Z}{a}\right)^{3/2}\left(27 - 18\frac{Zr}{a} + 2\frac{Z^2r^2}{a^2}\right)e^{-Zr/3a}$$

$$3p_z = \frac{2^{1/2}}{81\pi^{1/2}}\left(\frac{Z}{a}\right)^{5/2}\left(6 - \frac{Zr}{a}\right)re^{-Zr/3a}\cos\theta$$

$$3p_x = \frac{2^{1/2}}{81\pi^{1/2}}\left(\frac{Z}{a}\right)^{5/2}\left(6 - \frac{Zr}{a}\right)re^{-Zr/3a}\sin\theta\cos\phi$$

$$3p_y = \frac{2^{1/2}}{81\pi^{1/2}}\left(\frac{Z}{a}\right)^{5/2}\left(6 - \frac{Zr}{a}\right)re^{-Zr/3a}\sin\theta\sin\phi$$

$$3d_{z^2} = \frac{1}{81(6\pi)^{1/2}}\left(\frac{Z}{a}\right)^{7/2} r^2 e^{-Zr/3a}(3\cos^2\theta - 1)$$

$$3d_{xz} = \frac{2^{1/2}}{81\pi^{1/2}}\left(\frac{Z}{a}\right)^{7/2} r^2 e^{-Zr/3a}\sin\theta\cos\theta\cos\phi$$

$$3d_{yz} = \frac{2^{1/2}}{81\pi^{1/2}}\left(\frac{Z}{a}\right)^{7/2} r^2 e^{-Zr/3a}\sin\theta\cos\theta\sin\phi$$

$$3d_{x^2-y^2} = \frac{1}{81(2\pi)^{1/2}}\left(\frac{Z}{a}\right)^{7/2} r^2 e^{-Zr/3a}\sin^2\theta\cos 2\phi$$

$$3d_{xy} = \frac{1}{81(2\pi)^{1/2}}\left(\frac{Z}{a}\right)^{7/2} r^2 e^{-Zr/3a}\sin^2\theta\sin 2\phi$$

Levine, I. N. *Quantum Chemistry*, 7th ed.

Separable Hamiltonian

Consider the particle in 2-dimensional box, specified by the potential

$$V(x) = \begin{cases} 0, & 0 \leq x < L_x, \ \ 0 \leq y < L_y, \\ \infty, & \text{otherwise.} \end{cases}$$

The Hamiltonian inside the box can be split into x- and y- components,

$$\hat{H} = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} - \frac{\hbar^2}{2m}\frac{\partial^2}{\partial y^2} = \hat{H}_x + \hat{H}_y,$$

which allows the Schrödinger equation to be solved by the separation of variables. We assume a solution of the form

$$\psi(x, y) = f(x)g(y),$$

which leads to

$$-\frac{\hbar^2}{2m}\left(\frac{1}{f(x)}\frac{\partial^2 f(x)}{\partial x^2} + \frac{1}{g(y)}\frac{\partial^2 g(y)}{\partial y^2} \right) = E.$$

19

Separable Hamiltonian

Rearranging the equation gives

$$-\frac{\hbar^2}{2m}\frac{1}{f(x)}\frac{\partial^2 f(x)}{\partial x^2} = E + \frac{\hbar^2}{2m}\frac{1}{g(y)}\frac{\partial^2 g(y)}{\partial y^2} = \text{const.}$$

To clarify the physical meaning of the constant, we take the leftmost component and rearrange the equation into

$$-\frac{\hbar^2}{2m}\frac{d^2 f(x)}{dx^2} = (\text{const})f(x),$$

which is just the particle in a box problem for the x-direction. Hence, the constant can be thought as "the energy of the x-component".

Separable Hamiltonian

The same logic can be applied to the y-direction, and we can conclude

$$E = E_x + E_y,$$

where E_x and E_y are the energies assigned to each dimension.

$$\hat{H}_x f(x) = -\frac{\hbar^2}{2m}\frac{d^2 f(x)}{dx^2} = E_x f(x), \quad \hat{H}_y g(y) = -\frac{\hbar^2}{2m}\frac{d^2 g(y)}{dy^2} = E_y g(y).$$

The normalized solutions are

$$f_{n_x}(x) = \sqrt{\frac{2}{L_x}}\sin\left(\frac{n_x \pi x}{L_x}\right), \quad g_{n_y}(y) = \sqrt{\frac{2}{L_y}}\sin\left(\frac{n_y \pi y}{L_y}\right),$$

with quantum numbers n_x and n_y.

Separable Hamiltonian

The full solution can be reconstructed as

$$\psi_{n_x,n_y}(x,y) = f_{n_x}(x)g_{n_y}(y) = \sqrt{\frac{4}{L_xL_y}}\sin\left(\frac{n_x\pi x}{L_x}\right)\sin\left(\frac{n_y\pi y}{L_y}\right),$$

and the energy eigenvalue for each solution is, of course,

$$E_{n_x,n_y} = E_{x,n_x} + E_{y,n_y} = \frac{\pi^2\hbar^2}{2m}\left(\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2}\right).$$

This observation can be generalized into Schrödinger equations that can be separated into independent components:

$$\hat{H}(x_1, x_2, x_3 \cdots) = \hat{H}_1(x_1) + \hat{H}_2(x_2) + \hat{H}_3(x_3) + \cdots = \sum_j \hat{H}_j(x_j).$$

22

Separable Hamiltonian

1. Separately solve the Schrödinger equation for each component of the Hamiltonian. Each solution has its own quantum number n_j.

$$\hat{H}_j(x_j)\psi_{x_j,n_j}(x_j) = E_{x_j,n_j}(x_j)\psi_{x_j,n_j}(x_j).$$

2. The full solution for the total Hamiltonian can then be constructed by multiplying the solutions of individual components:

$$\psi_{\{n_1,n_2,n_3\cdots\}}(x_1,x_2,x_3\cdots) = \psi_{x_1,n_1}(x_1)\psi_{x_2,n_2}(x_2)\psi_{x_3,n_3}(x_3)\cdots = \prod_j \psi_{x_j,n_j}(x_j).$$

3. The corresponding energy eigenvalue is the sum of individual energies:

$$E_{\{n_1,n_2,n_3\cdots\}} = E_{x_1,n_1} + E_{x_2,n_2} + E_{x_3,n_3} + \cdots = \sum_j E_{x_j,n_j}.$$

This observation will be crucial in developing methods to numerically solve Schrödinger equations for atoms and molecules.

23