

for $\frac{d\psi}{dx}$, we have:



$$\left. \frac{d\psi}{dx} \right|_{x=n+\frac{1}{2}} = \frac{\psi_{n+1} - \psi_n}{a} \quad \left. \frac{d\psi}{dx} \right|_{x=n-\frac{1}{2}} = \frac{\psi_n - \psi_{n-1}}{a} \rightarrow \left. \frac{d^2\psi}{dx^2} \right|_{x=n} = \frac{\left. \frac{d\psi}{dx} \right|_{n+\frac{1}{2}} - \left. \frac{d\psi}{dx} \right|_{n-\frac{1}{2}}}{a}$$

$$\rightarrow \left. \frac{d^2\psi}{dx^2} \right|_{x=n} = \frac{\psi_{n+1} - 2\psi_n + \psi_{n-1}}{a^2}$$

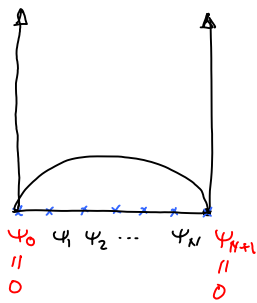
So we can write:

$$i\hbar \frac{d}{dt} \psi_n = \underbrace{\frac{-\hbar^2}{2ma^2}}_{t_0} (\psi_{n-1} - 2\psi_n + \psi_{n+1}) + U(x_n) \psi_n$$

$$i\hbar \frac{d}{dt} \psi_n = -t_0 \psi_{n-1} + 2t_0 \psi_n - t_0 \psi_{n+1} + U(x_n) \psi_n$$

$$i\hbar \frac{d}{dt} \begin{bmatrix} \psi_1 \\ \psi_2 \\ \psi_3 \\ \vdots \\ \psi_N \end{bmatrix} = \begin{bmatrix} 2t_0 + U(x_1) & -t_0 & 0 & 0 & \dots & 0 \\ -t_0 & 2t_0 + U(x_2) & -t_0 & 0 & \dots & 0 \\ 0 & -t_0 & 2t_0 + U(x_3) & -t_0 & & \\ 0 & 0 & \dots & \dots & \dots & -t_0 \\ 0 & 0 & \dots & \dots & -t_0 & 2t_0 + U(x_N) \end{bmatrix} \begin{bmatrix} \psi_1 \\ \psi_2 \\ \psi_3 \\ \vdots \\ \psi_N \end{bmatrix}$$

$$[H] = \begin{bmatrix} 2t_0 + U(x_1) & -t_0 & 0 & 0 & \dots & 0 \\ -t_0 & 2t_0 + U(x_2) & -t_0 & 0 & \dots & 0 \\ 0 & -t_0 & 2t_0 + U(x_3) & -t_0 & & \\ 0 & 0 & \dots & \dots & \dots & -t_0 \\ 0 & 0 & \dots & \dots & -t_0 & 2t_0 + U(x_N) \end{bmatrix}$$



=> so at the two ends we have:

$$\begin{cases} -t_0 \psi_0 + (2t_0 + U_1) \psi_1 - t_0 \psi_2 & \xrightarrow[\text{with}]{\text{replace}} (2t_0 + U_1) \psi_1 - t_0 \psi_2 \\ -t_0 \psi_{N-1} + (2t_0 + U_N) \psi_N - t_0 \psi_{N+1} & \longrightarrow -t_0 \psi_{N-1} + (2t_0 + U_N) \psi_N \end{cases}$$

This was for box boundary condition. For **periodic boundary** conditions, like a particle on a ring, we have:

$$\psi_0 = \psi_N \text{ and } \psi_{N+1} = \psi_1 \text{ so we have:}$$

$$\begin{aligned} -t_0 \psi_0 + (2t_0 + U_1) \psi_1 - t_0 \psi_2 & \xrightarrow[\text{with}]{\text{replace}} -t_0 \psi_N + (2t_0 + U_1) \psi_1 - t_0 \psi_2 \\ -t_0 \psi_{N-1} + (2t_0 + U_N) \psi_N - t_0 \psi_{N+1} & \longrightarrow -t_0 \psi_{N-1} + (2t_0 + U_N) \psi_N - t_0 \psi_1 \end{aligned}$$

So $[H]$ for each case looks different:

For Box boundary condition:

$$[H] = \begin{bmatrix} 2t_0 + U(x_1) & -t_0 & 0 & 0 & \dots & 0 \\ -t_0 & 2t_0 + U(x_2) & -t_0 & 0 & \dots & 0 \\ 0 & -t_0 & 2t_0 + U(x_3) & -t_0 & & \\ 0 & 0 & \dots & \dots & \dots & -t_0 \\ 0 & 0 & \dots & \dots & -t_0 & 2t_0 + U(x_N) \end{bmatrix}$$

For Periodic boundary condition:

$$[H] = \begin{bmatrix} 2t_0 + U(x_1) & -t_0 & 0 & 0 & \dots & -t_0 \\ -t_0 & 2t_0 + U(x_2) & -t_0 & 0 & \dots & 0 \\ 0 & -t_0 & 2t_0 + U(x_3) & -t_0 & & \\ 0 & 0 & \dots & \dots & \dots & -t_0 \\ -t_0 & 0 & \dots & \dots & -t_0 & 2t_0 + U(x_N) \end{bmatrix}$$

Notice that $H = H^\dagger$ (reminder $H^\dagger \equiv (H^*)^T$)

which means H is hermitian. This is normally true for all physical Hamiltonians.

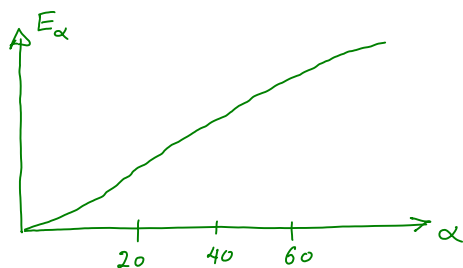
Periodic versus Box boundary condition

Box

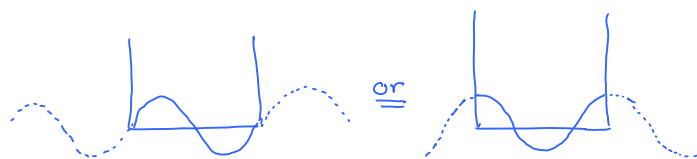


$$\psi_n = \sin \frac{n\pi x}{L} \quad n=1,2,\dots$$

Box B.C. \Rightarrow Non-degenerate eigenvalues



Periodic

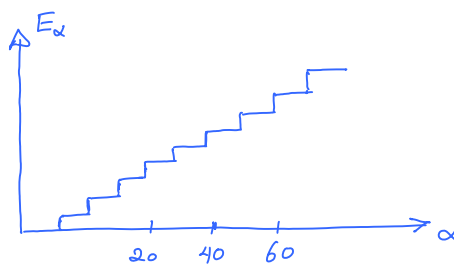


$$\psi_n = \sin \frac{2n\pi x}{L} \quad n=1,2,\dots$$

or $\cos \frac{2n\pi x}{L}$

} Degenerate states

Periodic B.C. \Rightarrow degenerate eigenvalues



Numerical versus Analytic Eigenvalues

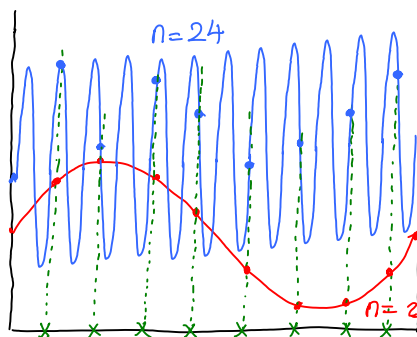
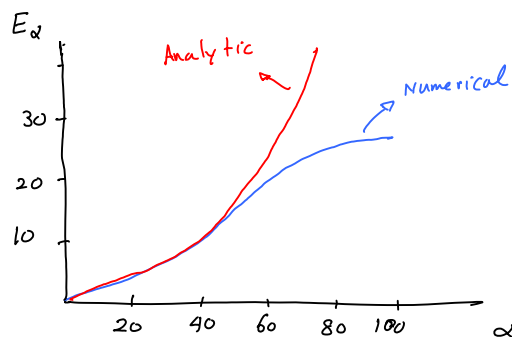
Consider for example a particle in a box. The eigenvalues are:

$$E_n = \frac{\hbar^2 k_n^2}{2m} = \frac{\hbar^2}{2m} \left(\frac{n\pi}{L} \right)^2$$

The eigenfunctions are $\sin \frac{n\pi x}{L}$.

So at very high energies (n large), the eigenfunction oscillates very fast and the wide lattice spacing doesn't capture the whole changes.

Note: If we define n lattice points, $[H]$ is $n \times n$, and it has only n eigenfunctions. So we don't get all the eigenfunctions to describe high energy eigenstates that have rapidly changing eigenfunctions.



\rightarrow Blue points don't show the correct wavefunction \times

\rightarrow Red points show the shape of the wavefunction well \checkmark

Let's go back to our Schrödinger equation now:

$$-\frac{\hbar^2}{2m} \frac{d^2 \psi}{dx^2} + U\psi = i\hbar \frac{\partial \psi}{\partial t}$$

$$\left(-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + U \right) \psi = i\hbar \frac{\partial \psi}{\partial t}$$

$$H\psi = i\hbar \frac{\partial \psi}{\partial t}$$

we converted this equation to a numerical matrix form:

$$[H]\{\psi\} = i\hbar \frac{\partial}{\partial t} \{\psi\}$$

\downarrow \swarrow
 $n \times n$ tri-diagonal matrix $n \times 1$ vector

Then to get rid of the time derivative, we solved the eigenvalue problem:

$$[H]\{\alpha\} = E_\alpha \{\alpha\}$$

This will give us the eigenvalues E_α and also the eigenfunction $\{\alpha\}$.

The wavefunction is then the superposition of these eigenfunctions:

$$\{\psi\} = \sum_{\alpha} C_{\alpha} \{\alpha\} e^{-E_{\alpha} t / \hbar}$$

Be careful that $\{\}$ means a vector whose components correspond to a lattice point in real space:

$$\{\psi\} \equiv \begin{bmatrix} \psi(x_1) \\ \psi(x_2) \\ \vdots \\ \psi(x_N) \end{bmatrix} \equiv \begin{bmatrix} \psi_1 \\ \psi_2 \\ \vdots \\ \psi_N \end{bmatrix}$$

But α refers to different eigenfunctions. For example, for a particle

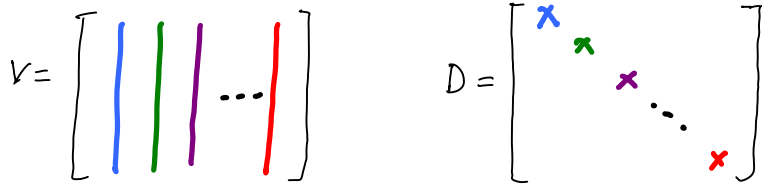
in a box $\alpha = \sin \frac{\pi x}{L}, \sin \frac{2\pi x}{L}, \dots = \sin \frac{n\pi x}{L} \quad n=1,2,3, \dots$

So for a particle in a box the above equation is:

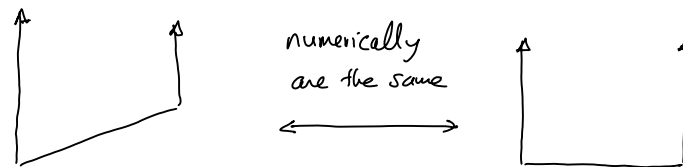
$$\begin{bmatrix} \psi_1 \\ \psi_2 \\ \vdots \\ \psi_N \end{bmatrix} = C_1 \begin{bmatrix} \sin \frac{\pi x_1}{L} \\ \sin \frac{\pi x_2}{L} \\ \vdots \\ \sin \frac{\pi x_N}{L} \end{bmatrix} e^{-E_1 t / \hbar} + C_2 \begin{bmatrix} \sin \frac{2\pi x_1}{L} \\ \sin \frac{2\pi x_2}{L} \\ \vdots \\ \sin \frac{2\pi x_N}{L} \end{bmatrix} e^{-E_2 t / \hbar} + \dots$$

It is computationally very straightforward to calculate eigenvalues and eigenfunctions. In MATLAB you can use this function:

$[V, D] = \text{eig}(H)$
 eigenvectors as columns of a square matrix \rightarrow eigenvalues in a diagonal matrix



The big advantage of numerical method is that once you develop a code to solve a particular problem, you can easily adopt it to solve another problem of the same nature. For example the *slanted well* is a complex problem to solve involving *Airy functions*. But numerically it is very much like an infinite square well.

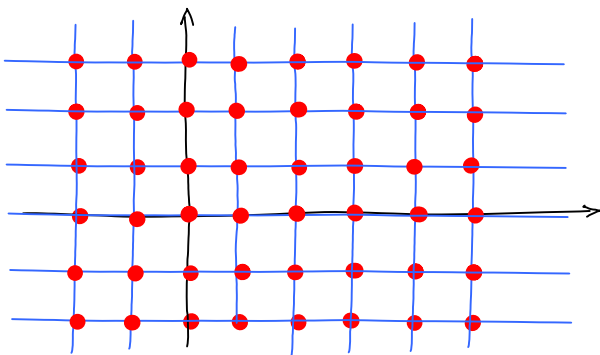


Two-dimensional problems

In 2D, our Hamiltonian operator looks like:

$$H = -\frac{\hbar^2}{2m} \left(\frac{d^2}{dx^2} + \frac{d^2}{dy^2} \right) + U(x, y)$$

We can now easily extend our finite difference method:



The main problem now is the increased number of points that results in a large matrix. For example: $100 \times 100 = 10\,000$ points!

But if the potential is separable, we can separate the 2D problem into two 1D problems:

$$U(x,y) = U_x + U_y \longrightarrow \Psi(x,y) = X(x)Y(y)$$

How:

$$-\frac{\hbar^2}{2m} \left(\frac{d^2 \Psi}{dx^2} + \frac{d^2 \Psi}{dy^2} \right) + V(x,y) \Psi(x,y) = E \Psi(x,y)$$

Substitute: $U = U_x + U_y$; $\Psi(x,y) = X(x)Y(y) \Rightarrow$

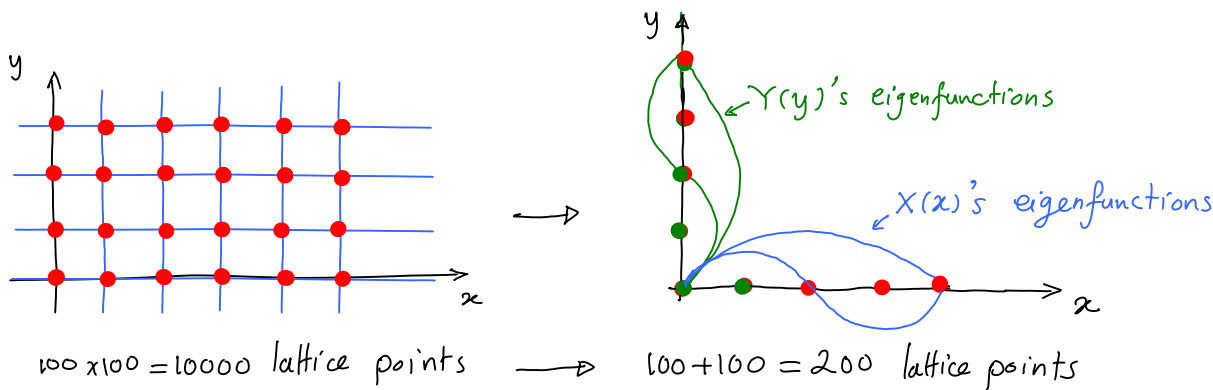
$$-\frac{\hbar^2}{2m} \left(Y \frac{d^2 X}{dx^2} + X \frac{d^2 Y}{dy^2} \right) + (U_x + U_y) X Y = E X Y$$

divide by XY :

$$\underbrace{-\frac{1}{X} \frac{\hbar^2}{2m} \frac{d^2 X}{dx^2} + U_x}_{E_x} - \underbrace{\frac{1}{Y} \frac{\hbar^2}{2m} \frac{d^2 Y}{dy^2} + U_y}_{E_y} = E$$

$$\rightarrow \begin{cases} -\frac{\hbar^2}{2m} \frac{d^2 X}{dx^2} + U_x X = E_x X \\ -\frac{\hbar^2}{2m} \frac{d^2 Y}{dy^2} + U_y Y = E_y Y \end{cases} \quad \text{where } E_x + E_y = E$$

Numerically we have now two 1D lattice instead of a 2D lattice:



Numerically, if we split x and y axis now by 100 points, we will have 100 eigenvectors for X and 100 eigenvectors for Y (see the note on the section of "numerical versus analytic eigenvalues").

So $\Psi(x,y) = XY$ will have $100 \times 100 = 10000$ eigenfunctions.

$$\left. \begin{array}{l} X \rightarrow X_n \quad n=1,2, \dots, 100 \\ Y \rightarrow Y_m \quad m=1,2, \dots, 100 \end{array} \right\} \Psi_{nm} = X_n Y_m \quad \begin{array}{l} n=1,2, \dots, 100 \\ m=1,2, \dots, 100 \end{array} \rightarrow 10000 \text{ eigenfunctions}$$

So each (n,m) has a corresponding energy level. Some of these pairs may result in equal energy levels called degenerate states. For a 2D square well, for example, this happens if:

$$(n_1, m_1) \rightarrow \begin{cases} E_{n_1} = \frac{\hbar^2 n_1^2 \pi^2}{2mL^2} \\ E_{m_1} = \frac{\hbar^2 m_1^2 \pi^2}{2mL^2} \end{cases} \rightarrow E_1 = E_{n_1} + E_{m_1} = \frac{\hbar^2 \pi^2}{2mL^2} (n_1^2 + m_1^2)$$

$$(n_2, m_2) \rightarrow E_2 = E_{n_2} + E_{m_2} = \frac{\hbar^2 \pi^2}{2mL^2} (n_2^2 + m_2^2)$$

So if $(n_1^2 + m_1^2) = (n_2^2 + m_2^2) \rightarrow E_1 = E_2$ degenerate states.

For example: $E_{12} = E_{21}$

What about 3D: The same approach of separation of variables gives the eigenfunctions: $\Psi_{111}, \Psi_{112}, \dots$

Hydrogen Atom

This is 3D problem. We "wish" to use separation of variables to solve the problem.

But the potential is not separable in Cartesian coordinate:

$$H = -\frac{\hbar^2}{2m} \left(\frac{d^2}{dx^2} + \frac{d^2}{dy^2} + \frac{d^2}{dz^2} \right) - \frac{e^2}{4\pi\epsilon_0 \underbrace{\sqrt{x^2+y^2+z^2}}_{=r}}$$

We cannot separate $U(x,y,z) \neq U_x + U_y + U_z$.

But fortunately it can be separated in **spherical coordinate** as:

$$U = \frac{-e^2}{4\pi\epsilon_0 r}$$

Note that we can use similar approach for all atoms, but not with molecules because they don't have a spherical symmetry.

The Hamiltonian in spherical coordinate is:

$$-\frac{\hbar^2}{2m} \nabla^2 \psi + V\psi = E\psi \quad \xrightarrow[\text{coordinate}]{\text{in spherical}} \quad \psi = \psi(r, \theta, \varphi) \rightarrow$$

$$-\frac{\hbar^2}{2m} \left[\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial \psi}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \psi}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2 \psi}{\partial \varphi^2} \right] - \frac{e^2}{4\pi \epsilon_0 r} \psi = E\psi$$

$$\psi_{nlm}(r, \theta, \varphi) = R_n^l(r) \underbrace{\Theta_l^m(\theta) \Phi_m(\varphi)}_{\text{Spherical harmonics } Y_l^m(\theta, \varphi)} = R_n^l(r) Y_l^m(\theta, \varphi)$$

$$l=0 \left\{ Y_0^0 = \left(\frac{1}{4\pi} \right)^{1/2} \rightarrow \text{corresponding to } s \text{ orbital} \right.$$

$$l=1 \left\{ \begin{array}{l} Y_1^0 = \frac{1}{2} \left(\frac{3}{\pi} \right)^{1/2} \cos \theta \\ Y_1^{\pm 1} = \mp \frac{1}{2} \left(\frac{3}{2\pi} \right)^{1/2} \sin \theta e^{\pm i\varphi} \end{array} \right\} \rightarrow p \text{ orbitals}$$

$$l=2 \left\{ \begin{array}{l} \vdots \\ \vdots \end{array} \right\} \rightarrow d \text{ orbitals}$$

note that Y_l^m is the same for all atoms which results in isotropic behavior. It is only the radial term that changes.

For the radial equation, we have:

$$-\frac{\hbar^2}{2m} \left[\left(\frac{d^2}{dr^2} + \frac{2}{r} \frac{d}{dr} \right) \right] R(r) + \left(-\frac{\hbar^2}{2m} \frac{l(l+1)}{r^2} - \frac{e^2}{4\pi \epsilon_0 r} \right) R(r) = E R(r)$$

which can be simplified by defining $R(r) = \frac{f(r)}{r} \Rightarrow$

$$\frac{dR}{dr} = \frac{d}{dr} \left(\frac{f}{r} \right) = \frac{f'}{r} - \frac{f}{r^2}$$

$$\frac{d^2 R}{dr^2} = \frac{f''}{r} - \frac{f'}{r} - \frac{f'}{r^2} + \frac{2f}{r^3} = \frac{f''}{r} - \frac{2f'}{r} - \frac{2f}{r^3}$$

$$\text{So we have: } \left(\frac{d^2}{dr^2} + \frac{2}{r} \frac{d}{dr} \right) R(r) = \frac{f''}{r}$$

After substitution in the radial equation, we have:

$$-\frac{\hbar^2}{2m} \frac{d^2 f}{dr^2} - \underbrace{\frac{e^2}{4\pi\epsilon_0 r}}_{\text{"Coulomb potential"}} f(r) + \underbrace{\frac{\hbar^2}{2m} \frac{l(l+1)}{r^2}}_{\text{"Angular potential"}} f(r) = E f(r)$$

what about the numerical solution?

well, we again set up a discrete axis along the radial axis and solve the appropriate radial Hamiltonian matrix for each value of $l = 0, 1, 2, \dots$

