VII. Schrödinger Equation in 2D and 3D

2D

$$i\hbar\frac{\partial}{\partial t}\Psi(x,y,t) = \frac{-\hbar^2}{2m}\left[\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}\right]\Psi(x,y,t)$$

$\boxed{\text{TDSE}}$

$$+\,U(x,y,t)\,\Psi(x,y,t)$$

If $U(x,y)$ only^{+} (no time dependence),

$$\boxed{\frac{-\hbar^2}{2m}\left[\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}\right]\psi(x,y) + U(x,y)\,\psi(x,y) = E\,\psi(x,y)}$$

TISE for energy eigenstates and energy eigenvalues

An energy eigenstate evolves in time as $\psi_E(x,y)\,e^{-iEt/\hbar}$

3D

$$i\hbar\frac{\partial}{\partial t}\Psi(\vec{r},t) = \frac{-\hbar^2}{2m}\left[\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right]\Psi(\vec{r},t)$$

$\boxed{\text{TISE}}$

$$+\,U(x,y,z,t)\,\Psi(\vec{r},t)$$

$$= \frac{-\hbar^2}{2m}\nabla^2\Psi(\vec{r},t) + U(\vec{r},t)\,\Psi(\vec{r},t)$$

If $U(\vec{r},t) = U(\vec{r})^{+}$ only,

$$\boxed{\frac{-\hbar^2}{2m}\nabla^2\psi(\vec{r}) + U(\vec{r})\,\psi(\vec{r}) = E\,\psi(\vec{r})}$$

TISE for energy eigenstates and energy eigenvalues

An energy eigenstate evolves in time as $\psi_E(\vec{r})\,e^{-iEt/\hbar}$

$^{+}$ Separate $\Psi(\vec{r},t) = \psi(\vec{r})\cdot T(t)$ [See Ch. III]

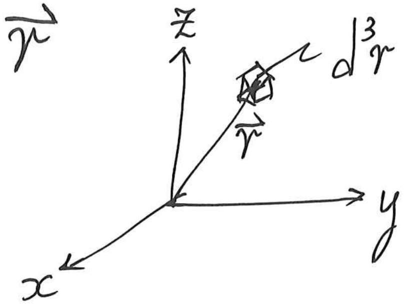
TISE + $\underbrace{\text{Boundary Conditions}}$

[$\psi(\vec{r})$ is single-valued, continuous; $\overbrace{\frac{\partial \Psi}{\partial x}, \frac{\partial \Psi}{\partial y}, \frac{\partial \Psi}{\partial z} \text{ continuous}}^{\text{except hitting } U=\infty}$]

- Bound states can be normalized

- $|\Psi(\vec{r},t)|^2 \, dx\, dy\, dz = |\Psi(\vec{r},t)|^2 \, d^3r$ (Born)

  = Prob. of finding particle in a volume element d^3r in the vicinity of position $\vec{r}$



- There are (unbound) states that cannot be normalized in usual way

  e.g. $e^{i\vec{k}\cdot\vec{r}}$ (plane wave for free particle)

  [c.f. e^{ikx} for 1D free particle]

A. Key Features in 2D/3D QM Problems (Solving TISE)

- Inspect $U(x,y)$ or $U(x,y,z)$ or $U(\vec{r})$ and check if separation of variables on $\psi(x,y)$ or $\psi(x,y,z)$ or $\psi(\vec{r})$ would work
- For nice $U(\vec{r})$, separation of variables[†] may work
- Energy eigenfunctions and eigenvalues: need more than one quantum numbers to label them
- Be aware of degeneracy (簡併)(简并)

[†] This is worthy of trying, whether it works or not will depend on the form of the potential energy function $U(\vec{r})$.

Degenerate $\Rightarrow$ $\underbrace{\text{One value of eigenenergy}}_{\text{two or more (different) eigenstates with same eigenenergy}}$

Solve $\hat{H}\psi = E\psi$ (plus B.C.'s)

Obtain: $\psi_1, \psi_2, \cdots, \psi_i, \psi_j, \cdots, \psi_n, \cdots$

$\updownarrow \quad \updownarrow \quad \updownarrow \quad \updownarrow \quad \updownarrow$

$E_1, E_2, \cdots, \underbrace{E_i, E_j}, \cdots, E_n, \cdots$

if $\underbrace{E_i = E_j \text{, but } \psi_i \neq \psi_j}_{\psi_i \text{ and } \psi_j \text{ have same eigenenergy}}$

(简并度)

<u>Degeneracy</u> (a label of energy) = Number of different ψ's with same energy

Degeneracy = 1 $\Rightarrow$ that energy has only one eigenstate ψ

If ψ_i and ψ_j share same energy, they are called <u>degenerate states</u>

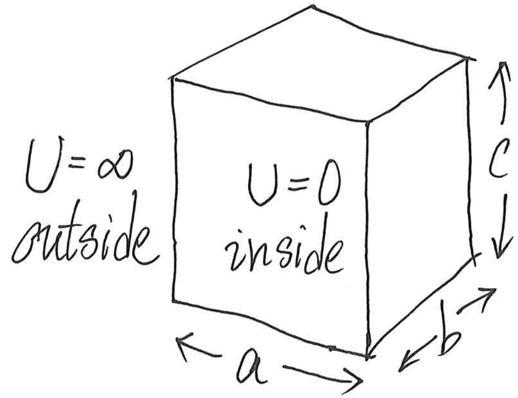
E.g. ψ_{2p_x}, ψ_{2p_y}, ψ_{2p_z} in hydrogen have the same energy (c.f. Chemistry Course)

E.g. $\psi_n(x)$ [all n] in 1D Box

$$\psi_n(x) \leftrightarrow E_n$$

only one $\psi_n(x)$ for each E_n ($\therefore$ Non-degenerate OR degeneracy $= 1$)

B. Example : 3D "Particle-in-an-infinite Box"



- Inspect $U(x,y,z)$

It has the special property that

$$\boxed{U(x,y,z) = U_1(x) + U_2(y) + U_3(z)}^{+}$$

where $U_1(x)$, $U_2(y)$, $U_3(z)$ are "1D Box" problems in x, y, z directions

E.g. $U_1(x) = \begin{cases} 0 , & 0 < x < a \\ \infty , & x \leq 0 , x \geq a \end{cases}$ and similarly for $U_2(y)$, $U_3(z)$

Solve TISE

$$-\frac{\hbar^2}{2m}\left[\frac{\partial^2}{\partial x^2}\psi + \frac{\partial^2}{\partial y^2}\psi + \frac{\partial^2}{\partial z^2}\psi\right] + \underbrace{U(x,y,z)}_{[U_1(x)+U_2(y)+U_3(z)]}\psi = E\psi$$

+ Not all $U(x,y,z)$ can be separated into SUMS this way. The effectiveness of separation of variables relies on this form.

- Write $\psi(\vec{r}) = \psi(x,y,z) = X(x)\cdot Y(y)\cdot Z(z)$ ← Very special form of product of three one-variable functions
- Substitute $\psi(\vec{r})$, TISE becomes

$$\underbrace{\underbrace{\left[\frac{-\hbar^2}{2m}\frac{1}{X(x)}\frac{d^2}{dx^2}X(x) + U_1(x)\right]}_{\text{involves } x \text{ only}}}_{=E_1 \text{ (a constant)}} + \underbrace{\underbrace{\left[\frac{-\hbar^2}{2m}\frac{1}{Y(y)}\frac{d^2}{dy^2}Y(y) + U_2(y)\right]}_{\text{involves } y \text{ only}}}_{=E_2 \text{ (a constant)}} + \underbrace{\underbrace{\left[\frac{-\hbar^2}{2m}\frac{1}{Z(z)}\frac{d^2}{dz^2}Z(z) + U_3(z)\right]}_{\text{involves } z \text{ only}}}_{=E_3 \text{ (a constant)}} = E$$

always hold [all x, y, z!]

Possible Only if: E_1 (a constant), E_2 (a constant), E_3 (a constant)

i.e.

$$\left.\begin{aligned} &\frac{-\hbar^2}{2m}\frac{d^2X(x)}{dx^2} + U_1(x)X(x) = E_1 X(x) \\ &\frac{-\hbar^2}{2m}\frac{d^2Y(y)}{dy^2} + U_2(y)Y(y) = E_2 Y(y) \\ &\frac{-\hbar^2}{2m}\frac{d^2Z(z)}{dz^2} + U_3(z)Z(z) = E_3 Z(z) \end{aligned}\right\}$$

3 problems, each is a 1D Box

AND

$$\boxed{E_1 + E_2 + E_3 = E}$$

- We solved the 1D Problems
- Allowed energies (energy eigenvalues) are

$$\underbrace{E_{n_1, n_2, n_3}}_{\substack{\text{need 3 quantum} \\ \text{numbers to label (specify)} \\ \text{one eigenvalue}}} = \frac{\pi^2 \hbar^2}{2m} \left(\underbrace{\frac{n_1^2}{a^2}}_{\substack{\text{from 1D Box} \\ \text{in } x}} + \underbrace{\frac{n_2^2}{b^2}}_{\substack{\text{from 1D Box} \\ \text{in } y}} + \underbrace{\frac{n_3^2}{c^2}}_{\substack{\text{from 1D Box} \\ \text{in } z}} \right)$$

Sum of 1D energy eigenvalues

where $n_1 = 1, 2, 3, \ldots$; $n_2 = 1, 2, 3, \ldots$; $n_3 = 1, 2, 3, \ldots$

- The corresponding energy eigenfunctions are

$$\psi_{n_1 n_2 n_3}(\vec{r}) = \psi_{n_1 n_2 n_3}(x, y, z) = \underbrace{\sqrt{\frac{8}{abc}}}_{\text{Normalization factor}} \underbrace{\sin\left(\frac{n_1 \pi x}{a}\right) \cdot \sin\left(\frac{n_2 \pi y}{b}\right) \cdot \sin\left(\frac{n_3 \pi z}{c}\right)}_{\text{Product of 1D Box energy eigenfunctions}}$$

$\sqrt{\frac{2}{a}} \cdot \sqrt{\frac{2}{b}} \cdot \sqrt{\frac{2}{c}}$

- Possible to have degenerate states
- Consider: $a = b \neq c$ [thus Box has higher symmetry than $a \neq b \neq c$]

$$E_{n_1 n_2 n_3} = \frac{\pi^2 \hbar^2}{2m}\left(\frac{n_1^2 + n_2^2}{a^2} + \frac{n_3^2}{c^2}\right)$$

- Ground state? $\psi_{111}(x,y,z) \leftrightarrow E_{111}$ (degeneracy = 1)
- Consider excited states characterized by

Different states

$$\psi_{211}(x,y,z) = \sqrt{\frac{8}{a^2 c}}\, \sin\left(\frac{2\pi x}{a}\right) \cdot \sin\left(\frac{\pi y}{a}\right) \cdot \sin\left(\frac{\pi z}{c}\right) \quad [n_1 = 2,\ n_2 = 1,\ n_3 = 1]$$

$$\psi_{121}(x,y,z) = \sqrt{\frac{8}{a^2 c}}\, \sin\left(\frac{\pi x}{a}\right) \cdot \sin\left(\frac{2\pi y}{a}\right) \cdot \sin\left(\frac{\pi z}{c}\right) \quad [n_1 = 1,\ n_2 = 2,\ n_3 = 1]$$

$$\underbrace{E_{211} = E_{121}}_{\text{Same energy}} = \frac{\pi^2 \hbar^2}{2m}\left(\frac{5}{a^2} + \frac{1}{c^2}\right)$$

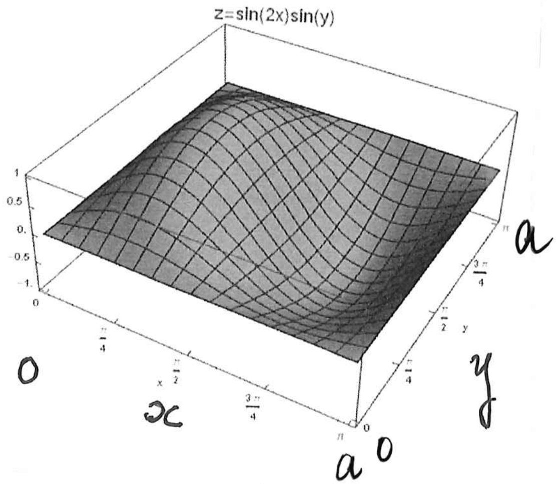
This energy (or called energy level) is degenerate with degeneracy = 2

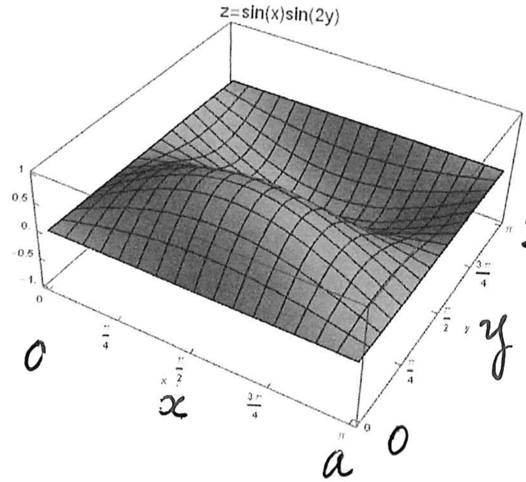
$n_1 = 2 \qquad n_2 = 1$

z-axis is: $\sin\left(\frac{2\pi x}{a}\right)\sin\left(\frac{\pi y}{a}\right)$,

$n_1 = 1 \qquad n_2 = 2$

$\sin\left(\frac{\pi x}{a}\right)\sin\left(\frac{2\pi y}{a}\right)$





They are different wavefunctions (states)

They correspond to the same energy eigenvalue.

- How about 2D isotropic harmonic oscillator $U(x,y)=\frac{1}{2}m\omega_0^2(x^2+y^2)$?
- How about 2D anisotropic oscillator $U(x,y)=\frac{1}{2}m\omega_{01}^2x^2+\frac{1}{2}m\omega_{02}^2y^2$?
- How about 2D finite box ? $U(x,y)=\begin{cases}0, & 0<x<a,\ 0<y<b \\ U_0, & \text{otherwise}\end{cases}$

  [Can this be expressed into $U_1(x)+U_2(y)$?]

- 2D isotropic oscillator

  $U(x,y)=\frac{1}{2}m\omega_0^2(x^2+y^2)$ in Cartesian coordinates Vs $U(x,y)=U(r,\theta)=\frac{1}{2}m\omega_0^2r^2$ in plane polar coordinates ?

- 3D versions of these questions ?

Summary

- TDSE and TISE in 2D, 3D
- Inspect $U(\vec{r})$ and think of Separation of Variables
- Method works if $U(\vec{r})$ can be expressed into sum of terms
- Depending on form of $U(\vec{r})$, Cartesian, plane polar, or spherical coordinates can be used
- Be aware of degeneracy!
  - Degeneracy = # different eigenstates corresponding to same energy eigenvalue
  - Non-degenerate: 1 eigenvalue $\leftrightarrow$ 1 eigenfunction (Degeneracy = 1)
  - Degeneracy is related to the symmetry of $U(x,y)$ or $U(x,y,z)$