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Operator

Eigenfunctions and Eigenvalues

$$\underbrace{\left[-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}+V(x)\right]}_{\hat{H}}\psi(x)=E\psi(x), \quad H=\frac{P_x^2}{2m}+V(x)$$

$$\hat{P}_q=\frac{\hbar}{i}\frac{\partial}{\partial q}=-i\hbar\frac{\partial}{\partial q} \qquad \hat{T}=\frac{\hat{P}_x^2}{2m}=-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}=-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}$$

$\Rightarrow \hat{H}=\hat{T}+\hat{V}=-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}+V(x)$

$\Rightarrow$ for 1D, one particle system $\left[-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}+V(x)\right]\psi_i=E_i\psi_i$

The 3-D, many-Particle Schrödinger Equation

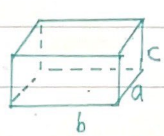
for one-particle $H=T+V=\frac{1}{2}(P_x^2+P_y^2+P_z^2)+V(x,y,z)$

$$\hat{H}=-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)+V(x,y,z) \Rightarrow -\frac{\hbar^2}{2m}\nabla^2\psi+V\psi=E\psi$$

3D system with n particles $T=\sum_{i=1}^{n}\frac{1}{2m_i}(P_{x_i}^2+P_{y_i}^2+P_{z_i}^2)$, $\hat{T}=-\sum_{i=1}^{n}\frac{\hbar^2}{2m_i}\nabla_i^2$

$$\hat{H}=-\sum_{i=1}^{n}\frac{\hbar^2}{2m_i}\nabla_i^2+V(x_1\cdots z_n)$$

The Particle in a 3-D Box



$$V(x,y,z)=0 \quad \begin{cases} 0<x<a \\ 0<y<b \\ 0<z<c \end{cases}$$

$V=\infty$ elsewhere

$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2\psi}{\partial x^2}+\frac{\partial^2\psi}{\partial y^2}+\frac{\partial^2\psi}{\partial z^2}\right)=E\psi$$

assume the solution can be written as $\psi(x,y,z)=f(x)g(y)h(z)$

then $-\frac{\hbar^2}{2m}(f''gh+fg''h+fgh'')-Efgh=0$ $\Big\downarrow \div fgh$

$$-\frac{\hbar^2}{2m}\left(\frac{f''}{f}+\frac{g''}{g}+\frac{h''}{h}\right)-E=0, \quad \underbrace{-\frac{\hbar^2}{2m}\frac{f''(x)}{f(x)}}_{E_x}=\frac{\hbar^2}{2m}\left[\underbrace{\frac{g''(y)}{g'(y)}}_{-E_y}+\underbrace{\frac{h''(z)}{h'(z)}}_{-E_z}\right]+E$$

$\Rightarrow E_x+E_y+E_z=E$

$\Rightarrow \frac{d^2f(x)}{dx^2}+\frac{2m}{\hbar^2}E_xf(x)=0 \qquad \frac{d^2g(y)}{dy^2}+\frac{2m}{\hbar^2}E_yg(y)=0 \qquad \frac{d^2h(z)}{dz^2}+\frac{2m}{\hbar^2}E_zh(z)=0$

$\Rightarrow f(x)=\sqrt{\frac{2}{a}}\sin\left(\frac{n_x\pi x}{a}\right) \qquad E_x=\frac{n_x^2h^2}{8ma^2}$

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$$\Rightarrow E = \frac{h^2}{8m}\left(\frac{n_x^2}{a^2} + \frac{n_y^2}{b^2} + \frac{n_z^2}{c^2}\right) \qquad \psi(x,y,z) = \sqrt{\frac{8}{abc}}\ \sin\left(\frac{n_x \pi x}{a}\right) \sin\left(\frac{n_y \pi y}{b}\right) \sin\left(\frac{n_z \pi z}{c}\right)$$

$$\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} |\psi|^2\, dx\,dy\,dz = \int_0^a |f(x)|^2 dx \int_0^b |g(y)|^2 dy \int_0^c |h(z)|^2 dz = 1$$

Degeneracy

for an n-fold degenerate energy level, there are n independent wave functions, each having the same energy eigenvalue W

$$\hat{H}\psi_n = W\psi_n$$

$$\hat{H}\left(\sum_1^n C_n\psi_n\right) = \hat{H}(C_1\psi_1) + \cdots \hat{H}(C_n\psi_n) = C_1\hat{H}\psi_1 + \cdots C_n\hat{H}\psi_n = C_1W\psi_1 + \cdots + C_nW\psi_n = W\left(\sum_{i=1}^n C_i\psi_i\right)$$

Average Values

many identical, noninteracting system each in the same state Ψ, $\langle B \rangle = \dfrac{\sum_{i=1}^{N} b_i}{N}$ observed value, number of system

$= \dfrac{\sum_b n_b b}{N}$ number of times

when N is very large, $\langle B \rangle = \sum_b \left(\frac{n_b}{N}\right) b = \sum_b P_b\, b$

$$\langle x \rangle = \int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} |\Psi(x,y,z,t)|^2 x\, dx\,dy\,dz$$

$$\langle B(x,y,z) \rangle = \int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} \Psi^* B \Psi\, dx\,dy\,dz$$

consider the special case where $\hat{B}\Psi = k\Psi$

$$\langle B \rangle = \int \Psi^* \hat{B} \Psi\, d\tau = \int \Psi^* k \Psi\, d\tau = k$$

$\langle A+B \rangle = \langle A \rangle + \langle B \rangle \qquad \langle cB \rangle = c\langle B \rangle \qquad \langle AB \rangle \neq \langle A \rangle \langle B \rangle$