

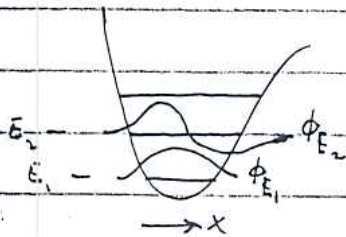
Chem. 1410
10 Sept. 07

Principles of Quantum Mechanics

Observable \mathcal{O} (Linear) Operator $\hat{\mathcal{O}}$ st. $\hat{\mathcal{O}} \phi_j(x) = \mathcal{O}_j \phi_j(x)$ ← Eigenvalue \mathcal{O}_j are only measurable values of \mathcal{O}

$\mathcal{O} = [p, x, L, \dots]$ $\phi_j(x)$ is eigenfunction of $\hat{\mathcal{O}}$ \mathcal{O}_j contains info about system prepared in state j .

For ex, let $\mathcal{O} = E$; $\hat{\mathcal{O}} = \hat{E} = \hat{H}$ = Hamiltonian operator: $\hat{H} \phi_{E_j}(x) = E_j \phi_{E_j}(x)$



Superposition States: Acceptable States other than "pure eigenfct." states exist

E.g. $\psi(x) = a_1 \phi_{E_1}(x) + a_2 \phi_{E_2}(x) + a_3 \phi_{E_3}(x) + \dots$ neglect for simplicity

↑
probability amplitude coefficients

measurement of energy yields $E_{1,2,3}$
w/ probability $|a_{1,2,3}|^2$

or, equivalently, $\langle E \rangle = \sum_{k=1}^3 |a_k|^2 E_k$

holds for eigenfct. of any \hat{Q}

To "prove" this, note additional property of the ϕ_{E_i} : Orthonormality $\int_{-\infty}^{\infty} \phi_{E_i}^*(x) \phi_{E_k}(x) dx = \delta_{ij}$

check:

$$1 = \int dx \psi^*(x) \psi(x) = \int dx (a_1^* \phi_{E_1}^* + a_2^* \phi_{E_2}^* + a_3^* \phi_{E_3}^*) (a_1 \phi_{E_1} + a_2 \phi_{E_2} + a_3 \phi_{E_3}) = \sum_{k=1}^3 |a_k|^2$$

Rule for computing Expectation values is then:

$$\int \psi^*(x) \hat{Q} \psi(x) dx = \langle \hat{Q} \rangle$$

for an example,
check:

$$\int dx \psi^* \hat{H} \psi = \int dx (a_1^* \phi_{E_1}^* + a_2^* \phi_{E_2}^* + a_3^* \phi_{E_3}^*) \hat{H} (a_1 \phi_{E_1} + a_2 \phi_{E_2} + a_3 \phi_{E_3}) = \sum_{k=1}^3 |a_k|^2 E_k$$

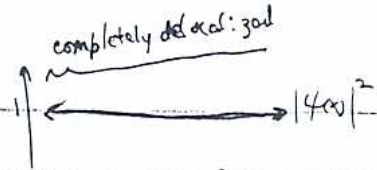
Two more postulates: (1) $\hat{p} = \frac{\hbar}{i} \frac{\partial}{\partial x}$ [Note eigenfct. $\frac{\hbar}{i} \frac{\partial}{\partial x} e^{ikx} = \hbar k e^{ikx}$]
(2) $\hat{x} = x$

Finally, Uncertainty Principle [Heisenberg]: can't measure position + momentum simultaneously w/ arbitrary precision

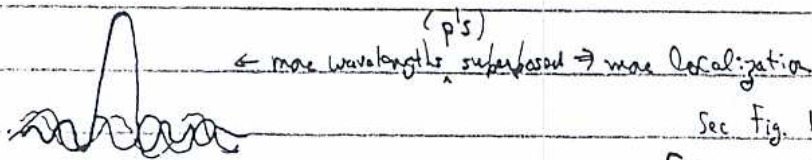
(2)

↪ [violates Newtonian world view]

Ex: $\psi(x) = e^{ikx}$ has definite momentum $\hbar k$, but $|\psi|^2 = 1$ anywhere



To build sharply localized function, need ^{to superpose} plane waves of many frequencies ["p's"]



See Fig. 11.21 Atkins

[Fig. 8.31, Atkins Ed. 8]

Mathematical Statement for Q.M.: $\Delta p \Delta x \geq \hbar/2$

(Note: $\Delta p_x \Delta y = 0$)

"Construction of Common Q.M. Operators [see Alberty + S. Feynman handouts]"

Construct \hat{H} ; recovers Schrödinger Eq.

Table 10.1 Classical Mechanical Observables and the Corresponding Quantum Mechanical Operators*

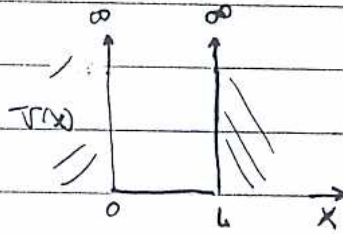
Observables		Operators	
Name	Symbol	Symbol	Operation
For one-dimensional systems			
Position	x	\hat{x}	Multiply by x
Position squared	x^2	\hat{x}^2	Multiply by x^2
Momentum	p_x	\hat{p}_x	$\frac{\hbar}{i} \frac{\partial}{\partial x}$
Momentum squared	p_x^2	\hat{p}_x^2	$-\hbar^2 \frac{\partial^2}{\partial x^2}$
Kinetic energy	$T = \frac{p_x^2}{2m}$	\hat{T}_x	$-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2}$
Potential energy	$V(x)$	$\hat{V}(x)$	Multiply by $V(x)$
Total energy	$E = T_x + V(x)$	\hat{H}	$-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x)$
For three-dimensional systems			
Position	r	\hat{r}	Multiply by r
Momentum	p	\hat{p}	$-i\hbar \left(i \frac{\partial}{\partial x} + j \frac{\partial}{\partial y} + k \frac{\partial}{\partial z} \right)$
Kinetic energy	T	\hat{T}	$-\frac{\hbar^2}{2m} \nabla^2$ $= -\frac{\hbar^2}{2m} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right)$
Potential energy	$V(x, y, z)$	$\hat{V}(x, y, z)$	Multiply by $V(x, y, z)$
Total energy	$E = T + V$	\hat{H}	$-\frac{\hbar^2}{2m} \nabla^2 + V(x, y, z)$
Angular momentum	$l_x = yp_z - zp_y$	\hat{L}_x	$-i\hbar \left(y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y} \right)$
	$l_y = zp_x - xp_z$	\hat{L}_y	$-i\hbar \left(z \frac{\partial}{\partial x} - x \frac{\partial}{\partial z} \right)$
	$l_z = xp_y - yp_x$	\hat{L}_z	$-i\hbar \left(x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x} \right)$

*Adapted from D. A. McQuarrie, *Quantum Chemistry*. Mill Valley, CA: University Science Books, 1983.

From Alberty + Silbey,
Physical Chemistry

Technique + Application

[E] 1-d Particle in a Box



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

General soltn is:

$$\psi(x) = A \sin kx + B \cos kx ; k = \sqrt{2mE}/\hbar$$

Impose (physical) B.C.: $\psi(x) = 0$ outside of box $\Rightarrow \psi(0) = \psi(L) = 0$

$\psi(x)$
must be
continuous

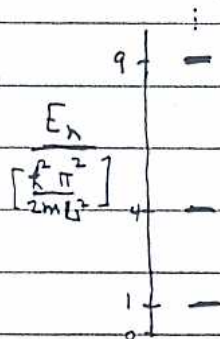
Thus $B=0$; k restricted to values $k_n = \frac{n\pi}{L}$; $n=1,2,3,\dots \Rightarrow \psi_n(x) = A \sin \frac{n\pi x}{L}$ $0 < x < L$

Note corresponding energy eigenvalues $E_n = \frac{\hbar^2 k_n^2}{2m} = \frac{\hbar^2 \pi^2 n^2}{2mL^2} = \frac{\hbar^2}{8mL^2} n^2$; $n=1,2,3,\dots$

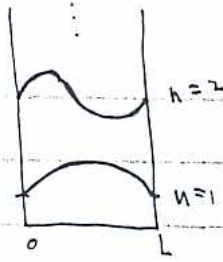
Finally, determine norm const. A : $1 = \int_{-\infty}^{\infty} |\psi_n(x)|^2 dx = A^2 \int_0^L dx \sin^2 \frac{n\pi x}{L} \Rightarrow A = \sqrt{\frac{2}{L}}$

Final eigenfunction expression is
$$\psi_n(x) = \begin{cases} 0 & x < 0 \\ \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right) & 0 < x < L \\ 0 & x > L \end{cases}$$

Study the solution: Energy level diagram



Eigenfunctions



[0] Confinement \Rightarrow Quantization!

Some features: (1) ψ_n are sin waves that "fit into the box" [vanish at $x=0, L$];

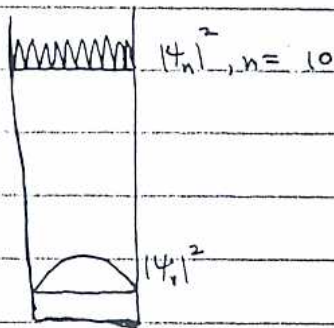
nodes in $\psi_n = n-1$

(2) ψ_1 = "ground state" has non-zero K.E = "Zero-point Energy" due to Uncertainty Principle, namely:

$$\Delta x \sim L \Rightarrow \Delta p \sim \hbar/L \sim \text{typical } p \quad [\text{note } \langle p \rangle = 0]$$

$$\Rightarrow E_{gs} \sim \frac{p^2}{2m} \sim \frac{\hbar^2}{2mL^2} \sim E_1$$

(3) For high n , probability distribution becomes essentially uniform [as is case for any classical trajectory of a P in B] \leftrightarrow Bohr correspondence principle



$$[4] E_{n+1} - E_n = \frac{\hbar^2}{8mL^2} (2n+1)$$

\leftarrow Notes: (i) ΔE increases w/ n

(ii) for fixed n , ΔE decreases as L or m increase

Example: Free Electron Model (Application to Bandstructure) \rightarrow to be continued!