Chem 1410
29 Aug. 07

Quantum Mechanics: Wavelike properties of matter contained in $\psi(x)$

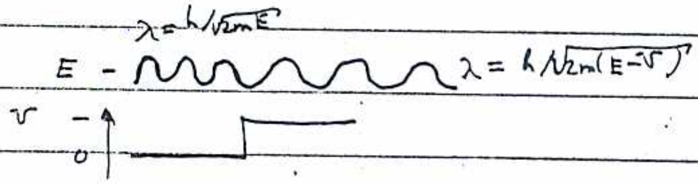
Schrödinger's Eq. [1926]: $\left[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x)\right]\psi(x) = E\,\psi(x)$ ← energy of particle; $\psi(x)$: wavefunction or state function for particle

Study free particle: $-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\psi(x) = E\,\psi(x) \Rightarrow \psi(x) = e^{\pm ikx} = \cos kx \pm i \sin kx \Rightarrow E = \frac{\hbar^2 k^2}{2m}$ or $k = \frac{\sqrt{2mE}}{\hbar}$

$\cos kx$, $\sin kx$ has wavelength $\lambda = \frac{2\pi}{k} = \frac{h}{\sqrt{2mE}} = \boxed{\frac{h}{p}}$ ✓

Next, consider particle moving in const. pot'l. V: $\left[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V\right]\psi(x) = E\,\psi(x) \Rightarrow k = \frac{\sqrt{2m(E-V)}}{\hbar}$

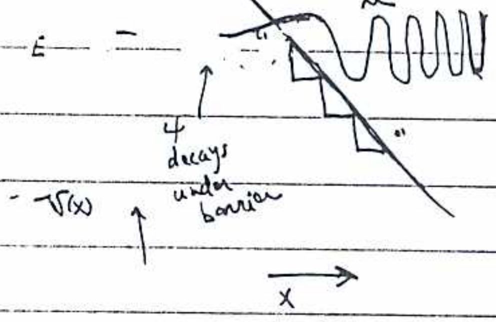
Thus



[← faster wiggles ↔ higher K.E.]

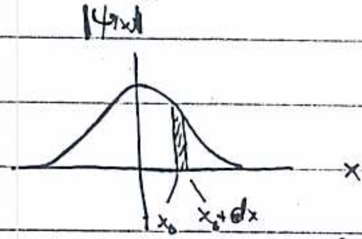
For non-const. pot'l, no const. λ sol'ns exist, but

$\lambda(x)$ = local wavelength $\psi \sim \sin(2\pi x/\lambda(x))$



Restrictions on the w.f.'s [$\leftrightarrow$ Quantization Conditions]

Born Interpretation : $\psi^*(x)\,\psi(x)$ = probability density



$|\psi_0(x)|^2 dx$ = prob. of observing between x_0, x_0+dx

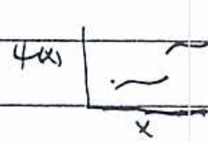
Born Interp $\Rightarrow$ Restrictions on w.f.:

(1) $\psi(x)$ finite everywhere

(2) $\psi(x)$ continuous everywhere

(3) $\psi'(x)$ continuous everywhere

(4) single-valued everywhere — ugh.



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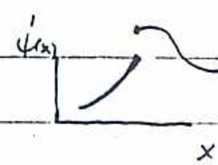
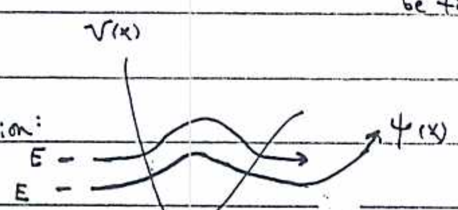


$$\psi''(x) = -\frac{2m}{\hbar^2}\left(E - V(x)\right)\psi(x)$$

for finite $V(x)$, $\psi''(x)$ must be finite everywhere.

These restrictions provide route to quantization:



$\leftarrow$ discrete # of special energies.

A Final Consequence of Born Interp.: $1 = \int dx\, \psi^*_{(x)} \psi_{(x)}$; i.e., normalization specified.

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Digression on Probability Concepts: Given an expt. [e.g. roll of dice] w/ n possible outcomes, each w/ probability P_j, then

$$P_j \equiv \frac{n_j}{n} \quad \text{as } n \to \infty$$

n_j ← # trials w/ outcome j

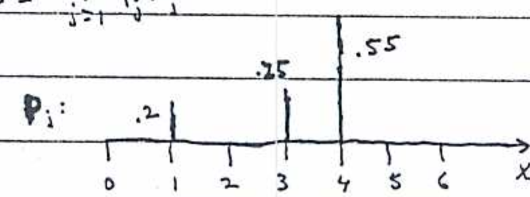
n ← total # trials

Note: [1] $1 = \sum_{j=1}^{n} P_j = \frac{1}{n} \sum_{j=1}^{n} n_j$

[2] Expectation Values: Let x_j be value of property X associated w/ possible outcome state j;

Then $\langle X \rangle = \sum_{j=1}^{n} P_j X_j$

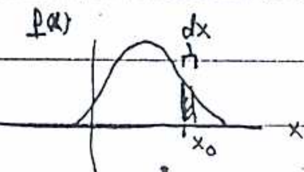
E.g., for discrete mass distribution



Here: $\langle X \rangle = (.2)(1) + (.25)3 + (.55)4 = 3.15$

NB: can compute $\langle X^2 \rangle$, etc., analogously.

[3] Generalization to Continuous Probability Distribution, $P(x)$



$P(x_0)dx$ = probability to find outcome state X in range $x_0 < x < x_0 + dx$

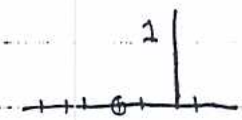
Properties: (i) $\int_{-\infty}^{\infty} P(x)dx = 1$

(ii) $\langle X^n \rangle = \int_{-\infty}^{\infty} dx\, P(x)\, x^n$, etc.

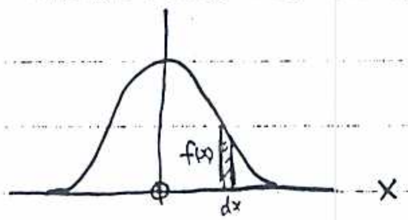
Note $\sigma_x^2 \geq 0$; thus $\boxed{\sigma_x^2} = \sum_{j=1}^{n} f_j \left[x_j^2 - 2x_j\bar{x} + \bar{x}^2\right] = \langle x^2 \rangle - 2\bar{x}\langle x \rangle + \bar{x}^2$

$$= \boxed{\langle x^2 \rangle - (\langle x \rangle)^2} \geq 0$$

Thus

$\langle x^2 \rangle \geq (\langle x \rangle)^2$ [Equality only when ]

(iii) continuous distributions, $f(x)$



probability density [cf. mass density]

$f(x)dx$ = probability to find outcome state in range x to $x+dx$

Then analogously to discrete state case

$$\int_{-\infty}^{\infty} dx\, f(x) = 1 \quad ; \quad \langle x^n \rangle = \int_{-\infty}^{\infty} dx\, f(x)\, x^n \quad ; \quad \sigma_x^2 = \int_{-\infty}^{\infty} dx\, f(x)\,[x - \langle x \rangle]^2$$

E.g., for Gaussian normal dist., $f(x) = Ae^{-x^2/2a^2}$, find A, $\langle x \rangle$, σ^2

$$1 = A \underbrace{\int_{-\infty}^{\infty} dx\, e^{-x^2/2a^2}}_{\sqrt{2\pi a^2}} \text{, so } A = \frac{1}{\sqrt{2\pi a^2}} .$$

Then

$$\langle x \rangle = A\int_{-\infty}^{\infty} dx\, x\, e^{-x^2/2a^2} = 0 \quad ; \quad \langle x^2 \rangle = \frac{1}{\sqrt{2\pi a^2}} \int_{-\infty}^{\infty} dx\, x^2 e^{-x^2/2a^2} = a^2$$

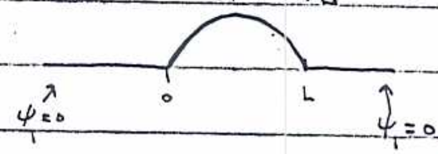
, so $\langle x^2 \rangle = \sigma^2 = a^2$; $\sigma = a \equiv$ "standard deviation"

Digression on Normalization: Examples

Normalization factor

$$\psi_1(x) = \sqrt{\frac{2}{L}}\,\sin\left(\frac{n\pi x}{L}\right)$$

(i) Particle in 1-d box



$$I = \int_0^L dx \left(\frac{2}{L}\right) \sin^2\left(\frac{n\pi x}{L}\right) \quad \checkmark$$

(ii) Hydrogen atom 1s state: $\psi(r) = \underset{\uparrow \text{ to be determined}}{N}\, e^{-r/a_0}$ $\quad$ [a_0 = Bohr radius]

$$I = N^2 \int d\underset{\sim}{r}\; e^{-2r/a_0} = 4\pi N^2 \underbrace{\int_0^\infty r^2 e^{-2r/a_0}\, dr}_{\frac{2!}{(2/a_0)^3}} \quad ; \text{Note } \int_0^\infty dr\, r^n e^{-\beta r} = \frac{n!}{\beta^{n+1}}$$

$$= \pi a_0^3 N^2 \;\Rightarrow\; \boxed{N = \sqrt{\frac{1}{\pi a_0^3}}}$$