Read all of pp 436 – 449 → light   11/19/01

Quantum – Molecular Structures & Interactions

↳ Basis of everything!

Bonding

Spectroscopy

Subfields relevant to biochemistry:

Molecular Dynamics – change over time

Molecular Mechanics – change to lowest E

<u>Wave-Particle Duality</u> electrons (and everything, but...) protons, neutrons

exhibit both particle and wave properties

Electron diffraction – clear demonstration of <u>wave</u>.

(just like x-ray diffraction, light diffraction).

<u>de Broglie</u>

$$\underbrace{\lambda}_{\text{wave}} = \underbrace{\frac{h}{mv}}_{\text{particle}} = \frac{\text{Planck's Const}}{\text{momentum of particle}}$$

<u>WAVE NATURE</u>

Wave function: $\psi = \psi(x, y, z, t)$ ← FULL DESCR

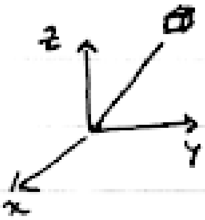
$= \psi(x, y, z)$ time-independent

← WE'LL FOCUS ON THIS

ψ is not useful for us

ψ^2 <u>is</u> useful → probability

predicts e^- distribution



Probability of finding the e^{-} in a small volume around x_0, y_0, z_0

$$\text{Prob} = \left[\psi_n(x_0, y_0, z_0)\right]^2 \Delta v$$

volume

$$\text{Prob for a finite volume} = \int \left[\psi_n(x,y,z)\right]^2 dv$$

integral over
x, y, AND z

Note that

$$\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} \left[\psi_n(x,y,z)\right]^2 dx\,dy\,dz = 1 = \int_{-\infty}^{\infty} \psi^2 dv$$

Q: $\Rightarrow$

"Probability" reflects the uncertainty principle.
We can only predict probabilities.

Note: ψ describes probability for <u>one</u> electron

Fortunately, we're often focusing on a single valence electron, in spectroscopy, for example.

pp. 449–451 Read. But don't get hung up.

New, but related, concept

Schrödinger $\quad \bar{z} = \int \psi_n \, z \, \psi_n \, d\tau$

Expectation value (for $\bar{z}$) — operator (for z)

Expectation value $\longleftrightarrow$ operator: associated

Predicts:

- momentum
- energy
- position
- dipole moment

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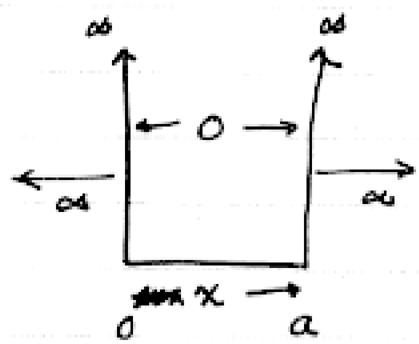
pp. 452–454 Give good, practical guidance. Come back to, if you need it.

Expectation value for E (energy)



Particle in a box.

Consider an $e^{\ominus}$ constrained as above. For $x > 0$ and $x < a$, then the $e^{\ominus}$'s potential energy is ZERO.

In this simple system, we define that if the $e^{\ominus}$ strays ≤ 0 or $\geq a$, then it's energy becomes infinite.

Result (at least classically): the $\bar{e}$ stays in the box

Q: Why "the box"?
What is it a model of? $\Rightarrow$ orbital
Not a perfect model, but...

Define: potential energy $= U_n(x)$ ← keep this 1D for simplicity

$$\bar{Z} = \int \psi_n \; Z \; \psi_n \, dv$$

$\bar{Z}$ ↓ Energy

Z ↑ "Hamiltonian" operator ↓ describes E

p. 450 shows you that $\mathcal{H}\psi = E\psi$

$$\underbrace{\left[-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + U(x)\right]}_{\mathcal{H}}\psi = E\psi \qquad (1D)$$

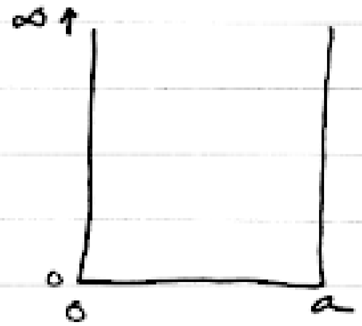
$$\left[-\frac{\hbar^2}{2m}\nabla^2 + U\right]\psi = E\psi \qquad (3D)$$

$\nabla^2 = \frac{d^2}{dx^2} + \frac{d^2}{dy^2} + \frac{d^2}{dz^2}$

Don't get excited...

So for particle in a box,

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2}\psi_n + U(x)\psi_n = E_n\psi_n$$



$U(x) = 0 \qquad 0 < x < a$

$U(x) = \infty \qquad x \leq 0 \quad x \geq a$

So outside the box, the particle will not exist (infinitely high energy). ψ outside $= 0$

We're left with $$-\frac{\hbar^2}{2m}\frac{\partial^2\psi}{\partial x^2}\psi_n + \cancel{0}\psi_n = E_n\psi_n$$

<u>Solution is:</u>

$$\psi = A \sin bx + B\cos bx$$

Boundary Conditions: when $x = 0 \quad \psi \to 0$

so

$$A\,\cancelto{0}{\sin(0)} + B\,\cancelto{1}{\cos(0)} = 0$$

$$\therefore \; B = 0$$

$\psi = A \sin bx \qquad$ but $\psi(a) = 0 = A \sin bx$

$$\Rightarrow \quad b\underset{\substack{\uparrow \\ (a)}}{x} = n\pi \qquad \therefore \; b = \frac{n\pi}{a}$$

$$\therefore \; \psi = A \sin\left(\frac{n\pi}{a}x\right)$$

FINALLY: $\int_0^a \psi^2(x)\,dx = 1$ why?

$$A^2 \int_0^a \sin^2\left(\frac{n\pi}{a}x\right) dx$$

$$A = \sqrt{\frac{2}{a}}$$

$\therefore$

$$\psi = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi}{a}x\right)$$