1/16/09

Aph 161 Quantum Mechanics tutorial

Outline:

- background
- "postulates" of QM
- applications #1: particle in a box
- applications #2: atomic orbitals

Is $\hbar$ relevant to biology?
sets lower bounds on size of organisms?
specific heats of solids, energy $\leftrightarrow$ wavelength of light

1) Background

Problems/Paradoxes that led to QM (some of them)

- discrete spectral lines, why don't e^- "orbiting" nuclei crash into the nucleus
- specific heats of solids - Law of Dulong + Petit - 1830's: all crystalline solids have specific heat = 3R @ high temp; goes to 0 @ 0 K
- photoelectric effect; is light a wave or a particle
- Davisson - Germer experiment - electron diffraction

$\Rightarrow$ read 1st 3 Chs of Feynmann lectures on QM - posted on website

~~2) "Postulates" of QM (hand-wavy version)~~

~~These~~

Theoretical responses to the above paradoxes:

- discrete spectral lines: Niels Bohr - energies/orbitals must be quantized $\Rightarrow E_n = -\frac{13.6}{n^2}\,eV$ (for hydrogen atom)

$$= -\frac{2\pi^2 m e^4}{h^2}\frac{1}{n^2}$$

- de Broglie "pilot waves"
attribute a wavelength to matter: $\lambda = \frac{h}{p} \leftarrow$ momentum
(use this + insist orbitals have to be integral #'s of λ's - recover

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2) "Postulates" of QM (hand-wavy version)

	Classical Mechanics	Quantum Mechanics
The "state" of the system	$\{\vec{q}_i, \vec{p}_i\}$ — $\vec{q}_i$: position/coordinates, $\vec{p}_i$: momentum • describe the whole system by writing down position, momentum for each particle ⇒ know all history + future of system (w/ Newton's laws) • deterministic	wave function: $\psi(\vec{r})$ or $\psi(\vec{r}_1, \ldots \vec{r}_n)$ for n particles
Evolution equations (time dependence/ series of the system)	$\dot{p}_i = -\frac{\partial H}{\partial q_i}$, $\dot{q}_i = \frac{\partial H}{\partial p_i}$ H = Hamiltonian (basically F=ma) (Lagrangian/Hamiltonian version of mechanics) ⇒ (digression: Feynman Nobel lecture – power of stating the same problem multiple ways)	time-dependent Schrodyer eqn: $\boxed{i\hbar\frac{\partial\psi}{\partial t} = \hat{H}\psi}$ • now the Hamiltonian is an operator • take this equation as an assertion for this class!
observables + measurements	Any mechanical variable we might be interested in is a function of $\{p_i, q_i\}$ eg. Energy for harmonic oscillator $= \frac{p^2}{2m} + \frac{1}{2}kq^2$ angular momentum $\vec{L} = \vec{r} \times \vec{p}$	• $\lvert\psi(x)\rvert^2 dx$ = probability that the particle will be found between x & $x + dx$ ⇒ not deterministic! probability density • the "expected value" of an observable $\hat{C}$ is given by $\boxed{\langle\psi\lvert\hat{C}\rvert\psi\rangle = \int \psi^*(x)\hat{C}\psi(x)\,dx}$ basically a weighted avg, weighted by the probability • An observable could be energy, ...

~~observables & measurements~~

more on observables in QM:

in QM observables are represented by operators, eg:

momentum $\vec{p} = -i\hbar\vec{\nabla}$ or in 1D $p_x = -i\hbar\frac{d}{dx}$

energy might be $\hat{H} = \frac{i\hbar p^2}{2m} + \frac{1}{2}kx^2$

angular momentum $\hat{L} = \vec{r}\times\vec{p}$ but replace $\vec{p}$ by $i\hbar\frac{d}{dx}$ or something

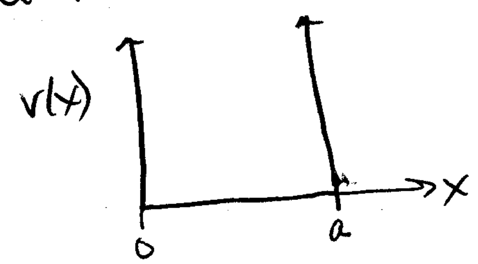
Free electron gas model:

look up the bulk moduli for Na, Li, K, etc - ~~they~~ it's not such a bad ~~~~ model to say they're boxes containing free electrons; so we'll model pigments like lycopene as one long box of free electrons

the other extreme of models: atomic orbital theories:

s, p, d, etc orbitals for an atom - these are the angular parts of the wave ~~equation~~ equations; radially they decay exponentially; so another model is ~~~~ the total ψ for a molecule is a sum of the wave functions for the individual atoms - there's only a small perturbation in bonding

3) Particle in a box in 1D:



$$V(x) = \begin{cases} 0 & 0 < x < a \\ \infty & \text{otherwise} \end{cases}$$

time-independent Schrödinger eqn:

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

$0 < x < a$:

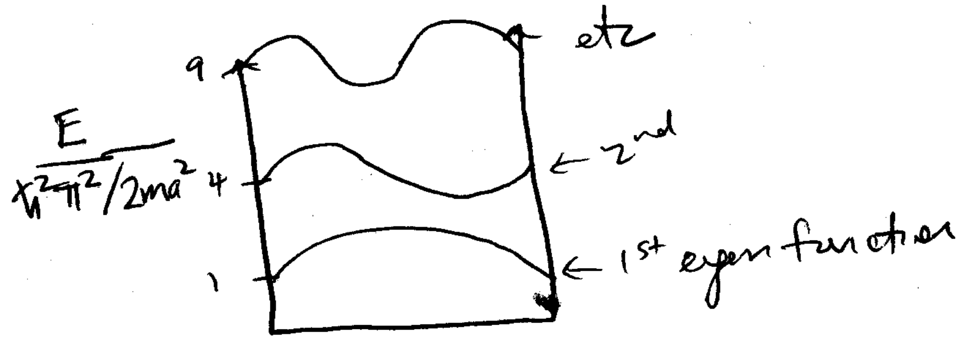
$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} = E\psi \rightarrow \frac{d^2\psi}{dx^2} + \frac{2mE}{\hbar^2}\psi = 0$$

$$\Rightarrow \psi(x) = A\cos\sqrt{\frac{2mE}{\hbar^2}}x + B\sin\sqrt{\frac{2mE}{\hbar^2}}x$$

impose boundary conditions:

$\psi(0) = \psi(a) = 0 \quad \Rightarrow \quad \psi(x) = B \sin \sqrt{\frac{2mE}{\hbar^2}}\, x$

and $\sqrt{\frac{2mE}{\hbar^2}}\, a = n\pi \Rightarrow \boxed{E_n = \frac{\hbar^2 n^2 \pi^2}{2ma^2}}$



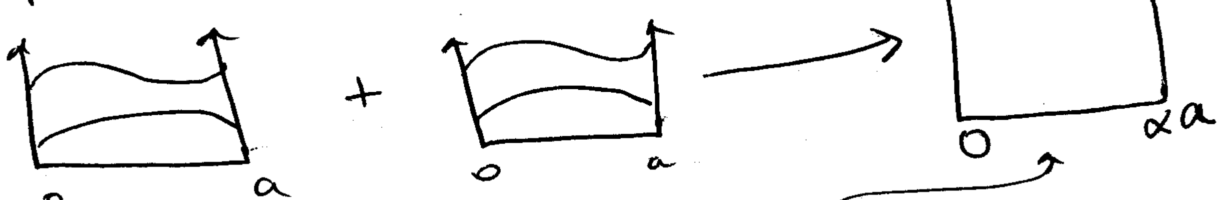
Now: toy model for a molecular bond:

bond energy = diff. between energies of the atoms separated and the energies of them together

molecule w/ 2 electrons in it - have to have opposite spins... (Pauli principle - one electron per state, where each ~~state~~ energy level has 2 states, one for each spin)

atom one

atom 2



both e^- are in the lowest energy state!

in the 2 separate atoms, n=1 for both, so total energy is $E = \frac{2\hbar^2\pi^2}{2ma^2}$

What about in the "molecule"? n=1 still!

$$E = 2\,\frac{\hbar^2\pi^2}{2m(\alpha a)^2}$$

there's 2 electrons

the size has changed! this parameter sets the energy ~~scale~~ scale for any particle

$$\text{so } E_{bond} = 2\left(\frac{\hbar^2\pi^2}{2m\alpha^2 a^2} - \frac{\hbar^2\pi^2}{2ma^2}\right) = \frac{\hbar^2\pi^2}{ma^2}\left(\frac{1-\alpha^2}{\alpha^2}\right)$$

$\alpha > 1$ so this term is negative

What is α usually? Size of a CC bond ~ 1.3 Å

↳ carbon-carbon

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energy of a typical molecular bond: a glucose is worth $\approx 2800 \frac{kJ}{mol}$

$\therefore 100-200 \frac{kJ}{mol} \approx 5\,eV/\text{bond}$

$$E_{bond} = \frac{\hbar^2 \pi^2}{ma^2}\left(\frac{1-\alpha^2}{\alpha^2}\right) \approx \frac{1}{4\cancel{\pi^2}} \frac{(6\times10^{-34}\,J\cdot s)^2 \cancel{\pi^2}}{(9\times10^{-31}\,kg)(10^{-10}\,m)^2}\underbrace{\left(\frac{1-\alpha^2}{\alpha^2}\right)}_{}$$

negative - α must be >1 or the molecule is smaller than the 2 atoms separately (not physically relevant)

$$\approx -\frac{36}{4}\,\frac{10^{-68}}{10^{-30}\,10^{-20}}$$

$$\approx -9\times10^{-18} \approx -10^{-17}\,J\left(\frac{1-\alpha^2}{\alpha^2}\right)$$

(about a factor of 5 too large, but still close!)

(and negative because it's a bonding orbital)

for ex,

Let $\alpha = 2$: then $\frac{1-\alpha^2}{\alpha^2} = 3/4$ so $E_{bond} = -\frac{3}{4}\times10^{-17}\,J$

Plan of action:

- Background;
- "Postulates" of QM;
- Application #1: Particle in a Box
  Application #2: Atomic orbitals;

Hints leading to QM:

- Discrete spectral lines;
- Specific heats of solids (Law of Dulong and Petit, 3R);
- Photoelectric effect;
- Davisson-Gerner experiment (electron diffraction);

Theoretical Responses:

- Discrete spectral lines: Niels Bohr → $E_n = -\frac{13.6}{n^2} eV = -\frac{2\pi^2 me^4}{h^2}\frac{1}{n^2}$;
- De Broglie: "pilot waves"

  Attribute a wavelength to matter: $\lambda = \frac{h}{p}$;

	Classical Mechanics	**Quantum Mechanics**
1) The "state" of a system	$\{\vec{q}_i, \vec{p}_i\}$	"wave function" $\psi(\vec{x})$
2) Evolution Equations	$\dot{p}_i = -\frac{\partial H}{\partial q_i}$; $\dot{q}_i = \frac{\partial H}{\partial p_i}$	$i\hbar\frac{\partial\psi}{\partial t} = \hat{H}\psi$
3) Observables and measurements	Any mechanical variable we might be interested in is a function of p's and q's, e.g. $E = \frac{p^2}{2m} + \frac{1}{2}kq^2$	i) $\lvert\psi(x)\rvert^2 dx \equiv$ probability that particle will be found between x and x+dx ii) "Expected" value of an observable, $\hat{C}$, is given by $\left\langle\psi\middle\lvert\hat{C}\middle\rvert\psi\right\rangle = \int\psi^*(x)\hat{C}\psi$

Question: What observables?

In QM, observables are represented by "operators"

3D: $\vec{p} = -i\hbar\vec{\nabla}$; 1D: $p_x = -i\hbar\frac{d}{dx}$

Particle in a box:

Schrödinger equation:

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

V(x) = 0

by rearranging: $\frac{d^2\psi}{dx^2}+\frac{2mE}{\hbar^2}\psi = 0 \;\rightarrow \psi = A\cos\sqrt{\frac{2mE}{\hbar^2}}x + B\sin\sqrt{\frac{2mE}{\hbar^2}}x$

Boundary conditions: ψ(0)= ψ(na)=0 → ditch cosine

$$\sqrt{\frac{2mE}{\hbar^2}}a = n\pi \rightarrow \boxed{E_n = \frac{\hbar^2\pi^2 n^2}{2ma^2}}$$

Toy model of molecular binding:

$$E_{2\text{"atoms"}} = 2\times\frac{\hbar^2\pi^2}{2ma^2} \qquad E_{molecule} = 2\times\frac{\hbar^2\pi^2}{2m(\alpha a)^2}$$

$$E_{bond} = 2\cdot\left(\frac{\hbar^2\pi^2}{2m\alpha^2 a^2}-\frac{\hbar^2\pi^2}{2ma^2}\right) = \frac{\hbar^2\pi^2}{ma^2}\left(\frac{1-\alpha^2}{\alpha^2}\right)$$

$$E_{bond} \approx \frac{(6\times 10^{-34}\,J\cdot s)^2\pi^2}{4\pi^2(9\times 10^{-31}\,kg)(10^{-10}\,m)^2} = \frac{36}{4}\frac{10^{-68}}{10^{-30}10^{-20}} = 9\times 10^{-18}\,J \approx 10^{-17}\,J$$