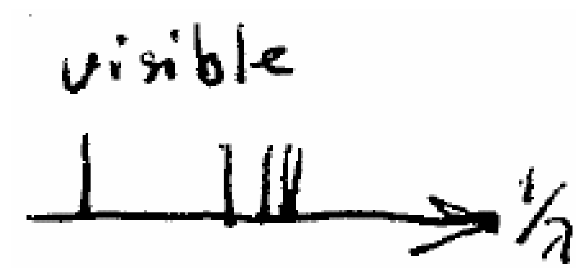
Structural Chemistry-2009 update -- Engel Ch. 12, also: Atkins Ch.9, alternate: Hanna, House, Blinder

To understand structure must come to terms with
atoms ↔ make molecules and of course then with
electrons/nuclei ↔ make up atoms!

Study of interaction of small particles ⇒
Quantum Mechanics →
Here "Quantum Chemistry" → Molecular scale theory
Also explains: Spectroscopy, Dynamics, Binding, Conformation…
big issue particles ↔ waves   frequency $\nu = c/\lambda$ wavelength

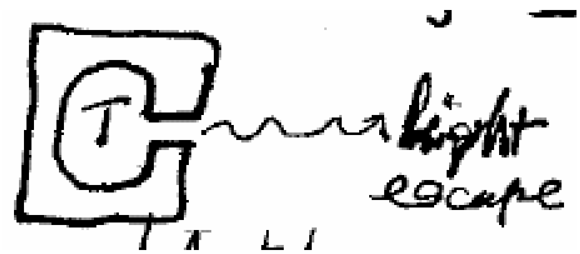
Why a special mechanics for small particles?
19^{th} century "everything worked out"
Newton mechanics – continuous
Maxwell relations (E & M)

Some little problems:
a. Excite elements in discharge – emission spectra, only at specific wavelengths

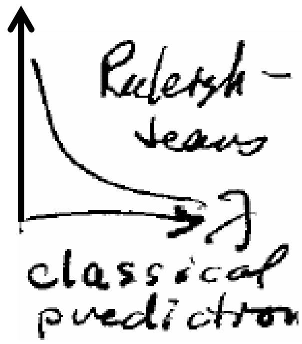


H-atom: $1/\lambda = R\,(1/n_1^2 - 1/n_2^2)$ vis- Balmer $n_1 = 2$
Others: Lyman – uv n_1=1, Paschen near IR etc.
$R = 109{,}677\ cm^{-1}$ – why discrete?

b. Black-body radiation



– if all possible wavelengths possible, probability would blow up at short λ



Concept—can get more short waves in a cavity

If all λ equally probable

Actual Shape (energy distribution with λ) observed rises with dec. λ to maximum, then steep fall off at short λ

Observations:

Stefan-Boltzmann – Energy density ~ T^4

$M = \sigma T^4$ $\sigma \sim 5.67 \times 10^{-8}\ Wm^{-2}\ K^{-4}$

Wein – distribution maximum depend inversely on T

$\lambda_{max}T$ = constant = 2.9×10^{-3} m K

Several people tried to derive it classically – fail

Planck → assume oscillators could only have energies

$E \sim 0, h\nu, 2h\nu, 3h\nu, \ldots$ – restriction, non-classical

h – constant – function to distributions

$\nu = c/\lambda$ → frequency

Then used Statistical-Thermo ideas to get distribution

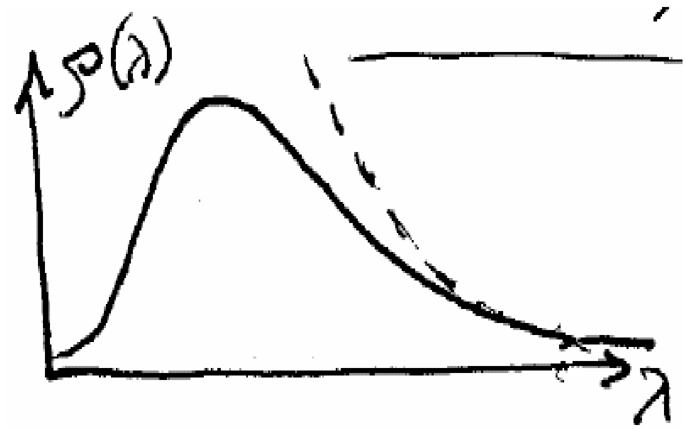
$$\rho(\lambda) = \left(\frac{8\pi hc}{\lambda^5}\right)\left(\frac{1}{e^{hc/\lambda kT}-1}\right)$$

energy density from "hole" as function λ (and T)

Test: long λ – $h\nu/kT \to 0$

Mult. top/bot. by $e^{-hc/\lambda kT}$, expand $e^{-x} = 1 - x + 1/2x^2$ etc.

$$\rho(\lambda) \sim \left(\frac{8\pi hc}{\lambda^5}\right)\left(\frac{1 - {}^{hc}/_{\lambda kT} + \cdots}{1 - 1 + {}^{hc}/_{\lambda kT} + \cdots}\right)$$



$$\sim \left(\frac{8\pi hc}{\lambda^5}\right)\left(\frac{\lambda kT}{hc} - \cdots\right)$$

$\sim 8\pi kT/\lambda^4$ ⇒ This is classical (Wein displacement) result fits long λ behavior

Short λ -- $\rho(\lambda) \cong (8\pi hc/\lambda^5)(e^{-hc/kT\lambda})$

as λ increased exponential term builds from zero to be much greater than 1-simplify

<u>In between</u> long - short λ,

ρ(λ) must have a maximum

max: $(d\rho/d\lambda) = 0 = [-5/\lambda^6 - (hc/kT\lambda^5)(-1/\lambda^2)]$

→ $\lambda_{max}T$ = constant = hc/5k -- Stefan-Boltzmann

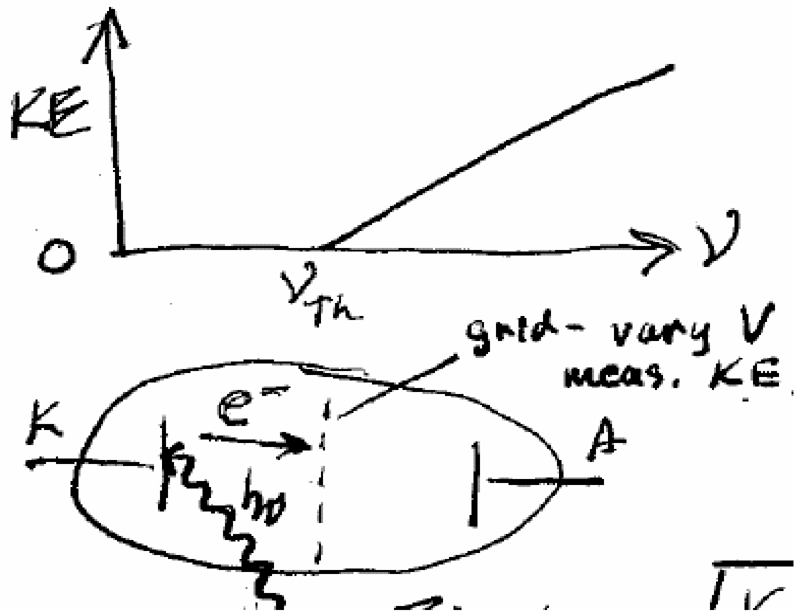
Result:

a) $h = 6.626 \times 10^{-34}$ J·s - note: this is an <u>angular momentum</u>

b) form of ρ(λ) fits observation "perfectly"

Justify assumption E = 0, hν, 2hν, etc. by fitting observation (not "proven")

Photoelectric Effect – Einstein explain-- light on metal,
electrons emitted



K.E. of electrons depend on ν

– long λ → no elect.

–– ν_{th} – threshold for appearance

-- K.E. linear dep. on ν

– Intensity not affect E, just number of electrons (current)

→ light acting like a particle

$$K.E. = \tfrac{1}{2} m \upsilon_e^2 = h(\nu - \nu_{Th}) = h\nu - \Phi$$

Φ – work function

So far: Energy limited to discrete values – Planck hν
Light (wave) behave particle – Einstein photelectric

key – threshold – frequency ⇔ energy
– intensity (classically E-field)
⇒ number of electrons, not energy

Complement: Davisson-Germer
e-beam – fixed energy onto
(metal) ordered surface

diffract → at specific angles due to periodic structure
→ analogous to diffract x-rays or light from grating
electrons are particles → behave as a wave

Combine → Louis de Broglie: $\lambda = h/p$ or $p = h/\lambda$

momentum of particle relate to $1/\lambda = \nu/c$

(or frequency of light relate to its momentum)

$\nu \quad \leftrightarrow \quad p$

Wave-Particle Duality – Central to Schrödinger QM

– property of small particles / high energies

Catch: a wave has no position so specify $\lambda \rightarrow x$ problem

Also: if particle localize can't oscillate $\rightarrow \nu$ problem

Heisenberg propose this to be fundamental limit

$\Delta p_x \Delta x \geq \hbar/2$ position and momentum complementary variables

Uncertainty principle – cannot know both x, p_x precisely

So now: have energy limited (quantized)

have light behave like particles

particle like light (quantized)

Big Deal – not continuous like classical

So what about those line spectra?

Somehow light / frequency limited -- discrete

Atoms (Rutherford) became clear dense nucleus (+)

electrons must be outside – postulate in "orbits"?

Bohr postulate (we moved back a decade – 1913)

a) Energy (light) emit only when change orbits

b) Frequency of light jump orbits

$\Delta E/h = \nu$ (relate to energy, E – like Einstein)

c) "Orbit" → relate electrostatic attraction e^- and p^+ to centripetal force

* d) Angular momentum restricted $nh/2\pi$ n = 0,1,2, ..

Look up derivation – fairly simple

$E = T + V = 1/2m\upsilon^2 - Ze^2/r$

c) equate coulomb-centripetal forces: $-Ze^2/r^2 = m(-\upsilon^2/r)$

solve: $m\upsilon^2 = Ze^2/r$ then plug in: $E = -Ze^2/2r$

d) substitute angular moment. assump: $r \cdot p = r \cdot mv = n\hbar$

$r = n^2\hbar^2/Ze^2m$ where: $\hbar = h/2\pi$ & $m\upsilon^2 = Ze^2/r = n^2\hbar^2/mr^2$

$$E = -Z^2e^4m/2n^2\hbar^2 \Rightarrow \Delta E = h\nu = R(1/n_1^2 - 1/n_2^2)$$

For Z=1 Rydberg: $R = e^4m/2\hbar^2$ in J (norm. in cm^{-1})

Bohr result explain H-atom discrete line spectra

$E \sim 1/n^2$ $\Delta E \sim R(1/n_1^2 - 1/n_2^2)$

Also worked for He^+, Li^{2+} etc. 1-e atoms

Depended on assuming angular momentum quantized

This is same as assume – fixed orbits

<u>Recall de Broglie</u> $\lambda = h/p = h/m\upsilon$ for particle

if particle on a ring $2\pi r = n\lambda$

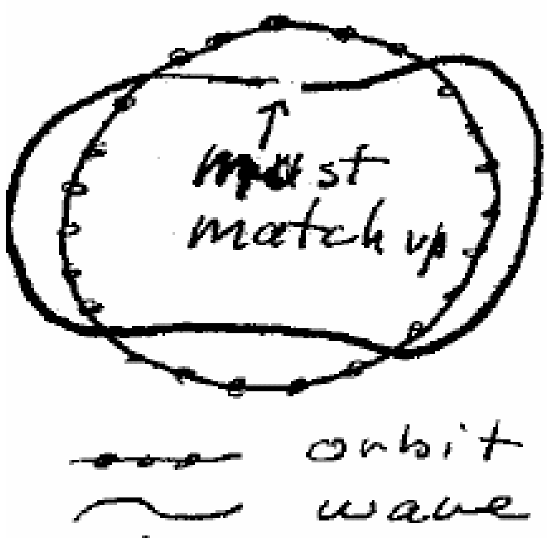
circumference have integer

number wave lengths

plug in: $2\pi r = n(h/m\upsilon)$

→ $m\upsilon r = n\hbar$ matches

Bohr's assumption (*10 years later*)



Again waves ↔ particles are key

With this set-up time was right to generalize

Bohr model great for H / fail for He^0

Problem → assumption <u>pseudo classical</u>

<u>1926</u>

Schrödinger developed a wave – mechanics

treat particles with wave properties

(relate to wave equation of Maxwell but different)

Heisenberg same time did a matrix – mechanics

fully consistent but judged more difficult concept

[Dirac later added relativity – source of spin]

Postulates – simplest approach - wave–quantum mech.

idea just like Thermo – postulate set of rules

– derive properties

– test against observables

Catch – initially must just accept, no rationale, then test

→little physical picture → See Atkins QM book

Postulate 1: State of a system fully described by a wavefunction: $\psi(\mathbf{r}_1, \mathbf{r}_2, \ldots t)$

> variables ($\mathbf{r}_1$, $\mathbf{r}_2$ - xyz coord. particle 1, 2, t = time)
> Anything not in wave fct. cannot be known in QM

Shorthand – represent state by quant. num. $\psi_{n,\ell,m,}$. . .

– or observables $\psi_{a,b,c}$ - *helpful for us, not w/f*

Alternative: $|n\,\ell\,m_\ell\,\ldots\rangle$ vector bracket from Heisenberg

Postulate 2: Observables correspond to operators Ω

summary:	constant:	$c \to c\bullet$	*concept: mult.* ψ
	variable:	$x \to x\bullet$	e.g. position
	function:	$f(x) \to f(x)\bullet$	e.g. PE: V(x)
	momentum:	$p_x \to -(ih/2\pi)d/dx\bullet = -i\hbar\, d/dx$	

Operators act on w/f – typical: multiplication, derivation

$[\alpha, \beta] = [\alpha\beta - \beta\alpha]$ – commutator,

Constraint is that $[x, p_x]\psi = [xp_x - p_x x]\psi = i\hbar\,\psi$

recall: $d/dx(y\psi)=(yd/dx)\psi+(dy/dx)\psi$

here x, p_x do not commute, since $[x, p_x]\psi \neq 0$

Properties: if $\Omega f(x) = w f(x)$ → *eigenvalue equation*

if operate Ω or $f(x)$ and result is w, a constant $*f(x)$

f is *eigenfunction* of Ω with *eigenvalue* w

Many possibilities → examples:

a) let **A** = d/dx

$\mathbf{A}e^{ax} = ae^{ax}$ $f = e^{ax}$ eigenfunction of **A**

$\mathbf{A}e^{ax^2} = 2ax\, e^{ax^2}$ $f' = e^{ax^2}$ not eigenfunction of **A**

2ax not a constant

b) or $\mathbf{B} = d^2/dx^2$

$\mathbf{B} \sin bx = -b^2 \sin bx$ g = sin bx is eigenfunction **B**

$\mathbf{B}\, e^{ax} = a^2e^{ax}$ $g' = e^{ax}$ also eigenfunction **B**

Could also do linear combinations

$\{f_n\}$ set of eigenfunction of Ω

if complete set $g(x) = \sum_{n=1} c_n f_n$ and let $\Omega f_n = w_n f_n$

then $\Omega g = \Omega \sum c_n f_n = \sum_n c_n \Omega f_n = \sum_n c_n w_n f_n$

This is not an eigenfct relation unless $w_n = w$ all w_n

$\Omega g = \Omega \sum c'_n f_n \neq cg$

$= w \sum c_n f_n = wg$ if all w_n equal

$\Rightarrow$ degenerate (product of symmetry)

Evaluating Observables

Postulate 3: If system is described by ψ_i and ψ_i is an eigenfunction of α, where α is operator corresponding to observable a

Then every measurement yield a_i, the eigenvalue

$\alpha\psi_i = a_i\psi_i$

ψ_i – set of eigenfunction

a_i – corresponding eigenvalue, for operator α

Postulate 4: If ψ is not eigenfunction then the average observed value is "expectation value"

$$\langle\alpha\rangle = \frac{\int \psi^* \alpha\, \psi\, d\tau}{\int \psi^*\, \psi\, d\tau}$$

ψ^* -- complex conjugate ψ , change $i \rightarrow -i$

τ – integrate over all variables

ex: a) let $\psi = e^{ax}$ evaluate p_x – momentum

$-i\hbar\, d/dx\, e^{ax} = (-i\hbar a)\, e^{ax}$

this is eigenvalue equation $\rightarrow \langle p_x\rangle = -i\hbar a$

b) let $\psi = \cos ax$

$-i\hbar\, d/dx \cos ax = i\hbar a \sin ax$ not eigenvalue

$$\langle p_x\rangle = \frac{\int (\cos ax)\frac{\hbar}{i}\frac{d}{dx}(\cos ax)\,dx}{\int \cos^2 ax\,dx} = \frac{\frac{-a\hbar}{i}\int_{-\infty}^{\infty}\cos ax\ \sin ax\ dx}{\int_{-\infty}^{\infty}\cos^2 ax\,dx} = 0$$

(numerator odd function, symmetric integral zero)

[meaning: p_x is $\rightarrow$ or $\leftarrow$ so average cancels out]

Schrödinger equation – many ways to get

– here use postulates --> create an Energy operator

"Hamiltonian" – classical operator for total Energy

$H = T + V = \frac{1}{2} mv^2 + V(x) = p^2/2m + V(x)$ -->KE+PE

Quantum Mechanics

$\boldsymbol{H} = \boldsymbol{T} + \boldsymbol{V} = (-\hbar^2/2m)\, d^2/dx^2 + \mathbf{V}(x)$ → 1-D

$\boldsymbol{H} = -\hbar^2/2m\, \nabla^2 + \boldsymbol{V}(x,y,z)$ 3-D Hamiltonian operator

$\nabla^2 = d^2/dx^2 + d^2/dy^2 + d^2dz^2$ Laplacian = $\nabla \cdot \nabla$

$\mathbf{r} = x\mathbf{i} + y\mathbf{j} + z\mathbf{k}$ → $\nabla = d/dx\, \mathbf{i} + d/dy\, \mathbf{j} + d/dz\, \mathbf{k}$ - vector op.

$\mathbf{H}\psi = E\psi = [(-\hbar^2/2m)\, \nabla^2 + V(\mathbf{x,y,z})]\psi = E\psi$ "gradient"

If ψ is eigenfct of **H** then eigen values (E)→total energy

Use these eigenvalue properties:

Expand arbitrary wavefcts in eigenfct of operator α

$\alpha f_n = a\, f_n$ $\{f_n\}$ → complete set

$\psi = \sum_n c_n f_n$

$\langle\alpha\rangle = \int \psi^* \alpha\, \psi\, d\tau \,/ \int \psi^* \psi\, d\tau$ → expectation value

but f_n are normalized and orthogonal (orthonormal--later)

$$\int \psi^*\psi\, d\tau = \sum_n \sum_m \int (c_n^* f_n^*)(c_m f_m)\, d\tau$$

$$= \sum_n \sum_m c_n^* c_m \int f_n^* f_m\, d\tau$$

$$= \sum_n |c_n|^2 = 1$$

$$\int f_n^* f_m\, d\tau = \delta_{nm} \begin{cases} =1 & n = m \\ =0 & n \neq m \end{cases}$$

similarly

$$\int \psi^* \alpha \psi \, d\tau = \sum_n \sum_m \int c_n^* f_n^* \alpha c_m f_m$$

$$= \sum_{n,m} c_n^* c_m a_m \delta_{nm}$$

$$\langle\alpha\rangle = \sum_n |c_n|^2 a_n$$

→ weighted sum of eigenvalues → expectation value

(<u>Note</u>: integral not necessary, if know eigenvalues)

Note 2: time is not in the above equation as given so →

<u>Postulate</u> 5: <u>Time evolution</u> of $\psi(x,y,z, \ldots t)$ is

$i\hbar \, \partial\psi/\partial t = \boldsymbol{H}\psi$ H → total Hamiltonian

time dependent Schrödinger → equ. for spectroscopy

if $\boldsymbol{H} \neq \boldsymbol{H}(t)$ let $\psi_i(x,y,z,t) = e^{-iE_it/\hbar}\phi(x,y,z)$

$i\hbar \, \partial/\partial t \, e^{-iEt/\hbar}\phi = \boldsymbol{H}e^{-iEt/\hbar}\phi$

$i\hbar(-iE/\hbar) \, e^{-iEt/\hbar}\phi = e^{-iEt/\hbar}\boldsymbol{H}\,\phi$ --> cancel $e^{-iEt/\hbar}$, *out of op.*

result, get back: $E\phi = \boldsymbol{H}\phi$ – time independent

so in general <u>for H without time dependence</u>

can just use time independent result

Spectroscopy→ light interaction is time dependent

Properties of operators

Hamiltonian operators – have real egienvalues (i.e. can be measured) hence all observables correspond to Hermitian operators (not vice versa)

Hermitian definition: $\int \psi_m^* \Omega \psi_n d\tau = \{\int \psi_n^* \Omega \psi_m d\tau\}^*$

equivalent to: $\int \psi_m^* \Omega \psi_n d\tau = \int (\Omega \psi_m)^* \psi_n d\tau$

to simplify → change notation $\langle m|\Omega|n\rangle = \int \psi_m^* \Omega \psi_n d\tau$

↑ ↑

bracket – Dirac notation

Orthonormality $\langle n|m\rangle = \delta_{nm} = \int \psi_n^* \psi_n d\tau$

Hermiticity $\langle m|\Omega|n\rangle = \langle n|R|m\rangle^*$

a) Prove: eigenvalues of Hermitian operator are real

$\Omega |n\rangle = \omega_n|n\rangle$ operator left by $\langle n|$

$\omega_n = \langle n|\Omega|n\rangle = \langle n|\Omega|n\rangle^* = \omega^*$ → real

b) Prove: eigenfunction of Hermitian op. are orthogonal

$\Omega |n\rangle = \omega_n|n\rangle$ $\Omega |m\rangle = \omega_m|m\rangle$

$\langle m|\Omega|n\rangle = \omega_n\langle m|n\rangle$ $\langle n|\Omega|m\rangle = \omega_m\langle m|n\rangle$

c.c. and subtract (recall, c.c --> take neg. of all i)

$\langle m|\Omega|n\rangle - \langle n|\Omega|m\rangle^* = (\omega_n - \omega_m)\langle n|m\rangle$

$\Rightarrow \omega_n = \omega_m$ or $\langle n|m\rangle = 0$ – orthogonal

important result - generalize operator form

Important

c) If two operators have simultaneous, arbitrarily precise eigenvalues in one state, then this is an eigenfunction of both and the operators commute.

i.e. $\mathbf{A}\psi = a\psi$ and $\mathbf{B}\psi = b\psi$

$\mathbf{AB}\psi = \mathbf{A}b\psi = b\mathbf{A}\psi = ba\psi = ab\psi = a(\mathbf{B}\psi) = \mathbf{B}(a\psi) = \mathbf{BA}\psi$

$\therefore [\mathbf{A}, \mathbf{B}] = 0$

* prove to yourself the converse –

$[\mathbf{A}, \mathbf{B}] = 0 \rightarrow \psi$ eigenfunction of both $\mathbf{A}$, $\mathbf{B}$

Relate back to Uncertainty

This proves that momentum, position cannot be measured with arbitrary accuracy because $[x, p_x] = i\hbar$

however since $[x,y] = 0 \rightarrow$ can be measured

$\therefore$ complementary operators do not commute