Chemistry 542 -- Fall 2001 -- Lecturer: Tim Keiderling

Introductory Quantum Mechanics for Chemistry

Monday -- August 20

Review: Syllabus/handout
  Fundamentals course - assume you had undergraduate quantum mechanics
    expect you to review basics/historical on own as we will go fast at first
  Homework essential (in our opinion) for mastery. Expect to spend 10+ hours/week
  Exams reflect lectures; problem oriented mostly
  NO MAKE-UP EXAMS/--time to be professional--Excused absences
    treated on individual basis (*minimum:* doctor note)

Text: **Levine** - popular with students, worked out problems
  source of much, not all homework (grade for method **not** answer)

Extra readings are important -- see syllabus and reserve list

Topics: See syllabus p. 3
  Our approach will be postulate prop. QM, work out example problems, apply to atoms and molecules.

Survey: Please hand in at end of class -- we schedule an extra session important to give practice in problem solving and provide make-up classes, etc.

HISTORICAL BACKGROUND -- *Levine 1, Atkins 1,2, R&S - 1*

19th century physics had it under control

Newtonian mechanics explain particle behavior-- eqn of motion to predict (p,x) at t

Maxwell's eqn summarize all E-M radiation -- light seen as having wave properties

Mechanics and deterministic behavior (Levine 1.4, R&S 1.3)

Newton's second law $F = ma = m(d^2x/dt^2) = m(dv/dt) = - dV(x)/dx$

Relate force to potential energy and determine x(t), v(t)

Example 1

Total energy--Hamilton's equation: $H = T + V = p^2/2m + V(x)$

$dH/dt = (dx/dt)[m(d^2x/dt^2) + (dV/dx)]$,

function in parentheses => 0 = F - ma, energy conserved (time independent)

Wednesday-- August 22

Wave motion: $A(x,t) = A_o \cos(kx-\omega t)$ $k = 2\pi/\lambda$, $\omega = 2\pi/\tau$

Increase energy, increase amplitude - A_o → $KE \sim d^2A/dt^2$ $PE \sim A^2$

Basic property--Waves diffract--picture1--$n\lambda = d \sin\theta$

Standing waves must fit the box--example2

Wave equation: $d^2A/dx^2 = (1/v_p)^2 \, d^2A/dt^2$

Goal of physics -- explain all of nature, so scale should not matter, if theory good

Correspondence -- expect microscopic ↔ macroscopic

i.e. should be possible to scale up using a consistent set of physical laws

Catch-- scale -- a few things were not working and they tended toward the microscopic

Black body radiation -- Planck postulate energy **not** continuous, smallest unit -- $h\nu$

this extrapolates from Wien law: $\lambda_m T = k$, good at short λ: λ_m from $\delta\rho/\delta\lambda = 0$

to Rayleigh-Jeans density of states, based on longer λ fit fewer oscillators in cavity,

but as shorten λ have more options for fit: $\rho(\lambda) = 8\pi kT/\lambda^4$,

was good at long at λ, $\nu = c/\lambda$, but disaster at short λ,

high frequency : $8\pi\nu^2 kT/c^3$ — blows up (uv catastrophe)

PICTURE2

Planck restricted energy of oscillators to $h\nu$, Boltzman relationship model population, high frequency oscillators have exponential fall off in population with higher frequency, then formulated BB energy density as:

$$\rho(\nu) = \left(\frac{8\pi h\nu^3}{c^3}\right)\frac{e^{-h\nu/kT}}{(1-e^{-h\nu/kT})}$$

This quantum hypothesis is also useful to explain low temperature heat capacity

Photo electric effect -- Einstein goes one step further, quantize light, make it particulate

$(1/2)\ mv^2 = h\nu - \Phi$ = K.E. of photo emitted electron

picture3

K.E. is independent of intensity of light, number of electrons increases with intensity.

Φ -- work function, property of material, no electrons until $h\nu > \Phi$,

independent of the intensity -- photon energy is $h\nu$, but light beam energy is classically the square of amplitude, or total energy is the sum of the energies of the photons

Wave-particle duality -- deBroglie --postulated particle to behave as waves, have λ

$\lambda = h/p$ p = mv but for light p = mc, rationalize: $h/mc = hc/mc^2 = hc/h\nu = c/\nu = \lambda$

Davisson and Germer then showed e-diffract in metals and Thompson in polymer

Uncertainty Principle (Heisenberg) -- principle of indeterminancy

-- what can/cannot know, fundamental limitation of quantum systems

fundamental difference from classical - no trajectories or predictions with time

consider x and p_x -- complementary observables - only one can be precisely known

with wave-particle duality problem clear:

know p_x perfectly: $p_x = h/\lambda \rightarrow$ single $\lambda \Rightarrow$ plane wave, no localization

$\Delta p_x = 0 \rightarrow \Delta x = \infty$

picture 4

know x perfectly $\rightarrow$ wave must be δ-function

Fourier analysis (FT) says this corresponds to linear super position of all λ -- interference of wavelengths all but x cancel other x value

thus total localization $\Delta x = 0$, but $\Delta\lambda = \infty \Rightarrow \Delta p = \infty$

in between -- Δx restricted and Δp restricted -- few λ's

IMPORTANT Uncertainty is an intrinsic property of quantum systems

-- not dependent on "gedanken"   exp. or measurement conditions or whatever
Correspondence comes with fact that $\Delta x \Delta p_x \geq \hbar/2$
for macroscopic systems $\hbar/2$ is very small so that
Newtonian trajectories work as well as we can measure them
Note: this is a statement of what can know or what is complete knowledge--
basis for definition of a quantum state

Aside--(parallel development) in **Atomic spectra**
Atoms when excited emitted line spectra--not classical (which would be continuous)
Balmer, Rydberg, Ritz--numerologists, found patterns based on $1/\lambda$ and integers
H-atom: $\nu/c = 1/\lambda = R(1/n_1^2 - 1/n_2^2)$ where : $R \sim 10^5 cm^{-1}$ is the Rydberg
general (Ritz): $1/\lambda = T_1 - T_2 \rightarrow$ light given off depends on differences of
atomic constants since light $\leftrightarrow h\nu$ energy (Einstein)$\leftrightarrow$T-energy levels

Bohr postulate elect restricted to E-level $\rightarrow$ stationary orbits
Spectra from e- jump between levels-process unknown- but then emit -- $h\nu = \Delta E$
also required: angular momentum integer multiple of $nh/2\pi$
(ratio of energy of e^- to frequency of orbit = hn/2)
put this together by use classical mechanics for $e^- \leftrightarrow$
centrifugal force balance by electrostatic attraction
worked for H atom, failed for all else - especially. molecules

Friday -- August 25

Schroedinger Equation Plausibility -- R&S 1.10
Since particle is a wave, use general wave function:
$\Psi(x,t) \sim \exp[i(kx-\omega t)]$ -- since complex, $\Psi(x,t)^2$ is constant--could be probability
recall : $p = h/\lambda = (h/2\pi)k$ and $E = (h/2\pi)\omega$ substitute and get w/f in particle properties
$\Psi(x,t) \sim \exp[2\pi i/h(px-Et)]$
Differentiate: $d\,\Psi(x,t)/dt = -2\pi i/h\, E\, \Psi(x,t)$
$d^2\,\Psi(x,t)/dx^2 = (2\pi ip/h)^2\, \Psi(x,t) = 2m(2\pi i/h)^2\, E\, \Psi(x,t)$ from $E = p^2/2m$
rearrange to $(ih/2\pi)\, d\,\Psi(x,t)/dt = E\,\Psi(x,t) = -(h/2\pi)^2\, d^2\,\Psi(x,t)/dx^2$
this is the Schroedinger Equation, shows the $E=p^2/2m$ relationship makes natural the first time derivative to go with the second space derivative
This is not a derivation, just a plausibility demonstration, consistent with all above

AND IT WORKS!