Lecture #3: Wavepacket, Heisenberg Uncertainty Principle & Bohr Model of H atom

I. **Uncertainty Principle**
II. **Bohr Model**
III. **Discussion: Solving Linear Homogeneous Differential Equations With Constant Coefficients**

I. Uncertainty Principle_Uncertainty principle:

To locate an electron with position error Δx, light of short wavelength λ (λ~Δx, for good resolution) should be used. But the photon has momentum p=h/λ, some of which is transferred to the electron thus changing the electron's momentum (Δp). Using lower λ light may increase the resolution (Δx↓) but this leads to p↑ and hence a Δp↑. Generalized via the Heisenberg Uncertainty Principle: $\mathbf{\Delta P_x \Delta x = h/4\pi = \hbar/2}$. Note your text is in error "**h**" should be "**ħ**". Eq. 3.43 on p. 90 shows the correct equation.
Other variable pairs also obey uncertainty principle: $\mathbf{\Delta E\, \Delta t \geq \hbar/2}$ *relates linewidths to state lifetimes, i.e. collisional broadening*.

For δE = HWHM of a transition line, and spontaneous emission lifetime τ from an excited state the Heisenberg principle relates δE (natural linewidths) and τ.

$\delta E\, \tau \approx \frac{\hbar}{2}$ Multiply both sides by 2 and divide by τ. Now 2δE = FWHM, but let's just represent this as δE. Thus we've change definition of δE from HWHM to FWHM.

$\delta E \approx \frac{\hbar}{\tau}$ $\quad E = hc\tilde{\nu}$ $\quad \delta\tilde{\nu} \approx \frac{\delta E}{hc}$ we can do this since E changes linearly with $\tilde{\nu}$

E = hc/λ we **cannot** say same for E and λ: $\delta E \neq \frac{hc}{\delta\lambda}$

Same for the relationship between λ and $\tilde{\nu}$, you would need to differentiate $\tilde{\nu}$ = 1/λ
$d\tilde{\nu} = -1/\lambda^2\, d\lambda$, Thus, if the linewidth of a dye laser at 600.000 nm is 0.050 cm^{-1}, what is the linewidth in nm?
Answer: $d\lambda = -\lambda^2\, d\tilde{\nu} = (600\ nm)^2(1\ cm/10^7\ nm)\,(0.050\ cm^{-1}) = 0.0018\ nm \sim 0.002\ nm$.
(note the negative sign is taken care of by opposite directions of $\tilde{\nu}$ and λ.)

Thus: $\delta\tilde{\nu} \approx \frac{\hbar}{\tau hc} \approx \frac{1/2\pi c}{\tau} \approx \frac{5.3\,cm^{-1}}{\tau(in\ ps)}$ careful this is a "unit specific" *can* formula

What is the linewidth in cm^{-1} for lifetime that is only 25 ps:

II. Bohr Model Bohr combined the Rutherford nuclear model of the atom (massive nucleus with electron orbiting in circular orbit) with planck's quantization condition. He related the ν (radiation frequency) from planck's relation to the frequency of rotation of electron about nucleus, by quantizing the angular momentum utilizing Debroglie wavelengths $\mathbf{l = mvr = nh/2\pi = n\hbar}$ and was able to reproduce the Rydberg Equation. His

postulates are: (1) The electron moves around nucleus of +e charge in circular orbit of constant energy *so called stationary states* (standing waves), classically they would have spiralled to nucleus since electron moving in field would emit radiation and decelerate (2) only orbits allowed are those with l = nħ (3) Transitions between the stationary states, radiation is emitted or absorbed by condiditon $\Delta E = h\nu$ *Bohr Freq. Condition*
Deriving the Rydberg Formula from the Bohr Postulate:
If these stationary states are truly fixed orbits, then the Coulombic attraction ($-e^2/\{4\pi\varepsilon_0 r^2\}$) should balance the repulsive centrifugal force (mv^2/r):

$$-\frac{e^2}{4\pi\varepsilon_0 r^2} + \frac{mv^2}{r} = 0 \quad (1)$$

$$\frac{mv^2}{r} = \frac{e^2}{4\pi\varepsilon_0 r^2} \quad (2)$$

The total energy is the sum of the kinetic ($\frac{1}{2}mv^2$) and potential (Coulombic = Force * radius):

$$E = \frac{mv^2}{2} - \frac{e^2}{4\pi\varepsilon_0 r} \quad (3)$$

$$sub\ 2\ into\ 3: E = -\frac{e^2}{8\pi\varepsilon_0 r} \quad (4)$$

Imposing boundary conditions: An integral number of wavelengths must match circumfrence of path (Debroglie waves must be in phase for each revolution, otherwise quantum interference cancels amplitue, nonstationary state): $n\lambda = 2\pi r$ **(5)**
If we substitute the deBroglie wavelength for the electron we obtain: $m_e vr = n\hbar$ **(6)**
Solving equation 6 for v and inserting this into equation 2 and solving for r, will yield:

$$r = \frac{4\pi\varepsilon_0 n^2\hbar^2}{m e^2} \quad (7)$$

which for n=1 is $\mathbf{a_0}$ (first bohr orbit)

$$= \frac{4\pi(8.8419\times10^{-12}C^2N^{-1}m^{-2})(1.055\times10^{-34}Js)^2}{(9.109\times10^{-31}kg)(1.6022\times10^{-19}C)^2} = 52.92 \text{ pm}$$

Thus we may insert 7 into 4 to get: $\mathbf{E_n = -[me^4/\{8\varepsilon_0^2h^2\}](1/n^2) =}$ **(8)**

Thus for a Transition: $\Delta E = \frac{m_e e^4}{8\varepsilon_0^2 h^2}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) = h\nu$ (9) **Bohr Frequency Condition ΔE = hν**

$E = h\nu$, $c=\lambda\nu$, $E=hc\tilde{\nu}$ so converting the equation to waveno units:

$$\tilde{\nu} = \frac{m_e e^4}{8\varepsilon_0^2 c h^3}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) = \textit{transition frequency in waveno} \qquad \textbf{(10)}$$

Thus comparing the empirical Rydberg expression to Bohr’s theoretical expression .

$$\tilde{\nu}_n = R_H\left\{\frac{1}{n_1^2} - \frac{1}{n_2^2}\right\} \qquad \textit{(Rydberg)}$$

yielded a value for R: $R_\infty = \frac{m_e e^4}{8\varepsilon_0^2 c h^3}$ = 109737.3 cm^{-1} consistent with experimental value of 109677.6 cm^{-1}

--------------- Discussion ----------------------

III. SOLVING LINEAR HOMOGENEOUS DIFFERENTIAL EQUATIONS WITH CONSTANT COEFFICIENTS

Motivation: The Shrodinger Equation is a linear homogeneous diffy-Q: **(H+E)y = 0**

Solving linear homogeneous differential equation with constant coefficients

In this course there is no need to solve diffy-Q since we will give solution but if you did have to solve a *linear* (Due to fact that function y occurs to first order) *homogeneous* (due to fact that there is no constant term, i.e. $(D^n + D^{n-1} + \ldots D)y + cy = 0$) differential equations the steps are:

1. Convert differential expressions to D operator
2. Divide through by function (y) on both sides and relable **D** as variable *m* (auxilary equation)
3. Solve auxilary equation for m
4. Note general solution is: $y = c_1\exp\{m_1x\}+c_2\exp\{m_2x\}+c_3\exp\{m_3x\}+\ldots$.
5. Use Euler relation ($e^{ix}=\cos x+i\sin x$) to simplify if you desire:i.e. replace complex expression with real ones, noting that the coefficients may become complex.

i.e.

$$\frac{d^3y}{dx^3} + \frac{dy}{dx} = 0$$

$\mathbf{D}^3y + \mathbf{D}y = 0 \rightarrow m^3 + m = 0, \rightarrow m(m^2+1) = 0, \rightarrow m = 0,+i,-i$

thus $y = c_1e^{0x}+c_2e^{ix}+c_3e^{-ix} = c_1 + (c_2e^{ix}+c_3e^{-ix})$

Euler relation: $e^{ix} = \cos x + i\sin x$, thus $(c_2e^{ix}+c_3e^{-ix}) = c_2\cos x+c_3\cos x+c_2 i\sin x-c_3 i\sin x$

$(c_2+c_3)\cos x+(c_2-c_3)i\sin x = c_2'\cos x+c_3'\sin x$, thus $y = c_1+c_2'\cos x+c_3'\sin x$

we just drop the primes since we are speaking of general solutions and write:

$y = c_1+c_2\cos x+c_3\sin x$

For the function:

$$\frac{d^2y}{dx^2} - 6\frac{dy}{dx} + 25y = 0$$

auxiliary equation: $m^2-6m+25 = 0$, we solve this via quadratic equation

$$m = \frac{6 \pm \sqrt{36 - 100}}{2} = \frac{6 \pm 8i}{2} = 3 \pm 4i$$

$y = c_1e^{\{3+4i\}x}+c_2e^{\{3-4i\}x} = e^{3x}(c_1e^{4ix}+c_2e^{-4ix})$

$= e^{3x}(c_1\cos 4x+c_2\cos 4x+c_1\sin 4x-c_2\sin 4x)$

$= e^{3x}(\{c_1+c_2\}\cos 4x+ \{c_1-c_2\}\cos 4x)$

$= e^{3x}(c_1'\cos 4x+c_2'\sin 4x)$

(drop primes since c_1 & c_2 arbitrary)

$= e^{3x}(c_1\cos 4x+c_2\sin 4x)$