In-Class notes Jun 27, 2023 ①

I) HW 1 this weekend

II) YouTube - Statistician Tiramisu

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III

Recipe for deriving S. Eqn

1) Guess a cons. of en statement for system

2) replace

nebulous wave number

PEDb $\underline{p} \Rightarrow \hbar \underline{k}$

$E_{sys}, E_{TOT} \Rightarrow \hbar \omega$

in (1)

3) (2) $\Rightarrow$ system dispn relation $\Rightarrow$ $\boxed{\omega = fn(\underline{k})}$

4) Assume that your system $\Leftrightarrow$ single travelling wave

$\Rightarrow$ $\boxed{\text{wave fn } \psi = A e^{i(\underline{k}\cdot\underline{x} - \omega t)}}$ (*)

a) 1 travelling wave,

b)

5) TAKE APPROP. (3)

derivatives, play w/ possibilities ⇒ "operate" on $A e^{i k \cdot x - \omega t}$ to expose your

Dispn. reln.

$$\boxed{\omega = \omega(\underline{k})}$$

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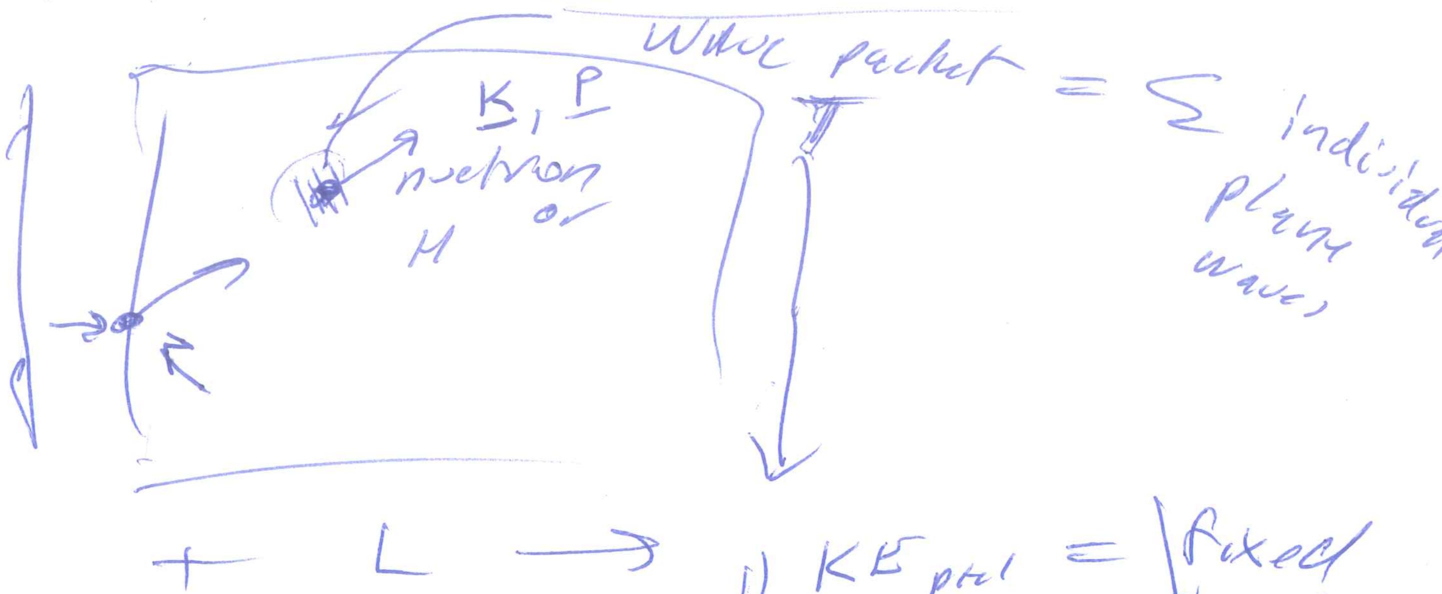
ex. particle translating in a force-free space.



1) KE_{ptcl} = fixed

Rel $\boxed{\frac{P \cdot P}{2m} = E_0}$

3) $\frac{\hbar^2 \underline{k}\cdot\underline{k}}{2m} = \hbar\omega$ (4)

Dispn rlni:

$\Rightarrow$ $$\boxed{\omega = \frac{\hbar}{2m}\underline{k}\cdot\underline{k}}$$ (4*)

4) Assume wave-ptcl dynamics of ptcl is some captured via

$$\boxed{\psi(x, t) = A e^{i(\underline{k}\cdot\underline{x} - \omega t)}}$$

5) $\psi_t = -\omega A i e^{i(k\cdot x - \omega t)}$

$= \boxed{-i\omega \psi}$ (2*)

$\psi_{x} = A(ik) e^{i(\cdot)}$

$\psi_{xx} = -k^2 A e^{i(\cdot)}$

$= \boxed{-k^2 \psi}$ (3*)

$\omega = \frac{\hbar}{2m} k^2$ $\quad \psi_{,t} = -i\omega\psi \quad \psi_{,xx} = -k^2\psi$

$\psi_{,t} = -\frac{i\hbar}{2m} k^2 \psi$

$\psi_{,xx} \longrightarrow \psi_{,t} = \frac{i\hbar}{2m}\psi_{,xx}$

1) $(\psi_{,t} = -i\omega\psi)(i) \Rightarrow i\psi_{,t} = \omega\psi$

2) $(\psi_{,xx} = -k^2\psi)\cdot\left(\frac{-\hbar}{2m}\right) \Rightarrow -\frac{\hbar}{2m}\psi_{,xx} = \frac{k^2\hbar}{2m}\psi$

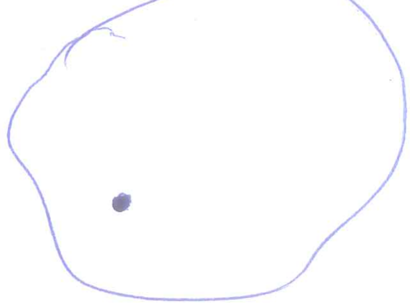
3) $\boxed{\omega = \frac{\hbar}{2m}k^2}$

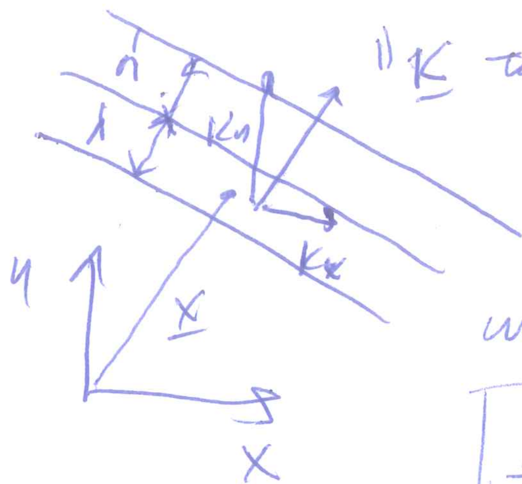
4) ∴ since

$\omega\psi = \frac{k^2\hbar}{2m}\psi$

then

$\boxed{i\psi_{,t} = \frac{-\hbar}{2m}\psi_{,xx}}$





$\parallel \underline{K}$ wave vector $\underline{\text{dir'n}}$ of wave train

$|\underline{K}| = \frac{2\pi}{\lambda}$

wave train

$$\underline{K} \cdot \underline{X} = K_x x + K_y y$$

Backup notes 1/27/23 ①

Review and ~~sta~~ connecting dots

1) $S(N,V,E) = k_B \ln \Omega(N,V,E)$ — use I Gas model to est

2) We want to ~~calc~~ $\Omega(N,V,E)$

3) for N Ideal Gas ptcls in Box

= Non-interacting

(1) $E^{(1\,ptcl)}(n_x, n_y, n_z) = \frac{h^2}{8mL^2}(n_x^2 + n_y^2 + n_z^2)$ ← SE

$\therefore\ E_{TOT,\,N\,ptc} = \sum_{i=1}^{N} E^{(ptcl\ i)}$

=

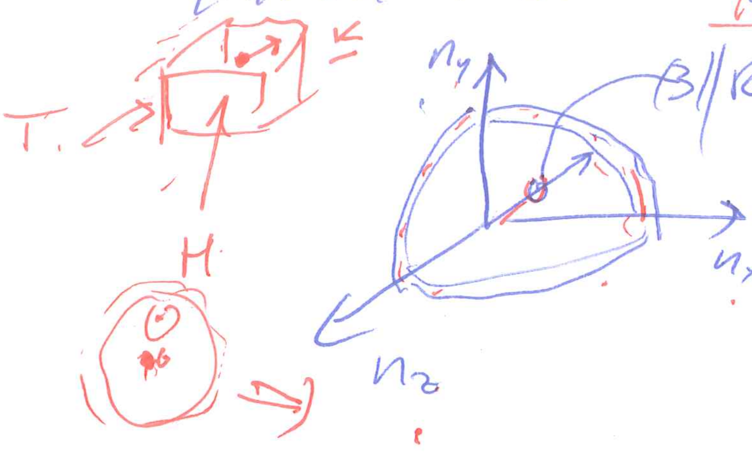
1 part ⇒ exposes dynamics of com. ⇒

2 part ⇒ expose QM. of e about fixed nucleus

4) Given (1) Geometric

(1) allows a geometric calcn. of $\Omega^{(1)}(\ )$

B) $R^2 = n_x^2 + n_y^2 + n_z^2 = E_{BOX,\,N}$ = fixed, subject to QC.



Schrodinger model of H atom

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5) When you look @ origin of (1) = S.E. for single ptcl potential free in box, questions arise

a) $\frac{p^{(1)} \cdot p^{(1)}}{2m} = E^{(1)} =$ fixed = Av.

$= \frac{E_{TOT}}{N} \frac{N_{pt}}{} =$ Avg en per ptcl

where Matom

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atom / molecule · M_{ATOM}

Q1) for composite obj. like atoms / molec what about energy ass'd w/ electrons; Q2 is there multiplicity include in (1)?

Q1 = electronic energy

Q2 = if not / why not include

Q3) ⇒ ch 6. partition ⇒

Q3) [ANS. NO.]

Q3) How would we include this?

Q4) is it a good approx

(B)

to neglect KE + PE of electrons buzzing around atom/molecule?

~~Q5) How do we ~~account~~~~

Q5) For other problems where electron energy is important, how do we tackle that?

Q6) ~~ANS~~: IT TURNS OUT we can address Q3) – Q5) ~~via a~~ by combining Schrodinger's Quantum analysis of the e- energy states in a (stationary) H atom with the single ptcl model leading to (1)

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Q Model — Schrodinger ...

1) e^-

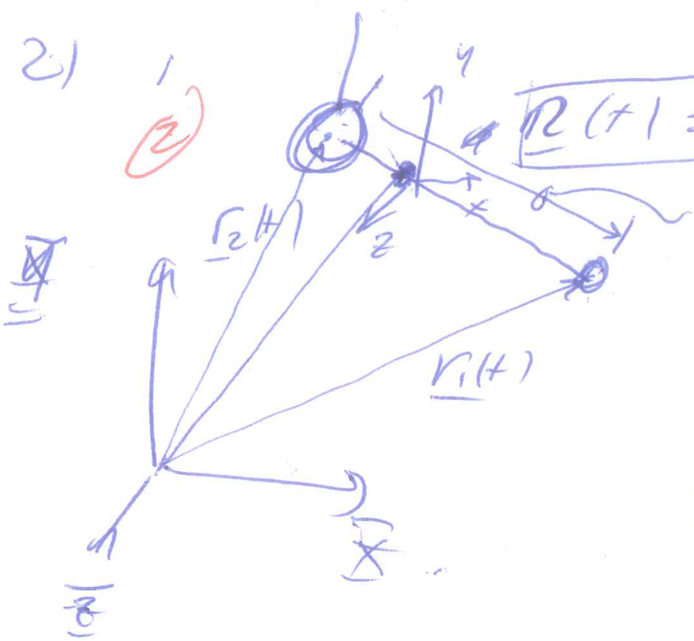
(1) neutron + proton (+)

nucleus

Demtroder ch. 5

1A

2) (2)



$$\underline{R}(t) = R_{com}(t)$$

$r(t) = r_1 - r_2$

(3)

$$\underline{r}_1 = \underline{R} + \frac{m_2}{M}\underline{r}$$

$$\underline{r}_2 = \underline{R} - \frac{m_1}{M}\underline{r}$$

$$\hat{H}_{tot}|\psi_{tot}\rangle = E_{tot}|\psi\rangle_{tot}$$

$$\hat{H} = \frac{\hat{p}_{nuc}\cdot\hat{p}_{nuc}}{2M}$$

Demtroder — KE nucl — cons — KE e — conv energy — pot. en. — H in the Schr. eqn.

(4)

a) $H = \frac{\underline{p}_{nuc}\cdot\underline{p}_{nuc}}{2m_n} + \frac{p_e\cdot p_e}{2m_e} - \frac{e^2}{4\pi\epsilon_0 r} = E_{const}$

b) ⇒ corresp. S.E.

(5)

$$-\frac{\hbar^2}{2m_n}\nabla_2^2\psi_{tot} - \frac{\hbar^2}{2m_e}\nabla_1\psi_{tot} - \frac{e^2}{4\pi\epsilon_0 r} = E_{tot}\psi_{tot}$$

1B

c) Xform to COM coords

assume

d) $\Psi_{TOT} = \Psi_n(X)\,\Psi_e(x)$ ⇐ only possible when random dynamics of constituent state index physically — motion of each uncorrelated

e) $E_{TOT} = E_{nuc} + E_{elect}$

⇓ seven DOF variables

e) $\rightarrow \; -\frac{\hbar^2}{2M}\nabla_n^2\Psi_n = E_n\Psi_n$

$\rightarrow \; \frac{\hbar^2}{\mu}\nabla_e^2\Psi_e$ ~~= E_e Ψ_e~~

(B)

$$\frac{\hbar^2}{2M}\left[\frac{\partial^2}{\partial X^2} + \frac{\partial^2}{\partial Y^2} + \frac{\partial^2}{\partial Z^2}\right]\Psi_{TOT} + \frac{\hbar^2}{2\mu}[\;]\Psi_{TOT}$$

$$+ E_{POT}(r)\,\Psi_{TOT} = -E_{TOT}\Psi_{TOT}$$

$-E_0\Psi_{TOT}$

$M = M_n + M_e \qquad \mu = \frac{M_e}{M}$

d) Ass (A) $\Psi_{TOT} = \Psi_{COM}(X)\,\Psi_e(x)$

ALSO $E_0 = E_n + E_e$ (8)

(7) ⇒ $\frac{\hbar^2}{2M}\nabla_R^2\Psi = -E_n\Psi$ ⇐ com. energy eqn $\frac{p_m \cdot p_m}{2M} = E_n$

→ $\frac{\hbar^2}{2\mu}\nabla_r^2\Psi_e = -E_e\Psi_e + E_{POT}(r)\,\Psi_e$ ⇐ electron eqn $\frac{p_e \cdot p_e}{2\mu} + V_{POT}(r) = E_e$