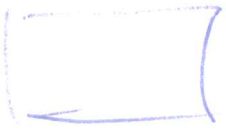
PROB NOTES | 11/30/23 | ⓪

Q M

Derivation of Schrodinger Eqns for random dynamics of Hydrogen atom nucleus & H atom electron in a heated box

(+) 1 SET-UP FOR ~~THE~~ RIGOROUS PATHINTS SINGLE IDEAL GAS particle in a heated box [chap. 1].

I) Simplest Particle in box



⇒

A) examples of an important initial insight into

B) how to gain intuition into QM and Q. chem states

we're focusing on H atom in heated box

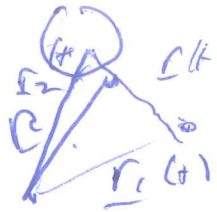
C) Born-Oppenheimer shows that H dynamics can be separated into the q/dyn. of the COM ≅ nucleus & b/ dyn. of electron about C.O.M ≅ nucleus

nucleus/COM S.E.Q.N.:

(1) $$i\hbar \psi_{N,t}(\underline{X}_2,t) = -\frac{\hbar^2}{2M}\nabla_N^2 \psi_N(\underline{X}_2,t)$$

(2) $M = m_N + m_e$

electron S.E.



$$i\hbar \psi_{e,t}(\underline{x}_1,t) = -\frac{\hbar^2}{2\mu}\nabla_e^2 \psi_e(\underline{x}_1,t) + V_{coulomb}(\underline{x}_1,t)\,\psi_e(\underline{x}_1,t)$$

$$V_{coulomb} = \frac{e^{-1}}{4\pi\epsilon_0 r}$$

$\underline{X}_1 = \underline{r}_1(t) = \underline{X}_e(t)$

$\underline{X}_2 = \underline{r}_2(t) = \underline{X}_N(t)$

$\underline{r} = \underline{x}$

$\mu = \frac{m_e m_N}{M}$ = reduced mass $\cong m_e$

II) Derivation of (1) & (2)

A) (1) & (2) are products of:
cons. of energy for composite body

$$\frac{P_N \cdot P_N}{2M_N} + \frac{P_e \cdot P_e}{2m_e} + V_{Coul}(r_1, r_2, t) \quad (2.1)$$

$$= E_0 \Psi$$

B) Assump 1: $\Psi_H(r_1, r_2, t) = \Psi_N(X, t) \cdot \Psi_e(x, t)$ (2.2)

① statistically - assing random dynamics of electron is independent of random dyn of nucleus

Assump 2: $E_0 = E_N + E_e$ (2.3)

② physically, were assing that the energetics/dynamics of the electron are indep. of that of the nucleus.

③ Based on Dentsoder's treatment of H atom, uncoupled energetics appears to be a reasonable assumption (at least under, e.g., Low temp conditions)

C) Using/Replacing

(3.1)
$$\begin{aligned} \underline{P}_N &= \hbar \underline{K}_N \\ E_N &= \hbar \omega_N \\ \underline{P}_e &= \hbar \underline{K}_e \\ E_e &= \hbar \omega_e \end{aligned}$$

Planck - Einstein - De Broglie postulates

in (2.1) Leads to a dispersion relation for H atom.

D) Rather than using our heuristic derivation of S eqn, Let's use the equivalent replacement / operator structure:

(3.2)
$$\frac{\hbar^2}{2M_N} \underline{K}_N \cdot \underline{K}_N \Rightarrow (-i\hbar)^2 \nabla_N^2$$

$$\frac{\hbar^2}{2M_e} \underline{K}_e \cdot \underline{K}_e \Rightarrow (-i\hbar)^2 \nabla_e^2$$

$$\nabla_N^2 = \frac{\partial^2}{\partial X_1^2} + \frac{\partial^2}{\partial Y_1^2} + \frac{\partial^2}{\partial Z_1^2}$$

$$\nabla_e^2 = \frac{\partial^2}{\partial X_2^2} + \frac{\partial^2}{\partial Y_2^2} + \frac{\partial^2}{\partial Z_2^2}$$

Rivera

As we began to piece together in Jan 27 Lecture more later

E) ~~Using (3.2)~~

F) CRUCIAL ASIDE "Wave operators" FN.

A) a) (vector) Momentum operator $= \hat{\underline{P}} = -i\hbar\nabla$ (3.3)

↑ vector gradient

b) kinetic energy operator = (4.1) $\hat{E}_{kin} = \frac{\hat{p}^2}{2m} = \frac{\hat{p}\cdot\hat{p}}{2m} \Rightarrow \frac{\hat{p}\cdot\hat{p}}{2m} = \frac{(-i\hbar\nabla)\cdot(-i\hbar\nabla)}{2m}$ Laplacian

c) Energy operator = (4.2) $\hat{H} = \frac{\hat{p}\cdot\hat{p}}{2m} + \hat{V}_{pot}(\underline{x},t)$ Hamiltonian

d) vector position operator = $\hat{\underline{x}} = \hat{\underline{r}} = \underline{x}$ (4.3)

e) vector angular momentum operator = $\hat{\underline{L}} = \hat{\underline{r}} \times \hat{\underline{p}} = \hat{\underline{r}} \times (-i\hbar\nabla)$

f) potential energy operator = $\hat{V}_{pot}$ (4.4) $\hat{V}_{pot}\psi = V_{pot}\psi$ (4.5)

B) Quick/incomplete Factoids re. wave fn operators

a) We'll come back to this q.f/as necessary

C) 2nd Recipe for solving a system Schrödinger EQN

1) Guess/state conc. of energy for your system

2)

2) Write down associated ~~Energy eq~~ Sch. eqn in the generic form:

$$\hat{H}_{sys}\psi_{sys} = i\hbar\psi_{sys,t} \qquad (5.1)$$

Note we could use the usual 'wave vector' notation

$$|\psi\rangle(\underline{x},t) \Leftrightarrow \psi(\underline{x},t) \qquad (5.2)$$

↑ represent all coordinates of all energetic constituents in system

3) Restate $\hat{H}_{sys}$ in terms of wave fn operators highlighted pp 4-5.

V) Let's Apply this recipe to our ~~H~~ H atom in a box.

A) cons. of energy:

$$\frac{\underline{P}_N \cdot \underline{P}_N}{2M_N} + \frac{\underline{P}_e \cdot \underline{P}_e}{2M_e} + V_{pot}(\underline{r}_1(t), \underline{r}_2(t)) = E_0 \quad (6.1)$$

☺ THIS version assumes H atom HAS THERMALLY equilibrated w/ Heated walls, i.e., the random atomic motion is statistically stationary

B) Restate as generic S. Eqn.:

$$\hat{H}|\psi\rangle = i\hbar \frac{\partial}{\partial t}|\psi\rangle$$

STEP 3

either or, ~~Pay~~ based on (6.1):

$$\left(\frac{\hat{\underline{P}}_N \cdot \hat{\underline{P}}_N}{2M_N} + \frac{\hat{\underline{P}}_e \cdot \hat{\underline{P}}_e}{2M_e} + \hat{V}_{pot}\right)|\psi_{sys}\rangle = i\hbar \frac{\partial}{\partial t}|\psi_{sys}\rangle \quad (6.2)$$

C) a) Assume statistically indep. (random) nuclear dynamics and electron dynamics; see eq. (2.2)

b) Equivalently, assume uncoupled nuclear and electron dynamics see eq. (2.3)

∴ Use (2.2) ~~and (2.3)~~ in (6.2):

(~~AS usual~~) and restate operators in (3.3) thru (4.2)

a) $\langle\psi\rangle^2$ = probability density functions $\Rightarrow$ $|\psi_{sys}\rangle = |\psi_N\rangle \cdot |\psi_e\rangle$ ⇐ Assume statistically indep.

(7.1) $\left[\frac{(-i\hbar)^2}{2M_N}\nabla_N^2 + \frac{(i\hbar)^2}{2m_e}\nabla_e^2 + V_{pot}(\underline{r}_1, \underline{r}_2)\right] \psi_N(\underline{x}_2, t) \cdot \psi_e(\underline{x}_1, t)$

b) prob & statistics

joint pdf of 2 random obls z_1 & z_2

$p(z_1, z_2) = p(z_1) \cdot p(z_2)$ = $(E_N + E_e)\,\psi_N(\underline{x}_2, t)\,\psi_e(\underline{x}_1, t)$

(7.2) = $i\hbar\left[\psi_{N,t}\,\psi_e + \psi_N\,\psi_{e,t}\right]$

or

$\left(-\frac{\hbar^2}{2M_N}\nabla_N^2\psi_N\right)\psi_e - \left(\frac{\hbar^2}{2m_e}\nabla_e^2\psi_e\right)\psi_N + V_{pot}\,\psi_N\,\psi_e$

$= i\hbar\left[\psi_{N,t}\,\psi_e + \psi_N\,\psi_{e,t}\right]$

$= E_N\,\psi_N\,\psi_e + E_e\,\psi_N\,\psi_e$

(7.3) (7.2) / $\psi_e\psi_N$ ⇒ $\frac{-\hbar^2\nabla_N^2\psi_N}{2M_N\psi_N} - \frac{\hbar^2\nabla_e^2\psi_e}{2m_e\psi_e} + V_{pot} = E_N + E_e$

(7.4) Separate (7.3) INTO STATISTICALLY / DYNAMICALLY INDEP eqns, 1 for nucleus, 1 for electron:

$-\frac{\hbar^2\nabla_N^2\psi_N}{2M_N\psi_N} = E_N$

or

(7.3) $\Rightarrow$ (7.2) $\Rightarrow$

$\psi_N \psi_e$

$$(7.3)\quad -\frac{\hbar^2}{2M_N}\frac{\nabla_N^2\psi_N}{\psi_N} - \frac{\hbar^2\nabla_e^2\psi_e}{2m_e\psi_e} + V_{pot} = i\hbar\frac{\psi_{N,t}}{\psi_N} + i\hbar\frac{\psi_{e,t}}{\psi_e}$$

(7.3), by eq. (7.2) and (7.3)

(7.4) Assumes statistically indep, uncoupled dynamics for nucleus & electron; so we can break (7.3) into 2 separate ~~(illegible)~~ S.eqns, ~~(illegible)~~ one for nucleus, one for electron

$$\Rightarrow -\frac{\hbar^2}{2M_N}\frac{\nabla_N^2\psi_N}{\psi_N} = i\hbar\frac{\psi_{N,t}}{\psi_N} \qquad (\text{nucleus})$$

$$\Rightarrow -\frac{\hbar^2}{2m_e}\frac{\nabla_e^2\psi_e}{\psi_e} + V_{pot} = i\hbar\frac{\psi_{e,t}}{\psi_e} \qquad (\text{electron})$$

(7.5) or

nucleus $$\boxed{-\frac{\hbar^2}{2M_N}\nabla^2\psi_N = i\hbar\psi_{N,t}} \qquad (8.1)$$

electron $$\boxed{-\frac{\hbar^2}{2m_e}\nabla^2\psi_e + V_{pot}\psi_e = i\hbar\psi_{e,t}} \qquad (8.2)$$

IV | ORIGIN OF STATIONARY Schrodinger eqn.

A) UNDER experimental conditions where microscale dynamics are random statistically stationary i.e., mean values of measured QTYS are nominally fixed, we can assume that the system wave fn, or component wave fn is time-independent

B) UNDER THOSE conditions, we apparently look for wave fns that have the form of standing waves. [THE complex squares of wave fn which corresponds to the space-dependent probability density of observing the constituents of the system at specified locations w/in the modeled problem is then time-independent.]

c) UNDER THESE CONDITIONS, a) ASSUME THAT

$$\psi(x,t) = \tilde{\psi}(x)\, e^{i\omega t} \qquad (10.1)$$

or $|\psi\rangle = |\tilde{\psi}\rangle e^{i\omega t}$

b) PLUG (10.1) INTO time-dep S. Eqn TO GET

$$\hat{H}|\tilde{\psi}\rangle e^{i\omega t} = i\hbar \frac{\partial}{\partial t}|\psi(x,t)\rangle$$

$$= i\hbar |\tilde{\psi}(x)|(i\omega)\, e^{i\omega t}$$

$$\Rightarrow \boxed{\hat{H}|\tilde{\psi}\rangle = \hbar\omega|\tilde{\psi}\rangle} \qquad (10.2)$$

c) USING PROB postulate, restate $\hbar\omega$ as E:

$$\boxed{\hat{H}|\tilde{\psi}\rangle = E|\tilde{\psi}\rangle} \qquad (10.3)$$

stationary S. EQN

VII) SO, GOING BACK TO H ATOM IN HEATED BOX PROBLEM, LET'S:

a) FOCUS ONLY ON THE random dynamics OF THE nucleus

b) LET'S ASSUME THAT THE NUCLEUS HAS equilibrated W/ THE HEATED WALLS, i.e., IT'S RANDOM MOTION IS statistically stationary

c) so ~~USING~~ Assuming

$$\text{and} \quad \boxed{\begin{aligned} \psi_N(\underline{x}_2, t) &= \tilde{\psi}_N(\underline{x}_2)\, e^{-i\omega_N t} \\ \psi_e(\underline{x}_1, t) &= \tilde{\psi}_e(\underline{x}_1)\, e^{-i\omega_e t} \end{aligned}} \quad (11.1)$$

and using these in (8.1) & (8.2).

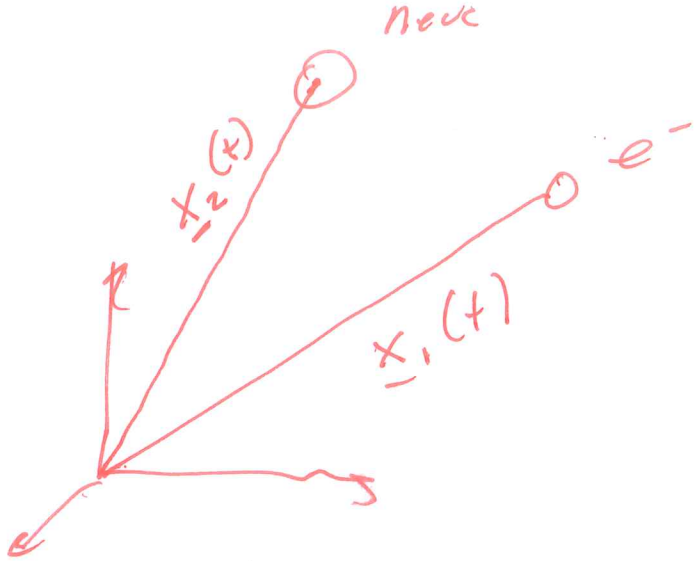
has finally ~~gg~~ leads to:

$$(11.2) \quad \boxed{\frac{\hbar^2}{2m} \nabla_N^2 \tilde{\psi}_N(\underline{x}_2) = E_N \tilde{\psi}_N(\underline{x}_2)} \Leftarrow \text{S.E nucleus}$$

$$(11.3) \quad \boxed{\frac{\hbar^2}{2m} \nabla_e^2 \tilde{\psi}_e(\underline{x}_1) + V_{pot}(\underline{x}_1, \underline{x}_2)\, \tilde{\psi}_e(\underline{x}_1) = E_e \tilde{\psi}_e(\underline{x}_1)} \Uparrow \text{S.E electron}$$

where

$$\boxed{\begin{aligned} \nabla_N^2 &= \frac{\partial^2}{\partial x_2^2} + \frac{\partial^2}{\partial y_2^2} + \frac{\partial^2}{\partial z_2^2} \\ \nabla_e^2 &= \frac{\partial^2}{\partial x_1^2} + \frac{\partial^2}{\partial y_1^2} + \frac{\partial^2}{\partial z_1^2} \end{aligned}}$$



$$\underline{x}_2 = x_2 \hat{i} + y_2 \hat{j} + z_2 \hat{k}$$

similar $\underline{x}_1$