QM Lecture 19

PERTURBATIONS TO THE HYDROGEN ATOM

RELATIVISTIC KINETIC ENERGY

- BOHR MODEL: e^- VEL $\beta = \frac{v}{c} = \alpha Z$

Z: ATOMIC #

α: FINE STRUCTURE CONST. $\sim \frac{1}{137}$

$Z = 1$: $v = \frac{1}{137} c$ SEMI-REL

NOW $H = K + V$

$$K = \underbrace{\frac{\hat{P}_p^2}{2m_p}}_{\text{CLASSICAL}} + \overbrace{\left\{ \left(\hat{P}_e^2 c^2 + m_e^2 c^4 \right)^{\frac{1}{2}} - m_e c^2 \right\}}^{\text{REL. K.E.}}$$

* WANT: LEADING MOM. CORR.

$$\left(p_e^2 c^2 + m_e^2 c^4 \right)^{\frac{1}{2}} - m_e c^2$$

$$= m_e c^2 \left(\frac{p_e^2}{m_e^2 c^2} + 1 \right)^{\frac{1}{2}} - m_e c^2$$

$$\simeq m_e c^2 \left(1 + \frac{p_e^2}{2 m_e^2 c^2} - \frac{1}{8} \frac{p_e^4}{m_e^4 c^4} + \dots \right) - m_e c^2$$

$$= \underbrace{\frac{p_e^2}{2 m_e}}_{\text{CLASS.}} - \underbrace{\frac{1}{8} \frac{\left(p_e^2 \right)^2}{m_e^3 c^2}}_{\text{CORR.}} + \dots$$

RECALL: HYDROGENIC IN COM VARS

$$\hat{H}_0 = \frac{\vec{p}^2}{2\mu} - \frac{Ze^2}{|\vec{r}|}$$

NOW ALSO: $\hat{H}_1 = \frac{-(\vec{p}^2)^2}{8m_e^3c^2}$

* NB: $H_1 \sim (\text{VEC. LENGTH})^2 \Rightarrow$ ROT INV.

$\Rightarrow$ $[H_1, L] = 0$

$\therefore$ $\hat{H}_1$ MAT. EL. DIAG. IN UNPERT. BASIS

* COMPUTE LEADING EN. CORR. (how?)

$$E^1_{n,\ell} = -\langle n,\ell,m| \frac{(p^2)^2}{8m_e^3c^2} |n,\ell,m\rangle$$

METHODS

(1) DIRECT $(p^2)^2 \longrightarrow (-\hbar^2\nabla^2)^2$ & ACT. (Legendre & Laguerre $\Rightarrow$ hard!)

(2) TRICK: ASIDE $\mu = \frac{Zm_p m_e}{Zm_p + m_e} = \frac{Zm_p m_e}{Zm_p\left(1 + \frac{m_e}{Zm_p}\right)} \simeq m_e\left(1 - \frac{m_e}{Zm_p}\right)$

CORR $O\left(\frac{m_e}{Zm_p}\right)$

$\simeq \frac{1}{1800Z}$

$\ll \frac{1}{137}$

$$\frac{-(\hat{p}^2)^2}{8m_e^3c^2} = -\frac{1}{2m_ec^2}\left(\frac{p^2}{2m_e}\right)^2$$

$$= -\frac{1}{2m_ec^2}\left(H_0 + \frac{Ze^2}{|\vec{r}|}\right)^2$$

FIRST TERM GIVES E_n^0

$$\therefore \quad E_{n,l}^1 = -\frac{1}{2m_e c^2}\left\{ (E_n^0)^2 + 2E_n^0 \langle nlm | \frac{Ze^2}{|\hat{r}|} | nlm \rangle + \langle nlm | \frac{(Ze^2)^2}{|\hat{r}|^2} | nlm \rangle \right\}$$

STILL HARD!

TRICK 2

TAYLOR
$$E_n(\gamma) = E_n\Big|_{\gamma=0} + \underbrace{\gamma\left(\frac{dE_n}{d\gamma}\right)\Big|_{\gamma=0}}_{\text{FIRST CORR, } E_n^1} + \frac{1}{2!}\gamma^2\left(\frac{d^2E_n}{d\gamma^2}\right)_{\gamma=0} + \cdots$$

LET
$$\hat{H}' = \frac{\hat{P}^2}{2\mu} - \frac{(Ze^2-\gamma)}{|\hat{r}|} = H_0 + \frac{\gamma}{|\vec{r}|}$$

(by redef. of $Ze^2-\gamma$) $\quad E_n' = \frac{-\mu(Ze^2-\gamma)^2}{2\hbar^2 n^2}$

$$\frac{dE_n'}{d\gamma} = \frac{2\mu(Ze^2-\gamma)}{2\hbar^2 n^2}$$

$$\therefore (E_n')' = \gamma \frac{\mu Z e^2}{\hbar^2 n^2}$$

$$\Rightarrow \langle nlm | \frac{1}{|\vec{r}|} | nlm \rangle = \frac{\mu Z e^2}{\hbar^2 n^2} = \frac{\mu c \alpha}{\hbar}\left(\frac{Z}{n^2}\right) = \frac{Z}{a_0 n} \qquad \left(\alpha = \frac{ke^2}{\hbar c}\right)$$

$$\Rightarrow \langle nlm | \frac{Ze^2}{|\vec{r}|} | nlm \rangle = \frac{\mu Z^2 e^4}{n^2\hbar^2} = -2E_n^0$$

$\frac{1}{r^2}$ TERM SIMILAR TRICK

$$\left[-\frac{\hbar^2}{2\mu}\frac{d^2}{dr^2} + \frac{\ell(\ell+1)\hbar^2}{2\mu r^2} + V(r)\right] u_{E,\ell}(r) = E_{n,\ell}\, u_{E,\ell}(r)$$

SO PERT CAN BE THOUGHT OF AS

$$\frac{\ell(\ell+1)\hbar^2}{2\mu r^2} + \frac{\gamma}{r^2} =: \frac{\ell'(\ell'+1)\hbar^2}{2\mu r^2} \quad (*)$$

(again, the trick is to change a const. that multiplies a term already in H)

$$E = -\frac{\mu Z^2 e^4}{2\hbar^2(1+\ell+n_r)^2} \Longrightarrow E_n' = -\frac{\mu Z^2 e^4}{2\hbar^2(1+\ell'+n_r)^2}$$

$$\left.\frac{dE_n'}{d\gamma}\right|_{\gamma=0} = \left.\left(\frac{dE_n'}{d\ell'}\right)\right|_{\ell'=\ell} \left.\left(\frac{d\ell'}{d\gamma}\right)\right|_{\ell'=\ell} = \frac{\mu Z^2 e^4}{\hbar^2(1+\ell+n_r)^3} \left.\left(\frac{d\ell'}{d\gamma}\right)\right|_{\ell'=\ell}$$

$$(*) \Rightarrow \frac{d\gamma}{d\ell'} = \frac{(2\ell'+1)\hbar^2}{2\mu} \Longrightarrow \left.\left(\frac{d\ell'}{d\gamma}\right)\right|_{\ell'=\ell} = \frac{\mu}{(\ell+\frac{1}{2})\hbar^2}$$

$$\therefore E_n' = \langle n\ell m|\frac{\gamma}{r^2}|n\ell m\rangle = \gamma\left(\frac{dE_n'}{d\gamma}\right)_{\gamma=0} = \gamma\frac{\mu^2 Z^2 e^4}{\hbar^4 n^3}\frac{1}{(\ell+\frac{1}{2})}$$

$$\therefore \langle n\ell m|\frac{(Ze^2)^2}{r^2}|n\ell m\rangle = \frac{\mu^2(Ze^2)^4}{\hbar^4 n^3}\frac{1}{(\ell+\frac{1}{2})} = \frac{4(E_n^0)^2 n}{\ell+\frac{1}{2}}$$

CONCLUSION

$$E' = -\frac{1}{2m_e c^2}(E_n^0)^2\left\{1 - 4 + \frac{4n}{\ell+\frac{1}{2}}\right\}$$

BREAKS ℓ DEGEN!

$$E' = -\frac{1}{2}\frac{\mu^2}{m_e}c^2 Z^2\alpha^4\left\{-\frac{3}{4n^4} + \frac{1}{n^3(\ell+\frac{1}{2})}\right\}$$

↳ m_e IN BOOK

QUANTUM MECHANICS & SYMMETRY GROUPS

(i) STATES $|\psi\rangle$ ARE VECTORS IN CMPLX V.S. $\mathcal{H}$.

- $\mathcal{H}$ HAS A MAP $\langle \cdot | \cdot \rangle : \mathcal{H}^* \times \mathcal{H} \longrightarrow \mathbb{C}$ SATIS:

  1. $\langle \phi | \psi \rangle = \langle \psi | \phi \rangle^*$
     $\langle \phi | \left(\xi_1 |\psi_1\rangle + \xi_2 |\psi_2\rangle \right) = \xi_1 \langle \phi | \psi_1 \rangle + \xi_2 \langle \phi | \psi_2 \rangle$
     & SIM. FOR CONJ.

  2. $\langle \psi | \psi \rangle \geq 0$ w/ $= 0 \iff |\psi\rangle = 0 \in \mathcal{H}$

- FOR PHYSICAL STATES WE TAKE $\langle \psi | \psi \rangle = 1$.

(ii) OBSERVABLES ARE REP'D BY HERM. LIN. OPS $\mathcal{O} : \mathcal{H} \longrightarrow \mathcal{H}$

- A STATE $|\psi\rangle$ HAS A DEFINITE VALUE $\psi_\mathcal{O} \in \mathbb{C}$ IF

$$\mathcal{O} |\psi\rangle = \psi_\mathcal{O} |\psi\rangle$$

  I.E. IT IS AN EIGENVECTOR.

- FACT $\mathcal{O}^+ = \mathcal{O} \Rightarrow \psi_\mathcal{O} \in \mathbb{R}$ & E-VECS $|\psi\rangle, |\phi\rangle$ w $\psi_\mathcal{O} \neq \phi_\mathcal{O}$ HAVE $\langle \phi | \psi \rangle = 0$.

(iii) PROBABILITIES SYSTEM IN $|\psi\rangle$, EXP'T DONE TO DET. WHETHER IT IS IN ANY ONE OF ORTH. RAYS $|\psi_i\rangle$, THE PROB. IT IS IN $|\psi_i\rangle$ IS $|\langle \psi | \psi_i \rangle|^2$.

- IF $|\psi_i\rangle$ AN ORTH. BASIS, PROBS SUM TO ONE

$$\sum_i |\langle \psi | \psi_i \rangle|^2 = 1$$

SYMMETRY GROUPS

(some operation can do on the system that doesn't change anything that we can observe about it)

SYMMETRY

ALICE (A) & BOB (B) LOOK AT SAME SYSTEM

FROM DIFFERENT PERSPECTIVES. CHG OF PERS = C.o.P

A: $|\psi_A\rangle$. PROB TO BE FOUND IN $|\psi_{A,i}\rangle$ IS $|\langle\psi_A|\psi_{A,i}\rangle|^2$.

$\updownarrow$ C.O.P $\qquad\qquad\qquad\qquad \updownarrow$ C.O.P. $\qquad\qquad$ $\|$

B: $|\psi_B\rangle$. " " " " " $|\psi_{B,i}\rangle$ IS $|\langle\psi_B|\psi_{B,i}\rangle|^2$.

JUST C.O.P. $\Rightarrow$ PHYS. SAME $\Rightarrow$ = SIGN ABOVE

<u>E.G.</u> Z-AXIS VS X-AX. IN STERN-GERLACH

<u>WIGNER 30'S</u> $|\psi_A\rangle$ $|\psi_B\rangle$ REL BY UNITARY LIN. OP.

$$|\psi_A\rangle = \mathcal{U}|\psi_B\rangle \qquad \mathcal{U}: \mathcal{H}\longrightarrow\mathcal{H} \quad \text{ST.} \quad \mathcal{U}^\dagger\mathcal{U} = \mathbb{1}$$

<u>NOTE</u> $|\langle\psi|\phi\rangle|^2 \Rightarrow |\langle\psi'|\phi'\rangle|^2 = |\langle\psi'|\mathcal{U}^\dagger\mathcal{U}|\phi'\rangle|^2 = |\langle\psi|\phi\rangle|^2$

<u>A</u> SYMMETRY IS NON-TRIVIAL A UNITARY LIN. OP $\mathcal{U}: \mathcal{H}\longrightarrow\mathcal{H}$

SYMMETRY GROUP

* SUPPOSE CHARLIE (C) HAS DIFF. PERS.

THEN $\exists$ $|\psi_C\rangle = \mathcal{U}_C|\psi_A\rangle$ $\quad \mathcal{U}_C^\dagger\mathcal{U}_C = \mathbb{1}$ $\quad \mathcal{U}_C$ A SYM.

& $\therefore$ $|\psi_C\rangle = \mathcal{U}_C\mathcal{U}|\psi_B\rangle$. BUT $(\mathcal{U}_C\mathcal{U})^\dagger\mathcal{U}_C\mathcal{U} = \mathcal{U}^\dagger\mathcal{U}_C^\dagger\mathcal{U}_C\mathcal{U} = \mathbb{1}$

$\Rightarrow$ $\mathcal{U}_C\mathcal{U}$ A SYM!

* GENERALLY

$S = \{\text{SET OF SYMM}\}$

FACTS ABOUT S

1) $\mathcal{U}^{\dagger} = \mathcal{U}^{-1} \in S \quad \forall \mathcal{U} \in S$ (it is a unitary lin op)

2) $\mathcal{U}_1 \mathcal{U}_2 \in S \quad \forall \mathcal{U}_1, \mathcal{U}_2 \in S$

PROOF

i) PROD. LIN OPS IS LIN.

ii) $(\mathcal{U}_1\mathcal{U}_2)^{\dagger}\mathcal{U}_1\mathcal{U}_2 = \mathcal{U}_2^{\dagger}\mathcal{U}_1^{\dagger}\mathcal{U}_1\mathcal{U}_2 = \mathbb{1} \implies \mathcal{U}_1\mathcal{U}_2$ UNITARY

3) $\mathbb{1} \in S$

4) $\mathcal{U}_1(\mathcal{U}_2\mathcal{U}_3) = (\mathcal{U}_1\mathcal{U}_2)\mathcal{U}_3 \quad \forall \mathcal{U}_1, \mathcal{U}_2, \mathcal{U}_3 \in S$

closure, assoc, identity, inverse

$\implies (S, \cdot)$ FORM A GROUP

WHERE $\cdot$ IS COMP. OF MAPS, OR MAT MULT.

SYMMETRIES FORM A GROUP! (symmetry group)

EXAMPLES

GROUP

$(\mathbb{Z}, +)$

$(\mathbb{Q}, \cdot)$ ($\frac{1}{2} \notin \mathbb{Z}$ is $\in \mathbb{Q}$)

$(\mathbb{Q}, +)$

$(\mathbb{Z}_{12}, +)$ "CLOCK ADD."
EG $7+6=1$

$\mathcal{U}(1) := (S, \cdot)$
$S = \{e^{i\theta} \mid \theta \in [0, 2\pi]\}$

SPATIAL ROT.

ROT ABOUT z-AXIS
(subgroup!)

NOT GROUP

$(\mathbb{Z}, \cdot)$ ($\exists\, z \in \mathbb{Z}$ S.T. $\frac{1}{z} \notin \mathbb{Z}$)

CONTINUOUS GROUPS

* $\mathcal{U} \in S$ IS FUNC OF CONT. PARAMS ϵ
* FOR ϵ REAL & $\epsilon \ll 1$, $\mathcal{U} = \mathbb{1} + i\epsilon T$ w T HERMITIAN.
* MANY OBSERVABLES RELATED TO SYMM.
  - SPATIAL ROT. GROUP $\longleftrightarrow$ ANG. MOM $\hat{L}$
  - GROUP OF TIME TRANS $\longleftrightarrow$ ENERGY OP $\hat{H}$
  - GROUP OF SPATIAL TRANS $\longleftrightarrow$ MOM. $\hat{P}_x$ $\hat{P}_y$ $\hat{P}_z$

NOETHER'S THM: FOR EVERY CONTINUOUS SYMM. $\exists$ A CONSERVATION LAW!

$\hat{L}$, $\hat{H}$, $\hat{P}_x$, $\hat{P}_y$, $\hat{P}_z$, ALL TRUE!

GAUGE "SYMMETRY" NOT SYMMETRY IN TECHNICAL SENSE.