TIME-INDEPENDENT PERTURBATION THEORY

OR

STATIONARY PERTURBATION THEORY

THE RAYLEIGH-SCHRÖDINGER FORMALISM

- USEFUL WHEN A TIME-INDEPENDENT PERTURBATION ACTS ON A SYSTEM (THE UNPERTURBED SYSTEM) WHOSE DYNAMICS IS KNOWN.

THE DISTURBANCE CHANGES THE ENERGY LEVELS AND THE STATIONARY STATES OF THE UNPERTURBED SYSTEM.

$$H = \underbrace{H_0}_{\text{UNPERTURBED SYSTEM}} + \underbrace{\lambda W}_{\text{PERTURBATION}} \quad , \quad \text{WITH} \quad \lambda \ll 1$$

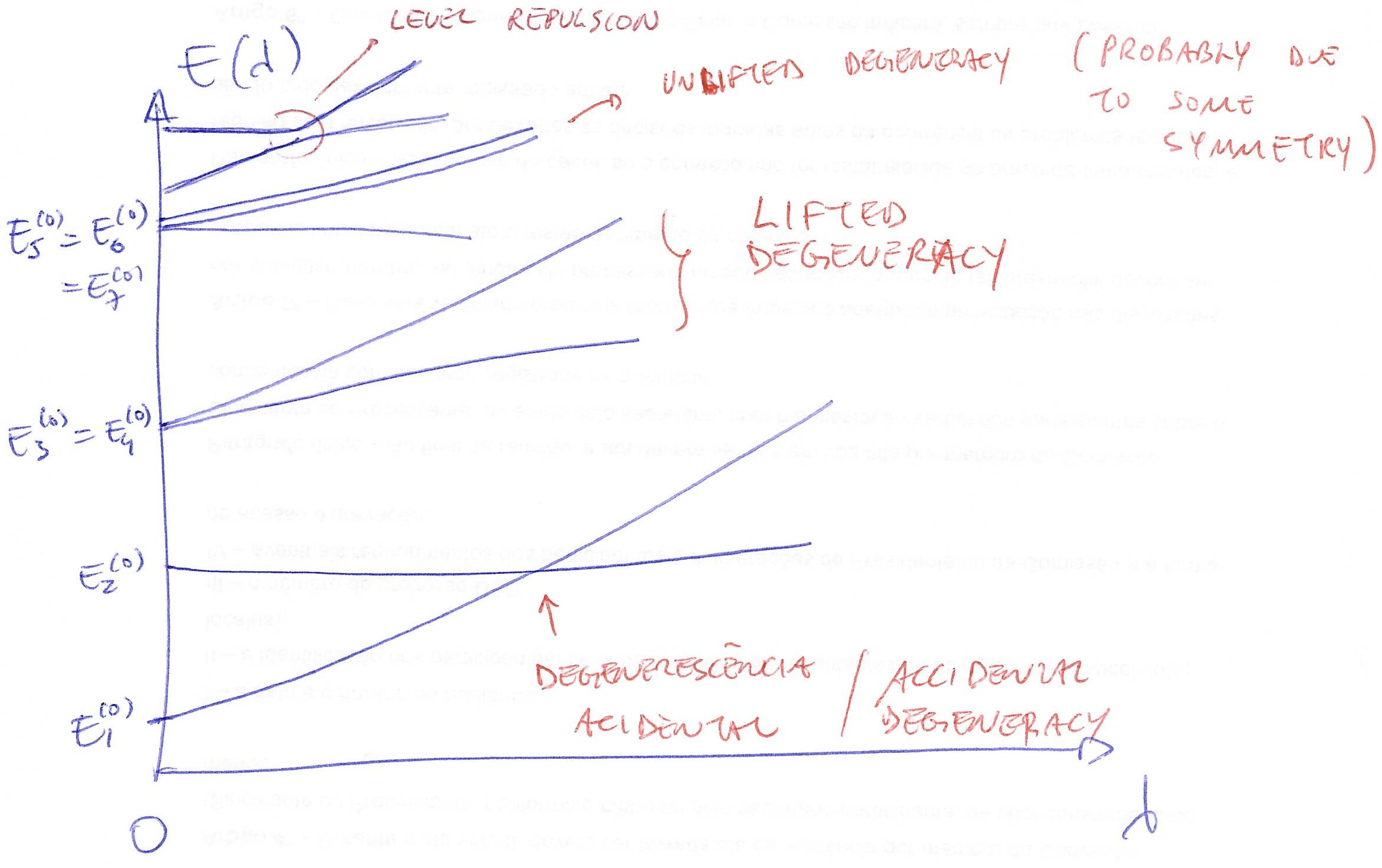
IT IS COMMON TO SEE $H = H_0 + V$ $(V = \lambda W)$

WHERE V IS A PERTURBATION. THIS MEANS THE THE ENERGY GAPS OF H_0 ARE TYPICALLY MUCH GREATER THAN THOSE OF V

(WHICH MEANS WE HAVE TO BE CAREFUL WHEN DEALING WITH DEGENERATE STATES OF H_0.)

* LET' US FIRST DEAL WITH NON-DEGENERATE PERTURBATION THEORY, I.E., THE SPECTRUM OF H_0 IS NON-DEGENERATE.

WHAT DO WE EXPECT TO HAPPEN WITH THE SPECTRUM OF $H = H_0 + \lambda W$ AS A FUNCTION OF λ?



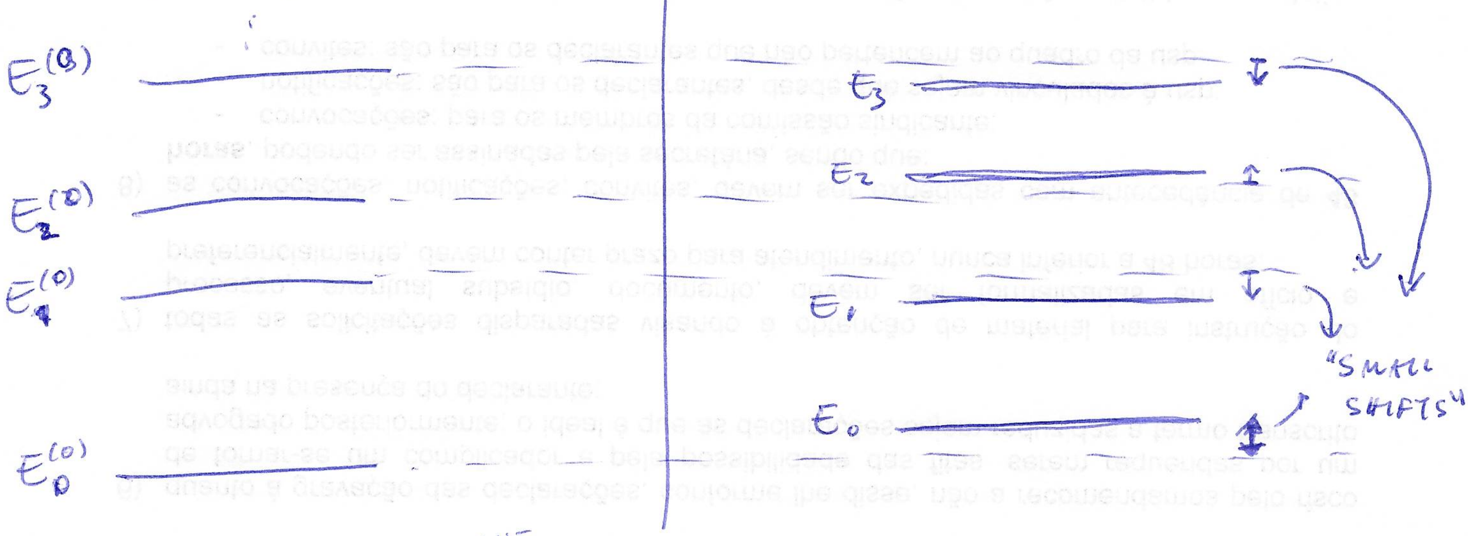
- SPECTRUM OF H_0 IS FULLY KNOWN

$$H_0 |\varphi_m^{(0)}\rangle = E_m^{(0)} |\varphi_m^{(0)}\rangle$$

$E_n^{(0)} \neq E_m^{(0)}$ IF $n \neq m$ (NON-DEGENERATE)

WE WANT $H|\varphi_m\rangle = E_m |\varphi_m\rangle$; $m = 0, 1, 2 \dots$

$H = H_0$ | $H = H_0 + \lambda W$



AS THE STATES OF THE UNPERTURBED H_0 FORM A BASIS, THEN

$$|\varphi_m\rangle = \sum_j c_{mj} |\varphi_j^{(0)}\rangle$$

EVIDENTLY, $\begin{cases} c_{mj} \equiv c_{mj}(\lambda) \\ E_m \equiv E_m(\lambda) \end{cases}$

IF NOTHING PATHOLOGIC HAPPENS, THEN THERE IS A TAYLOR SERIES

$$E_m(\lambda) = E_m(0) + \frac{\partial E_m}{\partial \lambda}\Big|_{\lambda=0} \lambda + E_m''(0)\frac{\lambda^2}{2!} + \cdots$$

$$\equiv E_m^{(0)} + \lambda E_m^{(1)} + \lambda^2 E_m^{(2)} + \lambda^3 E_m^{(3)} + \cdots$$

- HERE, WE ASSUME $E_m(\lambda)$ TO BE A HOLOMORPHIC FUNCTION. THUS, THE TAYLOR SERIES EXIST AND IS CONVERGENT.

ALTERNATIVELY, ONE CAN USE CAUCHY CONVERGENCE CRITERION TO VERIFY IF THE TAYLOR SERIES IS CONVERGENT.

$\sum_m a_m$ IS CONVERGENT IF FOR EVERY $\epsilon > 0$ THERE IS A POSITIVE N SUCH THAT FOR ALL $M \geq m \geq N$ WE HAVE

$$\left| \sum_{k=m}^{M} a_m \right| < \epsilon .$$

HERE $a_m = \lambda^m E_j^{(m)}$

YET ALTERNATIVELY, ONE CAN SIMPLY USE THE CRITERION

$$\sum_{k=0}^{N} \lambda^k E_m^{(k)} - E_m(\lambda) = O(\lambda^{N+1})$$

LIKEWISE,

$$c_{m,j}(\lambda) = c_{m,j}^{(0)} + \lambda c_{m,j}^{(1)} + \lambda^2 c_{m,j}^{(2)} + \cdots$$

AND, THEREFORE,

$$|\psi_m\rangle = \sum_j c_{m,j}(\lambda)\, |\varphi_j^{(0)}\rangle = \sum_{jk} \lambda^k c_{m,j}^{(k)} |\varphi_j^{(0)}\rangle$$

$$= \underbrace{\sum_j c_{m,j}^{(0)} |\varphi_j^{(0)}\rangle}_{\text{ZEROTH ORDER CORRECTION}} + \lambda \underbrace{\overbrace{\sum_j c_{m,j}^{(1)} |\varphi_j^{(0)}\rangle}^{|\psi_m^{(1)}\rangle}}_{\text{1st ORDER CORRECTION}} + \lambda^2 \underbrace{\overbrace{\sum_j c_{m,j}^{(2)} |\varphi_j^{(0)}\rangle}^{|\psi_m^{(2)}\rangle}}_{\text{2ND ORDER CORRECTION}} + \cdots$$

FOR $\lambda \to 0$, WE EXPECT $c_{m,j}^{(0)} = \delta_{m,j}$

$$\Rightarrow \quad |\psi_m\rangle = |\psi_m^{(0)}\rangle + \lambda |\psi_m^{(1)}\rangle + \lambda^2 |\psi_m^{(2)}\rangle + \cdots$$

(UP TO NORMALIZATION)

WHERE $|\psi_m^{(k)}\rangle = \sum_j c_{m,j}^{(k)} |\varphi_j^{(0)}\rangle$

NOW, WE APPLY IT ON THE TIME-INDEPENDENT SCHRÖDINGER EQUATION

$$H|\varphi_m\rangle = E_m|\varphi_m\rangle$$

$$\Rightarrow \left(H_0 + \lambda W\right)\left(|\varphi_m^{(0)}\rangle + \lambda|\varphi_m^{(1)}\rangle + \lambda^2|\varphi_m^{(2)}\rangle + \cdots \right) =$$

$$\left(E_m^{(0)} + \lambda E_m^{(1)} + \lambda^2 E_m^{(2)} + \cdots\right)\left(|\varphi_m^{(0)}\rangle + \lambda|\varphi_m^{(1)}\rangle + \lambda^2|\varphi_m^{(2)}\rangle + \cdots\right)$$

AS THIS EQUATION IS A POLYNOMIAL FOR λ, THEN

λ^0: $\quad H_0|\varphi_m^{(0)}\rangle = E_m^{(0)}|\varphi_m^{(0)}\rangle \rightarrow \left(H_0 - E_m^{(0)}\right)|\varphi_m^{(0)}\rangle = 0$

λ^1: $\quad H_0|\varphi_m^{(1)}\rangle + W|\varphi_m^{(0)}\rangle = E_m^{(0)}|\varphi_m^{(1)}\rangle + E_m^{(1)}|\varphi_m^{(0)}\rangle$

λ^2: $\quad H_0|\varphi_m^{(2)}\rangle + W|\varphi_m^{(1)}\rangle = E_m^{(0)}|\varphi_m^{(2)}\rangle + E_m^{(1)}|\varphi_m^{(1)}\rangle + E_m^{(2)}|\varphi_m^{(0)}\rangle$

$\vdots$

SOLVE THE PROBLEM ORDER BY ORDER IN λ STARTING FROM THE LOWEST ORDER

<u>NORMALIZATION</u>:

$$\langle\varphi_m|\varphi_m\rangle = 1 = N^2\left(\langle\varphi_m^{(0)}| + \lambda\langle\varphi_m^{(1)}| + \lambda^2\langle\varphi_m^{(2)}| + \cdots\right)\left(|\varphi_m^{(0)}\rangle + \lambda|\varphi_m^{(1)}\rangle + \lambda^2|\varphi_m^{(2)}\rangle + \cdots\right)$$

$$= N^2\Big(1 + \lambda\left(\langle 1|0\rangle + \langle 0|1\rangle\right) + \lambda^2\left(\langle 0|2\rangle + \langle 1|1\rangle + \langle 2|0\rangle\right) + \cdots\Big)$$

* ESCOLHA DA FASE DE $|\varphi_m\rangle$

CONVENIENTLY, WE CHOOSE $\langle\varphi_m^{(0)}|\varphi_m\rangle \in \mathbb{R}$

THUS,

$$\langle \varphi_m^{(0)} | \left(|\varphi_n^{(0)}\rangle + \lambda |\varphi_n^{(1)}\rangle + \lambda^2 |\varphi_n^{(2)}\rangle + \cdots \right)$$

$$= 1 + \lambda \langle 0|1\rangle + \lambda^2 \langle 0|2\rangle + \cdots \in \mathbb{R}, \ \forall \lambda$$

$$\Rightarrow \langle \varphi_n^{(0)} | \varphi_m^{(j)} \rangle \in \mathbb{R}, \ \forall j$$

FROM NORMALIZATION

$$1 = N^2 \left(1 + \lambda \underbrace{\left(\langle 1|0\rangle + \langle 0|1\rangle \right)}_{=0} + \lambda^2 (\cdots) + \cdots \right)$$

SINCE $\langle 0|1\rangle$ IS REAL $\Rightarrow$ $\boxed{\langle 0|1\rangle = 0}$

LIKEWISE FOR THE 2ND ORDER IN λ:

$$\langle 0|2\rangle + \langle 2|0\rangle + \langle 1|1\rangle$$

AGAIN, CHOOSE $\langle 0|2\rangle = 0$. IN FACT, LET US CHOOSE $\langle 0|k\rangle = 0, \ \forall k \neq 0$

THIS MEANS THAT

$$|\varphi_m^{(k)}\rangle = \sum_j c_{mj}^{(k)} |\varphi_j^{(0)}\rangle = \sum_{j \neq m} c_{mj}^{(k)} |\varphi_j^{(0)}\rangle$$

BECAUSE WE WANT THE PERTURBATIONS TO BE <u>ORTHOGONAL</u> TO THE UNPERTURBED STATE

THUS, UP TO 2ND ORDER, THE NORMALIZATION IS

$$1 = N^2\left(1 + 0 + \lambda^2\langle 1|1\rangle\right)$$

COMING BACK TO THE SCHRÖDINGER EQ.

ZEROTH ORDER: $H_0|\varphi_n^{(0)}\rangle = E_n^{(0)}|\varphi_n^{(0)}\rangle$

1ST ORDER: $H_0|\varphi_n^{(1)}\rangle + W|\varphi_n^{(0)}\rangle = E_n^{(0)}|\varphi_n^{(1)}\rangle + E_n^{(1)}|\varphi_n^{(0)}\rangle$

TO SOLVE FOR $E_n^{(1)}$, THEN $\langle\varphi_n^{(0)}|$ (1ST ORDER EQUATION)

$$\cancelto{0}{\underbrace{\langle\varphi_n^{(0)}|H_0}_{E_n^{(0)}\langle\varphi_n^{(0)}|}|\varphi_n^{(1)}\rangle} + \langle\varphi_n^{(0)}|W|\varphi_n^{(0)}\rangle =$$

$$E_n^{(0)}\cancelto{0}{\langle\varphi_n^{(0)}|\varphi_n^{(1)}\rangle} + E_n^{(1)}\cancelto{1}{\langle\varphi_n^{(0)}|\varphi_n^{(0)}\rangle}$$

$$\Rightarrow \boxed{E_n^{(1)} = \langle\varphi_n^{(0)}|W|\varphi_n^{(0)}\rangle}$$

THE CORRECTION IN ENERGY IS THE EXPECTATION VALUE OF THE PERTURBATION ON THE CORRESPONDING UNPERTURBED STATE.

NOTICE $E = E^{(0)} + \lambda E^{(1)} + \dots$

$$\Rightarrow \lambda E^{(1)} = \lambda\langle 0|W|0\rangle = \langle 0|\lambda W|0\rangle = \langle 0|V|0\rangle$$
$$= \Delta E^{(1)}$$

THE 1st ORDER CORRECTION TO THE STATE IS OBTAINED AS FOLLOWS

$$H_0|\varphi_m^{(1)}\rangle + W|\varphi_m^{(0)}\rangle = E_m^{(0)}|\varphi_m^{(1)}\rangle + E_m^{(1)}|\varphi_m^{(0)}\rangle$$

$$\Rightarrow H_0\left(\sum_{j\neq m} C_{mj}^{(1)}|\varphi_j^{(0)}\rangle\right) + W|\varphi_m^{(0)}\rangle = E_m^{(0)}\left(\sum_{j\neq m} C_{mj}^{(1)}|\varphi_j^{(0)}\rangle\right) + E_m^{(1)}|\varphi_m^{(0)}\rangle$$

$$\Rightarrow \underset{k\neq m}{\langle\varphi_k^{(0)}|}\left(W|\varphi_m^{(0)}\rangle = \sum_{j\neq m} C_{mj}^{(1)}\left(E_m^{(0)} - E_j^{(0)}\right)|\varphi_j^{(0)}\rangle + E_m^{(1)}|\varphi_m^{(0)}\rangle\right)$$

$$\Rightarrow \langle\varphi_k^{(0)}|W|\varphi_m^{(0)}\rangle = C_{mk}^{(1)}\left(E_m^{(0)} - E_k^{(0)}\right)$$

$$\Rightarrow C_{mk}^{(1)} = \frac{\langle\varphi_k^{(0)}|W|\varphi_m^{(0)}\rangle}{E_m^{(0)} - E_k^{(0)}}$$

$$\Rightarrow \boxed{|\varphi_m^{(1)}\rangle = \sum_{j\neq m} \frac{\langle\varphi_j^{(0)}|W|\varphi_m^{(0)}\rangle}{E_m^{(0)} - E_j^{(0)}}|\varphi_j^{(0)}\rangle}$$

THUS, UP TO 1st ORDER IN λ

$$|\varphi_m\rangle = |\varphi_m^{(0)}\rangle + \sum_{j\neq m} \frac{\langle\varphi_j^{(0)}|\lambda W|\varphi_m^{(0)}\rangle}{E_m^{(0)} - E_j^{(0)}}|\varphi_j^{(0)}\rangle$$

THESE RESULTS ARE ACCURATE IF

$$\underbrace{\lambda \langle \varphi_{k \neq m}^{(0)}| W | \varphi_m^{(0)} \rangle}_{\downarrow} \ll | E_m^{(0)} - E_k^{(0)} |$$

WHEN $m \to$ ENERGY DOES NOT CHANGE MUCH

WHEN $k \to$ STATE " " " "

ONCE WE HAVE THE 1ST ORDER CORRECTIONS TO THE ENERGY AND STATE, WE CAN PROCEED TO THE 2ND ORDER CORRECTIONS.

IN ENERGY:

$$\langle \varphi_m^{(0)} | \left(H_0 |\varphi_m^{(2)}\rangle + W |\varphi_m^{(1)}\rangle = E_m^{(0)} |\varphi_m^{(2)}\rangle + E_m^{(1)} |\varphi_m^{(1)}\rangle + E_m^{(2)} |\varphi_m^{(0)}\rangle \right)$$

$$E_m^{(0)} \cancel{\langle \varphi_m^{(0)} | \varphi_m^{(2)} \rangle} + \langle \varphi_m^{(0)} | W | \varphi_m^{(1)} \rangle = E_m^{(0)} \cancel{\langle \varphi_m^{(0)} | \varphi_m^{(2)} \rangle} + E_m^{(1)} \cancel{\langle \varphi_m^{(0)} | \varphi_m^{(1)} \rangle} + E_m^{(2)}$$

0 0 0

$$\Rightarrow E_m^{(2)} = \langle \varphi_m^{(0)} | W \left(\sum_{j \neq m} \frac{\langle \varphi_j^{(0)} | W | \varphi_m^{(0)} \rangle}{E_m^{(0)} - E_j^{(0)}} | \varphi_j^{(0)} \rangle \right)$$

$$\boxed{E_m^{(2)} = \sum_{j \neq m} \frac{|\langle \varphi_j^{(0)} | W | \varphi_m^{(0)} \rangle|^2}{E_m^{(0)} - E_j^{(0)}}}$$

IN SUM,

$$\boxed{E_m = E_m^{(0)} + \langle \varphi_m^{(0)} | \lambda W | \varphi_m^{(0)} \rangle + \sum_{j \neq m} \frac{\langle \varphi_m^{(0)} | \lambda W | \varphi_j^{(0)} \rangle \langle \varphi_j^{(0)} | \lambda W | \varphi_m^{(0)} \rangle}{E_m^{(0)} - E_j^{(0)}} + O(\lambda^3)}$$

WE CAN NOW COMPUTE THE CORRECTION TO THE STATE (WHICH IS NOT SOMETHING THAT IS USUALLY NEEDED IN PRACTICE)

AS $|\varphi_m^{(k)}\rangle = \sum_{j\neq m} c_{mj}^{(k)} |\varphi_j^{(0)}\rangle$ AND $(H_0 - E_m^{(0)})|2\rangle + (W - E_m^{(1)})|1\rangle = E_m^{(2)}|0\rangle$

$$\Rightarrow \sum_{j\neq m} c_{mj}^{(2)}\left(E_j^{(0)}-E_m^{(0)}\right)|\varphi_j^{(0)}\rangle + \sum_{j\neq m} c_{mj}^{(1)}\left(W-E_m^{(1)}\right)|\varphi_j^{(0)}\rangle = E_m^{(2)}|\varphi_m^{(0)}\rangle$$

$\langle\varphi_k^{(0)}| \Rightarrow$ ($k\neq m$)

$$c_{mk}^{(2)}\left(E_k^{(0)}-E_m^{(0)}\right) + \sum_{j\neq m} c_{mj}^{(1)}\langle\varphi_k^{(0)}|W|\varphi_j^{(0)}\rangle = c_{mk}^{(1)}E_m^{(1)}$$

$$\Rightarrow c_{mk}^{(2)} = \sum_{j\neq m} \frac{\langle\varphi_j^{(0)}|W|\varphi_m^{(0)}\rangle\langle\varphi_k^{(0)}|W|\varphi_j^{(0)}\rangle}{\left(E_m^{(0)}-E_j^{(0)}\right)\left(E_m^{(0)}-E_k^{(0)}\right)} - \frac{\langle\varphi_k^{(0)}|W|\varphi_m^{(0)}\rangle\langle\varphi_m^{(0)}|W|\varphi_m^{(0)}\rangle}{\left(E_m^{(0)}-E_k^{(0)}\right)^2}$$

$$= \sum_{j\neq m}\frac{W_{kj}\,W_{jm}}{\left(E_m^{(0)}-E_j^{(0)}\right)\left(E_m^{(0)}-E_k^{(0)}\right)} - \frac{W_{km}\,W_{mm}}{\left(E_m^{(0)}-E_k^{(0)}\right)^2}$$

IN SUM,

$$\boxed{|\varphi_m\rangle = |\varphi_m^{(0)}\rangle + \sum_{j\neq m}\left[\frac{\langle\varphi_j^{(0)}|\lambda W|\varphi_m^{(0)}\rangle}{E_m^{(0)}-E_j^{(0)}}\left(1 - \frac{\langle\varphi_m^{(0)}|\lambda W|\varphi_m^{(0)}\rangle}{E_m^{(0)}-E_j^{(0)}}\right) + \sum_{k\neq m}\frac{\langle\varphi_j^{(0)}|\lambda W|\varphi_k^{(0)}\rangle\langle\varphi_k^{(0)}|\lambda W|\varphi_m^{(0)}\rangle}{\left(E_m^{(0)}-E_k^{(0)}\right)\left(E_m^{(0)}-E_j^{(0)}\right)}\right]|\varphi_m^{(0)}\rangle + O(\lambda^3)}$$

HOWEVER, UP TO 2ND ORDER, THE NORMALIZATION CONSTANT IS DIFFERENT FROM 1 AND HAS TO BE WORKED OUT (SEE PAGE 7)

EXAMPLE: $H = \underbrace{\frac{P^2}{2m} + \frac{m\omega^2}{2} X^2}_{H_0} + \underbrace{\lambda X}_{\text{PERTURBATION}}$

THIS PROBLEM HAS EXACT SOLUTION AS IT IS A SIMPLE HARMONIC OSCILLATOR SHIFTED FROM ORIGIN

$$H = \frac{P^2}{2m} + \frac{1}{2} m\omega^2 \left(X + \frac{\lambda}{m\omega^2} \right)^2 - \frac{\lambda^2}{2m\omega^2}$$

THUS, ENERGIES $= E_n = \hbar\omega(n + \frac{1}{2}) - \frac{\lambda^2}{2m\omega^2}$ (EXACT)

EIGENSTATES: SAME AS THOSE OF H_0 BUT SHIFTED

$$x \to x + \frac{\lambda}{m\omega^2}$$

$$|\varphi_n^{(0)}\rangle \to |\varphi_n\rangle = e^{i P \frac{\Delta x}{\hbar}} |\varphi_n^{(0)}\rangle = \underbrace{e^{i P \frac{\lambda}{m\omega^2 \hbar}}}_{\text{SPATIAL TRANSLATION OPERATOR}} |\varphi_n^{(0)}\rangle$$

PERTURBATION THEORY: RECALL THAT

$$\begin{cases} X = \sqrt{\frac{\hbar}{2m\omega}} (a + a^\dagger) \\ P = i \sqrt{\frac{\hbar m\omega}{2}} (a^\dagger - a) \end{cases}$$

$$H_0 = \hbar\omega(a^\dagger a + \tfrac{1}{2})$$

$$V = \lambda X = \lambda \sqrt{\frac{\hbar}{2m\omega}} (a^\dagger + a)$$

$$a|\varphi_n^{(0)}\rangle = \sqrt{n}\, |\varphi_{n-1}^{(0)}\rangle$$

$$a^\dagger|\varphi_n^{(0)}\rangle = \sqrt{n+1}\, |\varphi_{n+1}^{(0)}\rangle$$

1st ORDER: $E_n^{(1)} = \langle \varphi_n^{(0)} | \lambda X | \varphi_n^{(0)} \rangle = 0$ (NO CORRECTION IN 1st ORDER)

2ND ORDER: $E_n^{(2)} = \sum_{j\neq n} \frac{|\langle \varphi_j^{(0)} | \lambda X | \varphi_n^{(0)} \rangle|^2}{(n-j)\hbar\omega}$

BUT $\langle \varphi_j^{(0)} | X | \varphi_n^{(0)} \rangle = \sqrt{\frac{\hbar}{2m\omega}} \left(\underbrace{\langle \varphi_j^{(0)} | a | \varphi_n^{(0)} \rangle}_{\sqrt{n}\,\delta_{j,n-1}} + \underbrace{\langle j | a^+ | n \rangle}_{\sqrt{n+1}\,\delta_{j,n+1}} \right)$

$$\Rightarrow E_n^{(2)} = \frac{\lambda^2 \hbar}{2m\omega} \times \left(\frac{n}{\hbar\omega} + \frac{n+1}{(-\hbar\omega)} \right) = \frac{-\lambda^2}{2m\omega^2}$$

(JUST LIKE THE EXACT RESULT)

CORRECTION TO THE STATE

UP TO 1ST ORDER: $|\varphi_n\rangle = |\varphi_n^{(0)}\rangle + \sum_{j\neq n} \frac{\langle \varphi_j^{(0)} | \lambda X | \varphi_n^{(0)} \rangle}{E_n^{(0)} - E_j^{(0)}} |\varphi_j^{(0)}\rangle$

$$\Rightarrow |\varphi_n\rangle = |\varphi_n^{(0)}\rangle + \lambda \sqrt{\frac{n\hbar}{2m\omega}} \frac{|\varphi_{n-1}^{(0)}\rangle}{\hbar\omega} + \lambda \sqrt{\frac{(n+1)\hbar}{2m\omega}} \frac{|\varphi_{n+1}^{(0)}\rangle}{(-\hbar\omega)}$$

HOW ABOUT THE EXACT STATE?

$$|\varphi_n\rangle = e^{\frac{i P \lambda}{\hbar m \omega^2}} |\varphi_n^{(0)}\rangle = \left(1 + \frac{i P \lambda}{\hbar m \omega^2} + O(\lambda^2) \right) |\varphi_n^{(0)}\rangle$$

$$= |\varphi_n^{(0)}\rangle - \sqrt{\frac{\hbar m \omega}{2}} (a^+ - a) \frac{\lambda}{\hbar m \omega^2} |\varphi_n^{(0)}\rangle + O(\lambda^2)$$

$$= |\varphi_n^{(0)}\rangle + \sqrt{\frac{\hbar n}{2m\omega}} \frac{|\varphi_{n-1}^{(0)}\rangle}{\hbar\omega} - \sqrt{\frac{\hbar(n+1)}{2m\omega}} \frac{|\varphi_{n+1}^{(0)}\rangle}{\hbar\omega} + O(\lambda^2)$$

WHICH MATCHES THE RESULT FROM PERT. THEORY.

ESTIMATING THE ERROR WHEN CORRECTING THE ENERGY

- SUPPOSE YOU COMPUTE THE CORRECTION TO THE ENERGY IN 1st ORDER. WHAT IS THE ERROR ASSOCIATED TO THIS CORRECTION.

ANSWER: IF THE TAYLOR SERIES EXISTS AND CONVERGES RAPIDLY, THE 2ND ORDER CORRECTION GIVES US A GOOD ESTIMATE FOR THIS ERROR

$$E_m = E_m^{(0)} + E_m^{(1)} + \text{ERROR}$$

$$\text{ERROR} \sim E_m^{(2)} = \sum_{j\neq m} \frac{\left|\langle \varphi_j^{(0)} | \lambda W | \varphi_m^{(0)} \rangle\right|^2}{E_m^{(0)} - E_j^{(0)}} \leq \frac{1}{\Delta E_m^{(0)}} \sum_{j\neq m} |W_{jm}|^2$$

WHERE $\Delta E^{(0)} = \min \left\{ E_m^{(0)} - E_j^{(0)} \right\}\Big|_{\text{WITH } j\neq m}$ ≡ SMALLEST ENERGY GAP IN THE SPECTRUM OF H_0

IN ADDITION $\sum_{j\neq m} |W_{jm}|^2 = \sum_j |W_{jm}|^2 - |W_{mm}|^2$

BUT $\sum_j |W_{jm}|^2 = \sum_j W_{mj} W_{jm} = \sum_j \langle \varphi_m^{(0)} | W\lambda | \varphi_j^{(0)} \rangle \langle \varphi_j^{(0)} | \lambda W | \varphi_m^{(0)} \rangle = \langle \varphi_m^{(0)} | (\lambda W)^2 | \varphi_m^{(0)} \rangle$

$$\boxed{\Rightarrow \text{ERROR} \sim \frac{1}{\Delta E_m^{(0)}} (\Delta W)_m^2}$$

WHERE $(\Delta W)_m^2 = \langle \varphi_m^{(0)} | (\lambda W)^2 | \varphi_m^{(0)} \rangle - \left| \langle \varphi_m^{(0)} | \lambda W | \varphi_m^{(0)} \rangle \right|^2$

= DISPERSION OF THE PERTURBATION ON THE UNPERTURBED STATE

DEGENERATE PERTURBATION THEORY

SAY THERE IS A LEVEL OF H_0 WHICH IS DEGENERATE (g_m TIMES DEGENERATE)

$$H_0 |\varphi^{(0)}_{m,\alpha}\rangle = E^{(0)}_m |\varphi^{(0)}_{m,\alpha}\rangle , \quad \alpha = 1, 2, \cdots, g_m$$

AS IN THE NON-DEGENERATE CASE (SEE PAGE 5)

ZEROTH-ORDER : $H_0 |\phi^{(0)}_{m,\alpha}\rangle = E^{(0)}_m |\phi^{(0)}_{m,\alpha}\rangle$

WHERE $$|\phi^{(0)}_{m,\alpha}\rangle = \sum_{\beta=1}^{g_m} d_{\alpha\beta,m} |\varphi^{(0)}_{m,\beta}\rangle$$

AND WE REQUIRE $\langle \phi^{(0)}_{m,\alpha} | \phi^{(0)}_{m,\beta}\rangle = \delta_{\alpha\beta}$

THIS IS A TRIVIAL RESULT AS ANY LINEAR COMBINATION ~~FROM~~ OF DEGENERATE EIGENSTATES IS ALSO AN EIGENSTATE

1st ORDER : $H_0 |\phi^{(1)}_{m\alpha}\rangle + W |\phi^{(0)}_{m\alpha}\rangle = E^{(0)}_m |\phi^{(1)}_{m\alpha}\rangle + E^{(1)}_{m\alpha} |\phi^{(0)}_{m\alpha}\rangle$

THE CORRECTION MAY DEPEND ON α, i.e., THE PERTURBATION MAY LIFT THE DEGENERACY

PROJECTING ONTO $\langle \varphi^{(0)}_{m\beta}|$

$$\Rightarrow \underbrace{\langle \varphi^{(0)}_{m\beta} | H_0 | \phi^{(1)}_{m\alpha}\rangle}_{\cancel{E^{(0)}_m \langle \varphi^{(0)}_{m\beta} | \phi^{(1)}_{m\alpha}\rangle}} + \langle \varphi^{(0)}_{m\beta} | W | \phi^{(0)}_{m\alpha}\rangle = \cancel{E^{(0)}_m \langle \varphi^{(0)}_{m\beta} | \phi^{(1)}_{m\alpha}\rangle} + E^{(1)}_{m\alpha} \underbrace{\langle \varphi^{(0)}_{m\beta} | \phi^{(0)}_{m\alpha}\rangle}_{d_{\alpha\beta,m}}$$

$$\Rightarrow \sum_{\gamma} \langle \varphi^{(0)}_{m\beta} | W | \varphi^{(0)}_{m\gamma} \rangle d_{\alpha\gamma} = E^{(1)}_{m\alpha} d_{\alpha\beta,m}$$

$$\Rightarrow \sum_{\gamma} W_{\beta\gamma\,(m)} d_{\alpha\gamma} = E^{(1)}_{m\alpha} d_{\alpha\beta(m)}$$

NOTICE SUB-INDICES α AND m ARE DOING NOTHING.

THIS IS ANALOGOUS TO $\sum_{\alpha} W_{\beta\gamma} d_{\gamma} = E^{(1)} d_{\beta}$

OR, IN MATRIX REPRESENTATION, $\mathbb{W} \vec{d} = E^{(1)} \vec{d}$.

$\Rightarrow$ IN, 1st ORDER, WE NEED TO DIAGONALIZE $\mathbb{W}$ IN THE DEGENERATE SUBSPACE

$\Rightarrow$ DET $\left(\mathbb{W} - \mathbb{1} E^{(1)} \right) = 0 \to g_m$ EIGENVALUES $E^{(1)}_{\alpha}$, $\alpha = 1, 2, \dots, g_m$

THE CORRESPONDING EIGENVECTORS OF $\mathbb{W}$ CORRESPOND TO THE ZEROTH ORDER $\{ |\phi^{(0)}_{m\alpha}\rangle \}$

CORRECTIONS TO THE STATES AND/OR FURTHER CORRECTIONS ARE OBTAINED IN SIMILAR WAY AS IN THE NON-DEGENERATE CASE

EXEMPLE: ZEEMAN EFFECT (NEGLECTING SPIN! LATER WE WILL ADD IT)

(SPLITTING OF SPECTRAL LINES DUE TO A MAGNETIC FIELD)

$H = H_0 + \lambda W$, H = HYDROGEN ATOM IN A CONSTANT MAGNETIC FIELD

$= \frac{1}{2m} \left| \vec{p} - q\vec{A} \right|^2 - \frac{q^2}{r}$, $\boxed{q = -e}$ WHERE $\vec{B} = \nabla \times \vec{A}$ VECTOR POTENTIAL

$= \frac{p^2}{2m} - \frac{q}{2m}\left(\vec{p}\cdot\vec{A} + \vec{A}\cdot\vec{p}\right) - \frac{q^2}{r} + \frac{q^2 A^2}{2m}$

TAKE $\vec{A} = \frac{B_0}{2}(-y, x, 0)$ (SYMMETRIC GAUGE)

$\Rightarrow \boxed{\vec{B} = B_0 \hat{z}}$

THE EFFECTS OF THE MAGNETIC FIELD ARE ASSUMED TO BE WEAK

$\Rightarrow H_0 = \frac{1}{2m} p^2 - \frac{q^2}{r}$ (UNPERTURBED H ATOM)

$\lambda W = -\frac{q}{2m}\left(\vec{p}\cdot\vec{A} + \vec{A}\cdot\vec{p}\right) + \underbrace{\frac{1}{2m} q^2 A^2}$

NEGLECT → ONLY IMPORTANT IN 2^{ND} ORDER CORRECTIONS

* SHOW THAT ~~[scribbled]~~ $\vec{p}\cdot\vec{A} = \vec{A}\cdot\vec{p}$

$\vec{p}\cdot\vec{A} = p_x\left(-\frac{B_0 y}{2}\right) + p_y\left(\frac{B_0 x}{2}\right) = B_0 \frac{x}{2} p_y + \left(-\frac{B_0 y}{2}\right) p_x = \vec{A}\cdot\vec{p}$

THIS IS A "GENERIC" RESULT BECAUSE $\nabla\cdot\vec{A} = 0$

$\vec{p}\cdot\vec{A}\,\psi = -i\hbar\nabla\cdot(\vec{A}\psi) = -i\hbar\underbrace{(\nabla\cdot\vec{A})}_{=0}\psi - i\hbar\vec{A}\cdot\nabla\psi = \vec{A}\cdot\vec{p}\,\psi$

$\Rightarrow \lambda W = -\frac{q}{m}\vec{A}\cdot\vec{p} = -\frac{q}{m}\frac{B_0}{2}\left(x p_y - y p_x\right) = -\frac{q B_0}{2m} L_z$ (q → $(-e)$)

$g_L = 1$ (GYROMAGNETIC FACTOR)

→ BOHR MAGNETON $\mu_B \equiv \frac{\hbar e}{2m_e}$ $\Rightarrow$ $\boxed{\lambda W = + B_0 \mu_B \frac{L_z}{\hbar} = -\vec{\mu}_L\cdot\vec{B}}$

$-g_L \mu_B \frac{\vec{L}}{\hbar} = \vec{\mu}_L$ = MAGNETIC MOMENT DUE TO THE ORBITAL ANGULAR MOMENTUM

RECALLING THE H ATOM

$$E_n^{(0)} = -\frac{Ry}{n^2} \quad , \qquad Ry \equiv \text{RYDBERG UNIT OF ENERGY} = 13.605\,693\ldots \text{ eV}$$

$n = 1, 2, 3 \ldots$

DEGENERACIES : $g_n = n^2$, $\{|\varphi^{(0)}_{n,\alpha}\rangle\} = \{|n\,\ell\, m\rangle\}$, $\alpha = 1, 2, \ldots, g_n$

LEVEL $n = 1$ (NON-DEGENERATE)

$n = 2$ ($g_n = 4$, $\ell = 0$, $m = 0$ AND $\ell = 1$, $m = -1, 0, 1$)

1ST ORDER CORRECTION

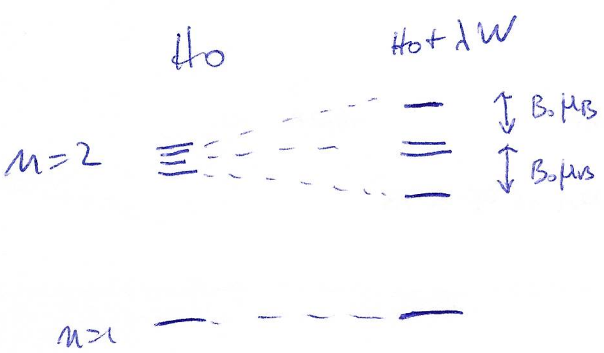
$$n = 1 \rightarrow \quad E^{(1)}_{n=1} = \langle \varphi_1^{(0)} | \left(-\frac{B_0 \mu_B}{\hbar} L_z \right) \underbrace{|\varphi_1^{(0)}\rangle}_{\hbar m |\varphi_1^{(0)}\rangle,\ m \to 0} = 0$$

$$\underline{n=2} \rightarrow \{|n\,\ell\,m\rangle\} = \left\{ \begin{array}{l} |2\,0\,0\rangle \\ |2\,1\,-1\rangle \\ |2\,1\,0\rangle \\ |2\,1\,+1\rangle \end{array} \right.$$

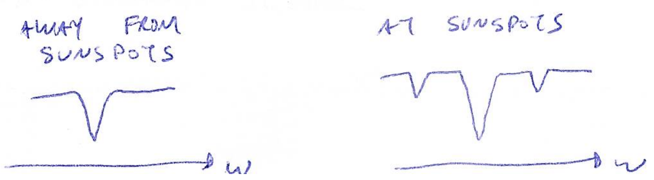
$\rightarrow$ PROJECT λW ON THIS SUBSPACE

$$\langle 2\,\ell' m' | \lambda W | 2\,\ell\, m\rangle = -\frac{B_0 \mu_B}{\hbar} \delta_{\ell\ell'} \delta_{m m'} (m\hbar)$$

$$\Rightarrow \lambda W = \begin{array}{c} \begin{array}{cccc} |200\rangle & |21{-1}\rangle & |210\rangle & |211\rangle \end{array} \\ \left(\begin{array}{c|ccc} 0 & 0 & 0 & 0 \\ \hline 0 & B_0\mu_B & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & -B_0\mu_B \end{array} \right) \end{array}$$



CURIOSITY : THIS SPLITTING IS OBSERVED IN THE ABSORPTION SPECTRUM OF THE SUN IN SUNSPOTS WHERE THE MAGNETIC FIELD IS "HIGH"



EXAMPLE: STARK EFFECT

(SHIFTING AND SPLITTING OF SPECTRAL LINES DUE TO ELECTRIC FIELD)

H ≡ HYDROGEN ATOM IN AN EXTERNAL CONSTANT ELECTRIC FIELD

$$H = \frac{p^2}{2m_e} - \frac{q^2}{r} + q\phi \quad , \quad \vec{E} = -\nabla\phi = E_0\hat{z} \quad , \quad \phi \equiv \text{SCALAR POTENTIAL} \Rightarrow \phi = -E_0 z$$

$$= H_0 + \underbrace{eE_0 r\cos\theta}_{\lambda W}$$

1st ORDER CORRECTION

$\underline{n=1}$ → $\langle 100 | eE_0 r\cos\theta | 100\rangle = \int d\vec{r}\, \psi^*_{100}(\vec{r})\, eE_0 r\cos\theta\, \psi_{100}(\vec{r})$

$$\psi_{100} = R_{10}(r)\, Y_{00}(\theta,\phi) \quad , \quad R_{10} = \frac{2e^{-r/a_0}}{a_0^{3/2}} \quad , \quad a_0 \equiv \text{BOHR RADIUS} = \frac{\hbar^2}{m_e e^2}$$

$$Y_{00} = \sqrt{\frac{1}{4\pi}}$$

NOTICE THAT

$$Y_{10} = \sqrt{\frac{3}{4\pi}}\cos\theta$$

$$Y_{1\pm1} = \sqrt{\frac{3}{8\pi}}\sin\theta\, e^{\pm i\phi}$$

$$\Rightarrow \langle 100 | \lambda W | 100\rangle \propto \int d\Omega\, Y^*_{00} Y_{10} Y_{00} \propto \int d\Omega\, Y_{10} = 0$$

NO CORRECTION IN 1st ORDER TO THE n=1 LEVEL

$\underline{n=2}$ → $\langle 2 l' m' | \lambda W | 2 l m\rangle$ NOTICE THAT $[W, L_z] \propto [z, L_z] = 0$

$$\Rightarrow \langle 2l'm' | WL_z - L_z W | 2lm\rangle = 0 = \hbar(m-m')\langle 2l'm' | W | 2lm\rangle$$

$\Rightarrow$ IF $m \neq m'$ $\Rightarrow \langle 2l'm' | W | 2lm\rangle = 0$

↓

REGRA DE SELEÇÃO

$\langle l'm' | W | lm\rangle = 0$

SE $m \neq m'$

$$\Rightarrow \lambda W = \begin{array}{c} \\ \\ \\ \\ \end{array}\begin{array}{cccc} 200 & 21\text{-}1 & 210 & 211 \end{array}$$

$$\lambda W = \left(\begin{array}{c|cccc} & 200 & 21\text{-}1 & 210 & 211 \\ \hline & (?) & 0 & (?) & 0 \\ & 0 & (?) & 0 & 0 \\ & (?) & 0 & (?) & 0 \\ & 0 & 0 & 0 & (?) \end{array}\right)$$

COMPUTE THE MATRIX ELEMENTS

$$\langle 200|\lambda W|200\rangle \propto \int d\Omega\, Y_{00}^{*} \cos\theta\, Y_{00} \propto \int_0^{\pi} d\theta \sin\theta\cos\theta = 0$$

$$\langle 210|\lambda W|210\rangle \propto \int_0^{\pi} d\theta \sin\theta\cos^3\theta \propto \int_0^{\pi} d\theta\,(e^{i\theta}-e^{-i\theta})(e^{3i\theta}+3e^{i\theta}+3e^{-i\theta}+e^{-3i\theta})$$

$$= \int_0^{\pi} d\theta\; e^{4i\theta} - e^{-4i\theta} + 2e^{2i\theta} - 2e^{-2i\theta} + 3 - 3 \propto \sum_g \int_0^{\pi} d\theta\, e^{\pm i g\theta}$$

$= 0$ FOR g EVEN

$= 0$

$$\langle 21\pm1|\lambda W|21\pm1\rangle \propto \int_0^{\pi} d\theta \sin\theta\, \sin\theta\cos\theta\sin\theta$$

$$\propto \int_0^{\pi} (e^{3i\theta}-3e^{+i\theta}+3e^{-i\theta}-3e^{-3i\theta})(e^{i\theta}+e^{-i\theta}) \propto \sum_g \int_0^{\pi} e^{ig\theta} = 0$$

WITH g EVEN

$= 0$

$\Rightarrow$ ALL DIAGONAL TERMS ARE VANISHING

FINALLY, $$\langle 200|\lambda W|210\rangle = eE_0 \underbrace{\int_0^{\infty} dr\, r^2 R_{20}^{*}(r)\, r\, R_{21}(r)}_{I_R} * \underbrace{\int d\Omega\, Y_{00}^{*} \cos\theta\, Y_{10}}_{I_\Omega}$$

$$R_{20} = \left(\frac{1}{2a_0}\right)^{\frac{3}{2}} \left(2 - \frac{r}{a_0}\right) e^{-\frac{r}{2a_0}}$$

$$R_{21} = \left(\frac{1}{2a_0}\right)^{3/2} \frac{r}{\sqrt{3}\,a_0}\, e^{-\frac{r}{2a_0}}$$

$$I_R = \left(\frac{1}{2a_0}\right)^3 \int_0^{\infty} dr\, r^2 \left(2 - \frac{r}{a_0}\right) \frac{r^2}{\sqrt{3}\,a_0}\, e^{-\frac{r}{a_0}}$$

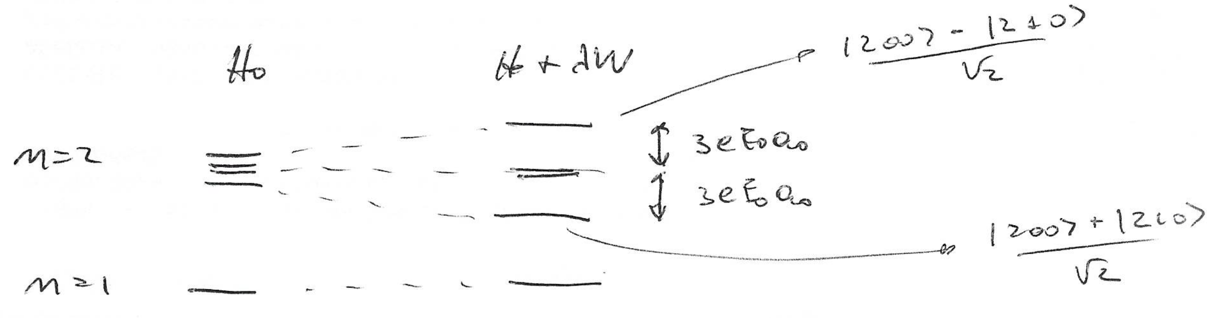
VARIABLE CHANGING: $x = \frac{r}{a_0}$

$$= \frac{a_0}{8\sqrt{3}} \int_0^{\infty} dx\, x^4 (2-x)\, e^{-x} = \frac{a_0}{8\sqrt{3}} \Big[2\underbrace{\int_0^{\infty} dx\, x^4 e^{-x}}_{4!} - \underbrace{\int_0^{\infty} dx\, x^5 e^{-x}}_{5!} \Big] = -\frac{9a_0}{\sqrt{3}}$$

$$I_\Omega = \int d\Omega\, \frac{1}{\sqrt{4\pi}} \sqrt{\frac{4\pi}{3}}\, Y_{10}^{*}\, Y_{10} = \frac{1}{\sqrt{3}}$$

$$\Rightarrow \boxed{\langle 200|\lambda W|210\rangle = -3eE_0 a_0} \quad \Rightarrow \lambda W = \begin{pmatrix} 0 & 0 & \star & 0 \\ 0 & 0 & 0 & 0 \\ \star & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix}$$

AUTO-VALORES: $0, 0, \pm\star$, $\star = -3eE_0 a_0$



*OBS: NO EXPERIMENTO, OS ESTADOS $|200\rangle$ e $\{|21m\rangle\}$ NÃO SÃO DEGENERADOS. HÁ SPIN-ÓRBITA E LAMB SHIFT

RELATIVISTIC CORRECTION TO THE HYDROGEN ATOM
(FINE STRUCTURE)

FINE STRUCTURE

$$H = mc^2 + \frac{P^2}{2m} + V(r) - W_F$$

m = ELECTRON + PROTON REDUCED REST MASS ≃ ELECTRON REST MASS

$$V(r) = \frac{-e^2}{4\pi\epsilon_0 r} = -\frac{\hbar^2}{m a_0^2}\left(\frac{a_0}{r}\right)$$

WHERE $a_0 \equiv \frac{4\pi\epsilon_0 \hbar^2}{m e^2}$ = BOHR RADIUS ≃ 0.529 177 210 Å

IN ADDITION $\alpha = \frac{e^2}{4\pi\epsilon_0 \hbar c} = \frac{e^2}{2\epsilon_0 h c} \simeq \frac{1}{137.035\,999\,177} \simeq \frac{1}{137}$

IS THE FINE STRUCTURE CONSTANT

THUS, $a_0 = \frac{\hbar}{mc}\frac{1}{\alpha} \Rightarrow \boxed{V(r) = -\alpha^2 mc^2\left(\frac{a_0}{r}\right)}$

$$W_F = \underbrace{-\frac{P^4}{8m^3c^2}}_{W_v} + \underbrace{\frac{1}{2m^2c^2}\frac{1}{r}\frac{dV}{dr}\vec{L}\cdot\vec{S}}_{W_{SO}} + \underbrace{\frac{\hbar^2}{8m^2c^2}\nabla^2 V}_{W_D}$$

W_v: RELATIVISTIC CORRECTION TO THE KINETIC ENERGY

W_{SO}: SPIN-ORBIT COUPLING

W_D: DARWIN TERM

ORIGIN AND ORDER OF MAGNITUDE OF THE PERTURBING TERMS

W_v: $$E=\sqrt{(pc)^2+(mc^2)^2} = mc^2\left(1+\frac{1}{2}\frac{p^2c^2}{m^2c^4}-\frac{1}{8}\frac{p^4c^4}{m^4c^8}+\cdots\right)$$

$$\simeq mc^2+\frac{p^2}{2m}-\frac{1}{8}\frac{p^4}{m^3c^2}$$

ORDER OF MAGNITUDE

$$W_v = -\frac{1}{8}mc^2\left(\frac{p}{mc}\right)^4 = \boxed{-\frac{\alpha^4}{8}mc^2\left(\frac{a_0}{\hbar}p\right)^4 = W_v}$$

CLASSICAL CIRCULAR ORBIT $\dfrac{mv^2}{r}=\dfrac{e^2}{4\pi\epsilon_0 r^2}$

IN (OR NOT TOO FAR FROM) THE GROUND STATE

$r\simeq a_0$

$$\Rightarrow \frac{p^2}{m a_0}=\frac{e^2}{4\pi\epsilon_0 a_0^2} \Rightarrow \left(\frac{a_0 p}{\hbar}\right)^2=\frac{e^2 m a_0}{\hbar^2 4\pi\epsilon_0}=\frac{m}{\hbar^2}(\hbar c\alpha)\frac{\hbar}{mc\alpha}=1$$

$\Rightarrow W_v \sim \alpha^4 mc^2$ (HOW DOES IT COMPARE WITH H_0?)

$H_0=\dfrac{p^2}{2m}+V(r)$ FROM VIRIAL THEOREM

$2\langle T\rangle = n\langle V\rangle$, WHERE $V=ar^n$

$\Rightarrow 2\left\langle \dfrac{p^2}{2m}\right\rangle = -\langle V\rangle$

$\Rightarrow H_0 \sim \frac{1}{2}V(r)$, $r=a_0$

$\rightarrow -\dfrac{\alpha^2}{2}mc^2$

FINALLY, $\boxed{\dfrac{W_v}{H_0}\sim\dfrac{\alpha^4 mc^2}{\alpha^2 mc^2}=\alpha^2} \Rightarrow \dfrac{W_v}{H_0}\sim\left(\dfrac{1}{137}\right)^2$

INTERESTINGLY, $\dfrac{W_v}{H_0}\sim\dfrac{p^4/m^3c^2}{p^2/m}=\dfrac{p^2}{m^2c^2}=\left(\dfrac{v}{c}\right)^2$

$\Rightarrow$ IN THE GROUND STATE, $\boxed{v\sim\alpha c}$

W_{SO}: IN THE PROTON'S REFERENCE FRAME, THE ELECTRON SEES AN ELECTRIC FIELD $\vec{E} = -\frac{1}{e}\frac{dV}{dr}\hat{r}$

HOWEVER, DUE TO LORENTZ TRANSFORMATION, IN THE ELECTRON'S REFERENCE FRAME, THE ELECTRON SEES A MAGNETIC FIELD $B \sim -\frac{\gamma}{c^2}\vec{v}\times\vec{E} \sim -\frac{1}{c^2}\vec{v}\times\vec{E}$

THIS IS THE TRANSFORMATION FOR CONSTANT $\vec{v}$

HOWEVER, FOR A CIRCULAR MOTION, THE CORRECT TRANSFORMATION PICKS UP A $\frac{1}{2}$ FACTOR (KNOWN AS THOMAS' FACTOR)

$$\Rightarrow \vec{B} \simeq -\frac{1}{2c^2}\vec{v}\times\vec{E}$$

THIS MAGNETIC FIELD INTERACTS WITH THE ELECTRON'S SPIN

$$\Rightarrow W_{SO} = -\vec{\mu}_S \cdot \vec{B}$$

, $\vec{\mu}_S$ = ELECTRON'S SPIN MAGNETIC MOMENT

$$= -g\mu_B\frac{\vec{\sigma}}{2} = g\mu_B\frac{\vec{S}}{\hbar}$$

GYROMAGNETIC FACTOR $= 2.002\ 319\ 304\ 360\ 92(36)$

BOHR MAGNETON $= \frac{e\hbar}{2m_e}$

$\mu_B \simeq 9{,}27\cdot 10^{-24}\,\frac{J}{T}$

$\simeq 9{,}27\cdot 10^{-21}\,\frac{Erg}{G}$

$\simeq 5.79\cdot 10^{-5}\,\frac{eV}{T}$

$= \frac{1}{2}\underbrace{\left(\frac{e\hbar}{m_e}\right)}_{\text{ATOMIC UNIT}}$

$V = -\underbrace{e}_{\text{ELECTRON'S CHARGE}}\underbrace{\phi}_{\text{POTENTIAL DUE TO THE PROTON}}$

$$\vec{E} = -\nabla\phi = -\frac{d\phi}{dr}\hat{r} = \left(\frac{1}{e}\frac{dV}{dr}\right)\frac{\vec{r}}{r}$$

$$\Rightarrow W_{SO} = -\left(-g\frac{e\hbar}{2m}\right)\frac{\vec{S}}{\hbar}\cdot\frac{-1}{2c^2}\left(\vec{v}\times\left(+\frac{1}{e}\right)\frac{dV}{dr}\frac{\vec{r}}{r}\right)$$

$$= \frac{-g}{4}\frac{1}{m^2c^2}\frac{1}{r}\frac{dV}{dr}\vec{S}\cdot(\vec{p}\times\vec{r})$$

$$= \frac{1}{2}\frac{1}{m^2c^2}\frac{1}{r}\frac{dV}{dr}\vec{S}\cdot(\vec{r}\times\vec{p})$$

$$\Rightarrow \boxed{W_{SO} = \frac{1}{2m^2c^2}\frac{1}{r}\frac{dV}{dr}\vec{L}\cdot\vec{S}}$$

ORDER OF MAGNITUDE

$$\boxed{W_{SO} = \frac{1}{2} mc^2 \frac{1}{m^3c^4} \frac{e^2}{4\pi\varepsilon_0 r^3} \hbar^2 \left(\frac{\vec{S}\cdot\vec{L}}{\hbar^2}\right)}$$

$$= \frac{1}{2} mc^2 \underbrace{\left(\frac{\hbar^2 e^2}{m^3c^4 4\pi\varepsilon_0 a_0^3}\right)}_{\frac{\hbar^2}{m^3c^4}\hbar c\alpha \frac{m^3c^3\alpha^3}{\hbar^3} = \alpha^4} \left(\frac{a_0}{r}\right)^3 \left(\frac{\vec{S}\cdot\vec{L}}{\hbar^2}\right) = \boxed{\frac{\alpha^4}{2} mc^2 \left(\frac{a_0}{r}\right)^3 \left(\frac{\vec{S}\cdot\vec{L}}{\hbar^2}\right)}$$

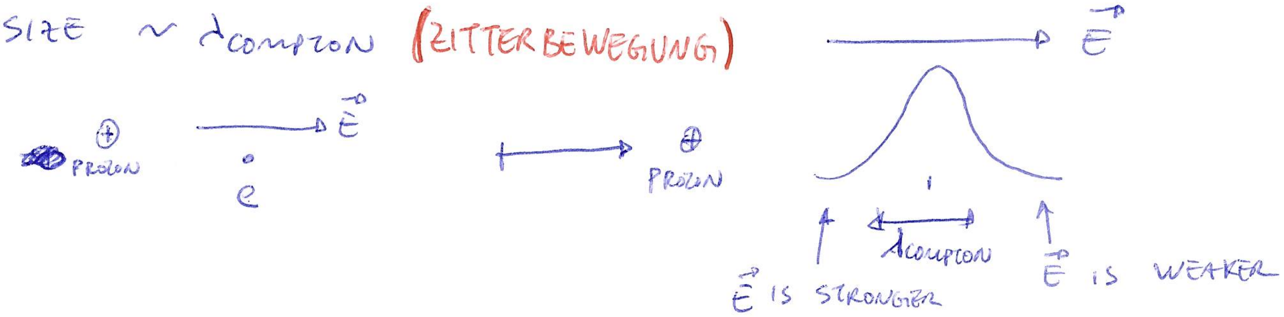
NOT TOO FAR FROM THE GROUND STATE, $r \simeq a_0$ $S \simeq L \simeq \hbar$

$W_{SO} \sim \alpha^4 mc^2$ COMPARING WITH $H_0 \sim \alpha^2 mc^2$

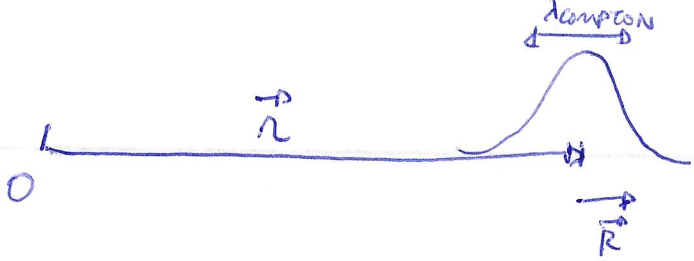
$$\Rightarrow \boxed{\frac{W_{SO}}{H_0} \sim \alpha^2}$$

W_D: IN RELATIVISTIC QUANTUM MECHANICS, IT IS IMPOSSIBLE TO LOCALIZE A PARTICLE IN A REGION SMALLER THAN ITS COMPTON WAVELENGTH $\lambda_{COMPTON}$.

THE PARTICLE "JITTERS" SMEARING OUT ~~ITS~~ ITS POSITION AROUND ITS CENTER OF MASS IN A REGION OF SIZE $\sim \lambda_{COMPTON}$ (ZITTERBEWEGUNG)



THEN, WE HAVE TO TAKE INTO ACCOUNT THAT THE e^- IS NOT A PUNCTUAL PARTICLE



$$H_{INT} = \int d\vec{R}\, \rho(\vec{R})\, \underbrace{\phi(\vec{r}+\vec{R})}_{\phi(\vec{r}) + \sum_i \frac{\partial \phi}{\partial r_i} R_i + \frac{1}{2}\sum_{ij} \frac{\partial^2 \phi}{\partial r_i \partial r_j} R_i R_j + \cdots}$$

$$= \phi(\vec{r}) \overbrace{\int d\vec{R}\, \rho(\vec{R})}^{-e}$$

$$+ \sum_i \frac{\partial \phi}{\partial r_i} \int d\vec{R}\, \rho(\vec{R}) R_i = 0 \quad \text{(SYMMETRICALLY DISTRIBUTED)}$$

$$+ \frac{1}{2} \sum_{ij} \frac{\partial^2 \phi}{\partial r_i \partial r_j} \underbrace{\int d\vec{R}\, \rho(\vec{R}) R_i R_j}_{(-e)\,\delta_{ij}\, \overline{R_i^2}}$$

BUT $\overline{R_i^2} = \frac{1}{3}\overline{R^2} = \frac{1}{3}\left(\overline{R_x^2} + \overline{R_y^2} + \overline{R_z^2}\right)$ BECAUSE $\overline{R_x^2} = \overline{R_y^2} = \overline{R_z^2}$

AND $\overline{R^2} \simeq \lambda_{COMPTON}^2$

$$\Rightarrow H_{INT} = -e\phi(\vec{r}) + \frac{1}{6}\left(\sum_i \frac{\partial^2 \phi}{\partial r_i^2}\right)\left(-e\,\lambda_{COMPTON}^2\right)$$

$$= V(\vec{r}) + \underbrace{\frac{1}{6}\nabla^2 V \left(\lambda_{COMPTON}^2\right)}_{W_D}$$

$$V(\vec{r}) \to \frac{-e^2}{4\pi\epsilon_0 r}$$

THE COMPTON WAVELENGTH:

IT IS THE WAVELENGTH OF A PHOTON WHOSE ENERGY IS THAT OF THE PARTICLE REST MASS

$$E = mc^2 = \hbar\omega = h\nu = h\frac{c}{\lambda_{compton}} \Rightarrow \boxed{\lambda_{compton} = \frac{h}{mc}}$$

$$\Rightarrow W_D = \frac{1}{6}\nabla^2 V\left(\frac{h}{mc}\right)^2 = \frac{h^2}{6m^2c^2}\nabla^2 V$$

THE CORRECT DARWIN TERM IS $\frac{\hbar^2}{8m^2c^2}\nabla^2 V$.

THE CORRECT PREFACTOR CANNOT BE CAPTURED BY OUR SIMPLE REASONING. ONE MUST CAREFULLY EXPAND DIRAC'S EQUATION TO OBTAIN IT.

$$\text{SINCE } \nabla^2 V = \nabla\cdot\nabla V = \nabla\cdot(-(-e)\vec{E}) = e\nabla\cdot\vec{E} = e\frac{\rho_{proton}(\vec{r})}{\epsilon_0}$$

$$= \frac{e^2}{\epsilon_0}\delta^{(3)}(\vec{r})$$

$$\Rightarrow \boxed{W_D = \frac{\hbar^2}{8m^2c^2}4\pi\left(\frac{e^2}{4\pi\epsilon_0}\right)\delta^{(3)}(\vec{r})}$$

ALTERNATIVELY, WE COULD HAVE USED THAT

$$\nabla^2\left(\frac{1}{r}\right) = -4\pi\delta^{(3)}(\vec{r})$$

$$\delta^{(3)}(\vec{r}) = \delta(x)\,\delta(y)\,\delta(z)$$

$$= \frac{1}{r^2}\delta(r)\,\delta(\cos\theta - 1)\,\delta(\phi)$$

$$= \frac{\delta(r)\,\cancel{\delta(\theta)}\,\delta(\phi)}{r^2 \sin\theta}$$

ORDER OF MAGNITUDE

$$W_D = \frac{\pi}{2}\frac{\hbar^2}{m^2c^2}(\alpha\hbar c)\frac{1}{a_0^3}\left(a_0^3\,\delta^{(3)}(\vec{r})\right)$$

$$\Rightarrow \boxed{W_D = \alpha^4\frac{\pi}{2}mc^2\left(a_0^3\,\delta^{(3)}(\vec{r})\right)}$$

BECAUSE OF $\delta(\vec{r})$, W_D AFFECTS ONLY WAVEFUNCTIONS WHICH ARE ~~[illegible]~~ (NON VANISHING) AT THE ORIGIN $\Rightarrow$ ONLY S-WAVES

$$\psi_{n\ell m}(\vec{r}=0) = 0 \quad \text{IF } \ell \neq 0$$

$$\psi_{n00}(\vec{r})$$

$$\Delta E = \langle \psi_{100} | W_D | \psi_{100} \rangle = \alpha^2 \frac{\pi}{2} mc^2 \int \underbrace{a_0^3 \delta^{(3)}(\vec{r}) |\psi_{100}(\vec{r})|^2 d\vec{r}}_{|\psi_{100}(0)|^2 a_0^3 = \frac{1}{\pi a_0^3} a_0^3 = \frac{1}{\pi}}$$ 26

$$\psi_{1s}(\vec{r}) = \frac{1}{\sqrt{\pi}} \frac{e^{-r/a_0}}{a_0^{3/2}}$$

H-ATOM ENERGIES:

$$E_n = -\frac{m e^4}{2(4\pi\epsilon_0)\hbar^2} \times \frac{1}{n^2} = -\frac{R_y}{n^2} \simeq -\frac{13.6\,eV}{n^2}$$

$$= -\frac{\hbar^2}{2 m a_0^2} \times \frac{1}{n^2} = -\frac{1}{2} \alpha^2 mc^2 \frac{1}{n^2}$$

$$\Rightarrow \boxed{\frac{\Delta E_{DARWIN}}{E_{100}} \; \alpha^2}$$

PERTURBATION THEORY

- COMPUTE THE PERTURBATION TO THE H-ATOM DUE TO OR FINE STRUCTURE CORRECTIONS

$$H = H_0 + W_F \quad ; \quad H_0 = \frac{P^2}{2m} - \frac{e^2}{4\pi\epsilon_0 r} = \text{H-ATOM}$$ UNPERTURBED

$$W_F = \underbrace{-\frac{\alpha^4}{8} mc^2 \left(\frac{a_0 P}{\hbar}\right)^4}_{W_v} + \underbrace{\frac{\alpha^4}{2} mc^2 \left(\frac{a_0}{r}\right)^3 \left(\frac{\vec{S}\cdot\vec{L}}{\hbar^2}\right)}_{W_{SO}} + \underbrace{\frac{\alpha^4 \pi}{2} mc^2 \left(a_0^3 \delta(\vec{r})\right)}_{W_D}$$

ALL THE TERMS ARE OF SAME ORDER $\frac{W_{v,SO,D}}{H_0} \sim \alpha^2$

UNPERTURBED H ATOM

$$H_0 |n\ell m\rangle = E_n^{(0)} |n\ell m\rangle \; ; \quad \boxed{E_n^{(0)} = \frac{\alpha^2}{2} \frac{mc^2}{n^2}}$$

$$\langle \vec{r} | n\ell m\rangle = \psi_{n\ell m}(\vec{r}) = R_{n\ell}(r)\, Y_{\ell m}(\theta,\phi)$$

DEGENERACY $\quad g_n = \begin{cases} n^2, & (\text{NO SPIN}) \quad |n\ell m\rangle \\ 2n^2, & (e^- \text{ SPIN}) \quad |n\ell m\sigma\rangle \\ 4n^2, & (e^- + \text{PROTON SPINS}) \quad |n\ell m\sigma\tau\rangle \end{cases}$

- NOTICE THAT W_F DOES NOT "SEE" THE PROTON'S SPIN.
- NOTICE THAT ONLY W_{SO} "SEES" THE e^-'s SPIN.

GROUND STATE $(n=1)$

1st ORDER DEGENERATE PERTURBATION THEORY

GROUND-STATE MULTIPLET = $\{|100\,\sigma\tau\rangle\} \longrightarrow \{|\sigma\tau\rangle\}$

$g_1 = 4$ (THE PROTON SPIN DEGENERACY IS NOT LIFTED)

MATRIX ELEMENT: $\langle \sigma'\tau' | W_F | \sigma\tau\rangle = \underbrace{\langle \sigma' | W_F | \sigma\rangle}_{\text{YIELDS TO A 2x2 MATRIX}} \underbrace{\langle \tau' | \tau\rangle}_{\delta_{\tau'\tau}}$

$$\langle \sigma' | W_F | \sigma\rangle \longleftrightarrow \begin{pmatrix} \langle 100+|W_F|100+\rangle & \langle 100+|W_F|100-\rangle \\ \langle 100-|W_F|100-\rangle & \langle 100-|W_F|100-\rangle \end{pmatrix}$$

WE NEED TO DIAGONALIZE THIS MATRIX

- EASY! IT IS DIAGONAL. ONLY W_{SO} CAN GIVE NON-DIAGONAL TERMS. HOWEVER, $\langle W_{SO}\rangle_{100} = 0$ BECAUSE THE ORBITAL ANGULAR MOMENTUM VANISHES.

$$\langle 100\,\sigma' | W_{SO} | 100\,\sigma \rangle \approx \underbrace{\langle 100 | \vec{L} | 100 \rangle}_{=0 \text{ BECAUSE } l=0=m} \cdot \langle \sigma' | \vec{S} | \sigma \rangle$$

$$\Rightarrow \langle W_F \rangle_{100} = \delta_{\sigma\sigma'}\,\delta_{\tau\tau'} \langle 100 | W_v + W_D | 100 \rangle$$

$$\langle 100 | W_v | 100 \rangle = \langle 100 | \left(-\frac{\alpha^4}{8} mc^2\right)\left(\frac{a_0 P}{\hbar}\right)^4 | 100 \rangle$$

* USEFUL TRICK: $H_0 = \frac{P^2}{2m} + V(r) \Rightarrow P^2 = 2m(H_0 - V)$

$$\left(\frac{a_0 P}{\hbar}\right)^4 = \frac{4m^2 a_0^4}{\hbar^4}\left(H_0^2 - H_0 V - V H_0 + V^2\right)$$

$$\Rightarrow \langle nlm | \left(\frac{a_0 P}{\hbar}\right)^4 | nlm \rangle = 4m^2 \frac{1}{(\alpha m c)^4} \langle H_0^2 - H_0 V - V H_0 + V^2 \rangle$$

$$= \frac{4}{\alpha^4 (mc^2)^2}\left(\left(E_n^{(0)}\right)^2 - 2E_n^{(0)} \langle V \rangle + \langle V^2 \rangle \right)$$

RECALL THAT $V(r) = -\alpha^2 mc^2 \left(\frac{a_0}{r}\right)$ (SEE PAGE 20)

ALSO, $E_n^{(0)} = -\frac{\alpha^2 mc^2}{2n^2}$

$$\Rightarrow \begin{cases} \langle V \rangle = -\alpha^2 mc^2 \langle \frac{a_0}{r} \rangle \\ \langle V^2 \rangle = \alpha^4 (mc^2)^2 \langle \left(\frac{a_0}{r}\right)^2 \rangle \end{cases}$$

$$\Rightarrow \langle W_v \rangle = -\frac{\alpha^4}{8} mc^2 \left[\frac{4}{\alpha^4 (mc^2)^2}\right]\left(\frac{\alpha^4 (mc^2)^2}{4n^4} - 2\frac{\alpha^4 (mc^2)^2}{2n^2}\langle \frac{a_0}{r} \rangle + \alpha^4 (mc^2)^2 \langle \frac{a_0^2}{r^2} \rangle \right)$$

$$\Rightarrow \boxed{\langle nlm | W_v | nlm \rangle = -\frac{\alpha^4 mc^2}{8}\left(\frac{1}{n^4} - \frac{4}{n^2}\langle \frac{a_0}{r} \rangle + 4 \langle \left(\frac{a_0}{r}\right)^2 \rangle \right)}$$

FOR THE GROUND STATE $(n=1)$ WE NEED

$$\langle \frac{a_0}{r} \rangle = \int_0^\infty dr\, r^2 R_{10}^2(r) \left(\frac{a_0}{r}\right) \overset{x = r/a_0}{=} \int_0^\infty dx\, x^2\, 4e^{-2x} \frac{1}{x} = 1$$

$$\langle \left(\frac{a_0}{r}\right)^2 \rangle = \int_0^\infty dx\, x^2\, 4e^{-2x} \frac{1}{x^2} = 2$$

$$\Rightarrow \langle W_v \rangle_{100} = -\frac{\alpha^4 mc^2}{8}\left(1 - 4\cdot 1 + 4\cdot 2\right) = -\frac{5}{8}\alpha^4 mc^2$$

NOW W_D:

$$\boxed{\langle nlm | W_D | nlm \rangle} = \frac{\alpha^4 \pi}{2} mc^2 \underbrace{\langle nlm | a_0^3 \delta(\vec{r}) | nlm \rangle}_{\delta_{l,0}\,\delta_{m,0}\, \underbrace{\langle n00 | a_0^3 \delta(\vec{r}) | n00 \rangle}_{a_0^3 R_{n0}^2(0)\, \underbrace{Y_{00}^2(0,0)}_{\frac{1}{4\pi}}}}$$

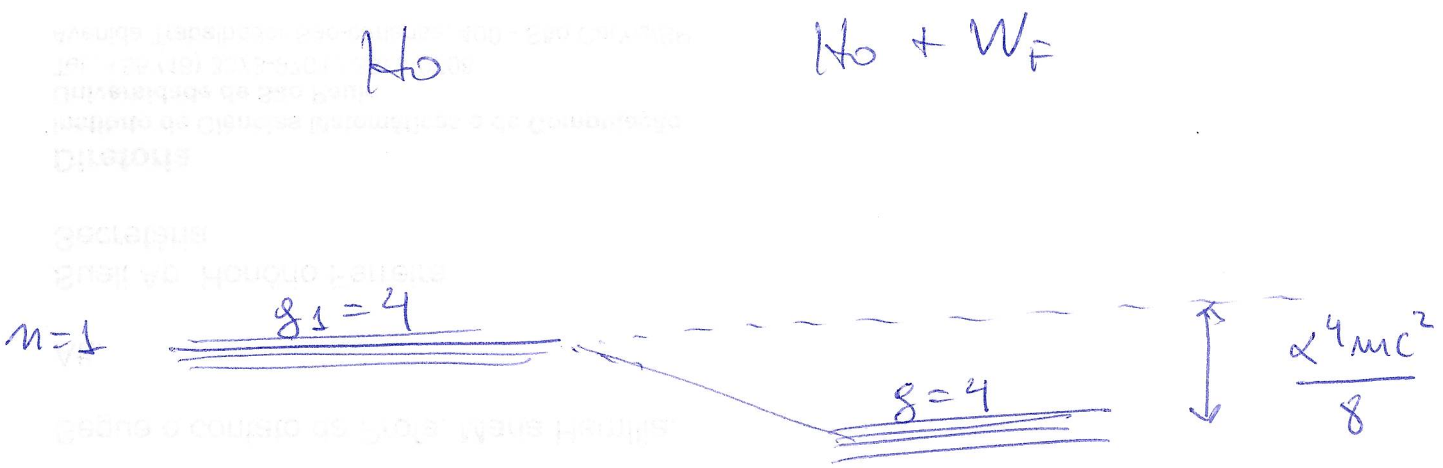
$$\boxed{= \frac{\alpha^4 mc^2}{8} a_0^3 R_{n0}^2(0)\, \delta_{l,0}\, \delta_{m,0}}$$

FOR $n=1$ $\left(R_{10} = \frac{1}{a_0^{3/2}} 2 e^{-\frac{r}{a_0}}\right)$

$$\Rightarrow \langle W_D \rangle_{100} = \frac{\alpha^4 mc^2}{2}$$

FINALLY, $\langle W_F \rangle = -\frac{1}{8}\alpha^4 mc^2$

ENERGY DIAGRAM (OR GROTRIAN DIAGRAM)



THE STATES REMAIN DEGENERATE

IN SUM, THE MATRIX ELEMENTS OF INTEREST OF 3 TERMS OF W_F ARE CONVENIENTLY WRITTEN AS

(29.a)

• W_σ: $\langle n l m \sigma' \tau' | W_\sigma | n l m \sigma \tau \rangle = \delta_{\sigma\sigma'} \delta_{\tau\tau'} \underbrace{\langle n l m | W_\sigma | n l m \rangle}_{\langle W_\sigma \rangle}$

$$\boxed{\langle W_\sigma \rangle = \frac{-\alpha^4}{8} mc^2 \left(\frac{1}{n^4} - \frac{4}{n^2} \left\langle \frac{a_0}{r} \right\rangle + 4 \left\langle \left(\frac{a_0}{r}\right)^2 \right\rangle \right)}$$

• W_D: LIKEWISE, $\boxed{\langle W_D \rangle_{l=0} = \frac{\alpha^4}{8} mc^2 \left(\overbrace{a_0^3 R_{n0}^2(0)}^{4/n^3} \right) = -\alpha^2 \frac{E_n^{(0)}}{n}}$

• W_{SO}: $\langle n l m' \sigma' \tau' | \frac{\alpha^4}{2} mc^2 \left(\frac{a_0}{r}\right)^3 \left(\frac{\vec{S}\cdot\vec{L}}{\hbar^2}\right) | n l m \sigma \tau \rangle$

$= \langle n l m' \sigma' | \frac{\alpha^4}{2} mc^2 \left(\frac{a_0}{r}\right)^3 \frac{\vec{S}\cdot\vec{L}}{\hbar^2} | n l m \sigma \rangle \delta_{\tau\tau'}$ DOES NOT "USE" THE PROTON'S SPIN

SINCE $\frac{1}{r}$ AND $\vec{L}$ ACT ON DISJOINT SUBSPACES, THEN

$= \frac{\alpha^4}{2} mc^2 \left\langle \left(\frac{a_0}{r}\right)^3 \right\rangle \langle m' \sigma' | \frac{\vec{S}\cdot\vec{L}}{\hbar^2} | m \sigma \rangle$ → NON VANISHING ONLY FOR $l \geq 1$

$\int_0^\infty dr\, r^2 \left(\frac{a_0}{r}\right)^3 R_{nl}^2(r)$

→ $\{|m\sigma\rangle\}$ IS NOT THE EIGEN BASIS OF $\vec{S}\cdot\vec{L}$

WE NEED TO USE THE BASIS OF THE TOTAL ANGULAR MOMENTUM $\vec{J} = \vec{L} + \vec{S}$ BECAUSE

$\vec{S}\cdot\vec{L} = \frac{1}{2}\left(J^2 - S^2 - L^2\right)$

$= \frac{1}{2}\left(J^2 - \hbar^2(s(s+1) - l(l+1))\right)$

SINCE J IS EITHER $l - \frac{1}{2}$ OR $l + \frac{1}{2}$

⇒ EINGENVALUES OF $\frac{\vec{S}\cdot\vec{L}}{\hbar^2}$ ARE

$$\begin{cases} \frac{1}{2}\left[\left(l+\frac{1}{2}\right)\left(l+\frac{3}{2}\right) - l(l+1) - \frac{1}{2}\left(\frac{1}{2}+1\right)\right] & (J = l + 1/2) \\ \frac{1}{2}\left[\left(l-\frac{1}{2}\right)\left(l+\frac{1}{2}\right) - l(l+1) - \frac{1}{2}\left(\frac{1}{2}+1\right)\right] & (J = l - \frac{1}{2}) \end{cases}$$

$= \frac{1}{2}\begin{cases} l & (J = l + \frac{1}{2}) \to \text{DEGENERACY } g = 2J+1 = 2l+2 \\ -l-1 & (J = l - \frac{1}{2}) \to \quad " \quad g = 2l \end{cases}$

FINALLY, $\boxed{\langle W_{SO} \rangle = \frac{\alpha^4}{4} mc^2 \left\langle \left(\frac{a_0}{r}\right)^3 \right\rangle * \begin{cases} l & (J = l + \frac{1}{2}) \\ -l-1 & (J = l - \frac{1}{2}) \end{cases}}$

N=2 LEVEL

$g_2 = 16$ STATES (INCLUDING PROTON + e^- SPINS)

$$\left\{\begin{array}{l}\psi_{200} = R_{20} Y_{00} \\ \psi_{21m} = R_{21} Y_{1m}\end{array}\right. \quad \text{WHERE} \quad \begin{array}{l} R_{20} = \dfrac{1}{(2a_0)^{3/2}}\left(2 - \dfrac{r}{a_0}\right) e^{-\frac{r}{2a_0}} \\ R_{21} = \dfrac{1}{\sqrt{3}\,(2a_0)^{3/2}}\left(\dfrac{r}{a_0}\right) e^{-\frac{r}{2a_0}}\end{array}$$

IT IS USEFUL TO NOTICE THAT $[L^2, W_F] = 0$

PROOF: a) $[W_{\sigma}, L^2] \propto [P^4, L^2] = P^2[P^2, L^2] + [P^2, L^2]P^2$

BUT $[P^2, L^2] \propto [H_0 - V(r), L^2]$

SINCE $V(r) = \dfrac{-e^2}{4\pi\epsilon_0 r}$ AND $\vec{L} = i\hbar\left(\hat{\theta}\dfrac{1}{\sin\theta}\dfrac{\partial}{\partial\phi} - \hat{\phi}\dfrac{\partial}{\partial\theta}\right)$

SINCE $\vec{L}$ DOES NOT INVOLVE $\frac{\partial}{\partial r}$ $\Rightarrow [V(r), \vec{L}] = 0 \Rightarrow [V(r), L^2] = 0$

NATURALLY, $[H_0, L^2] = 0$

$\Rightarrow [P^2, L^2] = 0 \Rightarrow [P^4, L^2] = 0 \Rightarrow [W_{\sigma}, L^2] = 0$

b) $[W_{SO}, L^2] = [f(r)\,\vec{L}\cdot\vec{S}, L^2]$ NATURALLY, $[L^2, \vec{S}] = 0 = [\vec{L}, L^2]$

AND $[f(r), L] = 0$ (ITEM (a))

$\Rightarrow [W_{SO}, L^2] = 0$

c) $[W_D, L^2] \propto [\delta(\vec{r}), L^2]$ SINCE $\delta(\vec{r})$ IS ROTATIONALLY INVARIANT $\Rightarrow [\delta(\vec{r}), \vec{L}] = 0$

$= 0$

SINCE $[L^2, W_F] = 0 \Rightarrow$ COMMON BASIS

ALSO, THE PERTURBATION WILL NOT MIX DIFFERENT ORBITAL ANGULAR MOMENTUM STATES

- $\langle n'l'm_l'\sigma'\tau' | [W_F, L^2] | n l m_l \sigma\tau\rangle = \hbar^2[l(l+1) - l'(l'+1)]\langle n'l'm_l'\sigma'\tau' | W_F | n l m_l \sigma\tau\rangle = 0$

$\Rightarrow \langle l' | W_F | l\rangle = 0$ IF $l \neq l'$

THUS THE MATRIX W_F IN THE $\underline{n=2}$ SUBSPACE IS

$$\langle W_F \rangle = \left(\begin{array}{c|c} \begin{matrix} 2\times 2 \\ (\ell=0) \end{matrix} & 0 \\ \hline 0 & \begin{matrix} 6\times 6 \\ (\ell=1) \end{matrix} \end{array} \right) \otimes \underbrace{\mathbb{1}_{2\times 2}}_{\text{DUE TO PROTON SPIN}}$$

(BLOCK DIAGONAL)

$\underline{\text{SUB-SPACE } \ell=0}$ (S-WAVE) : $\{|200\sigma\rangle\} \longmapsto \{|\sigma\rangle\}$

W_v : $\langle W_v \rangle_{200}\, \delta_{\sigma\sigma'} = \langle 200 | W_v | 200 \rangle\, \delta_{\sigma\sigma'}$

$$= -\frac{\alpha^4 mc^2}{8} \left(\frac{1}{16} - \left\langle \frac{a_0}{r} \right\rangle_{200} + 4 \left\langle \left(\frac{a_0}{r}\right)^2 \right\rangle_{200} \right) \delta_{\sigma\sigma'}$$

$$\left\langle \frac{a_0}{r} \right\rangle_{200} = \int_0^\infty dr\, r^2 R_{20}^2(r) \left(\frac{a_0}{r} \right) = \int_0^\infty dx\, x^2 \frac{1}{8} (2-x)^2 e^{-x} \frac{1}{x} = \frac{1}{4}$$

$$\left\langle \left(\frac{a_0}{r} \right)^2 \right\rangle_{200} = \int_0^\infty dx\, \frac{(2-x)^2}{8} e^{-x} = \frac{1}{4}$$

$$\Rightarrow \langle W_v \rangle_{200} = -\frac{\alpha^4 mc^2}{8} \left(\frac{1}{16} - \frac{1}{4} + 1 \right) = \alpha^4 mc^2 \left(-\frac{13}{128} \right)$$

W_{SO} :

$\langle W_{SO} \rangle_{200} = 0$ BECAUSE $\ell = 0$

W_D : $\langle W_D \rangle_{200} = \dfrac{\alpha^4 mc^2}{8} \times a_0^3 R_{20}^2(0) = \dfrac{\alpha^4 mc^2}{16}$

FINALLY, $\boxed{\langle W_F \rangle_{200} = -\dfrac{5}{128} \alpha^4 mc^2}$

NOW WE NEED TO WORK OUT THE

SUBSPACE $21m$

$\ell = 1$ (P-WAVE)

MATRIX ELEMENT: $\langle 2 1 m' \sigma' | W_F | 2 1 m \sigma \rangle$

W_r: $\langle 21m'\sigma' | W_r | 21m\sigma \rangle = \langle 21m\sigma | W_r | 21m\sigma \rangle \delta_{\sigma\sigma'} \delta_{mm'}$

$$\langle W_r \rangle = -\frac{\alpha^4 mc^2}{8}\left(\frac{1}{16} - \left\langle \frac{a_0}{r} \right\rangle_{21m} + 4 \left\langle \left(\frac{a_0}{r}\right)^2 \right\rangle_{21m} \right)$$

$$\left\langle \frac{a_0}{r} \right\rangle_{21m} = \int_0^\infty dr\, r^2 R_{21}^2(r) \left(\frac{a_0}{r}\right) = \int_0^\infty dx\, x^2 \frac{1}{3\cdot 8} x^2 e^{-x} \frac{1}{x} = \frac{1}{4}$$

$$\left\langle \left(\frac{a_0}{r}\right)^2 \right\rangle_{21m} = \int_0^\infty dx\, \frac{x^2 e^{-x}}{3\cdot 8} = \frac{1}{12}$$

$$\langle W_r \rangle = -\frac{\alpha^4 mc^2}{8}\left(\frac{1}{16} - \frac{1}{4} + \frac{4}{12} \right) = -\frac{7}{384}\alpha^4 mc^2$$

W_D: $\langle W_D \rangle_{21m} = 0$ (ONLY S-WAVES ARE AFFECTED ($\ell = 0$))

W_{SO}: $\langle W_{SO} \rangle = \frac{\alpha^4 mc^2}{2} {}_{21m'\sigma'}\left\langle \left(\frac{a_0}{r}\right)^3 \left(\frac{\vec{L}\cdot\vec{S}}{\hbar^2}\right) \right\rangle_{21m\sigma}$

NOTICE THAT $\vec{L}\cdot\vec{S} = L_x S_x + L_y S_y + L_z S_z$

THE KETS $|n \ell m \sigma\rangle$ ARE EIGENKETS OF L_z AND S_z

BUT NOT OF L_x, S_x, L_y OR S_y

IT IS THEN NEEDED TO DIAGONALIZE $\vec{L}\cdot\vec{S}$

USEFUL TRICK: $\vec{L}\cdot\vec{S} = \frac{1}{2}\left[(\vec{L}+\vec{S})^2 - L^2 - S^2 \right] = \frac{1}{2}\left(J^2 - L^2 - S^2 \right)$

WHERE $\vec{J} = \vec{L} + \vec{S}$ TOTAL ANGULAR MOMENTUM

THEN IN THE BASIS OF THE $\vec{J}$, $\vec{L}\cdot\vec{S}$ IS DIAGONAL

AS $L = 1$ AND $S = \frac{1}{2}$ $\Rightarrow$ J IS $\frac{1}{2}$ OR $\frac{3}{2}$

CHANGE OF BASIS $\{ |m\sigma\rangle \} \longrightarrow \{ |J m_J\rangle \}$

$m = -1, 0, 1$

$\sigma = -\frac{1}{2}, +\frac{1}{2}$

$\longmapsto$

$J = \frac{1}{2}$: $m_J = -\frac{1}{2}, \frac{1}{2}$

$J = \frac{3}{2}$: $m_J = -\frac{3}{2}, -\frac{1}{2}, \frac{1}{2}, \frac{3}{2}$

MATRIX ELEMENTS OF W_{SO}:

$$\langle 2\,1\,m'\sigma' | \left(\frac{a_0}{r}\right)^3 \frac{\vec{L}\cdot\vec{S}}{\hbar^2} | 2\,1\,m\sigma\rangle = \langle 2 1 | \left(\frac{a_0}{r}\right)^3 | 2 1\rangle \langle m'\sigma' | \frac{\vec{L}\cdot\vec{S}}{\hbar^2} | m\sigma\rangle$$

$$\langle 2 1 | \left(\frac{a_0}{r}\right)^3 | 2 1\rangle = \int_0^\infty dr\, r^2 R_{21}^2(r) \left(\frac{a_0}{r}\right)^3 = \int_0^\infty dx \frac{x e^{-x}}{3\cdot 8} = \frac{1}{24}$$

$$\langle m'\sigma' | \frac{\vec{L}\cdot\vec{S}}{\hbar^2} | m\sigma\rangle \longmapsto \langle J' m_J' | \frac{1}{2\hbar^2}\left(J^2 - L^2 - S^2\right) | J m_J\rangle$$

$$= \delta_{JJ'}\delta_{m_J' m_J} \underbrace{\left(\frac{J(J+1) - 2 - \frac{3}{4}}{2}\right)}_{\begin{cases} -1, & \text{FOR } J = 1/2 \\ +\frac{1}{2}, & \text{FOR } J = 3/2 \end{cases}}$$

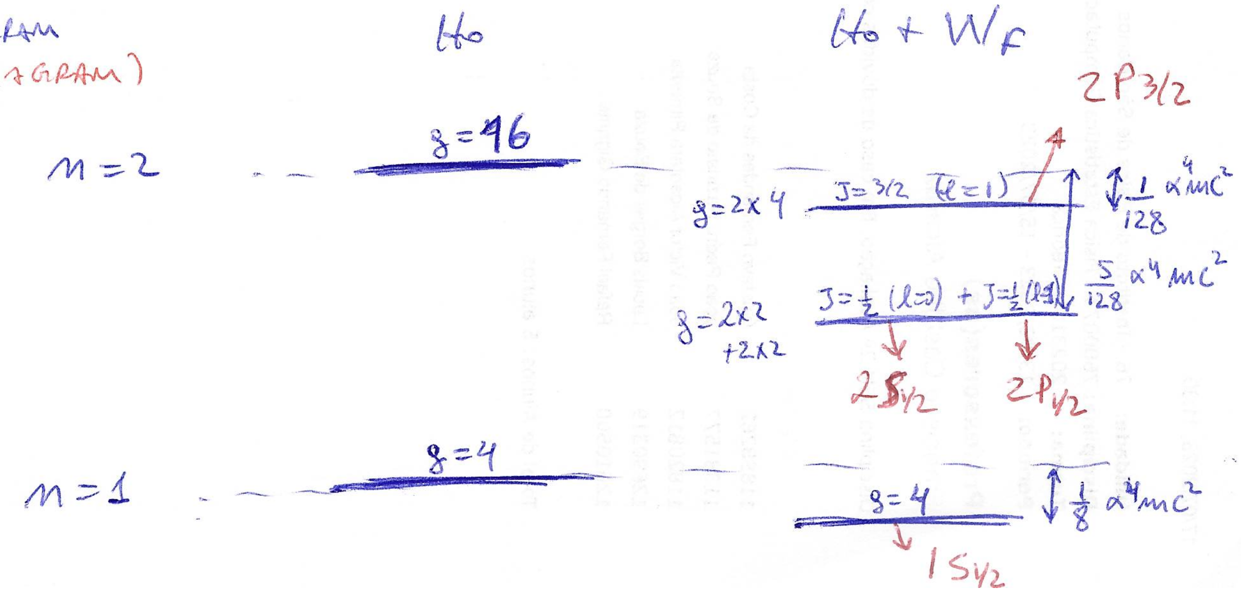
$$\Rightarrow \langle W_{SO}\rangle \rightarrow \frac{\alpha^2 mc^2}{2} \times \frac{1}{24} \times \begin{cases} -1, & J = 1/2 \\ +\frac{1}{2}, & J = 3/2 \end{cases}$$

IN SUM,

$$\langle W_F\rangle = \left(\begin{array}{c|c} \begin{matrix}2\times 2\\(\ell=0)\end{matrix} & 0 \\ \hline 0 & \begin{matrix}6\times 6\\(\ell=1)\end{matrix} \end{array}\right) = \left(\begin{array}{c|cc} \mathbb{1}_{2\times 2} & & 0 \\ \hline 0 & \begin{matrix}2\times 2\\(J=1/2)\end{matrix} & 0 \\ & 0 & \begin{matrix}4\times 4\\(J=3/2)\end{matrix} \end{array}\right)$$

$$\xrightarrow{\text{DIAGONALIZE}} \left(\begin{array}{c|cc} -\frac{5}{128}\mathbb{1}_{2\times 2} & & 0 \\ \hline 0 & -\frac{5}{128}\mathbb{1}_{2\times 2} & \\ & & -\frac{1}{128}\mathbb{1}_{4\times 4} \end{array}\right) \alpha^4 mc^2$$

ENERGY DIAGRAM
(OR GROTRIAN DIAGRAM)



HOW ABOUT THE OTHER LEVELS $n>2$?

$\langle W_\sigma \rangle$ can be OBTAINED GENERICALLY

$\times \quad \left\langle \frac{a_0}{r} \right\rangle_{nlm} = \frac{1}{n^2}$

$\times \quad \left\langle \left(\frac{a_0}{r}\right)^2 \right\rangle_{nlm} = \frac{1}{n^3}\frac{1}{l+\frac{1}{2}}$

$\times \quad \left\langle \left(\frac{a}{r}\right)^3 \right\rangle_{nlm} = \frac{1}{n^3}\frac{1}{l(l+1)(l+\frac{1}{2})} \qquad (\text{FOR } l \geq 1)$

$$\Rightarrow \langle W_\sigma \rangle_{nlm} = -\frac{\alpha^4 mc^2}{8}\left(\frac{1}{n^4} - \frac{4}{n^4} + \frac{4}{n^3(l+\frac{1}{2})}\right) = \boxed{+\frac{\alpha^2}{n}E_n^{(0)}\left(\frac{1}{l+\frac{1}{2}} - \frac{3}{4n}\right)}$$

$$\Rightarrow \boxed{\langle W_D \rangle_{nlm} = -\alpha^2 \frac{E_n^{(0)}}{n}\delta_{l,0}}$$

FOR W_{SO}, WE NEED TO CHANGE BASIS: $\{|nm\sigma\rangle\} \to \{|J\, m_J\rangle\}$

$$\langle W_{SO} \rangle_{nlm\sigma} \longrightarrow \langle W_{SO} \rangle_{nlJm_J} = \frac{\alpha^4 mc^2}{4}\frac{1}{n^3 l(l+1)(l+\frac{1}{2})}\begin{cases} l & (J=l+1/2) \\ -l-1 & (J=l-1/2)\end{cases} \times (1-\delta_{l,0})$$

$$\boxed{= \frac{\alpha^2}{n}E_n^{(0)}\frac{(1-\delta_{l,0})}{l(l+1)(2l+1)} \times \begin{cases} -l & (J=l+\frac{1}{2}) \\ +l+1 & (J=l-\frac{1}{2})\end{cases}}$$

$$\boxed{\Rightarrow \langle W_F \rangle \to E^{(1)}_{nlJ} = \alpha^2 \frac{E_n^{(0)}}{n}\left[-\delta_{l,0} + \frac{1}{l+\frac{1}{2}} - \frac{3}{4n} + \frac{(1-\delta_{l0})}{2l+1}\begin{cases} \frac{-1}{l+1} & (J=l+\frac{1}{2}) \\ \frac{1}{l} & (J=l-\frac{1}{2})\end{cases}\right]}$$

THIS CAN BE FURTHER SIMPLIFIED

$$l=0 \text{ CASE} \Rightarrow E^{(1)}_{mlJ} = \frac{\alpha^2 E^{(0)}_m}{m}\left[\frac{-3}{4m} \overbrace{- 1 + 2}^{1}\right] = \frac{\alpha E^{(0)}_m}{m}\left[\frac{-3}{4m} + \frac{1}{J+\frac{1}{2}}\right]$$

WITH $J=\frac{1}{2}$ BECAUSE $l=0$
$\Rightarrow \vec{J} = \vec{L} + \vec{S} = \frac{\vec{1}}{2}$

$$\text{CASE } l\neq 0 \Rightarrow E^{(1)}_{mlJ} = \frac{\alpha^2 E^{(0)}_m}{m}\Bigg[\frac{-3}{4m} + \underbrace{\frac{1}{l+\frac{1}{2}} + \frac{1}{2(l+\frac{1}{2})}\begin{cases} -\frac{1}{l+1} & (J=l+1/2) \\ \frac{1}{l} & (J=l-\frac{1}{2})\end{cases}}\Bigg]$$

- $J=l+\frac{1}{2} \rightarrow \frac{1}{l+\frac{1}{2}}\left[1-\frac{1}{2}\frac{1}{(l+1)}\right] = \frac{2l+1}{2(l+\frac{1}{2})(l+1)} = \frac{1}{l+1}$

$$= \frac{1}{J+\frac{1}{2}}$$

- $J=l-\frac{1}{2} \rightarrow \frac{1}{l+\frac{1}{2}}\left(1+\frac{1}{2l}\right) = \frac{2l+1}{(2l+1)l} = \frac{1}{l} = \frac{1}{J+\frac{1}{2}}$

$\Rightarrow$ IN ALL CASES, IT ENDS UP EQUAL TO $\frac{1}{J+\frac{1}{2}}$

$$\Rightarrow \boxed{E^{(1)}_{mlJ} = \frac{\alpha^2}{m} E^{(0)}_m\left[\frac{1}{J+\frac{1}{2}} - \frac{3}{4m}\right]}$$

MINIMUM VALUE OF $J=\frac{1}{2} \Rightarrow \frac{1}{J+\frac{1}{2}} - \frac{3}{4m} = 1-\frac{3}{4m} > 0$ BECAUSE $m\geq 1$

MAXIMUM VALUE OF $J = l+\frac{1}{2} = m-\frac{1}{2} \Rightarrow \frac{1}{J+\frac{1}{2}} - \frac{3}{4m} = \frac{1}{m} - \frac{3}{4m} = \frac{1}{4m} > 0$

THEREFORE, $\boxed{E^{(1)}_{mlJ} < 0}$ THE FINE-STRUCTURE CORRECTION ALWAYS LOWERS THE ENERGY

$$\Rightarrow \boxed{E_{mlJ} = E^{(0)}_m\left[1+\frac{\alpha^2}{m}\left(\frac{1}{J+\frac{1}{2}} - \frac{3}{4m}\right)\right]}$$

A GENERIC LEVEL m HAS

QUANTUM NUMBERS $\underbrace{m, l, m}_{\text{USUAL H-ATOM}},\ \underbrace{\sigma}_{e^-\text{ SPIN}},\ \underbrace{\tau}_{\text{PROTON SPIN}}$

DEGENERACY $= g_m = 4m^2$

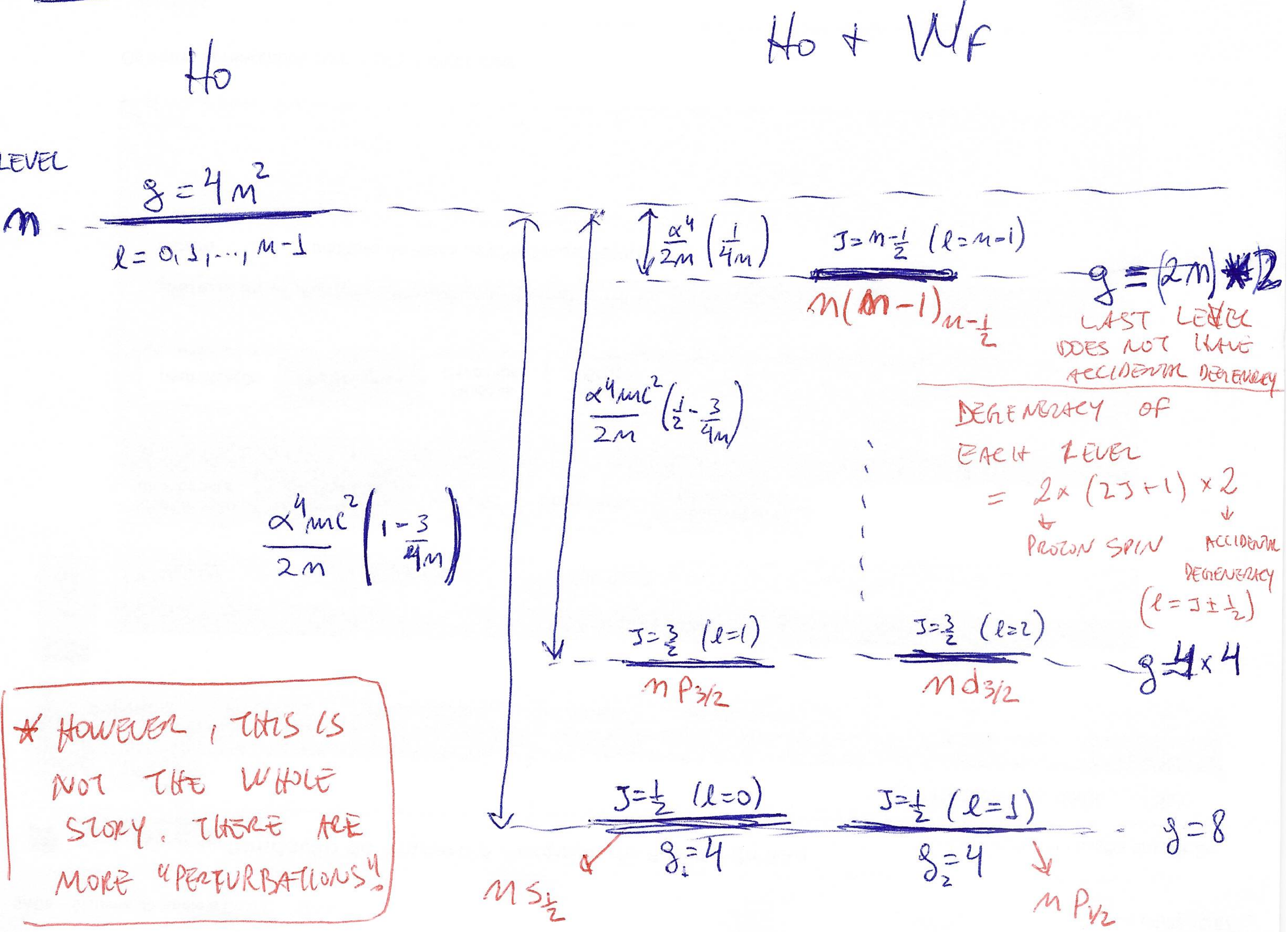
HOWEVER, THE USEFUL QUANTUM NUMBERS ARE

$$m, l, J, m_J, \tau \quad , \quad \vec{J} = \vec{S} + \vec{L}$$

DUE TO THE FINE-STRUCTURE PERTURBATION, THE DEGENERACY IS LIFTED BECAUSE $E^{(1)}_{m l J m_J \tau}$ DEPENDS ON J

HOW MANY NEW LEVELS APPEAR? $\Rightarrow$ J GOES FROM $\frac{1}{2}$ TO $m-\frac{1}{2}$ $\Rightarrow$ m LEVELS

ENERGY DIAGRAM (OR GROTRIAN DIAGRAM)



* HOWEVER, THIS IS NOT THE WHOLE STORY. THERE ARE MORE "PERTURBATIONS"!

THE ACCIDENTAL DEGENERACY

OF LEVELS $n(\ell)_J$ AND $n(\ell+1)_J$
$(J=\ell+\frac{1}{2})$ $(J=\ell-\frac{1}{2})$

IS ALSO A DEGENERACY IN THE

DIRAC'S EQUATION.

HOWEVER, NATURE LIFTS THIS DEGENERACY

AS SHOWN BY THE NOBEL-PRIZE-WINNING

EXPERIMENT BY LAMB AND RETHERFORD (1947).

THEY FOUND THAT LEVELS $2P_{\frac{1}{2}}$ AND $2S_{\frac{1}{2}}$

ARE NOT DEGENERATED.

THEY FOUND THAT $E_{2S_{\frac{1}{2}}} - E_{2P_{\frac{1}{2}}} = 4{,}372 \times 10^{-6}\,eV$

$\sim 1057\,MHz$

$\sim 28\,cm$

THIS SHIFT DOWN OF
THE $2P_{\frac{1}{2}}$ LEVEL IS KNOWN AS THE "LAMB SHIFT".

THE EXPLANATION OF THIS EFFECT (DUE TO HANS BETHE)

LED TO THE DEVELOPMENT OF THE
QUANTUM ELECTRODYNAMICS (QED) BY, MAINLY,
DUE TO FEYNMAN, SCHWINGER, AND TOMONAGA
(FROM WHICH THEY WERE AWARDED THE NOBEL PRIZE)

HYPER-FINE STRUCTURE

FINE-STRUCTURE: RELATIVISTIC CORRECTIONS

HYPER FINE STRUCTURE: QUANTUM VERSION OF "INTERNAL" CLASSICAL MAGNETIC DIPOLE EFFECTS AND ELECTRIC QUADRUPOLE EFFECTS

FOR THE H-ATOMS (OR NUCLEI WITH TOTAL SPIN $\leq 1/2$) DO NOT HAVE FINITE ELECTRIC QUADRUPOLE MOMENT.

HERE WE CONSIDER ONLY H-ATOM, $\Rightarrow$ NO ELECTRIC QUADRUPOLE, AND ONLY THE 1S LEVEL ($n=1$)

THE HYPER FINE HAMILTONIAN (CLASSICALLY)

HAMILTONIAN OF AN e^- ON AN ~~MAGNETIC FIELD~~ ELECTRIC + MAGNETIC FIELD

$$H = \frac{1}{2m}\left|\vec{p} + e\vec{A}\right|^2 - e\phi(\vec{r}) - \vec{\mu}_{S_e}\cdot\vec{B} \qquad (q=-e)$$

WHERE $\vec{B} = \nabla\times\vec{A}$ AND $\vec{E} = -\nabla\phi$

HERE $\vec{E}$ IS THE ELECTRIC FIELD DUE TO THE PROTON

$$\Rightarrow \phi = \frac{e}{4\pi\varepsilon_0 r}$$

$\vec{B}$ IS THE MAGNETIC FIELD DUE TO THE PROTON'S SPIN

PROTON'S MAGNETIC MOMENT

$$= \frac{\mu_0}{4\pi}\left[\frac{3\vec{r}(\vec{\mu}_p\cdot\vec{r})}{r^5} - \frac{\vec{\mu}_p}{r^3}\right], \qquad \vec{\mu}_p = +g_p\,\mu_N\,\frac{\vec{S}_p}{\hbar}$$

PROTON'S SPIN

GYROMAGNETIC FACTOR $\simeq 5.5856946893(16)$

NUCLEAR MAGNETON $= \dfrac{e\hbar}{2M_p}$, M_p: PROTON MASS

$= \dfrac{m_e}{M_p}\mu_B$

$$\Rightarrow \boxed{\vec{A} = \frac{\mu_0}{4\pi}\,\frac{\vec{\mu}_p\times\vec{r}}{r^3}},$$

EXERCISE: PROVE THAT $\nabla \times \vec{A} = \frac{\mu_0}{4\pi}\left[\frac{3\vec{r}(\vec{\mu}_p \cdot \vec{r})}{r^5} - \frac{\vec{\mu}_p}{r^3}\right]$

HINT: $\nabla \times (\vec{A} \wedge \vec{B}) = \vec{A}(\nabla \cdot \vec{B}) - \vec{B}(\nabla \cdot \vec{A}) + (\vec{B} \cdot \nabla)\vec{A} - (\vec{A} \cdot \nabla)\vec{B}$

THEREFORE,

$$H = \underbrace{\frac{p^2}{2m} - e\phi(\vec{r})}_{H_0} + \frac{2e\vec{A} \cdot \vec{p}}{2m} - g\mu_B \frac{\vec{S}_e}{\hbar} \cdot (\nabla \times \vec{A}) + O(\vec{A}^2)$$

$$\vec{A} \cdot \vec{p} \propto (\vec{\mu}_p \times \vec{r}) \cdot \vec{p} = \vec{\mu}_p \cdot (\vec{r} \times \vec{p}) = \vec{\mu}_p \cdot \vec{L}$$

THUS, THE TERM $\frac{e}{m} \vec{A} \cdot \vec{p}$ YIELDS TO

$$\boxed{H_1 = \frac{\mu_0}{4\pi} \frac{e}{m r^3} \vec{\mu}_p \cdot \vec{L} = \frac{\mu_0}{4\pi\hbar} 2\left(\frac{\hbar e}{2m}\right) \frac{\vec{\mu}_p \cdot \vec{L}}{r^3} = \frac{2\mu_0 \mu_B}{4\pi\hbar} \frac{\vec{\mu}_p \cdot \vec{L}}{r^3}}$$

THE PROTON'S SPIN GENERATES A MAGNETIC FIELD WHICH INTERACTS WITH THE ORBITAL ANGULAR MOMENTUM OF THE ELECTRON.

THE OTHER PERTURBING TERM IS

$$\boxed{H_2 = -\vec{\mu}_{se} \cdot \vec{B} = -\vec{\mu}_{se} \cdot (\nabla \times \vec{A})}$$

THAT SAME MAGNETIC FIELD INTERACTS WITH THE ELECTRON'S SPIN.

HOWEVER, $\nabla \times \vec{A} = \vec{B}$ + ANOTHER TERM NOT TAKEN INTO ACCOUNT SO FAR

THIS TERM IS DUE TO THE PROTON MAGNETIC FIELD INSIDE THE PROTON. ACTUALLY, THE VECTOR POTENTIAL $\vec{A}$ OF A UNIFORMLY MAGNETIZED SPHERE IS

$$\vec{A} = \frac{\mu_0}{4\pi} \vec{\mu} \times \vec{r} \begin{cases} \frac{1}{r^3}, & r > R \\ \frac{1}{R^3}, & r < R \end{cases}$$

WHERE R IS THE RADIUS SPHERE

TAKING $R \to 0$ YIELDS TO

$$\vec{B} = \frac{\mu_0}{4\pi}\left[\underbrace{\frac{3(\vec{\mu}_p \cdot \vec{r})\vec{r}}{r^5} - \frac{\vec{\mu}_p}{r^3}}_{\text{DIPOLE MAGNETIC FIELD}} + \underbrace{\frac{8\pi}{3} \vec{\mu}_p \delta^{(3)}(\vec{r})}_{\text{MAGNETIC FIELD INSIDE THE PROTON (WHICH IS A "POINT" PARTICLE HERE}}\right]$$

THIS EXTRA TERM $[\propto \delta(\vec{r})]$ CAN BE DERIVED IN MANY (NON TRIVIAL) WAYS. A "FAST" ONE IS THE FOLLOWING:

$$\vec{A} = \frac{\mu_0}{4\pi} \frac{\vec{\mu}_p \times \vec{r}}{r^3} = -\frac{\mu_0}{4\pi} \vec{\mu}_p \times \nabla\left(\frac{1}{r}\right)$$

USING THAT

$$\nabla \times (\vec{A} \times \vec{B}) = \vec{A}(\nabla \cdot \vec{B}) - (\vec{A} \cdot \nabla)\vec{B} - \vec{B}(\nabla \cdot \vec{A}) + (\vec{B} \cdot \nabla)\vec{A}$$

$$\Rightarrow \vec{B} = \nabla \times \vec{A} = -\frac{\mu_0}{4\pi} \nabla \times \left(\vec{\mu}_p \times \nabla\left(\frac{1}{r}\right)\right)$$

$$= -\frac{\mu_0}{4\pi}\left[\vec{\mu}_p\left(\nabla \cdot \nabla\left(\frac{1}{r}\right)\right) - (\vec{\mu}_p \cdot \nabla)\nabla\left(\frac{1}{r}\right) - 0 + 0\right]$$

BECAUSE $\partial_{r_j} \vec{\mu}_p = 0$

NOW WE HAVE TO BE VERY CAREFUL

$$\boxed{\nabla \cdot \nabla\left(\frac{1}{r}\right) = \nabla^2\left(\frac{1}{r}\right) = -4\pi\, \delta^{(3)}(\vec{r})}$$

→ NOTICE THAT, SOMEHOW, $\frac{\partial^2}{\partial x^2}\left(\frac{1}{r}\right) = \frac{\partial^2}{\partial y^2}\left(\frac{1}{r}\right) = \frac{\partial^2}{\partial z^2}\left(\frac{1}{r}\right) = -\frac{4\pi}{3}\delta(\vec{r})$

A SIMILAR FACTOR APPEARS ON THE 2ND TERM

$$(\vec{\mu}_p \cdot \nabla)\nabla\left(\frac{1}{r}\right) = (\mu_x \partial_x + \mu_y \partial_y + \mu_z \partial_z)\left(\hat{x}\,\partial_x\left(\frac{1}{r}\right) + \hat{y}\,\partial_y\left(\frac{1}{r}\right) + \hat{z}\,\partial_z\left(\frac{1}{r}\right)\right)$$

$$= \hat{x}\left[\mu_x \underbrace{\partial^2_{x^2}\left(\frac{1}{r}\right)}_{-\frac{4\pi}{3}\delta(\vec{r}) + \frac{3x^2}{r^5} - \frac{1}{r^3}} + \mu_y \underbrace{\partial^2_{xy}\left(\frac{1}{r}\right)}_{\frac{3xy}{r^5}} + \mu_z \underbrace{\partial^2_{xz}\left(\frac{1}{r}\right)}_{\frac{3xz}{r^5}}\right] + \hat{y}[\dots] + \hat{z}[\dots]$$

$$= \hat{x}\left[-\frac{4\pi}{3}\mu_x \delta(\vec{r}) + \frac{3x}{r^5}[\mu_x x + \mu_y y + \mu_z z] - \frac{\mu_x}{r^3}\right] + \hat{y}[\dots] + \hat{z}[\dots]$$

$$= \frac{3(\vec{\mu}_p \cdot \vec{r})\vec{r}}{r^5} - \frac{\vec{\mu}_p}{r^3} - \frac{4\pi}{3}\vec{\mu}_p \delta(\vec{r})$$

$$\Rightarrow \vec{B} = -\frac{\mu_0}{4\pi}\left[-4\pi \vec{\mu}_p \delta(\vec{r}) - 3(\vec{\mu}_p \cdot \vec{r})\frac{\vec{r}}{r^5} + \frac{\vec{\mu}_p}{r^3} + \frac{4\pi}{3}\vec{\mu}_p \delta(\vec{r})\right]$$

$$\boxed{\vec{B} = \frac{\mu_0}{4\pi}\left[3(\vec{\mu}_p \cdot \vec{r})\frac{\vec{r}}{r^5} - \frac{\vec{\mu}_p}{r^3} + \frac{8\pi}{3}\vec{\mu}_p \delta(\vec{r})\right]}$$

FINALLY, $H_2 = -\vec{\mu}_{S_e} \cdot \vec{B} = +\frac{\mu_0}{4\pi} \mu_B \mu_N g_e g_p \frac{\vec{S}_e}{\hbar} \cdot \left[\underbrace{\frac{3(\vec{S}_p \cdot \vec{r})\vec{r}}{\hbar r^5} - \frac{\vec{S}_p}{\hbar r^3}}_{\text{DIPOLE-DIPOLE INTERACTION}} + \frac{8\pi \delta(\vec{r})}{3} \frac{\vec{S}_p}{\hbar}\right]$

ORDER OF MAGNITUDE

$$H_1 = \frac{2\mu_0 \mu_B}{4\pi a_0^3}\left(\frac{a_0^3}{r^3}\right) g_P \mu_N \left(\frac{\vec{S}_P \cdot \vec{L}}{\hbar^2}\right) = 2\frac{m}{M_P} g_P \frac{\mu_B^2 \mu_0}{4\pi a_0^3}\left(\frac{a_0}{r}\right)^3\left(\frac{\vec{S}_P\cdot\vec{L}}{\hbar^2}\right)$$

USE THAT $\mu_0 = \frac{1}{\epsilon_0 c^2}$

RECALL THAT $a_0 = \frac{\hbar}{\alpha m c}$ AND $\alpha = e^2/4\pi\epsilon_0\hbar c$

$$\Rightarrow \frac{\mu_0 \mu_B^2}{4\pi a_0^3} = \frac{\mu_B^2}{4\pi\epsilon_0 a_0^3 c^2} = \frac{e^2\hbar^2}{4m^2c^2 4\pi\epsilon_0 a_0^3} = \frac{1}{4} mc^2\alpha^4$$

$$\Rightarrow H_1 = \frac{1}{2}\frac{m}{M_P} g_P \times \left(\alpha^4 mc^2\right)\left(\frac{a_0}{r}\right)^3\left(\frac{\vec{S}_P\cdot\vec{L}}{\hbar^2}\right)$$

THEREFORE, IT IS $\sim \frac{m}{M_P} \sim \frac{1}{2000}$ SMALLER THAN THE FINE-STRUCTURE CORRECTIONS

LIKEWISE,

$$H_2 = +\frac{\mu_0}{4\pi}\frac{m}{M_P}\frac{\mu_B^2}{a_0^3} g_e g_P \frac{\vec{S}_e}{\hbar}\cdot\left[3\left(\frac{a_0}{r}\right)^3\left(\frac{\vec{S}_P}{\hbar}\cdot\hat{n}\right)\hat{n} - \left(\frac{a_0}{r}\right)^3\frac{\vec{S}_P}{\hbar} + \frac{8\pi}{3}\left(a_0^3\delta^{(3)}(\vec{r})\right)\frac{\vec{S}_P}{\hbar}\right]$$

$$\boxed{H_2 = +\frac{1}{4} g_e g_P\left(\frac{m}{M_P}\right)\left(\alpha^4 mc^2\right)\frac{\vec{S}_e}{\hbar}\cdot\left[\left(\frac{a_0}{r}\right)^3\left(3\left(\frac{\vec{S}_P\cdot\hat{n}}{\hbar}\right)\hat{n} - \frac{\vec{S}_P}{\hbar}\right) + \frac{8\pi}{3}\left(a_0^3\delta^{(3)}(\vec{r})\right)\frac{\vec{S}_P}{\hbar}\right]}$$

WHICH IS OF THE SAME ORDER AS H_1

FINALLY,

$$\boxed{H = H_0 + \underbrace{W_F}_{W_{mv} + W_{SO} + W_D} + \underbrace{W_{HF}}_{H_1 + H_2}}$$

PERTURBATION THEORY ON THE 1S LEVEL

THE STATES ARE $\{ |n\, l\, m\rangle \otimes \underbrace{|S_e, \sigma\rangle}_{e^-\text{'s SPIN}} \otimes \underbrace{|S_p, \tau\rangle}_{\text{PROTON'S SPIN}} \}$

FOR THE $n=1$ LEVEL $\Rightarrow$ $|n\, l\, m\rangle = |1\,0\,0\rangle$

$\Rightarrow$ GROUND MULTIPLET IS $\{ |1\,0\,0, S_e\, \sigma, S_p\, \tau\rangle \} \equiv \{ |\sigma, \tau\rangle \}$

RECALL THAT, BECAUSE $l=0$, THE FINE-STRUCTURE PERTURBATION DOES <u>NOT</u> LIFT THE 4-FOLD DEGENERACY

FOR THE SAME REASON, $H_1 \propto \vec{S}_p \cdot \vec{L}$ VANISHES!

$$\boxed{\langle 1\,0\,0\, \sigma' \tau' | H_1 | 1\,0\,0\, \sigma \tau \rangle = 0}$$

HOWEVER, H_2 DOES NOT INVOLVE $\vec{L}$. WE THEN EXPECT FINITE CORRECTIONS

LET US WORK OUT THE DIPOLE-DIPOLE INTERACTION WHICH IS PROPORTIONAL TO $\vec{S}_e \cdot [3(\vec{S}_p \cdot \hat{n})\hat{n} - \vec{S}_p] = 3(\vec{S}_p \cdot \hat{n})(\vec{S}_e \cdot \hat{n}) - \vec{S}_e \cdot \vec{S}_p = W_{2a}$

$$\vec{S}_p \cdot \hat{n} = S_{px}\, s\theta c\phi + S_{py}\, s\theta s\phi + S_{pz}\, c\theta$$
$$\vec{S}_e \cdot \hat{n} = S_{ex}\, s\theta c\phi + S_{ey}\, s\theta s\phi + S_{ez}\, c\theta$$

$$\Rightarrow W_{2a} = S_{px} S_{ex} (3 s^2\theta c^2\phi - 1) + S_{py} S_{ey} (3 s^2\theta s^2\phi - 1) + S_{pz} S_{ez} (3 c^2\theta - 1)$$
$$+ 3(S_{px} S_{ey} + S_{py} S_{ex})\, s^2\theta\, c\phi\, s\phi + 3(S_{px} S_{ez} + S_{pz} S_{ex})\, c\theta\, s\theta\, c\phi$$
$$+ 3(S_{py} S_{ez} + S_{pz} S_{ey})\, c\theta\, s\theta\, s\phi$$

THE CORRESPONDING MATRIX ELEMENT IS

$$\langle 1\,0\,0\, \sigma' \tau' | W_{2a} | 1\,0\,0\, \sigma \tau \rangle = \langle 1\,0\,0 | s^2\theta c^2\phi - 1 | 1\,0\,0\rangle \langle \sigma' \tau' | S_{px} S_{ex} | \sigma \tau \rangle + \cdots +$$
$$\langle 1\,0\,0 | c\theta\, s\theta\, s\phi | 1\,0\,0\rangle \langle \sigma' \tau' | S_{py} S_{ez} + S_{pz} S_{ey} | \sigma \tau \rangle$$

WE THEN NEED TO COMPUTE THE ANGULAR INTEGRALS $\langle l m | f(\theta,\phi) | l m \rangle = \langle 00 | f(\theta,\phi) | 00 \rangle$

$$= \int d\Omega \, Y_{00}^*(\theta,\phi) f(\theta,\phi) Y_{00}(\theta,\phi)$$

$$= \frac{1}{4\pi} \int d\Omega \, f(\theta,\phi) = \frac{1}{4\pi} \int f(\theta,\phi) \sin\theta \, d\theta \, d\phi$$

INTERESTINGLY, ALL ANGULAR INTEGRALS VANISH.

$$\int (3\cos^2\phi \, s^2\theta - 1) s\theta \, d\theta \, d\phi = 0$$

$$\int (3 s^2\theta s^2\phi - 1) s\theta \, d\theta \, d\phi = 0$$

$$\int (3c^2\theta - 1) s\theta \, d\theta \, d\phi = \int \sqrt{\frac{16\pi}{5}} \, Y_{20}(\theta,\phi) \, d\Omega = 0$$

$$\int s^2\theta \, c\phi s\phi \, s\theta \, d\theta \, d\phi = 0$$

$$\int c\theta s\theta c\phi \, s\theta \, d\theta \, d\phi = 0$$

$$\int c\theta s\theta s\phi \, s\theta \, d\theta \, d\phi = 0$$

THUS, ONLY $H_{2b} = \overbrace{+\frac{1}{4} g_e g_p \left(\frac{m}{m_p}\right) (\alpha^4 mc^2) \times \frac{8\pi}{3} (a_0^3 \delta(\vec{r}))}^{G} \left(\frac{\vec{S}_p \cdot \vec{S}_e}{\hbar^2}\right)$

CONTRIBUTES

THE MATRIX ELEMENTS ARE $G \langle 100 \sigma' \tau' | a_0^3 \delta(\vec{r}) \frac{\vec{S}_p \cdot \vec{S}_e}{\hbar^2} | 100 \sigma \tau \rangle$

$$= G |\psi_{100}(0)|^2 \langle \sigma' \tau' | \frac{\vec{S}_p \cdot \vec{S}_e}{\hbar^2} | \sigma \tau \rangle = \frac{G}{\pi} \langle \sigma' \tau' | \frac{\vec{S}_p \cdot \vec{S}_e}{\hbar^2} | \sigma \tau \rangle$$

NOW WE USE THAT $\vec{S}_p \cdot \vec{S}_e = \frac{1}{2} \left(|\vec{F}|^2 - |\vec{S}_p|^2 - |\vec{S}_e|^2 \right)$ WHERE $\vec{F} = \vec{S}_p + \vec{S}_e$

$$= \frac{1}{2} \left(F^2 - \hbar^2 \tfrac{1}{2}(\tfrac{1}{2}+1) \times 2 \right) = \frac{1}{2} F^2 - \hbar^2 \frac{3}{4}$$

AND $\vec{F}$ CAN BE $\vec{0}$ OR $\vec{1}$ ⇒ POSSIBLE EIGENVALUES: $F=1 \to \frac{\hbar^2}{2} 1(1+1) - \frac{3\hbar^2}{4}$

$$= \frac{1}{4}\hbar^2$$

$F=0 \to \hbar^2 0 - \frac{3}{4}\hbar^2$

$$= -\frac{3}{4}\hbar^2$$

$\vec{0}$ ↓ SINGLET $(g=1)$ $\left\{ \frac{|+-\rangle - |-+\rangle}{\sqrt{2}} \right\}$

$\vec{1}$ ↓ TRIPLET $(g=3)$ $\left\{ |++\rangle, \ \frac{|+-\rangle + |-+\rangle}{\sqrt{2}}, \ |--\rangle \right\}$

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$$H_{2D} = \left(\begin{array}{c|ccc} -\frac{3}{4} & 0 & 0 & 0 \\ \hline 0 & \frac{1}{4} & 0 & 0 \\ 0 & 0 & \frac{1}{4} & 0 \\ 0 & 0 & 0 & \frac{1}{4} \end{array}\right) * \frac{C}{\pi}$$

$$\Delta E = E_{TRIPLET} - E_{SINGLET} = \frac{C}{\pi}\left(\frac{1}{4} - \left(-\frac{3}{4}\right)\right) = \left(\frac{2}{3} g_e g_p \frac{m}{M_p} \alpha^4\right) mc^2$$

$\frac{m}{M_p} \to \frac{1}{1836.15267}$ $\qquad mc^2 \to 510.999$ KeV

$$\boxed{\Delta E \simeq 5.88426 \times 10^{-6}\ eV}$$

CORRESPONDING FREQUENCY : $\nu = \frac{\Delta E}{h} = 1.422\,807 \times 10^9$ Hz

$h \to 4.135\,667\,696\ \frac{eV}{Hz}$

MEASURED VALUE : $1.420\,405\,751\,768(1)$ GHz

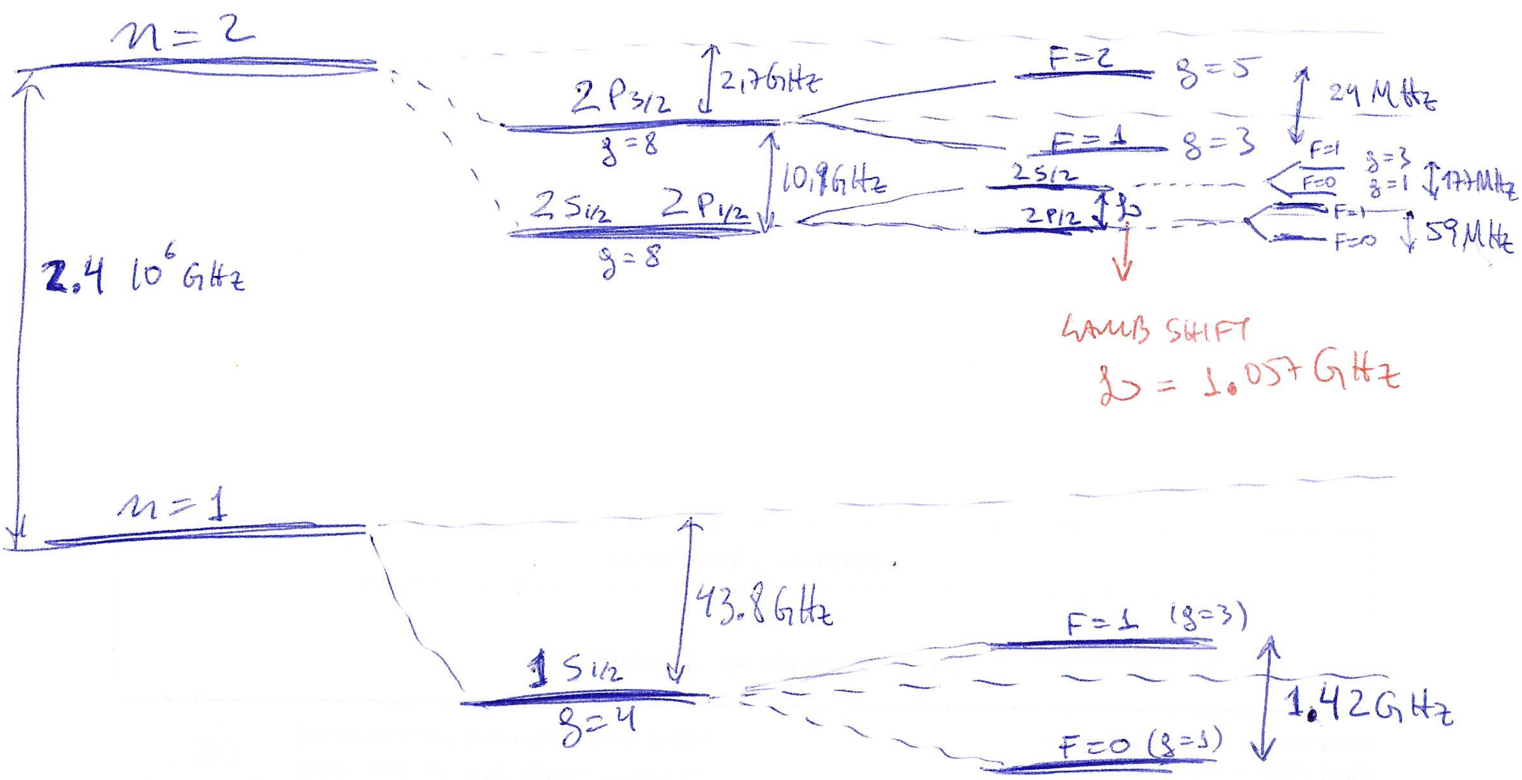
CORRESPONDING TO $\lambda = c/\nu \simeq 21$ cm

"RADIO ASTRONOMY"

RELEVANT TO ASTRONOMY

ENERGY DIAGRAM : $H = H_0 + W_F + W_{HF}$ + (LAMB SHIFT)

H_0 $\qquad$ $H_0 + W_F$ $\qquad$ $H_0 + W_F + W_{HF}$ + LAMB SHIFT $\{\mathcal{S}\}$



ZEEMAN EFFECT ON THE H-ATOM

$$H = H_0 + W_F + W_{HF} + W_B$$

(NO LAMB SHIFT, WE WILL FOCUS ON THE $n=1$ LEVEL)

$$W_B = -\underbrace{(\vec{\mu}_L + \vec{\mu}_{S_e} + \vec{\mu}_{S_p})}\cdot\vec{B}$$

TOTAL MAGNETIC MOMENT DUE TO THE ELECTRON'S ORBITAL + SPIN ANGULAR MOMENTUM AND THE PROTON'S SPIN ANGULAR MOMENTUM

DUE TO THE ELECTRON'S NEGATIVE CHARGE

$$\vec{\mu}_L + \vec{\mu}_{S_e} = -\mu_B\left(g_e\frac{\vec{L}}{\hbar} + g_s\frac{\vec{S}_e}{\hbar}\right)$$

$$\vec{\mu}_{S_p} = g_p\,\mu_N\frac{\vec{S}_p}{\hbar} = \left(\frac{m}{M_p}\right)g_p\,\mu_B\frac{\vec{S}_p}{\hbar}$$

VERY SMALL $\Rightarrow$ NEGLECT

$$\Rightarrow \boxed{W_B \cong \mu_B B\left(g_e\frac{L_z}{\hbar} + g_e\frac{S_z}{\hbar}\right)}$$

SINCE $\vec{B} = B\hat{z}$

FOR THE 1S LEVEL, $l=0 \Rightarrow L_z \to 0$

$H_0 + W_F \to$ DEGENERATED STATES

$W_{HF} + W_B$ WILL LIFT THE DEGENERACY

FOR THE $n=1$ LEVEL, ONLY THE DIRAC-DELTA TERM OF W_{HF} CONTRIBUTES

$$\Rightarrow W_{HF} = H_{2b} = \frac{1}{4}g_e g_p\left(\frac{m}{M_p}\right)(\alpha^4 mc^2)\left(\frac{8\pi}{3}a_0^3\,\delta(\vec{r})\right)\left(\frac{\vec{S}_p\cdot\vec{S}_e}{\hbar^2}\right)$$

$$= C\,a_0^3\,\delta(\vec{r})\left(\frac{\vec{S}_p\cdot\vec{S}_e}{\hbar^2}\right)$$

PROBLEM TO SOLVE

$$\underbrace{H_0 + W_F}_{\text{UNPERTURBED}} + \underbrace{C_1\, a_0^3 \delta(\vec{r}) \left(\frac{\vec{S}_p \cdot \vec{S}_e}{\hbar^2}\right) + 2\omega S_z}_{\text{PERTURBATION}}$$

WHERE $2\omega = \dfrac{\mu_B g_e B}{\hbar}$

$$= \frac{e\cancel{\hbar}}{\cancel{2}m} \frac{\cancel{g_e} B}{\cancel{\hbar}} \simeq \frac{eB}{m}$$

IT IS "SOMEWHAT" CONVENIEN TO WORK ON THE BASIS OF $\vec{F} = \vec{S}_p + \vec{S}_e$

1S LEVEL: $\{|100\sigma\tau\rangle\} \mapsto \{|\sigma\tau\rangle\} \xrightarrow[\text{TO}]{\text{CHANGE}} \{|Fm\rangle\}$

$S_e^z|\sigma\tau\rangle = \frac{\hbar}{2}\sigma|\sigma\tau\rangle$ $\qquad F^2|Fm\rangle = \hbar^2 F(F+1)|Fm\rangle$

$S_p^z|\sigma\tau\rangle = \frac{\hbar}{2}\tau|\sigma\tau\rangle$ $\qquad F_z|Fm\rangle = \hbar m|Fm\rangle$

1st ORDER PERTURBATION THEORY $\to$ PROJECT THE PERTURBATION ONTO DE DEGENERATE GROUND-STATE MANYFOLD

- THE RADIAL INTEGRATION IS SIMPLE

$$\langle 100\, F'm' |\, C_1 a_0^3 \delta(\vec{r})\, \frac{\vec{S}_p\cdot\vec{S}_e}{\hbar^2}\, | 100\, Fm\rangle = C_1 \underbrace{a_0^3 |\psi_{100}(0)|^2}_{\frac{1}{\pi}} \langle F'm' | \frac{\vec{S}_p\cdot\vec{S}_e}{\hbar} | Fm\rangle$$

$$= \frac{C}{\pi} \langle F'm' | \frac{1}{2} \frac{(F^2 - S_p^2 - S_e^2)}{\hbar^2} | Fm\rangle$$

$$= \frac{C}{\pi}\left(\frac{1}{2}F(F+1) - \frac{3}{4}\right)\delta_{FF'}\,\delta_{mm'}$$

RECALL THAT $\{|Fm\rangle\} = \{\underbrace{|11\rangle, |10\rangle, |1-1\rangle}_{\text{TRIPLET}}, \underbrace{|00\rangle}_{\text{SINGLET}}\}$

$|11\rangle = |++\rangle$, $|10\rangle = \dfrac{|+-\rangle + |-+\rangle}{\sqrt{2}}$, $|1-1\rangle = |--\rangle$, $|00\rangle = \dfrac{|+-\rangle - |-+\rangle}{\sqrt{2}}$

NOW, THE ZEEMAN PERTURBATION

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- $2\omega S_z |0,0\rangle_{Fm} = 2\omega S_z \left(\frac{|+-\rangle - |-+\rangle}{\sqrt{2}} \right)_{\sigma\tau} = \hbar\omega \left(\frac{|+-\rangle + |-+\rangle}{\sqrt{2}} \right)$
$= \hbar\omega |1,0\rangle$

- $2\omega S_z |1,-1\rangle = 2\omega S_z |--\rangle = -\hbar\omega |--\rangle = -\hbar\omega |1,-1\rangle$

- $2\omega S_z |1,0\rangle = 2\omega S_z \left(\frac{|+-\rangle + |-+\rangle}{\sqrt{2}} \right) = \hbar\omega \left(\frac{|+-\rangle - |-+\rangle}{\sqrt{2}} \right) = \hbar\omega |0,0\rangle$

- $2\omega S_z |1,1\rangle = 2\omega S_z |++\rangle = \hbar\omega |++\rangle = \hbar\omega |1,1\rangle$

THUS, THE CORRESPONDING MATRIX IS

$$\begin{array}{cccc} |11\rangle & |10\rangle & |1-1\rangle & |00\rangle \end{array}$$
$$\left(\begin{array}{ccc|c} \frac{G}{4\pi}+\hbar\omega & 0 & 0 & 0 \\ 0 & \frac{G}{4\pi} & 0 & \hbar\omega \\ 0 & 0 & \frac{G}{4\pi}-\hbar\omega & 0 \\ \hline 0 & \hbar\omega & 0 & -\frac{3G}{4\pi} \end{array}\right) \xrightarrow{\text{REARRANGIN}} \begin{array}{c} \begin{array}{cccc} |11\rangle & |1-1\rangle & |10\rangle & |00\rangle \end{array} \\ \left(\begin{array}{cc|cc} \frac{G}{4\pi}+\hbar\omega & 0 & \multicolumn{2}{c}{\multirow{2}{*}{0}} \\ 0 & \frac{G}{4\pi}-\hbar\omega & & \\ \hline \multicolumn{2}{c|}{\multirow{2}{*}{0}} & G/4\pi & \hbar\omega \\ & & \hbar\omega & -3G/4\pi \end{array}\right) \end{array}$$

$\Rightarrow$ STATES $|1,1\rangle = |++\rangle$ AND $|1,-1\rangle = |--\rangle$ ARE EIGENSTATES WITH EIGENENERGIES $\frac{G}{4\pi} \pm \hbar\omega$, RESPECTIVELY

- THE $S_z = 0$ SUBSPACE: $\begin{pmatrix} \frac{G}{4\pi} & \hbar\omega \\ \hbar\omega & -\frac{3G}{4\pi} \end{pmatrix} = -\frac{G}{4\pi}\mathbb{1} + \hbar\omega\sigma^x + \frac{G}{2\pi}\sigma^z$

$= -\frac{G}{4\pi}\mathbb{1} + \sqrt{\hbar^2\omega^2 + \left(\frac{G}{2\pi}\right)^2}\left(\sin\theta\,\sigma^x + \cos\theta\,\sigma^z\right)$

$\cos\theta = \frac{G/2\pi}{\sqrt{\hbar^2\omega^2 + (G/2\pi)^2}}$

$\sin\theta = \frac{\hbar\omega}{\sqrt{\hbar^2\omega^2 + (G/2\pi)^2}}$

$\Rightarrow$ EIGENSTATE $|\nearrow\rangle = \cos\frac{\theta}{2}|1,0\rangle + \sin\frac{\theta}{2}|00\rangle$

$E_{\nearrow} = +\sqrt{(\hbar\omega)^2 + (G/2\pi)^2} - \frac{G}{4\pi}$

$\Rightarrow$ EIGENSTATE $|\swarrow\rangle = +\sin\frac{\theta}{2}|1,0\rangle - \cos\theta|00\rangle$

$E_{\swarrow} = -\frac{G}{4\pi} - \sqrt{(\hbar\omega)^2 + \left(\frac{G}{2\pi}\right)^2}$

ENERGY DIAGRAM (GROTRIAN DIAGRAM)