PERTURBATION OF HYDROGEN

SPECTROSCOPY OF HYDROGEN ATOM PLAYED CRUCIAL ROLE FOR DEVELOPMENT OF QUANTUM MECHANICS AND FOR PERTURBATION THEORY IN PARTICULAR

ENERGY LEVELS OF H CAN NOW BE MEASURED WITH 15 DIGITS PRECISION, PROVIDING ONE OF THE BEST TESTS FOR QUANTUM THEORY

OVERVIEW:

PERTURBATIONS CAUSED BY INTERNAL FIELDS
[BETWEEN PROTON + ELECTRON]

- FINE STRUCTURE
  - RELATIVISTIC CORRECTION
  - SPIN-ORBIT COUPLING
- HYPERFINE STRUCTURE

PERTURBATIONS CAUSED BY EXTERNAL FIELDS

- STARK EFFECT [EXT. $\vec{E}$-FIELD]
- ZEEMAN EFFECT [EXT. $\vec{B}$-FIELD]

⇨ PRESENTATIONS

[SECT. 4.2 GRIFFITHS]

REVIEW OF HYDROGEN ATOM

UNPERTURBED H-ATOM HAMILTONIAN:

$$\boxed{H^{(0)} = -\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{4\pi\epsilon_0}\frac{1}{r}}$$

[KINETIC ENERGY + COULOMB POTENTIAL TERM]

m: REDUCED MASS

$$\nabla^2 \equiv \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

∇: Del
Nabla

ϵ_0: PERMITTIVITY OF FREE SPACE

$\epsilon_0 = 8.854 \cdot 10^{-12}\ \frac{C^2}{N}m^2$

[CAPABILITY OF VACUUM TO PERMIT ELECTRIC FIELD LINES]

UNPERTURBED H-ATOM EIGENVALUE EQUATION:

$$H^{(0)}\,|nlm\rangle^{(0)} = E_n^{(0)}\,|nlm\rangle^{(0)}$$

UNPERTURBED EIGENSTATES:

$$|nlm\rangle^{(0)} = R_{nl}(r)\,Y_l^m(\theta,\phi)$$

UNPERTURBED EIGENVALUES:

$$E_n^{(0)} = -\frac{m}{2\hbar^2}\left(\frac{e^2}{4\pi\epsilon_0}\right)^2\frac{1}{n^2} \quad , n=1,2,3,\dots$$

$$= -\frac{1}{2}\frac{1}{n^2}\frac{e^2}{4\pi\epsilon_0}\frac{1}{a_0}$$

WITH BOHR RADIUS

$$a_0 \equiv \frac{4\pi\epsilon_0\hbar^2}{m\,e^2} = 0.529 \cdot 10^{-10}\,m$$

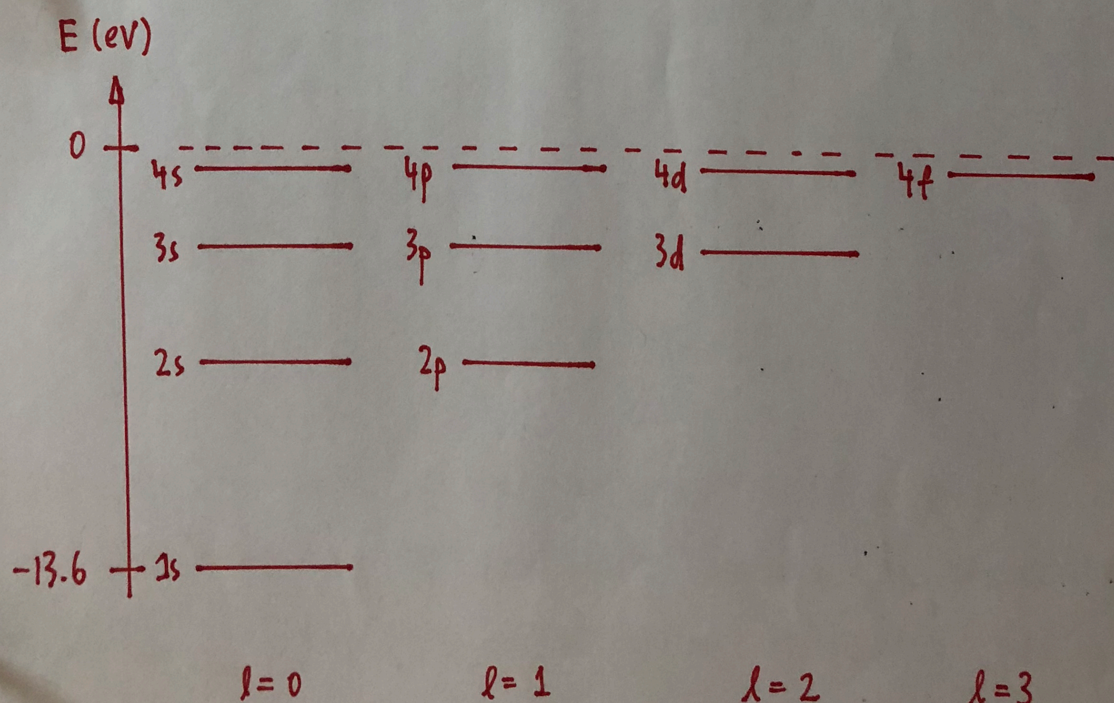
[$E_n^{(0)}$ INDEPENDENT OF l, m]

- DEGENERACY OF EACH LEVEL IS n^2
- WE SUSPECT THAT, ONCE PERTURBATIONS ARE TURNED ON, ENERGY LEVELS WILL SHIFT AND DEGENERACIES WILL BE [PARTIALLY] LIFTED
- IN FOLLOWING WE WILL FOCUS ON FINDING ENERGY CORRECTIONS ONLY [NOT EIGENSTATE CORRECTIONS]; FOR THIS WE WILL BE USING UNPERTURBED EIGENSTATES

$\ell = 0, \dots, n-1$

$m = -\ell, \dots, +\ell$

ENERGY LEVEL DIAGRAM OF HYDROGEN FOR $n=1$ TO $n=4$



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CONVENIENT EXPRESSION:

$$E_n^{(0)} = -\frac{1}{2}\frac{1}{n^2}\alpha^2 \overbrace{m_e c^2}^{\text{ELECTRON REST ENERGY} = 511\text{ keV}}$$

$$\alpha \equiv \frac{e^2}{4\pi\epsilon_0 \hbar c} = 1/137 \quad \text{"FINESTRUCTURE CONSTANT"}$$

EXAMPLE: GROUND STATE

$$E_1^{(0)} = -\frac{1}{2}\frac{1}{1^2}\left(\frac{1}{137}\right)^2 (511{,}000\text{ eV}) = -13.6\text{ eV}$$

RECALL VIRIAL THEOREM FOR H: $\boxed{\langle T\rangle = -E_n}$ KINETIC ENERGY

[HANDOUT]

$\langle V\rangle = 2E_n$

[GRIFFITHS, PROB. 4.40 AND EQS. (4.190), (4.191)]

THUS, IN H ATOM, TOTAL ENERGY IS ROUGHLY SPLIT BETWEEN KINETIC AND POTENTIAL ENERGY:

$$\frac{1}{2}m_e v^2 \approx \frac{1}{2}\frac{1}{n^2}\alpha^2 m_e c^2$$

1

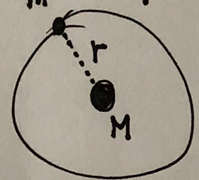
$$\frac{v}{c} \approx \alpha = 1/137$$

- ELECTRON MOVES, ROUGHLY, WITH 1% OF SPEED OF LIGHT
- LARGE ENOUGH FOR RELATIVISTIC CORRECTIONS TO BECOME IMPORTANT
- SMALL ENOUGH FOR APPLICATION OF PERTURBATION THEORY

VIRIAL THEOREM [RUDOLF CLAUSIUS (1822 - 1888)]

SUPPOSE THAT :
- YOU HAVE A FINITE COLLECTION OF POINT PARTICLES
- TIME AVERAGES OF TOTAL KINETIC ENERGY AND TOTAL POTENTIAL ENERGY ARE WELL DEFINED
- POSITION AND VELOCITIES OF ALL PARTICLES ARE BOUNDED FOR ALL TIME

SIMPLE EXAMPLE: PLANET ORBITING STAR ON CIRCULAR ORBIT



$V = -G\frac{mM}{r}$

$m \ll M$

$$\left.\begin{aligned}\vec{F}_G &= -G\frac{mM}{r^2}\\ \vec{F}_{cp} &= -\frac{mv^2}{r}\end{aligned}\right\} \quad \frac{mv^2}{r} = G\frac{mM}{r^2}$$

$$\underbrace{T}_{\text{KINETIC ENERGY OF LIGHT PARTICLE}} = \frac{mv^2}{2} = G\frac{mM}{2r} = -\frac{1}{2}V$$

GENERALIZED VERSION OF THIS RESULT IS CALLED :

$$\boxed{\begin{array}{c}\text{VIRIAL THEOREM}\\ \langle T\rangle = -\frac{1}{2}\langle V\rangle\end{array}}$$

- FOR A PROOF IN CLASSICAL PHYSICS, SEE H. GOLDSTEIN, "CLASSICAL MECHANICS" (ADDISON-WESLEY, 1950)
- IT IS APPLIED IN ASTROPHYSICS, STATISTICAL MECHANICS, QUANTUM MECHANICS

NOW CONSIDER H GROUND STATE :

$$E_{g.s.} = \boxed{-\frac{1}{2}\underbrace{\frac{1}{n^2}}_{1}\frac{e^2}{4\pi\epsilon_0}\frac{1}{a_0}} \quad ; \quad \psi_{g.s.} = \frac{1}{\sqrt{\pi}\, a_0^{3/2}} e^{-r/a_0}$$

AVERAGE POTENTIAL ENERGY :

$$\langle V \rangle = -\frac{e^2}{4\pi\epsilon_0}\int \psi^*_{g.s.}\frac{1}{r}\psi_{g.s}\, dV = -\frac{e^2}{4\pi^2\epsilon_0 a_0^3}\int_0^\infty e^{-2r/a_0}\frac{1}{r}4\pi r^2 dr$$

$$= -\frac{e^2}{\pi\epsilon_0 a_0^3}\underbrace{\int_0^\infty e^{-2r/a_0} r\, dr}$$

$$= \underbrace{\left[-\frac{a_0}{2}e^{-2r/a_0} r\right]_0^\infty}_{=0} + \frac{a_0}{2}\int_0^\infty e^{-2r/a_0} dr$$

$$= -\frac{a_0^2}{4}\left[e^{-2r/a_0}\right]_0^\infty = \frac{a_0^2}{4}$$

$$= \boxed{-\frac{e^2}{4\pi\epsilon_0 a_0}}$$

IT FOLLOWS THAT : $E_{g.s.} = +\frac{1}{2}\langle V \rangle$ AND

$$\langle T \rangle = E_{g.s.} - \langle V \rangle = -\frac{1}{2}\langle V \rangle$$

[VIRIAL THEOREM]

FROM NOW ON, WE WILL ASSUME THAT THE PROTON IS INFINITELY HEAVY;

ONLY FOR THE UNPERTURBED ENERGIES IS IT RIGOROUS TO USE THE REDUCED MASS OF THE ELECTRON; THIS REPLACEMENT IS NOT CORRECT FOR THE PERTURBATIONS, WHICH ARE RELATIVISTIC

SINCE $m_p \gg m_e$, AND SINCE WHAT WE WILL CALCULATE ARE ALREADY CORRECTIONS, WE WILL NOT WORRY ABOUT IT

[SEE p. 1213/1214 IN COHEN-TANNOUDJI, QUANTUM MECHANICS]

FINE STRUCTURE : RELATIVISTIC CORRECTION

FIRST TERM IN UNPERTURBED HAMILTONIAN : $T = -\frac{\hbar^2}{2m_e}\nabla^2$

DROP "e"

[CLASSICAL KINETIC ENERGY]

REPLACE BY RELATIVISTIC KINETIC ENERGY

$$T = \underbrace{\frac{m_e c^2}{\sqrt{1 - v^2/c^2}}}_{\text{TOTAL RELATIVISTIC ENERGY}} - \underbrace{m_e c^2}_{\text{REST ENERGY}} = \sqrt{p^2c^2 + m_e^2 c^4} - m_e c^2$$

TOTAL RELATIVISTIC ENERGY [EXCLUDING POTENTIAL E; NOT OF CONCERN IN FIRST TERM]

WITH

$$p = \frac{m_e v}{\sqrt{1 - v^2/c^2}}$$

RELATIVISTIC LINEAR MOMENTUM

$$= \sqrt{\frac{p^2 c^2 m_e^2 c^4}{m_e^2 c^4} + m_e^2 c^4} - m_e c^2$$

$$= m_e c^2 \left[\sqrt{\frac{p^2}{m_e^2 c^2} + 1} - 1\right]$$

EXPAND SQUARE ROOT IN POWERS OF SMALL NUMBER $x \equiv \frac{p}{m_e c}$

$$\frac{p}{m_e c} = \underbrace{\frac{m_e v}{m_e c}}_{\substack{\text{SMALL} \\ 1\%}} \frac{\overbrace{1}^{\approx 1}}{\sqrt{1 - v^2/c^2}}$$

$$\sqrt{1+x^2} \approx 1 + \frac{x^2}{2} - \frac{x^4}{8} + \dots$$

$$\Rightarrow \quad T = m_e c^2 \left[\cancel{1} + \frac{1}{2}\frac{p^2}{m_e^2 c^2} - \frac{1}{8}\frac{p^4}{m_e^4 c^4} + \dots - \cancel{1} \right]$$

RELATIVISTIC LINEAR MOMENTUM! WHICH WE ASSOCIATE WITH QUANTUM OPERATOR $p \to i\hbar\nabla$

$$= \underbrace{\frac{p^2}{2m_e}}_{\text{1. TERM IN HAMILTONIAN}} - \underbrace{\frac{p^4}{8m_e^3c^2}}_{\text{LOWEST ORDER RELATIVISTIC CORRECTION}} + \dots$$

PERTURBING HAMILTONIAN: $H_r' = -\dfrac{p^4}{8m_e^3c^2}$

- PERTURBATION IS NEGATIVE: INCREASES BINDING ENERGY [LARGER MAGNITUDE]

- PERTURBATION SMALLER THAN UNPERTURBED HAMILTONIAN BY 2 ORDERS OF MAGNITUDE IN $p/m_e c \approx v/c \approx \alpha$

- WE EXPECT ENERGY CORRECTION TO BE SMALLER BY 2 ORDERS OF MAGNITUDE IN α COMPARED TO UNPERTURBED ENERGIES

SHOULD WE NOW USE NON-DEGENERATE OR DEGENERATE PERTURBATION THEORY ?

HYDROGEN LEVELS ARE DEGENERATE WITH RESPECT TO ℓ AND m

HOWEVER, REMEMBER EARLIER THEOREM

- EIGENFUNCTIONS $|n\ell m\rangle^{(0)}$ ARE SIMULTANEOUS EIGENFUNCTIONS OF $H^{(0)}$ AND $\vec{L}^2, L_z$, WITH DISTINCT EIGENVALUES (ℓ, m)

- $\vec{L}^2, L_z$ ARE HERMETIAN OPERATORS THAT COMMUTE WITH $\vec{p}^{\,2}$ [$H^{(0)}$] AND $\vec{p}^{\,4}$ [PERTURBATION]

  $\Rightarrow$ SEE HOMEWORK #3

$\to$ $|n\ell m\rangle^{(0)}$ ARE ALREADY THE "GOOD" SOLUTIONS THAT CAN BE USED IN NON-DEGENERATE PERTURBATION THEORY

FIRST-ORDER NON-DEGENERATE PERTURBATION THEORY:

$$E_{rel}^{(1)} = \langle \psi_{nlm}^{(0)} | H' | \psi_{nlm}^{(0)} \rangle = -\frac{1}{8m_e^3c^2} \langle \psi_{nlm}^{(0)} | p^4 | \psi_{nlm}^{(0)} \rangle$$

$$= -\frac{1}{8m_e^3c^2} \langle p^2 \psi_{nlm}^{(0)} | p^2 \psi_{nlm}^{(0)} \rangle$$

SINCE p^2 IS HERMETIAN:

$$\langle \psi_1 | \hat{A} \psi_2 \rangle = \langle \hat{A} \psi_1 | \psi_2 \rangle = \langle \psi_2 | \hat{A} \psi_1 \rangle^*$$

FROM EQUATION FOR UNPERTURBED STATES:

$$\left[\frac{p^2}{2m_e} - \frac{e^2}{4\pi\epsilon_0 r} \right] \psi_{nlm}^{(0)} = E_n^{(0)} \psi_{nlm}^{(0)}$$

$$p^2 \psi_{nlm}^{(0)} = 2m_e \left[E_n^{(0)} + \frac{e^2}{4\pi\epsilon_0 r} \right] \psi_{nlm}^{(0)}$$

$$E_{rel}^{(1)} = -\frac{1}{8m_e^3c^2} 4m_e^2 \langle \psi_{nlm}^{(0)} | \underbrace{\left(E_n^{(0)} + \frac{e^2}{4\pi\epsilon_0 r} \right)\left(E_n^{(0)} + \frac{e^2}{4\pi\epsilon_0 r} \right)}_{[E_n^{(0)}]^2 + 2E_n^{(0)} \frac{e^2}{4\pi\epsilon_0 r} + \left(\frac{e^2}{4\pi\epsilon_0 r} \right)^2} | \psi_{nlm}^{(0)} \rangle$$

$$= -\frac{1}{2m_ec^2} \left[[E_n^{(0)}]^2 + 2E_n^{(0)} \frac{e^2}{4\pi\epsilon_0} \left\langle \frac{1}{r} \right\rangle_{nl} + \left(\frac{e^2}{4\pi\epsilon_0} \right)^2 \left\langle \frac{1}{r^2} \right\rangle_{nl} \right]$$

WHERE $\langle f(r) \rangle_{nl} \equiv \langle \psi_{nlm}^{(0)} | f(r) | \psi_{nlm}^{(0)} \rangle$

$\langle Y_\ell^m | Y_{\ell'}^{m'} \rangle = \delta_{\ell\ell'} \delta_{mm'}$

RECALL $\psi_{n\ell m}^{(0)} = R_{n\ell}(r)\, Y_\ell^m(\theta,\phi)$

$\Rightarrow$ $\langle \frac{1}{r} \rangle$ AND $\langle \frac{1}{r^2} \rangle$ WILL ONLY DEPEND ON RADIAL WAVE FUNCTION AND THUS ON n, ℓ [DROP QUANTUM NUMBER m]

CALCULATION OF MATRIX ELEMENTS:

(i) $\langle \frac{1}{r} \rangle_{n\ell} = \int_0^\infty \frac{1}{r} R_{n\ell}^2(r)\, r^2\, dr$

RECALL VIRIAL THEOREM FOR H:

$$\langle V \rangle = 2E_n$$

$$\langle -\frac{e^2}{4\pi\epsilon_0}\frac{1}{r} \rangle = -\frac{e^2}{4\pi\epsilon_0}\langle \frac{1}{r} \rangle$$

$$2E_n = -2\,\frac{m_e}{2\hbar^2}\left(\frac{e^2}{4\pi\epsilon_0}\right)^2 \frac{1}{n^2}$$

$$\Rightarrow \langle \frac{1}{r} \rangle = \underbrace{\frac{m_e e^2}{4\pi\epsilon_0 \hbar^2}}_{= 1/a_0} \cdot \frac{1}{n^2} = \frac{1}{a_0 n^2}$$

(ii) $\langle \frac{1}{r^2} \rangle_{n\ell} = \int_0^\infty \frac{1}{r^2} R_{n\ell}^2(r)\, r^2\, dr = \frac{1}{(\ell + \frac{1}{2})\, n^3 a_0^2}$ [PROB. 6.33 GRIFFITHS]

TO SIMPLIFY THINGS:

$$E_n^{(0)} = -\frac{1}{n^2}\,\frac{1}{2}\,\frac{e^2}{4\pi\epsilon_0}\,\frac{1}{a_0} = \overbrace{-\frac{1}{2n^2}\,\alpha^2 m_e c^2}^{\text{SEE EARLIER}} \Rightarrow \frac{e^2}{4\pi\epsilon_0} = a_0 \alpha^2 m_e c^2$$

PUT EVERYTHING TOGETHER:

$$E^{(1)}_{rel} = -\frac{1}{2m_ec^2}\Bigg[\frac{\alpha^4 m_e^2 c^4}{4n^4} + 2\overbrace{\left(-\tfrac{1}{2}\right)\frac{1}{n^2}\alpha^2 m_ec^2}^{E_n^{(0)}}\ \overbrace{a_0\alpha^2 m_ec^2}^{\frac{e^2}{4\pi\epsilon_0}}\ \overbrace{\frac{1}{n^2a_0}}^{\langle\frac{1}{r}\rangle_{nl}}$$

$$+ a_0^2\alpha^4 m_e^2 c^4 \frac{1}{(l+\frac{1}{2})n^3a_0^2}\Bigg]$$

$$= -\frac{1}{8}\frac{m_ec^2}{n^4}\alpha^4 + \frac{1}{2}\frac{1}{n^4}\alpha^4 m_ec^2 - \frac{1}{2}m_ec^2\alpha^4\frac{1}{l+\frac{1}{2}}\frac{1}{n^3}$$

$$= -\frac{1}{2}m_ec^2\alpha^4\Bigg[\underbrace{\frac{1}{4n^4} - \frac{1}{n^4}}_{-\frac{3}{4n^4}} + \frac{1}{n^3(l+\frac{1}{2})}\Bigg]$$

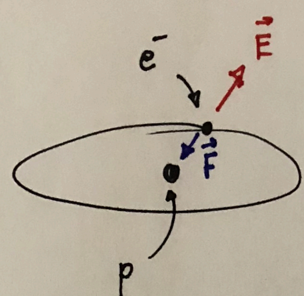
GRIFFITHS, EQ. (6.57)

$$\boxed{E^{(1)}_{rel} = -\frac{1}{2}m_ec^2\alpha^4\left[\frac{1}{n^3(l+\frac{1}{2})} - \frac{3}{4n^4}\right] = -\frac{\left[E_n^{(0)}\right]^2}{2m_ec^2}\left[\frac{4n}{l+\frac{1}{2}} - 3\right]}$$

AS EXPECTED, RELATIVISTIC CORRECTION IS SMALLER THAN BOHR ENERGY BY A FACTOR OF α^2: $E_n^{(0)} = -\frac{1}{2}m_ec^2\alpha^2\frac{1}{n^2}$

FINE STRUCTURE : SPIN - ORBIT COUPLING

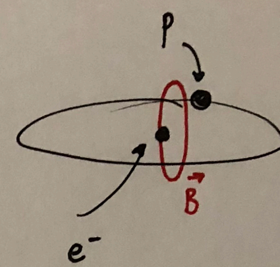
IN PROTON REST FRAME:



- ELECTRON EXPERIENCES PURELY ELECTRIC FIELD FROM PROTON
- SPIN - ORBIT COUPLING ARISES FROM INTERACTION BETWEEN PROTON ELECTRIC FIELD WITH ELECTRON ELECTRIC DIPOLE MOMENT

[SUPER MESSY SINCE
$d_e < -2 \cdot 10^{-29}$ e·cm]

IN ELECTRON REST FRAME



- $\vec{E}$ IN CENTER OF CURRENT LOOP IS ZERO
- ELECTRON EXPERIENCES PURELY MAGNETIC FIELD GENERATED BY PROTON
- SPIN-ORBIT COUPLING ARISES FROM INTERACTION BETWEEN MAGNETIC FIELD WITH ELECTRON MAGNETIC DIPOLE MOMENT

IN STANDARD MODEL, ELECTRON EDM ARISES FROM VIOLATION OF PARITY AND TIME REVERSAL INVARIANCE

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d_e IS A MEASURE OF THE AVERAGE DISPLACEMENT OF CHARGE FROM THE CENTER OF MASS; ONLY DISPLACEMENT ALONG SPIN AXIS CONTRIBUTES TO d_e, BECAUSE SPIN AVERAGES OTHER COMPONENTS TO ZERO

INTERACTION OF NUCLEAR MAGNETIC DIPOLE MOMENT WITH MAGNETIC FIELD GENERATED BY ELECTRON:

$\longrightarrow$ HYPERFINE STRUCTURE

$\mu_0 = 4\pi\, 10^{-7}\ N s^2/C^2$
PERMEABILITY OF FREE SPACE

MAGNETIC FIELD AT CENTER OF LOOP:

$$B = \frac{\mu_0 I}{2r}$$ "BIOT - SAVART LAW"

CURRENT OF PROTON WITH CHARGE $+e$ ORBITING IN PERIOD $T = 2\pi r / v_p$

$$= \frac{\mu_0}{2r} \underbrace{\frac{e}{2\pi r} v_p}_{I}$$

NOW: $v_p^{\text{ELECTRON REST FRAME}} = v_{e^-}^{\text{PROTON REST FRAME}}$

ELECTRON ORBITAL ANGULAR MOMENTUM : $L = m_e v_e r \Rightarrow v_e = \dfrac{L}{m_e r}$

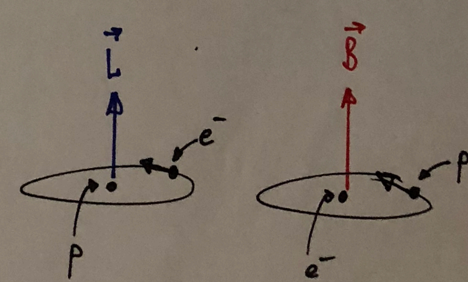
WE FIND:

$$B = \frac{\mu_0}{2r} \frac{e L}{2\pi r^2 m_e} = \frac{\mu_0 e L}{4\pi\, m_e r^3} = \frac{e L}{4\pi \epsilon_0 m_e c^2 r^3}$$

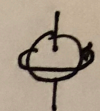
$$c^2 = \frac{1}{\epsilon_0 \mu_0}$$

$\vec{B}$ AND $\vec{L}$ POINT INTO SAME DIRECTION:

$$\vec{B} = \frac{e}{4\pi\epsilon_0 m_e c^2 r^3} \vec{L}$$



SPIN-ORBIT INTERACTION ENERGY



$\vec{\mu} \equiv i\vec{A}$

CLASSICALLY :

- EACH VOLUME ELEMENT OF A ROTATING CHARGED SPHERE REPRESENTS A CURRENT LOOP THAT CONTRIBUTES TO A MAGNETIC FIELD
- OVERALL EFFECT IS CREATION OF A MAGNETIC DIPOLE WITH POLES OF EQUAL MAGNITUDE, BUT OPPOSITE POLARITY

ELECTRON MAGNETIC DIPOLE MOMENT : $\vec{\mu} = -g\dfrac{e}{2m_e}\underbrace{\vec{S}}_{\text{ELECTRON SPIN}}$

[DIRAC EQUATION GIVES : $\vec{\mu} = -\dfrac{e}{m_e}\vec{S}$; SEE ALSO FOOTNOTE 12 ON p. 273 IN GRIFFITHS]

SPIN-ORBIT INTERACTION ENERGY IS CAUSED BY TORQUE EXERTED BY MAGNETIC FIELD [GENERATED BY ORBITING PROTON] ON INTRINSIC SPIN MAGNETIC DIPOLE MOMENT (μ) OF ELECTRON [IN ELECTRON INSTANTANEOUS REST FRAME]

$$H'_{so} = E_{so} = -\vec{\mu}\cdot\vec{B} = -\Big(\overbrace{-\underbrace{\frac{e}{2m_e}}_{\text{WRONG BY FACTOR OF 2}}\vec{S}}^{\text{CLASS. RESULT}}\Big)\overbrace{\underbrace{\frac{e}{4\pi\epsilon_0 m_e c^2 r^3}}_{}\vec{L}}^{\text{ORBITAL MOTION}} = \underbrace{\frac{e^2}{8\pi\epsilon_0 m_e^2 c^2 r^3}\vec{L}\cdot\vec{S}}_{\text{CORRECT RESULT}}$$

ACCOUNT FOR FACT THAT ENERGY IS LOWER WHEN $\vec{\mu}$ AND $\vec{B}$ ARE ALIGNED

ANOTHER FACTOR OF $\frac{1}{2}$ IS MISSING BECAUSE e^- IS NOT IN AN INERTIAL REFERENCE FRAME; "THOMAS PRECESSION" CORRECTION

CONSIDER ANGULAR MOMENTA:

- BECAUSE OF $\vec{L}\cdot\vec{S}$ PERTURBATION TERM IN TOTAL HAMILTONIAN, NEITHER $\vec{L}$ NOR $\vec{S}$ ARE SEPARATELY CONSERVED

IN THE ABSENCE OF SPIN-ORBIT INTERACTION, AND OF ANY TORQUES, $\vec{L}$ AND $\vec{S}$ WOULD BE CONSERVED [ℓ, m_ℓ, m_s];

BUT WITH A $\overset{\text{UNIFORM}}{\vec{B}}$-FIELD, WHOSE ORIENTATION AND STRENGTH ARE GIVEN BY $\vec{L}$, A TORQUE ACTS ON SPIN MAGNETIC DIPOLE MOMENT

SUCH TORQUE WILL CHANGE THE DIRECTION, BUT NOT THE MAGNITUDE, OF $\vec{S}$; NOR WILL REACTION TORQUE ACTING ON $\vec{L}$ CHANGE ITS MAGNITUDE

$\Rightarrow$ ORIENTATIONS OF $\vec{L}$ AND $\vec{S}$ WILL BE CHANGED [z-COMPONENTS]

- L_z AND S_z DO NOT COMMUTE WITH $H'_{SO} \sim \vec{L}\cdot\vec{S}$

- IF WE USE FUNCTIONS $\psi^{(0)}_{n\ell m_\ell m_s}$ AS OUR UNPERTURBED BASIS,

THE MATRIX $\begin{pmatrix} W_{aa} & W_{ab} & \cdots \\ W_{ba} & W_{bb} & \\ \vdots & & \ddots \end{pmatrix}$ WILL <u>NOT</u> HAVE A DIAGONAL FORM

[REMEMBER THE EARLIER THEOREM]

- CALCULATION BECOMES GREATLY SIMPLIFIED IF A "GOOD" BASIS CAN BE FOUND FOR WHICH THE MATRIX IS DIAGONAL

[SO THAT WE CAN USE NON-DEGENERATE PERTURBATION THEORY]

- WE NEED TO FIND A BASIS APPROPRIATE FOR OPERATORS THAT COMMUTE WITH $H^{(0)}$ AND $H'_{SO} \sim \vec{L}\cdot\vec{S}$

- LET'S INTRODUCE TOTAL ANGULAR MOMENTUM $\vec{J} = \vec{L} + \vec{S}$;

  $H'_{SO} \sim \vec{L}\cdot\vec{S}$ COMMUTES WITH $\vec{L}^2, \vec{S}^2, \vec{J}, J_z$;

  ALSO: $\vec{J}^2 = \vec{L}^2 + \vec{S}^2 + 2\vec{L}\cdot\vec{S} \Rightarrow \vec{L}\cdot\vec{S} = \frac{1}{2}\left[\vec{J}^2 - \vec{L}^2 - \vec{S}^2\right]$

- CONSIDER NOW FUNCTIONS $\psi^{(0)}_{nljm_j}$ WHICH ARE EIGENSTATES OF OPERATORS $H^{(0)}, \vec{L}^2, \vec{S}^2, \vec{J}^2, J_z$ WITH EIGENVALUES $E_n^{(0)}$, $l(l+1)\hbar^2$, $\frac{3}{4}\hbar^2$, $j(j+1)\hbar^2$, $m_j\hbar$

  FROM ANGULAR MOMENTUM COUPLING, ALLOWED VALUES ARE:

  $$j = l \pm \frac{1}{2} \quad \text{FOR } l \neq 0$$
  $$j = \frac{1}{2} \quad \text{FOR } l = 0$$

- WE CAN CONSTRUCT THESE FROM LINEAR COMBINATIONS:

$$\psi^{(0)}_{nljm_j} = \sum_{m_l m_s} \underbrace{\langle l\, s\, m_l\, m_s \,|\, j\, m \rangle}_{\substack{\text{CLEBSCH-GORDAN}\\ \text{COEFFICIENTS}}} \psi^{(0)}_{nlm_lm_s} \quad , \quad s = \frac{1}{2}$$

- THESE FORM A "GOOD" BASIS IN WHICH THE PERTURBATION MATRIX IS DIAGONAL

FIRST-ORDER NON-DEGENERATE PERTURBATION THEORY:

$$E_{SO}^{(1)} = \langle \Psi_{nlsjm_j}^{(0)} | H'_{SO} | \Psi_{nlsjm_j}^{(0)} \rangle = \frac{e^2}{8\pi\epsilon_0 m_e^2 c^2} \langle \Psi_{nlsjm_j}^{(0)} | \frac{1}{r^3} \vec{L}\cdot\vec{S} | \Psi_{nljsm_j}^{(0)} \rangle$$

SINCE $\vec{j}$ IS CONSERVED

$$= \frac{e^2}{16\pi\epsilon_0 m_e^2 c^2} \underbrace{\langle \frac{1}{r^3} \rangle_{nl}}_{= \frac{1}{l(l+\frac{1}{2})(l+1)n^3 a_0^3}} \underbrace{\langle \Psi_{lsjm_j}^{(0)} | \vec{J}^2 - \vec{L}^2 - \vec{S}^2 | \Psi_{lsjm_j}^{(0)} \rangle}_{= \hbar^2 [j(j+1) - l(l+1) - s(s+1)]}$$

$s = \frac{1}{2}$

[GRIFFITHS, PROB. 6.35c]

USE: $\frac{e^2}{4\pi\epsilon_0} = a_0 \alpha^2 m_e c^2$ AND $a_0 = \frac{\hbar}{\alpha m_e c}$

$$E_{SO}^{(1)} = \left[\frac{a_0 \alpha^2 m_e^2 c^2 \hbar^2}{4 m_e^2 c^2 a_0^3 n^3} \frac{j(j+1) - l(l+1) - 3/4}{l(l+1)(l+\frac{1}{2})} \right] = \frac{\alpha^2 m_e^2 c^2 \alpha^2 m_e^2 c^2}{\hbar^2 4 m_e^2 c^2} \hbar^2 \frac{1}{n^3} \frac{j(j+1) - l(l+1) - 3/4}{l(l+1)(l+\frac{1}{2})}$$

$$\boxed{E_{SO}^{(1)} = \frac{\alpha^4}{4} m_e c^2 \frac{1}{n^3} \frac{j(j+1) - l(l+1) - 3/4}{l(l+1)(l+1/2)} = \frac{[E_n^{(0)}]^2}{m_e c^2} n \frac{j(j+1) - l(l+1) - 3/4}{l(l+1)(l+1/2)}}$$

- $|l - \frac{1}{2}| \leq j \leq l + 1/2 \rightarrow j = l \pm \frac{1}{2}$
- $l \neq 0$

- SMALLER THAN BOHR ENERGY BY FACTOR α^2 [SIMILAR TO RELATIVISTIC CORRECTION]

- FOR $l=0$, NO MAGNETIC FIELD IS GENERATED, i.e., THERE IS NO SPIN-ORBIT COUPLING FOR STATES WITH NO ORBITAL ANGULAR MOMENTUM

- IN THE EQUATION: $l=0$ IMPLIES $j=\frac{1}{2}$, i.e., THE NUMERATOR ALSO BECOMES ZERO [NO ∞ IS PRODUCED]

- AMBIGUITY CAN BE FORMALLY REMOVED BY INTRODUCING A "DARWIN" TERM.

COMPLETE FINE STRUCTURE : $E^{(1)}_{rel} + E^{(1)}_{so}$

$$E^{(1)}_{fs} = E^{(1)}_{rel} + E^{(1)}_{so} = -\frac{1}{2}\alpha^4 m_e c^2 \frac{1}{n^3}\left[\frac{1}{j+\frac{1}{2}} - \frac{3}{4n}\right]$$

PROBLEM 6.17 GRIFFITHS

$$= \underbrace{\frac{[E^{(0)}_n]^2}{2m_e c^2}}_{1.809\cdot 10^{-4}\, eV/n^4}\left[3 - \frac{4n}{j+\frac{1}{2}}\right] *$$

RESULT DEPENDS ON n AND j, BUT NOT ℓ ["$\ell=0$" PROBLEM HAS DISAPPEARED]

TOTAL PERTURBED ENERGIES:

HYDROGEN-LIKE ATOM CHARGE

$$E_{nj} = E^{(0)}_n\left[1 + \frac{(Z\alpha)^2}{n^2}\left(\frac{n}{j+\frac{1}{2}} - \frac{3}{4}\right)\right] \quad \text{WITH} \begin{cases} j = \frac{1}{2} & (\ell=0) \\ j = \ell \pm \frac{1}{2} & (\ell \neq 0) \end{cases}$$

UNPERTURBED ENERGIES: $E^{(0)}_n = -\frac{1}{2} m_e c^2 \frac{(Z\alpha)^2}{n^2}$, $n = 1, 2, 3, \ldots$

[EQ. (C.28) IN COHEN-TANNOUDJI]

- FINE STRUCTURE BREAKS DEGENERACY IN j FOR GIVEN n, BUT THERE IS STILL DEGENERACY IN ℓ

- m_ℓ AND m_s ARE NO LONGER GOOD QUANTUM NUMBERS [SINCE $\vec{L}$ AND $\vec{S}$ ARE NOT CONSERVED]; GOOD QUANTUM NUMBERS ARE: n, ℓ, s, j, m_j [$\vec{J}$ IS CONSERVED]

- FOR EXACT H FINESTRUCTURE FORMULA, OBTAINED WITHOUT PERTURBATION THEORY, USING DIRAC EQUATION, SEE PROB. 6.19 IN GRIFFITHS

EXAMPLE

CALCULATE:

(i) UNPERTURBED ENERGIES FOR $n = 1, 2, 3$

(ii) FIRST-ORDER ENERGY SHIFTS, $E_{fs}^{(1)}$, FROM FINE STRUCTURE

(iii) SKETCH LEVELS [UNPERTURBED, PERTURBED]

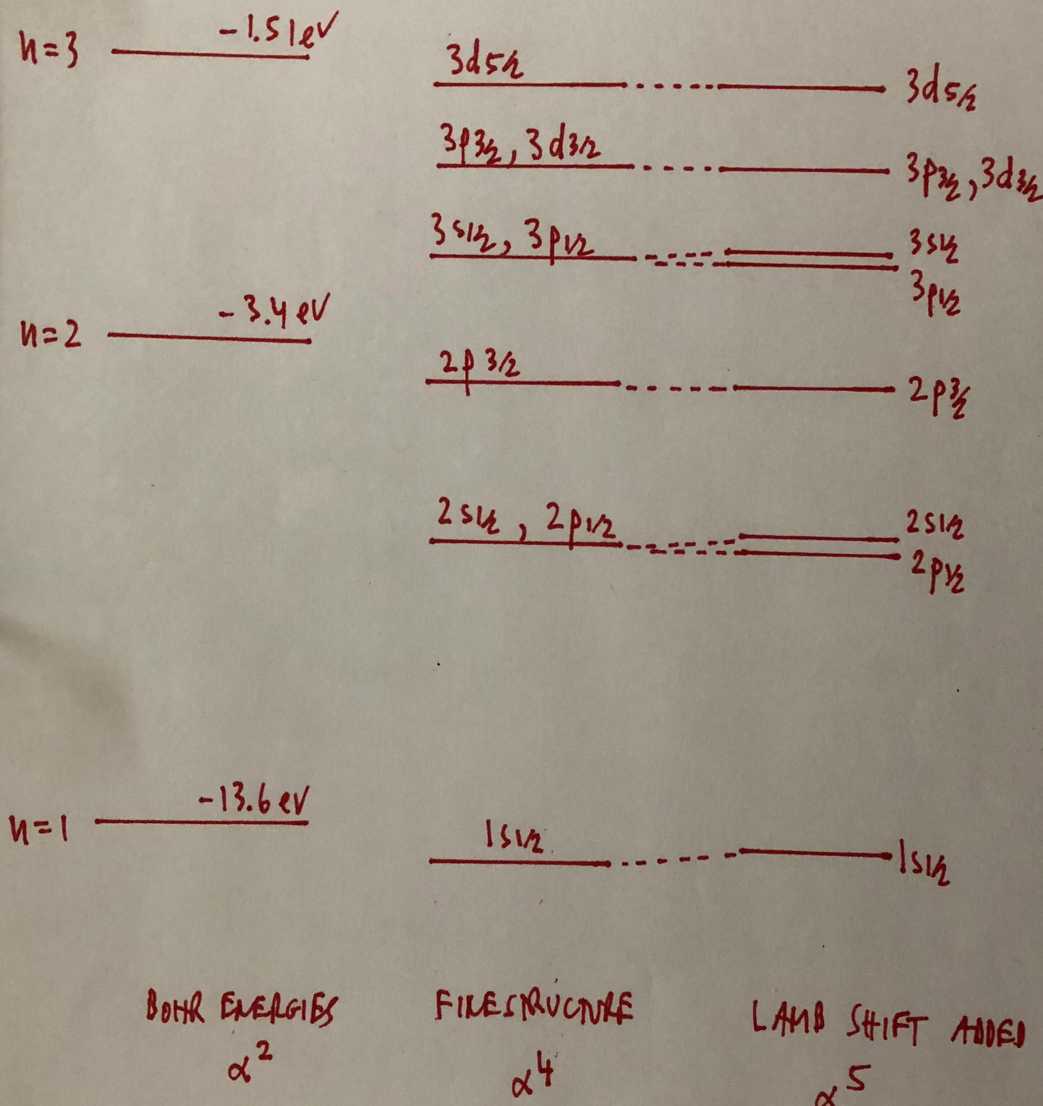
(i)

n	$E_n^{(0)}$ (eV)	$E_n^{(0)} + E_{fs}^{(1)}$ (eV)
1	-13.60569253	-13.60587253
2	-3.401423133	-3.40145633
3	-1.511743614	$-$

(ii)

n	l	j	$E_{fs}^{(1)}$ (eV)	
1	s	1/2	$-1.8 \cdot 10^{-4}$	
2	s	1/2	$-5.6 \cdot 10^{-5}$	DEGENERATE
2	p	1/2	$-5.6 \cdot 10^{-5}$	
2	p	3/2	$-1.1 \cdot 10^{-5}$	
3	s	1/2	$-2.0 \cdot 10^{-5}$	DEGENERATE
3	p	1/2	$-2.0 \cdot 10^{-5}$	
3	p	3/2	$-6.7 \cdot 10^{-6}$	DEGENERATE
3	d	3/2	$-6.7 \cdot 10^{-6}$	
3	d	5/2	$-2.2 \cdot 10^{-6}$	

- ALL SHIFTS ARE NEGATIVE
- DEGENERACY IN l REMAINS



LAMB SHIFT: CAUSED BY QUANTIZATION OF THE ELECTROMAGNETIC FIELD [QUANTUM ELECTRODYNAMICS]; CAUSES $S_{1/2}$ LEVELS TO SHIFT UP SLIGHTLY [BREAKS DEGENERACY IN ℓ]

[STUDENT PROJECT]

WILLIS LAMB, NOBEL PRIZE 1955

COMMENTS

(i) ELECTRON MAGNETIC DIPOLE MOMENT : $\vec{\mu}_e = -\frac{e}{2m_e}\vec{S}_e \cdot g_e^{\approx 2.00}$

PROTON MAGNETIC DIPOLE MOMENT : $\vec{\mu}_p = \frac{e}{2m_p}\vec{S}_p \cdot g_p^{\approx 5.59}$

$\vec{\mu}_p \ll \vec{\mu}_e$ BECAUSE OF MASS DIFFERENCE

[PROTON MADE UP OF THREE QUARKS]

PROTON MAGNETIC DIPOLE MOMENT INVOLVES A NUMBER OF INTERACTIONS:

(1) BETWEEN $\vec{\mu}_p$ AND MAGNETIC FIELD GENERATED AT PROTON BY ORBITING ELECTRON

(2) BETWEEN $\vec{\mu}_p$ AND $\vec{\mu}_e$ [i.e., BETWEEN $\vec{\mu}_e$ AND MAGNETIC FIELD GENERATED BY $\vec{\mu}_p$, OR VICE VERSA]

(3) "FERMI'S CONTACT TERM" → SEE COHEN-TANNOUDJI, p. 1219

⇒ HYPERFINE STRUCTURE : CORRECTION IS OF ORDER $\frac{m_e}{m_p}\alpha^4$

21-CM LINE IN ASTRONOMY MAPS
HYDROGEN IN GALAXY

(ii) WHEN ATOM IS PLACED IN EXTERNAL $\vec{B}$-FIELD:

$$H' = -(\underbrace{\vec{\mu}_\ell + \vec{\mu}_e}_{\text{MAGNETIC DIPOLE MOMENT OF ATOM}})\vec{B}_{EXT} = \frac{e}{2m_e}(\vec{L} + 2\vec{S})\vec{B}_{EXT}$$

ASSOCIATED WITH ORBITAL MOTION

⇒ ZEEMAN EFFECT

[SEC. 6.4 GRIFFITHS]

FINAL COMMENT:

ASSUMING THAT THE PROTON IS INFINITELY HEAVY, THE HAMILTONIAN ENTERING THE DIRAC EQUATION CAN BE EXPANDED AS:

$$H = m_e c^2 + \underbrace{\frac{\vec{p}^{\,2}}{2m_e} + V(r)}_{H_0} \underbrace{- \frac{\vec{p}^{\,4}}{8 m_e^3 c^2}}_{H'_{rel}} + \underbrace{\frac{e^2}{8\pi\epsilon_0} \frac{1}{m_e^2 c^2} \frac{1}{r^3} \vec{L} \cdot \vec{S}}_{H'_{so}} + \ldots$$

ONLY FOR THIS TERM, IF THERE IS NO PERTURBATION, MAY WE REPLACE $m_e \to \mu$ [REDUCED MASS] TO TAKE FINITE PROTON MASS INTO ACCOUNT

SOLVING THE DIRAC EQUATION GIVES THE CORRECT ENERGIES; WITHOUT USING PERTURBATION THEORY

THE ADVANTAGES OF PERTURBATION THEORY ARE:

- IDENTIFIES PHYSICS EFFECTS INVOLVED
- LET'S US ESTIMATE QUANTITATIVELY THESE DIFFERENT CONTRIBUTIONS
- HELPS US ESTIMATE THESE EFFECTS IN MANY-ELECTRON ATOMS [DIRAC EQUATION CANNOT BE SOLVED]

[COHEN-TANNOUDJI, p. 1214]