

Quantum Comeback - III Finale - 3

Time Independent Perturbation Theory

Non-degenerate perturbation theory

Suppose we have solved the time-independent Schrödinger equation for some potential,

$$H^0 \psi_n^0 = E_n^0 \psi_n^0.$$

and we obtain a complete set of orthonormal eigenfunctions ψ_n^0 .

$$\langle \psi_m^0 | \psi_n^0 \rangle = \delta_{mn}.$$

and the corresponding eigen values E_n^0 .

Now, what if we perturb the Potential slightly? How to get the new TISE?, New eigen functions and Eigen values?

$$H \psi_n = E_n \psi_n - ??$$

Not all potentials are easy to solve exactly - (Not much worth it also). Hence, if we know a potential's solutions, and the potential we need is a slightly modified version of the first potential, then instead of solving the Schrödinger equation, we can use the Perturbation Theory to get approx. solutions, which suffice for our needs.

Let us see how this works:

Let us define the new perturbed Hamiltonian :

$$H = H^0 + \lambda H'$$

where H' is the perturbation.

Note: Always the superscript of '0' depicts unperturbed

We will now write Ψ_n and E_n as power series in λ .

$$\Psi_n = \Psi_n^0 + \lambda \Psi_n^1 + \lambda^2 \Psi_n^2 + \dots$$

$$E_n = E_n^0 + \lambda E_n^1 + \lambda^2 E_n^2 + \dots$$

Here, E_n^1 is the first-order correction to the n^{th} eigenvalue and Ψ_n^1 is the " for n^{th} eigen function.

Thus, $E_n^2 + \Psi_n^2$ are second order corrections.

Plugging the power series in the Hamiltonian expression,

$$(H^0 + \lambda H') [\Psi_n^0 + \lambda \Psi_n^1 + \lambda^2 \Psi_n^2 + \dots] = (E_n^0 + \lambda E_n^1 + \lambda^2 E_n^2).$$

$$[\Psi_n^0 + \lambda \Psi_n^1 + \lambda^2 \Psi_n^2 + \dots]$$

Collecting like powers

of λ , we get :

$$H^0 \Psi_n^0 + \lambda (H^0 \Psi_n^1 + H' \Psi_n^0) + \lambda^2 (H^0 \Psi_n^2 + H' \Psi_n^1) +$$

$$\lambda^3 (H^0 \Psi_n^3 + H' \Psi_n^2) + \dots = E_n^0 \Psi_n^0 + \lambda (E_n^0 \Psi_n^1 + E_n^1 \Psi_n^0) + \lambda^3 (E_n^0 \Psi_n^3 + E_n^1 \Psi_n^2 + E_n^2 \Psi_n^1) + \dots$$

The lowest order (λ^0) yields nothing new.

The first order, however, is :

$$H^0 \Psi_n^1 + H' \Psi_n^0 = E_n^0 \Psi_n^1 + E_n^1 \Psi_n^0.$$

Second order:

$$H^0 \Psi_n^2 + H^1 \Psi_n^1 = E_n^0 \Psi_n^2 + E_n^1 \Psi_n^1 + E_n^2 \Psi_n^0$$

Let us dive into each of these 2 orders, one-by-one.

First Order Theory

Writing the first order equation again:

$$H^0 \Psi_n^1 + H^1 \Psi_n^0 = E_n^0 \Psi_n^1 + E_n^1 \Psi_n^0.$$

Taking inner product with $\langle \Psi_n^0 |$.

$$\langle \Psi_n^0 | H^0 \Psi_n^1 \rangle + \langle \Psi_n^0 | H^1 \Psi_n^0 \rangle = \langle \Psi_n^0 | E_n^0 \Psi_n^1 \rangle + \langle \Psi_n^0 | E_n^1 \Psi_n^0 \rangle$$

$$\Rightarrow \langle H^0 \Psi_n^0 | \Psi_n^1 \rangle \text{ (Hermiticity } H^0) = E_n^0 \langle \Psi_n^0 | \Psi_n^1 \rangle$$

and $\langle \Psi_n^0 | \Psi_n^0 \rangle = 1$.

$$\therefore \cancel{\langle \Psi_n^0 | H^0 \Psi_n^1 \rangle} + \langle \Psi_n^0 | H^1 \Psi_n^0 \rangle = \cancel{\langle \Psi_n^0 | E_n^0 \Psi_n^1 \rangle} + \langle \Psi_n^0 | E_n^1 \Psi_n^0 \rangle_1$$

$$\therefore \langle \Psi_n^0 | H^1 | \Psi_n^0 \rangle = E_n^1$$

Fundamental result of first order perturbation theory.

The first-order correction to the energy is the expectation value of the perturbation, in the unperturbed state.

Now, first order correction to the wave function:

$$\underbrace{(H^0 - E_n^0)}_{?} \Psi_n^1 = - (H^1 - E_n^1) \Psi_n^0 \rightarrow \begin{array}{l} \text{Rewrote the first order} \\ \text{equation.} \end{array}$$

\downarrow Known function

Hence, leads to an inhomogeneous differential equation for Ψ_n^1 .

The unperturbed wave functions constitute a complete set, so Ψ_n^1 can be written as a linear combination of them.

$$\Psi_n^1 = \sum_{m \neq n} C_m^{(n)} \Psi_m^0$$

Putting this in the earlier equation,

$$\sum_{m \neq n} (E_m^0 - E_n^0) C_m^{(n)} \langle \Psi_l^0 | \Psi_m^0 \rangle = - \langle \Psi_l^0 | H' | \Psi_n^0 \rangle + E_n^1 \langle \Psi_l^0 | \Psi_n^0 \rangle$$

0 for $l=n$
 1 for $l \neq n = m$
 0 for $l \neq n = m$

If $l=n$, [How does it make the left side zero?]

$$E_n^1 = \langle \Psi_n^0 | H' | \Psi_n^0 \rangle \rightarrow \text{already got this.}$$

see above blue for clarity ...

$$\text{If } l \neq n, (E_l^0 - E_n^0) C_{(l)}^{(n)} = - \langle \Psi_l^0 | H' | \Psi_n^0 \rangle$$

$$C_m^{(n)} = \frac{\langle \Psi_m^0 | H' | \Psi_n^0 \rangle}{E_n^0 - E_m^0}$$

$$\therefore \Psi_n^1 = \sum_{m \neq n} \frac{\langle \Psi_m^0 | H' | \Psi_n^0 \rangle}{(E_n^0 - E_m^0)} \Psi_m^0$$

As long $m \neq n$, Ψ_n^1 's denominator is safe. (Non-degenerate). But what if energy levels are degenerate?

Welcome to degenerate perturbation theory!

But before that, we'll finish the second order...

$$\langle \Psi_n^0 | H^0 \Psi_n^2 \rangle + \langle \Psi_n^0 | H' \Psi \rangle = E_n^0 \langle \Psi_n^0 | \Psi_n^2 \rangle$$

$$+ E_n^1 \langle \psi_n^0 | \psi_n^1 \rangle + E_n^2 \langle \psi_n^0 | \psi_n^0 \rangle$$

Again, we'll exploit the Hermiticity of H^0 .

$$\langle \psi_n^0 | H^0 \psi_n^2 \rangle = \langle H^0 \psi_n^0 | \psi_n^2 \rangle = E_n^0 \langle \psi_n^0 | \psi_n^1 \rangle$$

$$\therefore E_n^2 = \langle \psi_n^0 | H' | \psi_n^1 \rangle - E_n^1 \langle \psi_n^0 | \psi_n^1 \rangle$$

But,

$$\langle \psi_n^0 | \psi_n^1 \rangle = \sum_{m \neq n} c_m^{(n)} \langle \psi_n^0 | \psi_m^0 \rangle = 0$$

$$\begin{aligned} E_n^2 &= \langle \psi_n^0 | H' | \psi_n^1 \rangle = \sum_{n \neq m} c_m^{(n)} \langle \psi_n^0 | H' | \psi_m^0 \rangle \\ &= \sum_{m \neq n} \frac{\langle \psi_m^0 | H' | \psi_n^0 \rangle \langle \psi_n^0 | H' | \psi_m^0 \rangle}{E_n^0 - E_m^0} \end{aligned}$$

or finally,

$$E_n^2 = \sum_{m \neq n} \frac{|\langle \psi_m^0 | H' | \psi_n^0 \rangle|^2}{E_n^0 - E_m^0}$$

Now, we'll jump to the degenerate part:

Two fold Degeneracy

$$H^0 \psi_a^0 = E^0 \psi_a^0, \quad H^0 \psi_b^0 = E^0 \psi_b^0, \quad \langle \psi_a^0 | \psi_b^0 \rangle = 0$$

Now, $\Psi^0 = \alpha \psi_a^0 + \beta \psi_b^0$ (a linear combination of these degenerate states)

Even this will follow this: $H^0 \Psi^0 = E^0 \Psi^0$.

Now a perturbation will break the degeneracy.

As we increase the value of λ from 0 to 1, the common unperturbed energy E^0 splits into 2. When we go the other direction, the "upper" state reduces to "one" linear combination, and the "lower" state reduces to some linear combination of states, but we do not know what these states are.

These "good" states are defined as the limit of the true eigen states as the perturbation is switched off ($\lambda \rightarrow 0$).

But if that's the case, then we have to solve exactly \rightarrow which we don't want (Any we're lazy, hehehe)

For now, let's just write the "good" unperturbed states in a generic form:

$$H\Psi = E\Psi, \text{ with } H = H^0 + \lambda H'$$

$$\text{and } E = E^0 + \lambda E^1 + \lambda^2 E^2 + \dots; \Psi = \Psi^0 + \lambda \Psi^1 + \lambda^2 \Psi^2 + \dots$$

Plugging these in $H\Psi = E\Psi$, collecting like powers of λ

$$H^0\Psi^0 + \lambda(H^0\Psi^1 + H^1\Psi^0) + \dots = E^0\Psi^0 + \lambda(E^0\Psi^1 + E^1\Psi^0) + \dots$$

$$\text{But } H^0\Psi^0 = E^0\Psi^0.$$

$$\therefore H^0\Psi^1 + H^1\Psi^0 = E^0\Psi^1 + E^1\Psi^0 \quad (\text{at order 1})$$

Taking inner product of the above equation with $\langle \Psi_a^0 |$,

$$\langle \Psi_a^0 | H^0 \Psi^1 \rangle + \langle \Psi_a^0 | H^1 \Psi^0 \rangle = \langle \Psi_a^0 | E^0 \Psi^1 \rangle + \langle \Psi_a^0 | E^1 \Psi^0 \rangle$$

Using the Hermiticity of H^0 ,

$$\langle \Psi_a^0 | H^0 \Psi^1 \rangle = E^0 \langle \Psi_a^0 | \Psi^1 \rangle$$

$$\therefore \langle \Psi_a^0 | H^1 \Psi^0 \rangle = E^1 \langle \Psi_a^0 | \Psi^0 \rangle.$$

$$\text{Now, putting } \Psi^0 = \alpha \Psi_a^0 + \beta \Psi_b^0.$$

$$\alpha \langle \Psi_a^0 | H' | \Psi_a^0 \rangle + \beta \langle \Psi_a^0 | H' | \Psi_b^0 \rangle = \alpha E'$$

Or, more compactly,

$$\alpha W_{aa} + \beta W_{ab} = \alpha E'$$

$$\text{where, } W_{ij} = \langle \Psi_i^0 | H' | \Psi_j^0 \rangle, \quad (i,j=a,b)$$

Now, inner product of the above equation with $\langle \Psi_b^0 |$ gets

$$\alpha W_{ba} + \beta W_{bb} = \beta E'$$

As we know, W 's are the matrix elements of H' , w.r.t the unperturbed wave functions Ψ_a^0 & Ψ_b^0 .

$$W : \begin{bmatrix} W_{aa} & W_{ab} \\ W_{ba} & W_{bb} \end{bmatrix} \begin{bmatrix} \alpha \\ \beta \end{bmatrix} = E' \begin{bmatrix} \alpha \\ \beta \end{bmatrix}$$

The eigen values of the matrix W give us the first-order corrections to energy E' , and the corresponding eigenvectors tell us the coefficients α and β that determine the "good" states.

$$\begin{vmatrix} W_{aa} - E' & W_{ab} \\ W_{ba} & W_{bb} - E' \end{vmatrix} = 0 \Rightarrow (W_{aa} - E_1)(W_{bb} - E_1) - W_{ab}W_{ba} = 0$$

$\Rightarrow |W_{ab}| = |W_{ba}|$ as W matrix must be Hermitian.

$$\therefore E_{\pm}' = \frac{1}{2} \left[W_{aa} + W_{bb} \pm \sqrt{(W_{aa} - W_{bb})^2 + 4|W_{ab}|^2} \right]$$

This is the fundamental result of degenerate perturbation theory

The two roots correspond to two perturbed energies.

If $W_{ab} = 0$, then the 2 eigen vectors are:

$\begin{bmatrix} 1 \\ 0 \end{bmatrix}$ and $\begin{bmatrix} 0 \\ 1 \end{bmatrix}$; and the energies:

$$E_+^1 = W_{aa} = \langle \Psi_a^0 | H' | \Psi_a^0 \rangle ; E_-^1 = W_{bb} = \langle \Psi_b^0 | H' | \Psi_b^0 \rangle.$$

This is exactly what we would've obtained in the non-degenerate theory. Turns out, as $\alpha = \beta = 1$, $\Psi_a^0 + \Psi_b^0$ are themselves the good states.

If we somehow "guess" the good states from the start, then we can use non degenerate theory only. There is a theorem that helps us in this regard:

Theorem of "good states":

Let A be a Hermitian operator that commutes with H^0 and H' .

If Ψ_a^0 and Ψ_b^0 (the degenerate eigenfunctions of H^0) are also eigen functions of A , with distinct eigenvalues,

$$A \Psi_a^0 = \mu \Psi_a^0 ; A \Psi_b^0 = \nu \Psi_b^0 , \nu \neq \mu,$$

then Ψ_a^0 and Ψ_b^0 are the "good" states ...

Proof for this theorem:

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Proof: Since $H(\lambda) = H^0 + \lambda H'$ and A commute, there exist simultaneous eigenstates $\psi_\gamma(\lambda)$ where

$$H(\lambda) \psi_\gamma(\lambda) = E(\lambda) \psi_\gamma(\lambda) \text{ and } A \psi_\gamma(\lambda) = \gamma \psi_\gamma(\lambda). \quad (7.36)$$

The fact that A is hermitian means

$$\langle \Psi_a^0 | A \psi_\gamma(\lambda) \rangle = \langle A \Psi_a^0 | \psi_\gamma(\lambda) \rangle$$

$$\gamma \langle \Psi_a^0 | \psi_\gamma(\lambda) \rangle = \mu^* \langle \Psi_a^0 | \psi_\gamma(\lambda) \rangle \quad (7.37)$$

$$(\gamma - \mu) \langle \Psi_a^0 | \psi_\gamma(\lambda) \rangle = 0, \quad (7.38)$$

(making use of the fact that μ is real). This holds true for any value of λ and taking the limit as $\lambda \rightarrow 0$ we have

$$\langle \psi_a^0 | \psi_\gamma(0) \rangle = 0 \text{ unless } \gamma = \mu,$$

and similarly

$$\langle \psi_b^0 | \psi_\gamma(0) \rangle = 0 \text{ unless } \gamma = \nu.$$

Now the good states are linear combinations of ψ_a^0 and ψ_b^0 : $\psi_\gamma(0) = \alpha \psi_a^0 + \beta \psi_b^0$. From above it follows that either $\gamma = \mu$, in which case $\beta = \langle \psi_b^0 | \psi_\gamma(0) \rangle = 0$ and the good state is simply ψ_a^0 , or $\gamma = \nu$ and the good state is ψ_b^0 . QED

Once we identify the "good" states, we can use these as our unperturbed states and apply ordinary non-degenerate perturbation theory.

Moral: If you're faced with degenerate states,

- Look around for some Hermitian operator A , that commutes with H^0 and H'
- Pick the simultaneous eigenfunctions of A and H^0 as your "good" unperturbed states
- Now use ordinary first-order perturbation theory.
- If you can't find A , then use this:

$$E_{\pm} = \frac{1}{2} \left[(W_{aa} + W_{bb}) \pm \sqrt{(W_{aa} - W_{bb})^2 + 4|W_{ab}|^2} \right]$$

Higher Order Degeneracy

In case of n -fold degeneracy, we look for eigenvalues of the $n \times n$ matrix:

$$\langle \psi_i^0 | H' | \psi_j^0 \rangle.$$

for example, three fold: $\psi_a^0, \psi_b^0, \psi_c^0$.

$$\therefore W = \begin{bmatrix} W_{aa} & W_{ab} & W_{ac} \end{bmatrix} \begin{bmatrix} \alpha \\ \beta \\ \gamma \end{bmatrix}$$

$$\begin{vmatrix} W_{ba} & W_{bb} & W_{bc} \\ W_{ca} & W_{cb} & W_{cc} \end{vmatrix} \begin{pmatrix} \beta \\ \gamma \end{pmatrix} = E' \begin{pmatrix} \beta \\ \gamma \end{pmatrix}$$

and the good states are the corresponding eigen vectors:

$$\Psi^o = \alpha \Psi_a^o + \beta \Psi_b^o + \gamma \Psi_c^o.$$

Fine Structure of Hydrogen

In our study of Hydrogen, we saw the Bohr Hamiltonian :

$$H_{\text{Bohr}} = -\frac{\hbar^2}{2m} \nabla^2 - \frac{e^2}{4\pi\epsilon_0 r}$$

To correct this for the motion of nucleus, just replace m with reduced mass.

More significant is the so-called fine-structure, which is actually due to 2 Mechanisms :

- Relativistic correction
- Spin-orbit Coupling

Compared to Bohr energies, fine structures is a tiny perturbation, smaller by a factor of α^2 , where

$$\alpha \equiv \frac{e^2}{4\pi\epsilon_0 hc} \approx \frac{1}{137.036} \quad \text{and } \alpha \rightarrow \text{fine structure constant}$$

Still smaller is the Lamb shift - associated with quantisation of electric field,

Yet smaller is the Hyperfine structure - due to the interaction between the magnetic dipole moments of the proton and the electron.

$$\begin{aligned}
 \text{Bohr energies:} & \quad \alpha^2 mc^2 \\
 \text{Fine structures:} & \quad \alpha^4 mc^2 \\
 \text{Lamb shift:} & \quad \alpha^5 mc^2 \\
 \text{Hyperfine splitting:} & \quad \left(\frac{m}{m_p}\right) \alpha^4 mc^2.
 \end{aligned}$$

Now, we will study the fine structures of Hydrogen as an application to the time-independent perturbation theory.

1. Relativistic correction

$$T = \frac{1}{2} mv^2 = \frac{p^2}{2m}$$

putting $p \rightarrow -i\hbar \nabla$,

$$T = -\frac{\hbar^2}{2m} \nabla^2$$

But these are classical expressions for T .

$$\text{Relativistic: } T = \frac{mc^2}{\sqrt{1 - (v^2/c^2)}} - mc^2$$

Now, we need to express T in terms of p , which is:

$$p = \frac{mv}{\sqrt{1 - (v/c)^2}}$$

Notice this:

$$\begin{aligned}
 \underbrace{p^2 c^2 + m^2 c^4}_{= \frac{m^2 v^2 c^2}{1 - (v/c)^2} + m^2 c^4} &= \frac{m^2 v^2 c^2}{1 - (v/c)^2} + m^2 c^4 \\
 &= \frac{m^2 v^2 c^2 + m^2 c^4 [1 - (v/c)^2]}{1 - (v/c)^2} = \frac{m^2 c^4}{1 - (v/c)^2} = \underline{(T + mc^2)^2}
 \end{aligned}$$

$$\therefore T = \frac{1}{2} \frac{p^2}{m} = \frac{1}{2} \frac{m v^2}{1 - (v/c)^2} = \frac{1}{2} \frac{m^2 c^2}{1 - (v/c)^2}$$

$$\therefore 1 + mc = \sqrt{P^2 c^2 + m^2 c^4}$$

$$\text{and } T = \sqrt{P^2 c^2 + m^2 c^4} - mc^2.$$

$$T = \left[\sqrt{1 + \left(\frac{P}{mc}\right)^2} - 1 \right] mc^2.$$

Expanding T in small powers of P/mc ,

$$\begin{aligned} T &= mc^2 \left[1 + \frac{1}{2} \left(\frac{P}{mc} \right)^2 - \frac{1}{8} \left(\frac{P}{mc} \right)^4 + \dots - 1 \right] \\ &= \frac{P^2}{2m} + \frac{P^4}{8m^3 c^2} + \dots \end{aligned}$$

The lowest-order relativistic correction to the Hamiltonian is therefore :

$$H'_R = -\frac{P^4}{8m^3 c^2}.$$

In the first-order perturbation theory, the correction to E_n is given by the expectation value of H' in the unperturbed state :

$$\begin{aligned} E_\psi' &= \langle H'_R \rangle = -\frac{1}{8m^3 c^2} \langle \psi | P^4 \psi \rangle \\ &= -\frac{1}{8m^3 c^2} \langle P^2 \psi | P^2 \psi \rangle \end{aligned}$$

Now, the Schrödinger equation for the unperturbed states says:

$$P^2 \psi = 2m(E - V) \psi.$$

$$\therefore E_\psi' = -\frac{1}{2mc^2} \langle (E - V)^2 \rangle = \frac{-1}{2mc^2} [E^2 - 2E \langle V \rangle + \langle V^2 \rangle]$$

So far it was general. Now we need for hydrogen. So.

we will plug in $V(r) = -\frac{e^2}{4\pi\epsilon_0 r}$:

$$E_r' = \frac{-1}{2mc^2} \left[E_n^2 + 2E_n \left(\frac{e^2}{4\pi\epsilon_0} \right) \left\langle \frac{1}{r} \right\rangle + \left(\frac{e^2}{4\pi\epsilon_0} \right)^2 \left\langle \frac{1}{r^2} \right\rangle \right]$$

where E_n = Bohr energy of the state.

Now to complete, we need the expectation values of $\langle \frac{1}{r} \rangle$ and $\langle \frac{1}{r^2} \rangle$.

$$\left\langle \frac{1}{r} \right\rangle = \frac{1}{n^2 a} \quad \text{and} \quad \left\langle \frac{1}{r^2} \right\rangle = \frac{1}{(\ell+1/2)n^3 a^2}$$

$$\therefore E_r' = -\frac{1}{2mc^2} \left[E_n^2 + 2E_n \left(\frac{e^2}{4\pi\epsilon_0} \right) \frac{1}{n^2 a} + \left(\frac{e^2}{4\pi\epsilon_0} \right)^2 \times \frac{1}{(\ell+1/2)n^3 a^2} \right]$$

$$\text{Using } E_n = -\left[\frac{m_e}{2\hbar} \left(\frac{e^2}{4\pi\epsilon_0} \right)^2 \right] \frac{1}{n^2} = \frac{E_1}{n^2},$$

$$E_r' = -\frac{(E_n)^2}{2mc^2} \left[\frac{4n}{\ell+1/2} - 3 \right]$$

Evidently, the relativistic correction is smaller than E_n by $E_n/mc^2 \rightarrow \sim 2 \times 10^{-5}$.

2. Spin Orbit Coupling

To the electron that's spinning around a nucleus, it appears as if the positively charged nucleus goes around it.

This orbiting positive charge sets up a magnetic field \vec{B} and sets up a torque in the spinning electron's frame.

This tends the electron to align its magnetic moment (μ) along the direction of the field.

The Hamiltonian :

$$H = -\vec{\mu} \cdot \vec{B}.$$

Before we begin, we need to figure out B of proton and μ of electron.

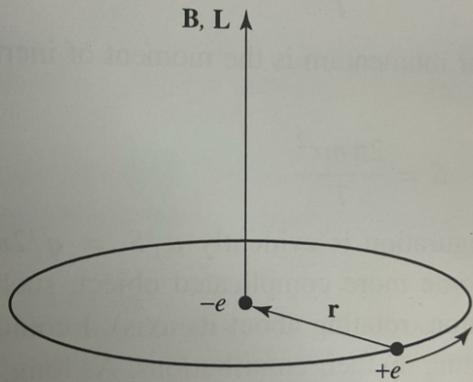


Figure 7.6: Hydrogen atom, from the electron's perspective.

1. Mag. field \vec{B} of the proton:

Picturing the proton as a continuous current loop, its magnetic field can be calculated from the Biot-Savart's Law:

$$B = \frac{\mu_0 I}{2r}$$

with effective current $I = e/T$, where e = charge of electron, T = time period of orbit

The orbital angular momentum of the electron (in the rest frame of the nucleus) is $L = mv r = 2\pi mr^2/T$.

Both \vec{B} and \vec{L} point in the same direction so,

$$\vec{B} = \frac{1}{4\pi\epsilon_0} \frac{e}{mc^2 r^3} \vec{L}.$$

1. Dipole moment of electron μ : (of a ring) = $\mu = IA$

$$\therefore \mu = \frac{q\pi r^2}{T} \quad (\text{Spin})$$

If the mass of the ring is m , its angular momentum is the moment of inertia (mr^2) times the angular velocity ($2\pi/T$):

$$S = \frac{2\pi mr^2}{T}$$

We know that $\vec{S} = \mu$. $\therefore \vec{\mu} = \frac{q}{2m} \vec{S}$. (it is independent of r and T)

$$\therefore \vec{\mu} = \left(\frac{q}{2m}\right) \vec{S}$$

That was purely classical it seems... Turns out, the e^- 's mag. moment is twice its classical value.

$$\therefore \vec{\mu}_e = -\frac{e}{m} \vec{S}. \quad \text{Explained by Dirac...}$$

$$\therefore H = \frac{e^2}{4\pi G_0} \frac{1}{m^2 c^2 r^3} \vec{S} \cdot \vec{L}. \quad \text{But this is not an inertial system - it accelerates}$$

Thomas precession:

$$H'_{SO} = \left(\frac{e^2}{8\pi G_0}\right) \frac{1}{m^2 c^2 r^3} \vec{S} \cdot \vec{L}.$$

Total angular momentum = $J = S + L$

H'_{SO} does commute with J .

$$J^2 = (\vec{L} + \vec{S}) \cdot (\vec{L} + \vec{S}) = L^2 + S^2 + 2 \vec{L} \cdot \vec{S}.$$

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

\therefore Eigenvalues of $\vec{L} \cdot \vec{S}$: $\frac{\hbar^2}{2} [j(j+1) - l(l+1) - s(s+1)]$

$$\left\langle \frac{1}{r^3} \right\rangle = \frac{1}{l(l+1)r_0(l+1) n^3 a^3}$$

$$\therefore E_{SO}' = \langle H'_{SO} \rangle = \frac{e^2}{2} \frac{1}{n^3} \underbrace{(\frac{\hbar^2}{2})(j(j+1) - l(l+1) - 3/4)}$$

$$8\pi\epsilon_0 m^-c^-\ell(\ell+1/2)(\ell+1)n^3a^3$$

$$E_{so}^I = \frac{(E_n)^2}{mc^2} \left\{ n \frac{[j(j+1) - \ell(\ell+1) - 3/4]}{\ell(\ell+1/2)(\ell+1)} \right\}$$

$$E_{fs}^I = \frac{(E_n)^2}{2mc^2} \left(3 - \frac{4n}{j+1/2} \right)$$

Combining this with the Bohr formula, we obtain the grand result for the energy levels of hydrogen, including fine structure

$$E_{nj} = -\frac{13.6\text{eV}}{n^2} \left[1 + \frac{\alpha^2}{n^2} \left(\frac{n}{j+1/2} - \frac{3}{4} \right) \right] //$$

