PHY 742 Quantum Mechanics II
12-12:50 PM MWF Olin 103

Plan for Lecture 3
Approximate solutions for stationary states
Perturbation theory (Chap. 12 C)

1. Summary of results for non-degenerate problem
2. Perturbation theory for the case of degenerate zero order eigenvalues
3. Examples

Course schedule for Spring 2022

(Preliminary schedule -- subject to frequent adjustment.)

	Lecture date	Reading	Topic	HW	Due date
1	Mon: 01/10/2022	Chap. 12	Approximate solutions for stationary states -- The variational approach	#1	01/14/2022
2	Wed: 01/12/2022	Chap. 12 C	Approximate solutions for stationary states -- Perturbation theory	#2	01/19/2022
3	Fri: 01/14/2022	Chap. 12 D	Approximate solutions for stationary states -- Degenerate perturbation theory	#3	01/21/2022
	Mon: 01/17/2022		MLK Holiday -- no class		

PHY 742 -- Assignment #3

January 14, 2022

Read Chapter 12, part D in **Carlson's** textbook.

1. Work problem 9 at the end of chapter 12.

Methods for finding approximate solutions to the time-independent Schrödinger equation

Review of non-degenerate perturbation formalism --

Problem to solve – $$H\left|n\right\rangle = E_n\left|n\right\rangle$$

For a Hamiltonian of the form $$H = H^0 + \epsilon H^1$$

Here H^0 denotes a Hamiltonian whose eigenstates we know

$$H^0\left|n^0\right\rangle = E_n^0\left|n^0\right\rangle$$

H^1 denotes another contribution to the Hamiltonian scaled by a small number ϵ

$$H\left|n\right\rangle = E_n\left|n\right\rangle$$

$$H = H^0 + \epsilon H^1$$

Assume: $\left|n\right\rangle = \left|n^0\right\rangle + \epsilon\left|n^1\right\rangle + \epsilon^2\left|n^2\right\rangle + \ldots$

$$E_n = E_n^0 + \epsilon E_n^1 + \epsilon^2 E_n^2 + \ldots$$

First order formula --

$$E_n^1 = \left\langle n^0 \middle| H^1 \middle| n^0 \right\rangle$$

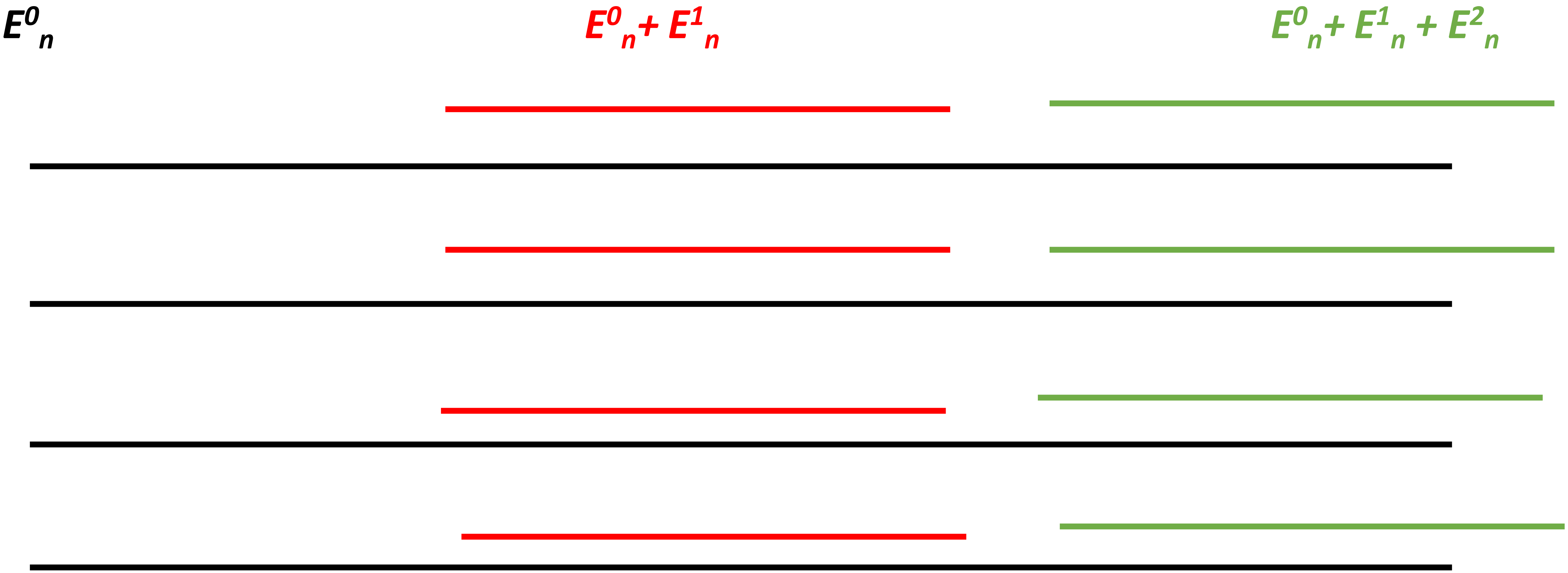
$$\left| n^1 \right\rangle = \sum_{m \neq n} \left(\frac{\left\langle m^0 \middle| H_1 \middle| n^0 \right\rangle}{E_n^0 - E_m^0} \right) \left| m^0 \right\rangle$$

Second order formula --

$$E_n^2 = \left\langle n^0 \middle| H^1 \middle| n^1 \right\rangle = \sum_{m \neq n} \frac{\left\langle n^0 \middle| H^1 \middle| m^0 \right\rangle \left\langle m^0 \middle| H^1 \middle| n^0 \right\rangle}{E_n^0 - E_m^0}$$

$$\left| n^2 \right\rangle = \sum_{m \neq n} \left| m^0 \right\rangle \sum_{l \neq n} \frac{\left\langle m^0 \middle| H^1 \middle| l^0 \right\rangle \left\langle l^0 \middle| H^1 \middle| n^0 \right\rangle}{\left(E_n^0 - E_m^0\right)\left(E_n^0 - E_l^0\right)} - \sum_{m \neq n} \left| m^0 \right\rangle \frac{\left\langle m^0 \middle| H^1 \middle| n^0 \right\rangle \left\langle n^0 \middle| H^1 \middle| n^0 \right\rangle}{\left(E_n^0 - E_m^0\right)^2} - \frac{1}{2} \left| n^0 \right\rangle \sum_{m \neq n} \frac{\left| \left\langle m^0 \middle| H^1 \middle| n^0 \right\rangle \right|^2}{\left(E_n^0 - E_m^0\right)^2}$$

Qualitative behavior of non-degenerate perturbation theory



Perturbation theory in the case that the zero states are degenerate

Cannot use non-degenerate formalism because even in first order, the expressions diverge.

First order formula --

$$E_n^1 = \left\langle n^0 \middle| H^1 \middle| n^0 \right\rangle$$

$$\left| n^1 \right\rangle = \sum_{m \neq n} \left(\frac{\left\langle m^0 \middle| H_1 \middle| n^0 \right\rangle}{E_n^0 - E_m^0} \right) \left| m^0 \right\rangle$$

Approximation schemes for solving the time-independent Schrödinger equation

$$H\left|n\right\rangle = E_n\left|n\right\rangle$$

$$H = H^0 + \epsilon H^1$$

In general, we approach the problem using the complete basis set of H^0:

$$H^0\left|n^0\right\rangle = E_n^0\left|n^0\right\rangle$$

However, consider the case when

$$E_{n_a}^0 = E_{n_b}^0 \ldots . E_{n_N}^0$$

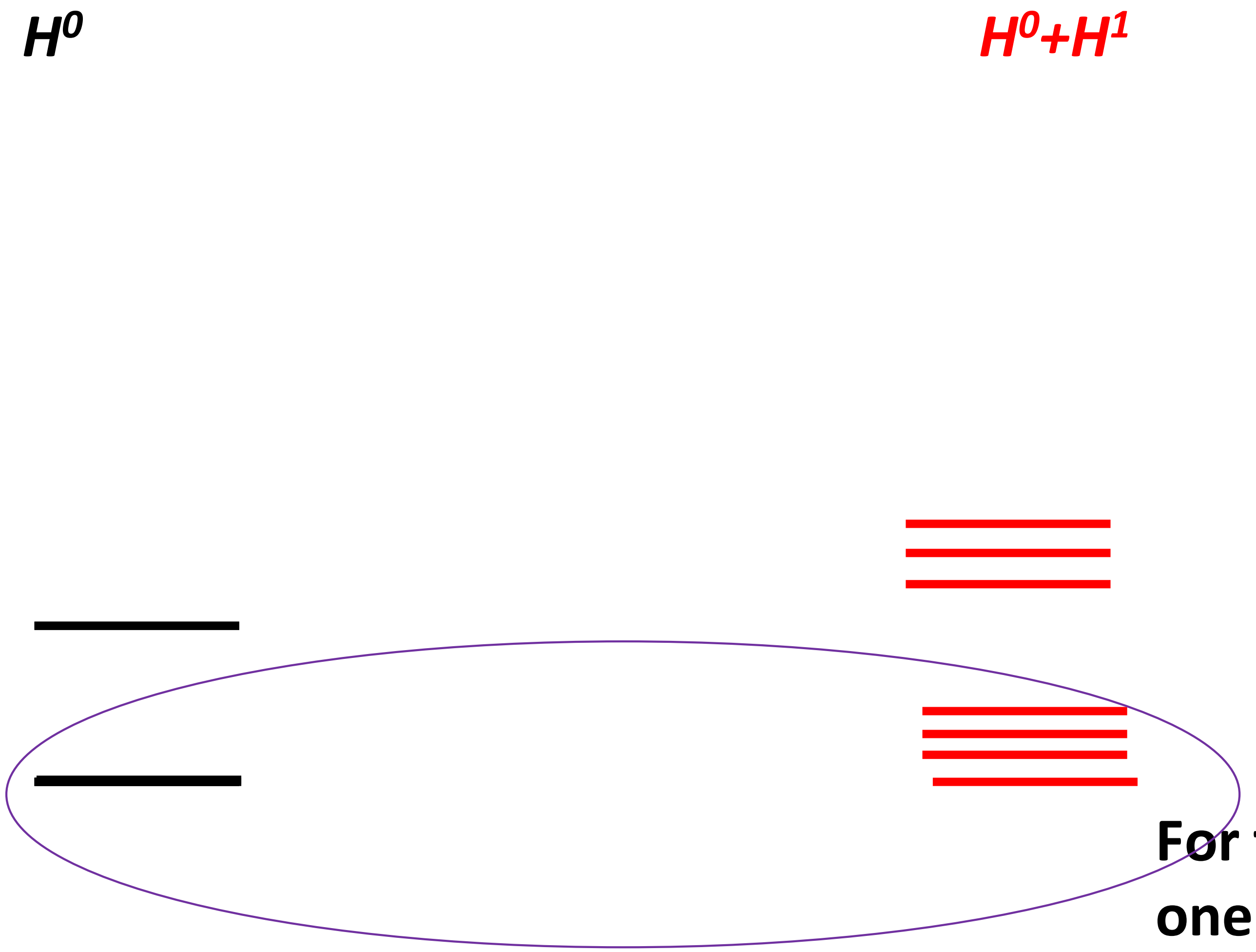
Degenerate perturbation theory,

considering the effects on the N-fold degenerate states:

$\left|n_a^0\right\rangle, \left|n_b^0\right\rangle, \ldots \left|n_N^0\right\rangle$ where $E_{n_a}^0 = E_{n_b}^0 \ldots = E_{n_N}^0$

For $i = 1, 2, \ldots N$, assume $\left|n_i^1\right\rangle = \sum_{j=1}^{N} C_j^i \left|n_j^0\right\rangle$

$\Rightarrow$ The N first-order wavefunctions will be the eigenstates of the $N \times N$ matrix $\left\langle n_j^0 \right| H^0 + H^1 \left| n_i^0 \right\rangle$



For the moment, we will focus on one degenerate zero order state

Example of degenerate perturbation theory for a H atom in the degenerate states

$$\left|nlm\right\rangle = \left|200\right\rangle, \left|21-1\right\rangle, \left|210\right\rangle, \left|211\right\rangle$$

all having zero-order energies $E_2^0 = -\frac{e^2}{2a_0}\frac{1}{2^2}$

In this case, consider a perturbation caused by an electrostatic field F directed along the z-axis causing polarization of the electron:

$$H^1 = eFr\ \cos\theta$$

Matrix elements:

$$\left\langle 2lm\right|H^1\left|2l'm'\right\rangle = -3eFa_0\delta_{|l-l'|1}\delta_{m0}\delta_{m'0}$$

Details:

$$\left\langle 200\right|H^1\left|210\right\rangle = \frac{eF}{16a_0^4}\int_0^\infty r^4 dr\left(2-\frac{r}{a_0}\right)e^{-r/a_0}\int_{-1}^{1}\cos^2\theta\ d\cos\theta$$

$$= -3eFa_0$$

Degenerate perturbation theory example for the Stark effect -- continued

Matrix elements: $\quad |200\rangle \; |210\rangle \; |21-1\rangle \; |211\rangle$

$$\langle 2lm|H^1|2l'm'\rangle = \begin{matrix} \langle 200| \\ \langle 210| \\ \langle 21-1| \\ \langle 211| \end{matrix} \begin{pmatrix} 0 & -3eFa_0 & 0 & 0 \\ -3eFa_0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix}$$

Eigenvalues of $\langle 2lm|H^0 + H^1|2l'm'\rangle$:

$$E_2^0 \quad \text{for} \quad |21\pm1\rangle$$

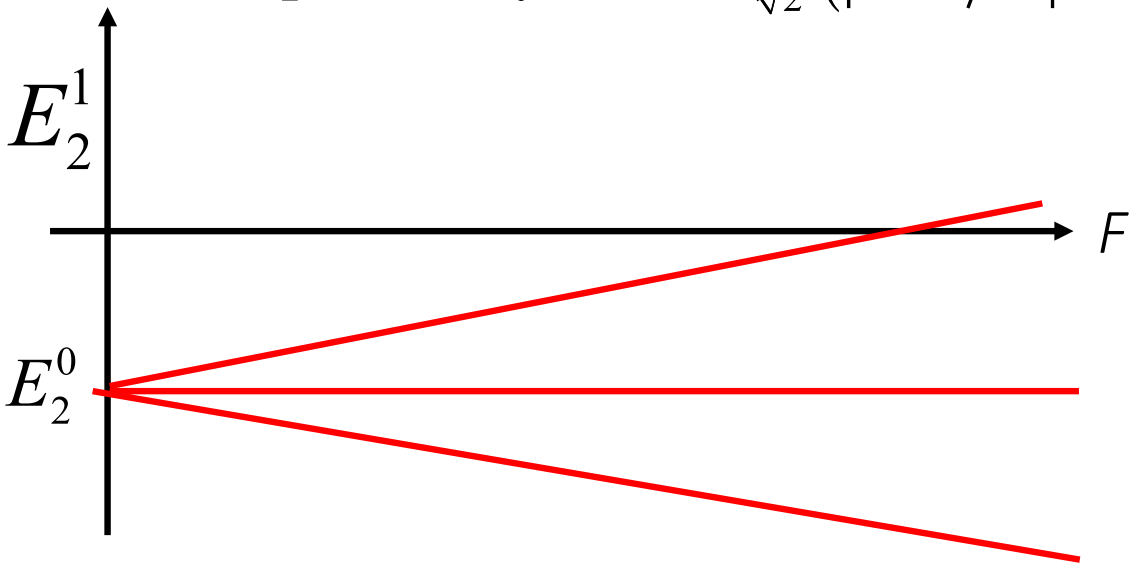
$$E_2^0 - 3eFa_0 \quad \text{for} \quad \tfrac{1}{\sqrt{2}}\left(|200\rangle + |210\rangle\right)$$

$$E_2^0 + 3eFa_0 \quad \text{for} \quad \tfrac{1}{\sqrt{2}}\left(|200\rangle - |210\rangle\right)$$

Degenerate perturbation theory example for the Stark effect -- continued

Eigenvalues of $\langle 2lm | H^0 + H^1 | 2l'm' \rangle$:

$$E_2^1 = \begin{cases} E_2^0 & \text{for } |21\pm1\rangle \\ E_2^0 - 3eFa_0 & \text{for } \frac{1}{\sqrt{2}}\left(|200\rangle + |210\rangle\right) \\ E_2^0 + 3eFa_0 & \text{for } \frac{1}{\sqrt{2}}\left(|200\rangle - |210\rangle\right) \end{cases}$$



Degenerate perturbation theory example for effects of a constant magnetic field B on an atom

$$H = \frac{\left(\mathbf{p} + \frac{e}{c}\mathbf{A}\right)^2}{2m} + V(r) + \frac{e}{mc}\mathbf{B}\cdot\mathbf{S}$$

Vector potential $\mathbf{A} = \frac{1}{2}\mathbf{r}\times\mathbf{B}$

$$H^0 = \frac{\mathbf{p}^2}{2m} + V(r)$$

Keeping only terms to linear order in $\mathbf{B}$:

$$H^1 = \frac{e}{2mc}\left(\mathbf{L} + 2\mathbf{S}\right)\cdot\mathbf{B}$$

Detail:

$$\frac{1}{2}\mathbf{p}\cdot\mathbf{r}\times\mathbf{B} + \frac{1}{2}\mathbf{r}\times\mathbf{B}\cdot\mathbf{p} = \mathbf{L}\cdot\mathbf{B}$$

Degenerate perturbation theory example for effects of a constant magnetic field B on an atom -- continued

For atoms with total orbital momentum L and total spin S:

$$\mathbf{L}^2 \left| LM;SM_S \right\rangle = \hbar^2 L(L+1) \left| LM;SM_S \right\rangle \qquad L_z \left| LM;SM_S \right\rangle = \hbar M \left| LM;SM_S \right\rangle$$

$$\mathbf{S}^2 \left| LM;SM_S \right\rangle = \hbar^2 S(S+1) \left| LM;SM_S \right\rangle \qquad S_z \left| LM;SM_S \right\rangle = \hbar M_S \left| LM;SM_S \right\rangle$$

These states have a degeneracy of $(2L+1)(2S+1)$

Degenerate perturbation theory matrix for first order:

$$\left\langle LM;SM_S \right| H^1 \left| LM';SM_S' \right\rangle = \frac{e\hbar B}{2mc}\left(M + 2M_S\right)\delta_{MM'}\delta_{M_S M_S'}$$

Example: atomic term: ${}^3P$

values of $\left\langle LM;SM_S \right| H^1 \left| LM';SM_S' \right\rangle / (e\hbar B / 2mc)$

	$M_S = -1$	0	1
$M = -1$	-3	-1	1
$M = 0$	-2	0	2
$M = 1$	-1	1	3

Paschen-Back effect

Example of degenerate perturbation theory in the treatment of the term values of multi-electron atoms:

$$\mathcal{H} = \underbrace{\sum_i h(\mathbf{r}_i)}_{\text{single electron terms}} + \sum_{i,j<i} \frac{e^2}{\underbrace{|\mathbf{r}_i - \mathbf{r}_j|}_{\text{electron-electron interaction}}} \qquad h(\mathbf{r}_i) \equiv -\frac{\hbar^2}{2m}\nabla_i^2 - \frac{Ze^2}{r_i}$$

Evaluating expectation values: $\langle LM|\mathcal{H}|LM\rangle$ for $2p^2$

$$E(P) = e^2\left(\mathcal{R}^0(2p,2p;2p,2p) - \frac{5}{25}\mathcal{R}^2(2p,2p;2p,2p)\right)$$

$$E(D) = e^2\left(\mathcal{R}^0(2p,2p;2p,2p) + \frac{1}{25}\mathcal{R}^2(2p,2p;2p,2p)\right)$$

$$E(S) = e^2\left(\mathcal{R}^0(2p,2p;2p,2p) + \frac{10}{25}\mathcal{R}^2(2p,2p;2p,2p)\right)$$

Example of degenerate perturbation theory in the treatment of the effects of spin-orbit interaction:

$$H_{SO} = G(r)\mathbf{S}\cdot\mathbf{L}$$

$$\text{Note that:}\quad \mathbf{J}=\mathbf{S}+\mathbf{L}$$

$$\mathbf{J}^2 = \mathbf{S}^2 + \mathbf{L}^2 + 2\mathbf{S}\cdot\mathbf{L}$$

$$\left\langle JM;ls\middle|H_{SO}\middle|JM;ls\right\rangle = G(r)\left\langle JM;ls\middle|\mathbf{S}\cdot\mathbf{L}\middle|JM;ls\right\rangle$$

$$= \frac{\hbar^2 G(r)}{2}\Big(j(j+1)-s(s+1)-l(l+1)\Big)$$

J=l+1/2:

$$\left\langle \left(l+\tfrac{1}{2}\right)M;ls\middle|H_{SO}\middle|\left(l+\tfrac{1}{2}\right)M;ls\right\rangle = \frac{\hbar^2 G(r)}{2}l$$

J=l-1/2:

$$\left\langle \left(l-\tfrac{1}{2}\right)M;ls\middle|H_{SO}\middle|\left(l-\tfrac{1}{2}\right)M;ls\right\rangle = -\frac{\hbar^2 G(r)}{2}(l+1)$$

Degenerate perturbation theory example for effects of a constant magnetic field B on an atom – including the effects of spin-orbit interaction

$$H=\frac{\left(\mathbf{p}+\frac{e}{c}\mathbf{A}\right)^2}{2m}+V(r)+G(r)\mathbf{S}\cdot\mathbf{L}+\frac{e}{mc}\mathbf{B}\cdot\mathbf{S}$$

$$H^0=\frac{\mathbf{p}^2}{2m}+V(r)$$

Keeping only terms to linear order in $\mathbf{B}$:

$$H^1=G(r)\mathbf{S}\cdot\mathbf{L}+\frac{e}{2mc}\left(\mathbf{L}+2\mathbf{S}\right)\cdot\mathbf{B}$$

$$=\frac{G(r)}{2}\left(\mathbf{J}^2-\mathbf{L}^2-\mathbf{S}^2\right)+\frac{e}{2mc}\left(\mathbf{J}+\mathbf{S}\right)\cdot\mathbf{B}$$