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 & D)

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.

9. A hydrogen atom in some combination of the $n = 2$ states is placed in an electric field which adds a perturbation $W = \frac{1}{2}\lambda\left(X^2 - Y^2\right)$ where λ is small. Ignore any spin-orbit or hyperfine splitting of the hydrogen atom; *i.e.*, treat all $n = 2$ states of hydrogen as perfectly degenerate before W is included.
   (a) Find all non-vanishing matrix elements $\langle 2l'm' | W | 2lm \rangle$ for this interaction.
   (b) Find the perturbed eigenstates and eigenenergies of the $n = 2$ states to zeroth and first order in λ respectively.

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 --

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

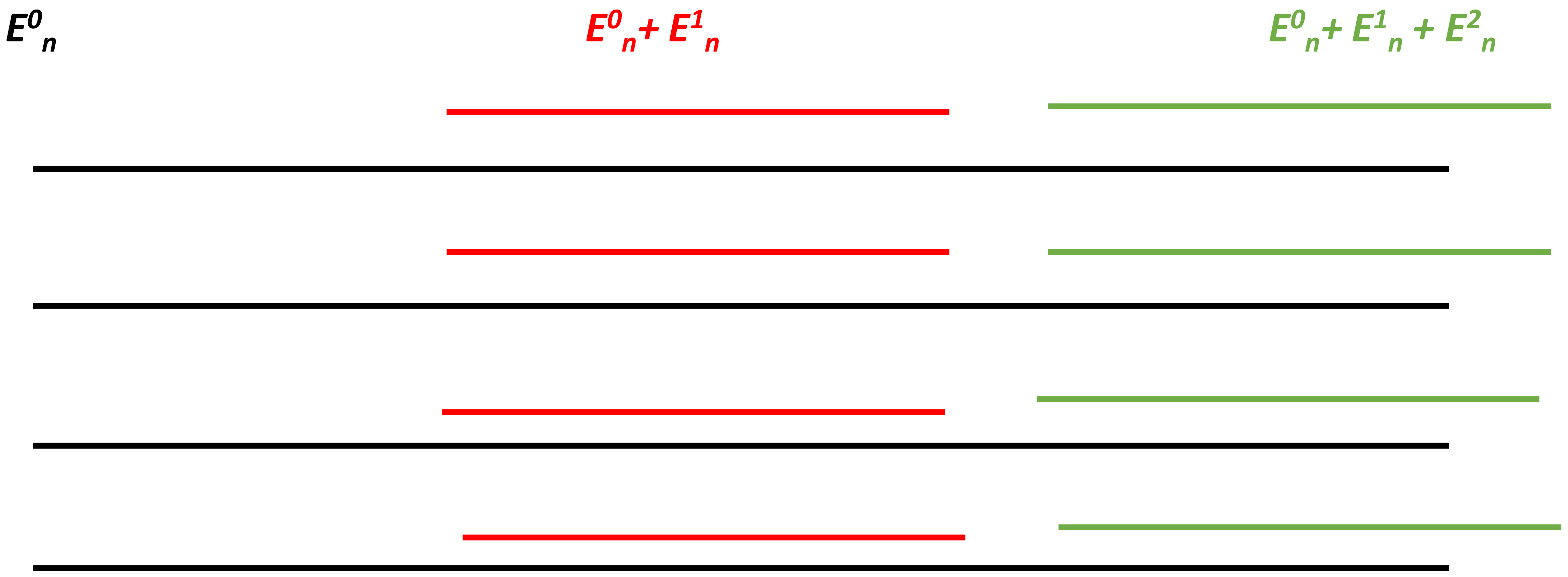
$$\left| n^1 \right\rangle = \sum_{m \neq n} \left(\frac{\left\langle m^0 \middle| H_1 \middle| n^0 \right\rangle}{E_n^0 - E_m^0} \right) \left| m^0 \right\rangle$$

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,

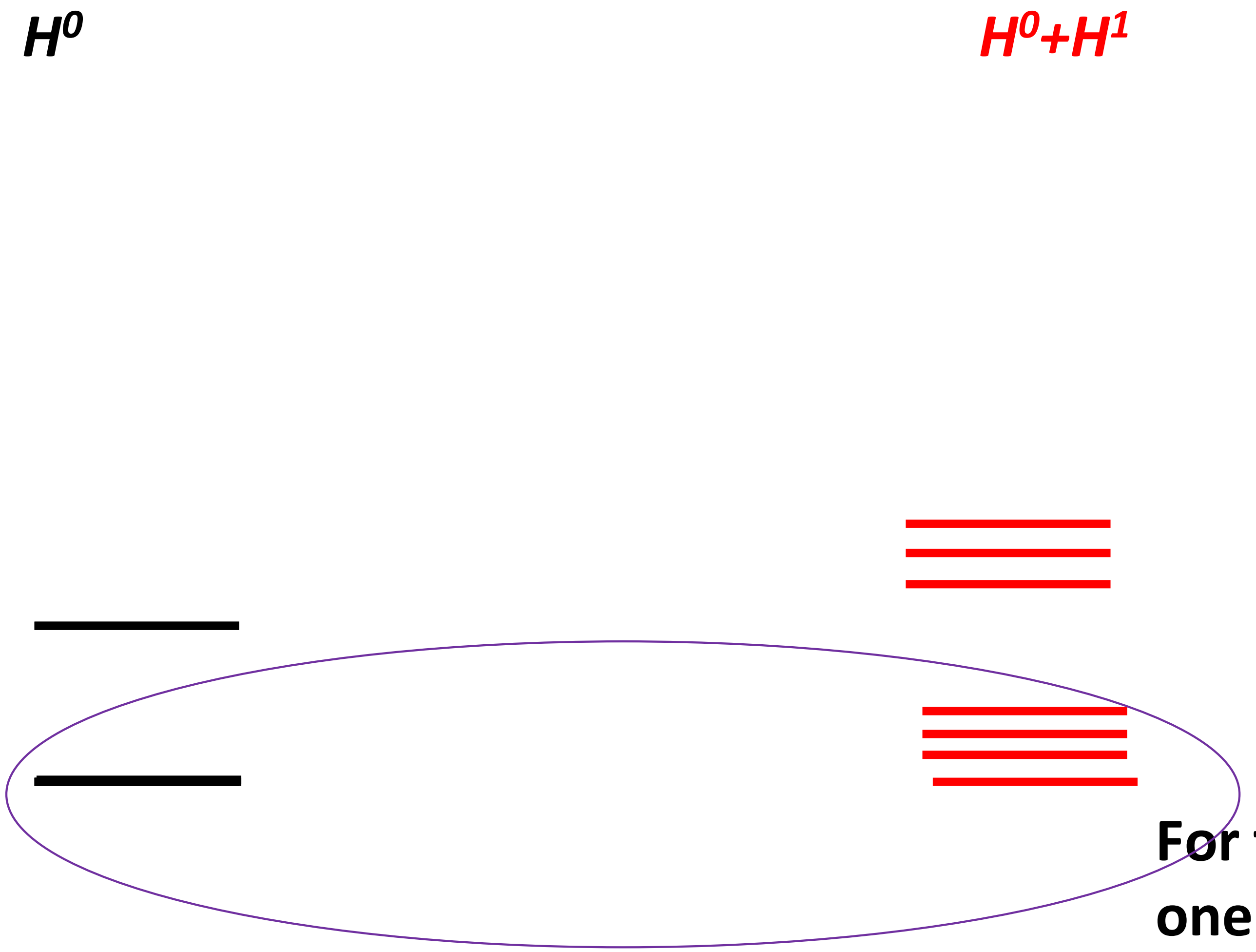
considering the effects on the N-fold degenerate states:

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

For $i = 1, 2, ...N,$ 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

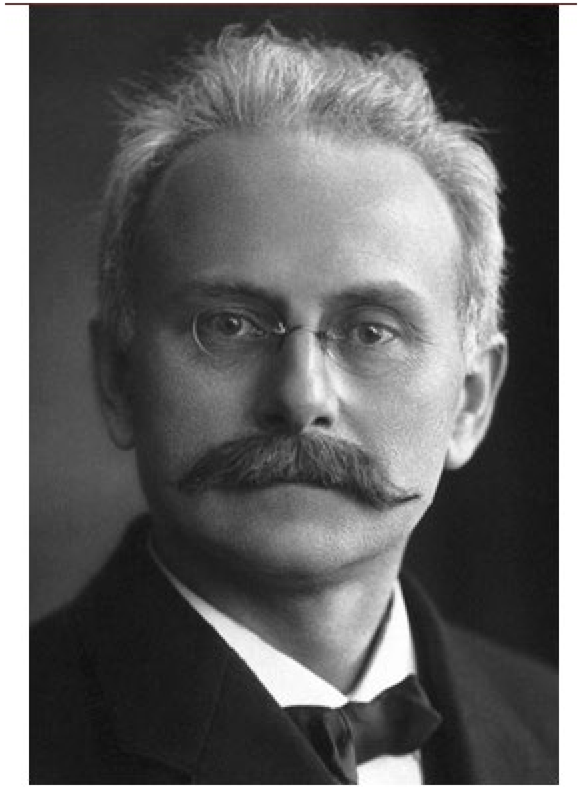


Photo from the Nobel Foundation archive.

Johannes Stark

Prize share: 1/1

The Nobel Prize in Physics 1919 was awarded to Johannes Stark "for his discovery of the Doppler effect in canal rays and the splitting of spectral lines in electric fields."

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: $\quad |200\rangle \quad |210\rangle \quad |21{-1}\rangle \quad |211\rangle$

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

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

$$E_2^0 \quad \text{for} \quad |21\pm 1\rangle$$

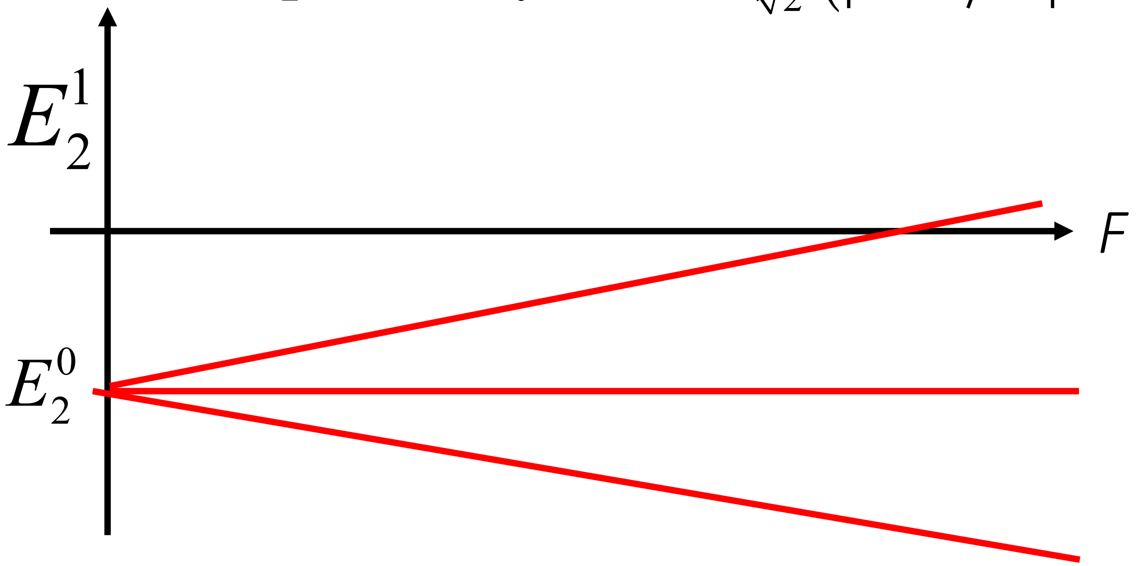
$$E_2^0 - 3eFa_0 \quad \text{for} \quad \tfrac{1}{\sqrt{2}}\left(|200\rangle + |210\rangle\right)$$

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

Degenerate perturbation theory example for the Stark effect -- continued

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

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



Note that the treatment in the previous slides is called the linear Stark effect. (why?)

What happens when you apply an electrostatic field to a H atom in its ground state?

1. **No effect**
2. **Small effect**
3. **Large effect**

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:

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

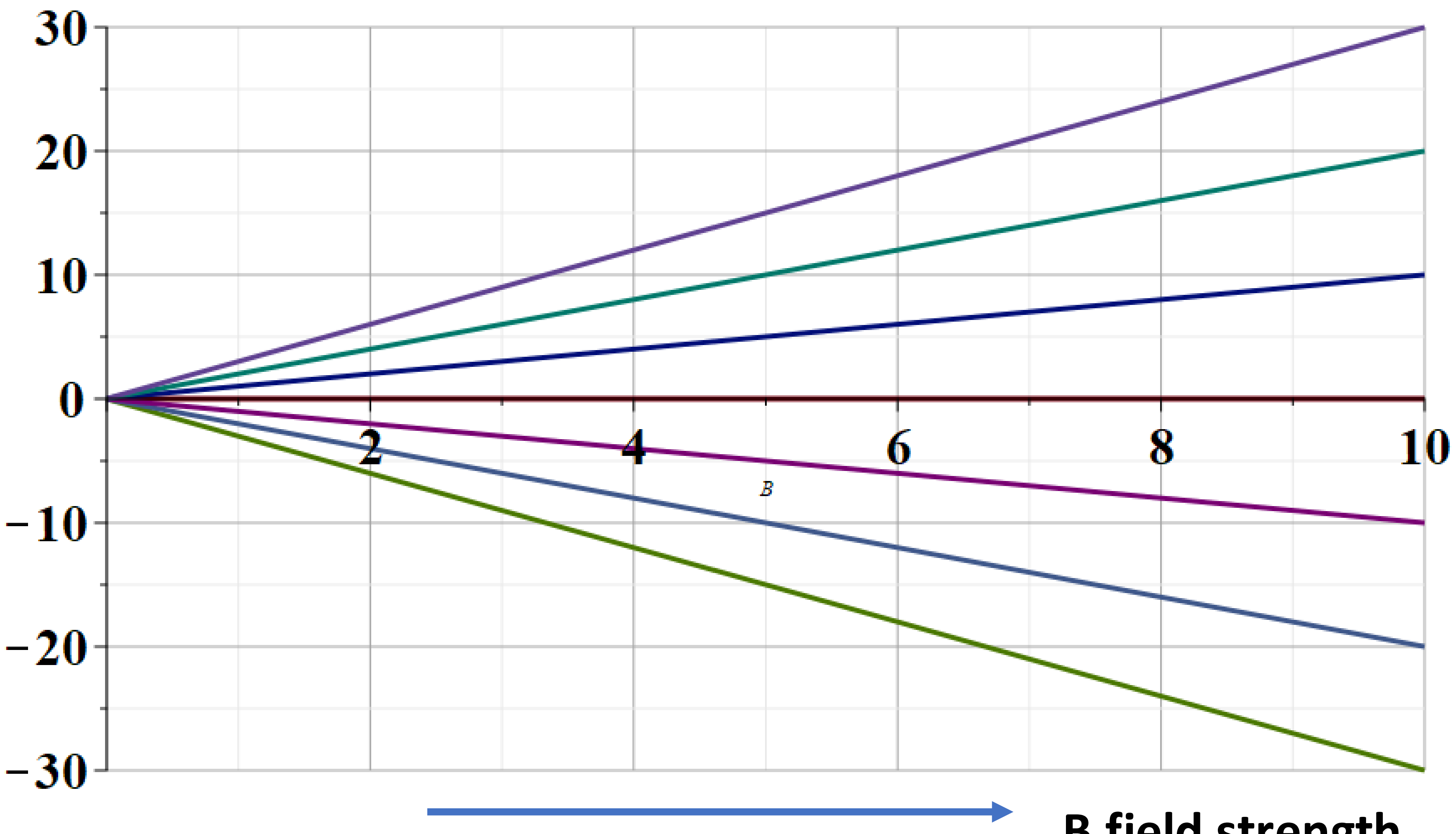
Example: atomic term: ^3P

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

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

Paschen-Back effect

Energy eigenvalues of L=1,S=1 atom (without spin-orbit interaction) in a magnetic field



M	M_s
1	1
0	1
-1	1 or 1 0
0	0
1	-1 or -1 0
0	-1
-1	-1

B field strength

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:

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

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

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

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

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

J=l+1/2:

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

J=l-1/2:

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

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 $\mathbf{B}$:

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

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