Name _____

Finding Splitting in the Hydrogen Atom Energy Spectrum due to an External Magnetic Field (Zeeman Effect)-PART II

The focus in degenerate perturbation theory is on ensuring that $\hat{H}'$ is diagonal in each degenerate subspace of $\hat{H}^0$. The degeneracy in $\hat{H}^0$ is $2n^2$ fold for each n. Our focus is always on a fixed n. The radial basis states are always $R_{nl}(r)$, which are solutions to the radial part of the time-independent Schrödinger equation for $\hat{H}^0$. We will learn how to determine a "good" angular basis.

1 Definition

For a given unperturbed Hamiltonian $\hat{H}^0$ and perturbation $\hat{H}'$, a **"good"** basis consists of a complete set of eigenstates of $\hat{H}^0$ that diagonalizes $\hat{H}'$ in each degenerate subspace of $\hat{H}^0$ ($\hat{H}^0$ remains diagonal everywhere since the basis states are eigenstates of $\hat{H}^0$).

- Once you have a "good" basis for a given $\hat{H}^0$ and $\hat{H}'$, you can use the same expressions that you use in non-degenerate perturbation theory for perturbative corrections.

2 Notes for this tutorial:

* If you are not familiar with the steps to determine a "good" basis for finding corrections to the unperturbed energies when the energy spectrum has degeneracy, please work through the pretest, tutorial and posttest for Basics of Degenerate Perturbation Theory before working on this tutorial.

* A Hermitian operator $\hat{Q}$ has the property $Q_{ij} = (Q_{ji})^*$. Here * denotes the complex conjugate.

* For the matrix representation of a Hermitian operator $\hat{Q}$ in a given basis, we will use "=" or "is equal to" instead of "$\doteq$" or "is represented by" as in the notation below

$$\hat{Q} = \begin{pmatrix} Q_{11} & Q_{12} & Q_{13} \\ Q_{21} & Q_{22} & Q_{23} \\ Q_{31} & Q_{32} & Q_{33} \end{pmatrix} \quad \text{is equivalent to} \quad \hat{Q} \doteq \begin{pmatrix} Q_{11} & Q_{12} & Q_{13} \\ Q_{21} & Q_{22} & Q_{23} \\ Q_{31} & Q_{32} & Q_{33} \end{pmatrix}.$$

* In this tutorial, "degeneracy" indicates degeneracy in the unperturbed energy eigenvalue spectrum, i.e., the fact that more than one distinct energy eigenstate can have the same energy eigenvalue. For example, if

$$\hat{H}^0|\psi_a\rangle = E_a|\psi_a\rangle \qquad \text{and} \qquad \hat{H}^0|\psi_b\rangle = E_a|\psi_b\rangle,$$

  $|\psi_a\rangle$ and $|\psi_b\rangle$ are degenerate eigenstates of the Hamiltonian $\hat{H}^0$ since they correspond to the same energy E_a.

* We will only consider the bound states of the hydrogen atom.

* The unperturbed bound state energies E_n are given by $E_n = -\frac{13.6\text{eV}}{n^2}$, $n = 1, 2, 3, \ldots$.

* **For any basis we choose, the radial parts of the wavefunctions R_{nl} (for given quantum numbers n and l) will always be chosen to be the radial parts of a complete set of eigenstates of $\hat{H}^0$. In other words, our focus will be on the choice of the angular part of the wavefunction in order to find a "good" basis for degenerate perturbation theory for the given $\hat{H}^0$ and $\hat{H}'$ for the hydrogen atom.**

* We will restrict our focus to a finite subspace of the infinite dimensional Hilbert space.
  - As an example of a degenerate subspace of the unperturbed Hamiltonian $\hat{H}^0$, only the subspace with the principal quantum number $n = 2$ will be considered.
  - The results can be generalized to any quantum number n.
* The external magnetic field will be chosen to be a uniform, time independent field along the $\hat{z}$ direction given by $\vec{B} = B_{ext}\hat{z}$.
* We will account for the coupling of the external magnetic field with both the orbital and spin angular momentum.
* We will use the following notations interchangeably to write states in the uncoupled representation (in which basis states are eigenstates of $\hat{L}^2$, $\hat{S}^2$, $\hat{L}_Z$, and $\hat{S}_Z$) with a given set of quantum numbers (notation for quantum numbers is standard):
  - $|n\ l\ s\ m_l\ m_s\rangle$
  - $|l,\ m_l\rangle|s,\ m_s\rangle$ (if n is fixed)
  - $|l,\ m_l,\ m_s\rangle$ (if n and s are fixed)
* $\vec{J} = \vec{L} + \vec{S}$
* We will use the following notations interchangeably to write states in the coupled representation (in which basis vectors are eigenstates of $\hat{L}^2$, $\hat{S}^2$, $\hat{J}^2$, and $\hat{J}_Z$) with a given set of quantum numbers (notation for quantum numbers is standard):
  - $|n\ l\ s\ j\ m_j\rangle$
  - $|l,\ s,\ j,\ m_j\rangle$ (if n is fixed)
  - $|l,\ j,\ m_j\rangle$ (if n and s are fixed)
* In both Part I and Part II of this tutorial, we will consider the case in which $s = \frac{1}{2}$ so this quantum number may be suppressed in writing a state (e.g., $|l\ m_l\ m_s\rangle$ or $|l\ j\ m_j\rangle$).

3 Physical Constants

Below is a list of physical constants used in this tutorial.

Planck's constant:	$\hbar$	=	1.05×10^{-34} J s
Mass of the electron:	m	=	9.11×10^{-31} kg
Charge of an electron (magnitude):	e	=	1.60×10^{-19} C
Speed of light:	c	=	2.99×10^{8} m/s
Permittivity of space:	ϵ_0	=	8.85×10^{-12} C^2/J m
Bohr radius:	a	=	$\frac{4\pi\epsilon_0\hbar^2}{me^2} = 0.529 \times 10^{-10}$ m
Bohr magneton:	μ_B	=	$\frac{e\hbar}{2m} = 5.79 \times 10^{-5}$ eV/T
Fine structure constant:	α	=	$\frac{e^2}{4\pi\epsilon_0\hbar c} \approx \frac{1}{137} = 7.30 \times 10^{-3}$

NOTE : The following equations may be helpful.

$$E_n^1 = \langle \psi_n^0 | \hat{H}' | \psi_n^0 \rangle$$

$$|\psi_n^1\rangle = \sum_{m \neq n} \frac{\langle \psi_m^0 | \hat{H}' | \psi_n^0 \rangle}{(E_n^0 - E_m^0)} |\psi_m^0\rangle$$

$$\hat{S}^2 |s\ m_s\rangle = \hbar^2 s(s+1) |s\ m_s\rangle \qquad \hat{S}_z |s\ m_s\rangle = \hbar m_s |s\ m_s\rangle$$

$$\hat{S}_\pm |s\ m_s\rangle = \hbar \sqrt{s(s+1) - m_s(m_s \pm 1))} |s\ m_s \pm 1\rangle$$

$$\hat{L}^2 |l\ m_l\rangle = \hbar^2 l(l+1) |l\ m_l\rangle \qquad \hat{L}_z |l\ m_l\rangle = \hbar m_l |l\ m_l\rangle$$

$$\hat{L}_\pm |l\ m_l\rangle = \hbar \sqrt{l(l+1) - m_l(m_l \pm 1))} |l\ m_l \pm 1\rangle$$

$$\vec{J} = \vec{L} + \vec{S}$$

$$\hat{J}^2 |l,\ s,\ j,\ m_j\rangle = \hbar^2 j(j+1) |l,\ s,\ j,\ m_j\rangle \qquad \hat{J}_z |l,\ s,\ j\ m_j\rangle = \hbar m_j |l,\ s,\ j,\ m_j\rangle$$

$$\hat{S}^2 |l,\ s,\ j,\ m_j\rangle = \hbar^2 s(s+1) |l,\ s,\ j,\ m_j\rangle \qquad \hat{L}^2 |l,\ s,\ j\ m_j\rangle = \hbar^2 l(l+1) |l,\ s,\ j,\ m_j\rangle$$

$$\vec{L} \cdot \vec{S} = \frac{1}{2}(\hat{J}^2 - \hat{S}^2 - \hat{L}^2) = \frac{1}{2}(\hat{L}_+ \hat{S}_- + \hat{L}_- \hat{S}_+) + \hat{L}_z \hat{S}_z$$

4 Objectives:

Upon completion of this tutorial, you should be able to do the following for the hydrogen atom:

1. Identify the unperturbed Hamiltonian $\hat{H}^0$ and the perturbing Hamiltonian $\hat{H}'$.
2. Identify the degeneracy in the unperturbed Hamiltonian $\hat{H}^0$ in each degenerate subspace corresponding to a principal quantum number n.
3. Determine a "good" basis for finding the corrections to the unperturbed energies of the hydrogen atom for only the fine structure perturbation $\hat{H}'_{fs}$.
4. Find the first order corrections to energies due to the fine structure perturbation $\hat{H}'_{fs}$.
5. Determine a "good" basis for finding the corrections to the unperturbed energies of the hydrogen atom due to the Zeeman effect (including in intermediate, strong, and weak magnetic field).
6. Find the first order corrections to energies in the intermediate field Zeeman effect.
7. Find the first order corrections to energies in the strong field Zeeman effect.
8. Find the first order corrections to energies in the weak field Zeeman effect.

5 The Hydrogen Atom Placed in an External Magnetic Field

The Hamiltonian of the hydrogen atom placed in an external magnetic field is

$$\hat{H} = \hat{H}^0 + \hat{H}'_r + \hat{H}'_{SO} + \hat{H}'_Z = \hat{H}^0 + \hat{H}'_{fs} + \hat{H}'_Z \tag{1}$$

in which

- $\hat{H}^0 = \frac{\hat{p}^2}{2m} - \frac{e^2}{4\pi\epsilon_0}\left(\frac{1}{r}\right)$ accounts only for the interaction of the electron with the nucleus via Coulomb attraction
- $\hat{H}'_r = -\frac{\hat{p}^4}{8m^3c^2}$ is the relativistic correction term
- $\hat{H}'_{SO} = \frac{e^2}{8\pi\epsilon_0}\frac{1}{m^2c^2r^3}\vec{L}\cdot\vec{S}$ is the spin-orbit interaction term

and combining the relativistic and spin-orbit terms

- $\hat{H}'_{fs} = \hat{H}'_{SO} + \hat{H}'_r$ is the fine structure term
- $\hat{H}'_Z = \frac{\mu_B B_{ext}}{\hbar}(\hat{L}_z + 2\hat{S}_z)$ is the Zeeman term, in which $\vec{B}_{ext} = B_{ext}\hat{z}$.

6 Perturbation Theory

- In order to find the first order corrections to the energies due to a perturbation $\hat{H}'$, we must first find a "good" basis for the given $\hat{H}^0$ and $\hat{H}'$.
- A "good" basis is defined as one which satisfies the following two conditions:
  1. The entire unperturbed Hamiltonian $\hat{H}^0$ is diagonal (i.e., basis states are eigenstates of $\hat{H}^0$).
     - We know from Part I of this tutorial that the unperturbed Hamiltonian matrix $\hat{H}^0$ is diagonal if the coupled or uncoupled representation or any arbitrary complete orthonormal basis found with linear combinations of a complete set of the coupled or uncoupled states with the same principal quantum number n is chosen as the angular basis (as a consequence of the spherical symmetry of $\hat{H}^0$ and the unperturbed energy only depending on n as $E_n = -\frac{13.6 \text{ eV}}{n^2}$).
  2. The perturbing Hamiltonian $\hat{H}'$ is diagonal in each degenerate subspace of $\hat{H}^0$.
     - We always choose R_{nl} as the radial part of the basis and focus on the angular basis for determining a "good" basis for a given $\hat{H}^0$ and $\hat{H}'$.
     - We shall consider several types of perturbing Hamiltonian, $\hat{H}'$, and determine whether the coupled representation, the uncoupled representation, some special orthonormal basis constructed with linear combinations of the coupled or the uncoupled states, or any arbitrary complete orthonormal basis constructed with linear combinations of the coupled or the uncoupled states with the same principal quantum number n and the same l diagonalizes $\hat{H}'$ in each degenerate subspace of $\hat{H}^0$.
- In Part I, we found:
  - $\hat{H}^0$ (spherically symmetric with energy only depending on n as $E_n = -\frac{13.6 \text{ eV}}{n^2}$) is diagonal if the coupled representation, the uncoupled representation, or any arbitrarycomplete orthonormal basis constructed with linear combinations of a complete set of states in the coupled or the uncoupled representation (with the same n) is chosen as the angular basis.
  - $\hat{H}'_r$ (spherically symmetric with energy depending on both n and l) is diagonal in each degenerate subspace of $\hat{H}^0$ if the coupled representation, the uncoupled representation, or any arbitrary complete orthonormal basis constructed with linear combinations of states with the same n and l in the coupled or the uncoupled representation is chosen as the angular basis.
  - $\hat{H}'_{SO}$ is diagonal in each degenerate subspace of $\hat{H}^0$ if the coupled representation is chosen as the angular basis.
  - $\hat{H}'_Z$ is diagonal if the uncoupled representation is chosen as the angular basis.

6.1 The Hydrogen Atom in an External Magnetic Field

- In order to find the corrections to the unperturbed energies in the presence of an external magnetic field, we shall consider the following two terms in the Hamiltonian perturbatively:

$$\hat{H}' = \hat{H}'_{fs} + \hat{H}'_Z \tag{2}$$

in which $\hat{H}'_{fs}$ is the fine structure correction term and $\hat{H}'_Z$ is the Zeeman term incorporating the effect of the external magnetic field.

- The perturbative corrections due to these terms are small compared to the unperturbed energies due to $\hat{H}^0$, but both terms are important in terms of determining splittings in the energy spectrum so that they should both be considered simultaneously.

- Let's first consider the fine structure. Here is the order in which we shall proceed:

I. Determining a "good" angular basis and corrections to the energies for **ONLY** the fine structure perturbation $\hat{H}'_{fs}$.

   – The fine structure correction $\hat{H}'_{fs}$ is made up of two mechanisms: $\hat{H}'_{fs} = \hat{H}'_r + \hat{H}'_{SO}$, in which $\hat{H}'_r$ is the relativistic correction term and $\hat{H}'_{SO}$ is the spin-orbit interaction term (due to the coupling of the orbital and spin angular momenta of the electron).

II. Determining a "good" angular basis and corrections to the energies for **ONLY** the Zeeman perturbation $\hat{H}'_Z$.

   – The Zeeman effect in the hydrogen atom (or any atom) is the splitting of the energy spectrum as a result of placing the atom in an external magnetic field.

III. Determining a "good" angular basis and corrections to the energies for **BOTH** the fine structure and Zeeman perturbations combined: $\hat{H}' = \hat{H}'_{fs} + \hat{H}'_Z$.

   – In this tutorial we will learn about three cases with $\hat{H}' = \hat{H}'_{fs} + \hat{H}'_Z$:

      * **CASE 1: The Intermediate Field Zeeman Effect**
         · The intermediate field Zeeman effect describes a situation when the first-order corrections to the energies due to the spin-orbit coupling term $\hat{H}'_{fs}$ and the Zeeman term $\hat{H}'_Z$ in $\hat{H}'$ are comparable to one another. (We will use the notations $E'_Z \approx E'_{fs}$ to denote the intermediate field Zeeman effect).

   – along with two limiting cases:

      * **CASE 2: The Strong Field Zeeman Effect ($E'_Z \gg E'_{fs}$)**
         · The strong field Zeeman effect describes a situation when the first-order corrections to the energies due to the Zeeman term is stronger than the first-order corrections to the energies due to the spin-orbit coupling term in $\hat{H}'$. (We will use the notation $E'_Z \gg E'_{fs}$ to denote the strong field Zeeman effect).

      * **CASE 3: The Weak Field Zeeman Effect ($E'_{fs} \gg E'_Z$)**
         · The weak field Zeeman effect describes a situation when the first-order corrections to the energies due to the spin-orbit coupling term is stronger than the first-order corrections to the energies due to the Zeeman term in $\hat{H}'$. (We will use the notation $E'_{fs} \gg E'_Z$ to denote the weak field Zeeman effect)

I. Determining a "GOOD" Angular Basis and Corrections to the Energies for ONLY the Fine Structure Perturbation $\hat{H}'_{fs}$.

As noted, the fine structure perturbation is comprised of two mechanisms: the relativistic correction $\hat{H}'_r$ and the spin-orbit interaction $\hat{H}'_{SO}$:

$$\hat{H}'_{fs} = \hat{H}'_r + \hat{H}'_{SO}. \tag{3}$$

We shall discuss each separately and then find the first order corrections to the energies of the hydrogen atom due to the combined effect of the relativistic correction and the spin-orbit interaction.

Relativistic Correction

6.2 Finding a "GOOD" Basis for the Relativistic Correction Term as a Perturbation for the Hydrogen Atom

A perturbation $\hat{H}'_r$ acts on a hydrogen atom with the unperturbed Hamiltonian $\hat{H}^0 = -\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{4\pi\epsilon_0}\frac{1}{r}$ such that the relativistic correction term in the Hamiltonian is

$$\hat{H}'_r = -\frac{\hat{p}^4}{8m^3c^2}. \tag{4}$$

1. For the perturbation $\hat{H}'_r$, will a "good" angular basis for finding the corrections to the energies be the coupled representation, the uncoupled representation, or any arbitrary complete orthonormal basis constructed with linear combinations of the coupled or uncoupled states with the same principal quantum number n and the same l? Explain.

Consider the following conversation regarding finding a "good" basis for the relativistic term $\hat{H}'_r$ as a perturbation on $\hat{H}^0$ for the hydrogen atom.

Student 1: We found that for a fixed n the **spherically symmetric** unperturbed Hamiltonian $\hat{H}^0$ is diagonal in the coupled or the uncoupled representation, as well as in any arbitrary complete orthonormal basis constructed with linear combinations of states in the coupled representation or the uncoupled representation. Since the relativistic correction $\hat{H}'_r$ is also spherically symmetric, $\hat{H}'_r$ will also be diagonal in the coupled or the uncoupled representation, as well as in any arbitrary complete orthonormal basis constructed with linear combinations of basis states with the same n and l in the coupled representation or the uncoupled representation.

Student 2: I agree. $\hat{H}^0 = \frac{\hat{p}^2}{2m} - \frac{e^2}{4\pi\epsilon_0}(\frac{1}{r})$ and $\hat{H}'_r$ is proportional to $\hat{p}^4$. Both terms are spherically symmetric because $[\hat{H}^0, \vec{\hat{L}}] = 0$ and $[\hat{H}'_r, \vec{\hat{L}}] = 0$. However, the eigenvalues of $\hat{H}^0$ only depend on n while the eigenvalues of $\hat{H}'$ depend on both n and l. Thus, $\hat{H}'_r$ will also be diagonal in both the coupled and the uncoupled representation, as well as any arbitrary complete orthonormal basis constructed with linear combinations of states in the coupled representation or the uncoupled representation.

Student 3: I disagree with both Student 1 and Student 2. The fact that $\hat{H}'_r$ is spherically symmetric is not enough information to determine whether the coupled or uncoupled representation or both will form a "good" angular basis.

Student 4: I agree with Student 1 and Student 2. For finding the corrections to the energies due to the perturbation $\hat{H}'_r$, a "good" angular basis can be chosen to be the coupled representation, the uncoupled representation, or any arbitrary complete orthonormal basis found with linear combinations of the coupled or uncoupled states with the same principal quantum number n and the same l.

Explain why you agree or disagree with each student.

The relativistic correction term $\hat{H}'_r$ is spherically symmetric and its energy eigenvalues depend on the quantum numbers n and l, and therefore the coupled representation, the uncoupled representation, or any arbitrary complete orthonormal basis constructed with linear combinations of states with a fixed n and l in the coupled or the uncoupled representation will form a "good" basis. For example, using the same reasoning as for the unperturbed Hamiltonian $\hat{H}^0$ and the example when $\hat{H}'$ was proportional to $\delta(r)$ in Part I of this tutorial, for a given n and l, $\hat{H}'_r$ will be a diagonal in each degenerate subspace of $\hat{H}^0$ because the angular part of the matrix elements of $\hat{H}'_r$ will involve $\langle l, j, m_j | l', j', m'_j \rangle = \delta_{l,l'}\delta_{j,j'}\delta_{m_j,m'_j}$ if we choose the coupled representation or $\langle l, m_l, m_s | l', m'_l, m'_s \rangle = \delta_{l,l'}\delta_{m_l,m'_l}\delta_{m_s,m'_s}$ if we choose the uncoupled representation. The off-diagonal matrix elements will be zero due to the Kronecker deltas in either case.

**** Check your answers to question 1. ****

1. The coupled representation, the uncoupled representation, or any arbitrary complete orthonormal basis constructed with linear combinations of states with the same n and l in the coupled or the uncoupled representation with the same principal quantum number n and the same l will form a "good" angular basis for finding the corrections to the energies of the hydrogen atom due to the spherically symmetric relativistic correction term $\hat{H}'_r = -\frac{\hat{p}^4}{8m^3c^2}$.

If your answer to question 1 does not match with the checkpoint, go back and reconcile any differences.

6.3 First Order Corrections to the Energy Spectrum of the Hydrogen Atom Due to the Relativistic Correction Term Using Perturbation Theory

Now that we have determined that the coupled representation, the uncoupled representation, or any arbitrary complete orthonormal basis constructed with linear combinations of states in the coupled or the uncoupled representation form a "good" angular basis for $\hat{H}'_r$ as the perturbation, we can determine the corrections to the energies.

- Let $\{|\psi_n\rangle\}$ represent a "good" basis set in which the quantum numbers to describe the angular part of the $\{|\psi_n\rangle\}$ have been suppressed (those quantum numbers will depend, e.g., on whether we choose the coupled or uncoupled representation for the angular part).
- If $\{|\psi_n\rangle\}$ forms a "good" basis for $\hat{H}'_r$ as a perturbation on the unperturbed Hamiltonian $\hat{H}^0$, then the first order correction to the energy due to $\hat{H}'_r$ is given by (using the fact that $\hat{p}^2$ is Hermitian, i.e., $(\hat{p}^2)^\dagger = \hat{p}^2$)

$$E'_r = \langle \psi_n | \hat{H}'_r | \psi_n \rangle = \langle \psi_n | -\frac{\hat{p}^4}{8m^3c^2} | \psi_n \rangle = -\frac{1}{8m^3c^2} \langle \hat{p}^2\psi_n | \hat{p}^2\psi_n \rangle. \tag{5}$$

Consider the following statement regarding evaluating $\hat{p}^2|\psi_n\rangle$.
Student 1: We evaluate $\hat{p}^2|\psi_n\rangle$ by considering the Time-Independent Schrödinger Equation or TISE for the unperturbed Hamiltonian $\hat{H}^0|\psi_n\rangle = E_n|\psi_n\rangle$. Using the TISE $[\frac{\hat{p}^2}{2m} + V(r)]|\psi_n\rangle = E_n|\psi_n\rangle$, rearranging and solving for $\hat{p}^2|\psi_n\rangle$ gives $\hat{p}^2|\psi_n\rangle = 2m[E_n - V(r)]|\psi_n\rangle$ which is helpful in evaluating E'_r in equation (5). Using $\langle \hat{p}^2\psi_n | \hat{p}^2\psi_n \rangle = (2m)^2 \langle \psi_n | [E_n - V(r)]^2 | \psi_n \rangle$, in which $V(r)$ for the hydrogen atom is proportional to $\frac{1}{r}$, we can find the first order corrections to the energies due to $\hat{H}'_r$ in Eq. (5).
Do you agree with Student 1's approach? Explain your reasoning.

Student 1's method is helpful in determining $\hat{p}^2|\psi_n\rangle$. The first order correction to the energy due to $\hat{H}'_r$ in the "good" basis $\{|\psi_n\rangle\}$ is given by

$$E'_r = -\frac{1}{8m^3c^2}\langle\hat{p}^2\psi_n|\hat{p}^2\psi_n\rangle = -\frac{1}{8m^3c^2}\langle\psi_n|[2m(E_n - V(r))]^2|\psi_n\rangle = -\frac{1}{2mc^2}\langle\psi_n|E_n^2 - 2E_nV(r) + (V(r))^2|\psi_n\rangle. \quad (6)$$

For the Coulomb potential energy $V(r) = -\dfrac{1}{4\pi\epsilon_0}\left(\dfrac{e^2}{r}\right)$, the first order correction to the energy becomes

$$E'_r = -\frac{1}{2mc^2}\langle\psi_n|\left[E_n^2 + 2E_n\frac{e^2}{4\pi\epsilon_0}\left(\frac{1}{r}\right) + \left(\frac{e^2}{4\pi\epsilon_0}\right)^2\left(\frac{1}{r^2}\right)\right]|\psi_n\rangle. \quad (7)$$

It can be shown that using the radial part of the wavefunction R_{nl} (for a given n and l) for the unperturbed Hamiltonian $\hat{H}^0$ for the hydrogen atom yields

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

with Bohr radius

$$a = \frac{4\pi\epsilon_0\hbar^2}{me^2}.$$

The first order correction to the n^{th} energy state E_n due to the relativistic correction is

$$E'_r = -\frac{E_n^2}{2mc^2}\left[\frac{4n}{l+1/2} - 3\right]. \quad (8)$$

In one to two sentences, summarize what you have learned about the "good" angular basis states for finding the first order corrections to the energy spectrum of the hydrogen atom due to the relativistic correction $\hat{H}'_r$ (pertaining to whether the coupled representation, the uncoupled representation, or any arbitrary complete orthonormal basis found with linear combinations of states with the same principal quantum number n and the same l in the coupled or uncoupled representation form a "good" angular basis or all of them form a "good" angular basis).

Summary: Finding a "GOOD" Angular Basis for the Relativistic Correction

- The perturbation matrix due to the relativistic correction $\hat{H}'_r$ is a diagonal matrix in the degenerate subspace of $\hat{H}^0$ in both the coupled and the uncoupled representation, or in any arbitrary complete orthonormal basis constructed with linear combinations of the coupled or uncoupled states with the same principal quantum number n and the same l.
- The coupled representation, the uncoupled representation, or any arbitrary complete orthonormal basis constructed with linear combinations of the coupled or uncoupled states with the same principal quantum number n and the same l form a "good" basis for finding corrections to the energies.

Hamiltonian	Uncoupled Representation (for a fixed n)	Is Uncoupled Representation a "Good" Basis?	Coupled Representation (for a fixed n)	Is Coupled Representation a "Good" Basis?	Is Any Arbitrary Complete Orthonormal Basis Constructed with Linear Combinations of a Complete Set of States with the Same n and l in the Coupled or Uncoupled Representation a "Good" Basis?	Energy
$\hat{H}^0$	Diagonal	—	Diagonal	—	—	$E_n = -\frac{13.6\text{eV}}{n^2}$
$\hat{H}'_r$	Diagonal	Yes	Diagonal	Yes	Yes	$E'_r = -\frac{E_n^2}{2mc^2}\left[\frac{4n}{l+1/2} - 3\right]$

Spin-orbit Interaction

6.4 Finding a "GOOD" Angular Basis for the Spin-orbit Interaction Correction to the Energy Spectrum of the Hydrogen Atom in Perturbation Theory

A perturbation $\hat{H}'_{SO}$ acts on a hydrogen atom with the unperturbed Hamiltonian $\hat{H}^0 = -\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{4\pi\epsilon_0}\frac{1}{r}$ such that the spin-orbit interaction term in the Hamiltonian is

$$\hat{H}'_{SO} = \frac{e^2}{8\pi\epsilon_0}\frac{1}{m^2c^2r^3}\vec{L}\cdot\vec{S}. \tag{9}$$

2. In each degenerate subspace of $\hat{H}^0$, the off-diagonal matrix elements of $\hat{H}'_{SO}$ should be zero in a "good" basis. Does the coupled or the uncoupled representation, or any arbitrary complete orthonormal basis found with linear combinations of the coupled or uncoupled states with the same principal quantum number n form a "good" angular basis for finding the corrections to the energies? Explain.

Consider the following conversation about finding a "good" angular basis for the hydrogen atom due to the spin-orbit interaction term as the perturbation.
Student 1: The spin-orbit interaction term is proportional to $\vec{L}\cdot\vec{S}$. Does the coupled or uncoupled representation, or any arbitrary complete orthonormal basis found with their linear combination form a "good" angular basis for finding the corrections to the energies?
Student 2: Since $\vec{L}\cdot\vec{S} = \hat{L}_x\hat{S}_x + \hat{L}_y\hat{S}_y + \hat{L}_z\hat{S}_z$, the uncoupled representation must be a "good" basis because the basis states in the uncoupled representation are eigenstates of both $\hat{S}_z$ and $\hat{L}_z$.
Student 3: I disagree with Student 2. $\vec{S}\cdot\vec{L}$ is diagonal in the coupled representation because $J^2 = (\vec{L}+\vec{S})\cdot(\vec{L}+\vec{S}) = \hat{L}^2 + \hat{S}^2 + 2\vec{L}\cdot\vec{S}$ which implies $\vec{L}\cdot\vec{S} = \frac{1}{2}(\hat{J}^2 - \hat{S}^2 - \hat{L}^2)$. The basis states in the coupled representation are eigenstates of $\hat{J}^2$, $\hat{S}^2$, and $\hat{L}^2$ and hence eigenstates of $\vec{L}\cdot\vec{S}$.
Student 4 I agree with Student 3. $\hat{H}'_{SO}$ is diagonal in each degenerate subspace of $\hat{H}^0$ when the coupled representation is chosen as the basis, but not when the uncoupled representation is chosen as the basis. The coupled representation forms a "good" basis for the given $\hat{H}^0$ and $\hat{H}'_{SO}$.

Do you agree with Student 2 or Student 3? Explain.

(If you need further help with why $\vec{S}\cdot\vec{L}$ is diagonal in the coupled representation, see Part I of this tutorial.)

**** Check your answer to question 2. ****

2. The coupled representation forms a "good" angular basis for finding the corrections to the energies of the hydrogen atom due to the spin-orbit interaction term $\hat{H}'_{SO}$.

If your answer to question 2 does not match with the checkpoint, go back and reconcile any differences.

6.5 First Order Corrections to the Energy Spectrum of the Hydrogen Atom in Perturbation Theory Due to the Spin-orbit Interaction

Student 3 is correct in the preceding conversation in stating that the coupled representation will form a "good" angular basis for finding the correction to the energy due to the spin-orbit interaction as a perturbation. The first order corrections to the energies due to the spin-orbit interaction in a "good" basis are given by

$$E'_{SO} = \langle n\ l\ s\ j\ m_j|\hat{H}'_{SO}|n\ l\ s\ j\ m_j\rangle = \left(\frac{e^2}{8\pi\epsilon_0}\right)\frac{1}{m^2c^2}\langle n\ l\ s\ j\ m_j|\frac{1}{r^3}\vec{L}\cdot\vec{S}|n\ l\ s\ j\ m_j\rangle$$

$$E'_{SO} = A\langle n\ l\ s\ j\ m_j|\frac{1}{r^3}\vec{L}\cdot\vec{S}|n\ l\ s\ j\ m_j\rangle \tag{10}$$

where $A = \left(\frac{e^2}{8\pi\epsilon_0}\right)\frac{1}{m^2c^2}$.

Separating the radial ($R_{nl}(r)$) and angular parts of eigenstates $\{|\psi\rangle\}$ of $\hat{H}^0$ in the coupled representation, the angular part is

$$\left\langle l\ s\ j\ m_j\left|\vec{L}\cdot\vec{S}\right|l\ s\ j\ m_j\right\rangle = \left\langle l\ s\ j\ m_j\left|\frac{\hat{J}^2-\hat{L}^2-\hat{S}^2}{2}\right|l\ s\ j\ m_j\right\rangle = \frac{\hbar^2}{2}[j(j+1)-l(l+1)-s(s+1)] \tag{11}$$

and the radial part is

$$\left\langle n\ l\left|\frac{1}{r^3}\right|n\ l\right\rangle = \frac{1}{l(l+1)(l+1/2)n^3a^3}. \tag{12}$$

Thus, combining equations (10), (11), and (12), the first order correction to the energy due to the spin-orbit interaction is

$$E'_{SO} = \frac{E_n^2}{mc^2}\left[\frac{n(j(j+1)-l(l+1)-3/4)}{l(l+1)(l+1/2)}\right]. \tag{13}$$

In one to two sentences, summarize what you have learned about the "good" states for finding the first order corrections to the energy spectrum of the hydrogen atom due to the spin-orbit interaction $\hat{H}'_{SO}$ (pertaining to whether the coupled representation, the uncoupled representation, or any arbitrary complete orthonormal basis found with linear combinations of states with a fixed principal quantum number n in the coupled or uncoupled representation form a "good" basis).

Summary: Finding a "GOOD" Angular Basis for the Spin-orbit Interaction Term $\hat{H}'_{SO}$

- $\hat{H}'_{SO} = A\frac{1}{r^3}(\vec{L}\cdot\vec{S}) = A\frac{1}{r^3}\left[\frac{1}{2}(\hat{J}^2 - \hat{L}^2 - \hat{S}^2)\right]$ is diagonal in the each degenerate subspace of $\hat{H}^0$ in the coupled representation.
  - The basis states in the coupled representation are eigenstates of $\hat{J}^2$, $\hat{L}^2$ and $\hat{S}^2$ and hence $\hat{H}'_{SO}$ is diagonal in each degenerate subspace of $\hat{H}^0$ if the coupled representation is chosen as the angular basis.
- The coupled representation forms a "good" angular basis for finding the corrections to the energies of the hydrogen atom due to $\hat{H}'_{SO}$.

Hamiltonian	Uncoupled Representation (for a fixed n)	Is the Uncoupled Representation a "Good" Basis?	Coupled Representation (for a fixed n)	Is the Coupled Representation a "Good" Basis?	Is Any Arbitrary Complete Orthonormal Basis Constructed with Linear Combinations of a Complete Set of States with the Same n and l in the Coupled or Uncoupled Representation a "Good" Basis?	Energy
$\hat{H}^0$	Diagonal	—	Diagonal	—	—	$E_n = -\frac{13.6\text{eV}}{n^2}$
$\hat{H}'_r$	Diagonal	Yes	Diagonal	Yes	Yes	$E'_r = -\frac{E_n^2}{2mc^2}\left[\frac{4n}{l+1/2} - 3\right]$
$\hat{H}'_{SO}$	Not Diagonal	No	Diagonal	Yes	No	$E'_{SO} = \frac{E_n^2}{mc^2}\left[\frac{n(j(j+1)-l(l+1-3/4))}{l(l+1)(l+1/2)}\right]$

Fine Structure Correction

6.6 Finding a "Good" Angular Basis for the Fine Structure Correction Term to the Energy Spectrum of the Hydrogen Atom in Perturbation Theory

Consider the following conversation regarding finding a "good" angular basis for fine structure term $\hat{H}'_{fs} = \hat{H}'_r + \hat{H}'_{SO}$ as a perturbation on the unperturbed Hamiltonian $\hat{H}^0$.
Student 1: The fine structure term $\hat{H}'_{fs}$ is made up of two mechanisms: $\hat{H}'_{SO}$ and $\hat{H}'_r$. The "good" angular basis is one in which both $\hat{H}'_{SO}$ and $\hat{H}'_r$ are diagonal in each degenerate subspace of $\hat{H}^0$.
Student 2: I agree. In the preceding table, the coupled representation is a "good" angular basis for both the relativistic correction term $\hat{H}'_r$ and the spin-orbit interaction term $\hat{H}'_{SO}$, because $\hat{H}'_r$ and $\hat{H}'_{SO}$ are both diagonal in each degenerate subspace of $\hat{H}^0$ in the coupled representation. Therefore, the coupled representation forms a "good" angular basis for finding the corrections to the energies due to the fine structure term $\hat{H}'_{fs} = \hat{H}'_r + \hat{H}'_{SO}$.

Explain why you agree or disagree with each student.

6.7 First Order Corrections to the Energy Spectrum of the Hydrogen Atom in Perturbation Theory Due to the Fine Structure

Combining the first order corrections to the energies for the hydrogen atom due to the relativistic correction term in equation (8) and spin-orbit interaction term from equation (13) gives the first order correction to the energies due to the fine structure correction term in the hydrogen atom.

$$E'_{fs} = -\frac{E_n^2}{2mc^2}\left[\frac{4n}{(j+1/2)} - 3\right] \tag{14}$$

3. How many distinct energies does the $n = 2$ state split into? Explain. [Hint: How many possible values of j are there for the $n = 2$ subspace?]

**** Check your answer to question 3. ****

3. For $n = 2$, there are two possible values of j, $j = \{\frac{1}{2}, \frac{3}{2}\}$. The energies split into two distinct levels.

l	s	j	E'_{fs}	Number of States
0	$\frac{1}{2}$	$\frac{1}{2}$	$-\frac{5E_2^2}{2mc^2}$	2
1	$\frac{1}{2}$	$\frac{1}{2}$	$-\frac{5E_2^2}{2mc^2}$	2
1	$\frac{1}{2}$	$\frac{3}{2}$	$-\frac{E_2^2}{2mc^2}$	4

If your answers to question 3 do not match with the checkpoint, go back and reconcile any differences.

In one to two sentences, summarize what you have learned about the "good" angular basis states for finding the first order corrections to the energy spectrum of the hydrogen atom due to the fine structure term $\hat{H}'_{fs}$ (pertaining to whether the coupled representation, the uncoupled representation, or any arbitrary complete orthonormal basis found with linear combinations of states with a fixed principal quantum number n in the coupled or uncoupled representation form a "good" angular basis).

Summary: Finding a "GOOD" Angular Basis for the Fine Structure

- For the entire fine structure perturbation $\hat{H}' = \hat{H}'_r + \hat{H}'_{SO}$, the coupled representation forms a "good" angular basis because $\hat{H}'_{fs}$ is diagonal in each degenerate subspace of $\hat{H}^0$ in the coupled representation.

Hamiltonian	Uncoupled Representation (for a fixed n)	Is Uncoupled Representation a "Good" Basis?	Coupled Representation (for a fixed n)	Is Coupled Representation a "Good" Basis?	Is Any Arbitrary Complete Orthonormal Basis Constructed with Linear Combinations of a Complete Set of States with the Same n and l in the Coupled or Uncoupled Representation a "Good" Basis?	Energy
$\hat{H}^0$	Diagonal	—	Diagonal	—	—	$E_n = -\frac{13.6\text{eV}}{n^2}$
$\hat{H}'_r$	Diagonal	Yes	Diagonal	Yes	Yes	$E'_r = -\frac{E_n^2}{2mc^2}\left[\frac{4n}{l+1/2} - 3\right]$
$\hat{H}'_{SO}$	Not Diagonal	No	Diagonal	Yes	No	$E'_{SO} = \frac{E_n^2}{mc^2}\left[\frac{n(j(j+1)-l(l+1-3/4))}{l(l+1)(l+1/2)}\right]$
$\hat{H}'_{fs} = \hat{H}'_r + \hat{H}'_{SO}$	Not Diagonal	No	Diagonal	Yes	No	$E'_{fs} = -\frac{E_n^2}{2mc^2}\left[\frac{4n}{(j+1/2)} - 3\right]$

II. Determining a "GOOD" Angular Basis and Corrections to the Energies for ONLY the Zeeman Perturbation $\hat{H}'_Z$.

Zeeman Effect

6.8 Finding a "GOOD" Angular Basis for the Zeeman term as a Perturbation for the Hydrogen Atom

Note: Treating the Zeeman term as the only perturbation on the unperturbed Hamiltonian is a hypothetical case, one should always consider both the Zeeman term and the fine structure term when an external magnetic field is applied to the hydrogen atom. This hypothetical case is presented here to help when later we consider both the fine structure term and the Zeeman term as perturbations for the hydrogen atom.

- A perturbation $\hat{H}'_Z$ acts on a hydrogen atom with the unperturbed Hamiltonian $\hat{H}^0 = -\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{4\pi\epsilon_0}\frac{1}{r}$. The Zeeman perturbation term in the Hamiltonian is

$$\hat{H}'_Z = \frac{e}{2m}(\vec{L} + 2\vec{S}) \cdot \vec{B}_{ext} = \frac{\mu_B B_{ext}}{\hbar}(\hat{L}_z + 2\hat{S}_z) \tag{15}$$

  in which $\vec{B}_{ext} = B_{ext}\hat{z}$.

4. In each degenerate subspace of $\hat{H}^0$, the off-diagonal matrix elements of $\hat{H}'_Z$ will be zero in a "good" basis. Is a "good" angular basis for finding the corrections to the energies the coupled representation, the uncoupled representation, or any arbitrary complete orthonormal basis found with linear combinations of the coupled or uncoupled states with the same principal quantum number n? Explain.

Consider the following conversation regarding choosing a "good" basis when the perturbation is $\hat{H}'_Z = \frac{\mu_B B_{ext}}{\hbar}(\hat{L}_z + 2\hat{S}_z)$.
Student 1: When a perturbation $\hat{H}'_Z = \mu_B B_{ext}(\hat{L}_z + 2\hat{S}_z)$ acts on a hydrogen atom, the uncoupled representation is a "good" angular basis for finding the first order corrections to the energies.
Student 2: I disagree. We can use either the coupled or the uncoupled representation to find the first order corrections to the energies. Since $\hat{J}_Z = \hat{L}_z + \hat{S}_z$, the perturbation $\hat{H}'_Z = \mu_B B_{ext}(\hat{L}_z + 2\hat{S}_z)$ is not much different from $\hat{J}_Z$ and so the coupled representation is also a "good" angular basis.
Student 3: I only agree with Student 1. $\hat{J}_Z$ is diagonal in both the coupled and the uncoupled representation. However, $\hat{H}' = \mu_B B_{ext}(\hat{L}_z + 2\hat{S}_z) = \mu_B B_{ex}(\hat{J}_z + \hat{S}_z)$ is not proportional to $\hat{J}_z$. Therefore, $\hat{H}'_Z = \mu_B B_{ext}(\hat{L}_z + 2\hat{S}_z)$ is only diagonal in the uncoupled representation in which the basis states are eigenstates of $\hat{L}_z$ and $\hat{S}_z$.

Explain why you agree or disagree with each student.

(If you need further help with why $\hat{L}_z + 2\hat{S}_z$ is diagonal in the uncoupled representation and not the coupled representation, refer to the Part I of this tutorial.)

**** Check your answer to question 4. ****

4. The uncoupled representation forms a "good" basis for finding the corrections to the energies of the hydrogen atom due to only the Zeeman term $\hat{H}'_Z$.

If your answer to question 4 does not match with the checkpoint, go back and reconcile any differences.

6.9 First Order Corrections to the Energy Spectrum of the Hydrogen Atom in Perturbation Theory Due to the Zeeman Term

Student 1 and Student 3 are correct in the preceding conversation in stating that the uncoupled representation will form a "good" angular basis for $\hat{H}'_Z$ on $\hat{H}^0$.

5. What are the first order corrections to the energies due to the Zeeman term $\hat{H}'_Z$ using a "good" basis?

6. How many distinct energies does the $n = 2$ state split into when we take into account $\hat{H}'_Z$ as a perturbation on $\hat{H}^0$? Explain. [Hint: How many possible values of $m_l + 2m_s$ are there for $n = 2$?]

**** Check your answer to questions 5-6. ****

5. The first order corrections to the energies due to only the Zeeman term $\hat{H}'_Z$ using a "good" basis (the uncoupled representation) is given by

$$E'_Z = \mu_B B_{ext}(m_l + 2m_s) \tag{16}$$

6. There are 5 distinct energies. For the $n = 2$ subspace, there are three possible values of m_l $(-1, 0, 1)$ for $l = 1$ and one possible values of m_l (0) for $l = 0$. For each value of l, there are two possible values of m_s $(\frac{1}{2}, -\frac{1}{2})$.

l	m_l	m_s	Energy (E'_Z)
1	-1	$\frac{1}{2}$	0
	-1	$-\frac{1}{2}$	$-2\mu_B B_{ext}$
	0	$-\frac{1}{2}$	$-\mu_B B_{ext}$
	0	$\frac{1}{2}$	$\mu_B B_{ext}$
	1	$-\frac{1}{2}$	0
	1	$\frac{1}{2}$	$2\mu_B B_{ext}$
0	0	$-\frac{1}{2}$	$-\mu_B B_{ext}$
	0	$\frac{1}{2}$	$\mu_B B_{ext}$

If your answers to questions 5 and 6 do not match with the checkpoint, go back and reconcile any differences.

In one to two sentences, summarize what you have learned about the "good" states for finding the first order corrections to the energy spectrum of the hydrogen atom due to only the Zeeman term $\hat{H}'_Z$ (pertaining to whether the coupled representation, the uncoupled representation, or any arbitrary complete orthonormal basis found with linear combinations of states with a fixed principal quantum number n in the coupled or uncoupled representation form a "good" basis).

Summary: Finding a "GOOD" Angular Basis for Various Perturbations on $\hat{H}^0$

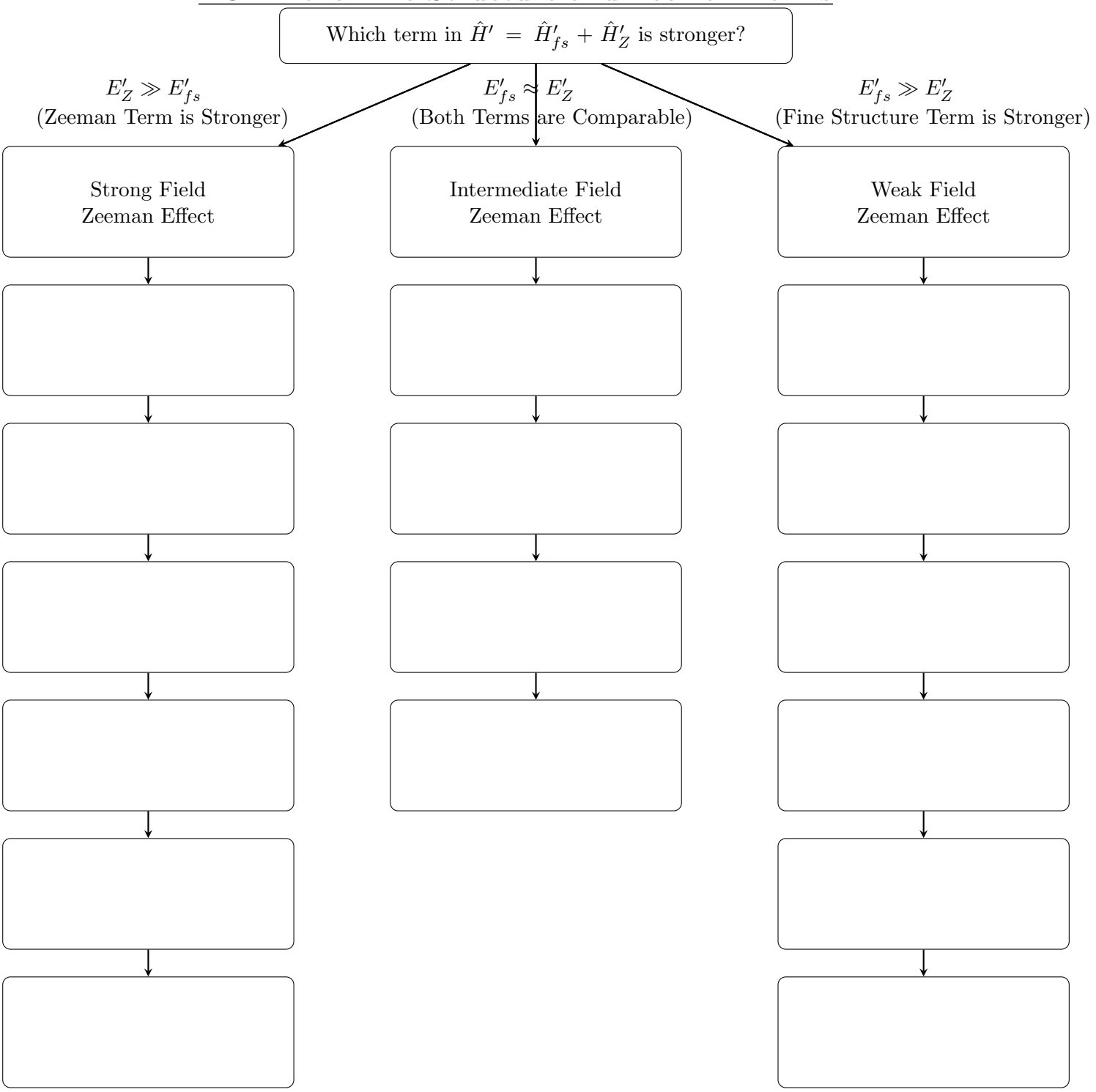
- $\hat{H}'_Z$ is diagonal in each degenerate subspace of $\hat{H}_0$ in the uncoupled representation.
  - The basis states in the uncoupled representation are eigenstates of $\hat{L}_z$ and $\hat{S}_z$
- The uncoupled representation forms a "good" angular basis for finding the corrections to the energies due to the Zeeman pertrubation $\hat{H}'_Z$.

Hamiltonian	Uncoupled Representation (for a fixed n)	Is the Uncoupled Representation a "Good" Basis?	Coupled Representation (for a fixed n)	Is the Coupled Representation a "Good" Basis?	Is Any Arbitrary Complete Orthonormal Basis Constructed with Linear Combination of a Complete Set of States with the Same n and l in the Coupled or Uncoupled Representation a "Good" Basis?	Energy
$\hat{H}^0$	Diagonal	—	Diagonal	—	—	$E_n = -\frac{13.6\text{eV}}{n^2}$
$\hat{H}'_r$	Diagonal	Yes	Diagonal	Yes	Yes	$E'_r = -\frac{E_n^2}{2mc^2}\left[\frac{4n}{l+1/2} - 3\right]$
$\hat{H}'_{SO}$	Not Diagonal	No	Diagonal	Yes	No	$E'_{SO} = \frac{E_n^2}{mc^2}\left[\frac{n(j(j+1)-l(l+1-3/4))}{l(l+1)(l+1/2)}\right]$
$\hat{H}'_{fs} = \hat{H}'_r + \hat{H}'_{SO}$	Not Diagonal	No	Diagonal	Yes	No	$E'_{fs} = -\frac{E_n^2}{2mc^2}\left[\frac{4n}{(j+1/2)} - 3\right]$
$\hat{H}'_Z$	Diagonal	Yes	Not Diagonal	No	No	$E'_Z = \mu B_{ext}(m_l + 2m_s)$

III. Determining a "GOOD" Angular Basis and Corrections to the Energies due to BOTH the Fine Structure and the Zeeman Perturbations $\hat{H}' = \hat{H}'_{fs} + \hat{H}'_Z$.

As we work through the remainder of the tutorial, we will fill in the following flowchart after each section regarding the intermediate, strong, and weak field Zeeman effect.

Determining a "GOOD" Angular Basis and Corrections to the Energies due to BOTH the Fine Structure and Zeeman Terms



CASE 1: Intermediate Field Zeeman Effect ($E'_{fs} \approx E'_Z$), when the fine structure term is comparable to the Zeeman term in $\hat{H}'$)

6.10 Finding a "Good" Angular Basis for the Intermediate Field Zeeman Effect

Consider the following conversation regarding whether the coupled or uncoupled representation forms a "good" angular basis for the intermediate field Zeeman effect (in order to find the first order corrections to the energies).
Student 1: In the intermediate field Zeeman effect, we must treat $\hat{H}'_{fs}$ and $\hat{H}'_Z$ on an equal footing. Does the coupled or uncoupled representation form a "good" angular basis?
Student 2: Since the coupled representation is a "good" angular basis for the fine structure term and the uncoupled representation is a "good" angular basis for the Zeeman term, both the coupled and uncoupled representation form "good" angular bases and are equally appropriate to find the first order corrections to the energies for $\hat{H}' = \hat{H}'_{fs} + \hat{H}'_Z$.
Student 3: I disagree with Student 2. You cannot consider different bases for different parts of $\hat{H}'$. If we choose the coupled representation, $\hat{H}' = \hat{H}'_{fs} + \hat{H}'_Z$ is not diagonal in each degenerate subspace of $\hat{H}^0$ since $\hat{H}'_Z$ is not diagonal in the coupled representation. Similarly, if we choose the uncoupled representation, $\hat{H}' = \hat{H}'_{fs} + \hat{H}'_Z$, is not diagonal in each degenerate subspace of $\hat{H}^0$ since $\hat{H}'_{fs}$ is not diagonal in the uncoupled representation. Neither of these representations forms a "good" basis.

Explain why you agree or disagree with Student 2 or Student 3.

Consider the following conversation regarding whether to choose the coupled representation or uncoupled representation as the angular basis for finding the corrections to the energies in the intermediate field Zeeman effect.
Student 1: In the intermediate field Zeeman effect, neither the coupled nor uncoupled representation forms a "good" angular basis. How do we determine the "good" angular basis?
Student 2: We can express $\hat{H}' = \hat{H}'_{fs} + \hat{H}'_Z$ initially in either the coupled or uncoupled representation, which will not be a "good" angular basis. Then, a "good" angular basis is found by diagonalizing $\hat{H}'$ in each degenerate subspace of $\hat{H}^0$. Thus, the "good" angular basis states will be linear combinations of the originally chosen angular basis states.

Do you agree with Student 2? Explain.

The angular basis states for $n = 2$ are listed below in the coupled representation (left), and each state in the coupled representation is given in terms of a linear combination of states in the uncoupled representation (right) using the Clebsch-Gordon table ($s = 1/2$).

	Coupled Representation $\lvert l,\ j,\ m_j\rangle$	Uncoupled Representation $\lvert l,\ m_l\rangle\lvert s,\ m_s\rangle$
$\lvert\psi_1\rangle$	$\left\lvert 0,\ \frac{1}{2},\ \frac{1}{2}\right\rangle$	$\lvert 0,\ 0\rangle \left\lvert \frac{1}{2},\ \frac{1}{2}\right\rangle$
$\lvert\psi_2\rangle$	$\left\lvert 0,\ \frac{1}{2},\ -\frac{1}{2}\right\rangle$	$\lvert 0,\ 0\rangle \left\lvert \frac{1}{2},\ -\frac{1}{2}\right\rangle$
$\lvert\psi_3\rangle$	$\left\lvert 1,\ \frac{3}{2},\ \frac{3}{2}\right\rangle$	$\lvert 1,\ 1\rangle \left\lvert \frac{1}{2},\ \frac{1}{2}\right\rangle$
$\lvert\psi_4\rangle$	$\left\lvert 1,\ \frac{3}{2},\ -\frac{3}{2}\right\rangle$	$\lvert 1,\ -1\rangle \left\lvert \frac{1}{2},\ -\frac{1}{2}\right\rangle$
$\lvert\psi_5\rangle$	$\left\lvert 1,\ \frac{3}{2},\ \frac{1}{2}\right\rangle$	$\sqrt{\frac{2}{3}}\lvert 1,\ 0\rangle \left\lvert \frac{1}{2},\ \frac{1}{2}\right\rangle + \sqrt{\frac{1}{3}}\lvert 1,\ 1\rangle \left\lvert \frac{1}{2},\ -\frac{1}{2}\right\rangle$
$\lvert\psi_6\rangle$	$\left\lvert 1,\ \frac{1}{2},\ \frac{1}{2}\right\rangle$	$-\sqrt{\frac{1}{3}}\lvert 1,\ 0\rangle \left\lvert \frac{1}{2},\ \frac{1}{2}\right\rangle + \sqrt{\frac{2}{3}}\lvert 1,\ 1\rangle \left\lvert \frac{1}{2},\ -\frac{1}{2}\right\rangle$
$\lvert\psi_7\rangle$	$\left\lvert 1,\ \frac{3}{2},\ -\frac{1}{2}\right\rangle$	$\sqrt{\frac{1}{3}}\lvert 1,\ -1\rangle \left\lvert \frac{1}{2},\ \frac{1}{2}\right\rangle + \sqrt{\frac{2}{3}}\lvert 1,\ 0\rangle \left\lvert \frac{1}{2},\ -\frac{1}{2}\right\rangle$
$\lvert\psi_8\rangle$	$\left\lvert 1,\ \frac{1}{2},\ -\frac{1}{2}\right\rangle$	$-\sqrt{\frac{2}{3}}\lvert 1,\ -1\rangle \left\lvert \frac{1}{2},\ \frac{1}{2}\right\rangle + \sqrt{\frac{1}{3}}\lvert 1\,0\rangle \left\lvert \frac{1}{2},\ -\frac{1}{2}\right\rangle$

Using the table above, the perturbing Hamiltonian $\hat{H}' = \hat{H}'_Z + \hat{H}'_{fs}$ in the coupled representation is given on the next page, in which $\gamma = \left(\frac{\alpha}{8}\right)^2$ 13.6 eV, $\alpha = \frac{e^2}{4\pi\epsilon_0\hbar c}$, $\beta = \mu_B B_{ext}$ and the angular basis states are chosen in the order $|\psi_1\rangle = |0,\ \frac{1}{2},\ \frac{1}{2}\rangle$, $|\psi_2\rangle = |0,\ \frac{1}{2},\ -\frac{1}{2}\rangle$, $|\psi_3\rangle = |1,\ \frac{3}{2},\ \frac{3}{2}\rangle$, $|\psi_4\rangle = |1,\ \frac{3}{2},\ -\frac{3}{2}\rangle$, $|\psi_5\rangle = |1,\ \frac{3}{2},\ \frac{1}{2}\rangle$, $|\psi_6\rangle = |1,\ \frac{1}{2},\ \frac{1}{2}\rangle$, $|\psi_7\rangle = |1,\ \frac{3}{2},\ -\frac{1}{2}\rangle$, and $|\psi_8\rangle = |1,\ \frac{1}{2},\ -\frac{1}{2}\rangle$:

$$\hat{H}' = -\begin{bmatrix} 5\gamma-\beta & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 5\gamma+\beta & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & \gamma-2\beta & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & \gamma+2\beta & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & \gamma-\frac{2}{3}\beta & \frac{\sqrt{2}}{3}\beta & 0 & 0 \\ 0 & 0 & 0 & 0 & \frac{\sqrt{2}}{3}\beta & 5\gamma-\frac{1}{3}\beta & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & \gamma+\frac{2}{3}\beta & \frac{\sqrt{2}}{3}\beta \\ 0 & 0 & 0 & 0 & 0 & 0 & \frac{\sqrt{2}}{3}\beta & 5\gamma+\frac{1}{3}\beta \end{bmatrix}$$

Consider the following conversation regarding diagonalizing the $\hat{H}' = \hat{H}'_{fs} + \hat{H}'_Z$ matrix in the $n = 2$ degenerate subspace of $\hat{H}^0$ for the intermediate field Zeeman effect.

Student 1: In the case of $n = 2$, $\hat{H}^0$ possesses an eight-fold degeneracy, which means that in order to find a "good" angular basis for the correction to the $n = 2$ energy spectrum, we must diagonalize the entire 8 x 8 $\hat{H}'$ matrix in the $n = 2$ degenerate subspace of $\hat{H}^0$.

Student 2: While it is true that we must diagonalize the $\hat{H}'$ matrix in the degenerate subspace of $\hat{H}^0$, we are fortunate that the symmetry of the hydrogen atom yields many zero off-diagonal matrix elements. Therefore, $\hat{H}'$ will be block diagonal in the degenerate subspaces of $\hat{H}^0$.

Student 3: I agree with Student 2. We must make an effort to diagonalize $\hat{H}'$ only in those block diagonal subspaces with smaller dimensions than the original 8×8 $\hat{H}'$ matrix in order to diagonalize the entire $\hat{H}'$ matrix in the degenerate subspace of $\hat{H}^0$ to obtain the "good" angular basis set.

Student 4: I agree with Student 1, Student 2, and Student 3. When I calculate the $\hat{H}'$ matrix for $n = 2$ in the coupled representation and the angular basis states are chosen in the order $|\psi_1\rangle = |0,\ \frac{1}{2},\ \frac{1}{2}\rangle$, $|\psi_2\rangle = |0,\ \frac{1}{2},\ -\frac{1}{2}\rangle$, $|\psi_3\rangle = |1,\ \frac{3}{2},\ \frac{3}{2}\rangle$, $|\psi_4\rangle = |1,\ \frac{3}{2},\ -\frac{3}{2}\rangle$, $|\psi_5\rangle = |1,\ \frac{3}{2},\ \frac{1}{2}\rangle$, $|\psi_6\rangle = |1,\ \frac{1}{2},\ \frac{1}{2}\rangle$, $|\psi_7\rangle = |1,\ \frac{3}{2},\ -\frac{1}{2}\rangle$, and $|\psi_8\rangle = |1,\ \frac{1}{2},\ -\frac{1}{2}\rangle$, I get the block diagonal matrix $\hat{H}'$ below

$$\hat{H}' = -\begin{bmatrix} 5\gamma-\beta & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 5\gamma+\beta & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & \gamma-2\beta & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & \gamma+2\beta & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & \gamma-\frac{2}{3}\beta & \frac{\sqrt{2}}{3}\beta & 0 & 0 \\ 0 & 0 & 0 & 0 & \frac{\sqrt{2}}{3}\beta & 5\gamma-\frac{1}{3}\beta & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & \gamma+\frac{2}{3}\beta & \frac{\sqrt{2}}{3}\beta \\ 0 & 0 & 0 & 0 & 0 & 0 & \frac{\sqrt{2}}{3}\beta & 5\gamma+\frac{1}{3}\beta \end{bmatrix}$$

We will only need to diagonalize the 2×2 matrices $-\begin{bmatrix} \gamma-\frac{2}{3}\beta & \frac{\sqrt{2}}{3}\beta \\ \frac{\sqrt{2}}{3}\beta & 5\gamma-\frac{1}{3}\beta \end{bmatrix}$ and $-\begin{bmatrix} \gamma+\frac{2}{3}\beta & \frac{\sqrt{2}}{3}\beta \\ \frac{\sqrt{2}}{3}\beta & 5\gamma+\frac{1}{3}\beta \end{bmatrix}$ to obtain the "good" angular basis.

Explain why you agree or disagree with each student.

6.11 First Order Corrections to the Energy Spectrum of the Hydrogen Atom in Perturbation Theory for the Intermediate Field Zeeman Effect

Consider the following conversation regarding whether choosing the coupled representation or the uncoupled representation as the initial angular basis and then carrying out a change of basis by diagonalizing $\hat{H}'$ in the degenerate subspace of $\hat{H}^0$ affects the corrections to the energies in the intermediate field Zeeman effect.
Student 1: When calculating the first order corrections to the energies in the intermediate field Zeeman effect, we can choose either the coupled or the uncoupled representation as the initial angular basis even if we know it is not a "good" angular basis. Then, a "good" angular basis will be found by diagonalizing $\hat{H}'$ in each degenerate subspace of $\hat{H}^0$. After diagonalizing $\hat{H}'$, the new basis is "good" and the first order corrections to the energies are the diagonal matrix elements.
Student 2: I disagree. Since the diagonal matrix elements of $\hat{H}'$ will depend on the choice of initial basis, a different choice of the initial basis in which we diagonalize $\hat{H}'$ in the degenerate subspace of $\hat{H}^0$ will change the first order corrections to the energies.
Student 3: I disagree with Student 2. After diagonalizing $\hat{H}'$ in each degenerate subspace of $\hat{H}^0$, a "good" basis is obtained and the first order correction to the energy will be the same regardless of which basis, e.g., the coupled or uncoupled representation, you had initially chosen. In a "good" basis, you will end up with the same diagonal matrix elements of $\hat{H}'$ which are the first order corrections to the energies.

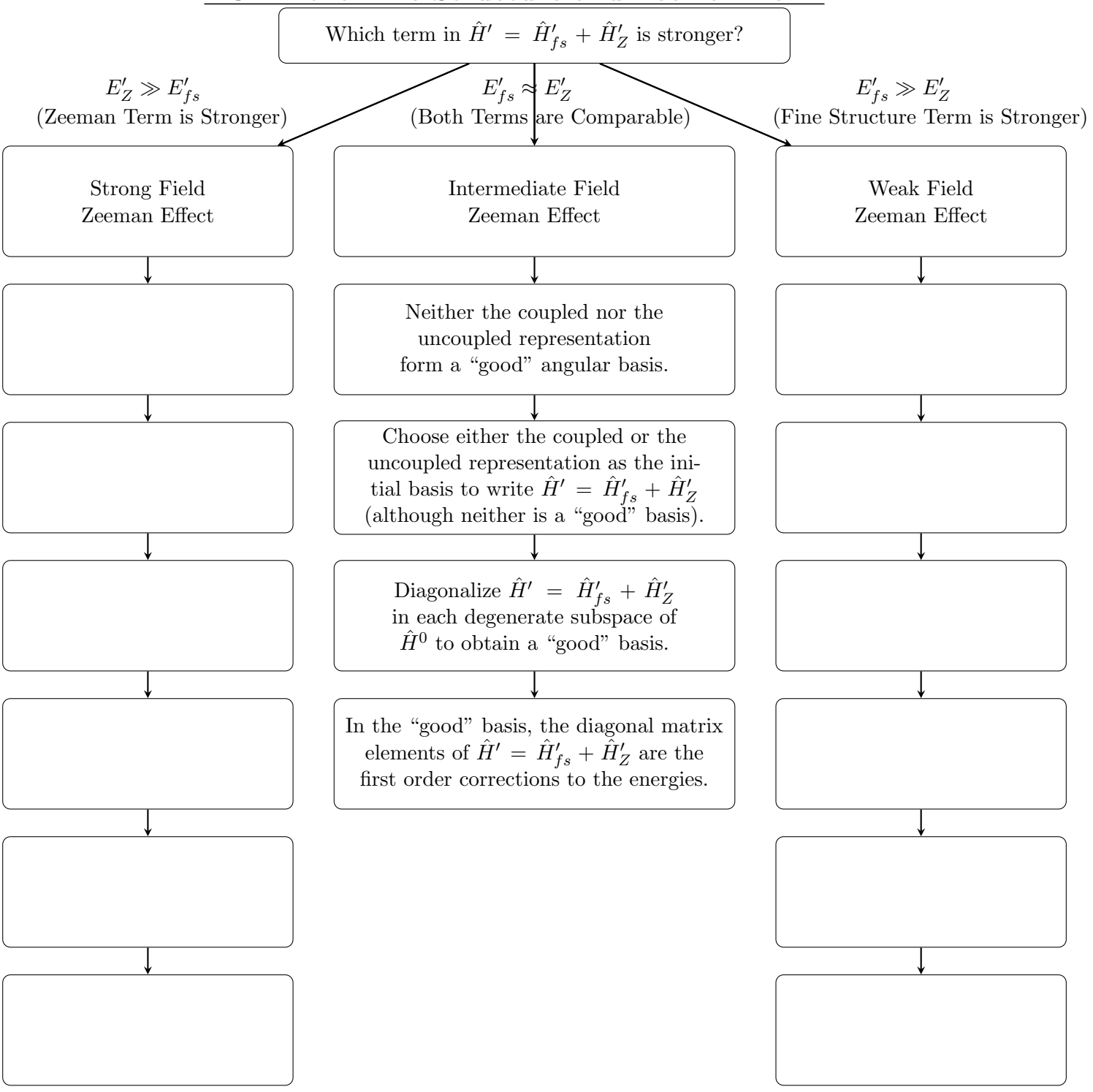
Explain why you agree or disagree with each student.

In one or two sentences, summarize what you have learned about the "good" angular basis states for finding the first order corrections to the energy spectrum of the hydrogen atom due to the intermediate field Zeeman effect (pertaining to whether the coupled representation, the uncoupled representation, or any arbitrary complete orthonormal basis constructed with linear combinations of a complete set of states with a fixed principal quantum number n in the coupled or uncoupled representation form a "good" angular basis).

Shortly, we shall calculate the first order corrections to the energies due to the intermediate field Zeeman effect. But before we do so, let's first consider the limiting cases when one perturbation is stronger than the other.

Review the following flowchart concerning a "good" angular basis and corrections to the energies for the intermediate field Zeeman effect. Using the intermediate field Zeeman effect as a guide, attempt to fill in the steps required to determine a "good" angular basis and corrections to the energies due to both the fine structure ($\hat{H}'_{fs}$) and Zeeman ($\hat{H}'_Z$) terms for the strong field Zeeman effect ($E'_Z \gg E'_{fs}$) and the weak field Zeeman effect ($E'_{fs} \gg E'_Z$). You can add or remove boxes in the flowchart if necessary.

Determining a "GOOD" Angular Basis and Corrections to the Energies due to BOTH the Fine Structure and Zeeman Term



Summary: Finding a "GOOD" Angular Basis for the Intermediate Field Zeeman Effect $\hat{H}' = \hat{H}'_Z + \hat{H}'_{fs}$

- Neither the coupled nor the uncoupled representation forms a "good" angular basis when $E'_Z \approx E'_{fs}$.
- To find a "good" angular basis for the intermediate field Zeeman effect $E'_Z \approx E'_{fs}$:
  - First choose either the coupled or the uncoupled representation as the basis.
  - Diagonalize $\hat{H}' = \hat{H}'_Z + \hat{H}'_{fs}$ in each degenerate subspace of $\hat{H}^0$.
  - The "good" basis will be a special linear combinations of the originally chosen basis set.

6.12 Limiting Cases

Consider the following conversation regarding finding a "good" basis when treating the perturbation in two steps.

Student 1: If we have a perturbation that has two terms in which one perturbation is stronger than the other, we can first take into account the correction due to the stronger perturbation and then take into account the weaker perturbation as a second perturbation.

Student 2: I agree. In the first step, we must find a "good" basis for $\hat{H}^0$ and $\hat{H}'_{strong}$, so $\hat{H}'_{strong}$ must be diagonal in each degenerate subspace of $\hat{H}^0$. Then in the second step, treat $\hat{H}^0_{strong} = \hat{H}^0 + \hat{H}'_{strong}$ as the unperturbed Hamiltonian and $\hat{H}'_{weak}$ as perturbation on $\hat{H}^0_{strong} = \hat{H}^0 + \hat{H}'_{strong}$. A "good" basis for step 2 is one in which $\hat{H}'_{weak}$ is diagonal in each degenerate subspace of $\hat{H}^0_{strong} = \hat{H}^0 + \hat{H}'_{strong}$.

Student 3: I disagree with Student 2. You cannot find one "good" basis for step 1 and a different "good" basis for step 2.

Student 4: I agree with Student 1 and Student 2. It is approprate to use a two step perturbation theory when one part of the perturbation is stronger than another if the error due to this two step process is negligible. If the basis after step 1 is not a "good" basis for step 2, we would need to diagonalize $\hat{H}'_{weak}$ in each degenerate subspace of $\hat{H}^0_{strong} = \hat{H}^0 + \hat{H}'_{strong}$ to find a "good" basis in step 2.

Explain why you agree or disagree with each student.

- Summary of Two-Step Approximation
  - **STEP 1:** First consider only the stronger perturbation $\hat{H}'_{strong}$ as a perturbation on $\hat{H}^0$.
    - Choose a basis in which $\hat{H}^0$ is diagonal and $\hat{H}'_{strong}$ is diagonal in each degenerate subspace of $\hat{H}^0$.
    - Determine the first order corrections to the energies E'_{strong} due to the stronger perturbation $\hat{H}'_{strong}$.
  - **STEP 2:** Consider the weaker perturbation $\hat{H}'_{weak}$ as a perturbation on the new unperturbed Hamiltonian $\hat{H}^0_{strong} = \hat{H}^0 + \hat{H}'_{strong}$.
    - Treat as the new unperturbed Hamiltonian $\hat{H}^0_{strong} = \hat{H}^0 + \hat{H}'_{strong}$.
    - Treat $E^0_{strong} = E^0 + E'_{strong}$ as the new unperturbed energies.
    - Determine the degeneracy of $\hat{H}^0_{strong} = \hat{H}^0 + \hat{H}'_{strong}$ (i.e., how many distinct states have the same energy $E^0_{strong,i}$).
    - Determine if $\hat{H}'_{weak}$ is diagonal in each degenerate subspace of $\hat{H}^0_{strong} = \hat{H}^0 + \hat{H}'_{strong}$.
      - If $\hat{H}'_{weak}$ is already diagonal in each degenerate subspace of $\hat{H}^0_{strong} = \hat{H}^0 + \hat{H}'_{strong}$ then the basis is "good" and the diagonal elements of $\hat{H}'_{weak}$ will give the corrections E'_{weak}.
      - If $\hat{H}'_{weak}$ is not diagonal in each degenerate subspace of $\hat{H}^0_{strong} = \hat{H}^0 + \hat{H}'_{strong}$, diagonalize $\hat{H}'_{weak}$ in each degenerate subspace of $\hat{H}^0_{strong}$ to find a "good" basis.

Consider the following conversation regarding approximating the corrections to the energy when one perturbation is stronger than the other.

Student 1: When the hydrogen atom is placed in an external magnetic field, we must consider both the Zeeman term and the fine structure term in the Hamiltonian as perturbations. Therefore, neither the coupled nor the uncoupled representation form a "good" basis. We must diagonalize the entire $\hat{H}' = \hat{H}'_Z + \hat{H}'_{fs}$ matrix in the degenerate subspace of $\hat{H}^0$.

Student 2: That is true. However, if one term is much stronger than the other, we can approximate the first order corrections to the energy using perturbation theory in two steps. In the first step, consider only the stronger perturbation. Then, as the second step, consider the weaker perturbation. This two-step approximation may simplify the process for finding a "good" basis and provide an alternative to diagonalizing the entire $\hat{H}' = \hat{H}'_Z + \hat{H}'_{fs}$ matrix in each degenerate subspace of $\hat{H}^0$.

Student 3: I agree with Student 2. We will find that in the limiting case, the first order corrections to the energies obtained using this two-step approximation match with the first order corrections to the energies obtained by diagonalizing the entire $\hat{H}' = \hat{H}'_Z + \hat{H}'_{fs}$ matrix in each degenerate subspace of $\hat{H}^0$ as in the intermediate field Zeeman effect when we take the appropriate limit.

Explain why you agree or disagree with each student.

All the students are correct in the preceding conversation. However, we will focus on the limiting cases and use the method described by Student 2 and Student 3.

- When $E'_Z \gg E'_{fs}$ or $E'_{fs} \gg E'_Z$, we can use a two step approximation to find the first order corrections to the energies of the hydrogen atom.
- Two-Step Approximation for the Strong and Weak Field Zeeman Effect
  - **CASE 2: Strong Field Zeeman Effect ($E'_Z \gg E'_{fs}$)**
    - The Zeeman term dominates.
      - **STEP 1:** Treat only $\hat{H}'_Z$ as the perturbation on $\hat{H}^0$.
      - **STEP 2:** Now, treat $\hat{H}'_{fs}$ as the perturbation on the new unperturbed Hamiltonian $\hat{H}^0_Z = \hat{H}^0 + \hat{H}'_Z$ after the first step.
  - **CASE 3: Weak Field Zeeman Effect ($E'_{fs} \gg E'_Z$)**
    - The fine structure term dominates.
      - **STEP 1:** Treat only $\hat{H}'_{fs}$ as the perturbation on $\hat{H}^0$.
      - **STEP 2:** Now, treat $\hat{H}'_Z$ as the perturbation on the new unperturbed Hamiltonian $\hat{H}^0_{fs} = \hat{H}^0 + \hat{H}'_{fs}$ after the first step.

CASE 2: Strong Field Zeeman Effect: Perturbation Theory in Two Steps to Find the Corrections to Energy Spectrum

6.12.1 Finding a "GOOD" Basis for the Strong Field Zeeman Effect in the Hydrogen Atom

STEP 1:
For the case $E'_Z \gg E'_{fs}$, in step 1, we treat only $\hat{H}'_Z$ as the perturbation on $\hat{H}^0$.

7. For the case $E'_Z \gg E'_{fs}$, what is a "good" angular basis for step 1 when we only consider $\hat{H}'_Z$ as perturbation? Explain.

8. Write an expression for the first order corrections to the energies due to only the stronger perturbation $\hat{H}'_Z$ acting on the unperturbed Hamiltonian $\hat{H}^0$ (once you have found a "good" basis). Here the first order corrections are the exact results for the energies for the Hamiltonian $\hat{H} = \hat{H}^0 + \hat{H}'_Z$ after STEP 1 since $\hat{H}^0$ and $\hat{H}'_Z$ commute (so $\hat{H}^0$ and $\hat{H}'_Z$ can be diagonalized simultaneously in a "good" basis).

STEP 2:
In the strong field when $E'_Z \gg E'_{fs}$, in step 2, the unperturbed Hamiltonian includes the Zeeman term and becomes

$$\hat{H}^0_Z = \hat{H}^0 + \hat{H}'_Z = -\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{4\pi\epsilon_0 r} + \frac{e}{2m}B_{ext}(\hat{L}_z + 2\hat{S}_z). \tag{17}$$

9. Is the $\hat{H}^0_Z$ matrix a diagonal matrix if the coupled representation or the uncoupled representation is chosen as the basis? Explain your reasoning. Your answer should be consistent with your response to question 7 above.

Now for the $n = 2$ subspace, take a look at the $\hat{H}^0_Z = \hat{H}^0 + \hat{H}'_Z$ and $\hat{H}'_{fs}$ matrices given below in which $E_2 = -\frac{13.6\text{eV}}{4}$ and the basis vectors are chosen in the **uncoupled representation** ($|l,\ m_l,\ m_s\rangle$) in the order $|\psi_1\rangle = |0,\ 0,\ \frac{1}{2}\rangle$, $\psi_2\rangle = |1,\ 0,\ -\frac{1}{2}\rangle$, $|\psi_3\rangle = |1,\ 1,\ \frac{1}{2}\rangle$, $|\psi_4\rangle = |1,\ 1,\ -\frac{1}{2}\rangle$, $|\psi_5\rangle = |1,\ 0,\ \frac{1}{2}\rangle$, $|\psi_6\rangle = |1,\ 0,\ -\frac{1}{2}\rangle$, $|\psi_7\rangle = |1,\ -1,\ \frac{1}{2}\rangle$, and $|\psi_8\rangle = |1,\ -1,\ -\frac{1}{2}\rangle$. Then answer questions 10-13 for the Strong field Zeeman effect.

$$\hat{H}^0_Z = \hat{H}^0 + \hat{H}'_Z = -\frac{13.6\text{eV}}{4}\begin{bmatrix} 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \end{bmatrix} + \mu_B B_{ext}\begin{bmatrix} 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 2 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & -2 \end{bmatrix}$$

$$\hat{H}_Z^0 = \begin{bmatrix} E_2+\mu_B B_{ext} & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & E_2-\mu_B B_{ext} & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & E_2+2\mu_B B_{ext} & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & E_2 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & E_2+\mu_B B_{ext} & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & E_2-\mu_B B_{ext} & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & E_2 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & E_2-2\mu_B B_{ext} \end{bmatrix} \tag{18}$$

$$\hat{H}'_{fs} = \hat{H}'_r + \hat{H}'_{SO} = \hat{H}'_{fs} = \frac{(-13.6\text{ eV})\alpha^2}{192} \begin{bmatrix} 15 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 15 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 3 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 11 & 4\sqrt{2} & 0 & 0 & 0 \\ 0 & 0 & 0 & 4\sqrt{2} & 7 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 7 & 4\sqrt{2} & 0 \\ 0 & 0 & 0 & 0 & 0 & 4\sqrt{2} & 11 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 3 \end{bmatrix} \tag{19}$$

10. Determine the degeneracy in the energy eigenvalues of the "new" unperturbed Hamiltonian $\hat{H}_Z^0 = \hat{H}^0 + \hat{H}'_Z$ after accounting for the stronger perturbation. Then circle the corresponding degenerate subspaces of $\hat{H}_Z^0 = \hat{H}^0 + \hat{H}'_Z$ (for the $n = 2$ subspace) in the preceding matrix representation in equation (18).

11. Identify the matrix elements of $\hat{H}'_{fs}$ in equation (19) that correspond to each degenerate subspace of $\hat{H}_Z^0 = \hat{H}^0 + \hat{H}'_Z$ in equation (18) and determine whether $\hat{H}'_{fs}$ is diagonal in each of these subspaces of $\hat{H}_Z^0$.

12. Determine whether the uncoupled representation chosen as the basis in question 9 is a "good" basis for the unperturbed Hamiltonian $\hat{H}_Z^0 = \hat{H}^0 + \hat{H}'_Z$ and the perturbation $\hat{H}'_{fs}$. Explain how you made the determination.

**** Check your answers to questions 7-10. ****

7. The uncoupled representation forms a "good" basis when only the Zeeman term $\hat{H}'_Z$ is the perturbation on the unperturbed Hamiltonian $\hat{H}^0$.
8. As we determined in equation (16), the first order corrections to the energies due to the Zeeman term $\hat{H}'_Z$ in the uncoupled representation are $E'_Z = \mu_B B_{ext}(m_l + 2m_s)$.
9. $\hat{H}^0_Z = \hat{H}^0 + \hat{H}'_Z$ is diagonal if the uncoupled representation is chosen as the basis.
10. $\hat{H}^0_Z = \hat{H}^0 + \hat{H}'_Z$ possesses three two-fold degeneracies (see equation 18) in the $n = 2$ subspace of $\hat{H}^0$. There are two distinct states that share the new unperturbed energies $E_2 + \mu B_{ext}$, $E_2 - \mu B_{ext}$, and E_2.
11. The perturbation $\hat{H}'_{fs}$ is diagonal in each degenerate subspace of $\hat{H}^0_Z = \hat{H}^0 + \hat{H}'_Z$ treated as the unperturbed Hamiltonian in step 2 of perturbation theory.
12. Yes. The uncoupled representation is a "good" angular basis in this case since $\hat{H}^0_Z = \hat{H}^0 + \hat{H}'_Z$ is diagonal and $\hat{H}'_{fs}$ is diagonal in each degenerate subspace of $\hat{H}^0_Z = \hat{H}^0 + \hat{H}'_Z$.

If your answers to questions 7-12 do not match with the checkpoint answers, go back and reconcile any differences.

For the following conversation, consider the $n = 2$ subspace for which the unperturbed Hamiltonian for the strong field Zeeman effect is $\hat{H}^0_Z = \hat{H}^0 + \hat{H}'_Z$ after the first step for the strong field Zeeman effect ($E'_Z \gg E'_{fs}$).
Student 1: In the limit $E'_Z \gg E'_{fs}$, we can only take the Zeeman term $\hat{H}'_Z$ as the perturbation first when we are using the two-step approximation. Then, after the first step, consider the unperturbed Hamiltonian as $\hat{H}^0_Z = \hat{H}^0 + \hat{H}'_Z$ with unperturbed energies $E^0_n = E_n + \mu B_{ext}(m_l + 2m_s)$, and consider the degeneracy left in E^0_n to determine the degenerate subspaces of $\hat{H}^0_Z$. In the second step, treat the fine structure part $\hat{H}'_{fs}$ as the perturbation on $\hat{H}^0_Z = \hat{H}^0 + \hat{H}'_Z$.
Student 2: What is the degeneracy left in the hydrogen atom energy spectrum when it is placed in a strong external magnetic field after accounting for only the Zeeman term $\hat{H}'_Z$ as the perturbation in the first step?
Student 3: In the $n = 2$ subspace, the $\hat{H}^0_Z = \hat{H}^0 + \hat{H}'_Z$ matrix is the following if the basis states are chosen in the uncoupled representation ($|l,\ m_l,\ m_s\rangle$) in the order $|\psi_1\rangle = |0,\ 0,\ \frac{1}{2}\rangle$, $|\psi_2\rangle = |0,\ 0,\ -\frac{1}{2}\rangle$,$|\psi_3\rangle = |1,\ 1,\ \frac{1}{2}\rangle$, $|\psi_4\rangle = |1,\ 1,\ -\frac{1}{2}\rangle$, $|\psi_5\rangle = |1,\ 0,\ \frac{1}{2}\rangle$, $|\psi_6\rangle = |1,\ 0,\ -\frac{1}{2}\rangle$, $|\psi_7\rangle = |1,\ -1,\ \frac{1}{2}\rangle$, and $|\psi_8\rangle = |1,\ -1,\ -\frac{1}{2}\rangle$

$$\hat{H}^0_Z = \begin{bmatrix} \boxed{E_2 + \mu_B B_{ext}} & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & \underline{E_2 - \mu_B B_{ext}} & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & E_2 + 2\mu_B B_{ext} & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & \textcircled{E_2} & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & \boxed{E_2 + \mu_B B_{ext}} & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & \underline{E_2 - \mu_B B_{ext}} & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & \textcircled{E_2} & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & E_2 - 2\mu_B B_{ext} \end{bmatrix}.$$

$\hat{H}^0_Z = \hat{H}^0 + \hat{H}'_Z$ has three separate two-fold degeneracies for the energies $E_2 + \mu_B B_{ext}, E_2 - \mu_B B_{ext}$, and E_2 as indicated by the boxed, underlined, and circled matrix elements of $\hat{H}^0_Z$ above.
Student 4: I agree with both Student 1 and Student 3. By considering the stronger perturbation $\hat{H}'_Z$ first, some of the degeneracies are broken and the eight-fold degeneracy in the energy spectrum of $\hat{H}^0$ has become three separate two-fold degeneracies plus two nondegenerate levels in the energy spectrum of $\hat{H}^0_Z = \hat{H}^0 + \hat{H}'_Z$.

Explain why you agree or disagree with each student.

Consider the following conversation regarding the case $E'_Z \gg E'_{fs}$ and treating the perturbation in two steps with the stronger Zeeman term considered as part of the unperturbed Hamiltonian $\hat{H}^0_Z = \hat{H}^0 + \hat{H}'_Z$ to find the corrections due to the weaker perturbation $\hat{H}'_{fs}$.

Student 1: Even in a two step process, how can we find a "good" basis easily when both the fine structure term $\hat{H}'_{fs}$ and the Zeeman term $\hat{H}'_Z$ are present? The "good" basis is one in which there are no off-diagonal matrix elements of $\hat{H}' = \hat{H}'_Z + \hat{H}'_{fs}$ in the degenerate subspace of $\hat{H}^0$. Since $\hat{H}'_{fs}$ is diagonal in the coupled representation and $\hat{H}'_Z$ is diagonal in the uncoupled representation, neither the coupled nor the uncoupled representation could possibly form a "good" basis when we have $\hat{H}' = \hat{H}'_Z + \hat{H}'_{fs}$.

Student 2: I agree. In step 1, when we only consider $\hat{H}'_Z$ as the perturbation on $\hat{H}^0$, we choose the uncoupled representation as the "good" basis. Once the uncoupled representation is chosen as the "good" basis, we are guaranteed to have off-diagonal matrix elements in the weaker fine structure perturbation matrix $\hat{H}'_{fs}$. Thus, the "good" basis for step 1 cannot be a "good" basis for step 2.

Student 3: Actually, once we treat the stronger Zeeman perturbation $\hat{H}'_Z$ in the first step, we lift some of the degeneracy in the energy spectrum of $\hat{H}^0$. There is still degeneracy in the energy spectrum $E^0_n = E_n + \mu_B B_{ext}(m_l + 2m_s)$ after the first step, but now the degeneracy is present in smaller subspaces of $\hat{H}^0$. For example, for the $n = 2$ subspace in step 2, $\hat{H}^0_Z = \hat{H}^0 + \hat{H}'_Z$ in the uncoupled representation is

$$\hat{H}^0_Z = \begin{bmatrix} \boxed{E_2 + \mu_B B_{ext}} & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & \underline{E_2 - \mu_B B_{ext}} & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & E_2 + 2\mu_B B_{ext} & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & \textcircled{E_2} & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & \boxed{E_2 + \mu_B B_{ext}} & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & \underline{E_2 - \mu_B B_{ext}} & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & \textcircled{E_2} & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & E_2 - 2\mu_B B_{ext} \end{bmatrix}.$$

In the uncoupled representation, $\hat{H}'_{fs}$ is not diagonal in the entire $n = 2$ subspace, but it is diagonal in each degenerate subspace of $\hat{H}^0_Z = \hat{H}^0 + \hat{H}'_Z$. In the $\hat{H}'_{fs}$ matrix below, the elements of the degenerate subspace of $\hat{H}^0_Z$ corresponding to the degenerate energy $E_2 + \mu_B B_{ext}$ are boxed. We see that $\hat{H}'_{fs}$ is diagonal in the 2×2 subspace corresponding to the degenerate energy $E_2 + \mu_B B_{ext}$.

$$\hat{H}'_{fs} = \frac{(-13.6 \text{ eV})\alpha^2}{192} \begin{bmatrix} \boxed{15} & 0 & 0 & 0 & \boxed{0} & 0 & 0 & 0 \\ 0 & 15 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 3 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 11 & 4\sqrt{2} & 0 & 0 & 0 \\ \boxed{0} & 0 & 0 & 4\sqrt{2} & \boxed{7} & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 7 & 4\sqrt{2} & 0 \\ 0 & 0 & 0 & 0 & 0 & 4\sqrt{2} & 11 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 3 \end{bmatrix}.$$

Similarly, $\hat{H}'_{fs}$ is diagonal in the degenerate subspace of $\hat{H}^0_Z$ for the degenerate energies E_2 and $E_2 - \mu_B B_{ext}$. Therefore, the uncoupled representation does form a "good" basis in this two step process.

Explain why you agree or disagree with each student.

Consider the following conversation regarding choosing the basis states in a different order to easily determine a "good" basis for the strong field Zeeman effect ($E'_Z \gg E'_{fs}$).

Student 1: In the strong field Zeeman effect, for the $n = 2$ subspace, we chose basis states in the uncoupled representation ($|l,\ m_l,\ m_s\rangle$) in the order $|\psi_1\rangle = |0,\ 0,\ \frac{1}{2}\rangle$, $|\psi_2\rangle = |0,\ 0,\ -\frac{1}{2}\rangle$,$|\psi_3\rangle = |1,\ 1,\ \frac{1}{2}\rangle$, $|\psi_4\rangle = |1,\ 1,\ -\frac{1}{2}\rangle$, $|\psi_5\rangle = |1,\ 0,\ \frac{1}{2}\rangle$, $|\psi_6\rangle = |1,\ 0,\ -\frac{1}{2}\rangle$, $|\psi_7\rangle = |1,\ -1,\ \frac{1}{2}\rangle$, and $|\psi_8\rangle = |1,\ -1,\ -\frac{1}{2}\rangle$ to write the $\hat{H}^0_Z = \hat{H}^0 + \hat{H}'_Z$ matrix in equation (18) and the $\hat{H}'_{fs}$ matrix in equation (19). Can we choose to write the basis states in a different order to make the $\hat{H}^0_Z = \hat{H}^0 + \hat{H}'_Z$ matrix such that the degenerate eigenvalues along the diagonal are adjacent? Doing so may make it easier to determine if we have a "good" basis.

Student 2: Yes. Suppose we choose the basis states in the order $|\psi_1\rangle = |0,\ 0,\ \frac{1}{2}\rangle$, $|\psi_2\rangle = |1,\ 0,\ \frac{1}{2}\rangle$, $|\psi_3\rangle = |0,\ 0,\ -\frac{1}{2}\rangle$, $|\psi_4\rangle = |1,\ 0,\ -\frac{1}{2}\rangle$, $|\psi_5\rangle = |1,\ 1,\ -\frac{1}{2}\rangle$, $|\psi_6\rangle = |1,\ -1,\ \frac{1}{2}\rangle$, $|\psi_7\rangle = |1,\ 1,\ \frac{1}{2}\rangle$, and $|\psi_8\rangle = |1,\ -1,\ -\frac{1}{2}\rangle$, then in the $n = 2$ subspace, the $\hat{H}^0_Z = \hat{H}^0 + \hat{H}'_Z$ matrix is

$$\hat{H}^0_Z = \begin{bmatrix} \boxed{E_2 + \mu_B B_{ext}} & \boxed{0} & 0 & 0 & 0 & 0 & 0 & 0 \\ \boxed{0} & \boxed{E_2 + \mu_B B_{ext}} & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & \boxed{E_2 - \mu_B B_{ext}} & \boxed{0} & 0 & 0 & 0 & 0 \\ 0 & 0 & \boxed{0} & \boxed{E_2 - \mu_B B_{ext}} & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & \boxed{E_2} & \boxed{0} & 0 & 0 \\ 0 & 0 & 0 & 0 & \boxed{0} & \boxed{E_2} & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & E_2 + 2\mu_B B_{ext} & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & E_2 - 2\mu_B B_{ext} \end{bmatrix}. \tag{20}$$

The degenerate subspaces of $\hat{H}^0_Z = \hat{H}^0 + \hat{H}'_Z$ are boxed. Each degenerate subspace of $\hat{H}^0_Z$ is diagonal. **Student 3:** I agree with Student 2. In order to determine if the "good" basis for step 1 is also a "good" basis for step 2, we must check that $\hat{H}'_{fs}$ is diagonal in each degenerate subspace of $\hat{H}^0_Z = \hat{H}^0 + \hat{H}'_Z$. When basis states are chosen in the order $|\phi_1\rangle = |0,\ 0,\ \frac{1}{2}\rangle$, $|\phi_2\rangle = |1,\ 0,\ \frac{1}{2}\rangle$, $|\phi_3\rangle = |0,\ 0,\ -\frac{1}{2}\rangle$, $|\phi_4\rangle = |1,\ 0,\ -\frac{1}{2}\rangle$, $|\phi_5\rangle = |1,\ 1,\ -\frac{1}{2}\rangle$, $|\phi_6\rangle = |1,\ -1,\ \frac{1}{2}\rangle$, $|\phi_7\rangle = |1,\ 1,\ \frac{1}{2}\rangle$, and $|\phi_8\rangle = |1,\ -1,\ -\frac{1}{2}\rangle$, the $\hat{H}'_{fs}$ matrix is

$$\hat{H}'_{fs} = \frac{(-13.6\text{eV})\alpha^2}{192} \begin{bmatrix} \boxed{15} & \boxed{0} & 0 & 0 & 0 & 0 & 0 & 0 \\ \boxed{0} & \boxed{7} & 0 & 0 & 4\sqrt{2} & 0 & 0 & 0 \\ 0 & 0 & \boxed{15} & \boxed{0} & 0 & 0 & 0 & 0 \\ 0 & 0 & \boxed{0} & \boxed{7} & 0 & 4\sqrt{2} & 0 & 0 \\ 0 & 4\sqrt{2} & 0 & 0 & \boxed{11} & \boxed{0} & 0 & 0 \\ 0 & 0 & 0 & 4\sqrt{2} & \boxed{0} & \boxed{11} & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 3 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 3 \end{bmatrix} \tag{21}$$

Now we can more easily see that $\hat{H}'_{fs}$ is diagonal in each degenerate subspace of $\hat{H}^0_Z = \hat{H}^0 + \hat{H}'_Z$.

Student 4: I disagree with Student 2 and Student 3. We are not permitted to write the basis states in any order we choose. If we change the order of the basis states, we change the first order corrections to the energies. Since the first order corrections to the energies are the diagonal matrix elements of the perturbation in a "good" basis, writing the basis states in a different order will produce incorrect first order corrections to the energies.

Student 3: No! Reordering the basis states just changes the order in which the unperturbed energies and their corrections appear, but corrections to each unperturbed energy will be the same. Remember that we need to reorder both $\hat{H}^0_Z$ and $\hat{H}'_{fs}$ matrices since the basis vectors must be chosen in the same order for all matrices.

Explain why you agree or disagree with each student.

Consider the following conversation regarding the off-diagonal matrix elements of $\hat{H}'fs$ in each degenerate subspace of $\hat{H}_Z^0$ in the strong field Zeeman effect ($E'_Z \gg E'_{fs}$).

Student 1: Since $\hat{H}'_Z$ is diagonal in the uncoupled representation and $\hat{H}'_{fs}$ is diagonal in the coupled representation, we were fortunate that after the first step in our two-step approximation, the off-diagonal matrix elements of $\hat{H}'_{fs}$ were zero in each degenerate subspace of $\hat{H}_Z^0 = \hat{H}^0 + \hat{H}'_Z$ in the uncoupled representation after step 1.

Student 2: I agree with Student 1. Considering $\hat{H}_Z^0 = \hat{H}^0 + \hat{H}'_Z$ as the new unperturbed Hamiltonian after the first step, the stronger perturbation $\hat{H}'_Z$ breaks some of the degeneracy in the energy spectrum of $\hat{H}^0$. In the second step in perturbation theory, the non-zero off-diagonal matrix elements of the weaker perturbation $\hat{H}'_{fs}$ are NOT in each degenerate subspace of $\hat{H}_Z^0 = \hat{H}^0 + \hat{H}'_Z$ when we consider the unperturbed Hamiltonian $\hat{H}_Z^0 = \hat{H}^0 + \hat{H}'_Z$ and the uncoupled representation as the basis.

Student 3: You are correct. We got lucky! After the first step, if the off-diagonal matrix elements of the weaker perturbation $\hat{H}'_{fs}$ were not zero in one or more of the degenerate subspaces of $\hat{H}_Z^0 = \hat{H}^0 + \hat{H}'_Z$, we would need to determine the "good" basis by diagonalizing $\hat{H}'_{fs}$ in each degenerate subspace of $\hat{H}_Z^0 = \hat{H}^0 + \hat{H}'_Z$ in the second step. The uncoupled representation would not have been a "good" basis.

Explain why you agree or disagree with each student.

6.12.2 Finding Corrections to the Energies for the Strong Field Zeeman Effect

After the first step, the unperturbed Hamiltonian including the Zeeman term is

$$\hat{H}_Z^0 = \hat{H}^0 + \hat{H}'_Z = -\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{4\pi\epsilon_0 r} + \frac{e}{2m}B_{ext}(L_z + 2S_z) \tag{22}$$

and the corresponding unperturbed energies are

$$E_Z^0 = -\frac{13.6\text{eV}}{n^2} + \mu_B B_{ext}(m_l + 2m_s) \tag{23}$$

13. After step 2, find one of the first order corrections to the energies due to the weaker perturbation $\hat{H}'_{fs}$ for the hydrogen atom placed in a strong external magnetic field for the $n = 2$ subspace.

**** Check your answers to question 13. ****

13. The first order corrections to the energies due to the fine structure term for the hydrogen atom placed in a strong external magnetic field for the $n = 2$ subspace are the diagonal elements of $\hat{H}'_{fs}$ in equation (21).

$$E'_1 = \frac{(-13.6\text{ eV})\alpha^2}{192}(15) \qquad E'_2 = \frac{(-13.6\text{ eV})\alpha^2}{192}(7)$$

$$E'_3 = \frac{(-13.6\text{ eV})\alpha^2}{192}(15) \qquad E'_4 = \frac{(-13.6\text{ eV})\alpha^2}{192}(7)$$

$$E'_5 = \frac{(-13.6\text{ eV})\alpha^2}{192}(11) \qquad E'_6 = \frac{(-13.6\text{ eV})\alpha^2}{192}(11)$$

$$E'_7 = \frac{(-13.6\text{ eV})\alpha^2}{192}(3) \qquad E'_8 = \frac{(-13.6\text{ eV})\alpha^2}{192}(3)$$

If your answers to question 13 do not match with the checkpoint answers, go back and reconcile any differences.

In one to two sentences, summarize what you have learned about the "good" angular basis states for finding the first order corrections to the energy spectrum of the hydrogen atom due to the strong field Zeeman effect (pertaining to whether the coupled representation, the uncoupled representation, or any arbitrary complete orthonormal basis constructed with linear combinations of states with a fixed principal quantum number n in the coupled or uncoupled representation form a "good" angular basis).

Summary: Finding a "GOOD" Angular Basis for the Strong Field Zeeman Effect ($E'_Z \gg E'_{fs}$)

- We can use a two step process in perturbation theory to find corrections to the hydrogen atom energy spectrum when $E'_Z \gg E'_{fs}$.

Step 1: Treat the stronger perturbation $\hat{H}'_Z$ as a perturbation on the unperturbed Hamiltonian $\hat{H}^0$.

- $\hat{H}'_Z$ is diagonal in the uncoupled representation.

Step 2: Treat the fine structure part of the Hamiltonian, $\hat{H}'_{fs}$, as a perturbation on the new unperturbed Hamiltonian $\hat{H}^0_Z = \hat{H}^0 + \hat{H}'_Z$.

- In the uncoupled representation, $\hat{H}'_{fs}$ is diagonal in each degenerate subspace of $\hat{H}^0_Z = \hat{H}^0 + \hat{H}'_Z$ (even though $\hat{H}'_{fs}$ has off-diagonal matrix elements in the uncoupled representation, they are not in each degenerate subspace of $\hat{H}^0_Z = \hat{H}^0 + \hat{H}'_Z$).

- The uncoupled representation forms a "good" angular basis for finding the corrections to the energies.

Review the following flowchart concerning the "good" basis and how to find the corrections to the energies for the intermediate and strong field Zeeman effect. Using the intermediate and strong field Zeeman effect as a guide, attempt to fill in the steps required to determine a "good" basis and corrections to the energies due to both the fine structure ($\hat{H}'_{fs}$) and Zeeman ($\hat{H}'_Z$) terms for the the weak field Zeeman effect ($E'_{fs} \gg E'_Z$). You may add or remove boxes in the flowchart if necessary.

Determining a "GOOD" Angular Basis and Corrections to the Energies due to BOTH the Fine Structure and Zeeman Effect

Which term in $\hat{H}' = \hat{H}'_{fs} + \hat{H}'_Z$ is stronger?

$E'_Z \gg E'_{fs}$ (Zeeman Term is Stronger)	$E'_{fs} \approx E'_Z$ (Both Terms are Comparable)	$E'_{fs} \gg E'_Z$ (Fine Structure Term is Stronger)
Strong Field Zeeman Effect	Intermediate Field Zeeman Effect	Weak Field Zeeman Effect
STEP 1: Treat $\hat{H}'_Z$ as a perturbation on $\hat{H}^0$.	Neither the coupled nor the uncoupled representation forms a "good" angular basis.	
$\hat{H}'_Z$ is diagonal in the uncoupled representation.	Choose either the coupled or the uncoupled representation as the initial basis to write $\hat{H}' = \hat{H}'_{fs} + \hat{H}'_Z$ (although neither is a "good" angular basis).	
STEP 2: Consider $\hat{H}' = \hat{H}'_{fs}$ as a perturbation on the unperturbed Hamiltonian $\hat{H}^0_Z = \hat{H}^0 + \hat{H}'_Z$.	Diagonalize $\hat{H}' = \hat{H}'_{fs} + \hat{H}'_Z$ in each degenerate subspace of $\hat{H}^0$ to obtain a "good" angular basis.	
$\hat{H}'_{fs}$ is diagonal in each degenerate subspace of $\hat{H}^0_Z = \hat{H}^0 + \hat{H}'_Z$ in the uncoupled representation.	In the "good" basis, the diagonal matrix elements of $\hat{H}' = \hat{H}'_{fs} + \hat{H}'_Z$ are the first order corrections to the energies.	
The uncoupled representation forms a "good" angular basis.		
In the uncoupled representation, the diagonal matrix elements of $\hat{H}'_{fs}$ are the first order corrections to the energies		

CASE 3: Weak Field Zeeman Effect: Perturbation Theory in Two Steps to Find the Corrections to the Energy Spectrum

6.12.3 Finding a "GOOD" Basis for the Weak Field Zeeman Effect ($E'_{fs} \gg E'_Z$)

STEP 1:

In step 1, for the case $E'_{fs} \gg E'_Z$, we treat only $\hat{H}'_{fs}$ as the perturbation on $\hat{H}^0$.

14. For the case $E'_{fs} \gg E'_Z$, what is the "good" angular basis for step 1 when we ignore $\hat{H}'_Z$? Explain.

15. Write an expression for the first order corrections to the energies due to the stronger perturbation $\hat{H}'_{fs}$.

STEP 2:

In the weak field when $E'_{fs} \gg E'_Z$, in step two, the unperturbed Hamiltonian including the fine structure term becomes

$$\hat{H}^0_{fs} = -\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{4\pi\epsilon_0 r} - \frac{\hat{p}^4}{8m^3c^2} + \left(\frac{e^2}{8\pi\epsilon_0}\right)\frac{1}{m^2c^2r^3}\vec{S}\cdot\vec{L}. \tag{24}$$

16. For $\hat{H}^0_{fs} = \hat{H}^0 + \hat{H}'_{fs}$, is $\hat{H}^0_{fs}$ diagonal if the angular basis is chosen to be the coupled representation, uncoupled representation, or neither? Explain your reasoning.

Now for the $n = 2$ subspace, take a look at the $\hat{H}^0_{fs} = \hat{H}^0 + \hat{H}'_{fs}$ and $\hat{H}'_Z$ matrices given below in the **coupled representation** ($|l,\ j,\ m_j\rangle$) in which $E_2 = -\frac{13.6\text{eV}}{4}$ and the basis states are chosen in the order $|\Phi_1\rangle = |1,\ \frac{3}{2},\ \frac{3}{2}\rangle$, $|\Phi_2\rangle = |1,\ \frac{3}{2},\ \frac{1}{2}\rangle$, $|\Phi_3\rangle = |1,\ \frac{3}{2},\ -\frac{1}{2}\rangle$, $|\Phi_4\rangle = |1,\ \frac{3}{2},\ -\frac{3}{2}\rangle$, $|\Phi_5\rangle = |1,\ \frac{1}{2},\ \frac{1}{2}\rangle$, $|\Phi_6\rangle = |1,\ \frac{1}{2},\ -\frac{1}{2}\rangle$, $|\Phi_7\rangle = |0,\ \frac{1}{2},\ \frac{1}{2}\rangle$ and $|\Phi_8\rangle = |0,\ \frac{1}{2},\ -\frac{1}{2}\rangle$. Then, answer questions 16-20 for the weak field Zeeman effect.

$$\hat{H}^0_{fs} = \hat{H}^0 + \hat{H}'_{fs}$$

$$\hat{H}^0_{fs} = E_2 \begin{bmatrix} 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \end{bmatrix} + \frac{E_2^2}{mc^2} \begin{bmatrix} -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & -1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & -5 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & -5 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & -5 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & -5 \end{bmatrix}$$

$$\hat{H}^0_{fs} = \begin{bmatrix} E_2 - \frac{E_2^2}{mc^2} & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & E_2 - \frac{E_2^2}{mc^2} & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & E_2 - \frac{E_2^2}{mc^2} & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & E_2 - \frac{E_2^2}{mc^2} & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & E_2 - \frac{5E_2^2}{mc^2} & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & E_2 - \frac{5E_2^2}{mc^2} & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & E_2 - \frac{5E_2^2}{mc^2} & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & E_2 - \frac{5E_2^2}{mc^2} \end{bmatrix} \tag{25}$$

$$\hat{H}'_Z = \mu_B B_{ext} \begin{bmatrix} 2 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & \frac{2}{3} & 0 & 0 & -\frac{\sqrt{2}}{3} & 0 & 0 & 0 \\ 0 & 0 & -\frac{2}{3} & 0 & 0 & -\frac{\sqrt{2}}{3} & 0 & 0 \\ 0 & 0 & 0 & -2 & 0 & 0 & 0 & 0 \\ 0 & -\frac{\sqrt{2}}{3} & 0 & 0 & \frac{1}{3} & 0 & 0 & 0 \\ 0 & 0 & -\frac{\sqrt{2}}{3} & 0 & 0 & -\frac{1}{3} & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & -1 \end{bmatrix} \tag{26}$$

17. In step 2, determine the degeneracy of the "new" unperturbed Hamiltonian $\hat{H}^0_{fs} = \hat{H}^0 + \hat{H}'_{fs}$ after accounting for the stronger perturbation and circle the corresponding degenerate subspaces in $\hat{H}^0_{fs} = \hat{H}^0 + \hat{H}'_{fs}$ for the $n = 2$ subspace in the preceding matrix representation in equation (25).

18. Identify the matrix elements of $\hat{H}'_Z$ in equation (26) that correspond to each degenerate subspace of $\hat{H}^0_{fs} = \hat{H}^0 + \hat{H}'_{fs}$ in equation (25) and determine whether $\hat{H}'_Z$ is diagonal in each of these subspaces of $\hat{H}^0_{fs}$

19. Determine whether the basis chosen in question 16 is a "good" angular basis for the unperturbed Hamiltonian $\hat{H}^0_{fs} = \hat{H}^0 + \hat{H}'_{fs}$ and the perturbation $\hat{H}'_Z$. Explain how you made the determination.

**** Check your answers to questions 14-19. ****

14. The coupled representation forms a "good" basis when only the fine structure term $\hat{H}'_{fs}$ is the perturbation on the unperturbed Hamiltonian $\hat{H}^0$

15. As we determined in equation (14), the first order corrections to the energies due to the fine structure term $\hat{H}'_{fs}$ in the coupled representation are $E'_{fs} = \frac{E_n^2}{mc^2}\left[3 - \frac{4n}{j+1/2}\right]$.

16. For a fixed n, $\hat{H}^0_{fs} = \hat{H}^0 + \hat{H}'_{fs}$ is diagonal in each degenerate subspace of $\hat{H}^0$ if the coupled representation is chosen as the angular basis.

17. $\hat{H}^0_{fs} = \hat{H}^0 + \hat{H}'_{fs}$ possesses two four-fold degeneracies in the $n = 2$ subspace. There are four distinct states that share the new unperturbed energies $E_2 - \frac{5E_2^2}{mc^2}$ and $E_2 - \frac{E_2^2}{mc^2}$.

18. The perturbation $\hat{H}'_Z$ is diagonal in each degenerate subspace of $\hat{H}^0_{fs} = \hat{H}^0 + \hat{H}'_{fs}$ treated as the unperturbed Hamiltonian in step 2 of perturbation theory.

19. Yes. The coupled representation is a "good" angular basis. In the second step, the new perturbation term $\hat{H}^0_{fs} = \hat{H}^0 + \hat{H}'_{fs}$ is diagonal in the coupled representation for a fixed n and the perturbation $\hat{H}'_Z$ is diagonal in each degenerate subspace of $\hat{H}^0_{fs} = \hat{H}^0 + \hat{H}'_{fs}$.

If your answers to questions 14-19 do not match with the checkpoint, go back and reconcile any differences.

Consider the following conversation regarding the weak field Zeeman effect ($E'_{fs} \gg E'_Z$) and finding a "good" basis for the two-step process in the weak field Zeeman effect ($E'_{fs} \gg E'_Z$).

Student 1: Since $\hat{H}'_Z = \mu_B B_{ext}(\hat{L}_z + 2\hat{S}_z)$, we cannot use the coupled representation as the angular basis. $\hat{H}'_Z$ is not diagonal in the coupled representation. To find the first order corrections to the energies, we must use the uncoupled representation since $\hat{H}'_Z$ is diagonal in the uncoupled representation.

Student 2: I don't see how either the coupled or uncoupled representation form a "good" angular basis when we have both $\hat{H}'_{fs}$ and $\hat{H}'_Z$. They simply cannot be diagonalized simultaneously in either basis. We must choose linear combinations of the states in the coupled or uncoupled representation so that the basis diagonalizes the sum of $\hat{H}'_{fs}$ and $\hat{H}'_Z$ in each degenerate subspace of $\hat{H}^0$.

Student 3: I agree with Student 2 only for the intermediate field Zeeman effect with $E'_{fs} \approx E'_Z$. In the weak field Zeeman effect in which $E'_{fs} \gg E'_Z$, we can use the two step approximation by considering only the stronger perturbation $\hat{H}'_{fs}$ in the first step. In the second step, we consider the "new" unperturbed Hamiltonian $\hat{H}^0_{fs} = \hat{H}^0 + \hat{H}'_{fs}$ and the perturbation $\hat{H}'_Z$. If the coupled representation is chosen as the angular basis, then in the $n = 2$ subspace, the $\hat{H}^0_{fs} = \hat{H}^0 + \hat{H}'_{fs}$ matrix is (the basis vectors are chosen the same order as in questions 17-19):

$$\hat{H}^0_{fs} = \left[\begin{array}{cccc|cccc} \boxed{E_2 - \frac{E_2^2}{mc^2}} & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & E_2 - \frac{E_2^2}{mc^2} & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & E_2 - \frac{E_2^2}{mc^2} & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & E_2 - \frac{E_2^2}{mc^2} & 0 & 0 & 0 & 0 \\ \hline 0 & 0 & 0 & 0 & \boxed{E_2 - \frac{5E_2^2}{mc^2}} & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & E_2 - \frac{5E_2^2}{mc^2} & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & E_2 - \frac{5E_2^2}{mc^2} & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & E_2 - \frac{5E_2^2}{mc^2} \end{array}\right]$$

Student 4: I agree with Student 3. $\hat{H}'_Z$ is diagonal in each degenerate subspace of $\hat{H}^0_{fs} = \hat{H}^0 + \hat{H}'_{fs}$ shown for the $n = 2$ subspace in the following matrix. Therefore, the coupled representation is a "good" basis in the limit $E'_{fs} \gg E'_Z$. When we use a two step process in the limit $E'_{fs} \gg E'_Z$, some degeneracy is lifted in the first step.

$$\hat{H}'_Z = \mu_B B_{ext} \left[\begin{array}{cccc|cccc} \boxed{2} & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & \frac{2}{3} & 0 & 0 & -\frac{\sqrt{2}}{3} & 0 & 0 & 0 \\ 0 & 0 & -\frac{2}{3} & 0 & 0 & -\frac{\sqrt{2}}{3} & 0 & 0 \\ 0 & 0 & 0 & -2 & 0 & 0 & 0 & 0 \\ \hline 0 & -\frac{\sqrt{2}}{3} & 0 & 0 & \boxed{\frac{1}{3}} & 0 & 0 & 0 \\ 0 & 0 & -\frac{\sqrt{2}}{3} & 0 & 0 & -\frac{1}{3} & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & -1 \end{array}\right]. \tag{27}$$

Explain why you agree or disagree with each student.

Consider the following conversation regarding the off-diagonal matrix elements of $\hat{H}'_Z$ in the degenerate subspace of $\hat{H}^0_{fs}$ in the weak field Zeeman effect ($E'_{fs} \gg E'_Z$).

Student 1: Since $\hat{H}'_Z$ is diagonal in the uncoupled representation and $\hat{H}'_{fs}$ is diagonal in the coupled representation for a fixed n, we were fortunate that, after the first step in our approximation, the off-diagonal matrix elements of $\hat{H}'_Z$ are zero in each degenerate subspace of $\hat{H}^0_{fs} = \hat{H}^0 + \hat{H}'_{fs}$.

Student 2: I agree with Student 1. The stronger perturbation $\hat{H}'_{fs}$ breaks some of the degeneracy in the energy spectrum of $\hat{H}^0$. When we consider $\hat{H}^0_{fs} = \hat{H}^0 + \hat{H}'_{fs}$ as the new unperturbed Hamiltonian in step 2, the non-zero off-diagonal matrix elements of $\hat{H}'_Z$ are not in the degenerate subspaces of $\hat{H}^0_{fs} = \hat{H}^0 + \hat{H}'_{fs}$.

Student 3: You are correct. We got lucky! In step 2, if the off-diagonal matrix elements of the weaker perturbation $\hat{H}'_Z$ were non-zero in any of the degenerate subspaces of $\hat{H}^0_{fs} = \hat{H}^0 + \hat{H}'_{fs}$, we would have needed to determine the "good" basis by diagonalizing $\hat{H}'_Z$ in each degenerate subspace of $\hat{H}^0_{fs} = \hat{H}^0 + \hat{H}'_{fs}$ that is not diagonal already after the first step.

Explain why you agree or disagree with each student.

6.12.4 Finding Corrections to the Energies for the Weak Field Zeeman Effect ($E'_{fs} \gg E'_Z$)

After the first step, the unperturbed Hamiltonian including the fine structure term is

$$\hat{H}^0_{fs} = -\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{4\pi\epsilon_0 r} - \frac{\hat{p}^4}{8m^3c^2} + \left(\frac{e^2}{8\pi\epsilon_0}\right)\frac{1}{m^2c^2r^3}\vec{S}\cdot\vec{L} \tag{28}$$

and the corresponding unperturbed energies are

$$E_{njm_j} = -\frac{13.6\text{eV}}{n^2} + \frac{E_n^2}{mc^2}\left[3 - \frac{4n}{j+1/2}\right] \tag{29}$$

20. After step 2, find one of the first order corrections to the energies due to the weaker perturbation $\hat{H}'_Z$ for the hydrogen atom placed in a weak external magnetic field for the $n = 2$ subspace.

**** Check your answers to question 20. ****

20. The first order corrections to the energies due to the Zeeman term only for the hydrogen atom placed in a weak external magnetic field for the $n = 2$ subspace are the diagonal elements of $\hat{H}'_Z$ in equation (27)

$$\begin{array}{rcl} E'_1 & = & 2\mu_B B_{ext} \\ E'_2 & = & \frac{2}{3}\mu_B B_{ext} \\ E'_3 & = & -\frac{2}{3}\mu_B B_{ext} \\ E'_4 & = & -2\mu_B B_{ext} \\ E'_5 & = & \frac{1}{3}\mu_B B_{ext} \\ E'_6 & = & -\frac{1}{3}\mu_B B_{ext} \\ E'_7 & = & \mu_B B_{ext} \\ E'_8 & = & -\mu_B B_{ext} \end{array}$$

If your answer to question 20 does not match with the checkpoint, go back and reconcile any differences.

In one to two sentences, summarize what you have learned about the "good" angular basis for finding the first order corrections to the energy spectrum of the hydrogen atom due to the weak field Zeeman effect (pertaining to whether the coupled representation, the uncoupled representation, or any arbitrary complete orthonormal basis constructed with linear combinations of states with a fixed principal quantum number n in the coupled or uncoupled representation form a "good" angular basis).

Summary: Finding a "GOOD" Angular Basis for the Weak Field Zeeman Effect ($E'_{fs} \gg E'_Z$)

- We can use a two step process for perturbation theory to find the corrections to the hydrogen atom energy spectrum for $E'_{fs} \gg E'_Z$.

Step 1: Treat the stronger perturbation $\hat{H}'_{fs}$ as the entire perturbation on the unperturbed Hamiltonian $\hat{H}^0$.

- $\hat{H}'_{fs}$ is diagonal in the coupled representation for a fixed n (in each degenerate subspace of $\hat{H}^0$).

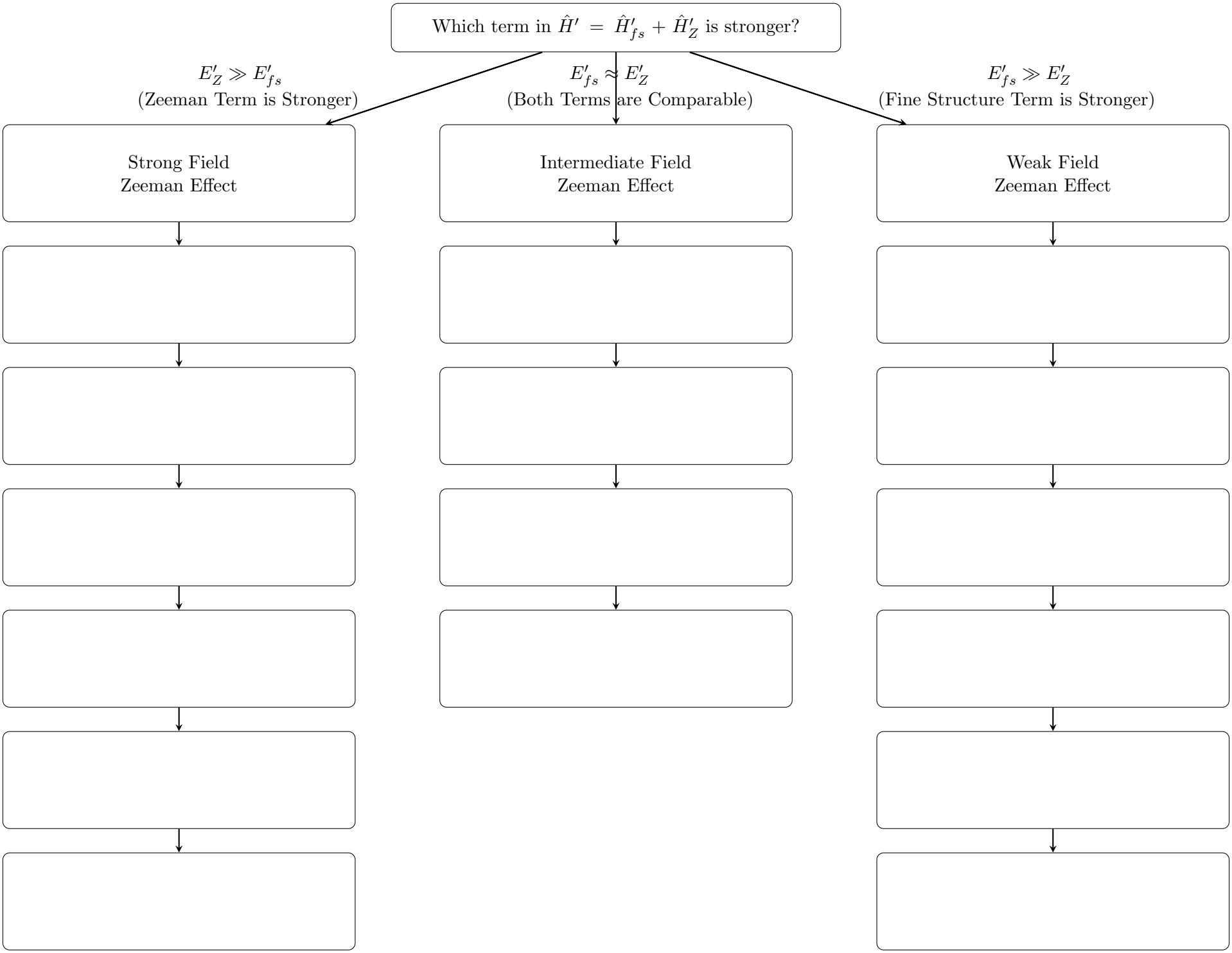
Step 2: Treat the Zeeman part of the Hamiltonian, $\hat{H}'_Z$, as the perturbation on the new unperturbed Hamiltonian $\hat{H}^0_{fs} = \hat{H}^0 + \hat{H}'_{fs}$.

- In the coupled representation, $\hat{H}'_Z$ is diagonal in each degenerate subspace of $\hat{H}^0_{fs} = \hat{H}^0 + \hat{H}'_{fs}$ (even though $\hat{H}'_Z$ has off-diagonal matrix elements in the coupled representation, they are not in the degenerate subspaces of $\hat{H}^0_{fs} = \hat{H}^0 + \hat{H}'_{fs}$).
- See equation (26) as an example for the $n = 2$ subspace.

- The coupled representation forms a "good" angular basis for finding the corrections to the energies.

Fill in the following flowchart concerning a "good" angular basis and how to find the corrections to the energies for the intermediate ($E'_{fs} \approx E'_Z$), strong ($E'_Z \gg E'_{fs}$), and weak field Zeeman effect ($E'_{fs} \gg E'_Z$).

Determining a "GOOD" Angular Basis and Corrections to the Energies Due to BOTH the Fine Structure and Zeeman Effect



Determining a "GOOD" Angular Basis and Corrections to the Energies Due to BOTH the Fine Structure and Zeeman Effect

Which term in $\hat{H}' = \hat{H}'_{fs} + \hat{H}'_Z$ is stronger?

$E'_Z \gg E'_{fs}$ (Zeeman Term is Stronger)

Strong Field Zeeman Effect

STEP 1: Treat $\hat{H}'_Z$ as a perturbation on $\hat{H}^0$.

$\hat{H}'_Z$ is diagonal in the uncoupled representation.

STEP 2: Consider $\hat{H}' = \hat{H}'_{fs}$ as a perturbation on the unperturbed Hamiltonian $\hat{H}^0_Z = \hat{H}^0 + \hat{H}'_Z$.

$\hat{H}'_{fs}$ is diagonal in each degenerate subspace of $\hat{H}^0_Z = \hat{H}^0 + \hat{H}'_Z$ in the uncoupled representation.

The uncoupled representation forms a "good" angular basis.

In the uncoupled representation, the diagonal matrix elements of $\hat{H}'_{fs}$ are the first order corrections to the energies

$E'_{fs} \approx E'_Z$ (Both Terms are Comparable)

Intermediate Field Zeeman Effect

Neither the coupled nor the uncoupled representations form a "good" angular basis.

Choose either the coupled or the uncoupled representation as the initial basis to write $\hat{H}' = \hat{H}'_{fs} + \hat{H}'_Z$ (although neither is a "good" basis).

Diagonalize $\hat{H}' = \hat{H}'_{fs} + \hat{H}'_Z$ in each degenerate subspace of $\hat{H}^0$ to obtain a "good" basis.

In the "good" basis, the diagonal matrix elements of $\hat{H}' = \hat{H}'_{fs} + \hat{H}'_Z$ are the first order corrections to the energies.

$E'_{fs} \gg E'_Z$ (Fine Structure Term is Stronger)

Weak Field Zeeman Effect

STEP 1: Treat $\hat{H}'_{fs}$ as a perturbation on $\hat{H}^0$.

$\hat{H}'_{fs}$ is diagonal in the coupled representation for a fixed n.

STEP 2: Consider $\hat{H}' = \hat{H}'_Z$ as a perturbation on the unperturbed Hamiltonian $\hat{H}^0_{fs} = \hat{H}^0 + \hat{H}'_{fs}$.

$\hat{H}'_Z$ is diagonal in each degenerate subspace of $\hat{H}^0_{fs} = \hat{H}^0 + \hat{H}'_{fs}$ in the coupled representation.

The coupled representation forms a "good" angular basis.

In the coupled representation, the diagonal matrix elements of $\hat{H}'_Z$ are the first order corrections to the energies

Fill in the following table for the Strong Field Zeeman Effect.

Strong Field Zeeman Effect

	Hamiltonian	Is the Matrix Diagonal or Non-Diagonal in the Uncoupled Representation? (for a fixed n)	Is the Uncoupled Representation a "Good" Basis?	Is the Matrix Diagonal or Non-Diagonal in the Coupled Representation? (for a fixed n)	Is the Coupled Representation a "Good" Basis?	Energy/ Energy Correction (Using the "Good" Basis)
Step 1	Unperturbed $\hat{H}^0$					
	Perturbation $\hat{H}'_Z$					
Step 2	Unperturbed $\hat{H}^0_Z = \hat{H}^0 + \hat{H}'_Z$					
	Perturbation $\hat{H}'_{fs}$					

Fill in the following table for the Weak Field Zeeman Effect.

Weak Field Zeeman Effect

	Hamiltonian	Is the Matrix Diagonal or Non-Diagonal in the Uncoupled Representation? (for a fixed n)	Is the Uncoupled Representation a "Good" Basis?	Is the Matrix Diagonal or Non-Diagonal in the Coupled Representation? (for a fixed n)	Is the Coupled Representation a "Good" Basis?	Energy/ Energy Correction (Using the "Good" Basis)
Step 1	Unperturbed $\hat{H}^0$					
	Perturbation $\hat{H}'_{fs}$					
Step 2	Unperturbed $\hat{H}^0_{fs} = \hat{H}^0 + \hat{H}'_{fs}$					
	Perturbation $\hat{H}'_Z$					

**** Check your answers to questions in the preceding tables.****

Strong Field Zeeman Effect

	Hamiltonian	Is the Matrix Diagonal or Non-Diagonal in the Uncoupled Representation? (for a fixed n)	Is the Uncoupled Representation a "Good" Basis?	Is the Matrix Diagonal or Non-Diagonal in the Coupled Representation? (for a fixed n)	Is the Coupled Representation a "Good" Basis?	Energy/ Energy Correction (Using the "Good" Basis)
Step 1	Unperturbed $\hat{H}^0$	Diagonal	Yes, because $\hat{H}'_Z$ is diagonal in each degenerate subspace of $\hat{H}^0$. (actually both $\hat{H}^0$ and $\hat{H}'_Z$ can be diagonalized simultaneously since $[\hat{H}^0, \hat{H}'_Z] = 0$).	Diagonal	No, because $\hat{H}'_Z$ is not diagonal in each degenerate subspace of $\hat{H}^0$.	$E^0 = -\frac{13.6\text{eV}}{n^2}$
	Perturbation $\hat{H}'_Z$	Diagonal		Non-Diagonal		$E'_Z = \mu_B B_{ext}(m_l + 2m_s)$
Step 2	Unperturbed $\hat{H}^0_Z = \hat{H}^0 + \hat{H}'_Z$	Diagonal	Yes, because $\hat{H}'_{fs}$ is diagonal in each degenerate subspace of $\hat{H}^0_Z = \hat{H}^0 + \hat{H}'_Z$.	Non-Diagonal	No, because $\hat{H}'_Z$ is not diagonal in each degenerate subspace of $\hat{H}^0$.	$E^0_Z = E^0 + E'_Z$ $= E^0 + \mu_B B_{ext}(m_l + 2m_s)$
	Perturbation $\hat{H}'_{fs}$	Non-diagonal		Diagonal		Use Clebsch-Gordon table table to express uncoupled states in the coupled basis to determine E'_{fs}.

Weak Field Zeeman Effect

	Hamiltonian	Is the Matrix Diagonal or Non-Diagonal in the Uncoupled Representation? (for a fixed n)	Is the Uncoupled Representation a "Good" Basis?	Is the Matrix Diagonal or Non-Diagonal in the Coupled Representation? (for a fixed n)	Is the Coupled Representation a "Good" Basis?	Energy/ Energy Correction (Using the "Good" Basis)
Step 1	Unperturbed $\hat{H}^0$	Diagonal	No, because $\hat{H}'_{fs}$ is not diagonal in each degenerate subspace of $\hat{H}^0$.	Diagonal	Yes, because $\hat{H}'_{fs}$ is diagonal in each degenerate subspace of $\hat{H}^0$.	$E^0 = -\frac{13.6\text{eV}}{n^2}$
	Perturbation $\hat{H}'_{fs}$	Non-Diagonal		Diagonal		$E'_{fs} = \frac{E_n^2}{2mc^2}\left[3 - \frac{4n}{(j+1/2)}\right]$
Step 2	Unperturbed $\hat{H}^0_{fs} = \hat{H}^0 + \hat{H}'_{fs}$	Non-Diagonal	No, because $\hat{H}'_{fs}$ is not diagonal in each degenerate subspace of $\hat{H}^0$.	Diagonal	Yes, because $\hat{H}'_Z$ is diagonal in each degenerate subspace of $\hat{H}^0_{fs} = \hat{H}^0 + \hat{H}'_{fs}$.	$E^0_{fs} = E^0 + E'_{fs}$ $= E^0 - \frac{E_n^2}{2mc^2}\left[\frac{4n}{(j+1/2)} - 3\right]$
	Perturbation $\hat{H}'_Z$	Diagonal		Non-Diagonal		Use Clebsch-Gordon table to express coupled states in the uncoupled basis to determine E'_Z

Summary: Finding a "GOOD" Basis for the Zeeman Effect in the Hydrogen Atom

- Intermediate Field Zeeman Effect ($E'_Z \approx E'_{fs}$)
  - Neither the coupled nor the uncoupled representation forms a "good" basis for finding corrections to the energies.
  - One needs to diagonalize $\hat{H}' = \hat{H}'_Z + \hat{H}'_{fs}$ in each degenerate subspace of $\hat{H}^0$ explicitly to find the "good" basis.
- Strong Field Zeeman Effect ($E'_Z \gg E'_{fs}$)
  - We can carry out perturbation theory in two steps.
  - The uncoupled representation forms a "good" basis for finding corrections to the energies.
- Weak Field Zeeman Effect ($E'_{fs} \gg E'_Z$)
  - We can carry out perturbation theory in two steps.
  - The coupled representation forms a "good" basis for finding corrections to the energies.

Hamiltonian	Uncoupled Representation (for a fixed n)	Is Uncoupled Representation a "Good" Basis?	Coupled Representation (for a fixed n)	Is Coupled Representation a "Good" Basis?	Is Any ArbitraryComplete Orthonormal Basis Found with Linear Combinations of a Complete Set of the Coupled or Uncoupled States a "Good" Basis? (with the same n and l)	Unperturbed Energy	First Order Correction to the Energy
$\hat{H}^0$	Diagonal	—	Diagonal	—	—	$E_n = -\frac{13.6\text{eV}}{n^2}$	-
$\hat{H}'_r$	Diagonal	Yes	Diagonal	Yes	Yes	E_n	$E'_r = -\frac{E_n^2}{2mc^2}\left[\frac{4n}{l+1/2} - 3\right]$
$\hat{H}'_{SO}$	Not Diagonal	No	Diagonal	Yes	No	E_n	$E'_{SO} = \frac{E_n^2}{mc^2}\left[\frac{n(j(j+1)-l(l+1-3/4))}{l(l+1)(l+1/2)}\right]$
$\hat{H}'_{fs} = \hat{H}'_r + \hat{H}'_{SO}$	Not Diagonal	No	Diagonal	Yes	No	E_n	$E'_{fs} = -\frac{E_n^2}{2mc^2}\left[\frac{4n}{(j+1/2)} - 3\right]$
$\hat{H}'_Z$	Diagonal	Yes	Not Diagonal	No	No	E_n	$E'_Z = \mu B_{ext}(m_l + 2m_s)$
$\hat{H}^0_Z = \hat{H}^0 + \hat{H}'_Z$	Diagonal	Yes	Not Diagonal	No	No	$E_n + \mu B_{ext}(m_l + 2m_s)$	Diagonal matrix elements of $\hat{H}'_{fs}$ in the uncoupled representation
$\hat{H}^0_{fs} = \hat{H}^0 + \hat{H}'_{fs}$	Not Diagonal	No	Diagonal	Yes	No	$E_n + \frac{E_n^2}{2mc^2}\left[3 - \frac{4n}{(j+1/2)}\right]$	Diagonal matrix elements of $\hat{H}'_Z$ in the coupled representation

7 Finding First Order Energy Corrections for the Intermediate Field Zeeman Effect Continued

Reconsider the following perturbing Hamiltonian $\hat{H}' = \hat{H}'_Z + \hat{H}'_{fs}$ in the coupled representation ($|l,\ j,\ m_j\rangle$) when $E'_{fs} \approx E'_Z$.

$$\hat{H}' = -\begin{bmatrix} 5\gamma-\beta & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 5\gamma+\beta & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & \gamma-2\beta & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & \gamma+2\beta & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & \gamma-\frac{2}{3}\beta & \frac{\sqrt{2}}{3}\beta & 0 & 0 \\ 0 & 0 & 0 & 0 & \frac{\sqrt{2}}{3}\beta & 5\gamma-\frac{1}{3}\beta & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & \gamma+\frac{2}{3}\beta & \frac{\sqrt{2}}{3}\beta \\ 0 & 0 & 0 & 0 & 0 & 0 & \frac{\sqrt{2}}{3}\beta & 5\gamma+\frac{1}{3}\beta \end{bmatrix} \tag{30}$$

in which $\gamma = \left(\frac{\alpha}{8}\right)^2$ 13.6 eV, $\alpha = \frac{e^2}{4\pi\epsilon_0\hbar c}$, $\beta = \mu_B B_{ext}$ and the basis states are chosen in the order of $|\psi_1\rangle = |0,\ \frac{1}{2},\ \frac{1}{2}\rangle$, $|\psi_2\rangle = |0,\ \frac{1}{2},\ -\frac{1}{2}\rangle$, $|\psi_3\rangle = |1,\ \frac{3}{2},\ \frac{3}{2}\rangle$, $|\psi_4\rangle = |1,\ \frac{3}{2},\ -\frac{3}{2}\rangle$, $|\psi_5\rangle = |1,\ \frac{3}{2},\ \frac{1}{2}\rangle$, $|\psi_6\rangle = |1,\ \frac{1}{2},\ \frac{1}{2}\rangle$, $|\psi_7\rangle = |1,\ \frac{3}{2},\ -\frac{1}{2}\rangle$, and $|\psi_8\rangle = |1,\ \frac{1}{2},\ -\frac{1}{2}\rangle$.

21. Explain in words how to find a "good" basis and corrections to the energies for the intermediate field Zeeman effect ($E'_{fs} \approx E'_Z$).

OPTIONAL: The final three questions in this tutorial are optional.

22. Determine the first order corrections to the energies for the intermediate field Zeeman effect ($E'_{fs} \approx E'_Z$) in which the perturbation $\hat{H}' = \hat{H}'_Z + \hat{H}'_{fs}$ in the coupled representation is given in equation (30).

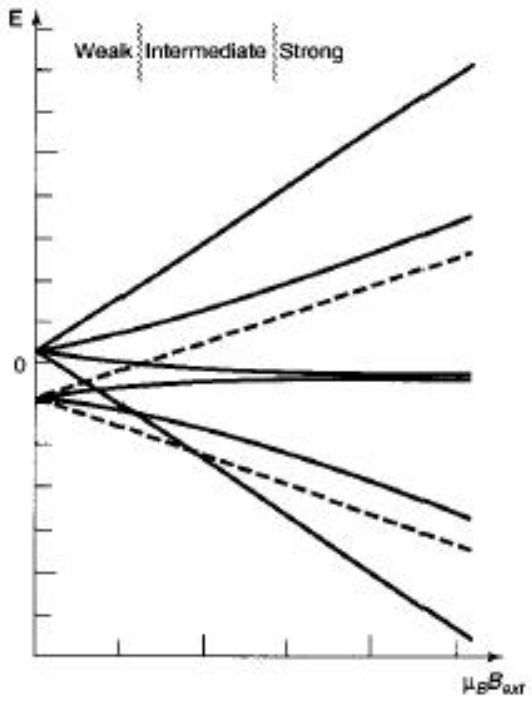
The energy levels for the $n = 2$ states of the hydrogen atom in the intermediate field Zeeman effect are given below.

Table 1: Energy Levels in the Intermediate Field Zeeman Effect ($n = 2$)

$$
\begin{array}{lcl}
\epsilon_1 & = & E_2 - 5\gamma + \beta \\
\epsilon_2 & = & E_2 - 5\gamma - \beta \\
\epsilon_3 & = & E_2 - \gamma + 2\beta \\
\epsilon_4 & = & E_2 - \gamma - 2\beta \\
\epsilon_5 & = & E_2 - 3\gamma + \beta/2 + \sqrt{4\gamma^2 + (2/3)\gamma\beta + \beta^2/4} \\
\epsilon_6 & = & E_2 - 3\gamma + \beta/2 - \sqrt{4\gamma^2 + (2/3)\gamma\beta + \beta^2/4} \\
\epsilon_7 & = & E_2 - 3\gamma - \beta/2 + \sqrt{4\gamma^2 - (2/3)\gamma\beta + \beta^2/4} \\
\epsilon_8 & = & E_2 - 3\gamma - \beta/2 - \sqrt{4\gamma^2 - (2/3)\gamma\beta + \beta^2/4}
\end{array}
$$

23. Use the appropriate Taylor series expansion to check that the corrections to the energies in the intermediate field Zeeman effect are consistent with the corrections found in the limiting cases of the strong and weak field Zeeman effects earlier.

24. Below is a graph of the splitting of the energy levels of the hydrogen atom for the weak, intermediate, and strong field Zeeman effect for the $n = 2$ subspace. Discuss whether the graph is consistent with what you have learned. Be sure to state whether the number of states is consistent in each regime (weak, strong, and intermediate field Zeeman effect).



[1]

[1]Griffiths, David J. *Introduction to Quantum Mechanics.* 2nd ed. Upper Saddle River, NJ: Pearson Prentice Hall, 2005. pg. 249

**** Check your answers to questions 21-24. ****

21. To find a "good" basis, we must diagonalize $\hat{H}'$ in the degenerate subspace of $\hat{H}^0$. This requires diagonalizing the 2×2 block diagonals $-\begin{bmatrix} \gamma - \frac{2}{3}\beta & \frac{\sqrt{2}}{3}\beta \\ \frac{\sqrt{2}}{3}\beta & 5\gamma - \frac{1}{3}\beta \end{bmatrix}$ and $-\begin{bmatrix} \gamma + \frac{2}{3}\beta & \frac{\sqrt{2}}{3}\beta \\ \frac{\sqrt{2}}{3}\beta & 5\gamma + \frac{1}{3}\beta \end{bmatrix}$. The "good" basis will be $\{|\psi_1\rangle, |\psi_2\rangle, |\psi_3\rangle, |\psi_4\rangle, a|\psi_5\rangle + b|\psi_6\rangle, c|\psi_5\rangle + d|\psi_6\rangle, e|\psi_7\rangle + f|\psi_8\rangle, g|\psi_7\rangle + h|\psi_8\rangle\}$, in which a, b, c, d, e, f, g, and h are obtained by diagonalizing the block diagonals.
The corrections to the energies in Table 1 are the diagonal matrix elements of $\hat{H}'$ in the "good" basis.
22.

$$\begin{array}{|rcl|}
\hline
E'_1 &=& 5\gamma - \beta \\
E'_2 &=& 5\gamma + \beta \\
E'_3 &=& \gamma - 2\beta \\
E'_4 &=& \gamma + 2\beta \\
E'_5 &=& 3\gamma - \beta/2 - \sqrt{4\gamma^2 + (2/3)\gamma\beta + \beta^2/4} \\
E'_6 &=& 3\gamma - \beta/2 + \sqrt{4\gamma^2 + (2/3)\gamma\beta + \beta^2/4} \\
E'_7 &=& 3\gamma + \beta/2 - \sqrt{4\gamma^2 - (2/3)\gamma\beta + \beta^2/4} \\
E'_8 &=& 3\gamma + \beta/2 + \sqrt{4\gamma^2 - (2/3)\gamma\beta + \beta^2/4} \\
\hline
\end{array}$$

23. In the strong field limit ($\beta \gg \gamma$), $\sqrt{4\gamma^2 \pm \frac{2}{3}\gamma\beta + \frac{1}{4}\beta^2} \approx \frac{1}{2}\beta \pm \frac{2}{3}\gamma$.

$$\begin{array}{|rcl|}
\hline
E'_1 &=& E_2 - 5\gamma + \beta \\
E'_2 &=& E_2 - 5\gamma - \beta \\
E'_3 &=& E_2 - \gamma + 2\beta \\
E'_4 &=& E_2 - \gamma - 2\beta \\
E'_5 &=& E_2 + \beta - \frac{7}{3}\gamma \\
E'_6 &=& E_2 - \frac{11}{3}\gamma \\
E'_7 &=& E_2 - \frac{11}{3}\gamma \\
E'_8 &=& E_2 - \beta - \frac{7}{3}\gamma \\
\hline
\end{array}$$

In the weak field limit ($\gamma \gg \beta$), $\sqrt{4\gamma^2 \pm \frac{2}{3}\gamma\beta + \frac{1}{4}\beta^2} \approx 2\gamma \pm \frac{1}{6}\beta$.

$$\begin{array}{|rcl|}
\hline
E'_1 &=& E_2 - 5\gamma + \beta \\
E'_2 &=& E_2 - 5\gamma - \beta \\
E'_3 &=& E_2 - \gamma + 2\beta \\
E'_4 &=& E_2 - \gamma - 2\beta \\
E'_5 &=& E_2 - \gamma + \frac{2}{3}\beta \\
E'_6 &=& E_2 - 5\gamma + \frac{1}{3}\beta \\
E'_7 &=& E_2 - \gamma - \frac{2}{3}\beta \\
E'_8 &=& E_2 - 5\gamma - \frac{1}{3}\beta \\
\hline
\end{array}$$

24. In the strong field, we found a two-fold degeneracy remaining in the energy spectrum after the two step approximation. In the weak field, we found no degeneracy remaining in the energy spectrum after the two step approximation. The results are consistent.

If your answers to questions 21-24 do not match with the checkpoint, go back and reconcile any differences.