Name _____

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

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 the perturbative corrections to the energies and energy eigenstates.

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 $\hat{Q}$ must satisfy 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:

1. Identify the degeneracy in the unperturbed Hamiltonian $\hat{H}^0$ in each degenerate subspace corresponding to a principal quantum number n.
2. In order to find the first order corrections to the unperturbed energies of the hydrogen atom in the presence of an external magnetic field, you should be able to determine:
   - the unperturbed Hamiltonian $\hat{H}^0$ in both the coupled and uncoupled representation (for a given principal quantum number n).
   - whether the relativistic correction term $\hat{H}'_r$ is diagonal if the coupled or uncoupled representation is chosen as the basis (for a given principal quantum number n).
   - whether the spin-orbit interaction term $\hat{H}'_{SO}$ is diagonal if the coupled or uncoupled representation is chosen as the basis (for a given principal quantum number n).
   - whether the Zeeman term $\hat{H}'_Z$ is diagonal if the coupled or uncoupled representation is chosen as the basis.
   - whether a "good" angular part of the basis (angular basis) for a given $\hat{H}^0$ and perturbation $\hat{H}'$ is the uncoupled representation, the coupled representation, or any arbitrary orthonormal basis found with linear combinations of a complete set of the coupled or the uncoupled states.

The following questions focus on finding the various quantum numbers for a given principal quantum number n.

1. Answer the following questions in the context of the hydrogen atom with Coulomb interaction between the electron and the nucleus (spin quantum number $s = \frac{1}{2}$ for the electron).
   (a) For $n = 1$, list the possible values of l and the corresponding possible values of m_l.

   (b) For $n = 1$, list the possible values of m_s for $s = \frac{1}{2}$.

   (c) For $n = 1$, list the possible values of j and the corresponding possible values of m_j.

   (d) For $n = 2$, list the possible values of l and the corresponding possible values of m_l.

   (e) For $n = 2$, list the possible values of m_s for $s = \frac{1}{2}$.

   (f) For $n = 2$, list the possible values of j and the corresponding possible values of m_j.

2. How many distinct states $|n\ l\ s\ m_l\ m_s\rangle$ are there in the uncoupled representation for $n = 2$?

3. How many distinct states $|n\ l\ s\ j\ m_j\rangle$ are there in the coupled representation for $n = 2$?

**** Check your answers to questions 1-3: ****

1a. $l = 0; m_l = 0$
1b. $m_s = \frac{1}{2}, -\frac{1}{2}$
1c. $j = \frac{1}{2}; m_j = \frac{1}{2}, -\frac{1}{2}$
1d. $l = 0; m_l = 0$ and $l = 1; m_l = -1, 0, 1$
1e. $m_s = \frac{1}{2}, -\frac{1}{2}$
1f. $j = \frac{1}{2}; m_j = \frac{1}{2}, -\frac{1}{2}$ (appears twice, once for $l = 0$ and once for $l = 1$) and $j = \frac{3}{2}; m_j = \frac{3}{2}, \frac{1}{2}, -\frac{1}{2}, -\frac{3}{2}$
2. There are eight distinct states in the uncoupled representation. $|n \;\; l \;\; s \;\; m_l \;\; m_s\rangle = \{|20\frac{1}{2}0\frac{1}{2}\rangle, |20\frac{1}{2}0-\frac{1}{2}\rangle, |21\frac{1}{2}1\frac{1}{2}\rangle, |21\frac{1}{2}1-\frac{1}{2}\rangle, |21\frac{1}{2}0\frac{1}{2}\rangle, |21\frac{1}{2}0-\frac{1}{2}\rangle, |21\frac{1}{2}-1\frac{1}{2}\rangle, |21\frac{1}{2}-1-\frac{1}{2}\rangle\}$
3. There are eight distinct states in the coupled representation. $|n \; l \; s \; j \; m_j\rangle = \{|21\frac{1}{2}\frac{3}{2}\frac{3}{2}\rangle, |21\frac{1}{2}\frac{3}{2}\frac{1}{2}\rangle, |21\frac{1}{2}\frac{3}{2}-\frac{1}{2}\rangle, |21\frac{1}{2}\frac{3}{2}-\frac{3}{2}\rangle, |21\frac{1}{2}\frac{1}{2}\frac{1}{2}\rangle, |21\frac{1}{2}\frac{1}{2}-\frac{1}{2}\rangle, |20\frac{1}{2}\frac{1}{2}\frac{1}{2}\rangle, |20\frac{1}{2}\frac{1}{2}-\frac{1}{2}\rangle\}$

If any of your answers do not match the checkpoint answers for questions 1-3, go back and reconcile any difference you may have.

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 Unperturbed Hamiltonian for Hydrogen Atom (only accounts for the interaction of the electron with the nucleus via Coulomb attraction)

$$\hat{H}^0 = \frac{\hat{p}^2}{2m} + V(r) = -\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{4\pi\epsilon_0}\left(\frac{1}{r}\right) \tag{2}$$

6.1 Degeneracy of the Unperturbed Hamiltonian $\hat{H}^0$

4. What is one complete set of quantum numbers that describe the eigenstates of $\hat{H}^0$ given by equation (2) (include spin degree of freedom)?

5. What is the unperturbed energy corresponding to $\hat{H}^0$ in equation (2) in terms of the principal quantum number n?

6. Based upon your answers to the two preceding questions, should there be degeneracy in the unperturbed spectrum of hydrogen atom given by equation (2)? Explain.

7. What is the degeneracy of an energy level with energy E_n for a given n (including degeneracy due to spin degrees of freedom)?

8. Circle **ALL** the representations below in which $\hat{H}^0$ is a diagonal matrix (fixed n).

   (a) the coupled representation

   (b) the uncoupled representation

   (c) any arbitrary complete orthonormal basis constructed with linear combinations of states in the coupled representation with the same n.

   (d) any arbitrary complete orthonormal basis constructed with linear combinations of states in the uncoupled representation with the same n.

   (e) Neither the coupled nor the uncoupled representation

   The entire infinite dimensional unperturbed Hamiltonian $\hat{H}^0$ is diagonal if eigenstates of $\hat{H}^0$ are chosen as basis states. In each degenerate subspace of $\hat{H}^0$ (fixed n), the $\hat{H}^0$ matrix is a constant ($-\frac{13.6\text{ eV}}{n^2}$) multiplied by the identity matrix of dimension $2n^2$. For example, the $\hat{H}^0$ matrix in the degenerate subspace for $n = 2$ is shown below when the basis states are eigenstates of $\hat{H}^0$.

$$\hat{H}^0 = \begin{bmatrix} -\frac{13.6\text{eV}}{4} & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & -\frac{13.6\text{eV}}{4} & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & -\frac{13.6\text{eV}}{4} & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & -\frac{13.6\text{eV}}{4} & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & -\frac{13.6\text{eV}}{4} & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & -\frac{13.6\text{eV}}{4} & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & -\frac{13.6\text{eV}}{4} & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & -\frac{13.6\text{eV}}{4} \end{bmatrix} \tag{3}$$

$$= -\frac{13.6\text{eV}}{4} \begin{bmatrix} 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \end{bmatrix} \tag{4}$$

9. (a) For the $\hat{H}^0$ matrix given above for $n = 2$, can you tell whether the coupled representation or the uncoupled representation is chosen as the basis? Explain why you can or cannot tell.

   (b) Can you tell whether the coupled or uncoupled representation was chosen as the basis if you are given the complete infinite dimensional, diagonal matrix for $\hat{H}^0$? Explain your answer.

- In this tutorial, the radial part of the basis states will always chosen to be $R_{nl}(r)$ for the hydrogen atom so the choice of a "good" basis focuses on choosing the angular basis appropriately.

Consider the following conversation regarding whether the unperturbed Hamiltonian $\hat{H}^0$ is diagonal if the coupled or the uncoupled representation is chosen as the angular basis for a given n.
Student 1: The unperturbed Hamiltonian $\hat{H}^0$ in equation (2) is only diagonal when the uncoupled representation is chosen as the basis.
Student 2: I disagree that the uncoupled representation is the only basis in which $\hat{H}^0$ is diagonal. $\hat{H}^0$ will also be diagonal when the coupled representation is chosen as the basis.
Student 3: I agree with Student 2. Angular basis states in both the coupled and the uncoupled representations are eigenstates of $\hat{H}^0$ since $\hat{H}^0$ is spherically symmetric with unperturbed energy only dependent on n. Furthermore, for a fixed n, any arbitrary complete orthogonal basis constructed using linear combinations of a complete set of the coupled or uncoupled states can also be chosen as the angular part of the eigenstates of $\hat{H}^0$ since the unperturbed energy only depends on n as $E_n = -\frac{13.6\text{ eV}}{n^2}$.
Student 2: Yes. And since $\hat{H}^0$ is a diagonal matrix in both the coupled and the uncoupled representations, there is no way to determine whether the basis states were chosen in the coupled or the uncoupled representation in equation (3).
Student 3: The unperturbed Hamiltonian $\hat{H}^0$ is identical in both the coupled and uncoupled representations. In fact, $\hat{H}^0$ is identical so long as, for a fixed n, we choose any arbitrary complete orthonormal basis constructed with linear combinations of states in the coupled or uncoupled representation.

Explain why you agree or disagree with each student.

In one to two sentences, summarize what you have learned about the unperturbed Hamiltonian $\hat{H}^0$ for the hydrogen atom in equation (2) (pertaining to whether $\hat{H}^0$ is diagonal if the coupled representation, the uncoupled representation, or any complete arbitrary 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).

**** Check your answers to questions 4-9: ****

4. n, l, m_l, s, m_s or n, l, s, j, m_j (If you omitted s, that is OK because s is fixed to $s = \frac{1}{2}$ for the electron in the hydrogen atom.)
5. $E_n = -\frac{13.6\text{eV}}{n^2}$
6. Yes, there is degeneracy in the energy spectrum of the hydrogen atom.
7. $2\sum_{l=0}^{n-1}(2l+1) = 2n^2$. (Since for each n, there are $(2l+1)$ values of m_l and the factor of 2 corresponds to the spin degeneracy.)
8. $\hat{H}^0$ will be diagonal if the coupled represenation, the uncoupled representation, or any complete arbitrary orthonormal basis constructed with linear combinations of states in the coupled representation or the uncoupled representation with the same principal quantum number n is chosen as the angular basis.
9. (a) and (b). The $\hat{H}^0$ matrix will be a diagonal matrix with the unperturbed energy E_n along the diagonal if the coupled representation, the uncoupled representation, or any complete arbitrary orthonormal basis constructed with linear combinations of states in the coupled representation or the uncoupled representation with the same principal quantum number n is chosen as the angular basis. There is no way to distinguish between these bases if we are only given the $\hat{H}^0$ matrix since the basis states are eigenstates of $\hat{H}^0$ in all these cases (so long as we do not take linear superpositions of states with different n).

If any of your answers do not match the checkpoint answers for questions 4-9, go back and reconcile any difference you may have.

Summary: The Unperturbed Hamiltonian of the Hydrogen Atom

- For a given unperturbed energy $E_n = -\frac{13.6\text{eV}}{n^2}$, there is a $2n^2$-fold degeneracy, i.e., there are $2n^2$ different states with the same energy E_n.
  - For $n = 2$, there is an 8-fold degeneracy, so 8 distinctly different states have the same energy $-\frac{13.6\text{ eV}}{4}$.
- For a fixed n, the unperturbed Hamiltonian $\hat{H}^0$ is diagonal if the coupled representation, the uncoupled representation, or any complete arbitrary orthonormal basis found with linear combinations of the coupled or uncoupled states with the same principal quantum number n is chosen as the angular basis.

Unperturbed Hamiltonian	Uncoupled Representation (for a fixed n)	Are States in the Uncoupled Representation the Angular Part of an Eigenstate of $\hat{H}^0$?	Coupled Representation (for a fixed n)	Are States in the Coupled Representation the Angular Part of an Eigenstate of $\hat{H}^0$?	Is Any Complete Set of Arbitrary Linear Combinations of Orthonormal States (with the same n) in the Coupled or Uncoupled Representation the Angular Part of an Eigenstate of $\hat{H}^0$	Unperturbed Energy
$\hat{H}^0$	Diagonal	Yes	Diagonal	Yes	Yes	$E_n = -\frac{13.6\text{eV}}{n^2}$

7 Perturbation Theory for the Hydrogen Atom in an External Magnetic Field

- For the hydrogen atom placed in an external magnetic field, we will treat the relativistic correction term $\hat{H}'_r$, the spin-orbit coupling term $\hat{H}'_{SO}$, and the Zeeman term $\hat{H}'_Z$ in the Hamiltonian as perturbations on $\hat{H}^0$ to find the corrections to the unperturbed energies (the Bohr energies $E_n = -\frac{13.6\text{eV}}{n^2}$).
- In order to find the corrections to the energies using perturbation theory when the unperturbed Hamiltonian $\hat{H}^0$ possesses degeneracy, we must ensure that the basis states are "**good**" states.
  - **Definition:** For a given $\hat{H}^0$ and $\hat{H}'$, a **"good"** basis consists of a complete set of eigenstates of $\hat{H}^0$ that diagonalizes $\hat{H}'$ in each degenerate subspace of $\hat{H}^0$ ($\hat{H}^0$ is diagonal everywhere).
- In order to determine if we have a "good" basis in each case, we can start by determining the matrix elements of the relativistic perturbation $\hat{H}'_r$, the spin-orbit perturbation $\hat{H}'_{SO}$, and the Zeeman perturbation $\hat{H}'_Z$ in the coupled and uncoupled representations and check whether the off-diagonal matrix elements of $\hat{H}'$ are zero in each degenerate subspace of $\hat{H}^0$.
- Given a perturbation $\hat{H}'$, if there are **non-zero off-diagonal matrix elements of $\hat{H}'$ in a degenerate subspace of $\hat{H}^0$** in the coupled and the uncoupled representations, neither is a "good" basis for the given $\hat{H}^0$ and $\hat{H}'$. In that case, we must diagonalize the $\hat{H}'$ matrix (in the initial basis) in each degenerate subspace of the $\hat{H}^0$ matrix explicitly to find a "good" basis.

7.1 Relativistic Correction

Before discussing the relativistic correction perturbation term, let's begin by considering a perturbation $\hat{H}' = \zeta\delta(r)$ that is spherically symmetric (in which ζ is a constant such that $\hat{H}'$ has the dimensions of energy). Recall that the unperturbed Hamiltonian $\hat{H}^0$ for the hydrogen atom is also spherically symmetric (with energy only depending on n) and keep this in mind as you consider the following conversation. Also, note that, in general, energies for spherically symmetric potential energies depend on both quantum numbers n and l.

Consider the following conversation regarding whether for the perturbation $\hat{H}' = \zeta\delta(r)$, the coupled representation, the uncoupled representation, or both form a "good" angular basis to find the first order corrections to the unperturbed energies of the hydrogen atom for a fixed n.
Student 1: When a perturbation $\hat{H}' = \zeta\delta(r)$ acts on a hydrogen atom with the unperturbed Hamiltonian $\hat{H}^0 = -\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{4\pi\epsilon_0}\left(\frac{1}{r}\right)$, to find the corrections to the energies, neither the coupled nor the uncoupled representations form a "good" angular basis.
Student 2: I agree. Since $\hat{H}'$ only depends on r, it means that n and l are the only "good" quantum numbers. Thus neither $\{j, m_j\}$ nor $\{m_l, m_s\}$ is a set of "good" quantum numbers. Neither the coupled nor the uncoupled representation forms a "good" angular basis.
Student 3: No, I disagree with both Student 1 and Student 2. Because $\hat{H}'$ is spherically symmetric, its off-diagonal matrix elements will be zero in each degenerate subspace of $\hat{H}^0$ in both the coupled and the uncoupled representations, whichever is chosen as the angular basis for a fixed n. $\hat{H}'$ will be diagonal whether we use the uncoupled representation $|m_l, m_s\rangle$ or the coupled representation $|j, m_j\rangle$ as the basis. This implies that the coupled or uncoupled representation each forms a "good" angular basis to find the corrections to the energies.
Student 4: I agree with Student 3. The reason the off-diagonal matrix elements of $\hat{H}'$ are zero in the degenerate subspace of $\hat{H}^0$ is that for each n, the matrix elements $\langle\psi'|\hat{H}'|\psi\rangle$ can be written as the product of the radial part and the angular part. If we choose the coupled representation, the angular part is $\langle l,\ j,\ m_j|l',\ j',\ m_j'\rangle = \delta_{l,l'}\delta_{j,j'}\delta_{m_j,m_j'}$. If we choose the uncoupled representation, the angular part is $\langle l,\ m_l,\ m_s|l',\ m_l',\ m_s'\rangle = \delta_{l,l'}\delta_{m_l,m_l'}\delta_{m_s,m_s'}$. Either way, the Kronecker delta implies that all off-diagonal matrix elements are zero for a fixed n. Thus, both the coupled and the uncoupled representation, or any arbitrary complete orthonormal basis found with linear combinations of a complete set of the coupled or uncoupled states for the same n and l form a "good" angular basis because $\hat{H}^0$ is diagonal and $\hat{H}' = \zeta\delta(r)$ is diagonal in the degenerate subspace of $\hat{H}^0$.

Explain why you agree or disagree with each student.

10. Is the relativistic correction term $\hat{H}_r' = -\frac{\hat{p}^4}{8m^3c^2}$ diagonal if the coupled representation, the uncoupled representation, or any arbitrary complete orthonormal basis constructed with linear combinations of a complete set of the coupled or uncoupled states with the same n and l is chosen as the angular basis? Explain. [Hint: $\hat{H}_r' = -\frac{\hat{p}^4}{8m^3c^2}$, $\hat{H}^0$, and $\hat{H}' = \zeta\delta(r)$ are all spherically symmetric and energies for spherically symmetric potential energies only depend on the quantum numbers n and l.]

7.2 Spin-Orbit Interaction

- The spin orbit coupling term in the Hamiltonian, $\hat{H}'_{SO}$, is proportional to $\vec{L}\cdot\vec{S}$. We can write $\vec{L}\cdot\vec{S}$ as $\vec{L}\cdot\vec{S} = \frac{1}{2}(\hat{J}^2 - \hat{S}^2 - \hat{L}^2)$ or $\vec{L}\cdot\vec{S} = \frac{1}{2}(\hat{L}_+\hat{S}_- + \hat{L}_-\hat{S}_+) + \hat{L}_z\hat{S}_z$. The expression that will be most beneficial in determining the matrix elements of $\hat{H}'_{SO}$ will depend on whether the coupled representation or the uncoupled representation is chosen as the basis.

11. If the coupled representation is chosen as the basis, which expression for $\vec{L}\cdot\vec{S}$ is more useful when evaluating the matrix elements of $\vec{L}\cdot\vec{S}$? Explain.

12. If the uncoupled representation is chosen as the basis, which expression for $\vec{L}\cdot\vec{S}$ is more useful when evaluating the matrix elements of $\vec{L}\cdot\vec{S}$? Explain.

- Let's evaluate the matrix elements of $\vec{L}\cdot\vec{S}$ in the coupled and the uncoupled representations in order to determine whether $\vec{L}\cdot\vec{S}$ is diagonal in each basis. This will help us later in determining a "good" angular basis when the perturbation is $\hat{H}'_{SO}$ (which is proportional to $\vec{L}\cdot\vec{S}$).

7.2.1 Coupled Representation

The spin-orbit coupling term in the Hamiltonian, $\hat{H}'_{SO}$, is proportional to $\vec{L}\cdot\vec{S}$. The expression $\vec{L}\cdot\vec{S} = \frac{1}{2}(\hat{J}^2 - \hat{S}^2 - \hat{L}^2)$ is most useful when expressing the matrix elements of $\hat{H}'_{SO}$ in the coupled representation.

13. Evaluate the following matrix elements useful for the perturbation $\hat{H}'_{SO}$, in which the states are written in the coupled representation $|n\ l\ s\ j\ m_j\rangle$.

    (a) $\langle 2\ 1\ \frac{1}{2}\ \frac{3}{2}\ \frac{1}{2}|\frac{1}{2}(\hat{J}^2 - \hat{S}^2 - \hat{L}^2)|2\ 1\ \frac{1}{2}\ \frac{3}{2}\ \frac{1}{2}\rangle$

    (b) $\langle 2\ 1\ \frac{1}{2}\ \frac{3}{2}\ \frac{1}{2}|\frac{1}{2}(\hat{J}^2 - \hat{S}^2 - \hat{L}^2)|2\ 1\ \frac{1}{2}\ \frac{3}{2}\ -\frac{1}{2}\rangle$

    (c) $\langle 2\ 1\ \frac{1}{2}\ \frac{3}{2}\ \frac{3}{2}|\frac{1}{2}(\hat{J}^2 - \hat{S}^2 - \hat{L}^2)|2\ 1\ \frac{1}{2}\ \frac{3}{2}\ -\frac{1}{2}\rangle$

14. Is $\hat{H}'_{SO}$ diagonal in each degenerate subspace of $\hat{H}^0$ (for a fixed n) if the coupled representation is chosen as the basis? [Hint: The answers to the preceding question may be helpful.]

7.2.2 Uncoupled Representation

The spin-orbit coupling term in the Hamiltonian, $\hat{H}'_{SO}$, is proportional to $\vec{L} \cdot \vec{S}$. The expression $\vec{L} \cdot \vec{S} = \frac{1}{2}(\hat{L}_+\hat{S}_- + \hat{L}_-\hat{S}_+) + \hat{S}_z\hat{L}_z$ is most useful when expressing the matrix elements of $\hat{H}'_{SO}$ in the uncoupled representation.

15. Evaluate the following expressions. (The states are written in the uncoupled representation $|n\ l\ s\ m_l\ m_s\rangle$).

    (a) $\hat{L}_-|2\ 1\ \frac{1}{2}\ -1\ \frac{1}{2}\rangle$

    (b) $\hat{L}_+|2\ 1\ \frac{1}{2}\ -1\ -\frac{1}{2}\rangle$

    (c) $\hat{S}_-|2\ 1\ \frac{1}{2}\ -1\ \frac{1}{2}\rangle$

    (d) $\hat{S}_+|2\ 1\ \frac{1}{2}\ -1\ \frac{1}{2}\rangle$

16. Evaluate the following matrix elements, in which the states are written in the uncoupled representation $|n\ l\ s\ m_l\ m_s\rangle$.

    (a) $\langle 2\ 1\ \frac{1}{2}\ -1\ \frac{1}{2}|(\hat{L}_+\hat{S}_- + \hat{L}_-\hat{S}_+)|2\ 1\ \frac{1}{2}\ -1\ \frac{1}{2}\rangle$

    (b) $\langle 2\ 1\ \frac{1}{2}\ 0\ -\frac{1}{2}|(\hat{L}_+\hat{S}_- + \hat{L}_-\hat{S}_+)|2\ 1\ \frac{1}{2}\ -1\ \frac{1}{2}\rangle$

17. Now let's evaluate the following matrix elements useful for the perturbation $\hat{H}'_{SO}$. We use the fact that $\vec{L}\cdot\vec{S}$ is proportional to $\frac{1}{2}(\hat{L}_+\hat{S}_- + \hat{L}_-\hat{S}_+) + \hat{L}_z\hat{S}_z$ in the uncoupled representation $|n\ l\ s\ m_l\ m_s\rangle$.

    (a) $\langle 2\ 1\ \frac{1}{2}\ -1\ \frac{1}{2}|\frac{1}{2}(\hat{L}_+\hat{S}_- + \hat{L}_-\hat{S}_+) + \hat{L}_z\hat{S}_z|2\ 1\ \frac{1}{2}\ -1\ \frac{1}{2}\rangle$

    (b) $\langle 2\ 1\ \frac{1}{2}\ 0\ -\frac{1}{2}|\frac{1}{2}(\hat{L}_+\hat{S}_- + \hat{L}_-\hat{S}_+) + \hat{L}_z\hat{S}_z|2\ 1\ \frac{1}{2}\ -1\ \frac{1}{2}\rangle$

18. Is $\hat{H}'_{SO}$ diagonal in each degenerate subspace of $\hat{H}^0$ (for a fixed n) if the uncoupled representation is chosen as the basis? [Hint: The answers to the preceding questions may be helpful.]

Consider the following conversation regarding whether the $\hat{H}'_{SO}$ matrix is a diagonal matrix if, for a fixed n, any arbitrary complete orthonormal basis found with linear combinations of a complete set of the coupled or uncoupled states is chosen as the basis.

Student 1: Since $\hat{H}'_{SO}$ is diagonal in each degenerate subspace of $\hat{H}^0$ in the coupled representation, any linear combinations of states in the coupled representation must also be eigenstates of $\hat{H}'_{SO}$. Thus, $\hat{H}'_{SO}$ is diagonal in the coupled representation in each degenerate subspace of $\hat{H}^0$ and also when any arbitrary complete orthonormal basis is constructed with linear combinations of a complete set of the coupled states.

Student 2: I disagree with Student 1. For example, in general, a linear combination of energy eigenstates is NOT an energy eigenstate. For example, if $|\psi_1\rangle$ and $|\psi_2\rangle$ are eigenstates of the operator $\hat{H}_{SO}$ with eigenvalues E_1 and E_2, respectively, then

$$\begin{aligned} \hat{H}|\psi_1\rangle &= E_1|\psi_1\rangle \\ \hat{H}|\psi_2\rangle &= E_2|\psi_2\rangle. \end{aligned}$$

The linear combination of $|\psi_1\rangle$ and $|\psi_2\rangle$ gives

$$\hat{H}(|\psi_1\rangle + \psi_2\rangle) \;=\; E_1|\psi_1\rangle + E_2|\psi_2\rangle \;\neq\; E(|\psi_1\rangle + |\psi_2\rangle).$$

Thus $\hat{H}(|\psi_1\rangle + \psi_2\rangle) \neq E(|\psi_1\rangle + \psi_2\rangle)$ unless $E_1 = E_2 = E$.

Student 3: I agree with Student 2. If we consider $\hat{H}'_{SO}$, which is proportional to $\frac{1}{2}(\hat{J}^2 - \hat{S}^2 - \hat{L}^2)$, then $\hat{H}'_{SO}$ is diagonal in each degenerate subspace of $\hat{H}^0$ in the coupled representation $|n\ l\ s\ j\ m_j\rangle$. However, in general, $\hat{H}'_{SO}$ is not diagonal in each degenerate subspace of $\hat{H}^0$ if linear combinations of states in the coupled representation, even with a fixed n, is chosen as the basis. For example, if we consider the states $|\psi_1\rangle = |2\ 1\ \frac{1}{2}\ \frac{3}{2}\ \frac{3}{2}\rangle$ and $|\psi_2\rangle = |2\ 0\ \frac{1}{2}\ \frac{1}{2}\ \frac{1}{2}\rangle$

$$\begin{aligned} \tfrac{1}{2}(\hat{J}^2 - \hat{S}^2 - \hat{L}^2)|\psi_1\rangle &= \tfrac{1}{2}(\hat{J}^2 - \hat{S}^2 - \hat{L}^2)\left|2\ 1\ \tfrac{1}{2}\ \tfrac{3}{2}\ \tfrac{3}{2}\right\rangle = \tfrac{\hbar^2}{2}\left|2\ 1\ \tfrac{1}{2}\ \tfrac{3}{2}\ \tfrac{3}{2}\right\rangle \\ \tfrac{1}{2}(\hat{J}^2 - \hat{S}^2 - \hat{L}^2)|\psi_2\rangle &= \tfrac{1}{2}(\hat{J}^2 - \hat{S}^2 - \hat{L}^2)\left|2\ 0\ \tfrac{1}{2}\ \tfrac{1}{2}\ \tfrac{1}{2}\right\rangle = 0\left|2\ 1\ \tfrac{1}{2}\ \tfrac{3}{2}\ \tfrac{3}{2}\right\rangle \end{aligned}$$

But the linear combination of $|\psi_1\rangle$ and $|\psi_2\rangle$, both in the $n = 2$ subspace, is not an eigenstate.

$$\begin{aligned} \tfrac{1}{2}(\hat{J}^2 - \hat{S}^2 - \hat{L}^2)(|\psi_1\rangle + |\psi_2\rangle) &= \tfrac{1}{2}(\hat{J}^2 - \hat{S}^2 - \hat{L}^2)(\left|2\ 1\ \tfrac{1}{2}\ \tfrac{3}{2}\ \tfrac{3}{2}\right\rangle + \left|2\ 0\ \tfrac{1}{2}\ \tfrac{1}{2}\ \tfrac{1}{2}\right\rangle) = \tfrac{\hbar^2}{2}\left|2\ 1\ \tfrac{1}{2}\ \tfrac{3}{2}\ \tfrac{3}{2}\right\rangle \\ &= \tfrac{\hbar^2}{2}|\psi_1\rangle \\ &\neq \text{Constant}(|\psi_1\rangle + |\psi_2\rangle) \end{aligned}$$

Explain why you agree or disagree with each student.

Consider the following conversation regarding whether the $\hat{H}'_{SO}$ is diagonal in each degenerate subspace of $\hat{H}^0$, for a fixed n, when any arbitrary complete orthonormal basis found with linear combinations of the coupled or uncoupled states is chosen as the angular basis.

Student 1: For a fixed n, the spin-orbit interaction term $\hat{H}'_{SO}$ is diagonal if the coupled representation is chosen as the basis. However, $\hat{H}'_{SO}$ is not diagonal in each degenerate subspace of $\hat{H}^0$ if the uncoupled representation or any arbitrary complete orthonormal basis found with linear combinations of the coupled or uncoupled states is chosen as the basis.

Student 2: I disagree. Since $\hat{H}'_{SO}$ is diagonal in each degenerate subspace of $\hat{H}^0$ in the coupled representation, then $\hat{H}'_{SO}$ must also be diagonal in each degenerate subspace of $\hat{H}^0$ if any arbitrary complete orthonormal basis constructed with linear combinations of the coupled states is chosen as the basis.

Student 3: I disagree with Student 2. For example, the states in the uncoupled representation can be constructed with linear combinations of states in the coupled representation. Therefore, if $\hat{H}'_{SO}$ were to be diagonal in each degenerate subspace of $\hat{H}^0$ when any arbitrary complete orthonormal basis constructed with linear combinations of the coupled states is chosen as the basis, then $\hat{H}'_{SO}$ would also be diagonal if the uncoupled representation were chosen as the basis. However, this is not the case because $\hat{H}'_{SO}$ is not diagonal in each degenerate subspace of $\hat{H}^0$ in the uncoupled representation. But, for a fixed n, $\hat{H}'_{SO}$ is diagonal in the coupled representation.

Student 1: I agree with Student 3. Also, if a matrix were diagonal if any arbitrary complete orthonormal basis constructed with linear combinations of the **coupled states** is chosen as the angular basis, then that matrix must also be diagonal when any complete orthogonal angular basis is chosen. Therefore, the matrix must also be diagonal if any arbitrary complete orthonormal basis constructed with linear combinations of the **uncoupled states** is chosen as the basis.

Explain why you agree or disagree with each student.

Student 1 and Student 3 are correct in the preceding conversation.

In one to two sentences, summarize what you have learned about the spin-orbit interaction term $\hat{H}'_{SO}$, which is proportional to $\vec{L} \cdot \vec{S}$ for the hydrogen atom (pertaining to whether $\hat{H}'_{SO}$ is diagonal in each degenerate subspace of $\hat{H}^0$, for a fixed n, if 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 is chosen as the basis).

SUMMARY: Spin-orbit Interaction ($\hat{H}'_{SO}$ proportional to $\vec{L} \cdot \vec{S}$)

- For a given n (in each degenerate subspace of $\hat{H}^0$), the spin-orbit interaction term in the Hamiltonian, $\hat{H}'_{SO}$, **is diagonal** if the **coupled representation** is chosen as the angular basis.
- For a given n (in each degenerate subspace of $\hat{H}^0$), the spin-orbit interaction term in the Hamiltonian, $\hat{H}'_{SO}$, **is NOT diagonal** if the **uncoupled representation** is chosen as the basis. (You must have found a non-zero off-diagonal matrix element in question 17.)

Hamiltonian $\hat{H}$	Uncoupled Representation (for a fixed n)	Are States in the Uncoupled Representation the Angular Part of Eigenstates of $\hat{H}^0$?	Coupled Representation (for a fixed n)	Are States in the Coupled Representation the Angular Part of Eigenstates of $\hat{H}^0$?	Is Any Arbitrary Linear Combination of Orthonormal States (with the same n and l) in the Coupled or Uncoupled Representation the Angular Part of an Eigenstate of $\hat{H}$
$\hat{H}^0$	Diagonal	Yes	Diagonal	Yes	Yes
$\hat{H}'_r$	Diagonal	Yes	Diagonal	Yes	Yes
$\hat{H}'_{SO}$	Not Diagonal	No	Diagonal	Yes	No

**** Check your answers to questions 10-18: ****

10. For a given n, $\hat{H}'_r$ in each degenerate subspace of $\hat{H}^0$ will be diagonal if 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 n and l is chosen as the angular basis.
11. If the coupled representation is chosen as the angular basis, $\vec{L}\cdot\vec{S} = \frac{1}{2}(\hat{J}^2 - \hat{S}^2 - \hat{L}^2)$ should be used since $|j,\ m_j\rangle$ is an eigenstate of $\hat{J}^2$, $\hat{S}^2$, and $\hat{L}^2$
12. If the uncoupled representation is chosen as the basis, $\vec{L}\cdot\vec{S} = \frac{1}{2}(\hat{L}_+\hat{S}_- + \hat{L}_-\hat{S}_+) + \hat{L}_z\hat{S}_z$ should be used since $|m_l,\ m_s\rangle$ is an eigenstate of $\hat{L}_z$ and $\hat{S}_z$ and the raising and lowering operators $\hat{L}_\pm$ and $\hat{S}_\pm$ act on the uncoupled states $|m_l,\ m_s\rangle$.
13a. $\frac{1}{2}\hbar^2$
13b. 0
13c. 0
14. For a fixed n, $\hat{H}'_{SO}$ is diagonal if the coupled representation is chosen as the basis. If the basis states are chosen in the coupled representation ($|l,\ j,\ m_j\rangle$) in the order $|\psi_1\rangle = |1,\ \frac{3}{2},\ \frac{3}{2}\rangle$, $|\psi_2\rangle = |1,\ \frac{3}{2},\ \frac{1}{2}\rangle$, $|\psi_3\rangle = |1,\ \frac{3}{2},\ -\frac{1}{2}\rangle$, $|\psi_4\rangle = |1,\ \frac{3}{2},\ -\frac{3}{2}\rangle$, $|\psi_5\rangle = |1,\ \frac{1}{2},\ \frac{1}{2}\rangle$, $|\psi_6\rangle = |1,\ \frac{1}{2},\ -\frac{1}{2}\rangle$, $|\psi_7\rangle = |0,\ \frac{1}{2},\ \frac{1}{2}\rangle$ and $|\psi_8\rangle = |0,\ \frac{1}{2},\ -\frac{1}{2}\rangle$, the $\hat{H}'_{SO}$ matrix for $n = 2$ is

$$\hat{H}'_{SO} = A\frac{1}{r^3}(\vec{L}\cdot\vec{S}) = \frac{2E_2^2}{3mc^2}\begin{bmatrix} 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & -2 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & -2 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \end{bmatrix}$$

15a. 0
15b. $\sqrt{2}\hbar|2\ 1\ \frac{1}{2}\ 0\ -\frac{1}{2}\rangle$
15c. $\hbar|2\ 1\ \frac{1}{2}\ -1\ -\frac{1}{2}\rangle$
15d. 0
16a. 0
16b. $\sqrt{2}\hbar^2$
17a. $-\frac{1}{2}\hbar^2$
17b. $\frac{\sqrt{2}}{2}\hbar^2$
18. For a fixed n, $\hat{H}'_{SO}$ is not diagonal if the uncoupled representation is chosen as the basis. 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 $|\psi_8\rangle = |1,\ -1,\ -\frac{1}{2}\rangle$, the $\hat{H}'_{SO}$ matrix is

$$\hat{H}'_{SO} = A\frac{1}{r^3}(\vec{L}\cdot\vec{S}) = \frac{\alpha^4 mc^2}{96}\begin{bmatrix} 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 & \sqrt{2} & 0 & 0 & 0 \\ 0 & 0 & 0 & \sqrt{2} & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & \sqrt{2} & 0 \\ 0 & 0 & 0 & 0 & 0 & \sqrt{2} & -1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \end{bmatrix}$$

If any of your answers do not match the checkpoint answers to questions 10-18, go back and reconcile any difference you may have.[1]

[1]For a fixed n, $\hat{H}'_{SO}$ is also diagonal if an orthonormal basis includes certain **special** linear combinations of states in the coupled representation corresponding to each degenerate subspace of $\hat{H}'_{SO}$. However, $\hat{H}'_{SO}$ is **NOT diagonal** if any arbitrary complete orthonormal basis constructed with linear combinations of states in the coupled representation with the same n is chosen as the angular basis. We will not focus on these issues in this tutorial since our goal is to find one "good" basis for perturbation theory.

7.3 Zeeman Effect

If the external magnetic field is chosen to be a uniform, time independent field along the $\hat{z}$ direction given by $\vec{B} = B_{ext}\hat{z}$, the Zeeman term in the Hamiltonian is

$$\hat{H}'_Z = \frac{\mu_B B_{ext}}{\hbar}(\hat{L}_z + 2\hat{S}_z). \tag{5}$$

Consider the following conversation regarding simplifying the hydrogen atom basis states in the coupled or uncoupled representation.
Student 1: When we write states in the coupled or uncoupled representation, we must write all the quantum numbers that represent the state $|n\ l\ s\ j\ m_j\rangle$ or $|n\ l\ s\ m_l\ m_s\rangle$.
Student 2: If we are dealing with an operator acting on the states that only depends on a subset of all the quantum numbers, we can express the states with only the relevant quantum numbers and suppress the other quantum numbers for convenience. Consider $\hat{H}'_Z = \frac{\mu_B B_{ext}}{\hbar}(\hat{L}_z + 2\hat{S}_z)$, where the relevant quantum numbers are m_l and m_s if n and s are fixed. We can abbreviate the state $|n\ l\ s\ m_l\ m_s\rangle$ as $|l,\ m_l,\ m_s\rangle$.
Student 3: I agree with Student 2. Additionally, if we know we are restricted to a particular set of quantum numbers or can determine the quantum numbers from the context, we can suppress those quantum numbers without loss of generality. For example, if we are considering an electron in the $n = 2$ degenerate subspace of $\hat{H}^0$, the state in the coupled representation $|n\ l\ s\ j\ m_j\rangle = |2\ 1\ \frac{1}{2}\ \frac{3}{2}\ \frac{3}{2}\rangle$ can be written as $|l,\ j,\ m_j\rangle = |1,\ \frac{3}{2},\ \frac{3}{2}\rangle$ since $s = \frac{1}{2}$.

Explain why you agree or disagree with each student.

7.3.1 Uncoupled Representation

19. Evaluate the following matrix elements of $\hat{H}'_Z$ in which the states are written in the uncoupled representation $|l,\ m_l,\ m_s\rangle$.

    (a) $\langle 0,\ 0,\ \frac{1}{2}|\frac{\mu_B B_{ext}}{\hbar}(\hat{L}_z + 2\hat{S}_z)|0,\ 0,\ \frac{1}{2}\rangle$

    (b) $\langle 0,\ 0,\ \frac{1}{2}|\frac{\mu_B B_{ext}}{\hbar}(\hat{L}_z + 2\hat{S}_z)|0,\ 0,\ -\frac{1}{2}\rangle$

    (c) $\langle 1,\ 1,\ \frac{1}{2}|\frac{\mu_B B_{ext}}{\hbar}(\hat{L}_z + 2\hat{S}_z)|1,\ 1,\ \frac{1}{2}\rangle$

    (d) $\langle 1,\ 1,\ \frac{1}{2}|\frac{\mu_B B_{ext}}{\hbar}(\hat{L}_z + 2\hat{S}_z)|1,\ -1,\ -\frac{1}{2}\rangle$

20. Is the $\hat{H}'_Z = \frac{\mu_B B_{ext}}{\hbar}(\hat{L}_z + 2\hat{S}_z)$ matrix a diagonal matrix if the uncoupled representation is chosen as the basis? [Hint: The answers to the preceding question may be helpful.]

7.3.2 Coupled Representation

In the following table, the angular states for $n = 2$ are listed 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.

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

21. Determine the following matrix elements given in the coupled representation ($|l,\ j,\ m_j\rangle$). If you need to first express the states in the uncoupled representation ($|l,\ m_l\rangle|s,\ m_s\rangle$) you can use the preceding table.

(a) $\langle\psi_3|\frac{\mu_B B_{ext}}{\hbar}(\hat{L}_z + 2\hat{S}_z)|\psi_3\rangle = \langle 1,\ \frac{3}{2},\ \frac{3}{2}|\frac{\mu_B B_{ext}}{\hbar}(\hat{L}_z + 2\hat{S}_z)|1,\ \frac{3}{2},\ \frac{3}{2}\rangle$

(b) $\langle\psi_5|\frac{\mu_B B_{ext}}{\hbar}(\hat{L}_z + 2\hat{S}_z)|\psi_6\rangle = \langle 1,\ \frac{3}{2},\ \frac{1}{2}|\frac{\mu_B B_{ext}}{\hbar}(\hat{L}_z + 2\hat{S}_z)|1,\ \frac{1}{2},\ \frac{1}{2}\rangle$

(c) $\langle\psi_5|\frac{\mu_B B_{ext}}{\hbar}(\hat{L}_z + 2\hat{S}_z)|\psi_1\rangle = \langle 1,\ \frac{3}{2},\ \frac{1}{2}|\frac{\mu_B B_{ext}}{\hbar}(\hat{L}_z + 2\hat{S}_z)|0,\ \frac{1}{2},\ \frac{1}{2}\rangle$

22. Is the $\hat{H}'_Z = \frac{\mu_B B_{ext}}{\hbar}(\hat{L}_z + 2\hat{S}_z)$ matrix a diagonal matrix if the coupled representation is chosen as the basis? [Hint: The answers to the preceding question may be helpful.]

Consider the following conversation regarding whether the $\hat{H}'_Z$ matrix is a diagonal matrix if any arbitrary complete orthonormal basis found with linear combinations of the coupled or uncoupled states is chosen as the basis.

Student 1: Since states in the uncoupled representation are eigenstates of $\hat{H}'_Z$, any linear combination of states in the uncoupled representation must also be eigenstates of $\hat{H}'_Z$. Thus, $\hat{H}'_Z$ is diagonal in the uncoupled representation and also when any arbitrary complete orthonormal basis is constructed with a linear combination of a complete set of the uncoupled states.

Student 2: I disagree with Student 1. If we consider $\hat{H}'_Z$ which is proportional to $(\hat{L}_z + 2\hat{S}_z)$, then states in the uncoupled representation $|n\ l\ s\ m_l\ m_s\rangle$ are eigenstates of $\hat{H}'_Z$. However, in general, linear combinations of states in the uncoupled representation are NOT eigenstates of $\hat{H}'_Z$. For example, if we consider the states $|\psi_1\rangle = |2\ 0\ \frac{1}{2}\ 0\frac{1}{2}\rangle$ and $|\psi_2\rangle = |2\ 0\ \frac{1}{2}\ 0\ -\frac{1}{2}\rangle$

$$
\begin{aligned}
(\hat{L}_z + 2\hat{S}_z)|\psi_1\rangle &= (\hat{L}_z + 2\hat{S}_z)\left|2\ 0\tfrac{1}{2}\ 0\ \tfrac{1}{2}\right\rangle = \hbar\left|2\ \ 0\tfrac{1}{2}\ 0\ \tfrac{1}{2}\right\rangle \\
(\hat{L}_z + 2\hat{S}_z)|\psi_2\rangle &= (\hat{L}_z + 2\hat{S}_z)\left|2\ 0\tfrac{1}{2}\ 0\ -\tfrac{1}{2}\right\rangle = -\hbar\left|2\ 0\tfrac{1}{2}\ 0\ -\tfrac{1}{2}\right\rangle
\end{aligned}
$$

But the linear combination of $|\psi_1\rangle$ and $|\psi_2\rangle$ is not an eigenstate.

$$
\begin{aligned}
(\hat{L}_z + 2\hat{S}_z)(|\psi_1\rangle + |\psi_2\rangle) &= (\hat{L}_z + 2\hat{S}_z)\left(\left|2\ 0\tfrac{1}{2}\ 0\tfrac{1}{2}\right\rangle + \left|2\ 0\ \tfrac{1}{2}\ 0\ -\tfrac{1}{2}\right\rangle\right) \\
&= \hbar\left[\left|2\ 0\tfrac{1}{2}\ 0\ \tfrac{1}{2}\right\rangle - \left|2\ 0\tfrac{1}{2}\ 0\ -\tfrac{1}{2}\right\rangle\right] \\
&= \hbar\left[|\psi_1\rangle - |\psi_2\rangle\right] \\
&\neq \text{Constant}(|\psi_1\rangle + |\psi_2\rangle)
\end{aligned}
$$

Explain why you agree or disagree with each student.

Consider the following conversation regarding whether the $\hat{H}'_Z$ matrix is a diagonal matrix if any arbitrary complete orthonormal basis constructed with linear combinations of a complete set of the coupled or uncoupled states is chosen as the angular basis.

Student 1: The Zeeman term $\hat{H}'_Z$ is diagonal if the uncoupled representation is chosen as the basis. However, $\hat{H}'_Z$ is not diagonal if the coupled representation or any arbitrary complete orthonormal basis constructed with linear combinations of the coupled or uncoupled states is chosen as the angular basis.

Student 2: I disagree. Since $\hat{H}'_Z$ is diagonal in the uncoupled representation, then $\hat{H}'_Z$ must also be diagonal if any arbitrary complete orthonormal basis constructed with linear combinations of the uncoupled states is chosen as the basis.

Student 3: I disagree with Student 2. For example, the states in the coupled representation can be constructed with linear combinations of states in the uncoupled representation. Therefore, if $\hat{H}'_Z$ were to be diagonal when any arbitrary complete orthonormal basis constructed with linear combinations of the uncoupled states is chosen as the basis, then $\hat{H}'_Z$ would also be diagonal if the coupled representation were chosen as the basis. However, this is not the case because $\hat{H}'_Z$ is not diagonal in the coupled representation. But $\hat{H}'_Z$ is diagonal in the uncoupled representation.

Student 1: I agree with Student 3. Also, if a matrix is diagonal if any arbitrary complete orthonormal basis constructed with linear combinations of the **coupled states** is chosen as the basis, then that matrix must also be diagonal when any complete orthonormal basis is chosen. Therefore, the matrix must also be diagonal if any arbitrary orthonormal angular basis constructed with a linear combination of the **uncoupled states** is chosen as the angular basis.

Explain why you agree or disagree with each student.

In one to two sentences, summarize what you have learned about the Zeeman term $\hat{H}'_Z = \frac{\mu_B B_{ext}}{\hbar}(\hat{L}_z + 2\hat{S}_z)$ for the hydrogen atom (pertaining to whether $\hat{H}'_Z$ is diagonal if the coupled representation, the uncoupled representation, or any arbitrary complete orthonormal basis constructed 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).

SUMMARY: Zeeman Effect

- For a given n, the Zeeman term in the Hamiltonian, $\hat{H}'_Z = \frac{\mu_B B_{ext}}{\hbar}(\hat{L}_z + 2\hat{S}_z)$, **is diagonal** if the **uncoupled representation** is chosen as the angular basis.
- For a given n, the Zeeman term in the Hamiltonian, $\hat{H}'_Z = \frac{\mu_B B_{ext}}{\hbar}(\hat{L}_z + 2\hat{S}_z)$, **is NOT diagonal** if the **coupled representation** is chosen as the angular basis. (You must have found some non-zero off-diagonal matrix elements in question 21.)

Hamiltonian $\hat{H}$	Uncoupled Representation (for a fixed n)	Are States in the Uncoupled Representation the Angular Part of Eigenstates of $\hat{H}^0$?	Coupled Representation (for a fixed n)	Are States in the Coupled Representation the Angular Part of Eigenstates of $\hat{H}^0$?	Is Any Arbitrary Linear Combination of Orthonormal States (with the same n and l) in the Coupled or Uncoupled Representation the Angular Part of an Eigenstate of $\hat{H}$
$\hat{H}^0$	Diagonal	Yes	Diagonal	Yes	Yes
$\hat{H}'_r$	Diagonal	Yes	Diagonal	Yes	Yes
$\hat{H}'_{SO}$	Not Diagonal	No	Diagonal	Yes	No
$\hat{H}'_Z$	Diagonal	Yes	Not Diagonal	No	No

**** Check your answers to questions 19-22: ****

19a. $\mu_B B_{ext}$
19b. 0
19c. $2\mu_B B_{ext}$
19d. 0
20. $\hat{H}'_Z$ is diagonal if the uncoupled representation is chosen as the basis. 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 $|\psi_8\rangle = |1,\ -1,\ -\frac{1}{2}\rangle$, the $\hat{H}'_Z$ matrix is

$$\hat{H}'_Z = \frac{\mu_B B_{ext}}{\hbar}(\hat{L}_z + 2\hat{S}_z) = \mu_B B_{ext} \begin{bmatrix} 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 2 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & -2 \end{bmatrix}$$

21a. $2\mu_B B_{ext}$
21b. $-\frac{\sqrt{2}}{3}\mu_B B_{ext}$
21c. 0
22. $\hat{H}'_Z$ is not diagonal if the coupled representation is chosen as the basis. If the basis states are chosen in the coupled representation ($|l,\ j,\ m_j\rangle$) in the order $|\psi_1\rangle = |1,\ \frac{3}{2},\ \frac{3}{2}\rangle$, $|\psi_2\rangle = |1,\ \frac{3}{2},\ \frac{1}{2}\rangle$, $|\psi_3\rangle = |1,\ \frac{3}{2},\ -\frac{1}{2}\rangle$, $|\psi_4\rangle = |1,\ \frac{3}{2},\ -\frac{3}{2}\rangle$, $|\psi_5\rangle = |1,\ \frac{1}{2},\ \frac{1}{2}\rangle$, $|\psi_6\rangle = |1,\ \frac{1}{2},\ -\frac{1}{2}\rangle$, $|\psi_7\rangle = |0,\ \frac{1}{2},\ \frac{1}{2}\rangle$ and $|\psi_8\rangle = |0,\ \frac{1}{2},\ -\frac{1}{2}\rangle$, the $\hat{H}'_Z$ matrix is

$$\hat{H}'_Z = \frac{\mu_B B_{ext}}{\hbar}(\hat{L}_z + 2\hat{S}_z) = \mu_B B_{ext} \begin{bmatrix} 2 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & \frac{2}{3} & 0 & 0 & -\frac{\sqrt{2}}{3} & 0 & 0 & 0 \\ 0 & 0 & -\frac{2}{3} & 0 & 0 & -\frac{\sqrt{2}}{3} & 0 & 0 \\ 0 & 0 & 0 & -2 & 0 & 0 & 0 & 0 \\ 0 & -\frac{\sqrt{2}}{3} & 0 & 0 & \frac{1}{3} & 0 & 0 & 0 \\ 0 & 0 & -\frac{\sqrt{2}}{3} & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & -1 \end{bmatrix}$$

If any of your answers do not match the checkpoint answers to questions 19-22, go back and reconcile any differences you may have.[2]

[2] $\hat{H}'_Z$ is also diagonal if an orthonormal basis includes certain **special** linear combination of states in the uncoupled representation corresponding to each degenerate subspace of $\hat{H}'_Z$. However, $\hat{H}'_Z$ is **NOT diagonal** if any arbitrary complete orthonormal basis constructed with linear combinations of states in the uncoupled representation with the same n is chosen as the basis. We will not focus on these issues in this tutorial since our goal is to find one "good" basis for perturbation theory.

8 Choosing a "Good" Basis

To find the first order corrections to the energies of the hydrogen atom in perturbation theory, we must first choose a "good" angular basis for the given $\hat{H}^0$ and $\hat{H}'$. Depending on the nature of the perturbation, the coupled representation, the uncoupled representation, or any arbitrary complete orthonormal basis constructed with linear combinations of the coupled or uncoupled states can form the "good" angular basis. Recall that the determination of a "good" basis depends on both $\hat{H}^0$ and $\hat{H}'$.

23. In the following questions, a perturbation $\hat{H}'$ acts on a hydrogen atom with the unperturbed Hamiltonian $\hat{H}^0 = -\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{4\pi\epsilon_0}\left(\frac{1}{r}\right)$. For each of the following perturbations, circle **ALL** of the representations that form a "good" angular basis. Assume that for all cases, the principal quantum number is fixed to $n = 2$. (A and C are constants which makes the dimensions of $\hat{H}'$ that of energy in each case.)

    (a) $\hat{H}' = C\delta(r)$

        i. Coupled representation
        ii. Uncoupled representation
        iii. Any arbitrary complete orthonormal basis constructed with linear combinations of states in the coupled representation with the same l (i.e., states with different l values are not mixed),
        iv. Any arbitrary complete orthonormal basis constructed with linear combinations of states in the uncoupled representation with the same l (i.e., states with different l values are not mixed),
        v. Neither coupled nor uncoupled representation

    (b) $\hat{H}' = C\hat{L}_z$

        i. Coupled representation
        ii. Uncoupled representation
        iii. Any arbitrary complete orthonormal basis constructed with linear combinations of states in the coupled representation with the same l (i.e., states with different l values are not mixed),
        iv. Any arbitrary complete orthonormal basis constructed with linear combinations of states in the uncoupled representation with the same l (i.e., states with different l values are not mixed),
        v. Neither coupled nor uncoupled representation

    (c) $\hat{H}' = C\hat{J}_z$

        i. Coupled representation
        ii. Uncoupled representation
        iii. Any arbitrary complete orthonormal basis constructed with linear combinations of states in the coupled representation with the same l (i.e., states with different l values are not mixed),
        iv. Any arbitrary complete orthonormal basis constructed with linear combinations of states in the uncoupled representation with the same l (i.e., states with different l values are not mixed),
        v. Neither coupled nor uncoupled representation

    (d) $\hat{H}' = C(\hat{L}_z + 2\hat{S}_z)$

        i. Coupled representation
        ii. Uncoupled representation
        iii. Any arbitrary complete orthonormal basis constructed with linear combinations of states in the coupled representation with the same l (i.e., states with different l values are not mixed),
        iv. Any arbitrary complete orthonormal basis constructed with linear combinations of states in the uncoupled representation with the same l (i.e., states with different l values are not mixed),
        v. Neither coupled nor uncoupled representation

(e) $\hat{H}' = C(\hat{L}_z + \hat{S}_z)$

i. Coupled representation
ii. Uncoupled representation
iii. Any arbitrary complete orthonormal basis constructed with linear combinations of states in the coupled representation with the same l (i.e., states with different l values are not mixed),
iv. Any arbitrary complete orthonormal basis constructed with linear combinations of states in the uncoupled representation with the same l (i.e., states with different l values are not mixed),
v. Neither coupled nor uncoupled representation

(f) $\hat{H}' = C(\vec{L} \cdot \vec{S})$

i. Coupled representation
ii. Uncoupled representation
iii. Any arbitrary complete orthonormal basis constructed with linear combinations of states in the coupled representation with the same l (i.e., states with different l values are not mixed),
iv. Any arbitrary complete orthonormal basis constructed with linear combinations of states in the uncoupled representation with the same l (i.e., states with different l values are not mixed),
v. Neither coupled nor uncoupled representation

(g) $\hat{H}' = C\left(\frac{1}{r^n}\right)$

i. Coupled representation
ii. Uncoupled representation
iii. Any arbitrary complete orthonormal basis constructed with linear combinations of states in the coupled representation with the same l (i.e., states with different l values are not mixed),
iv. Any arbitrary complete orthonormal basis constructed with linear combinations of states in the uncoupled representation with the same l (i.e., states with different l values are not mixed),
v. Neither coupled nor uncoupled representation

(h) $\hat{H}' = C\hat{p}^2$

i. Coupled representation
ii. Uncoupled representation
iii. Any arbitrary complete orthonormal basis constructed with linear combinations of states in the coupled representation with the same l (i.e., states with different l values are not mixed),
iv. Any arbitrary complete orthonormal basis constructed with linear combinations of states in the uncoupled representation with the same l (i.e., states with different l values are not mixed),
v. Neither coupled nor uncoupled representation

(i) $\hat{H}' = C\hat{p}^4$

i. Coupled representation
ii. Uncoupled representation
iii. Any arbitrary complete orthonormal basis constructed with linear combinations of states in the coupled representation with the same l (i.e., states with different l values are not mixed),
iv. Any arbitrary complete orthonormal basis constructed with linear combinations of states in the uncoupled representation with the same l (i.e., states with different l values are not mixed),
v. Neither coupled nor uncoupled representation

(j) $\hat{H}' = C(\hat{L}_z + 2\hat{S}_z) + A(\vec{L} \cdot \vec{S})$

i. Coupled representation
ii. Uncoupled representation
iii. Any arbitrary complete orthonormal basis constructed with linear combinations of states in the coupled representation with the same l (i.e., states with different l values are not mixed),
iv. Any arbitrary complete orthonormal basis constructed with linear combinations of states in the uncoupled representation with the same l (i.e., states with different l values are not mixed),
v. Neither coupled nor uncoupled representation

Consider the following conversation regarding determining a "good" angular basis for the perturbations $\hat{H}' = C(\hat{L}_z + \hat{S}_z)$ and $\hat{H}' = C\hat{J}_z$ acting on the hydrogen atom with the unperturbed Hamiltonian $\hat{H}^0 = -\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{4\pi\epsilon_0}\left(\frac{1}{r}\right)$.

Student 1: The uncoupled representation forms a "good" basis when the perturbation $\hat{H}' = C(\hat{L}_z + \hat{S}_z)$ acts on a hydrogen atom with the unperturbed Hamiltonian $\hat{H}^0 = -\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{4\pi\epsilon_0}\left(\frac{1}{r}\right)$.

Student 2: I agree. And the coupled representation forms a "good" basis when the perturbation $\hat{H}' = C\hat{J}_z$ acts on a hydrogen atom with the unperturbed Hamiltonian $\hat{H}^0 = -\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{4\pi\epsilon_0}\left(\frac{1}{r}\right)$.

Student 3: I agree with both Student 1 and Student 2, but both students are overlooking the fact that $\hat{J}_z = \hat{L}_z + \hat{S}_z$. The perturbation $\hat{H}' = C\hat{J}_z$ is identical to the perturbation $\hat{H}' = C(\hat{L}_z + \hat{S}_z)$. Therefore, both the coupled and uncoupled representations form a "good" basis for the perturbation $\hat{H}' = C(\hat{L}_z + \hat{S}_z) = C\hat{J}_z$.

Explain why you agree or disagree with each student.

Consider the following statement regarding whether any arbitrary orthonormal basis constructed with linear combinations of states in the coupled or uncoupled representation with the same principal quantum number n forms a "good" angular basis if both the coupled and uncoupled representations form a "good" angular basis.

Student 1: Since both the uncoupled and coupled representations form a "good" basis when the perturbation is $\hat{H}' = C(\hat{L}_z + \hat{S}_z)$, then any arbitrary complete orthonormal basis constructed with linear combinations of states in the uncoupled representation with the same n must form a "good" basis. Also, any arbitrary complete orthonormal basis constructed with linear combinations of states in the coupled representation with the same n must form a "good" basis.

Explain why you agree or disagree with the student.

Consider the following conversation regarding whether for the perturbation $\hat{H}' = C(\hat{L}_z + 2\hat{S}_z) + A(\vec{L} \cdot \vec{S})$, the coupled representation, the uncoupled representation, both the coupled and uncoupled representations, or neither the coupled nor uncoupled representation form a "good" angular basis to find the first order corrections to the unperturbed energies of the hydrogen atom.

Student 1: When the perturbation $\hat{H}' = C(\hat{L}_z + 2\hat{S}_z) + A(\vec{L} \cdot \vec{S})$ acts on a hydrogen atom with the unperturbed Hamiltonian $\hat{H}^0 = -\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{4\pi\epsilon_0}\left(\frac{1}{r}\right)$, to find the corrections to the energies, neither the coupled nor the uncoupled representations form a "good" angular basis.

Student 2: I disagree. Both the coupled and the uncoupled representations are "good" angular bases since $C(\hat{L}_z + 2\hat{S}_z)$ is diagonal in the coupled representation and $A(\vec{L} \cdot \vec{S})$ is diagonal in the uncoupled representation.

Student 3: I agree with Student 1. Neither the coupled nor uncoupled representation form a "good" angular basis to find the first order corrections to the unperturbed energies of the hydrogen atom due to the perturbation $\hat{H}' = C(\hat{L}_z + 2\hat{S}_z) + A(\vec{L} \cdot \vec{S})$. However, a "good" angular basis will be made up of some special linear combinations of states in the coupled representation that diagonalizes $\hat{H}'$ in each degenerate subspace of $\hat{H}^0$. These same angular basis states could be expressed as special linear combinations of states in the uncoupled representation.

Explain why you agree or disagree with each student.

**** Check your answers to question 23: ****

23a. i, ii, iii, iv
23b. ii
23c. i, ii
23d. ii
23e. i, ii
23f. i
23g. i, ii, iii, iv
23h. i, ii, iii, iv
23i. i, ii, iii, iv
23j. v

If any of your answers do not match the checkpoint answers to question 23, go back and reconcile any difference you may have.