Quantum Mechanics: Interesting Problems

Perturbations and Zeeman Splitting

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Problem 1

A spin-1 system has the Hamiltonian, $\hat{H} = A\hat{S}_z^2 + B\left(\hat{S}_x^2 - \hat{S}_y^2\right)$, with $B \ll A$.

(a) Write down the unperturbed Hamiltonian, $\hat{H}_0$, and solve for its eigenenergies and eigenstates.
(b) Find the perturbed energy levels to first order.
(c) Solve the problem exactly by diagonalizing the Hamiltonian. Compare the results to those obtained from perturbation theory.
(d) What does your answer in part (c) imply about higher order corrections for this system?

Solution

In this question, we shall use the following lemmas:

For $s = 1$, eigenvalues of $\hat{S}_z$ are 1,0,-1. We can thus construct the following operator

$$\hat{S}_z = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{bmatrix} \tag{1}$$

We then find the 'raising' and 'lowering' operators, $\hat{S}_+$ and $\hat{S}_-$ respectively. Knowing that

$$\hat{S}_\pm|m\rangle = \hbar\sqrt{s(s+1) - m(m\pm 1)}|m\pm 1\rangle \tag{2}$$

We can compute

$$\hat{S}_+ = \begin{bmatrix} \langle 1|\hat{S}_+|1\rangle & \langle 1|\hat{S}_+|0\rangle & \langle 1|\hat{S}_+|-1\rangle \\ \langle 0|\hat{S}_+|1\rangle & \langle 0|\hat{S}_+|0\rangle & \langle 0|\hat{S}_+|-1\rangle \\ \langle -1|\hat{S}_+|1\rangle & \langle -1|\hat{S}_+|0\rangle & \langle -1|\hat{S}_+|-1\rangle \end{bmatrix} = \hbar \begin{bmatrix} 0 & \sqrt{2} & 0 \\ 0 & 0 & \sqrt{2} \\ 0 & 0 & 0 \end{bmatrix} \tag{3}$$

$$\hat{S}_+ = \begin{bmatrix} \langle 1|\hat{S}_-|1\rangle & \langle 1|\hat{S}_-|0\rangle & \langle 1|\hat{S}_+|-1\rangle \\ \langle 0|\hat{S}_-|1\rangle & \langle 0|\hat{S}_-|0\rangle & \langle 0|\hat{S}_-|-1\rangle \\ \langle -1|\hat{S}_-|1\rangle & \langle -1|\hat{S}_-|0\rangle & \langle -1|\hat{S}_-|-1\rangle \end{bmatrix} = \hbar \begin{bmatrix} 0 & 0 & 0 \\ \sqrt{2} & 0 & 0 \\ 0 & \sqrt{2} & 0 \end{bmatrix} \tag{4}$$

We then use $\hat{S}_+$ and $\hat{S}_-$ to find $\hat{S}_x$ and $\hat{S}_y$:

$$\hat{S}_x = \frac{1}{2}\left(\hat{S}_+ + \hat{S}_-\right) = \frac{\hbar}{\sqrt{2}} \begin{bmatrix} 0 & 1 & 0 \\ 1 & 0 & 1 \\ 0 & 1 & 0 \end{bmatrix} \tag{5}$$

$$\hat{S}_y = \frac{1}{2i}\left(\hat{S}_+ - \hat{S}_-\right) \frac{i\hbar}{\sqrt{2}} \begin{bmatrix} 0 & -1 & 0 \\ 1 & 0 & -1 \\ 0 & 1 & 0 \end{bmatrix} \tag{6}$$

Part a

Since $B \ll A$, we can write

$$\hat{H} \approx \hat{H}_0 = A\hat{S}_z^2 = \boxed{A\hbar^2 \begin{bmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 1 \end{bmatrix}} \tag{7}$$

It is evident that eigenenergies are values on its diagonal, since it is already diagonalised, hence:

$$E_1 = A\hbar^2 \ \wedge \ E_2 = 0 \tag{8}$$

Eigenstates are χ_1, χ_2 and χ_3 which are also evident from the Hamiltonian:

$$\boxed{\vec{\chi}_1 = \begin{bmatrix}1\\0\\0\end{bmatrix} \ \wedge \ \vec{\chi}_2 = \begin{bmatrix}0\\0\\1\end{bmatrix} \ \wedge \ \vec{\chi}_3 = \begin{bmatrix}0\\1\\0\end{bmatrix}} \tag{9}$$

Corresponding to the eigenvalue $A\hbar^2$ ($\vec{\chi}_1$ and $\vec{\chi}_2$) and 0 ($\vec{\chi}_3$).

Part b

Using (5) and (6), we can express the perturbation as

$$\hat{H}' = B\left(\hat{S}_x^2 - \hat{S}_y^2\right) = \frac{B\hbar^2}{2}\left(\begin{bmatrix}1&0&1\\0&2&0\\1&0&1\end{bmatrix} + \begin{bmatrix}-1&0&1\\0&-2&0\\1&0&-1\end{bmatrix}\right) = \boxed{B\hbar^2\begin{bmatrix}0&0&1\\0&0&0\\1&0&0\end{bmatrix}} \tag{10}$$

Using Griffiths equation (7.9), with a modification for this problem:

$$E_1^3 = \langle\vec{\chi}_3|\hat{H}'|\vec{\chi}_3\rangle = 0 \tag{11}$$

For the ground state. For the degenerate state $E = B\hbar^2$, the expectation value (according to Griffiths 7.33) is simple since it is evident that $W_{11} = W_{22} = 0$:

$$E_1^1 = |W_{12}| = \langle\vec{\chi}_1|\hat{H}'|\vec{\chi}_2\rangle = \boxed{\pm B\hbar^2} \tag{12}$$

Which in turn means that the first approximation of the energy of the perturbed system is $\hbar^2 A$ for the ground state and $\hbar^2(A \pm B)$ for the only excited degenerate state.

Part c

The Hamiltonian can be explicitly computed:

$$\hat{H} = \hbar^2\begin{bmatrix}A&0&B\\0&0&0\\B&0&A\end{bmatrix} \tag{13}$$

Invoking the condition $det(\hat{H} - \lambda I_3) = 0$ we get

$$-\lambda(A-\lambda)^2 - \lambda B^2 = 0 \tag{14}$$

Which is evidently satisfied for $\lambda = 0$. Assuming $\lambda \neq 0$ we get

$$(A-\lambda)^2 = B^2 \implies \lambda = (A \pm B)\hbar^2 \tag{15}$$

For eigenvalue 0 we get an eigenvector

$$\vec{e}_1 = \begin{bmatrix}0\\1\\0\end{bmatrix} \tag{16}$$

For $(A+B)\hbar^2$ we get

$$\vec{e}_2 = \begin{bmatrix}1\\0\\-1\end{bmatrix} \tag{17}$$

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And for $(A-B)\,\hbar^2$ we get

$$\vec{e_3} = \begin{bmatrix} 1 \\ 0 \\ 1 \end{bmatrix}. \tag{18}$$

So

$$P = \begin{bmatrix} 0 & 1 & 1 \\ 1 & 0 & 0 \\ 0 & -1 & 1 \end{bmatrix} \tag{19}$$

And

$$P^{-1} = \frac{1}{2}\begin{bmatrix} 0 & 2 & 0 \\ 1 & 0 & -1 \\ 0 & 0 & 1 \end{bmatrix} \tag{20}$$

Calculating the diagonal matrix is thus simply

$$D = P^{-1}AP = \boxed{\hbar^2 \begin{bmatrix} A-B & 0 & 0 \\ 0 & A+B & 0 \\ 0 & 0 & 0 \end{bmatrix}} \tag{21}$$

So eigenvalues are $A \pm B$ and 0.

The entries of the diagonal matrix are equivalent to the approximate energy of the perturbed Hamiltonian for all eigenstates from part (b).

Part d

Since answers to part (b) and part (c) are identical, we can conclude that the sum of all higher-order corrections will be exactly zero.

Problem 2

Let $\hat{S}_1$ and $\hat{S}_2$ be the spin operators of two spin-1/2 particles and $\hat{S} = \hat{S}_1 + \hat{S}_2$, the spin of the two particle system.

(a) The unperturbed Hamiltonian of the two particle system is $\hat{H}_0 = \frac{\alpha}{\hbar^2}\left(\hat{S}_x^2 + \hat{S}_y^2 - \hat{S}_z^2\right)$. Find the eigenvalues and eigenvectors of this Hamiltonian.
(b) The system is perturbed by $\hat{H}' = \lambda\left(\hat{S}_{1x} - \hat{S}_{2x}\right)$. What are the perturbed energies to first order?

Solution

Part a

Using $\hat{S}^2 = \hat{S}_x^2 + \hat{S}_y^2 + \hat{S}_z^2$ the unperturbed Hamiltonian can be written in the form

$$\hat{H}_0 = \frac{\alpha}{\hbar^2}\left(\hat{S}^2 - 2\hat{S}_z^2\right) \tag{22}$$

We can find the eigenvalues of this Hamiltonian by first finding the eigenvalues of $\hat{S}^2$ and $\hat{S}_z^2$. Using Griffiths 4.135

$$\hat{S}^2\,|s\ m\rangle = \hbar^2 s(s+1)\,|s\ m\rangle \ \wedge\ \hat{S}_z^2\,|s\ m\rangle = \hbar^2 m^2\,|s\ m\rangle \tag{23}$$

Since the system has two particles, it has four possible eigenstates. It can happen (1) they are both spin up (2), (3) they are half spin-up half spin-down and (4) both spin down. more precisely:

$$\psi_1 = |\uparrow\uparrow\rangle = |1\ 1\rangle \tag{24}$$

$$\psi_2 = \frac{\sqrt{2}}{2}\left(|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle\right) = |1\ 0\rangle \tag{25}$$

$$\psi_3 = \frac{\sqrt{2}}{2}\left(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle\right) = |0\ 0\rangle \tag{26}$$

$$\psi_4 = |\downarrow\downarrow\rangle = |1\ -1\rangle \tag{27}$$

So, in the same order it holds:

$$\hat{S}^2\,|1\ 1\rangle = 2\hbar^2\,|1\ 1\rangle \ \wedge\ \hat{S}_z^2\,|1\ 1\rangle = \hbar^2\,|1\ 1\rangle \tag{28}$$

$$\hat{S}^2\,|1\ 0\rangle = 2\hbar^2\,|1\ 0\rangle \ \wedge\ \hat{S}_z^2\,|1\ 0\rangle = 0\cdot|1\ 0\rangle \tag{29}$$

$$\hat{S}^2\,|0\ 0\rangle = 0\cdot|0\ 0\rangle \ \wedge\ \hat{S}_z^2\,|0\ 0\rangle = 0\cdot|0\ 0\rangle \tag{30}$$

$$\hat{S}^2\,|1\ -1\rangle = 2\hbar^2\,|1\ -1\rangle \ \wedge\ \hat{S}_z^2\,|1\ -1\rangle = \hbar^2\,|1\ -1\rangle \tag{31}$$

Using these eigenvalues we obtain

$$\hat{H}_0\,|1\ 1\rangle = 0 \tag{32}$$

$$\hat{H}_0\,|1\ 0\rangle = 2\alpha\,|1\ 0\rangle \tag{33}$$

$$\hat{H}_0\,|1\ 1\rangle = 0 \tag{34}$$

$$\hat{H}_0\,|1\ 1\rangle = 0 \tag{35}$$

So, in total 4 eigenvalues, of which three are 0 and one is 2α. Their respective eigenstates are contained in equations (32)-(35).

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Part b

The perturbed energies for the one non-degenerate state can be calculated using the formula

$$E_n^1 = \langle\psi_n|\hat{H}'|\psi_n\rangle = \lambda\langle\psi_n|\hat{S}_{1x} - \hat{S}_{2x}|\psi_n\rangle \tag{36}$$

$$\implies E_2^1 = \lambda\left\langle \frac{\sqrt{2}}{2}\left(|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle\right)|\hat{S}_{1x}|\frac{\sqrt{2}}{2}\left(|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle\right)\right\rangle - \lambda\left\langle \frac{\sqrt{2}}{2}\left(|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle\right)|\hat{S}_{2x}|\frac{\sqrt{2}}{2}\left(|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle\right)\right\rangle \tag{37}$$

$\hat{S}_{1x}$ is only applied to the first particle and $\hat{S}_{2x}$ only to the second one, namely $\hat{S}_x|\uparrow\rangle = \frac{\hbar}{2}\downarrow$ and $\hat{S}_x|\downarrow\rangle = \frac{\hbar}{2}\uparrow$. So (37) this simplifies to

$$E_2^1 = \frac{\hbar\lambda}{4}\left(\left(|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle\right)|\left(|\downarrow\downarrow\rangle + |\uparrow\uparrow\rangle\right) - \left(|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle\right)|\left(|\uparrow\uparrow\rangle + |\downarrow\downarrow\rangle\right)\right) = \boxed{0} \tag{38}$$

Since the second eigenenergy is triple-degenerate, we must find a 3×3 matrix with entries W_{ab} where $a, b \in [1, 3, 4]$.

$$W = \begin{bmatrix} W_{11} & W_{13} & W_{14} \\ W_{31} & W_{33} & W_{34} \\ W_{41} & W_{43} & W_{44} \end{bmatrix} \tag{39}$$

Where, according to Griffiths 7.40

$$W_{ab} = \langle\psi_a^0|\hat{H}'|\psi_b^0\rangle \tag{40}$$

From (37) it is evident that $\langle\psi_a^0|\hat{H}'|\psi_a^0\rangle = 0$ for all a since $\hat{S}_x$ reverses the spin so the inner product would always be zero. For entries other than the diagonal, we have to apply brute force.

$$W_{13} = \langle\psi_1|\hat{H}'|\psi_3\rangle = \frac{\lambda\sqrt{2}}{2}\left(\langle|\uparrow\uparrow\rangle|\hat{S}_{1x}|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle\rangle - \langle|\uparrow\uparrow\rangle|\hat{S}_{2x}|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle\rangle\right) \tag{41}$$

$$\implies W_{13} = -\frac{\hbar\lambda\sqrt{2}}{4}\left(\langle\uparrow\uparrow|\uparrow\uparrow\rangle + \langle\uparrow\uparrow|\uparrow\uparrow\rangle\right) = -\frac{\hbar\lambda\sqrt{2}}{2} \tag{42}$$

Due to orthonormality. It is a similar process to show that $W_{31} = -\frac{\hbar\lambda\sqrt{2}}{2}$, and it is evidently symmetric. Furthermore, we begin to notice that the whole matrix W is symmetric, due to the operation we are applying! Namely, since we are merely flipping the direction of each spin, it should now matter to which eigenstate we apply the operator first. This is an analog of equal complex conjugates. Let us check for the remaining entries:

$$W_{14} = W_{41} = \langle\psi_1|\hat{H}'|\psi_4\rangle = \lambda\left(\langle|\uparrow\uparrow\rangle|\hat{S}_{1x}|\downarrow\downarrow\rangle\rangle - \langle|\uparrow\uparrow\rangle|\hat{S}_{2x}|\downarrow\downarrow\rangle\rangle\right) \tag{43}$$

$$\implies W_{14} = W_{41} = \frac{\hbar\lambda}{2}\left(\langle\uparrow\uparrow|\uparrow\downarrow\rangle - \langle\uparrow\uparrow|\downarrow\uparrow\rangle\right) = 0 - 0 = \boxed{0} \tag{44}$$

Due to orthonormality. And finally

$$W_{34} = W_{43} = \langle\psi_1|\hat{H}'|\psi_4\rangle = \frac{\lambda\sqrt{2}}{2}\left(\left(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle\right)|\hat{S}_{1x}|\downarrow\downarrow\rangle\rangle - \langle\left(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle\right)|\hat{S}_{2x}|\downarrow\downarrow\rangle\rangle\right) \tag{45}$$

$$\implies \frac{\hbar\lambda\sqrt{2}}{4}\left(\langle\uparrow\downarrow|\uparrow\downarrow\rangle\rangle + \langle\downarrow\uparrow|\downarrow\uparrow\rangle\right) = \boxed{\frac{\hbar\lambda\sqrt{2}}{2}} \tag{46}$$

Again, due to orthonormality. So our matrix is:

$$W = \begin{bmatrix} 0 & -\frac{\hbar\lambda\sqrt{2}}{2} & 0 \\ -\frac{\hbar\lambda\sqrt{2}}{2} & 0 & \frac{\hbar\lambda\sqrt{2}}{2} \\ 0 & \frac{\hbar\lambda\sqrt{2}}{2} & 0 \end{bmatrix} \tag{47}$$

The corrections to the energy are the eigenvalues of this matrix, or the solutions of the following equation

$$-x^3 - x\hbar^2\lambda^2 = 0 \implies x = 0 \ \vee \ x = \pm\hbar\lambda \tag{48}$$

Hence, the perturbed energies to first order are:

$$E_1' = 2\alpha \quad \text{(no correction to first order)} \tag{49}$$

$$E_2' = 0 \quad \text{(no correction to first order)} \tag{50}$$

$$E_3' = \lambda\hbar \tag{51}$$

$$E_4' = -\lambda\hbar \tag{52}$$

Problem 3

Griffiths 7.24

Consider the (eight) $n = 2$ states, $|2\ l\ j\ m_j\rangle$. Find the energy of each state, under weak-field Zeeman splitting, and construct a diagram like Figure 7.10 to show how the energies evolve as B_{ext} increases. Label each line clearly, and indicate its slope.

Solution

The eight possible states are:

$$\nu_1 = \left|2\ 1\ \frac{3}{2}\ \frac{3}{2}\right\rangle \tag{53}$$

$$\nu_2 = \left|2\ 1\ \frac{3}{2}\ \frac{1}{2}\right\rangle \tag{54}$$

$$\nu_3 = \left|2\ 1\ \frac{3}{2}\ -\frac{1}{2}\right\rangle \tag{55}$$

$$\nu_4 = \left|2\ 1\ \frac{3}{2}\ -\frac{3}{2}\right\rangle \tag{56}$$

$$\nu_5 = \left|2\ 1\ \frac{1}{2}\ \frac{1}{2}\right\rangle \tag{57}$$

$$\nu_6 = \left|2\ 1\ \frac{1}{2}\ -\frac{1}{2}\right\rangle \tag{58}$$

$$\nu_7 = \left|2\ 0\ \frac{1}{2}\ \frac{1}{2}\right\rangle \tag{59}$$

$$\nu_8 = \left|2\ 0\ \frac{1}{2}\ -\frac{1}{2}\right\rangle \tag{60}$$

Since the energies of these states only depend on n and j, and there are only two possible values of j, there will be just two energies, both of degeneracy four. By Griffiths 7.69, the energy can be calculated by

$$E(n,j) = -\frac{Ry}{n^2}\left(1 + \frac{\alpha^2}{n^2}\left(\frac{2n}{2j+1} - \frac{3}{4}\right)\right) \tag{61}$$

For the Rydberg constant $Ry \approx -13.6$ eV. So the two energies are

$$E^1 = E\left(2, \frac{3}{2}\right) = -\frac{Ry}{4}\left(1 + \frac{\alpha^2}{16}\right) \text{ for states } \nu_{1-4} \tag{62}$$

And

$$E^2 = E\left(2, \frac{1}{2}\right) = -\frac{Ry}{4}\left(1 + \frac{5\alpha^2}{16}\right) \text{ for states } \nu_{5-8} \tag{63}$$

Note that the superscripts 1 and 2 stand to separate the energies, and are not powers. The Landé g-factor can be calculated using the formula 7.78 from Griffiths:

$$g(j,l,s) = 1 + \frac{j(j+1) - l(l+1) + s(s+1)}{2j(j+1)} \tag{64}$$

So, respectively for each state ν_i for integer $i \in [1,8]$, it can be computed:

$$g_1 = g\left(\frac{3}{2}, 1, \frac{1}{2}\right) = 1 + \frac{\frac{15}{4} - 2 + \frac{3}{4}}{\frac{15}{2}} = \frac{4}{3} \tag{65}$$

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$$g_2 = g\left(\frac{3}{2}, 1, \frac{1}{2}\right) = 1 + \frac{\frac{15}{4} - 2 + \frac{3}{4}}{\frac{15}{2}} = \frac{4}{3} \tag{66}$$

$$g_3 = g\left(\frac{3}{2}, 1, \frac{1}{2}\right) = 1 + \frac{\frac{15}{4} - 2 + \frac{3}{4}}{\frac{15}{2}} = \frac{4}{3} \tag{67}$$

$$g_4 = g\left(\frac{3}{2}, 1, \frac{1}{2}\right) = 1 + \frac{\frac{15}{4} - 2 + \frac{3}{4}}{\frac{15}{2}} = \frac{4}{3} \tag{68}$$

$$g_5 = g\left(\frac{1}{2}, 1, \frac{1}{2}\right) = 1 + \frac{\frac{3}{4} - 2 + \frac{3}{4}}{\frac{3}{2}} = \frac{2}{3} \tag{69}$$

$$g_6 = g\left(\frac{1}{2}, 1, \frac{1}{2}\right) = 1 + \frac{\frac{3}{4} - 2 + \frac{3}{4}}{\frac{3}{2}} = \frac{2}{3} \tag{70}$$

$$g_7 = g\left(\frac{1}{2}, 0, \frac{1}{2}\right) = 1 + \frac{\frac{3}{4} + \frac{3}{4}}{\frac{3}{2}} = 2 \tag{71}$$

$$g_8 = g\left(\frac{1}{2}, 0, \frac{1}{2}\right) = 1 + \frac{\frac{3}{4} + \frac{3}{4}}{\frac{3}{2}} = 2 \tag{72}$$

The energy of each state can be found by combining E^1 or E^2 with the respective correction containing g. According to Griffiths (7.79) and (7.80):

$$E_i' = \frac{e\hbar g_i B_{ext} m_j}{2m} \tag{73}$$

For integer $i \in [1, 8]$. So the corrected energies for all the states are, respectively

$$E_1 = -\frac{Ry}{4}\left(1 + \frac{\alpha^2}{16}\right) + \frac{e\hbar}{m} B_{ext} \tag{74}$$

$$E_2 = -\frac{Ry}{4}\left(1 + \frac{\alpha^2}{16}\right) + \frac{e}{3m} B_{ext} \tag{75}$$

$$E_3 = -\frac{Ry}{4}\left(1 + \frac{\alpha^2}{16}\right) - \frac{e\hbar}{m} B_{ext} \tag{76}$$

$$E_4 = -\frac{Ry}{4}\left(1 + \frac{\alpha^2}{16}\right) + \frac{e\hbar}{3m} B_{ext} \tag{77}$$

$$E_5 = -\frac{Ry}{4}\left(1 + \frac{5\alpha^2}{16}\right) + \frac{e\hbar}{6m} B_{ext} \tag{78}$$

$$E_6 = -\frac{Ry}{4}\left(1 + \frac{5\alpha^2}{16}\right) - \frac{e\hbar}{6m} B_{ext} \tag{79}$$

$$E_7 = -\frac{Ry}{4}\left(1 + \frac{5\alpha^2}{16}\right) + \frac{e\hbar}{2m} B_{ext} \tag{80}$$

$$E_8 = -\frac{Ry}{4}\left(1 + \frac{5\alpha^2}{16}\right) - \frac{e\hbar}{2m} B_{ext} \tag{81}$$

For the graph, I shall use Griffiths technique, only that my slopes are factors of $\frac{m_j}{2}$ instead of m_j, as can be seen on figure 1. Weak field ($\vec{B}_{ext} \longrightarrow \vec{0}$) is assumed.

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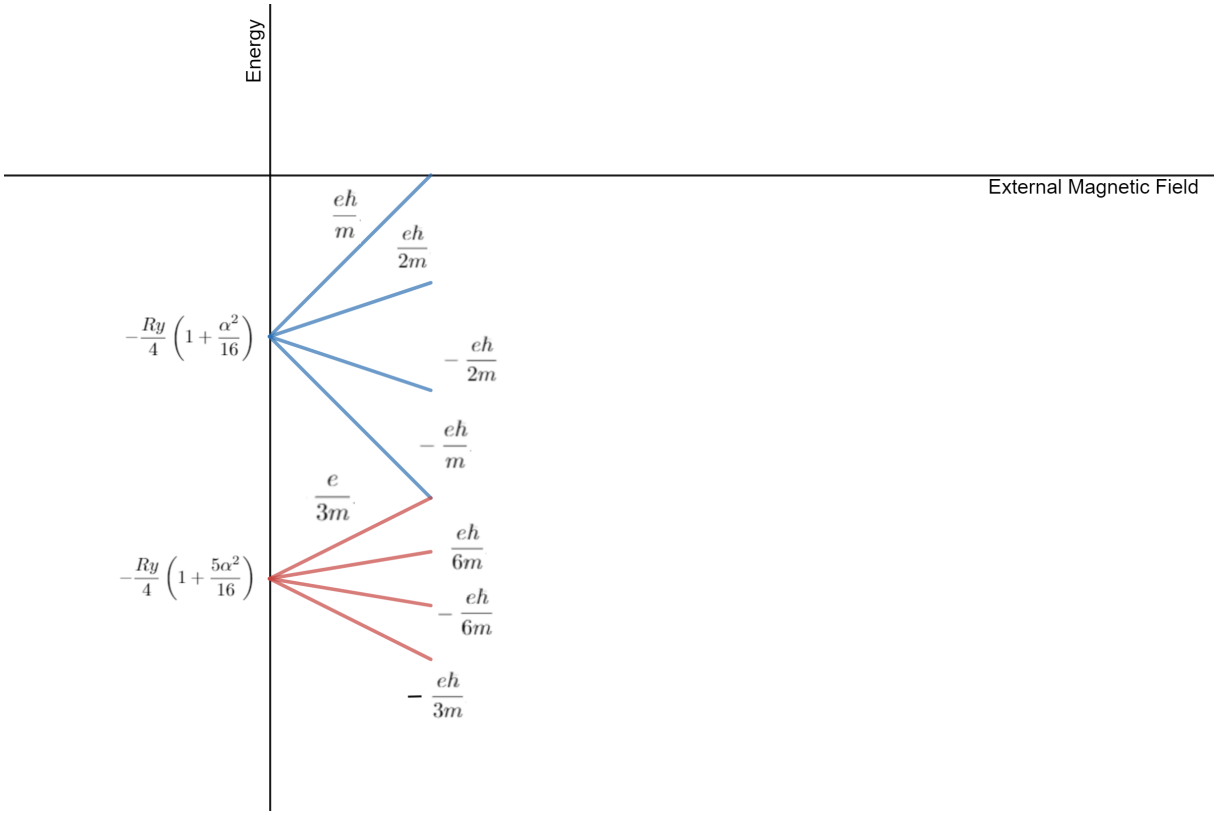

Figure 1: Lifting of degeneracies of $j = \frac{1}{2}$ and $j = \frac{3}{2}$ under weak-field Zeeman splitting

Problem 4

Griffiths 7.27

Consider the (eight) $n = 2$ states, $|2\ l\ m_l\ m_s\rangle$. Find the energy of each state, under strong-field Zeeman splitting. Express each answer as the sum of three terms: the Bohr energy, the fine-structure (proportional to α^2), and the Zeeman contribution (proportional to $\mu_B B_{ext}$). If you ignore fine structure altogether, how many distinct levels are there, and what are their degeneracies?

Solution

The Bohr energy can be calculated using Griffiths 4.70:

$$E_n = -\frac{Ry}{n^2} \tag{82}$$

Where $Ry \approx 13.6$ eV. Since all of our states satisfy $n = 2$, it holds that all eight Bohr energies are equal to

$$E_2 = -\frac{Ry}{4} \tag{83}$$

The energy due to the strong-field Zeeman splitting can be calculated using Griffiths 7.83:

$$E_z = \frac{e}{2m} B_{ext} \left(m_l + 2m_s\right) \tag{84}$$

The fine structure energy contribution can be calculated using Griffiths equation 7.86

$$E^1_{fs} = \frac{\alpha^2}{n^3}\left[\frac{3}{4n} - \frac{l\left(l+1\right) - m_l m_s}{l\left(l+\frac{1}{2}\right)\left(l+1\right)}\right] Ry \tag{85}$$

Which can also be simplifies for all states where $n = 2$ to:

$$E^1_{fs} = \frac{\alpha^2}{8}\left[\frac{3}{8} - \frac{2l\left(l+1\right) - 2m_l m_s}{l\left(2l+1\right)\left(l+1\right)}\right] Ry \tag{86}$$

So the overall energy will depend on l, m_l and m_s:

$$E_i = -\frac{Ry}{4} + \frac{e}{2m} B_{ext}\left(m_l + 2m_s\right) + \frac{\alpha^2}{8}\left[\frac{3}{8} - \frac{2l\left(l+1\right) - 2m_l m_s}{l\left(2l+1\right)\left(l+1\right)}\right] Ry \tag{87}$$

For integer $i \in [1, 8]$, or all cases. Note that l can take value 0 or 1, m_l can hence take values -1, 0 or 1 and m_s can only be either $\frac{1}{2}$ or $-\frac{1}{2}$. The eight states will then be:

$$\nu_1 = \left|2\ 1\ 1\ \frac{1}{2}\right\rangle \tag{88}$$

$$\nu_2 = \left|2\ 1\ 1\ -\frac{1}{2}\right\rangle \tag{89}$$

$$\nu_3 = \left|2\ 1\ 0\ \frac{1}{2}\right\rangle \tag{90}$$

$$\nu_4 = \left|2\ 1\ 0\ -\frac{1}{2}\right\rangle \tag{91}$$

$$\nu_5 = \left|2\ 1\ -1\ \frac{1}{2}\right\rangle \tag{92}$$

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$$\nu_6 = \left| 2\ 1\ -1\ -\frac{1}{2} \right\rangle \tag{93}$$

$$\nu_7 = \left| 2\ 0\ 0\ \frac{1}{2} \right\rangle \tag{94}$$

$$\nu_8 = \left| 2\ 0\ 0\ -\frac{1}{2} \right\rangle \tag{95}$$

Then (87) is evaluated for each state and the following energies are obtained:

$$E_1 = -\frac{Ry}{4} + \frac{e}{m}B_{ext} + \frac{\alpha^2}{8}\left[\frac{3}{8} - \frac{3}{6}\right] Ry = \boxed{-\left(1 + \frac{\alpha^2}{4}\right)\frac{Ry}{4} + \frac{e}{m}B_{ext}} \tag{96}$$

$$E_2 = -\frac{Ry}{4} + \frac{\alpha^2}{8}\left[\frac{3}{8} - \frac{5}{6}\right] Ry = \boxed{-\left(1 + \frac{11\alpha^2}{48}\right)\frac{Ry}{4}} \tag{97}$$

$$E_3 = -\frac{Ry}{4} + \frac{e}{2m}B_{ext} + \frac{\alpha^2}{8}\left[\frac{3}{8} - \frac{2}{3}\right] Ry = \boxed{-\left(1 + \frac{7\alpha^2}{48}\right)\frac{Ry}{4} + \frac{e}{2m}B_{ext}} \tag{98}$$

$$E_3 = -\frac{Ry}{4} + \frac{e}{2m}B_{ext} + \frac{\alpha^2}{8}\left[\frac{3}{8} - \frac{2}{3}\right] Ry = \boxed{-\left(1 + \frac{7\alpha^2}{48}\right)\frac{Ry}{4} - \frac{e}{2m}B_{ext}} \tag{99}$$

$$E_5 = -\frac{Ry}{4} + \frac{\alpha^2}{8}\left[\frac{3}{8} - \frac{5}{6}\right] Ry = \boxed{-\left(1 + \frac{11\alpha^2}{48}\right)\frac{Ry}{4}} \tag{100}$$

$$E_6 = -\frac{Ry}{4} - \frac{e}{m}B_{ext} + \frac{\alpha^2}{8}\left[\frac{3}{8} - \frac{3}{6}\right] Ry = \boxed{-\left(1 + \frac{\alpha^2}{4}\right)\frac{Ry}{4} - \frac{e}{m}B_{ext}} \tag{101}$$

$$E_7 = -\frac{Ry}{4} + \frac{e}{2m}B_{ext} + \frac{\alpha^2}{8}\left[\frac{3}{8} - 1\right] Ry = \boxed{-\left(1 + \frac{5\alpha^2}{16}\right)\frac{Ry}{4} + \frac{e}{2m}B_{ext}} \tag{102}$$

$$E_8 = -\frac{Ry}{4} - \frac{e}{2m}B_{ext} + \frac{\alpha^2}{8}\left[\frac{3}{8} - 1\right] Ry = \boxed{-\left(1 + \frac{5\alpha^2}{16}\right)\frac{Ry}{4} - \frac{e}{2m}B_{ext}} \tag{103}$$

Note that for cases E_7 and E_8 we have used the fact that the indeterminate form of $\frac{2l(l+1)-2m_l m_s}{l(2l+1)(l+1)}$ at $l = 0$ equals 1, as Griffiths mentioned (page 308).

Problem 5

Show that the intermediate field results we got in class reduce to the values from part (a) for weak fields ($\beta \ll \gamma$), and to the values you got in part (b) for strong fields ($\beta \gg \gamma$).

Solution

In class we got the following corrections of energies:

$$E_1 = -\frac{Ry}{4} - 5\gamma + \beta \tag{104}$$

$$E_2 = -\frac{Ry}{4} - 5\gamma - \beta \tag{105}$$

$$E_3 = -\frac{Ry}{4} - \gamma + 2\beta \tag{106}$$

$$E_4 = -\frac{Ry}{4} - \gamma - 2\beta \tag{107}$$

$$E_5 = -\frac{Ry}{4} - 3\gamma + \frac{\beta}{2} + \sqrt{4\gamma^2 + \frac{2}{3}\gamma\beta + \frac{\beta^2}{4}} \tag{108}$$

$$E_6 = -\frac{Ry}{4} - 3\gamma + \frac{\beta}{2} - \sqrt{4\gamma^2 + \frac{2}{3}\gamma\beta + \frac{\beta^2}{4}} \tag{109}$$

$$E_7 = -\frac{Ry}{4} - 3\gamma - \frac{\beta}{2} + \sqrt{4\gamma^2 - \frac{2}{3}\gamma\beta + \frac{\beta^2}{4}} \tag{110}$$

$$E_8 = -\frac{Ry}{4} - 3\gamma - \frac{\beta}{2} - \sqrt{4\gamma^2 - \frac{2}{3}\gamma\beta + \frac{\beta^2}{4}} \tag{111}$$

Where $\gamma = \left(\frac{\alpha}{8}\right)^2 Ry$ and $\beta = \frac{e}{2m}B_{ext}$. For weak fields this is approximately:

$$E_1 = -\frac{Ry}{4} - 5\gamma + \beta = \boxed{-\left(1 + \frac{5\alpha^2}{16}\right)\frac{Ry}{4} + \frac{e}{2m}B_{ext}} \tag{112}$$

$$E_2 = -\frac{Ry}{4} - 5\gamma - \beta = \boxed{-\left(1 + \frac{5\alpha^2}{16}\right)\frac{Ry}{4} - \frac{e}{2m}B_{ext}} \tag{113}$$

$$E_3 = -\frac{Ry}{4} - \gamma + 2\beta = \boxed{-\left(1 + \frac{\alpha^2}{16}\right)\frac{Ry}{4} + \frac{e}{m}B_{ext}} \tag{114}$$

$$E_4 = -\frac{Ry}{4} - \gamma - 2\beta = \boxed{-\left(1 + \frac{\alpha^2}{16}\right)\frac{Ry}{4} - \frac{e}{m}B_{ext}} \tag{115}$$

$$E_5 = -\frac{Ry}{4} - 3\gamma + \frac{\beta}{2} + 2\gamma\sqrt{1 + \frac{\beta}{6\gamma} + \frac{\beta^2}{16\gamma^2}} \approx -\frac{Ry}{4} - \gamma + \frac{\beta}{2} + \frac{\beta}{6} = \boxed{-\left(1 + \frac{\alpha^2}{16}\right)\frac{Ry}{4} + \frac{e}{3m}B_{ext}} \tag{116}$$

$$E_6 = -\frac{Ry}{4} - 3\gamma + \frac{\beta}{2} - 2\gamma\sqrt{1 + \frac{\beta}{6\gamma} + \frac{\beta^2}{16\gamma^2}} \approx -\frac{Ry}{4} - 5\gamma + \frac{\beta}{2} - \frac{\beta}{6} = \boxed{-\left(1 + \frac{5\alpha^2}{16}\right)\frac{Ry}{4} + \frac{e}{6m}B_{ext}} \tag{117}$$

$$E_7 = -\frac{Ry}{4} - 3\gamma - \frac{\beta}{2} + 2\gamma\sqrt{1 - \frac{\beta}{6\gamma} + \frac{\beta^2}{16\gamma^2}} \approx -\frac{Ry}{4} - \gamma - \frac{\beta}{2} - \frac{\beta}{6} = \boxed{-\left(1 + \frac{\alpha^2}{16}\right)\frac{Ry}{4} - \frac{e}{3m}B_{ext}} \tag{118}$$

Problem 5 continued on next page...

$$E_8 = -\frac{Ry}{4} - 3\gamma - \frac{\beta}{2} - 2\gamma\sqrt{1 - \frac{\beta}{6\gamma} + \frac{\beta^2}{16\gamma^2}} \approx -\frac{Ry}{4} - 5\gamma - \frac{\beta}{2} + \frac{\beta}{6} = \boxed{-\left(1 + \frac{5\alpha^2}{16}\right)\frac{Ry}{4} - \frac{e}{6m}B_{ext}} \quad (119)$$

Which are evidently the same results we obtained in part a) (not in the same order!).

For strong Zeeman splitting, the following applies:

$$E_1 = -\frac{Ry}{4} - 5\gamma + \beta = \boxed{-\left(1 + \frac{5\alpha^2}{16}\right)\frac{Ry}{4} + \frac{e}{2m}B_{ext}} \quad (120)$$

$$E_2 = -\frac{Ry}{4} - 5\gamma - \beta = \boxed{-\left(1 + \frac{5\alpha^2}{16}\right)\frac{Ry}{4} - \frac{e}{2m}B_{ext}} \quad (121)$$

$$E_3 = -\frac{Ry}{4} - \gamma + 2\beta = \boxed{-\left(1 + \frac{\alpha^2}{16}\right)\frac{Ry}{4} + \frac{e}{m}B_{ext}} \quad (122)$$

$$E_4 = -\frac{Ry}{4} - \gamma - 2\beta = \boxed{-\left(1 + \frac{\alpha^2}{16}\right)\frac{Ry}{4} - \frac{e}{m}B_{ext}} \quad (123)$$

$$E_5 = -\frac{Ry}{4} - 3\gamma + \frac{\beta}{2} + \frac{\beta}{2}\sqrt{1 + \frac{8\gamma}{3\beta} + \frac{16\gamma^2}{\beta^2}} \approx -\frac{Ry}{4} - \frac{7}{3}\gamma + \beta = \boxed{-\left(1 + \frac{7\alpha^2}{48}\right)\frac{Ry}{4} + \frac{e}{2m}B_{ext}} \quad (124)$$

$$E_6 = -\frac{Ry}{4} - 3\gamma + \frac{\beta}{2} - \frac{\beta}{2}\sqrt{1 + \frac{8\gamma}{3\beta} + \frac{16\gamma^2}{\beta^2}} \approx -\frac{Ry}{4} - \frac{11}{3}\gamma = \boxed{-\left(1 + \frac{11\alpha^2}{48}\right)\frac{Ry}{4}} \quad (125)$$

$$E_7 = -\frac{Ry}{4} - 3\gamma - \frac{\beta}{2} + \frac{\beta}{2}\sqrt{1 - \frac{8\gamma}{3\beta} + \frac{16\gamma^2}{\beta^2}} \approx -\frac{Ry}{4} - \frac{11}{3}\gamma\boxed{-\left(1 + \frac{11\alpha^2}{48}\right)\frac{Ry}{4}} \quad (126)$$

$$E_8 = -\frac{Ry}{4} - 3\gamma - \frac{\beta}{2} - \frac{\beta}{2}\sqrt{1 - \frac{8\gamma}{3\beta} + \frac{16\gamma^2}{\beta^2}} \approx -\frac{Ry}{4} - \frac{7}{3}\gamma - \beta = \boxed{-\left(1 + \frac{7\alpha^2}{48}\right)\frac{Ry}{4} - \frac{e}{2m}B_{ext}} \quad (127)$$

Which are evidently the same results we obtained in part a). Notice that in both approximations, we have neglected the terms with powers higher than 2, in both γ and β.

It follows from the results above, that the intermediate Zeeman splitting reduces to weak and strong field splitting, when appropriate limits are taken.

Problem 6

Griffiths 7.45

When an atom is placed in a uniform external electric field $\mathbf{E}_{ext}$, the energy levels are shifted-a phenomenon known as the Stark effect (it is the electrical analog to the Zeeman effect). In this problem we analyze the Stark effect for the $n = 1$ and $n = 2$ states of hydrogen. Let the field point in the z direction, so the potential energy of the electron is

$$H'_s = eE_{ext}z = eE_{ext}r\cos\theta$$

Treat this as a perturbation on the Bohr Hamiltonian (Equation 7.43). (Spin is irrelevant to this problem, so ignore it, and neglect the fine structure.)

(a) Show that the ground state energy is not affected by this perturbation, in first order.
(b) The first excited state is four-fold degenerate: ψ_{200}, ψ_{211}, ψ_{210}, ψ_{21-1}. Using degenerate perturbation theory, determine the first-order corrections to the energy. Into how many levels does E_2 split?
(c) What are the "good" wave functions for part (b)? Find the expectation value of the electric dipole moment $\mathbf{p}_e = -e\mathbf{r}$, in each of these "good" states. Notice that the results are independent of the applied field—evidently hydrogen in its first excited state can carry a *permanent* electric dipole moment.

Hint: There are lots of integrals in this problem, but almost all of them are zero. So study each one carefully, before you do any calculations: If the ϕ integral vanishes, there's not much point in doing the r and θ integrals! You can avoid those integrals altogether if you use the selection rules of Sections 6.4.3 and 6.7.2. *Partial answer:* $W_{13} = W_{31} = -3eaE_{ext}$; all other elements are zero.

Solution

Part a

The ground state wavefunction is

$$\psi_1 = \frac{1}{\sqrt{\pi a^3}}e^{-\frac{r}{a}} \tag{128}$$

And then the perturbation energy is

$$E' = \langle\psi_1|H'_s|\psi_1\rangle \tag{129}$$

This can be transformed into analytic form, in spherical coordinates:

$$E' = \frac{eE_{ext}}{\pi a^3}\iiint e^{-\frac{2r}{a}}r\cos\theta\mathrm{d}\tau = \frac{eE_{ext}}{\pi a^3}\iiint e^{-\frac{2r}{a}}r^3\cos\theta\sin\theta\mathrm{d}r\mathrm{d}\theta\mathrm{d}\phi = \boxed{0} \tag{130}$$

As given by WolframAlpha. This occurs because $\int_0^\pi \sin 2\theta\mathrm{d}\theta = 0$.

Part b

From Griffiths book, we know the analytic forms of all four eigenstates:

$$\begin{cases} \psi_{200} = \frac{1}{\sqrt{2\pi a}}\frac{1}{2a}\left(1-\frac{r}{2a}\right)e^{-\frac{r}{2a}} \\ \psi_{211} = -\frac{1}{\sqrt{\pi a}}\frac{1}{8a^2}re^{-\frac{r}{2a}}\sin\theta e^{i\phi} \\ \psi_{210} = \frac{1}{\sqrt{2\pi a}}\frac{1}{4a^2}re^{-\frac{r}{2a}}\cos\theta \\ \psi_{21-1} = \frac{1}{\sqrt{\pi a}}\frac{1}{8a^2}re^{-\frac{r}{2a}}\sin\theta e^{-i\phi} \end{cases} \tag{131}$$

Problem 6 continued on next page...

Since we have a 4×4 matrix, we have to compute 16 entries. Needless to say, I heavily relied on WolframAlpha here. However, one can notice that all but 2 entries in this matrix are zero, due to the specific combination of trigonometric integrals of functions which are odd on the interval. In particular, one can notice that when there is an odd power of $\sin\theta$ inside of an integral, the integral will compute to 0. This of course includes the complex exponential $e^{i\phi}$, since it is present in the integral $\int_0^{2\pi} e^{\pm i\phi}\mathrm{d}t$ which is zero. In particular:

$$\langle\psi_1|H_s'|\psi_1\rangle = \boxed{0} \tag{132}$$

$$\langle\psi_1|H_s'|\psi_2\rangle = \boxed{0} \tag{133}$$

$$\langle\psi_1|H_s'|\psi_3\rangle = \frac{eE_{ext}}{16\pi a^4}\iiint_{\text{all space}}\left(1-\frac{r}{2a}\right)r^3e^{-\frac{r}{a}}\sin\theta\cos^2\theta\mathrm{d}r\mathrm{d}\theta\mathrm{d}\phi = \boxed{-3aE_{ext}} \tag{134}$$

$$\langle\psi_2|H_s'|\psi_1\rangle = \boxed{0} \tag{135}$$

$$\langle\psi_2|H_s'|\psi_2\rangle = \boxed{0} \tag{136}$$

$$\langle\psi_2|H_s'|\psi_3\rangle = \boxed{0} \tag{137}$$

$$\langle\psi_2|H_s'|\psi_4\rangle = \boxed{0} \tag{138}$$

$$\langle\psi_3|H_s'|\psi_1\rangle = \langle\psi_1|H_s'|\psi_3\rangle = \boxed{-3aE_{ext}} \tag{139}$$

$$\langle\psi_3|H_s'|\psi_2\rangle = \boxed{0} \tag{140}$$

$$\langle\psi_3|H_s'|\psi_3\rangle = \boxed{0} \tag{141}$$

$$\langle\psi_3|H_s'|\psi_4\rangle = \boxed{0} \tag{142}$$

$$\langle\psi_4|H_s'|\psi1\rangle = \boxed{0} \tag{143}$$

$$\langle\psi_4|H_s'|\psi2\rangle = \boxed{0} \tag{144}$$

$$\langle\psi_4|H_s'|\psi3\rangle = \boxed{0} \tag{145}$$

$$\langle\psi_4|H_s'|\psi4\rangle = \boxed{0} \tag{146}$$

Where we have used the fact that inner product of ψ_1 and ψ_3 are symmetric with respect to the application of the operator due to commutativity of multiplication of real valued functions.
The matrix is then

$$W = -3aE_{ext}\begin{bmatrix}0&0&1&0\\0&0&0&0\\1&0&0&0\\0&0&0&0\end{bmatrix} \tag{147}$$

Whose eigenvalues are also calculated in WolframAlpha and are:

$$\lambda_1 = -3aE_{ext}\ ;\ \lambda_2 = 3aE_{ext}\ ;\ \lambda_3 = 0 \text{ with multiplicity 2} \tag{148}$$

Hence, the first order corrections are:

$$\Delta E_1 = -3aE_{ext}\ ;\ \Delta E_2 = 3aE_{ext}\ ;\ \Delta E_3 = 0 \tag{149}$$

So E_2 splits into <u>three</u> levels.

Part c

To find the good states, we need to find the eigenstates of W. For $\lambda_3 = 0$ the eigenvectors are:

$$\vec{e}_1 = \begin{bmatrix} 0 \\ 1 \\ 0 \\ 0 \end{bmatrix} \quad \wedge \quad \vec{e}_1 = \begin{bmatrix} 0 \\ 0 \\ 0 \\ 1 \end{bmatrix} \tag{150}$$

For $\lambda_2 = 3aE_{ext}$ there is one eigenvector

$$\vec{e}_2 = \frac{1}{\sqrt{2}} \begin{bmatrix} 1 \\ 0 \\ 1 \\ 0 \end{bmatrix} \tag{151}$$

And for $\lambda_1 = -3aE_{ext}$ there is one eigenvector

$$\vec{e}_3 = \frac{1}{\sqrt{2}} \begin{bmatrix} 1 \\ 0 \\ -1 \\ 0 \end{bmatrix} \tag{152}$$

Based on these, the good states are

$$\psi_{211};\ \psi_{21-1};\ \frac{1}{\sqrt{2}}\left(\psi_{200} + \psi_{210}\right);\ \frac{1}{\sqrt{2}}\left(\psi_{200} - \psi_{210}\right) \tag{153}$$

For the next part of the question, note that in spherical coordinates:

$$\mathbf{r} = r\left(\sin\theta\cos\phi\hat{i} + \sin\theta\sin\phi\hat{j} + \cos\theta\hat{k}\right) \tag{154}$$

Then:

$$\langle \mathbf{p} \rangle_1 = -e \iiint \psi_{211}^2 r \left(\sin\theta\cos\phi\hat{i} + \sin\theta\sin\phi\hat{j} + \cos\theta\hat{k}\right) \mathrm{d}\tau \tag{155}$$

Or

$$\langle \mathbf{p} \rangle_1 = \frac{e}{64\pi a^5} \left(\iiint e^{-\frac{r}{a}} r^3 \sin^3\theta e^{2i\phi} r\cos\phi \mathrm{d}\tau\ \hat{i} + \iiint e^{-\frac{r}{a}} \sin^3\theta e^{2i\phi} r\sin\phi \mathrm{d}\tau\ \hat{j} \right) \tag{156}$$

$$+ \left(\iiint e^{-\frac{r}{a}} r^3 \sin^2\theta e^{2i\phi} r\cos\theta \mathrm{d}\tau\ \hat{k} \right) \tag{157}$$

It is shown by WolframAlpha quickly that this integral over the whole space is zero, and that is because of the fact that $e^{2i\phi}$ is 2π periodic, evaluated over the interval $\phi \in [0, 2\pi]$. Since this term is also present in ψ_{21-1}, we can deduce that it holds

$$\langle \mathbf{p} \rangle_1 = \langle \mathbf{p} \rangle_2 = 0 \tag{158}$$

On the other hand

$$\frac{1}{2}\left(\psi_{200} + \psi_{210}\right)^2 = \frac{1}{2}\left(\psi_{200}^2 + 2\psi_{200}\psi_{210} + \psi_{210}^2\right) \tag{159}$$

It is quickly shown by WolframAlpha that it holds

$$\langle \mathbf{p} \rangle_{\psi_{200}} = \langle \mathbf{p} \rangle_{\psi_{210}} = 0 \tag{160}$$

So it holds that

$$\langle \mathbf{p} \rangle_3 = -e \iiint \psi_{200}\psi_{210}\mathbf{r}\mathrm{d}\tau \tag{161}$$

When evaluated over the whole space, this integral only survives in the $\hat{k}$ direction and it equals

$$\langle \mathbf{p} \rangle_3 = \boxed{3ea\hat{k}} \tag{162}$$

Thanks to the computational power of WolframAlpha.

Note that

$$\frac{1}{2}\left(\psi_{200}-\psi_{210}\right)^2=\frac{1}{2}\left(\psi_{200}+\psi_{210}\right)^2-\psi_{200}\psi_{210} \tag{163}$$

Hence from (160) and (161) it holds that

$$\langle\mathbf{p}\rangle_4=e\iiint\psi_{200}\psi_{210}\mathbf{r}\mathrm{d}\tau=\boxed{-3ea\hat{k}} \tag{164}$$

As it should be, since only the combination of the two states would generate a non-zero expectation value of $\mathbf{p}$, and the effective operator combinations are the same in magnitude, but opposite in sign ($\psi_{200}\psi_{210}$ and $-\psi_{200}\psi_{210}$. It also makes sense that the overall permanent dipole moment points 'upwards' or 'downwards'-whichever orientation that may be with respect to the direction polarisation of electron density.