

Part A: L-S Coupling and Term Symbols (Problems 1-5)

Problem 1

Question: An atom has a single valence electron in the $4f$ state. Determine the possible values of the total angular momentum quantum number J and write down the corresponding spectroscopic term symbols.

Solution:

1. **Identify quantum numbers:**

- Orbital angular momentum quantum number: $l = 3$ (for f state).
- Spin angular momentum quantum number: $s = 1/2$ (for a single electron).

2. **Determine L and S:**

- Since there is only one electron, the total orbital angular momentum $L = l = 3$.
- The total spin angular momentum $S = s = 1/2$.

3. **Calculate J:** The total angular momentum J is given by the vector sum of L and S : $J = L + S$.

$$J = |L - S|, \dots, L + S$$

4.

$$J = |3 - 1/2|, \dots, 3 + 1/2$$

5.

$$J = 5/2, \dots, 7/2$$

6.

The possible values for J are $5/2$ and $7/2$.

7. **Determine Term Symbol:** The general term symbol is $^{2S+1}L_J$.

- Spin Multiplicity: $2S + 1 = 2(1/2) + 1 = 2$.
- L-symbol: $L = 3$ corresponds to the F state.
- The two term symbols are:

$$^2F_{5/2} \quad \text{and} \quad ^2F_{7/2}$$

Problem 2

Question: A hypothetical atom has an electron configuration resulting in a total orbital angular momentum $L = 2$ and a total spin angular momentum $S = 1$.

- a) What is the spin multiplicity of this state?
- b) What are the possible values of the total angular momentum quantum number J ?
- c) Write down the full set of spectroscopic term symbols for this configuration.

Solution: a) **Spin Multiplicity:**

$$\text{Multiplicity} = 2S + 1$$

$$\text{Multiplicity} = 2(1) + 1 = 3$$

b) **Possible J values:**

$$J = |L - S|, \dots, L + S$$

$$J = |2 - 1|, \dots, 2 + 1$$

$$J = 1, 2, 3$$

The possible values for J are **1, 2, and 3**.

c) **Term Symbols:** The L-symbol for $L = 2$ is D . The multiplicity is 3. The term symbols are:

$${}^3D_1, \quad {}^3D_2, \quad {}^3D_3$$

Problem 3

Question: For a state with the term symbol ${}^4P_{5/2}$, determine the total orbital angular momentum L , the total spin angular momentum S , and the spin multiplicity.

Solution:

5. **Determine L:** The letter P in the term symbol corresponds to $L = 1$.

$$L = 1$$

6. **Determine Spin Multiplicity:** The superscript is the spin multiplicity, $2S + 1$.

$$2S + 1 = 4$$

7.

$$\text{Multiplicity} = 4$$

8. **Determine S:** Solve for S from the multiplicity.

$$2S + 1 = 4 \Rightarrow 2S = 3 \Rightarrow \mathbf{S = 3/2}$$

9. **Verify J:** The subscript is $J = 5/2$. We check if this is consistent with $L = 1$ and $S = 3/2$.

$$J_{\max} = L + S = 1 + 3/2 = 5/2$$

10.

$$J_{\min} = |L - S| = |1 - 3/2| = 1/2$$

11.

The possible J values are $1/2, 3/2, 5/2$. Since $5/2$ is one of the possible values, the term symbol is valid.

Problem 4

Question: Consider the $3d$ electron in a hydrogen-like atom.

a) What are the possible values of J ?

b) Which of the resulting fine structure states has the lower energy? Justify your answer.

Solution: a) **Possible J values:** * $l = 2$ (for d state), so $L = 2$.

* $s = 1/2$, so $S = 1/2$.

$$J = |L - S|, \dots, L + S$$

$$J = |2 - 1/2|, \dots, 2 + 1/2$$

$$J = 3/2, \dots, 5/2$$

The possible values for J are $3/2$ and $5/2$.

b) **Lower Energy State:** * The fine structure splitting is primarily due to the spin-orbit interaction, $\Delta E_{SO} \propto \mathbf{L} \cdot \mathbf{S}$.

* For a single electron, the spin-orbit coupling constant A is positive (normal order).

* The energy is lower for the state where $\mathbf{L}$ and $\mathbf{S}$ are anti-parallel, which corresponds to the **smaller** J value.

* Therefore, the state with the lower energy is $^2D_{3/2}$.

Problem 5

Question: The ground state of the Sodium (Na) atom has the electron configuration $1s^2 2s^2 2p^6 3s^1$. Determine the ground state term symbol.

Solution:

9. **Identify the valence electron:** The only electron outside the closed shells is the $3s$ electron.

10. **Determine L and S for the valence electron:**

– $l = 0$ (for s state), so $L = 0$.

– $s = 1/2$, so $S = 1/2$.

11. **Calculate J :**

$$J = |L - S|, \dots, L + S$$

12.

$$J = |0 - 1/2|, \dots, 0 + 1/2$$

13.

$$J = 1/2$$

14. **Determine Term Symbol:**

– Multiplicity: $2S + 1 = 2(1/2) + 1 = 2$.

– L -symbol: $L = 0$ corresponds to the S state.

– The ground state term symbol is $^2S_{1/2}$.

Part B: Spin-Orbit Interaction and Landé Interval Rule (Problems 6-10)

Problem 6

Question: A term in an atom is split into three fine structure levels with $J = 1, 2, 3$. The energy difference between the $J = 2$ and $J = 1$ levels is ΔE_{21} . According to the Landé Interval Rule, what is the energy difference between the $J = 3$ and $J = 2$ levels, ΔE_{32} , in terms of ΔE_{21} ?

Solution:

13. **State the Landé Interval Rule:** The energy splitting between successive levels J and $J - 1$ is proportional to the larger J value: $\Delta E(J, J - 1) = A \cdot J$, where A is the spin-orbit coupling constant.

14. **Apply the rule to ΔE_{21} :**

$$\Delta E_{21} = E_2 - E_1 = A \cdot 2$$

15.

$$A = \frac{\Delta E_{21}}{2}$$

16. **Apply the rule to ΔE_{32} :**

$$\Delta E_{32} = E_3 - E_2 = A \cdot 3$$

17. **Substitute A:**

$$\Delta E_{32} = \left(\frac{\Delta E_{21}}{2} \right) \cdot 3$$

18.

$$\Delta E_{32} = 1.5 \cdot \Delta E_{21}$$

Problem 7

Question: The spin-orbit interaction energy is given by $\Delta E_{SO} = \frac{A}{2} [J(J + 1) - L(L + 1) - S(S + 1)]$. Calculate the spin-orbit energy shift for the $^2P_{3/2}$ state of an atom, in terms of the coupling constant A .

Solution:

17. **Identify quantum numbers from the term symbol $^2P_{3/2}$:**

- $L = 1$ (from P state).
- $2S + 1 = 2 \Rightarrow S = 1/2$.
- $J = 3/2$.

18. **Substitute values into the ΔE_{SO} formula:**

$$\Delta E_{SO} = \frac{A}{2} [J(J+1) - L(L+1) - S(S+1)]$$

19.

$$\Delta E_{SO} = \frac{A}{2} \left[\frac{3}{2} \left(\frac{3}{2} + 1 \right) - 1(1+1) - \frac{1}{2} \left(\frac{1}{2} + 1 \right) \right]$$

20. Calculate the terms:

$$- J(J+1) = \frac{3}{2} \cdot \frac{5}{2} = \frac{15}{4}$$

$$- L(L+1) = 1 \cdot 2 = 2$$

$$- S(S+1) = \frac{1}{2} \cdot \frac{3}{2} = \frac{3}{4}$$

21. Calculate the bracketed term:

$$\left[\frac{15}{4} - 2 - \frac{3}{4} \right] = \left[\frac{15}{4} - \frac{8}{4} - \frac{3}{4} \right] = \frac{15 - 8 - 3}{4} = \frac{4}{4} = 1$$

22. Final ΔE_{SO} :

$$\Delta E_{SO} = \frac{A}{2} \cdot 1 = \frac{A}{2}$$

Problem 8

Question: For the same atom in Problem 7, calculate the spin-orbit energy shift for the $^2P_{1/2}$ state, and then find the total fine structure splitting ΔE between the $^2P_{3/2}$ and $^2P_{1/2}$ states.

Solution:

22. Identify quantum numbers for $^2P_{1/2}$:

$$- L = 1, S = 1/2, J = 1/2.$$

23. Calculate ΔE_{SO} for $^2P_{1/2}$:

$$\Delta E_{SO} = \frac{A}{2} [J(J+1) - L(L+1) - S(S+1)]$$

24.

$$\Delta E_{SO} = \frac{A}{2} \left[\frac{1}{2} \left(\frac{1}{2} + 1 \right) - 1(2) - \frac{1}{2} \left(\frac{3}{2} \right) \right]$$

25.

$$\Delta E_{SO} = \frac{A}{2} \left[\frac{3}{4} - 2 - \frac{3}{4} \right]$$

26.

$$\Delta E_{SO} = \frac{A}{2} [-2] = -A$$

27. Calculate the total fine structure splitting ΔE :

$$\Delta E = E(^2P_{3/2}) - E(^2P_{1/2})$$

28.

$$\Delta E = \Delta E_{SO}(^2P_{3/2}) - \Delta E_{SO}(^2P_{1/2})$$

29.

$$\Delta E = \frac{A}{2} - (-A) = \frac{A}{2} + A = \frac{3A}{2}$$

30. Alternatively, using the Landé Interval Rule for $J = 3/2$ and $J = 1/2$: $\Delta E = A \cdot J_{\max} = A \cdot (3/2) = 3A/2$. Note that the Landé rule applies to successive integer J values, but for a doublet $S = 1/2$, the splitting is simply $A(L + 1/2) = A(1 + 1/2) = 3A/2$.

Problem 9

Question: A ^3F term is split into three fine structure levels. If the energy difference between the highest and the middle level is 10 cm^{-1} , what is the energy difference between the middle and the lowest level?

Solution:

25. Determine L and S :

- $^3F \Rightarrow L = 3$ (from F state).
- $^3F \Rightarrow 2S + 1 = 3 \Rightarrow S = 1$.

26. Determine J values:

$$J = |L - S|, \dots, L + S$$

27.

$$J = |3 - 1|, \dots, 3 + 1$$

28.

$$J = 2, 3, 4$$

29.

The levels are ${}^3F_2$ (lowest), ${}^3F_3$ (middle), and ${}^3F_4$ (highest).

30. **Apply Landé Interval Rule:**

- Splitting between $J = 4$ and $J = 3$ (Highest and Middle):

$$\Delta E_{43} = E_4 - E_3 = A \cdot 4$$

- Splitting between $J = 3$ and $J = 2$ (Middle and Lowest):

$$\Delta E_{32} = E_3 - E_2 = A \cdot 3$$

31. **Use the given information:**

$$\Delta E_{43} = 10 \text{ cm}^{-1}$$

32.

$$A \cdot 4 = 10 \text{ cm}^{-1} \Rightarrow A = \frac{10}{4} = 2.5 \text{ cm}^{-1}$$

33. **Calculate the required splitting:**

$$\Delta E_{32} = A \cdot 3$$

34.

$$\Delta E_{32} = (2.5 \text{ cm}^{-1}) \cdot 3 = 7.5 \text{ cm}^{-1}$$

Problem 10

Question: The spin-orbit coupling constant A for a certain ${}^3D$ multiplet is 5×10^{-4} eV. Calculate the total energy separation between the lowest and the highest fine structure levels of this multiplet.

Solution:

30. **Determine L and S:**

- ${}^3D \Rightarrow L = 2.$
- ${}^3D \Rightarrow S = 1.$

31. **Determine J values:**

$$J = |L - S|, \dots, L + S$$

32.

$$J = |2 - 1|, \dots, 2 + 1$$

33.

$$J = 1, 2, 3$$

34.

The levels are $^3D_1$ (lowest), $^3D_2$ (middle), and $^3D_3$ (highest).

35. **Calculate the total separation ΔE_{total} :**

$$\Delta E_{\text{total}} = E_3 - E_1 = (E_3 - E_2) + (E_2 - E_1)$$

36. **Apply Landé Interval Rule:**

$$- \quad E_3 - E_2 = A \cdot 3$$

$$- \quad E_2 - E_1 = A \cdot 2$$

$$\Delta E_{\text{total}} = A \cdot 3 + A \cdot 2 = 5A$$

37. **Substitute the value of A:**

$$\Delta E_{\text{total}} = 5 \cdot (5 \times 10^{-4} \text{ eV})$$

38.

$$\Delta E_{\text{total}} = 25 \times 10^{-4} \text{ eV} \quad \text{or} \quad 2.5 \times 10^{-3} \text{ eV}$$

Part C: Fine Structure in Hydrogen-like Atoms (Problems 11-15)

Use the following constants for calculations in this section:

- Fine Structure Constant: $\alpha \approx 1/137$
- Rydberg Energy: $E_R = 13.6 \text{ eV}$

Problem 11

Question: The fine structure energy correction for a hydrogen-like atom with atomic number Z is given by the relativistic formula (from the Dirac equation, ignoring the Darwin term and mass correction for simplicity in this form):

$$\Delta E_{n,j} = \frac{E_n \alpha^2 Z^2}{n} \left(\frac{1}{j + 1/2} - \frac{3}{4n} \right)$$

where $E_n = -E_R Z^2 / n^2$. Calculate the fine structure splitting ΔE between the $2P_{3/2}$ and $2P_{1/2}$ states of the Hydrogen atom ($Z = 1$).

Solution:

35. Identify parameters:

- $Z = 1, n = 2$.
- $E_n = -E_R Z^2 / n^2 = -13.6/4 = -3.4 \text{ eV}$.
- $\alpha^2 \approx (1/137)^2 \approx 5.32 \times 10^{-5}$.

36. Calculate $\Delta E_{n,j}$ for $2P_{3/2}$ ($j = 3/2$):

$$\Delta E_{3/2} = \frac{E_n \alpha^2 Z^2}{n} \left(\frac{1}{3/2 + 1/2} - \frac{3}{4(2)} \right)$$

37.

$$\Delta E_{3/2} = \frac{E_n \alpha^2}{2} \left(\frac{1}{2} - \frac{3}{8} \right) = \frac{E_n \alpha^2}{2} \left(\frac{4-3}{8} \right) = \frac{E_n \alpha^2}{16}$$

38. Calculate $\Delta E_{n,j}$ for $2P_{1/2}$ ($j = 1/2$):

$$\Delta E_{1/2} = \frac{E_n \alpha^2 Z^2}{n} \left(\frac{1}{1/2 + 1/2} - \frac{3}{4(2)} \right)$$

39.

$$\Delta E_{1/2} = \frac{E_n \alpha^2}{2} \left(\frac{1}{1} - \frac{3}{8} \right) = \frac{E_n \alpha^2}{2} \left(\frac{8-3}{8} \right) = \frac{5E_n \alpha^2}{16}$$

40. Calculate the splitting ΔE :

$$\Delta E = \Delta E_{3/2} - \Delta E_{1/2}$$

41.

$$\Delta E = \frac{E_n \alpha^2}{16} - \frac{5E_n \alpha^2}{16} = -\frac{4E_n \alpha^2}{16} = -\frac{E_n \alpha^2}{4}$$

42. Substitute numerical values:

$$\Delta E = -\frac{(-3.4 \text{ eV}) \cdot (5.32 \times 10^{-5})}{4}$$

43.

$$\Delta E \approx 4.52 \times 10^{-5} \text{ eV}$$

Problem 12

Question: How does the fine structure splitting ΔE between the $2P_{3/2}$ and $2P_{1/2}$ states of a hydrogen-like ion scale with the atomic number Z ?

Solution:

40. **Recall the splitting formula (from Problem 11):**

$$\Delta E = -\frac{E_n \alpha^2 Z^2}{4}$$

41. **Recall the formula for E_n :**

$$E_n = -\frac{E_R Z^2}{n^2}$$

42. **Substitute E_n into the splitting formula:**

$$\Delta E = -\frac{1}{4} \left(-\frac{E_R Z^2}{n^2} \right) \alpha^2 Z^2$$

43.

$$\Delta E = \left(\frac{E_R \alpha^2}{4n^2} \right) Z^4$$

44. **Conclusion:** Since E_R , α , and n are constants, the fine structure splitting ΔE is proportional to Z^4 .

$$\Delta E \propto Z^4$$

Problem 13

Question: For a given principal quantum number n , the fine structure splitting is generally observed between states with different j values but the same l value (e.g., $2P_{1/2}$ and $2P_{3/2}$). Explain why the $2S_{1/2}$ and $2P_{1/2}$ states in Hydrogen are nearly degenerate (have almost the same energy) according to the Dirac theory.

Solution:

44. **Recall the Dirac Energy Formula:** The energy levels $E_{n,j}$ depend only on the principal quantum number n and the total angular momentum quantum number j .

$$E_{n,j} = -\frac{13.6Z^2}{n^2} \left[1 + \frac{\alpha^2 Z^2}{n} \left(\frac{1}{j + 1/2} - \frac{3}{4n} \right) \right]$$

45. **Compare the states:**

- $2S_{1/2}$: $n = 2, j = 1/2$.
- $2P_{1/2}$: $n = 2, j = 1/2$.

46. **Conclusion:** Since both states have the same n and the same j quantum numbers, the Dirac relativistic theory predicts that they have exactly the same energy. This is known as **accidental degeneracy** in the relativistic treatment.

- *Note for advanced context (not required for JAM, but for completeness):* The small energy difference that *does* exist between $2S_{1/2}$ and $2P_{1/2}$ is called the **Lamb Shift**, which is a quantum electrodynamics (QED) effect and is not accounted for by the Dirac equation alone.

Problem 14

Question: Calculate the ratio of the fine structure splitting of the $2P$ state in a singly ionized Helium atom (He^+) to that of the $2P$ state in a Hydrogen atom (H).

Solution:

47. **Identify parameters:**

- Hydrogen (H): $Z_H = 1$.
- Singly ionized Helium (He^+): $Z_{He} = 2$.
- Both are $n = 2$ states.

48. **Recall the scaling law (from Problem 12):**

$$\Delta E \propto Z^4$$

49. **Set up the ratio:**

$$\text{Ratio} = \frac{\Delta E(\text{He}^+)}{\Delta E(\text{H})} = \frac{Z_{He}^4}{Z_H^4}$$

50. **Substitute Z values:**

$$\text{Ratio} = \frac{2^4}{1^4} = \frac{16}{1}$$

51.

The ratio of the fine structure splitting is **16: 1**.

Problem 15

Question: The spin-orbit interaction energy is proportional to $1/n^3$. If the fine structure splitting of the $2P$ state in Hydrogen is ΔE_2 , what is the splitting ΔE_3 of the $3P$ state, assuming all other factors remain constant?

Solution:

51. **State the proportionality:** The spin-orbit splitting ΔE_{SO} is proportional to $1/n^3$.

$$\Delta E_{SO} \propto \frac{1}{n^3}$$

52. **Set up the ratio of splittings:**

$$\frac{\Delta E_3}{\Delta E_2} = \frac{1/n_3^3}{1/n_2^3} = \left(\frac{n_2}{n_3}\right)^3$$

53. **Identify principal quantum numbers:**

- $n_2 = 2$ (for $2P$ state).
- $n_3 = 3$ (for $3P$ state).

54. **Calculate the ratio:**

$$\frac{\Delta E_3}{\Delta E_2} = \left(\frac{2}{3}\right)^3 = \frac{8}{27}$$

55. **Express ΔE_3 in terms of ΔE_2 :**

$$\Delta E_3 = \frac{8}{27} \Delta E_2$$

Part D: Fine Structure in Alkali Atoms and Applications (Problems 16-20)

Problem 16

Question: The D-lines of Sodium (Na) arise from the transition $3P \rightarrow 3S$. Due to spin-orbit coupling, the $3P$ state is split into two levels, $3P_{3/2}$ and $3P_{1/2}$. If the splitting between these two levels is ΔE , express ΔE in terms of the spin-orbit coupling constant A .

Solution:

56. **Identify the state and quantum numbers:** The splitting occurs in the $3P$ state, which is a doublet ($S = 1/2$).

- $L = 1$ (for P state).

- $S = 1/2$.
- The two J states are $J_> = 3/2$ and $J_< = 1/2$.

57. **Use the general splitting formula for a doublet:** The energy splitting ΔE between $J = L + 1/2$ and $J = L - 1/2$ is given by:

$$\Delta E = \Delta E_{so}(J_>) - \Delta E_{so}(J_<)$$

58.

$$\Delta E = \frac{A}{2} [J_>(J_> + 1) - J_<(J_< + 1)]$$

- $J_>(J_> + 1) = \frac{3}{2} \cdot \frac{5}{2} = \frac{15}{4}$
- $J_<(J_< + 1) = \frac{1}{2} \cdot \frac{3}{2} = \frac{3}{4}$

$$\Delta E = \frac{A}{2} \left[\frac{15}{4} - \frac{3}{4} \right] = \frac{A}{2} \left[\frac{12}{4} \right] = \frac{A}{2} \cdot 3$$

-

$$\Delta E = \frac{3A}{2}$$

- *(This is the same result as Problem 8, confirming the general formula for P doublets).*

Problem 17

Question: The two D-lines of Sodium have wavelengths $\lambda_1 = 589.59$ nm and $\lambda_2 = 588.99$ nm. Calculate the fine structure splitting ΔE of the $3P$ state in cm^{-1} . Use: $c = 3 \times 10^{10}$ cm/s.

Solution:

58. **Calculate the wave numbers ($\bar{\nu}$):** The splitting is the difference in wave numbers.

$$\bar{\nu} = \frac{1}{\lambda}$$

59.

$$\bar{\nu}_1 = \frac{1}{589.59 \times 10^{-7} \text{ cm}} \quad (\text{since } 1 \text{ nm} = 10^{-7} \text{ cm})$$

60.

$$\bar{\nu}_2 = \frac{1}{588.99 \times 10^{-7} \text{ cm}}$$

61. Calculate the splitting ΔE in cm^{-1} :

$$\Delta E = |\bar{\nu}_2 - \bar{\nu}_1| = \left| \frac{1}{588.99 \times 10^{-7}} - \frac{1}{589.59 \times 10^{-7}} \right| \text{ cm}^{-1}$$

62.

$$\Delta E = \frac{10^7}{588.99 \cdot 589.59} \cdot (589.59 - 588.99) \text{ cm}^{-1}$$

63.

$$\Delta E = \frac{10^7}{347100} \cdot (0.60) \text{ cm}^{-1}$$

64.

$$\Delta E \approx 28.8 \times 0.60 \text{ cm}^{-1}$$

65.

$$\Delta E \approx 17.2 \text{ cm}^{-1}$$

66. (Alternatively, using the approximation $\Delta \bar{\nu} \approx \frac{\Delta \lambda}{\lambda^2}$ with $\lambda \approx 589.3 \text{ nm}$ and $\Delta \lambda = 0.60$ gives a similar result).

Problem 18

Question: The energy of an electron in an alkali atom can be approximated using the formula $E_n = -\frac{E_R}{(n^*)^2}$, where $n^* = n - \delta$ is the effective principal quantum number and δ is the quantum defect. If the ionization energy of the 3S state of Sodium ($n = 3$) is 5.14 eV, calculate the quantum defect δ for this state. Use: $E_R = 13.6 \text{ eV}$.

Solution:

60. **Relate Ionization Energy to E_n :** The ionization energy (IE) is the energy required to remove the electron, which is $|E_n|$.

$$|E_n| = 5.14 \text{ eV}$$

61. **Use the effective principal quantum number formula:**

$$|E_n| = \frac{E_R}{(n^*)^2}$$

62.

$$5.14 \text{ eV} = \frac{13.6 \text{ eV}}{(n^*)^2}$$

63. **Calculate n^* :**

$$(n^*)^2 = \frac{13.6}{5.14} \approx 2.646$$

64.

$$n^* = \sqrt{2.646} \approx 1.627$$

65. **Calculate the quantum defect δ :**

$$n^* = n - \delta \Rightarrow \delta = n - n^*$$

- For the 3S state, $n = 3$.

$$\delta = 3 - 1.627$$

-

$$\delta \approx \mathbf{1.373}$$

Problem 19

Question: The spin-orbit coupling constant A for the 3P state of Sodium is 11.5 cm^{-1} . Using the result from Problem 16, calculate the fine structure splitting ΔE in cm^{-1} . Compare this with the experimental value from Problem 17.

Solution:

64. **Recall the splitting formula for the 3P doublet (from Problem 16):**

$$\Delta E = \frac{3A}{2}$$

65. **Substitute the given value of A:**

$$\Delta E = \frac{3 \cdot (11.5 \text{ cm}^{-1})}{2}$$

66.

$$\Delta E = \frac{34.5}{2} \text{ cm}^{-1}$$

67.

$$\Delta E = 17.25 \text{ cm}^{-1}$$

68. **Comparison with experimental value (from Problem 17):**

- Calculated Splitting: 17.25 cm^{-1}
- Experimental Splitting: $\approx 17.2 \text{ cm}^{-1}$
- **Conclusion:** The calculated value of 17.25 cm^{-1} is in excellent agreement with the experimental value of 17.2 cm^{-1} , confirming the validity of the L-S coupling model and the spin-orbit interaction as the dominant cause of the fine structure splitting in alkali atoms.

Problem 20

Question: Consider a ^3P multiplet in an atom. If the lowest energy level is $^3P_0$, and the energy difference between $^3P_1$ and $^3P_0$ is 10 meV, what is the energy difference between $^3P_2$ and $^3P_1$?

Solution:

67. **Identify J values:** The multiplet has $J = 0, 1, 2$.

- Lowest level: $J = 0$ ($^3P_0$).
- Middle level: $J = 1$ ($^3P_1$).
- Highest level: $J = 2$ ($^3P_2$).

68. **Apply Landé Interval Rule:**

- Splitting between $J = 1$ and $J = 0$:

$$\Delta E_{10} = E_1 - E_0 = A \cdot 1$$

- Splitting between $J = 2$ and $J = 1$:

$$\Delta E_{21} = E_2 - E_1 = A \cdot 2$$

69. Use the given information:

$$\Delta E_{10} = 10 \text{ meV}$$

70.

$$A \cdot 1 = 10 \text{ meV} \Rightarrow A = 10 \text{ meV}$$

71. Calculate the required splitting ΔE_{21} :

$$\Delta E_{21} = A \cdot 2$$

72.

$$\Delta E_{21} = (10 \text{ meV}) \cdot 2$$

73.

$$\Delta E_{21} = \mathbf{20 \text{ meV}}$$

Summary of Formulas Used

Concept	Formula	Notes
Total Angular Momentum (J)	$J = L$	- S
Term Symbol	$^{2S+1}L_J$ $L=0$	,1,2,3 S, P, D, F
Spin-Orbit Energy Shift	$\Delta E_{SO} = \frac{A}{2} [J(J+1) - L(L+1) - S(S+1)]$ A is	the coupling constant.
Landé Interval Rule	$\Delta E(J, J-1) = E_J - E_{J-1} = A \cdot J$ Splitt	ing is proportional to the larger J.
H-like Fine Structure	$\Delta E \propto Z^4$ Split	ting scales with Z^4 for a given n .
Alkali Doublet Splitting	$\Delta E = \frac{3A}{2}$ (for P state) Splitt	ing between $P_{3/2}$ and $P_{1/2}$.
Quantum Defect	$E_n = -\frac{E_R}{(n-\delta)^2}$ Used fo	r calculating energy levels in alkali atoms.