

Question 1: Consider a 2-fold degenerate state with (normalized) eigen functions u_1 and u_2 . Consider a perturbation H' with

$$H'_{11} = \langle 1|H'|1 \rangle = 0, \quad H'_{22} = \langle 2|H'|2 \rangle = 0 \quad \text{and} \quad H'_{12} = H'_{21} = \sigma$$

Obtain the splitting and corresponding eigen function.

Solution 1: Let $\phi = c_1u_1 + c_2u_2$

We will have

$$\begin{aligned} c_1(H'_{11} - W^{(1)}) + c_2H'_{12} &= 0 \\ c_1H'_{21} + c_2(H'_{22} - W^{(1)}) &= 0 \end{aligned}$$

Thus

$$\begin{aligned} -c_1W^{(1)} + c_2\sigma &= 0 \\ c_1\sigma - c_2W^{(1)} &= 0 \end{aligned}$$

The secular equation is

$$\begin{vmatrix} -W^{(1)} & \sigma \\ \sigma & -W^{(1)} \end{vmatrix} = 0 \Rightarrow W^{(1)2} = \sigma^2$$

$\Rightarrow W^{(1)} = \pm\sigma$ (this is the perturbation)

For $W^{(1)} = +\sigma, c_1 = c_2 \Rightarrow \phi = \frac{1}{\sqrt{2}}(u_1 + u_2)$

For $W^{(1)} = -\sigma, c_1 = -c_2 \Rightarrow \phi = \frac{1}{\sqrt{2}}(u_1 - u_2)$

Question 2: Consider a 3-fold degenerate state with (normalized) eigenfunctions u_1, u_2 and u_3 .

Assume there is a perturbation H' and the only non-vanishing matrix elements are $(H')_{13} = g = (H')_{31}$. Calculate perturbation to eigenvalues and corresponding eigen functions.

Solution 2: Let $\phi = c_1u_1 + c_2u_2 + c_3u_3$

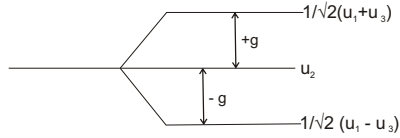
We will have

$$\begin{aligned} c_1(H'_{11} - W) + c_2H'_{12} + c_3H'_{13} &= 0 \\ c_2H'_{21} + c_2(H'_{22} - W) + c_3H'_{23} &= 0 \\ c_1H'_{31} + c_2H'_{32} + c_3(H'_{33} - W) &= 0 \end{aligned}$$

Thus

$$\begin{aligned} -c_1W + c_3g &= 0 \\ c_1g - c_2W &= 0 \\ c_1g - c_3W &= 0 \end{aligned}$$

If $c_2 \neq 0$ (and $c_1 = 0 = c_3$) then $W = 0$ and $\phi = u_2$



(The degeneracy is completely lifted).

Question 3: The $n = 2$ state of the hydrogen atom is 4 fold degenerate.

$$\begin{aligned} u_1 &= R_{20}(r)Y_{00}(\theta, \phi); u_2 = R_{21}(r)Y_{10}(\theta, \phi) \\ u_3 &= R_{21}(r)Y_{11}(\theta, \phi); u_4 = R_{21}(r)Y_{1,-1}(\theta, \phi) \end{aligned}$$

where $R_{nl}(r)Y_{lm}(\theta, \phi)$ are the normalized hydrogen atom wave functions. The atom is in a static electric field and the perturbation term is

$$H' = q\epsilon z = q\epsilon r \cos \theta \quad (q > 0)$$

q is the magnitude of electron charge and ϵ the strength of electric field which is in the z -direction only. Only non-vanishing matrix elements are:

$$\begin{aligned} H'_{12} &= H'_{21} = -g = -3q\epsilon a_0 \\ H'_{12} &= \int \int \int u_1^* H' u_2 d\tau \quad \text{etc} \end{aligned}$$

All other elements like H'_{11} , H'_{13} , H'_{23} , ... are zero. Calculate the perturbation and the corresponding wave functions.

Solution 3: Let $\phi = c_1 u_1 + c_2 u_2 + c_3 u_3 + c_4 u_4$

We will have

$$-c_1 W - c_2 g = 0$$

$$-c_1 g - c_2 W = 0$$

$$c_3(-W) = 0$$

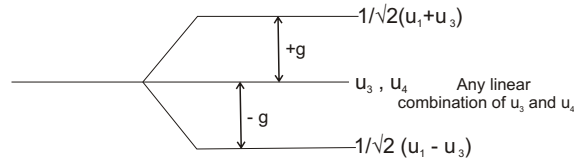
$$c_4(-W) = 0$$

Thus the secular determinant is

$$\begin{vmatrix} -W & -g & 0 & 0 \\ g & -W & 0 & 0 \\ 0 & 0 & -W & 0 \\ 0 & 0 & 0 & -W \end{vmatrix} = 0$$

The roots are $W = +g, -g, 0, 0$

The corresponding wave function are $\frac{1}{\sqrt{2}}(u_1 - u_2), \frac{1}{\sqrt{2}}(u_1 + u_2), c_3u_3 + c_4u_4$



The degeneracy is partially lifted. This is known as linear Stark effect.

Question 4: For a hydrogen atom placed in a weak uniform magnetic field (in the z-direction) the perturbation is given by $H' = \frac{\mu_B B}{\hbar} L_z$ where spin is neglected. Use degenerate state perturbation theory to calculate the splitting of the $n = 2$ and $n = 3$ levels.

Solution 4: The Hydrogen atom eigenfunctions are

$$\psi_{nlm}(r, \theta, \phi) = R_{nl}(r)Y_{lm}(\theta, \phi)$$

For $n = 2$ we have 4 wave functions

$$u_1 = R_{20}Y_{00}; u_2 = R_{21}Y_{00}; u_3 = R_{21}Y_{1,1}; u_4 = R_{21}Y_{1,-1}$$

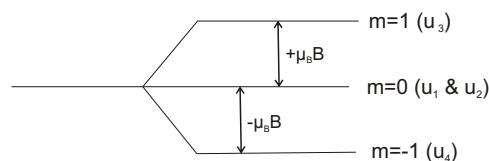
Now ψ_{nlm} are eigen functions of L_z .

$$L_z \psi_{nlm} = m\hbar \psi_{nlm}$$

Thus, we have a representation in which H' is diagonal and the diagonal elements are:

$$H'_{11} = 0, H'_{22} = 0, H'_{33} = +\mu_B B \text{ and } H'_{44} = -\mu_B B$$

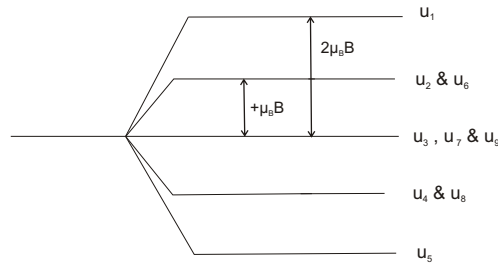
Thus the degeneracy is partially lifted



For $n = 3$, we will have wave functions:

$$\left. \begin{array}{l} u_1 = R_{32}Y_{22} \\ u_2 = R_{32}Y_{21} \\ u_3 = R_{32}Y_{20} \\ u_4 = R_{32}Y_{2,-1} \\ u_5 = R_{32}Y_{2,-2} \end{array} \right\} l = 2 \quad \left. \begin{array}{l} u_6 = R_{31}Y_{11} \\ u_7 = R_{31}Y_{10} \\ u_8 = R_{31}Y_{1,-1} \end{array} \right\} l = 1 \quad \text{and} \quad u_9 = R_{30}Y_{00}$$

Thus



Question 5: If we take into account the perturbation term is given by: $H' = \frac{\mu_B B}{\hbar} (L_z + 2S_z)$.

Calculate the perturbation to the state $\phi(n = 2, l = 1, j = \frac{3}{2}, m_j = \frac{1}{2}) = \begin{pmatrix} \sqrt{\frac{2}{3}} R_{21}Y_{10} \\ \sqrt{\frac{1}{3}} R_{21}Y_{11} \end{pmatrix}$

Solution 5: The pauli Operator is given by

$$\frac{\mu_B B}{\hbar} (L_z + 2S_z) = \frac{\mu_B B}{\hbar} \begin{pmatrix} L_z + \hbar & 0 \\ 0 & L_z - \hbar \end{pmatrix}$$

Thus

$$\begin{aligned} \Delta W &= \frac{\mu_B B}{\hbar} \left(\sqrt{\frac{2}{3}} R_{21}Y_{10} \sqrt{\frac{1}{3}} R_{21}Y_{11} \right) \begin{pmatrix} L_z + \hbar & 0 \\ 0 & L_z - \hbar \end{pmatrix} \begin{pmatrix} \sqrt{\frac{2}{3}} R_{21}Y_{10} \\ \sqrt{\frac{1}{3}} R_{21}Y_{11} \end{pmatrix} \\ &= \frac{\mu_B B}{\hbar} \left(\sqrt{\frac{2}{3}} R_{21}Y_{10} \sqrt{\frac{1}{3}} R_{21}Y_{11} \right) \begin{pmatrix} \hbar \sqrt{\frac{2}{3}} R_{21}Y_{10} \\ 0 \end{pmatrix} \\ &= \frac{2}{3} \mu_B B \end{aligned}$$

where the integration over entire space is assumed.