

Notes for Lectures in Quantum Mechanics *

Theoretical Explanation of Fine Structure of Hydrogen Atom

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1 Theoretical explanation of fine structure of H atom

The fine structure of H atom energy levels is fully explained by the Dirac theory. The Dirac equation for Coulomb potential can be solved exactly and makes predictions which are in complete agreement with the experiments. The non-relativistic limit of Dirac equation adds three correction terms to the Coulomb interaction of the Schrödinger theory. These are

1. Correction due to relativistic variation of mass

$$H_1 = -\frac{p^4}{8m^3c^2} \quad (1)$$

2. Spin orbit coupling

$$H_2 = -\frac{e}{2m^2c^2} \frac{1}{r} \frac{dV}{dr} (\vec{L} \cdot \vec{S}) \quad (2)$$

where $V(r)$ is the electric potential due to the nucleus and is equal to $\frac{e^2}{r}$ for the hydrogen atom. It is useful to keep it general as the method becomes applicable to alkali atoms and other one electron systems.

3. Darwin term

$$H_3 = \frac{\pi\hbar^2}{2m^2c^2} (Ze^2)\delta(r) \quad (3)$$

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Here we will be concerned with a perturbative treatment of these three terms within the framework of non-relativistic quantum mechanics.

We will now give outline of perturbative calculation for shift in energy due to the three terms H_1, H_2 and H_3 . The algebraic details will be skipped.

1 Corrections due to H_1 term ... 1/2

The perturbation term being invariant under rotations, commutes with the angular momentum operators and hence it does not connect states with different ℓm values. Being independent of spin also it does not connect states with different spin projections m_s . Thus

$$\langle n\ell' m'_\ell m'_s | H_1 | n\ell m_\ell m_s \rangle = 0 \quad (4)$$

if $\ell' \neq \ell$ or $m'_\ell \neq m_\ell$ or $m'_s \neq m_s$. Thus matrix of H_1 between different states with energy E_n is already diagonal and the corrections to a level with quantum numbers $n\ell m_\ell m_s$ is given by the diagonal elements

$$(\Delta E)_1 = \langle n\ell m_\ell m_s | H_1 | n\ell m_\ell m_s \rangle \quad (5)$$

$$= -\frac{1}{m^3 c^2} \langle n\ell m_\ell m_s | p^4 | n\ell m_\ell m_s \rangle \quad (6)$$

$$= -\frac{1}{m^3 c^2} \langle n\ell m_\ell m_s | p^2 p^2 | n\ell m_\ell m_s \rangle. \quad (7)$$

Noting that the state $|n\ell m_\ell m_s\rangle$ is an eigenstate of the unperturbed Hamiltonian $H_0 = \frac{p^2}{2m} - \frac{Ze^2}{r}$, we have

$$(p^2) |n\ell m_\ell m_s\rangle = (2m) \left(H_0 + \frac{Ze^2}{r} \right) |n\ell m_\ell m_s\rangle \quad (8)$$

$$= (2m) \left(E_n + \frac{Ze^2}{r} \right) |n\ell m_\ell m_s\rangle \quad (9)$$

. So that the correction takes the form

$$(\Delta E)_1 = -\frac{1}{2mc^2} \left\langle E_n^2 + 2E_n \frac{Ze^2}{r} + \left(\frac{Ze^2}{r} \right)^2 \right\rangle. \quad (10)$$

Computing averages of $1/r$ and $1/r^2$ gives the first order correction $(\Delta E)_1$.

2 Corrections due to spin orbit term

The term H_2 contains $\vec{L}\vec{S}$ which commutes with \vec{L}^2 but does not commute with L_z and S_z . Therefore its matrix elements between states with different m_ℓ and m_s values will be non zero. Calculation of corrections to energy, for a given ℓ , will require diagonalization of $(2\ell + 1) \times (2\ell + 1)$ matrices. This diagonalization can be avoided and computations can be simplified by considering states $|n, \ell jm\rangle$ with definite values of operators J^2, L^2, S^2, J_z , where $\vec{J} = \vec{L} + \vec{S}$ is the total angular momentum. All these operators commute with H_2 and hence the off diagonal terms in this basis set will be zero and the corrections to the energy levels, $(E)_2$ will be given by the diagonal elements $\langle n\ell jm | H_2 | n\ell jm \rangle$.

Squaring $\vec{J} = \vec{L} + \vec{S}$, we get useful relation

$$\vec{L} \cdot \vec{S} = \frac{1}{2}(\vec{J}^2 - \vec{L}^2 - \vec{S}^2) \quad (11)$$

and the states $|n\ell jm\rangle$ are eigenstates of the operators $\vec{L} \cdot \vec{S}$ and $\frac{1}{2}(j(j+1) - \ell(\ell+1) - \frac{1}{4})\hbar^2$ is the corresponding eigenvalue.

Therefore we have

$$\langle n\ell jm | H_2 | n\ell jm \rangle = \frac{\hbar^2}{2}(j(j+1) - \ell(\ell+1) - \frac{1}{4})\langle n\ell jm | \xi(r) | n\ell jm \rangle, \quad (12)$$

where $\xi(r)$ is given by

$$\xi(r) = \frac{1}{2m^2c^2} \left(\frac{Ze^2}{r} \right) \quad (13)$$

and $V(r) = Ze/r$ for the Coulomb potential due to the nucleus has been substituted.

For spin half case in hand, j can take two values $\ell\frac{1}{2}$ and we get

$$\langle n\ell jm | H_2 | n\ell jm \rangle = \frac{\hbar^2}{2} \langle \xi(r) \rangle \left(\frac{Ze^2}{r^3} \right) \begin{cases} \ell, & \text{if } j = \ell + \frac{1}{2}, \\ -\ell - 1, & \text{if } j = \ell - \frac{1}{2}. \end{cases} \quad (14)$$

and $\langle \xi(r) \rangle$ denotes the average value of $\xi(r)$ in state $|n\ell m\rangle$. For $\ell = 0$ the spin orbit term $\vec{L} \cdot \vec{S}$ becomes zero. For $\ell \neq 0$ we get

$$\langle \xi(r) \rangle = \frac{Ze^2}{2m^2c^2} \left\langle \frac{1}{r^3} \right\rangle \quad (15)$$

$$= \frac{Ze^2}{2m^2c^2} \frac{2Z^3}{a_0^3 n^3 \ell(\ell+1)(2\ell+1)}, \quad \ell \neq 0. \quad (16)$$

This completes the computation of shift in energy $(\Delta E)_2$ due to the spin orbit term.

3 Contribution of Darwin term

The radial wave function for orbital angular momentum $\ell = 0$, for small r behaves like r^ℓ and vanishes for $r = 0$. Due to the presence of the Dirac delta function, $\delta(r)$, the Darwin term contribution is proportional to $|u_{n\ell m}(0)|^2$ and becomes zero for states with $\ell = 0$. The correction to the energy due to the Darwin term, for n^{th} level with $\ell = 0$ is given by

$$\Delta E_3 = \left(\frac{\pi Ze^2 \hbar^2}{2m^2 c^2} \right) \langle n00 | \delta(\vec{r}) | n00 \rangle \quad (17)$$

$$= \left(\frac{\pi Ze^2 \hbar^2}{2m^2 c^2} \right) |u_{n00}(0)|^2 \quad (18)$$

$$= -E_n \frac{(Z\alpha)^2}{n}. \quad (19)$$

2 Summary of perturbative treatment

The three terms H_1, H_2, H_3 obtained from Dirac equation, have been treated as a perturbation to the Coulomb interaction Hamiltonian

$$H_0 = \frac{p^2}{2m} - \frac{e^2}{r} \quad (20)$$

of the non-relativistic Schrödinger theory, and the results in the first order are adequate to explain the experimental results on the fine structure of energy levels. A level with principal quantum number has degeneracy $2n^2$, and, in general, one is required to construct $2n^2 \times 2n^2$ matrix and obtain its eigenvalues. In practise it has been avoided by a suitable choice of basis for degenerate level.

The three corrections coming from the interaction terms H_1, H_2, H_3 are as follows.

$$\Delta E_1 = -E_n \left(\frac{Z\alpha}{n} \right)^2 \left(\frac{3}{4} - \frac{n}{\ell + 1/2} \right) \quad (21)$$

$$\Delta E_2 = E_n \frac{(Z\alpha)^2}{n\ell(\ell+1)(2\ell+1)} \times \begin{cases} -\ell - 1 & \ell \neq 0 \\ 0, & \ell = 0 \end{cases} \quad (22)$$

$$\Delta E_3 = \begin{cases} -E_n \frac{(Z\alpha)^2}{n}, & \ell = 0 \\ 0, & \ell \neq 0 \end{cases} \quad (23)$$

3 Sum of all the three contributions

Combining all the three corrections gives the final answer, which does not depend on ℓ , but depends only on j . The sum of the three corrections can be written as

$$(\Delta E)_{nj} = E_n \left(\frac{Z\alpha}{n} \right)^2 \left(\frac{n}{j + 1/2} - \frac{3}{4} \right), \quad (24)$$

and the final energy after relativistic corrections is given by

$$E_{nj} = E_n \left\{ 1 + \left(\frac{Z\alpha}{n} \right)^2 \left(\frac{n}{j + 1/2} - \frac{3}{4} \right) \right\}. \quad (25)$$