QM-23 Lecture Notes
Approximation Schemes for Time Independent Problems[*]
23.3 Fine structure of hydrogen atom levels

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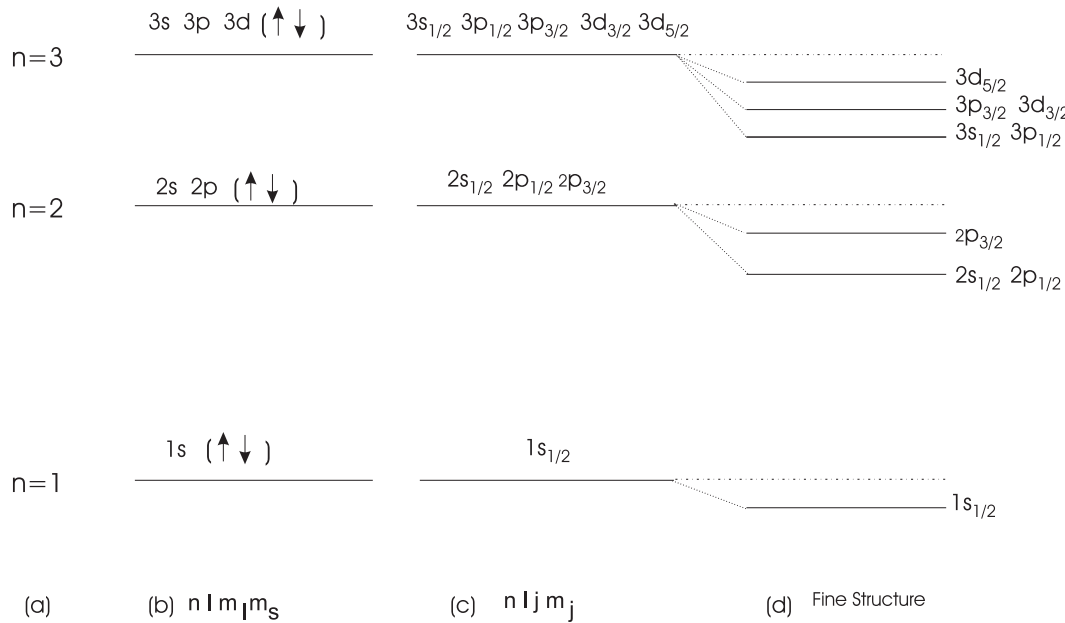akkhcu@gmail.com; kapoor.proofs@gmail.com

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§1   Observed structure of H atom energy levels

The first successful attempt to explain the H atom levels was by Bohr. In quantum mechanics the results are derived by solving the Schrodinger equation. The energy of a level with principal quantum number n is given by

$$En = \frac{\alpha^2 mc^2}{2n^2} \tag{1}$$

where $\alpha = e^2/(4\pi\epsilon_0)$ in si units, and is known as the fine structure constant. It is dimensionless and has a value $1/137.07$. The Schrödinger theory predicts that for a fixed value of the principal quantum number n, the angular momentum can take values $\ell = 0, 1, , (n1)$ and for each ℓ the z component of the angular momentum has $(2\ell + 1)$ values $m_\ell = \ell, \ell + 1, , \ell$. For each level corresponding to these combinations of $n\ell, m_\ell$ quantum numbers, the component of the spin of the electron along a specified directions can have two possible values to $\pm 1/2$. The energy depends only on n and hence there is a degeneracy of $2n^2$. For a few energy levels we schemetically show the set of quantum numbers in figure below.

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closely packed spectral lines. Translated in terms of energy levels, the fine structure refers to a fine splitting of energy levels, which is smaller approximately by a factor of α^2 as compared with the differences in Bohr levels with different n. The experimental results on fine structure of hydrogen atom energy levels can be summarised as follows.

The exact energies depend on j but do not depend on ℓ. Thus the H-atom levels, with the sane n but different j, get split by small amounts. However, the levels having same set of values for nj quantum numbers and different $\ell = j \pm 1/2$ remain degenerate, see Fig.4.1(d) Of course, there is no splitting between levels with different m_j (or m_s) values but same nj quantum numbers. So, for example, the structure of lowest three levels is as follows.

- The ground state level, $n = 1$, having $\ell = 0, j = 1/2$ only, receives corrections but there is no splitting as there is only one j value (=1/2) corresponding to $n = 1$.

- For $n = 2, \ell$ has values $0, 1$ and corresponding values of j are $1/2$, $3/2$. In the spectroscopic notation, nl_j , these levels are denoted by $2s_{\frac{1}{2}}, 2p_{\frac{1}{2}}, 2p_{\frac{3}{2}}$. The levels $2s_{\frac{1}{2}}$ and $2p_{\frac{1}{2}}$ remain degenerate but $2p_{\frac{3}{2}}$ receives a different correction and splits from the other levels. Thus $n = 2$ level splits into two levels corresponding to $j = 1/2, 3/2$.

- Similarly, for $n = 3$ in Schrödinger theory the levels $3s_{\frac{1}{2}}, 3p_{\frac{1}{2}}, 3p_{\frac{3}{2}}, 3d_{\frac{3}{2}}, 3d_{\frac{5}{2}}$ are all degenerate. These are seen to split into three groups of levels labelled by j values as given below.

$(a)\ 3s_{\frac{1}{2}}$ and $3p_{\frac{1}{2}}$ $\qquad (b)\ 3p_{\frac{3}{2}},\ 3d_{\frac{3}{2}}$ $\qquad (c)\ 3d_{\frac{5}{2}}$

The results described above are shown in figure, not to the scale, below. As already noted all the above splittings are small and are of the order

Boh r Levels : Quantum Numbers and Fine Structure Splitting

Fig. **1** Quantum numbers and fine structure

§2 Fine structure of H atom

Bohrs theory predicted spectral lines for hydrogen atom correctly. However, precise experiments showed that what was seen as a single spectral line in fact had a fine structure; most of the lines consist of several

of $\alpha^4 mc^2$. Lamb shift The Lamb shift refers to a very tiny splitting of energy levels with same nj and different ℓ values. The Lamb shift is of the order of $\alpha^5 mc^2$. For example, experimentally the levels $2s_{\frac{1}{2}}$ and $2p_{\frac{1}{2}}$ are not degenerate and the energy difference is given by

$$E(2s_{\frac{1}{2}})E(2p_{\frac{1}{2}})1057 text MHz. \tag{2}$$

§3   Hyperfine structure

The energy levels of Hydrogen atom after taking into account of of the fine structure and the Lamb shift appear as shown in figure below. Each of these levels have a hyperfine structure; each level splits further into two levels with energy differences $\sim \frac{m}{M}\alpha^4 mc^2$ where M is the proton mass. Order of magnitudes of various observed energy level splittings can be summarised as follows.

Bohr levels	Fine splitting	Lamb shift	Hyperfine splitting
$\alpha^2 mc^2$	$\alpha^4 mc^2$	$\alpha^5 mc^2$	$\left(\frac{m_e}{m_p}\right)\alpha^4 mc^2$
$\sim$ a few eV	~ 104 eV	~ 106 eV	~ 107 eV

The energy level diagram showing the fine structure, Lamb shift and the hyperfine structure, drawn schematically, is given below.
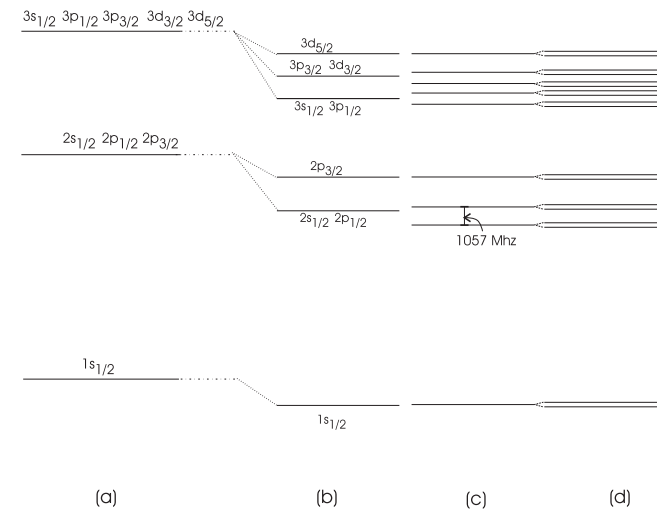
(a) Bohr Levels (b) Fine Structure (c) Lamb shift (d) Hyperfine Structure

Fig. **2**

§4   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 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

$$H_1 = -\frac{p^4}{8m^3c^2} \tag{3}$$

2. Spin orbit coupling

$$H_2 = -\frac{e}{2m^2c^2} \frac{1}{r} \frac{dV}{dr} (\vec{L} \cdot \vec{S}) \tag{4}$$

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

$$H_3 = \frac{\pi \hbar^2}{2m^2c^2}(Ze^2)\delta(r) \tag{5}$$

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.

Corrections due to H_1 term

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

$$\langle n\ell' m'_\ell m'_s | H_1 | n\ell m_\ell m_s \rangle = 0 \tag{6}$$

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 laready diagonal and the corrections to a level with quantum numbers $n\ell m_\ell m_s$ is given by the diagonal elements

$$
\begin{aligned}
(\Delta E)_1 &= \langle n\ell m_\ell m_s | H_1 | n\ell m_\ell m_s \rangle \tag{7} \\
&= -\frac{1}{m^3c^2} \langle n\ell m_\ell m_s | p^4 | n\ell m_\ell m_s \rangle \tag{8} \\
&= -\frac{1}{m^3c^2} \langle n\ell m_\ell m_s | p^2 p^2 | n\ell m_\ell m_s \rangle. \tag{9}
\end{aligned}
$$

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

$$
\begin{aligned}
(p^2)|n\ell m_\ell m_s\rangle &= (2m)\Big(H_0 + \frac{Ze^2}{r}\Big)|n\ell m_\ell m_s\rangle \tag{10} \\
&= (2m)\Big(E_n + \frac{Ze^2}{r}\Big)|n\ell m_\ell m_s\rangle \tag{11}
\end{aligned}
$$

. So that the correction takes the form

$$(\Delta E)_1 = -\frac{1}{2mc^2}\left\langle E_n^2 + 2E_n\frac{Ze^2}{r} + \left(\frac{Ze^2}{r}\right)^2 \right\rangle. \tag{12}$$

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

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 $(2\ell+1) \times (2\ell+1)$ martices. 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 $\langle nljm|H_2|nljm\rangle$. Squaring $\vec{J} = \vec{L} + \vec{S}$, we get useful relation

$$\vec{L} \cdot \vec{S} = \frac{1}{2}(\vec{J}^2 - \vec{L}^2 - \vec{S}^2) \tag{13}$$

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

$$\langle n\ell jm|H_2|n\ell jm\rangle = \frac{\hbar^2}{2}(j(j+1) - \ell(\ell+1) - \frac{1}{4})\langle n\ell jm|\xi(r)|n\ell jm\rangle, \tag{14}$$

where $\xi(r)$ is given by

$$\xi(r) = \frac{1}{2m^2c^2}\left(\frac{Ze^2}{r}\right) \tag{15}$$

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

$$\langle n\ell jm|H_2|n\ell jm\rangle = \frac{\hbar^2}{2}\langle \xi(r)\rangle\left(\frac{Ze^2}{r^3}\right)\begin{cases}\ell, & \text{if } j = \ell + \frac{1}{2}, \\ -\ell - 1, & \text{if } j = \ell - \frac{1}{2}.\end{cases} \tag{16}$$

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

$$\langle \xi(r)\rangle = \frac{Ze^2}{2m^2c^2}\left\langle \frac{1}{r^3}\right\rangle \tag{17}$$

$$= \frac{Ze^2}{2m^2c^2}\frac{2Z^3}{a_0^3 n^3 \ell(\ell+1)(2\ell+1)}, \quad \ell \neq 0. \tag{18}$$

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

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

$$\Delta E_3 = \left(\frac{\pi Ze^2\hbar^2}{2m^2c^2}\right)\langle n00|\delta(\vec{r})|n00\rangle \tag{19}$$

$$= \left(\frac{\pi Ze^2\hbar^2}{2m^2c^2}\right)|u_{n00}(0)|^2 \tag{20}$$

$$= -E_n\frac{(Z\alpha)^2}{n}. \tag{21}$$

§5 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

$$H_0 = \frac{p^2}{2m} - \frac{e^2}{r} \tag{22}$$

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.

$$\Delta E_1 = -E_n \Big(\frac{Z\alpha}{n}\Big)^2 \Big(\frac{3}{4} - \frac{n}{\ell + 1/2}\Big) \tag{23}$$

$$\Delta E_2 = E_n \frac{(Z\alpha)^2}{n\ell(\ell+1)(2\ell+1)} \times \begin{cases} -\ell - 1 & \ell \neq 0 \\ 0, & \ell = 0 \end{cases} \tag{24}$$

$$\Delta E_3 = \begin{cases} -E_n \frac{(Z\alpha)^2}{n}, & \ell = 0 \\ 0, & \ell \neq 0 \end{cases} \tag{25}$$

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

$$(\Delta E)_{nj} = E_n \Big(\frac{Z\alpha}{n}\Big)^2 \Big(\frac{n}{j + 1/2} - \frac{3}{4}\Big), \tag{26}$$

and the final energy after relativistic corrections is given by

$$E_{nj} = E_n \left\{ 1 + \Big(\frac{Z\alpha}{n}\Big)^2 \Big(\frac{n}{j + 1/2} - \frac{3}{4}\Big) \right\}. \tag{27}$$

§6   Hyperfine structure

The hyperfine structure comes from the interaction of electrons dipole moment with the magnetic field due to the spin dipole moment of the nucleus. The proton, like every charged spin half particle, carries a magnetic moment given by $\mu_p = \frac{ge}{2M_p c}\vec{S}$, where g called the gyromagnetic ratio, is found to be 5.59. The magnetic moment for the proton is very small compared to the magnetic moment of the electron because the mass M_p appears in the denominator. The hyperfine structure splitting works out to be proportional to the average value of $S_e \cdot S_p$. This operator

has diagonal matrix elements between states with total spin $\vec{S} = \vec{S}_e + \vec{S}_p$. The total spin for the electron proton system can be 0 (singlet) or 1 (triplet) and we write

$$\vec{S}_e \cdot \vec{S}_p = \frac{1}{2}(S^2 S_e^2 S_p^2) \tag{28}$$

$$= \begin{cases} \frac{1}{4}, & \text{for triplet } S = 1 \\ -\frac{3}{4}, & \text{for singlet } S = 0 \end{cases} \tag{29}$$

Thus the effect of hyperfine interactions is to split each level into two levels corresponding to total spin $S = 0, 1$. Assembling all the factors, this splitting works out to be very tiny, of the order of 10^{-6} eV. For the ground state of hydrogen atom, the photon emitted in transition from triplet to singlet has the wave length of 21cm, and is the famous 21 cm line is present everywhere in radiation in the universe. That 21 cm line should be observable in emission was predicted by Dutch astronomer H. C. van de Hulst in 1944.