The Fine Structure of the Hydrogen Atom

Whilst the predictions of the quantum model of hydrogen are a very good approximation to reality, it turns out that in high resolution spectra of hydrogen that the predicted lines are in fact split into sets of lines. This is the so called fine structure of hydrogen and means that we must have missed out something from the model we have written down.

When we wrote down the quantum model of the hydrogen atom we used the Schrödinger equation. The Schrödinger equation is the quantum equivalent to Newton's equation of motion in as much as it is non-relativistic. Just as with Newton's equations non-relativistic quantum mechanics is a good approximation under many circumstances. However, it is known to fail under other circumstances. The extension of quantum mechanics to make it relativistic was made by Dirac who replaced the Schrödinger equation with the Dirac equation. We will not try to solve the Dirac equation. Instead, as in the small velocity limit the Dirac equation tends towards the Schrödinger equation, we will treat the difference between the Dirac and Schrödinger equations as a series of perturbations to the Schrödinger equation. For historic reasons the different perturbations have been named.

Spin-Orbit Coupling

A charge moving creates a current.

A current creates a magnetic field.

From the electron's point of reference, the nucleus appears to be moving; therefore, the nucleus creates a magnetic field. Recall the electron with its spin has a magnetic moment. - i.e., it behaves like a bar magnet. The magnetic moment of the electron tries to align itself with the magnetic field that comes via the "orbiting" of the nucleus. This effect is the origin of **spin-orbit coupling**.

$$E_{so} = \frac{Ze^2\mu_0}{8\pi m_e^2}\frac{1}{r^3}\vec{s}\cdot\vec{\ell} = \xi(r)\vec{s}\cdot\vec{\ell}$$

where $\vec{s}$ is the spin angular momentum and $\vec{\ell}$ is the orbital angular momentum.

μ_0 - permittivity of free space.

The spin-coupling term affects the energy levels of the electrons in an atom. Sometimes the energy levels that were thought to be degenerate are split into separate energy levels because of spin-orbit coupling, e.g., $2p_z\alpha$ and $2p_z\beta$ are not degenerate when spin-orbit coupling is taken into account.

Comment: We have to treat the term E_{so} as perturbation on the hydrogen atom states. The first thing to note is that the perturbation breaks two fundamental symmetries of the Hamiltonian. These are the symmetries associated with changing the sign of the angular orbital momentum and the sign of the spin angular momentum. In the new model, changing the sign of one or the other on their own changes the sign of the perturbation, and it is only if both are changed simultaneously that the energy is unchanged. This less formal argument is born out by the fact that the perturbation no longer commutes with the operators associated with the z components of the orbital or spin angular momenta. This symmetry breaking means we need to seek the correct combination of the degenerate states given by the original simpler calculation to use in the perturbation calculation. It turns out that we have to invent a new type of angular momentum called the total angular momentum which is given by

$$\vec{J} = \vec{L} + \vec{S} \quad \Rightarrow \quad \left|\vec{J}\right|^2 = \left(\vec{L}+\vec{S}\right)^2 = \left|\vec{L}\right|^2 + \left|\vec{S}\right|^2 + 2\vec{L}\cdot\vec{S}$$

Consider the Hamiltonian

$$H = H_0 + H_{SO} = \frac{\nabla^2}{2m} - \frac{Z}{r} + \zeta(r)\,\vec{L}\cdot\vec{S}, \qquad \zeta(r) = \frac{Z\hbar^2 e^2}{2m^2 c^2}\frac{1}{r^3}$$

H.W. Examine the following relations:

$$\left[\hat{S}^2,\hat{L}^2\right]=\left[\hat{L}_z,\hat{L}^2\right]=\left[\hat{L}^2,\hat{S}_z\right]=\left[\hat{L}_z,\hat{S}_z\right]=\left[\hat{S}^2,\hat{L}_z\right]=\left[\hat{S}^2,\hat{S}_z\right]=0$$

$$\left[\hat{H}_o,\hat{L}^2\right]=\left[\hat{H}_o,\hat{S}^2\right]=\left[\hat{H}_o,\hat{L}_z\right]=\left[\hat{H}_o,\hat{S}_z\right]=\left[\hat{H}_o,\hat{J}^2\right]=\left[\hat{H}_o,\hat{J}_z\right]=0$$

$$\left[\vec{L}\cdot\vec{S},L^2\right]=\left[\vec{L}\cdot\vec{S},S^2\right]=\left[\vec{L}\cdot\vec{S},J^2\right]=\left[\vec{L}\cdot\vec{S},J_z\right]=0$$

But $\left[\vec{L}\cdot\vec{S},L_z\right]\neq 0,\quad\left[\vec{L}\cdot\vec{S},S_z\right]\neq 0$

H.W. discuss the origin of the term $\xi(r)$.

Conclusions:

1- For one or n-electrons system, both uncouple representation

$\left|\ell_i,m_{\ell i},s_i,m_{si}\right\rangle=\left|\ell_i,m_{\ell i}\right\rangle\left|s_i,m_{si}\right\rangle$ and the coupled representation $\left|\ell,s,j,m_j\right\rangle$ are

eigenfunctions of H_o and it is immaterial which representation is used.

2- $\left|\ell,m_\ell,s,m_s\right\rangle$ will not necessarily be an eigenfunctions of $\vec{L}\cdot\vec{S}$.

3- $\left|L,S,J,m_J\right\rangle$ is a simultaneous eigenfunctions of $\hat{J}^2$, $\hat{L}^2$, $\hat{S}^2$ and $\vec{L}\cdot\vec{S}$.

Term Symbols

Definitions

Total Spin Angular Momentum $\vec{S}$ – the sum of spin angular momenta for all of the electrons in the atom.

$$\vec{S}=\vec{s}_1+\vec{s}_2+\vec{s}_3+\cdots\quad\Rightarrow\quad\vec{S}=\sum_i\vec{s}_i\text{ - spin angular momenta added as vectors.}$$

Multiplicity – the number of possible spin states for an atom.

Total spin of singlet = 0   multiplicity = 1
Total spin of doublet = 1/2   multiplicity = 2
Total spin of triplet = 1   multiplicity = 3

In general, one can calculate the multiplicity if one know the total spin and vice versa

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

Total Orbital Angular Momentum $\vec{L}$ – the sum of orbital angular momenta for all of the electrons in the atom.

$$\vec{L}=\vec{\ell}_1+\vec{\ell}_2+\vec{\ell}_3+\cdots\quad\Rightarrow\quad\vec{L}=\sum_i\vec{\ell}_i\text{ - orbital angular momenta added as vectors.}$$

For two electrons, $\left|\vec{L}\right|=\ell_1+\ell_2,\ell_1+\ell_2-1,\ell_1+\ell_2-2,\cdots,\left|\ell_1-\ell_2\right|+1,\left|\ell_1-\ell_2\right|$

Total angular momentum $\vec{J}$ – the sum of the individual total angular momenta (Spin and orbital) for all of the electrons in the atom

The total angular momentum, $\vec{J}$, comes from the vector addition of $\vec{L}$ and $\vec{S}$.

$$\vec{J}=\vec{L}+\vec{S}$$

Thus $\left|\vec{J}\right|=L+S,L+S-1,L+S-2,\ldots,\left|L-S\right|$

The magnitudes are given by:

$$\left|\vec{L}\right|^2=\hbar^2 L(L+1),\quad\left|\vec{S}\right|^2=\hbar^2 S(S+1),\quad\left|\vec{J}\right|^2=\hbar^2 J(J+1)$$

And their z-component are quantized according to:

$$\vec{L}_z = M_L \hbar, \quad \vec{S}_z = M_S \hbar, \quad \vec{J}_z = M_J \hbar$$

The z-component quantum numbers are related to those of the individual electrons by the following addition rules:

$$M_L = \sum_i (m_\ell)_i, \quad M_S = \sum_i (m_s)_i, \quad M_J = M_L + M_S$$

Knowing M_L, M_S, and M_J, one can infer L, S, and J from the conditions:

$$M_L = L, L-1, \ldots 0, \ldots, -(L-1), -L$$
$$M_S = S, S-1, \ldots 0, \ldots, -(S-1), -S$$
$$M_J = J, J-1, \ldots 0, \ldots, -(J-1), -J$$

Term symbols are abbreviated way of describing an electronic state. Determining the electronic state is important because different states will have different energies. The differences in the energies come primarily from coupling of angular momenta such as spin-orbit coupling.

The term symbol has the following information.
  1.) multiplicity
  2.) total angular momentum, $\vec{J}$
  3.) total orbital angular momentum, $\vec{L}$
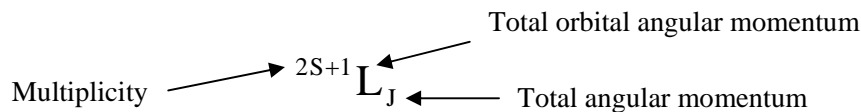
The orbital angular momentum is given as letter symbol.

L	0	1	2	3	4	5	etc…
symbol	S	P	D	F	G	H	etc…

Selection rules for the allowed transitions between energy levels

Change of the **principal quantum number:**
$$\Delta n = 0, \pm 1, \pm 2, \pm 3, \ldots$$
Change of the **azimuthal (orbital) quantum number:**
$$\Delta L = 0, \pm 1$$
Change of the **Spin quantum number:**
$$\Delta S = 0$$
Change of the **total angular quantum number:**
$$\Delta J = 0, \pm 1 \qquad \text{(The transition } J = 0 \rightarrow J = 0 \text{ is not allowed)}$$
Change of the **magnetic quantum number**
$$\Delta M_J = 0, \pm 1 \quad \text{(But if } \Delta J = 0, \text{ then the transition } M_J = 0 \rightarrow M_J = 0 \text{ is not allowed)}$$

These are electric dipole transitions; other transitions (quadrupole, octupole,..) occur but they are found to be much weaker. If the electric dipole transition involves just one electron, $\Delta L = \Delta \ell \neq 0$.
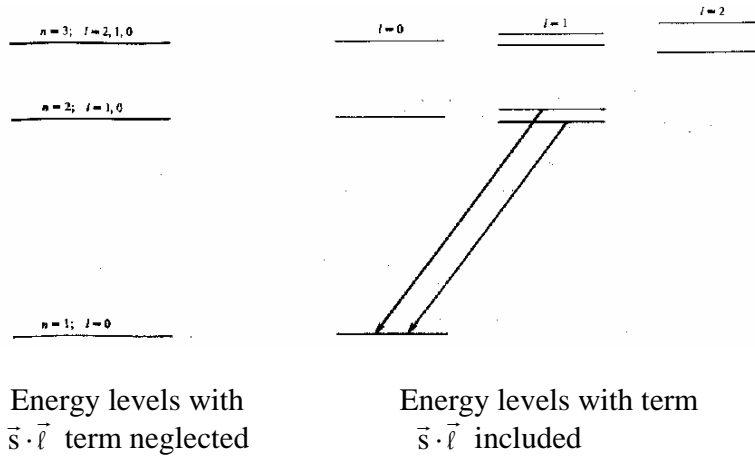
The transitions with $\Delta j = 0$ are very weak because they require a reversal of the direction of the spin relative to the orbital angular momentum of the electron. But the force that would produce such spin reversal is the spin-orbit interaction, which is a relatively weak force.

Example: Calculate the allowed values of $\vec{j}$ for p-electron.

Answer: For p-electron we have $\ell = 1$, then the allowed values of $\vec{j}$ for a p-electron are:

$$\vec{j} = \ell + s = 1 + \frac{1}{2} = \frac{3}{2}$$

$$\vec{j} = \ell - s = 1 - \frac{1}{2} = \frac{1}{2}$$

| Energy levels with | Energy levels with term |
| $\vec{s} \cdot \vec{\ell}$ term neglected | $\vec{s} \cdot \vec{\ell}$ included |

Example: Calculate the possible values of $\vec{L} \cdot \vec{S}$ for a p-electron.

Answer: Use the relation:

$$\vec{J} = \vec{L} + \vec{S} \quad \Rightarrow \quad \left|\vec{J}\right|^2 = \left(\vec{L} + \vec{S}\right)^2 = \left|\vec{L}\right|^2 + \left|\vec{S}\right|^2 + 2\vec{L} \cdot \vec{S}$$

$$\therefore \vec{L} \cdot \vec{S} = \frac{1}{2}\left[\left|\vec{J}\right|^2 - \left|\vec{L}\right|^2 - \left|\vec{S}\right|^2\right] = \frac{1}{2}[J(J+1) - L(L+1) - S(S+1)]$$

For $J = \frac{3}{2}$

$$\vec{L} \cdot \vec{S} = \frac{1}{2}\left[\frac{3}{2}(\frac{3}{2}+1) - 1(1+1) - \frac{1}{2}(\frac{1}{2}+1)\right] = \frac{1}{2}$$

For $J = \frac{1}{2}$

$$\vec{L} \cdot \vec{S} = \frac{1}{2}\left[\frac{1}{2}(\frac{1}{2}+1) - 1(1+1) - \frac{1}{2}(\frac{1}{2}+1)\right] = -1$$
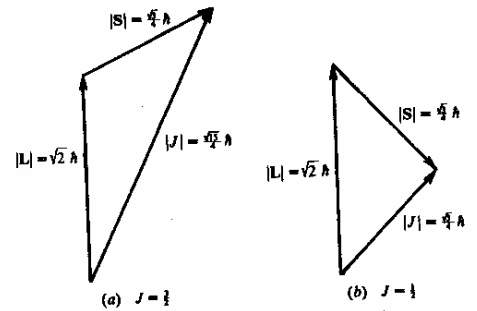
The following figure illustrates the relative orientation of the three vectors.

H.W. Calculate the value of $\xi(r)$ in the equation:

$$E_s = \xi(r)\vec{L} \cdot \vec{S}$$

for the two sodium D lines (5889.95 $\overset{o}{A}$, 5895.92 $\overset{o}{A}$) . Remember that the units of $\hbar$ is $eV \cdot s$

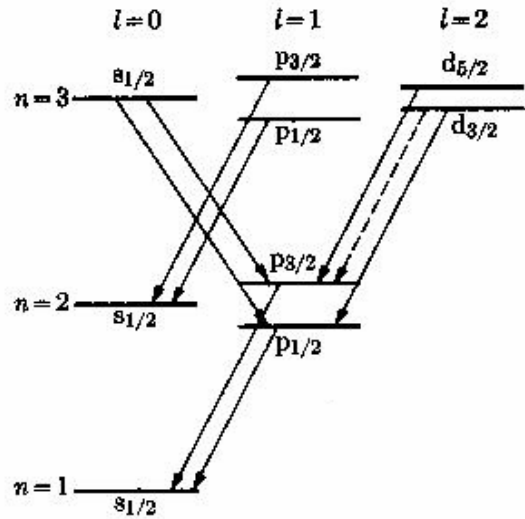[Ans: $\xi(r) = 3.28 \times 10^{27} \dfrac{1}{eV \cdot s^2}$]

Fig. 3–22. Spin-orbit splitting of energy levels and possible transitions. The dashed line indicates a transition with very low probability.

Note: The transition $3p \rightarrow 1s$ will be allowed but with low intensity compared with the transition $3p \rightarrow 2s$;

$$\frac{\text{Intensity } (1s \rightarrow 2p)}{\text{Intensity } (1s \rightarrow 3p)} = \frac{0.6243}{0.166} = 3.76$$

$$\frac{\text{Intensity } (2s \rightarrow 3p)}{\text{Intensity } (1s \rightarrow 3p)} = \frac{1/0.22}{1/1.64} = \frac{4.55}{0.61} = 7.46$$

24.6. Calculate **L·S** for a $^3F_2$ state.

For a $^3F_2$ state, $S = 1$, $L = 3$ and $J = 2$. From the result of Problem 22.1 we have

$$\mathbf{L \cdot S} = \tfrac{1}{2}[J(J+1) - L(L+1) - S(S+1)]\hbar^2 = \tfrac{1}{2}[2(2+1) - 3(3+1) - 1(1+1)]\hbar^2 = -4\hbar^2$$

24.7. Determine the transitions occurring from a ^3F state to a ^3D state with an **L·S** interaction present.

The relative sizes of the spin-orbit splittings are determined by evaluating

$$\mathbf{L \cdot S} = \tfrac{1}{2}[J(J+1) - L(L+1) - S(S+1)]\hbar^2$$

See Table 24-3, in which J is evaluated from (*22.4*).

Table 24-3

State	L	S	J	$\mathbf{L \cdot S}$
^3F	3	1	4, 3, 2	$3\hbar^2, -1\hbar^2, -4\hbar^2$
^3D	2	1	3, 2, 1	$2\hbar^2, -1\hbar^2, -3\hbar^2$

In this case the **L·S** interactions split each energy level into three parts, as shown in Fig. 24-4. The transitions satisfying the selection rule $\Delta J = 0, \pm 1$ (but no $0 \rightarrow 0$) are also shown. The transition rule $\Delta L = \pm 1$ is automatically satisfied.
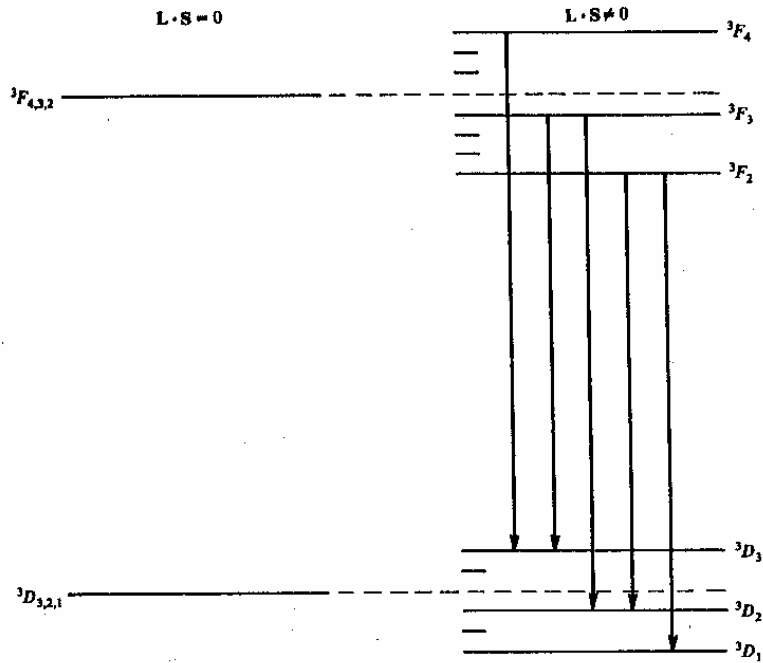
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Fig. 24-4

H.W. For an electron in P-state, calculate the matrix elements of the operator:

$$H^{(1)} = a\,\hat{L}.\hat{S}, \qquad\qquad a = \text{constant}$$

  i-   in the coupling representation.

For coupling states $\left| j, m_j \right\rangle$, **use** $\hat{L}.\hat{S} = \dfrac{1}{2}\left\{ \hat{J}^2 - \hat{L}^2 - \hat{S}^2 \right\}$

$$\left(\hat{L}.\hat{S} \right) = \frac{\hbar^2}{2}
\begin{array}{c}
 \\
'\left\langle \tfrac{3}{2},\tfrac{3}{2} \right| \\
'\left\langle \tfrac{3}{2},\tfrac{1}{2} \right| \\
'\left\langle \tfrac{3}{2},-\tfrac{1}{2} \right| \\
'\left\langle \tfrac{3}{2},-\tfrac{3}{2} \right| \\
'\left\langle \tfrac{1}{2},-\tfrac{1}{2} \right| \\
'\left\langle \tfrac{1}{2},\tfrac{1}{2} \right|
\end{array}
\begin{pmatrix}
1 & 0 & 0 & 0 & 0 & 0 \\
0 & 1 & 0 & 0 & 0 & 0 \\
0 & 0 & 1 & 0 & 0 & 0 \\
0 & 0 & 0 & 1 & 0 & 0 \\
0 & 0 & 0 & 0 & -2 & 0 \\
0 & 0 & 0 & 0 & 0 & -2
\end{pmatrix}$$

with column labels $\left| \tfrac{3}{2},\tfrac{3}{2} \right\rangle'$ $\left| \tfrac{3}{2},\tfrac{1}{2} \right\rangle'$ $\left| \tfrac{3}{2},-\tfrac{1}{2} \right\rangle'$ $\left| \tfrac{3}{2},-\tfrac{3}{2} \right\rangle'$ $\left| \tfrac{1}{2},-\tfrac{1}{2} \right\rangle'$ $\left| \tfrac{1}{2},\tfrac{1}{2} \right\rangle'$

b- In the uncoupling representation $\left| m_l, m_S \right\rangle$, **use** $\hat{L}.\hat{S} = \hat{L}_z \hat{S}_z + \dfrac{1}{2}\left(\hat{L}_+ \hat{S}_- + \hat{L}_- \hat{S}_+ \right)$

$$
\left(\hat{L}.\hat{S}\right) = \frac{\hbar^2}{2}
\begin{array}{c}
\\
\left\langle 1,\frac{1}{2}\right| \\
\left\langle 1,-\frac{1}{2}\right| \\
\left\langle 0,\frac{1}{2}\right| \\
\left\langle 0,-\frac{1}{2}\right| \\
\left\langle -1,\frac{1}{2}\right| \\
\left\langle -1,-\frac{1}{2}\right|
\end{array}
\begin{array}{cccccc}
\left|1,\frac{1}{2}\right\rangle & \left|1,-\frac{1}{2}\right\rangle & \left|0,\frac{1}{2}\right\rangle & \left|0,-\frac{1}{2}\right\rangle & \left|-1,\frac{1}{2}\right\rangle & \left|-1,-\frac{1}{2}\right\rangle \\
\begin{pmatrix}
1 & 0 & 0 & 0 & 0 & 0 \\
0 & -1 & \sqrt{2} & 0 & 0 & 0 \\
0 & \sqrt{2} & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & \sqrt{2} & 0 \\
0 & 0 & 0 & \sqrt{2} & -1 & 0 \\
0 & 0 & 0 & 0 & 0 & 1
\end{pmatrix}
\end{array}
$$

One-electron corrections of energy

The Hamiltonian

$$H_o = \frac{p^2}{2m} - \frac{Z}{r}$$

has the uncoupled wave function $\left| \ell, m_\ell, s, m_s \right\rangle = \left| \ell, m_\ell \right\rangle \left| s, m_s \right\rangle$ which identify the angular and spin parts of the wave function. m_ℓ is the projection quantum number associated with ℓ and m_s is the projection quantum number associated with *s* satisfies the relations:

$$\left\langle \ell', m_\ell', s', m_s' \left| \hat{L}^2 \right| \ell, m_\ell, s, m_s \right\rangle = \ell(\ell+1)\delta_{\ell\ell'}\delta_{ss'}\delta_{m_\ell m_\ell'}\delta_{m_s m_s'}$$

$$\left\langle \ell', m_\ell', s', m_s' \left| \hat{L}_z \right| \ell, m_\ell, s, m_s \right\rangle = m_\ell \delta_{\ell\ell'}\delta_{ss'}\delta_{m_\ell m_\ell'}\delta_{m_s m_s'}$$

$$\left\langle \ell', m_\ell', s', m_s' \left| \hat{S}^2 \right| \ell, m_\ell, s, m_s \right\rangle = s(s+1)\delta_{\ell\ell'}\delta_{ss'}\delta_{m_\ell m_\ell'}\delta_{m_s m_s'}$$

$$\left\langle \ell', m_\ell', s', m_s' \left| \hat{S}_z \right| \ell, m_\ell, s, m_s \right\rangle = m_s \delta_{\ell\ell'}\delta_{ss'}\delta_{m_\ell m_\ell'}\delta_{m_s m_s'}$$

Aslo, the wave function $\left| \ell, s, j, m_j \right\rangle$ in LS-coupling has similar relations:

$$\left\langle \ell', s', j', m_j' \left| \hat{L}^2 \right| \ell, s, j, m_j \right\rangle = \ell(\ell+1)\delta_{\ell\ell'}\delta_{ss'}\delta_{jj'}\delta_{m_j m_j'}$$

$$\left\langle \ell', s', j', m_j' \left| \hat{S}^2 \right| \ell, s, j, m_j \right\rangle = s(s+1)\delta_{\ell\ell'}\delta_{ss'}\delta_{jj'}\delta_{m_j m_j'}$$

$$\left\langle \ell', s', j', m_j' \left| \hat{J}^2 \right| \ell, s, j, m_j \right\rangle = j(j+1)\delta_{\ell\ell'}\delta_{ss'}\delta_{jj'}\delta_{m_j m_j'}$$

$$\left\langle \ell', s', j', m_j' \left| \hat{J}_z \right| \ell, s, j, m_j \right\rangle = m_j \delta_{\ell\ell'}\delta_{ss'}\delta_{jj'}\delta_{m_j m_j'}$$

In which $\vec{J} = \vec{L} + \vec{S}$, and

$$\hat{J}^2 = \hat{J}_x^2 + \hat{J}_y^2 + \hat{J}_z^2 = \hat{L}^2 + \hat{S}^2 + 2\hat{L}\hat{S} = \hat{L}^2 + \hat{S}^2 + 2\hat{L}_z\hat{S}_z + \hat{L}_+\hat{S}_- + \hat{L}_-\hat{S}_+,$$

Note that $\left| \ell, s, j, m_j \right\rangle$ are not eigenfunctions of $\hat{L}_z$ or $\hat{S}_z$. $\left| \ell, s, j, m_j \right\rangle$ are said to be in the coupled representation.

Example: For one-electron atoms work out the energy corrections due to the following terms: relativistic ($\hat{H}_r$), spin orbit ($\hat{H}_{LS}$), Darwin ($\hat{H}_D$). Give an example of the contributions of each term to the splitting of the n = 2 level of hydrogen.

$$\hat{H} = \hat{H}_o + \hat{H}_r + \hat{H}_{LS} + \hat{H}_D;$$

$$\hat{H}_r = -\frac{\hat{P}^4}{8m^3c^2},$$

$$\hat{H}_{LS} = \xi(r)\hat{L}\hat{S} = \frac{Z^2 e^2 \hbar^2}{2m^2c^2}\frac{1}{r^3}\hat{L}\hat{S},$$

$$\hat{H}_D = -\frac{Ze^2\hbar^2}{2m^2c^2}\left[\nabla^2\left(\frac{1}{r}\right)\right] = -\frac{Ze^2\hbar^2}{2m^2c^2}\left[-4\pi\delta(r)\right]$$

Spin-Orbit Coupling and Fine structure

This is explain the reason that the energy level with $\ell > 0$, split into two components, which could not be explained by the Schrödinger theory. Since this splitting is very small and can be only resolved with high resolution spectrographs, where the hydrogen lines appear as a fine substructure, it was named fine structure.

$$E_{LS} = \left\langle \hat{H}_{LS} \right\rangle = \frac{Ze^2\hbar^2}{2m^2c^2}\left\langle \frac{1}{r^3} \right\rangle \left\langle \hat{s}.\hat{\ell} \right\rangle, \quad \left\langle \frac{1}{r^3} \right\rangle = \frac{Z^3}{a_o^3}\{\frac{\alpha^2}{n^3\ell(\ell+\frac{1}{2})(\ell+1)}\}$$

$$= \frac{Z^4e^2\hbar^2}{4a_o^3m^2c^2}\{\frac{j(j+1)-\ell(\ell+1)-s(s+1)}{n^3\ell(\ell+\frac{1}{2})(\ell+1)}\}$$

$$= \frac{\alpha^2Z^4}{n^3}\{\frac{j(j+1)-\ell(\ell+1)-s(s+1)}{2\ell(\ell+\frac{1}{2})(\ell+1)}\} \quad \text{Ry}$$

$$\therefore E_{LS} = \frac{\alpha^2Z^4}{n^3}\{\frac{1}{2\ell(\ell+\frac{1}{2})(\ell+1)}\}\times \begin{cases} \ell & \text{spin up } j = \ell+\frac{1}{2} \\ -(\ell+1) & \text{spin down } j = \ell-\frac{1}{2} \end{cases}$$

where α is the fine structure constant and is given by:

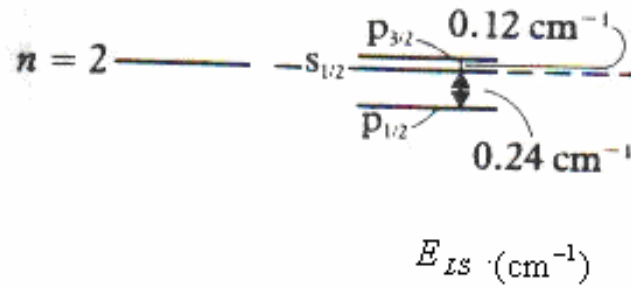$$\alpha = \frac{e^2}{\hbar c} \approx \frac{1}{137} \quad \Rightarrow \quad \alpha^2 = 5.33\times10^{-5},$$

And

$$a_o = \frac{\hbar^2}{me^2}, \quad \text{Ry} = \frac{1}{2}mc^2\left(\frac{e^2}{\hbar c}\right)^2 = 13.605 \text{ eV} = 109,737.311 \text{ cm}^{-1}$$

$$\Delta E_{LS} = E_{LS}(j+\frac{1}{2}) - E_{LS}(j-\frac{1}{2}) = \frac{\alpha^2Z^4}{n^3}\frac{1}{\ell(\ell+1)} = 5.33\times10^{-5}\frac{Z^4}{n^3}\frac{1}{\ell(\ell+1)} \text{ Ry}$$

Example: For the np levels of the H atom, we have $Z = 1$, and $\ell = 1$. From the above expression we therefore obtain for the fine structure splitting as:

n	E_n(Ry)	j	E_{LS} Ry(cm^{-1})	ΔE_{LS} (Ry)	ΔE_{LS}(cm^{-1})
2	-0.250	3/2	1.14E-6 (0.12)	3.33E-6	0.36
		1/2	-2.19E-6 (-0.24)		
3	-0.111	3/2		9.87E-7	0.12
		1/2			
4	0.0625	3/2		4.16E-7	0.044
		1/2			

This shows that:

1- Fine structure splitting are observed only for levels with $\ell > 0$, i.e. for p, d, f, levels, **not** for s-levels with $\ell = 0$.

2- The splitting is very small compared to the energy of the levels and justifies the name "fine structure."

3- The fine structure splitting decreases with increasing quantum numbers n and ℓ, but it increases proportionally to Z^2, or the product $Z^2 E_n$. Since the energies E of the levels with principal quantum number n follow the relation $E_n = -Z^2 / n^2$.

4- The energy levels split, depending on the orientation of the spin, into the two components with $j = \ell + \frac{1}{2}$ and $j = \ell - \frac{1}{2}$.

5- The fine structure may be regarded as Zeeman splitting due to the interaction of the magnetic spin moment with the internal magnetic field generated by the orbital motion of the electron.

Relativistic Mass Correction

The Relativistic Correction

Moving from the non-relativistic formula for the energy of an electron to the relativistic formula we make the change

$$mc^2 + \frac{p_e^2}{2m} \rightarrow \left(p^2 c^2 + m^2 c^4\right)^{1/2} = mc^2 \left(1 + \frac{p^2 c^2}{m^2 c^4}\right)^{1/2}.$$

$$p^2 = 0$$

Taylor expanding the square root around   , we find

$$\left(p^2c^2 + m^2c^4\right)^{1/2} = mc^2 + \frac{1}{2}\frac{p^2c^2}{mc^2} - \frac{1}{8}\frac{p^4c^4}{m^3c^6} + \cdots \approx mc^2 + \frac{p^2}{2m} - \frac{p^4}{8m^3c^2}$$

$$\frac{p^2}{2m}$$

So we have our next order correction term. Notice that   was just the lowest order correction
to mc^2 .

What about the ``reduced mass problem''? The proton is very non-relativistic so only the electron
term is important and the reduced mass is very close to the electron mass. We can therefore neglect
the small correction to the small correction and use

$$H_1 = -\frac{1}{8}\frac{p_e^4}{m^3c^2}.$$

According to special relativity, the kinetic energy (*i.e.*, the difference between the total energy and
the rest mass energy) of a particle of rest mass m and momentum p is

$$T = \sqrt{p^2c^2 + m^2c^4} - mc^2 = \frac{p^2}{2m} - \frac{p^4}{8m^3c^2} + \ldots$$

In the non-relativistic limit $p \ll mc$, we can expand the square-root in the above expression to
give

$$T = \frac{p^2}{2m}\left[1 - \frac{1}{4}\left(\frac{p}{mc}\right)^2 + \ldots\right]$$

The second term in the expansion of the kinetic energy is called the relativistic mass correction.
Notes: Neglecting the nuclear motion, the Hamiltonian with relativistic correction of the Hydrogen
atom is given by:

$$\hat{H} = \hat{H}_o + \hat{H}_r = -\frac{\hat{P}^2}{2m_e} - \frac{Ze^2}{r} - \frac{1}{2m_ec^2}\left(\frac{\hat{P}^2}{2m_e}\right)^2$$

With the notation:

$$\hat{H}_o = -\frac{\hat{P}^2}{2m_e} - \frac{Ze^2}{r} = E_n^{(0)}$$

Put $-\dfrac{\hat{P}^2}{2m_e} = E_n^{(0)} + \dfrac{Ze^2}{r}$, where $E_n^{(0)} = -\dfrac{Z^2}{n^2}$ Ry, then the first order correction will be:

$$E_r = \langle nlm' | \hat{H}' | nlm \rangle = -\frac{1}{2m_e c^2} \langle nlm' | \left(\frac{\hat{P}^2}{2m_e} \right)^2 | nlm \rangle$$

$$= -\frac{1}{2m_e c^2} \langle nlm' | \left(E_n^{(0)} + \frac{Ze^2}{r} \right) \left(E_n^{(0)} + \frac{Ze^2}{r} \right) | nlm \rangle ;$$

Using

$$\left(E_n^{(0)} + \frac{Ze^2}{r} \right) \left(E_n^{(0)} + \frac{Ze^2}{r} \right) = E_n^{(0)2} + E_n^{(0)} \frac{Ze^2}{r} + \frac{Ze^2}{r} E_n^{(0)} + \left(\frac{Ze^2}{r} \right)^2$$

Then

$$\Delta E_r = -\frac{1}{2m_e c^2} [\langle nlm' | E_n^{(0)2} | nlm \rangle + (Ze^2 \langle nlm' | E_n^{(0)} \frac{1}{r} | nlm \rangle$$

$$+ \langle nlm' | \frac{1}{r} E_n^{(0)} | nlm \rangle) + \left(Ze^2 \right)^2 \langle nlm' | \frac{1}{r^2} | nlm \rangle]$$

For the terms; the first one will be:

$$\langle nlm' | E_n^{(0)2} | nlm \rangle = \left(E_n^{(0)} \right)^2 \delta_{m'm}$$

The second and third terms will be:

$$\langle nlm' | E_n^{(0)} \frac{1}{r} | nlm \rangle = \langle nlm' | \frac{1}{r} E_n^{(0)} | nlm \rangle = E_n^{(0)} \langle nl | \frac{1}{r} | nl \rangle \delta_{m'm}$$

The fourth term will be:

$$\langle nlm' | \frac{1}{r^2} | nlm \rangle = \langle nl | \frac{1}{r^2} | nl \rangle \delta_{m'm}$$

The final correction is:

$$\Delta E_r = -\frac{\left(E_n^{(0)} \right)^2}{2m_e c^2} - \frac{Ze^2}{m_e c^2} E_n^{(0)} \langle nl | \frac{1}{r} | nl \rangle - \frac{\left(Ze^2 \right)^2}{2m_e c^2} \langle nl | \frac{1}{r^2} | nl \rangle$$

But we know:

$$\langle nl | \frac{1}{r} | nl \rangle = \frac{Z}{a_o} \frac{1}{n^2} \text{ Ry}, \qquad \langle nl | \frac{1}{r^2} | nl \rangle = \left(\frac{Z}{a_o} \right)^2 \frac{1}{n^3 (l + \frac{1}{2})} \text{ Ry}$$

Therefore:

$$E_r = \frac{Z^4 \alpha^2}{n^3} [\frac{3}{4n} - \frac{1}{(\ell + \frac{1}{2})}] \text{ Ry}$$

Comments:

1- The relativistic energy shift is maximum for the ground state of atoms ($n = 1$ and $\ell = 0$).

2- The correction depends on both quantum numbers n and ℓ. The $(n-1)$-fold degeneracy of states (n, ℓ), deduced from the Schrödinger theory is lifted by the relativistic correction.

3- At a given value of n, the electron comes closest the nucleus (and therefore acquires the largest velocity for small values of ℓ (the Sommerfeld orbits are then ellipses with large eccentricity). The increase in relativistic mass is then becomes maximum, which decreases the energy term value. For the maximum allowed $(\ell = n-1)$ the orbit is circular and the velocity of the electron has a constant medium value. the relativistic mass correction is then minimum.

Example: For H atom with $n =1$, $\ell = 0$ the magnitude of the relativistic correction is:

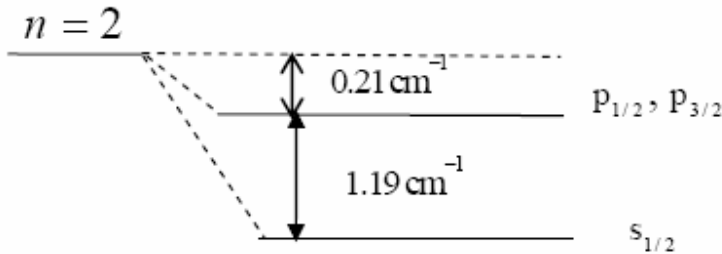$$\Delta E_r = E_1 \frac{5\alpha^2}{4} = -9.0\times10^{-4} \text{ eV} = 7.2 \text{ cm}^{-1}$$

For $n = 2$, $\ell = 0$ we obtain:

$$\Delta E_r = \frac{13}{16} E_2 \alpha^2 = -1.5\times10^{-4} \text{ eV} = 1.20 \text{ cm}^{-1}$$

For $n = 2$, $\ell = 1$ we obtain:

$$\Delta E_r = \frac{7}{48} E_2 \alpha^2 = -2.6\times10^{-5} \text{ eV} = 0.21 \text{ cm}^{-1}$$

As the numerical examples show, the relativistic mass correction only amounts to less than 10^{-4} of the Coulomb energy.

n	1	j	$\Delta E(\text{cm}^{-1})$
1	0	1/2	-1/4
2	0	1/2	-5/64
	1	1/2,3/2	-5/64, -1/64

Sum of Relativistic Fine Structure Corrections

Taken together the three relativistic corrections discussed above give an overall first order energy shift of

$$E_r + E_{LS} = -\frac{\alpha^2 Z^4}{n^3}\{\frac{1}{j+\frac{1}{2}} - \frac{3}{4n}\}\, \mathrm{Ry},$$
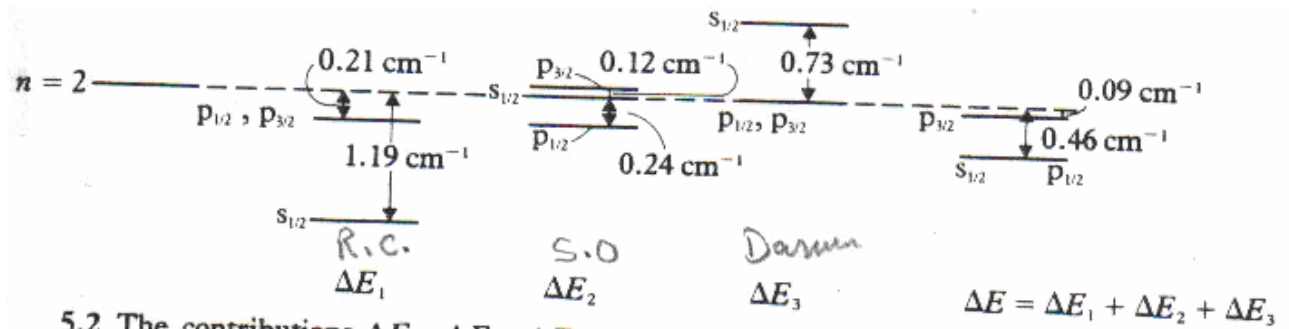
Darwin Correction ΔE_3

The third correction has no classical analogue is due to the highly non-classical dynamics of electrons near the nucleus. It can be shown that to first order it gives a correction to the energy of *l* = 0.

$$\hat{H}_D = -\frac{Ze^2\hbar^2}{2m^2c^2}\left[\nabla^2(\frac{1}{r})\right] = -\frac{Ze^2\hbar^2}{2m^2c^2}\left[-4\pi\delta(r)\right]$$

$$\langle\delta(r)\rangle = \langle n00|\delta(r)|n00\rangle = |\psi(0)|^2 = \frac{Z^3}{\pi n^3 a_o^3}$$

$$E_D = \langle\hat{H}_D\rangle = \frac{\alpha^2 Z^4}{n^3}\, \mathrm{Ry}$$

5.2 The contributions ΔE_1, ΔE_2, ΔE_3 to the splitting of the $n = 2$ level of hydrogen.
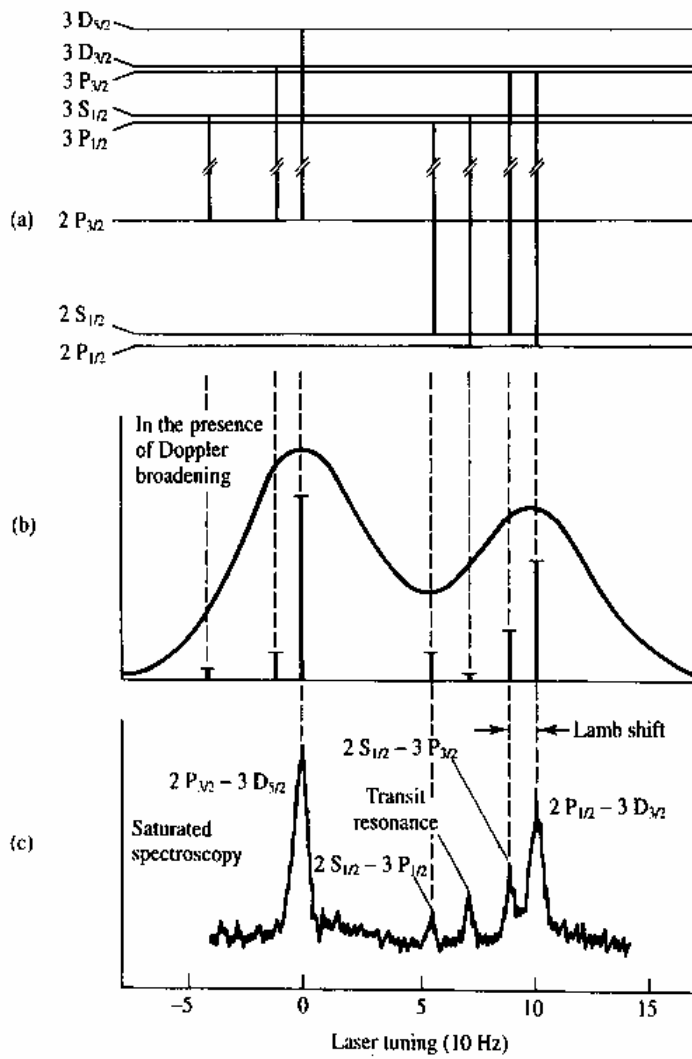
FIGURE 4.27

Fine structure of the H_α line. The seven transitions in the fine structure of the $n = 3$ to $n = 2$ transition are seen in (a). Their relative intensities are illustrated in (b) along with a poor resolution (from Doppler broadening) measurement. A high resolution measurement is shown in (c).