

## Revised One-electron system

### (Weissbluth Chapter 16)

### 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.

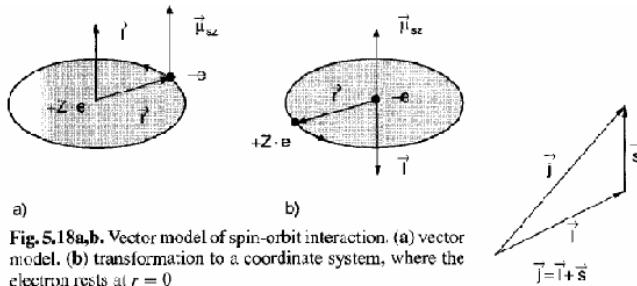
### Spin-Orbit Coupling

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**.

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

where  $\vec{s}$  is the spin angular momentum and  $\vec{l}$  is the orbital angular momentum.  
 $\mu_0$  - permittivity of free space.



**Fig. 5.18a,b.** Vector model of spin-orbit interaction. (a) vector model. (b) transformation to a coordinate system, where the electron rests at  $r = 0$

**Fig. 5.19.** Vector coupling of orbital angular momentum  $l$  and electron spin  $s$  to form the total angular momentum  $j$  of the electron

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:

- 1- The symmetries associated with changing the sign of the angular orbital momentum, and
- 2- 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

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

Consider the Hamiltonian

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

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

**H.W.** Find  $\vec{L} \cdot \vec{S} \left| m_\ell = 0, m_s = \frac{1}{2} \right\rangle$ , hence find  $\langle m_\ell, m_s | \vec{L} \cdot \vec{S} | 0, \frac{1}{2} \rangle$

**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 Å, 5895.92 Å). Remember that the units of  $\hbar$  is eV . s

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

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

**Hint:** you can use the following relations:

$$\hat{L}_\pm \equiv \hat{L}_x \pm i\hat{L}_y, \quad \hat{L}_\pm |\ell, m\rangle = \hbar \sqrt{\ell(\ell+1) - m(m \pm 1)} |\ell, m \pm 1\rangle,$$

$$\hat{L}_x = \frac{1}{2}(\hat{L}_+ + \hat{L}_-), \quad \hat{L}_y = \frac{1}{2i}(\hat{L}_+ - \hat{L}_-),$$

$$\begin{aligned} \vec{L} \cdot \vec{S} &= \hat{L}_z \hat{S}_z + \hat{L}_x \hat{S}_x + \hat{L}_y \hat{S}_y \\ &= \hat{L}_z \hat{S}_z + \frac{1}{2}(\hat{L}_+ + \hat{L}_-) \frac{1}{2}(\hat{S}_+ + \hat{S}_-) + \frac{1}{2i}(\hat{L}_+ - \hat{L}_-) \frac{1}{2i}(\hat{S}_+ - \hat{S}_-) \\ &= \hat{L}_z \hat{S}_z + \frac{1}{4}(\hat{L}_+ + \hat{L}_-)(\hat{S}_+ + \hat{S}_-) - \frac{1}{4}(\hat{L}_+ - \hat{L}_-)(\hat{S}_+ - \hat{S}_-) = \hat{L}_z \hat{S}_z + \frac{1}{2}(\hat{L}_+ \hat{S}_- + \hat{L}_- \hat{S}_+) \end{aligned}$$

To work out table 16.5 (Weissbluth Chapter 16)

a- in the coupling representation.

$$\text{For coupling states } |j, m_j\rangle, \text{ use } \hat{L} \hat{S} = \frac{1}{2} \{ \hat{J}^2 - \hat{L}^2 - \hat{S}^2 \}$$

$$(\hat{L}\hat{S}) = \frac{\hbar^2}{2} \begin{matrix} \langle \frac{3}{2}, \frac{3}{2} | \\ \langle \frac{3}{2}, \frac{1}{2} | \\ \langle \frac{3}{2}, -\frac{1}{2} | \\ \langle \frac{3}{2}, -\frac{3}{2} | \\ \langle \frac{1}{2}, -\frac{1}{2} | \\ \langle \frac{1}{2}, \frac{1}{2} | \end{matrix} \begin{pmatrix} \langle \frac{3}{2}, \frac{3}{2} | & \langle \frac{3}{2}, \frac{1}{2} | & \langle \frac{3}{2}, -\frac{1}{2} | & \langle \frac{3}{2}, -\frac{3}{2} | & \langle \frac{1}{2}, -\frac{1}{2} | & \langle \frac{1}{2}, \frac{1}{2} | \\ 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & -2 & 0 \\ 0 & 0 & 0 & 0 & 0 & -2 \end{pmatrix}$$

a- In the uncoupling representation  $|m_l, m_s\rangle$ , use  $\hat{L}\cdot\hat{S} = \hat{L}_z\hat{S}_z + \frac{1}{2}(\hat{L}_+\hat{S}_- + \hat{L}_-\hat{S}_+)$

$$(\hat{L}\hat{S}) = \frac{\hbar^2}{2} \begin{matrix} \langle 1, \frac{1}{2} | \\ \langle 1, -\frac{1}{2} | \\ \langle 0, \frac{1}{2} | \\ \langle 0, -\frac{1}{2} | \\ \langle -1, \frac{1}{2} | \\ \langle -1, -\frac{1}{2} | \end{matrix} \begin{pmatrix} \langle 1, \frac{1}{2} | & \langle 1, -\frac{1}{2} | & \langle 0, \frac{1}{2} | & \langle 0, -\frac{1}{2} | & \langle -1, \frac{1}{2} | & \langle -1, -\frac{1}{2} | \\ 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & -1 & \sqrt{2} & 0 & 0 & 0 \\ 0 & \sqrt{2} & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & \sqrt{2} & 0 \\ 0 & 0 & 0 & \sqrt{2} & -1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \end{pmatrix}$$

**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.

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

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

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

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

### 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.

$$\begin{aligned}
 E_{LS} &= \langle \hat{H}_{LS} \rangle = \frac{Ze^2\hbar^2}{2m^2c^2} \left\langle \frac{1}{r^3} \right\rangle \langle \hat{s} \cdot \hat{\ell} \rangle, \quad \left\langle \frac{1}{r^3} \right\rangle = \frac{Z^3}{a_o^3} \left\{ \frac{\alpha^2}{n^3 \ell(\ell + \frac{1}{2})(\ell + 1)} \right\} \\
 &= \frac{Z^4 e^2 \hbar^2}{4a_o^3 m^2 c^2} \left\{ \frac{j(j+1) - \ell(\ell+1) - s(s+1)}{n^3 \ell(\ell + \frac{1}{2})(\ell + 1)} \right\} \\
 &= \frac{\alpha^2 Z^4}{n^3} \left\{ \frac{j(j+1) - \ell(\ell+1) - s(s+1)}{2\ell(\ell + \frac{1}{2})(\ell + 1)} \right\} \text{ Ry} \\
 \therefore E_{LS} &= \frac{\alpha^2 Z^4}{n^3} \left\{ \frac{1}{2\ell(\ell + \frac{1}{2})(\ell + 1)} \right\} \times \begin{cases} \ell & \text{spin up } j = \ell + \frac{1}{2} \\ -(\ell + 1) & \text{spin down } j = \ell - \frac{1}{2} \end{cases}
 \end{aligned}$$

where  $\alpha$  is the fine structure constant and is given by:

$$\alpha = \frac{e^2}{\hbar c} \approx \frac{1}{137} \Rightarrow \alpha^2 = 5.33 \times 10^{-5},$$

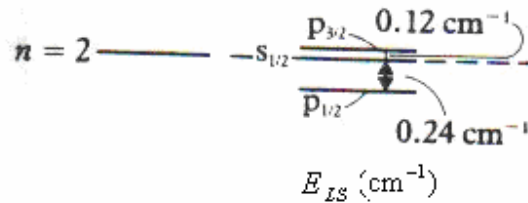
And

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

$$\Delta E_{LS} = E_{LS}(j + \frac{1}{2}) - E_{LS}(j - \frac{1}{2}) = \frac{\alpha^2 Z^4}{n^3} \frac{1}{\ell(\ell + 1)} = 5.33 \times 10^{-5} \frac{Z^4}{n^3} \frac{1}{\ell(\ell + 1)} \text{ Ry}$$

**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( $\text{cm}^{-1}$ )	$\Delta E_{LS}$ (Ry)	$\Delta E_{LS}$ ( $\text{cm}^{-1}$ )
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  $\ell$ , 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.

## The Relativistic Correction

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

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

Taylor expanding the square root around  $P^2$ , we find

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

So we have our next order correction term. Notice that  $\frac{P^2}{2m}$  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

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

⇒ In summary, 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

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

In the non-relativistic limit  $\mathbf{p} \ll m\mathbf{c}$ , we can expand the square-root in the above expression to give

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

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:

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

With the notation:

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

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

$$\begin{aligned} E_r &= \langle nlm | \hat{H} | nlm \rangle = -\frac{1}{2m_e c^2} \langle nlm | \left( \frac{\hat{P}^2}{2m_e} \right)^2 | nlm \rangle \\ &= -\frac{1}{2m_e c^2} \langle nlm | \left( E_n^{(0)} + \frac{Ze^2}{r} \right) \left( E_n^{(0)} + \frac{Ze^2}{r} \right) | nlm \rangle; \end{aligned}$$

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

$$\begin{aligned} \Delta E_r &= -\frac{1}{2m_e c^2} [\langle nlm | E_n^{(0)2} | nlm \rangle + (Ze^2 \langle nlm | E_n^{(0)} \frac{1}{r} | nlm \rangle \\ &\quad + \langle nlm | \frac{1}{r} E_n^{(0)} | nlm \rangle) + (Ze^2)^2 \langle nlm | \frac{1}{r^2} | nlm \rangle] \end{aligned}$$

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:

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

But we know:

$$\langle nl | \frac{1}{r} | nl \rangle = \frac{Z}{a_0} \frac{1}{n^2} \text{ Ry}, \quad \langle nl | \frac{1}{r^2} | nl \rangle = \left(\frac{Z}{a_0}\right)^2 \frac{1}{n^3(l + \frac{1}{2})} \text{ Ry}$$

Therefore:

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

### 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  $\ell$ . The  $(n - 1)$ -fold degeneracy of states  $(n, \ell)$ , 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  $\ell$  (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:

$$\Delta E_r = E_1 \frac{5\alpha^2}{4} = -9.0 \times 10^{-4} \text{ eV} = 7.2 \text{ cm}^{-1}$$

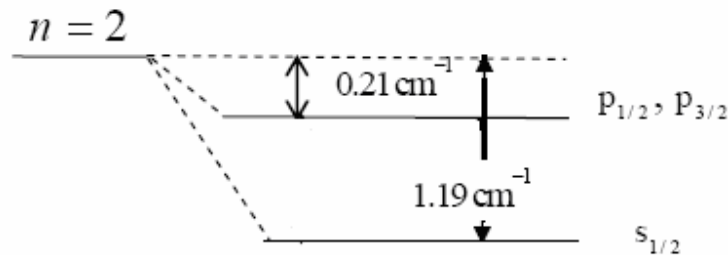
For  $n = 2$ ,  $\ell = 0$  we obtain:

$$\Delta E_r = \frac{13}{16} E_2 \alpha^2 = -1.5 \times 10^{-4} \text{ eV} = 1.20 \text{ cm}^{-1}$$

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

$$\Delta E_r = \frac{7}{48} E_2 \alpha^2 = -2.6 \times 10^{-5} \text{ eV} = 0.21 \text{ cm}^{-1}$$

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



for  $Z = 1$  and  $l = 1$

n	$\Delta E_{LS} (\text{cm}^{-1})$
2	0.36
3	0.12
4	0.044

n	l	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

$$E_r + E_{LS} = -\frac{\alpha^2 Z^4}{n^3} \left\{ \frac{1}{j + \frac{1}{2}} - \frac{3}{4n} \right\} \text{Ry},$$

### Darwin Correction $\Delta E_3$

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  $l = 0$ .

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

$$\langle \delta(r) \rangle = \langle n00 | \delta(r) | n00 \rangle = |\psi(0)|^2 = \frac{Z^3}{\pi n^3 a_0^3}$$

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

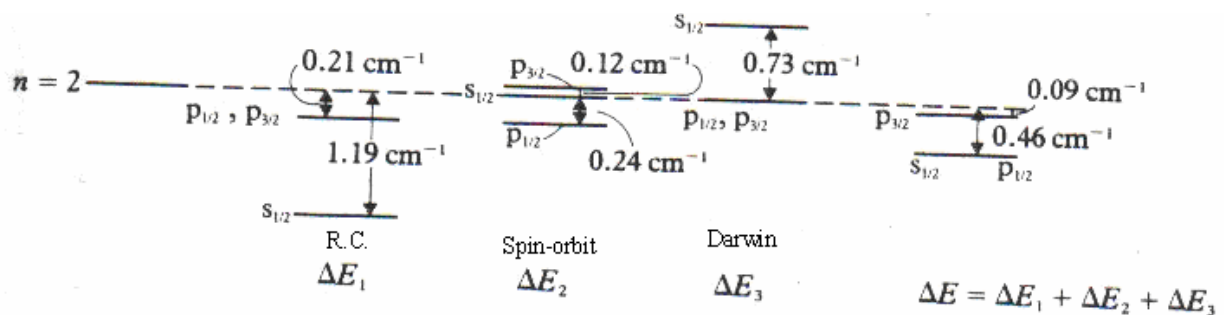


Figure: The contribution  $\Delta E_1, \Delta E_2, \Delta E_3$ , to the splitting of the  $n = 2$  level of hydrogen.