(10) Fine Structure (Energy level splitting) of Hydrogen Atoms

* The electron spin-orbital angular momentum coupling causes the hydrogen energy levels to shift and/or split to form fine structure. At the same time, relativity also introduces two correction terms to the energy levels: correction due to mass correction in relativity and correction called Darwin term, also due to relativity.

* Relativity-corrected Schrödinger equation:
We only consider this for hydrogen-like atom (ion) — the electron spin is ½, so the relativity-corrected Schrödinger equation is called the "Dirac equation". In absence of external field, the Hamiltonian operator is

$$\hat{H} = \hat{H}_0 + \Delta\hat{H}_m + \Delta\hat{H}_{ls} + \Delta\hat{H}_d$$

where $\hat{H}_0 = \frac{\hat{\vec{p}}^{\,2}}{2\mu} - \frac{1}{4\pi\varepsilon_0}\frac{Ze^2}{r}$ is the Hamiltonian operator in the non-relativity case (only consider electrostatic interaction between the nucleus and the single electron).

$$\Delta\hat{H}_m = -\frac{\hat{\vec{p}}^{\,4}}{8\mu^3c^2} = \frac{1}{2\mu c^2}\left(H_0 + \frac{Ze^2}{4\pi\varepsilon_0 r}\right)^2$$ is the operator

corresponding to the correction caused by the kinetic energy change due to the mass change in relativity.

$$\Delta\hat{H}_{ls} = \frac{1}{4\pi\varepsilon_0}\cdot\frac{Ze^2}{2\mu^2c^2r^3}\,\hat{\vec{s}}\cdot\hat{\vec{l}}$$. is the operator corresponding to the electron spin-orbit coupling interaction.

$$\Delta\hat{H}_d = -\frac{1}{4\pi\varepsilon_0}\frac{Ze^2\hbar^2}{4\mu^2c^2r^2}\frac{d}{dr}$$ is the operator

corresponding to a relativity correction, called Darwin term (in memory of C. Darwin).

* The relativity correction can be viewed as below: when a particle is at rest, its energy in relativity theory corresponding to the rest mass m_0 is given by $E_0 = m_0 c^2$, where c is light speed.

When the particle moves with a velocity v, then its energy becomes:

$$E = mc^2 = \frac{m_0 c^2}{\sqrt{1-\frac{v^2}{c^2}}}$$

i.e., the particle's mass becomes larger than its rest mass m_0.

The gained energy of E compared to E_0 is defined as the particle's kinetic energy:

$$E_K = E - E_0 = mc^2 - m_0 c^2 = m_0 c^2 \left(\frac{1}{\sqrt{1-v^2/c^2}} - 1\right).$$

This relativitic E_K is different than classical $E_K^{Classic} = \frac{1}{2} m_0 v^2$.

If $v \ll c$, then $E_K = m_0 c^2 \left(1 + \frac{1}{2} v^2/c^2 - 1\right) = \frac{1}{2} m_0 v^2$,

which turns into the classical expression.

In relativity, the momentum is

$$P = mv = \frac{m_0 v}{\sqrt{1-v^2/c^2}}.$$

∴ There exists such a relationship between E and P:

$$E = \sqrt{P^2c^2 + m_0^2 c^4} = \frac{m_0 c^2}{\sqrt{1-v^2/c^2}} = mc^2.$$

Expanding E and take approximation, we obtain

$$E = \sqrt{P^2c^2 + m_0^2 c^4} = m_0 c^2 \sqrt{1 + \frac{P^2 c^2}{m_0^2 c^4}} = m_0 c^2 \sqrt{1 + \left(\frac{P}{m_0 c}\right)^2}$$

$$= m_0 c^2 \left[1 + \frac{1}{2} \frac{P^2}{m_0^2 c^2} - \frac{1}{2} \times \frac{1}{4} \left(\frac{P^2}{m_0^2 c^2}\right)^2\right]$$

$$= m_0 c^2 + \frac{P^2}{2m_0} - \frac{P^4}{8 m_0^3 c^2}$$

The third term is the correction caused by relativity mass change

* For energy eigenvalue equation (i.e., stationary-state Schrödinger equation),

$$\hat{H}\psi = E\psi$$

If $\hat{H} = \hat{H}_0 + \Delta H$, and $\hat{H}_0$ eigenvalue equation can be solved exactly: $\hat{H}_0 \psi^{(0)} = E^{(0)} \psi^{(0)}$.

and if $\Delta\hat{H} << \hat{H}_0$, then we can use perturbation theory to solve the $\hat{H}$ equation approximately. Usually, this is based on the $\psi^{(0)}$ and $E^{(0)}$, and then make the first order correction to wave functions, and make the first and second order correction to the energy eigenvalues.

After 1st order correction, the wave function is

$$\psi_k = \psi_k^{(0)} + \sum_n{}' \frac{\Delta H_{nk}}{E_k^{(0)} - E_n^{(0)}} \psi_n^{(0)}$$

After two orders of correction, the energy eigenvalue is

$$E_k = E_k^{(0)} + \Delta H_{kk} + \sum_n{}' \frac{|\Delta H_{nk}|^2}{E_k^{(0)} - E_n^{(0)}}$$

where $\Delta H_{nk} = \int \psi_n^{(0)*} \Delta\hat{H} \psi_k^{(0)} d^3r \equiv \langle n|\Delta\hat{H}|k\rangle$

and $\sum_n{}'$ means to take sum but excluding $n=k$.

[If you are interested in the perturbation theory, you may check a QM book to learn it. We will just use its calculation results in our Spectroscopy class.]

* $\Delta\hat{H}_m$, $\Delta\hat{H}_{ls}$, and $\Delta\hat{H}_d$ terms of hydrogen atom are regarded as perturbations to $\hat{H}_0$ operator. The QM calculation results are:

$$\Delta E_m = \langle \Delta\hat{H}_m \rangle = -\frac{\alpha^4 Z^4 \mu c^2}{2n^3}\left[\frac{1}{l+1/2} - \frac{3}{4n}\right]$$

for all possible l (in SI unit)

$$\Delta E_{ls} = \begin{cases} \dfrac{\alpha^4 Z^4 \mu c^2}{4n^3} \cdot \dfrac{j(j+1) - l(l+1) - s(s+1)}{l(l+\frac{1}{2})(l+1)}, & l \neq 0 \\ 0, \quad l = 0 \end{cases} \quad \text{(in SI unit)}$$

$$\Delta E_d = \begin{cases} 0, & l \neq 0 \\ \dfrac{\alpha^4 Z^4 \mu c^2}{2n^3}, & l = 0 \end{cases} \quad \text{(in SI unit)}$$

* The sum of the relativity, $\hat{\vec{l}} \cdot \hat{\vec{s}}$ coupling, and Darwin terms are

$$\Delta E = \Delta E_m + \Delta E_{ls} + \Delta E_d$$

$$= -\frac{\alpha^4 Z^4 \mu c^2}{2n^3}\left[\frac{1}{j+1/2} - \frac{3}{4n}\right],$$

where $j = l \pm s = l \pm \frac{1}{2}$, $s = 1/2$ for single electron.

This is the result from Dirac equation, i.e., the relativity-corrected Schrödinger equation for $S = 1/2$ (spin) particles. In other words, this is the result for hydrogen and hydrogen-like atoms (ions), whose electron spin angular momentum is $S = 1/2$.

* Example, Hydrogen atom $n=2$ energy level split:

		ΔE_m	ΔE_d	ΔE_{ls}	ΔE
$S=\frac{1}{2}$, $l=1$,	$j=3/2$	$-7/24$	0	$1/6$	$-1/8$
	$j=1/2$	$-7/24$	0	$-1/3$	$-5/8$
$S=\frac{1}{2}$, $l=0$,	$j=1/2$	$-13/8$	1	0	$-5/8$.

unit: $\left(\frac{\alpha^4 Z^4 \mu c^2}{2n^3}\right)$.

Let's put in the real number to have an idea about the magnitude of energy splitting:

$$\alpha \approx \frac{1}{137}, \quad Z=1, \quad \mu \approx m_e = 9.1\times10^{-31}\,kg, \quad C=3\times10^8\,m/s$$

$n=2$.

$$\therefore \frac{\alpha^4 Z^4 \mu c^2}{2n^3} = \frac{\left(\frac{1}{137}\right)^4 \times 1^4 \times 9.1\times10^{-31}\times(3\times10^8)^2}{2\times 2^3} = 1.45\times10^{-23}\,J.$$

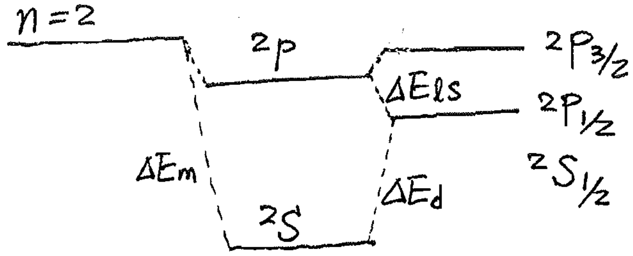
$\therefore$ The corresponding frequency is

$$\Delta\nu = \frac{\Delta E}{h} = \frac{1.45\times10^{-23}}{6.626\times10^{-34}} = 2.19\times10^{10}\,Hz = 2.19\times10^4\,MHz.$$

For H-atom $n=2$ energy levels:

2P energy level: $^2P_{3/2}$ and $^2P_{1/2}$ have a split of $\left(-\frac{1}{8}\right)-\left(-\frac{5}{8}\right) = -\frac{1}{2}\cdot\frac{\alpha^4 Z^4 \mu c^2}{2n^3}$

$$= -\frac{1}{2}\times 2.19\times10^4\,MHz = -1.09\times10^4\,MHz$$



Hydrogen $n=2$ energy level Fine Structure

3. Nucleus Influences and Hyperfine Structure

* In above atomic structure calculations, the nucleus has been treated as a point charge with certain mass. Only its electrostatic interaction with the electron is considered.
* However, in reality, the nucleus (even only consisting of one proton) is not a point mass or point charge. It has volume, charge distribution, spin angular momentum, magnetic moment. These properties cause the nucleus to interact with the magnetic and electric field produced by the electron, resulting in energy levels shift. splitting, and spectral lines to further splitting.
* Because the order of magnitude of these splittings is even smaller than the fine structure splitting, these splittings are called "Hyperfine Structure". The interactions that cause these hyperfine structures are called "hyperfine interaction".
* Table below lists a comparison of the order of magnitude of Coulomb potential, fine structure and hyperfine structure:

Interaction	Order of Magnitude of Energy Change		
	Hz	eV	cm^{-1}
Electrostatic Coulomb Force (Coarse Structure)	10^{15}	4	30,000
Fine Structure	$3\times10^{10}-3\times10^{13}$	$10^{-4}-10^{-1}$	$1-1{,}000$
Hyperfine Structure	$3\times10^{7}-3\times10^{10}$	$10^{-7}-10^{-4}$	$10^{-3}-1$

* In general, the fine structure is about 10^4 times smaller than coarse structure ($\alpha^2 \approx 10^4$), and the hyperfine structure is about 10^3 times smaller than the fine structure.

* A nucleus can have magnetic multipole moments and electric multipole moments. The moments that have major influences on atomic energy levels are magnetic dipole moment and the electric quadrupole moment of the nucleus. Their influences form the hyperfine structure.

* In addition, isotopes have the same nuclear charge but different nuclear mass, different nuclear charge distribution, and different nuclear volume. These factors will also influence atomic energy levels and spectral lines. Their magnitudes are similar to hyperfine structure.

* Here we will consider the hyperfine structure caused by the nuclear magnetic dipole moment and electric quadrupole moment, and the isotope shifts.

(1) Magnetic hyperfine structure (magnetic dipole moment)

* A nucleus has intrinsic spin angular momentum $\hat{\vec{I}}$.

The eigenvalue of $\hat{\vec{I}}^2$ is (analogy to electron spin)

$$|\hat{\vec{I}}^2| = I(I+1)\hbar^2, \quad (I \text{ can be integer or half-integer})$$

The eigenvalue of z-component $\hat{I}_z$ is

$$|\hat{I}_z| = m_I \hbar, \quad m_I = I, I-1, \cdots, -I$$

Associated with the nuclear spin angular momentum, the nuclear magnetic dipole moment $\hat{\mu}_I$ is

$$\hat{\mu}_I = g_I \frac{e}{2M_p} \hat{I} = g_I \frac{e\hbar}{2M_p} \sqrt{I(I+1)}$$

$$\hat{\mu}_{I,z} = g_I \frac{e}{2M_p} \hat{I}_z = g_I m_I \frac{e\hbar}{2M_p}$$

where M_p is the proton mass, and e is the electron charge.
Define a nuclear magneton μ_N as:

$$\mu_N \equiv \frac{e\hbar}{2M_p}$$

Since Bohr magneton $\mu_B \equiv \frac{e\hbar}{2m_e}$, the nuclear magneton is 3 order of magnitude smaller than the Bohr magneton:

$$\frac{\mu_N}{\mu_B} = \frac{m_e}{M_p} \approx \frac{1}{1836}$$

Using the nuclear magneton, the nuclear magnetic dipole moment and its z-component can be expressed as

$$\begin{cases} \mu_I = \sqrt{I(I+1)}\, g_I\, \mu_N \\ \mu_{I,z} = m_I\, g_I\, \mu_N . \end{cases}$$

<u>Example</u>: For proton (^1H): $I = 1/2$, $\mu_I = 2.79\mu_N$, $g_I = 5.58$.

For (^2D): $I = 1$, $\mu_I = 0.86\,\mu_N$, $g_I = 0.86$

For neutron (n): $I = 1/2$, $\mu_I = -1.91\,\mu_N$, $g_I = -3.82$.

* The nuclear magnetic dipole moment will interact with the magnetic field produced by the electron at the nucleus' position. This magnetic dipole interaction is given by a Hamiltonian operator: $\Delta\hat{H}_M = -\hat{\vec{\mu}}_I \cdot \hat{\vec{B}}_e$

$\because$ $\hat{\mu}_I \propto \hat{\vec{I}}$, and $\hat{\vec{B}} \propto \hat{\vec{J}}$ (i.e., electron-produced magnetic field $\vec{B}_e$ is proportional to electron total angular momentum $\hat{\vec{J}}$), $\therefore$ we can have

$$\Delta\hat{H}_M = A\,\hat{\vec{I}} \cdot \hat{\vec{J}}$$

This is a general expression of magnetic hyperfine interaction. A is called the magnetic hyperfine interaction constant.