Note: A is very different from α. The fine structure constant α is a universal constant ($\alpha \approx \frac{1}{137}$). But A can be different for different atomic states.

Now consider single electron atoms (hydrogen atom or hydrogen-like ions),

* If $\ell \neq 0$, the electron-produced magnetic field is

$$\vec{\hat{B}}_e' = \frac{(-e\vec{\hat{v}}) \times (-\vec{\hat{r}})}{cr^3} - \frac{1}{r^3}\left[\vec{\hat{\mu}}_s - \frac{3(\vec{\hat{\mu}}_s \cdot \hat{r})\vec{\hat{r}}}{r^2}\right], \quad r \neq 0$$

where the first term is the magnetic field produced by electron orbital motion, $\vec{v}$ is electron orbital motion velocity, $\vec{r}$ is the electron coordinates regarding nucleus as the origin; the second term is the magnetic field produced by the electron spin magnetic moment $\vec{\mu}_s$.

Since $\vec{\hat{\mu}}_s = -2\mu_B \vec{\hat{s}}$, and $-e\vec{\hat{r}} \times \frac{\vec{\hat{v}}}{c} = 2\mu_B \vec{\hat{\ell}}$,

($\vec{\hat{s}}$ and $\vec{\hat{\ell}}$ are electron's spin and orbital angular momentum)

We have $\vec{\hat{B}}_e' = -2\frac{\mu_B}{r^3}\left[\vec{\hat{\ell}} - \vec{\hat{s}} + 3\frac{(\vec{\hat{s}} \cdot \vec{\hat{r}})\vec{\hat{r}}}{r^2}\right]$

$$= -2\frac{\mu_B}{r^3}\vec{\hat{N}}$$

where $\vec{\hat{N}} = \vec{\hat{\ell}} - \vec{\hat{s}} + \frac{3(\vec{\hat{s}} \cdot \vec{\hat{r}})\vec{\hat{r}}}{r^2}$.

Since the angular momentum $\vec{\hat{N}}$ precesses around the electron total angular momentum $\vec{\hat{j}}$, the effective contribution is the projection of $\vec{\hat{N}}$ on the $\vec{\hat{j}}$ direction, Therefore, $\vec{\hat{B}}_e'$ should be $\vec{\hat{B}}_e = -\frac{2\mu_B}{r^3}\frac{\vec{\hat{N}} \cdot \vec{\hat{j}}}{\hat{j}(\hat{j}+1)}\vec{\hat{j}}$

∴ the Hamiltonian operator is

$$\Delta\hat{H}_M = \left(2\mu_B\frac{\mu_I}{I}\right)\frac{1}{r^3}\cdot\frac{\vec{\hat{N}} \cdot \vec{\hat{j}}}{\hat{j}(\hat{j}+1)}\vec{\hat{I}} \cdot \vec{\hat{j}}$$

The energy shift caused by this Hamiltonian operator can be derived by taking the mean of $\Delta \hat{H}_M$ in known electron wave function:

$$\Delta E_M = \langle \Delta \hat{H}_M \rangle = \frac{a_{\hat{j}}}{2} \left[F(F+1) - \hat{j}(\hat{j}+1) - I(I+1) \right]$$

Here F is the quantum number for the total angular momentum $\hat{\vec{F}}$ of the entire atom. (note: $\hat{\vec{j}}$ is the total angular momentum of electron)

$$\hat{\vec{F}} = \hat{\vec{I}} + \hat{\vec{J}} \quad , \qquad F = I+J, I+J-1, \cdots, |I-J|.$$

$\hat{\vec{F}}$ is conservative as long as no external field presents.

$\hat{\vec{I}}$ is the nuclear angular momentum,

$\hat{\vec{J}}$ is the total angular momentum of the electrons.

where $\hat{\vec{I}} \cdot \hat{\vec{J}} = \frac{1}{2} (\hat{\vec{F}}^2 - \hat{\vec{J}}^2 - \hat{\vec{I}}^2) = \frac{1}{2} [F(F+1) - J(J+1) - I(I+1)]$.

$$a_{\hat{j}} = \left(2\mu_B \frac{\mu_I}{I} \right) \left\langle \frac{1}{r^3} \right\rangle \frac{l(l+1)}{\hat{j}(\hat{j}+1)} \quad , \quad l \neq 0$$

* If $l=0$, then the magnetic hyperfine constant A is denoted as a_s which is given by

$$a_s = \left(2\mu_B \frac{\mu_I}{I} \right) \frac{8\pi}{3} |\psi(0)|^2, \quad l=0.$$

$\therefore \Delta E_M = \langle \Delta \hat{H}_M \rangle = \frac{a_s}{2} \left[F(F+1) - \hat{j}(\hat{j}+1) - I(I+1) \right]$
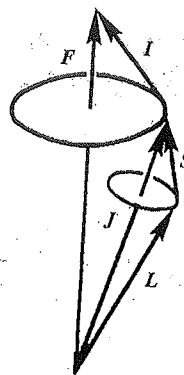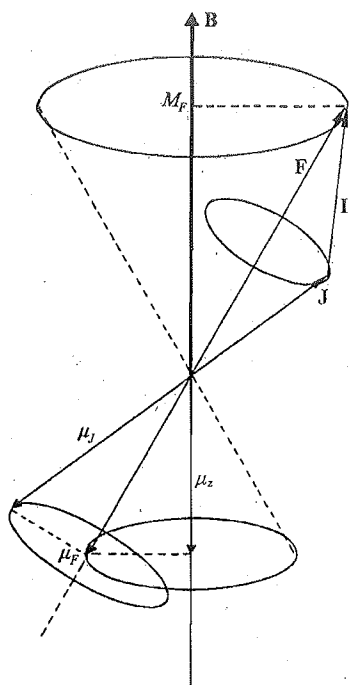
$\rightarrow$ a_s is proportional to the probability density $|\psi(0)|^2$ at the nucleus' position ($r=0$).

* Overall:

$$\Delta E_M = \begin{cases} \frac{a_s}{2} \left[F(F+1) - \hat{j}(\hat{j}+1) - I(I+1) \right], \quad l=0 \\ \qquad \text{where} \quad a_s = \left(2\mu_B \frac{\mu_I}{I} \right) \frac{8\pi}{3} |\psi(0)|^2 \\[2mm] \frac{a_{\hat{j}}}{2} \left[F(F+1) - J(J+1) - I(I+1) \right], \quad l \neq 0 \\ \qquad \text{where} \quad a_{\hat{j}} = \left(2\mu_B \frac{\mu_I}{I} \right) \left\langle \frac{1}{r^3} \right\rangle \frac{l(l+1)}{\hat{j}(\hat{j}+1)}. \end{cases}$$

Vector Model of Angular Momentum Coupling

$$\overrightarrow{\hat{\mu}_F} = \sqrt{F(F+1)}\, g_F\, \mu_N$$

$$\hat{\mu}_{F,z} = m_F\, g_F\, \mu_N \ , \quad m_F \doteq F, F-1, \cdots, -F.$$

Note: only when the electron wave function is known, we can calculate the hyperfine structure.

* <u>Example</u>: Hydrogen magnetic hyperfine structure (including hydrogen-like ions with nuclear charge Ze)

$$|\psi(0)|^2 = \frac{Z^3}{\pi a_1^3 n^3} \implies$$

$$a_S = \frac{1}{4\pi\varepsilon_0 c^2}\left(2\mu_B \frac{\mu_I}{\sqrt{I(I+1)}}\right)\frac{8}{3}\frac{Z^3}{a_1^3 n^3}, \quad \ell=0$$

For $\ell \neq 0$ $\left\langle \frac{1}{r^3}\right\rangle = \frac{Z^3}{a_1^3 n^3 (\ell+\frac{1}{2})\ell(\ell+1)} \implies$

$$a_j = \frac{1}{4\pi\varepsilon_0 c^2}\left(2\mu_B \frac{\mu_I}{\sqrt{I(I+1)}}\right)\left(\frac{Z}{a_1 n}\right)^3 \frac{1}{(\ell+\frac{1}{2})j(j+1)}, \quad \ell \neq 0$$

Let's consider the ground state of hydrogen: $1\ ^2S_{1/2}$.

$n=1,\ \ell=0,\ s=\frac{1}{2},\ j=\frac{1}{2}.\quad I=\frac{1}{2}.\quad \hat{\vec{I}}+\hat{\vec{J}} \implies \hat{\vec{F}}$

∵ $F = I+j,\ I+j-1,\ \cdots,\ |I-j|$

∴ $F = \frac{1}{2}+\frac{1}{2}=1, \quad F=\frac{1}{2}-\frac{1}{2}=0.$

i.e., $^2S_{1/2}$ ground state is split to two hyperfine levels.

for $F=1$, $\Delta E_M = \frac{a_S}{2}\left[1\times2-\frac{1}{2}\times\frac{3}{2}-\frac{1}{2}\times\frac{3}{2}\right]=\frac{1}{4}a_S$

for $F=0$, $\Delta E_M = \frac{a_S}{2}\left[0\times1-\frac{1}{2}\times\frac{3}{2}-\frac{1}{2}\times\frac{3}{2}\right]=-\frac{3}{4}a_S$

Hyperfine Splitting of hydrogen
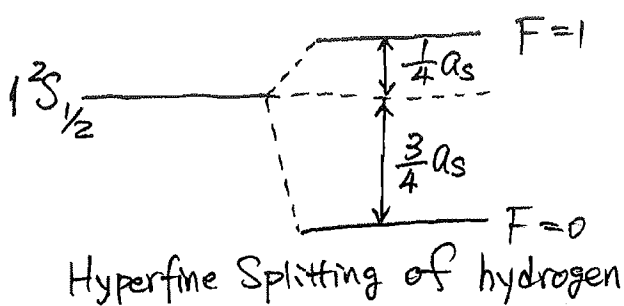
The energy separation between these two hyperfine splittings of hydrogen ground state is

$$\Delta[\Delta E_M(F=1)-\Delta E_M(F=0)]$$
$$= \frac{1}{4}a_S - \left(-\frac{3}{4}a_S\right) = a_S$$
$$= h\nu_H.$$

∴ The frequency corresponding to the transition between these two hyperfine splittings is

$$\nu_H = \frac{a_s}{h} = 1420.406 \text{ MHz} \approx 1.42 \text{ GHz}.$$

Corresponding wavelength $\lambda_H = \dfrac{c}{\nu_H} = 21 \text{ cm}.$

— This is the most famous hyperfine wavelength in the universe !!! It was the first and also the most frequently used wavelength/frequency in radiofrequency astronomy to detect the distribution of hydrogen atoms in the universe. Remember this: 1420 MHz or 21 cm.

☆ Application of Hydrogen hyperfine transition 1420 MHz: the hydrogen − maser.
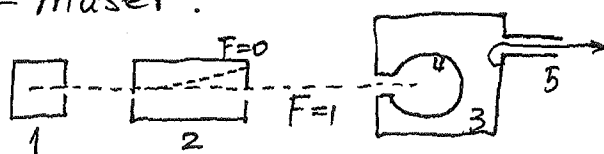
1: hydrogen atom source;   2: State − selector;
3: microwave harmonic oscillator; 4: Quartz cell
5: output of microwave

Working principle: hydrogen atoms coming from the sources are in the ground states $F=0$ and $F=1$. When they pass through the state selector, due to different magnetic moments, atoms on $F=1$ state will pass, while atoms on $F=0$ state will be kicked out of the beam. Thus, only $F=1$ atoms enter the quartz cell in the microwave harmonic oscillator. The oscillator is tuned to the hyperfine transition frequency $(F=1 \rightarrow F=0)$ 1420 MHz. Thus, self −oscillation will occur

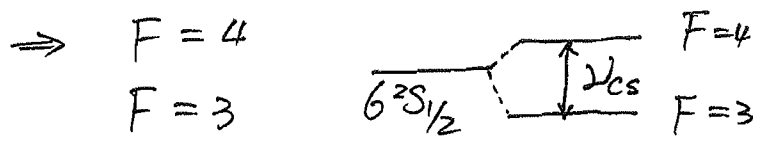and output EM waves with very high stability. (1×10^{-13})

$$\nu_H = 1420405751.786 \pm 0.028 \, Hz.$$

The H-maser has been used as secondary atomic clock to conduct many precise measurements. Unfortunately, the rep of H-master is not very good, so the H-maser is not primary atomic clock.

* ^{133}Cs hyperfine transition: (1967)

^{133}Cs: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^6 6s^1$
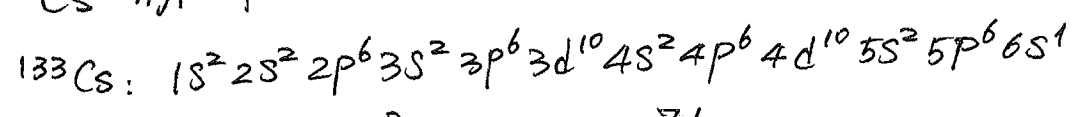
Ground state: $6\,^2S_{1/2}$, $\quad I = 7/2$

$\Rightarrow \quad F = 4$
$\qquad\quad F = 3$

$$\nu_{Cs} = 9192631770 \, Hz.$$

This is the definition of a <u>second</u> in 1967.

(2) Electric Hyperfine Structure.

Here we consider the electric quadrupole interaction between the nuclear electric quadrupole moment and the electric field produced by the electrons.

* Note: not all atoms have electric quadrupole interaction, because it needs two conditions to have it:

    1). nucleus has electric quadrupole moment Q

    2). the electric field produced by electrons must have non-zero gradient of electric field.

* Assume electron total angular momentum $\hat{J}$ goes z-direction, electron motion is symmetric around z-axis. Then the electric field gradient $\phi_z = -\frac{\partial E_z}{\partial z} = \frac{\partial^2 V_e}{\partial z^2}$.

Where V_e is the potential produced by the electron.

* QM results give the energy shift caused by the electric quadrupole interaction as:

$$\Delta E_Q = \frac{B}{4} \frac{\frac{3}{2} K(K+1) - 2I(I+1) J(J+1)}{I(2I-1) J(2J-1)} ,$$

Where $K = F(F+1) - J(J+1) - I(I+1)$.

And $B = eQ \left\langle \frac{\partial^2 V_e}{\partial z^2} \right\rangle$, is the electric quadrupole hyperfine constant. $\left\langle \frac{\partial^2 V_e}{\partial z^2} \right\rangle$ is the mean value of the electric field gradient produced by electron, and it is dependent on the wave function of electron motion.

* Hamiltonian operator for quadrupole interaction is

$$\Delta \hat{H}_Q = Q^{(2)} \cdot U^{(2)} \quad \Rightarrow \Delta E_Q = \langle \Delta \hat{H}_Q \rangle$$

* There is <u>no</u> electric quadrupole interaction in the following cases: 1). The electron is in S state, i.e., orbital angular momentum $L = 0$. Because wavefunction is spherically symmetric, the electric field gradient $\langle \frac{\partial^2 Ve}{\partial z^2} \rangle = 0$.

2). The nuclear angular momentum $I = 0$ or $\frac{1}{2}$, then the electric quadrupole $Q = 0$.

3). If electron total angular momentum $J = \frac{1}{2}$ or $J = 0$, then the electron wave function is spherically symmetric, the electric field gradient is zero at the nucleus.

* When consider the magnetic and the electric hyperfine interaction together, the sum of energy shift is

$$\Delta E = A \cdot \frac{K}{2} + B \cdot \frac{\frac{3}{2}K(K+1) - 2I(I+1)J(J+1)}{4I(2I-1)J(2J-1)}$$

where $K = F(F+1) - J(J+1) - I(I+1)$.

* For hydrogen atom, because $I = \frac{1}{2}$, for ^1H, $Q = 0$, so there is no electric quadrupole interaction.

For alkali atoms, $I > \frac{1}{2}$, $\therefore Q \neq 0$.
  However, ground state $^2S_{1/2} \Rightarrow \langle \frac{\partial^2 Ve}{\partial z^2} \rangle = 0$
  excited state $^2P_{1/2} \Rightarrow \langle \frac{\partial^2 Ve}{\partial z^2} \rangle = 0$

$\therefore$ there is no electric quadrupole interaction for $^2S_{1/2}$. $^2P_{1/2}$.
The lowest energy level that can have quadrupole interaction is $^2P_{3/2}$. $J > \frac{1}{2}$, $\ell > 0$, $I > \frac{1}{2}$.

(3) Isotope Shift.

* For different isotopes of the same element, the nuclear magnetic moments and electric moments can be different, so the hyperfine structure can be different for different isotopes. This belongs to the contents we just discussed above.

* In addition, the nuclear mass, volume are different for isotopes, so it will also cause small energy shift. This energy shift is called the isotope shift.

* There are two main effects in isotope shift: mass effect and volume effect. → for heavy elements   for light elements

* Isotope shift caused by mass effect:

Reduced mass in an atom is given by

$$\mu = \frac{m_e M}{m_e + M} = \frac{m_e}{1 + m_e/M} .$$

Using hydrogen as an example,

$$E_n = -\frac{\mu Z^2 e^4}{32 \pi^2 \varepsilon_0^2 \hbar^2 n^2} = -\frac{\alpha^2 Z^2 \mu c^2}{2 n^2} .$$

i.e., energy levels' energy is proportional to μ.

$$\therefore \quad \frac{\Delta E_n}{E_n} = \frac{\Delta \mu}{\mu} \approx \Delta\left(\frac{1}{1 + m_e/M}\right) \approx -\Delta(m_e/M) .$$

Consider Hydrogen, if we express E_0 as energy levels in infinit nuclear mass

$$E_0 = -\frac{\alpha^2 Z^2 m_e c^2}{2 n^2} = -R_\infty hc \frac{Z^2}{n^2} = -\frac{R_\infty hc}{n^2}$$

$\therefore$ the isotope shift for each isotope of hydrogen is

$$\Delta E = -E_0 \, \Delta(m_e/M) = -\frac{R_\infty hc Z^2}{n^2} \cdot \frac{m_e \, \delta M}{M(M + \delta M)}$$

* Isotope shift caused by nuclear volume effect:

* A nucleus has certain charge distribution within finite volume. The electrostatic interaction between this distributed charge and electron will be different than when assuming the nucleus as a point charge. This is because for S state electrons, wave function is non-zero at the nucleus position, i.e., $\psi(0) \neq 0$. When the electron is in the internal potential of the nucleus, the potential energy is not $-1/r$. A simple explanation is as follows:

* Assume the electron potential at position r from the center of the nucleus:

$$V(r) = \begin{cases} V_0(r) = -\frac{1}{4\pi\varepsilon_0} \cdot \frac{Ze^2}{r}, & r > R \\ \frac{1}{4\pi\varepsilon_0} \frac{Ze^2}{R}\left(-\frac{3}{2} + \frac{r^2}{2R^2}\right), & 0 \leq r \leq R \end{cases}$$

where R is the radius of the nucleus.

The energy correction Hamiltonian operator is

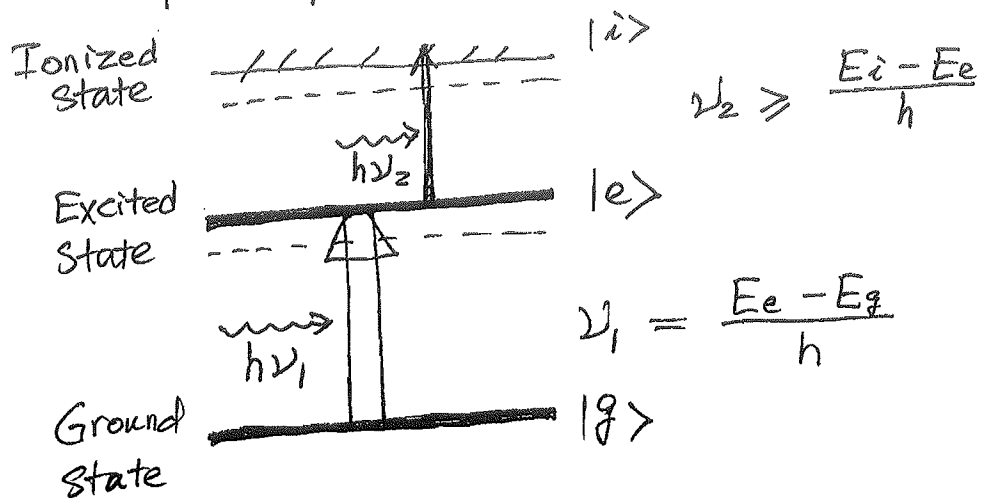$$\Delta \hat{H}_s = \hat{V}(r) - \hat{V_0}(r) = V(r) - V_0(r).$$

∴ The energy shift is

$$\Delta E_s = \langle \Delta \hat{H}_s \rangle = \int_0^\infty \psi^* [V(r) - V_0(r)] \psi \cdot 4\pi r^2 dr$$

$$= |\psi(0)|^2 \int_0^R [V(r) - V_0(r)] 4\pi r^2 dr.$$

∴ $$\Delta E_s = \frac{2\pi}{5} |\psi(0)|^2 \frac{1}{4\pi\varepsilon_0} Ze^2 R^2.$$

— This is the energy difference between a point charge and a charge sphere with radius of R. For different isotopes, R is different. So the energy shift between isotopes is

$$\delta(\Delta E_s) = \frac{4\pi}{5} |\psi(0)|^2 \frac{1}{4\pi\varepsilon_0} Ze^2 R^2 \frac{\delta R}{R}.$$

* Application of isotope shift — laser isotope separation

Ionized State — $|i\rangle$

$\nu_2 \geqslant \dfrac{E_i - E_e}{h}$

Excited State — $|e\rangle$

$h\nu_2$

$\nu_1 = \dfrac{E_e - E_g}{h}$

$h\nu_1$

Ground State — $|g\rangle$

Working principle: Use single frequency, high power laser with $h\nu_1$ to excite one isotope to the excited state, and then use the 2nd laser beam to ionize it. Once ionized, the ionized isotopes can be separated from other non-ionized isotopes.

An example is Uranium enrichment by laser isotope separation

— laser excite ^{235}U, and then ionize it.

— Ionized ^{235}U is deflected by an electric field, while ^{238}U remain neutral and pass to a different collector.

Appendix : Conversion from Atomic Unit to the SI Unit

* In the atomic unit, the energy correction caused by mass change in relativity theory is

$$\Delta E_m = - \frac{\alpha^2 Z^4}{n^3} \left[\frac{1}{\ell + \frac{1}{2}} - \frac{3}{4n} \right] \text{ for all possible } \ell$$

Converting to the SI unit,

$$\Delta E_m = - \frac{\alpha^2 Z^4}{n^3} hc R_H \left[\frac{1}{\ell + \frac{1}{2}} - \frac{3}{4n} \right],$$

where $\alpha = \frac{e^2}{4\pi\varepsilon_0 \hbar c}$ is fine structure constant

$R_H = \frac{\mu e^4}{(4\pi\varepsilon_0)^2 4\pi \hbar^3 c}$ is Rydberg constant for the hydrogen-like atoms, and $\mu = \frac{m_e M_N}{m_e + M_N}$ is reduced mass.

$$\therefore \Delta E_m = - \frac{e^4 Z^4 hc}{(4\pi\varepsilon_0)^2 \hbar^2 c^2 n^3} \frac{\mu e^4}{(4\pi\varepsilon_0)^2 4\pi \hbar^3 c} \left[\frac{1}{\ell + \frac{1}{2}} - \frac{3}{4n} \right]$$

$$= - \frac{(e^2)^4 Z^4 \mu c^2}{(4\pi\varepsilon_0)^4 \hbar^4 c^4 2 n^3} \left[\frac{1}{\ell + \frac{1}{2}} - \frac{3}{4n} \right]$$

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

* Similar derivation can be applied to $\Delta E_{\ell s}$ and ΔE_d.

$$\Delta E_{\ell s} = \frac{\alpha^2 Z^4}{n^3} \cdot \frac{1}{2} \frac{[j(j+1) - \ell(\ell+1) - s(s+1)]}{\ell(\ell + \frac{1}{2})(\ell+1)} \quad (a.u.)$$

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

$$\Delta E_d = \begin{cases} 0, & \ell \neq 0 \\ \frac{\alpha^2 Z^4}{n^3}, & \ell = 0 \end{cases} \quad (a.u.)$$

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