Quantum Mechanics - II

$\boxed{\text{Zeeman Effect}}$

Consider $1^2S_{\frac{1}{2}}$ hydrogen, apply external $\vec{B}_{ext} = B_0 \hat{z}$

Treat simultaneously the hyperfine + $\vec{B}_{ext}$ (no fine structure splitting)

$$H' = a\, \vec{I}\cdot\vec{S} - g_s \mu_0 B_0 S_z - g_p \mu_N B_0 I_z$$

$$a = 1420 \text{ MHz}, \quad k_1 \equiv -g_s \mu_0 B_0, \quad k_2 \equiv g_p \mu_N B_0,$$ $\left(k_1 >> k_2 \quad \because \frac{m_e}{m_p} \sim \frac{1}{2000}\right.$

$$\Rightarrow H' = a\, \vec{I}\cdot\vec{S} + k_1 S_z - k_2 I_z$$

$$= \frac{a}{2}\left[I_+ S_- + I_- S_+\right] + a\, I_z S_z + k_1 S_z - k_2 I_z$$

Without H', the ground state is $\underline{4\text{-fold}}$ degenerate.

$F = 1$ $(m_F = \pm 1, 0)$, $\quad F = 0$ $(m_F = 0)$

$\alpha = \begin{pmatrix}1\\0\end{pmatrix}$, for spin $\uparrow$, $\quad \beta = \begin{pmatrix}0\\1\end{pmatrix}$ for spin $\downarrow$

We can choose 4 basis

$$\psi_{1s} \times \{\alpha_e \alpha_p,\ \beta_e \beta_p,\ \alpha_e \beta_p,\ \beta_e \alpha_p\}$$

Then

$$\langle H' \rangle = \begin{array}{c|cccc} & \uparrow_e\uparrow_p & \downarrow_e\downarrow_p & \uparrow_e\downarrow_p & \downarrow_e\uparrow_p \\ \hline \uparrow_e\uparrow_p & \frac{a}{4}+\frac{k_1-k_2}{2} & 0 & 0 & 0 \\ \downarrow_e\downarrow_p & 0 & \frac{a}{4}-\frac{k_1-k_2}{2} & 0 & 0 \\ \uparrow_e\downarrow_p & 0 & 0 & -\frac{a}{4}+\frac{k_1+k_2}{2} & \frac{a}{2} \\ \downarrow_e\uparrow_p & 0 & 0 & \frac{a}{2} & -\frac{a}{4}-\frac{k_1+k_2}{2} \end{array}$$

The upper left $2\times 2 \Rightarrow$ $\lambda_1 = \frac{a}{4} + \frac{k_1-k_2}{2}$ $\quad (F=1,\ m_F = +1)$

$\lambda_4 = \frac{a}{4} - \frac{k_1-k_2}{2}$ $\quad (F=1,\ m_F = -1)$

the $\frac{a}{2}$ is from

$$\langle \alpha_e \beta_p | \frac{a}{2}(\cancel{I_+S_-} + I_-S_+) | \beta_e \alpha_p \rangle$$

$$= \frac{a}{2}\sqrt{\frac{1}{2}\left(\frac{3}{2}\right)-\left(-\frac{1}{2}\right)\left(-\frac{1}{2}+1\right)}\sqrt{\frac{1}{2}\left(\frac{3}{2}\right)-\frac{1}{2}\left(\frac{1}{2}-1\right)}\ \langle \alpha_e \beta_p | \alpha_e \beta_p \rangle = \frac{a}{2}$$

The lower right 2×2

$$0 = \begin{vmatrix} -\frac{a}{4}+\frac{k_1+k_2}{2}-\lambda & \frac{a}{2} \\ \frac{a}{2} & -\frac{a}{4}-\frac{k_1+k_2}{2}-\lambda \end{vmatrix} = \left(\frac{a}{4}+\lambda\right)^2-\left(\frac{k_1+k_2}{2}\right)^2-\frac{a^2}{4}$$

$$\Rightarrow \quad \lambda_\pm = -\frac{a}{4} \pm \frac{a}{2}\sqrt{1+\underbrace{\left(\frac{k_1+k_2}{a}\right)^2}_{z^2}} \qquad z \propto B_0$$

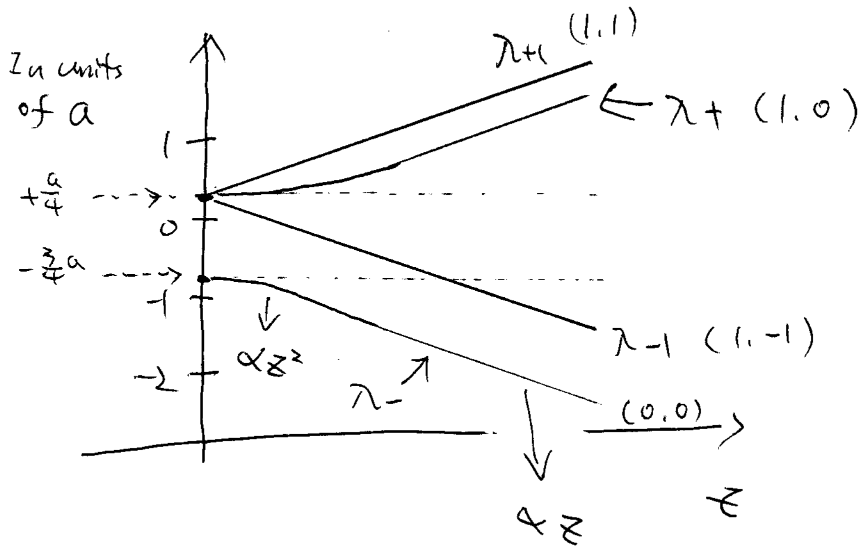
when $B_0 = 0$, $(z=0)$

$$\lambda_+ = \frac{a}{4} \qquad (F=1,\ m_F=0)$$

$$\lambda_- = -\frac{3a}{4} \qquad (F=0)$$

$z \ll 1 \quad \Rightarrow \quad \lambda_\pm \simeq -\frac{a}{4} \pm \frac{a}{2}\left(1+\frac{z^2}{2}\right)$ quadratic in B_0

$z \gg 1 \quad \Rightarrow \quad \lambda_\pm \simeq \pm \frac{a}{2} z$ linear in B_0



Also, it is easy to work out the eigenvector

$$\begin{pmatrix} a_\pm \\ b_\pm \end{pmatrix}, \qquad a_\pm^2 + b_\pm^2 = 1$$

$$a_\pm = \frac{1}{\sqrt{1+\left(z\mp\sqrt{1+z^2}\right)^2}}, \qquad b_\pm = \frac{-\left(z\mp\sqrt{1+z^2}\right)}{\sqrt{1+\left(z\mp\sqrt{1+z^2}\right)^2}}$$

when $z=0$, $a_+ = a_- = \frac{1}{\sqrt{2}}$, $b_+ = -b_- = \frac{1}{\sqrt{2}}$

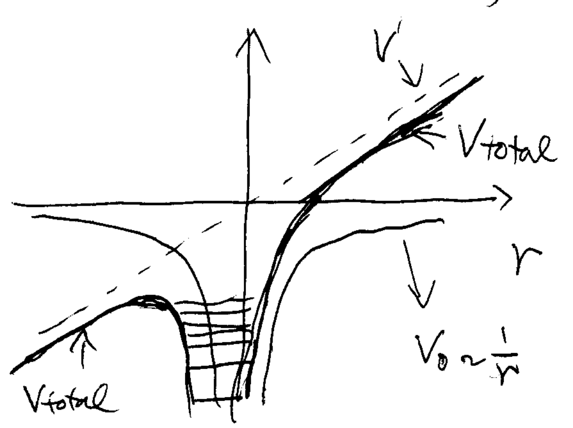
$z \gg 1$ $a_+ \to 1$, $a_- \to 0$, $b_+ \to 0$, $b_- \to -1$

☆ When B_0 is small, e and p spins are tightly coupled by hyperfine interaction $\Rightarrow$ neither m_I nor m_s are good quantum #. Only F and m_F are well-defined.

☆ However, for large B_0 ($z \gg 1$), e and p spin precess "seperately" about the external magnetic field, rather than about one another. $\Rightarrow$ F is no longer well defined, but m_I and m_s are "good quantum numbers".

☆ In more complicated case, one calculates (diagonalizes) the matrix on computer.!

$\boxed{\text{The Stark Effect}}$ $V' = |e|\,\vec{E}_{ext}\cdot\vec{r}$
for electron



Rigorously speaking:
No bound state is possible due to quantum tunnelling
(Especially the "Rydberg atom")
However, ground state in realistic Lab setup is O.K.

Consider weak electric field, ignore spin, and nondegenerate state $|u\rangle$

$$\Delta E^{(1)} = |e|\, \vec{E}_{ext} \cdot \langle u | \vec{r} | u \rangle$$

However, under parity $\mathbb{P}|u\rangle = \pm |u\rangle$

$$\langle u | \vec{r} | u \rangle = \langle u | (\mathbb{P}^{-1}\mathbb{P})\, \vec{r}\, (\mathbb{P}^{-1}\mathbb{P}) | u \rangle = \langle \pm u | \mathbb{P} \vec{r} \mathbb{P}^{-1} | \pm u \rangle$$

$$= -\langle u | \vec{r} | u \rangle = 0$$

Have to go to 2nd order perturbation

$$\Delta E^{(2)} = \sum_{n \neq 0} \frac{|\langle n |\, |e|\, \vec{E}_{ext} \cdot \vec{r}\, | 0 \rangle|^2}{E_0 - E_n}$$

since E_0 is the ground state energy, $E_n > E_0$

$\Rightarrow$ $\Delta E^{(2)}$ is always negative !!

Order of magnitude estimation:

$$E_0 - E_n \sim -\frac{e^2}{a_0^2}, \quad \langle 0 | \vec{r} | n \rangle \sim a_0$$

$$\Rightarrow \Delta E^{(2)} \sim -\frac{(|e| E_{ext} a_0)^2}{\frac{e^2}{a_0^2}} \sim -E_{ext}^2 a_0^3$$

p.s. Electric dipole moment of an atom is defined as

$$\vec{d} \equiv -\frac{\partial(\Delta E^{(2)})}{\partial \vec{E}_{ext}} \propto E_{ext}$$

if $E^{(1)}\ (\propto E_{ext})$ is nonvanishing

$$\Rightarrow \vec{d} = -\frac{\partial(\Delta E^{(1)})}{\partial \vec{E}_{ext}} \quad \text{independent of } E_{ext}$$

$\Rightarrow$ permerment EDM.

Now, consider the degenerate case.

$n=2$ hydrogen, ignoring the spin and Lamb shift for the moment : 4 degenerate states.

① 2S $\quad |n \ell m = 2\,0\,0\rangle$

② $2P, m_\ell=0 \quad |2\,1\,0\rangle$

③ $2P, m_\ell=+1 \quad |2\,1\,1\rangle$

④ $2P, m_\ell=-1 \quad |2\,1\,-1\rangle$

Let $\vec{E}_{ext} = E_{ext}\,\hat{z}$

then $$\langle H' \rangle = |e|\,E_{ext} \begin{pmatrix} 0 & a & 0 & 0 \\ a & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix}$$

where $a = \langle 200|\, z\, |210\rangle = \langle 200|\, |r|\cos\theta\, |210\rangle$

$$= \underbrace{\int_0^\infty r\, R_{21} R_{20} (r^2 dr)}_{= -\frac{3\sqrt{3}}{Z}} \underbrace{\int d\Omega\, (Y_1^0)^* \cos\theta\, Y_0^0}_{= \frac{1}{\sqrt{3}}} = -\frac{3}{Z}$$

It's easy to see that $\lambda_\pm = \pm \frac{3|e|E}{Z}$

and the eigenvectors $\varphi_\pm = \frac{1}{\sqrt{2}}\left(|210\rangle \pm |200\rangle \right)$

☆ In reality $2S$ & $2P_{\frac{1}{2}}$ seperate by the Lamb shift.

If Stark << Lamb → each level shift $\propto E_{ext}^2$

Stark $\gtrsim$ Lamb → each level shift $\propto E_{ext}$

Quantum Mechanics – II

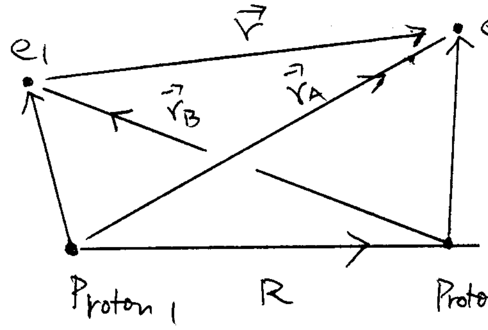
The Van der Waals interaction between 2 Hydrogen ($\sim R^{-6}$) (separated by distance $R \gg a_0$)

$\langle u|\vec{r}|u\rangle = 0 \Rightarrow$ no average EDM

However, for any intance $\vec{d}_1, \vec{d}_2 \neq 0$, which produce $\vec{E}_{dip} \sim \frac{\vec{d}}{R^3}$

Like stark eff. we need to go to 2nd order perturbation.

$$\Delta E^{(2)} \simeq -E^2 a_0^3 \simeq -a_0^3\left(\frac{d}{R^3}\right)^2 \simeq -\frac{a_0^3}{R^6}(e a_0)^2 \sim \boxed{-\frac{e^2 a_0^5}{R^6}}$$



$$\vec{r}_A = \vec{R} + \vec{r}_2$$
$$\vec{r}_B = -\vec{R} + \vec{r}_1$$
$$\vec{r} = \vec{r}_A - \vec{r}_1 = \vec{R} + \vec{r}_2 - \vec{r}_1$$

$$H = H_0 + H' = \left(\frac{p_1^2}{2} + \frac{p_2^2}{2} - \frac{1}{r_1} - \frac{1}{r_2}\right) + \left[\frac{1}{|R|} + \frac{1}{|r|} - \frac{1}{|r_A|} - \frac{1}{|r_B|}\right]$$

$$\frac{1}{|\vec{R}+\vec{r}_2|} = \frac{1}{\sqrt{R^2 + r_2^2 + 2\vec{r}_2\cdot\vec{R}}} = \frac{1}{R\sqrt{1 + \frac{2\vec{r}_2\cdot\vec{R}}{R^2} + \frac{r_2^2}{R^2}}} \sim \frac{1}{R}\left\{1 - \frac{\vec{r}_2\cdot\vec{R}}{R^2} + \frac{3}{8}\frac{(2\vec{r}_2\cdot\vec{R})^2}{R^4} - \frac{1}{2}\frac{r_2^2}{R^2} + \cdots\right]$$

$$\simeq \frac{1}{R} - \frac{\vec{r}_2\cdot\vec{R}}{R^3} + \frac{3}{2}\frac{(\vec{r}_2\cdot\vec{R})^2}{R^5} - \frac{r_2^2}{2R^3}$$

So

$$H' \simeq \frac{1}{R} + \left[\frac{1}{R} - \frac{(\vec{r}_2-\vec{r}_1)\cdot\vec{R}}{R^3} + \frac{3}{2}\frac{[(\vec{r}_2-\vec{r}_1)\cdot\vec{R}]^2}{R^5} - \frac{(\vec{r}_2-\vec{r}_1)^2}{2R^3}\right]$$
$$-\left[\frac{1}{R} - \frac{\vec{r}_2\cdot\vec{R}}{R^3} + \frac{3}{2}\frac{(\vec{r}_2\cdot\vec{R})^2}{R^5} - \frac{r_2^2}{2R^3}\right]$$
$$-\left[\frac{1}{R} + \frac{\vec{r}_1\cdot\vec{R}}{R^3} + \frac{3}{2}\frac{(\vec{r}_1\cdot\vec{R})^2}{R^5} - \frac{r_1^2}{2R^3}\right] + O\left(\frac{1}{R^4}\right)$$

$$= \frac{-3(\vec{r}_2\cdot\vec{R})(\vec{r}_1\cdot\vec{R}) + (\vec{r}_1\cdot\vec{r}_2)R^2}{R^5}$$

let $\vec{R} = R\hat{z}$, then

$$H' = \frac{1}{R^3}\left[-3 z_2 z_1 + (x_1 x_2 + y_1 y_2 + z_1 z_2)\right] = \frac{1}{R^3}\left[x_1 x_2 + y_1 y_2 - 2 z_1 z_2\right]$$

$$\psi_0 = u_{1s}(\vec{r}_1)\ u_{2s}(\vec{r}_2)$$

$$\Delta E^{(1)} = \frac{1}{R^3}\langle \psi_0 | x_1 x_2 + y_1 y_2 - 2 z_1 z_2 | \psi_0 \rangle = 0$$

$$\Delta E^{(2)} = \sum_{n\neq 0} \frac{\langle \psi_0 | H' | n\rangle\langle n | H' | \psi_0\rangle}{E_0 - E_n}$$

for each $|n\rangle$, $\ell = 1$, by <u>Wigner-Eckart theorem</u> (next topic)

$$E_0 = \underset{\text{1st H}}{\left(-\tfrac{1}{2}\right)} + \underset{\text{2nd H}}{\left(-\tfrac{1}{2}\right)} = -1, \qquad E_{np} = \left(-\frac{1}{2n^2}\right) + \left(-\frac{1}{2n^2}\right) = -\frac{1}{n^2}$$

$$\Rightarrow \quad E_{np} \geq -\frac{1}{4}$$

So
$$\Delta E^{(2)} = \sum_{n=2} \frac{\langle \psi_0 | H' | n\rangle\langle n | H' | \psi_0\rangle}{-1 - \left(-\frac{1}{n^2}\right)} \geq -\frac{4}{3}\sum_{n=2}^{\infty} \langle \psi_0 | H' | n_p\rangle\langle n_p | H' | \psi_0\rangle$$

denominator $\quad \underset{2p}{-\frac{3}{4}}, \quad \underset{3p}{-\frac{8}{9}}, \quad \underset{4p}{-\frac{15}{16}}, \quad \cdots$

$$\Rightarrow \quad -\frac{4}{3} \quad -\frac{9}{8} \quad -\frac{16}{15} \quad \cdots \text{ always negative}$$

Since all $\langle \psi_0 | H' | n\ell m\rangle = 0$ if $\ell \neq 1$, we can simply include all states

$$\Delta E^{(2)} \geq -\frac{4}{3}\underbrace{\sum_{m}}_{\text{all states}} \langle \psi_0 | H' \underbrace{| m\rangle\langle m |}_{= \mathbb{1}} H' | \psi_0\rangle = -\frac{4}{3}\langle \psi_0 | (H')^2 | \psi_0\rangle$$

$$(H')^2 = \frac{1}{R^6}\left[x_1^2 x_2^2 + y_1^2 y_2^2 + 4 z_1^2 z_2^2 + \underbrace{2 x_1 x_2 y_1 y_2 - 4 x_1 x_2 z_1 z_2 - 4 y_1 y_2 z_1 z_2}_{=0}\right]$$

$=0$ no contribution when sandwiched by $u_{1s}(\vec{r}_1)\ u_{1s}(\vec{r}_2)$

All we need to know is

$$\underbrace{\langle u_{1s}|x^2|u_{1s}\rangle^2}_{\langle\psi_1|x_1^2|\psi_1\rangle\langle\psi_2|x_2^2|\psi_2\rangle} + \langle u_{1s}|y^2|u_{1s}\rangle^2 + 4\langle u_{1s}|z^2|u_{1s}\rangle^2 = 6\times\left(\frac{\langle r^2\rangle}{3}\right)^2 = \frac{2}{3}\left(\langle r^2\rangle\right)^2$$

$$\Rightarrow \Delta E^{(2)} \geqslant -\frac{4}{3}\frac{1}{R^6}\frac{2}{3}\left(\langle r^2\rangle\right)^2 = -\frac{8}{R^6}$$

$$\left(= -\frac{8e^2a_0^5}{R^6} \quad \text{in ordinary units}\right)$$

Also, by variation method

$$\Delta E \leqslant -6.5\,\frac{e^2a_0^5}{R^6}$$

Van der Waals int. can occour between (for $R \lesssim 137a_0$)

1. an electron and a neutral atom
2. a neutral atom and a macroscopic conductor
3. 2 macroscopic conductors.

For $R > 137a_0$, retardation wash out $\rightarrow$ Casimir eff

$$\Rightarrow \frac{1}{R^7}$$

☆ This is not a fundamental force.
Just like the pions & the Yukawa int.