Parity of H-atom wave-functions

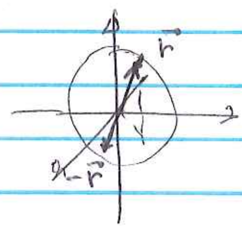
Parity operator $\hat{P}$: $\hat{P}\,\psi(\vec{r}) = \psi(-\vec{r})$

Since the Coulumb potential is spherically-symmetric, we expect that physically nothing changes if $\vec{r} \to -\vec{r}$

Thus, we may only have $\psi(\vec{r}) = \psi(-\vec{r})$ (even ~~fu~~ wave function) or $\psi(\vec{r}) = -\psi(-\vec{r})$ (odd wave function).

$$\psi_{nlm} = R_{nl}(r)\, Y_{lm}(\theta,\varphi)$$

In spherical coordinates



$$\vec{r} \longrightarrow -\vec{r}$$
$$r \longrightarrow r$$
$$\theta \longrightarrow \pi-\theta \qquad (\cos\theta \to -\cos\theta)$$
$$\varphi \longrightarrow \varphi+\pi$$

$$Y_{lm}(\theta,\varphi) = \underset{\text{(normalization)}}{N_{lm}}\, e^{im\varphi}\, P_l^m(\cos\theta)$$

$$e^{im\varphi} \xrightarrow{\varphi\to\varphi+\pi} e^{im(\varphi+\pi)} = e^{im\pi}\, e^{im\varphi} = (-1)^m e^{im\varphi}$$

$$P_{lm}(\cos\theta) \xrightarrow{\theta\to\pi-\theta} P_{lm}(-\cos\theta) = (-1)^{l+m} P_{lm}(\cos\theta)$$

$$Y_{lm}(\pi-\theta,\pi+\varphi) = (-1)^m(-1)^{l+m}\, Y_{lm}(\theta,\varphi) = (-1)^l\, Y_{lm}(\theta,\varphi)$$

$$\psi_{nlm}(-\vec{r}) = (-1)^l\, \psi_{nlm}(\vec{r})$$

If $l = 0, 2, 4\ldots$ $\psi_{nlm}(\vec{r})$ is even

$l = 1, 3, 5\ldots$ —— " —— odd

The values of n & m are irrelevant!

Hydrogen atom in the external electric field

Electro-dipole interaction: $\hat{H}' = +\vec{d}\,\vec{\mathcal{E}} = -e\,\vec{r}\,\vec{\mathcal{E}}$

electron dipole moment

Since by itself H-atom is symmetric, and only $\vec{\mathcal{E}}$ ~~has~~ provide a distinct direction, it is convenient to direct $\vec{\mathcal{E}}$ along z-axis

$$\hat{H}' = -ez\cdot\mathcal{E} = -e\mathcal{E}\,r\cos\theta$$

Unperturbed hydrogen wave functions

$$\psi_{100} = \frac{1}{\sqrt{\pi a^3}}\,e^{-r/a}$$ $n=1, l=0, m=0$, non degenerate S-state

$$\psi_{200} = \frac{1}{4\sqrt{2\pi a^3}}\,(2 - r/a)\,e^{-r/2a}$$ $n=2, l=0, m=0$ (S-state)

$$\psi_{210} = \frac{1}{4\sqrt{2\pi a^3}}\,\frac{r}{a}\,e^{-r/2a}\cos\theta$$ $n=2, l=1, m=0$

$$\psi_{21\pm1} \quad \frac{1}{8\sqrt{\pi a^3}}\,\frac{r}{a}\,e^{-r/2a}\sin\theta\,e^{\pm i\varphi}$$ $n=2, l=1, m=\pm1$

p-states

4x degenerate

First-order perturbation of the ground-state

$\langle\psi_{100}|\hat{H}'|\psi_{100}\rangle \Rightarrow \propto \langle \text{even} \,|\, z \,|\, \text{even}\rangle = 0$

no first-order correction

First excited state $n=2$, 4x degenerate

$\langle\psi_{2lm}|z|\psi_{2l'm'}\rangle$ $\quad z = r\cos\theta$, no φ-dependence $\Rightarrow m = m'$ for a non-zero result

$$\langle\psi_{2lm}|z|\psi_{2l'm'}\rangle = \langle\psi_{2lm}|z|\psi_{2l'm}\rangle\,\delta_{mm'}$$

Thus, ~~any~~ the non-zero matrix elements only for $m=m'$. (i.e. $\langle\psi_{2l0}|z|\psi_{2l'\pm1}\rangle = 0$)

$\langle\psi_{211}|z|\psi_{21-1}\rangle = 0$)

All diagonal terms are zero too
$\langle \psi_{nlm} | z | \psi_{nlm} \rangle = 0$ since z is odd

$$\int |\psi_{nlm}|^2 z \, d^3\vec{r} = 0$$

Thus, the only non-zero element is
$\langle \psi_{210} | z | \psi_{200} \rangle$ and its comp. conj.

lm	00	10	11	1-1
00	0	$V_\mathcal{E}$	0	0
10	$V_\mathcal{E}$	0	0	0
11	0	0	0	0
1-1	0	0	0	0

$$V_\mathcal{E} = -e\mathcal{E} \int \psi^*_{200}(\vec{r})\, \psi_{210}(\vec{r}) \cdot r\cos\theta \, d^3\vec{r} = 3ea\mathcal{E}$$

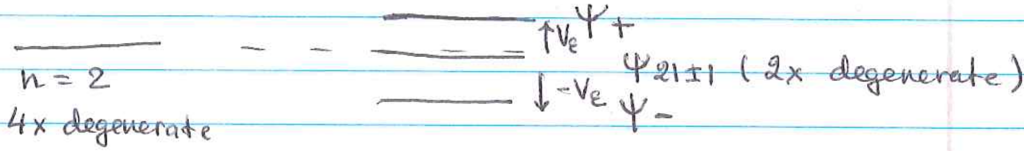
Clearly, the states $(1, \pm 1)$ are not affected by electric field, so their energy does not change. However, the states $|210\rangle$ and $|200\rangle$ get mixed.

Looking only on ψ_{210} and ψ_{200}
we have $H'\psi = \lambda\psi$ to diagonalize

$$\begin{pmatrix} -\lambda & V_\mathcal{E} \\ V_\mathcal{E} & -\lambda \end{pmatrix} \begin{pmatrix} \alpha \\ \beta \end{pmatrix} = 0 \qquad \psi = \alpha\psi_{210} + \beta\psi_{200}$$

$$\lambda_{1,2} = \pm V_\mathcal{E} = \pm 3ea\mathcal{E} \qquad \psi_\pm = \frac{1}{\sqrt{2}}(\psi_{210} \pm \psi_{200})$$

Electric field <u>partially</u> lifts the degeneracy



$E = 0$ $\qquad\qquad$ $\mathcal{E}_z \neq 0$

What about the second-order corrections?

Let's calculate (and estimate) the 2^{nd} order correction to the ground state ψ_{100}

$$E^{(2)}_{n=1} = \sum^{\infty}_{\substack{\text{all excited}\\\text{states}\\ n>1}} \frac{|\langle \psi_{100}|\hat{H}'|\psi_e\rangle|^2}{E^{(0)}_{n=1} - E^{(0)}_e} = e^2\mathcal{E}^2 \sum_e \frac{|\langle \psi_{100}|z|\psi_e\rangle|^2}{E^{(0)}_{n=1} - E^{(0)}_e}$$

To get the exact answer, we will need to calculate all the matrix elements and evaluate the sum. However, we can obtain a reasonably good estimate

$$E_R = |E^{(0)}_{n=1}| > |E^{(0)}_{n=1} - E^{(0)}_e| \geq |E^{(0)}_{n=1} - E^{(0)}_{n=2}| = \frac{3}{4} E_R$$

$$|E^{(2)}_{n=1}| = -E^{(2)}_{n=1} = e^2\mathcal{E}^2 \sum_e \frac{|\langle \psi_{100}|z|\psi_e\rangle|^2}{E^{(0)}_e - E^{(0)}_{n=1}} < \frac{e^2\mathcal{E}^2}{\frac{3}{4}E_R} \sum_e |\langle \psi_{100}|z|e\rangle|^2$$

Moreover, we know that $\langle \psi_{100}|z|\psi_{100}\rangle = 0$, so

$$\sum_e |\langle \psi_{100}|z|e\rangle|^2 = \sum_{\substack{\text{all states}\\ \psi_i}} |\langle \psi_{100}|z|\psi_i\rangle|^2 = \sum_{\text{all states}} \langle \psi_{100}|z|\psi_i\rangle\langle \psi_i|z|\psi_{100}\rangle$$

$$= \langle \psi_{100}|z^2|\psi_{100}\rangle \quad \text{- average value of } z^2$$

Can we simplify our calculations using symmetry considerations? Sure!

Since the ground state is spherically symmetric
$\langle x^2 \rangle = \langle y^2 \rangle = \langle z^2 \rangle = \frac{1}{3} r^2$

$$\langle r^2 \rangle = \int r^2 \varphi_{100}^2 \, d^3\vec{r} = \frac{4}{a^3} \int_0^\infty r^2 e^{-2r/a} r^2 dr = \frac{4}{a^3} \int_0^\infty r^4 e^{-2r/a} dr$$

$$= \frac{4}{a^3} \cdot \left(\frac{a}{2}\right)^5 \underbrace{\int_0^\infty x^4 e^{-x} dx}_{\text{Gamma function}} = \frac{a^2}{8} 4! = 3a^2$$

$$\Downarrow$$

$$\langle z^2 \rangle = a^2$$

Γ - function

$$\boxed{\int_0^\infty x^n e^{-x} dx = \Gamma(n+1) = n!}$$

Thus, we can put an upper bound on the second-order correction

$$\frac{e^2 \mathcal{E}^2 a^2}{E_R}$$

$$< |E_{n=1}^{(2)}| < \frac{4}{3} \frac{e^2 \mathcal{E}^2}{E_R} \cdot a^2 = \left\{ E_R = \frac{\hbar^2}{2ma^2} \right\} =$$

$$= \frac{4}{3} \mathcal{E}^2 \frac{2me^2}{\hbar^2} a^4 = \left\{ \frac{e^2}{4\pi\varepsilon_0} = \frac{\hbar^2}{ma} \right\} = \frac{8}{3} (4\pi\varepsilon_0) \mathcal{E}^2 a^3$$

The ~~second~~ exact correction $E_{n=1}^{(2)} = -\frac{9}{4} (4\pi\varepsilon_0) \mathcal{E}^2 a^3$

Our estimate is within ~20% accuracy limits.