ADVANCED CHEMISTRY

QUANTUM MECHANICS H.W. - WINTER - WEEK 9

Chapter 10

(14)

$$\hat{S}_z \alpha = \frac{1}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}_{2\times 2} \begin{pmatrix} 1 \\ 0 \end{pmatrix}_{2\times 1}$$

$$= \frac{1}{2} \begin{pmatrix} 1 \\ 0 \end{pmatrix} = \underline{\underline{\frac{1}{2}\alpha}}$$

$$\hat{S}_z \beta = \frac{1}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}_{2\times 2} \begin{pmatrix} 0 \\ 1 \end{pmatrix}_{2\times 1} = \frac{1}{2} \begin{pmatrix} 0 \\ -1 \end{pmatrix} = -\frac{1}{2} \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

$$= \underline{\underline{-\frac{1}{2}\beta}}$$

(16)

n	degeneracy w/o spin (n^2)	degeneracy w/ spin ($2n^2$)
1	1	2
2	4	8
3	9	18

(18)

$$\psi_{2s} = \frac{1}{4\pi\sqrt{2}} \left(\frac{Z}{a_0}\right)^{3/2} \left(2 - \frac{Zr}{a_0}\right) e^{-Zr/2a_0} = 0$$

Since $e^{-Zr/2a_0} \neq 0$ and the constants are non-zero

$$\Rightarrow \left(2 - \frac{Zr}{a_0}\right) = 0$$

$$\frac{Zr}{a_0} = 2 \qquad \underline{r = \frac{2a_0}{Z}}$$

$$\psi_{3s} = \frac{1}{81\sqrt{3\pi}} \left(\frac{Z}{a_0}\right)^{3/2} \left(27 - 18\frac{Zr}{a_0} + 2\left(\frac{Zr}{a_0}\right)^2\right) e^{-Zr/3a_0} = 0$$

$$\Rightarrow 27 - 18\left(\frac{Zr}{a_0}\right) + 2\left(\frac{Zr}{a_0}\right)^2 = 0$$

Let $\left(\frac{Zr}{a_0}\right) = n$

$$\Rightarrow 27 - 18n + 2n^2 = 0$$

$$\Rightarrow n = \frac{18 \pm \sqrt{(-18)^2 - 4(2)(27)}}{4} = \frac{18 \pm 10.3923}{4}$$

$n = 7.0981$; $n = 1.9019$

$\frac{Zr}{a_0} = 7.0981$ $\qquad$ $\frac{Zr}{a_0} = 1.9019$

$r = 7.0981 a_0$ $\qquad$ $r = \underline{1.9019 a_0}$

(19) The average distance for an orbital electron $\langle r \rangle$ can be given by

$$\langle r \rangle_{n\ell} = \int_0^\infty r\, P_{n\ell}(r)\, dr$$

$$= \frac{n^2 a_0}{Z}\left\{1 + \frac{1}{2}\left[1 - \frac{\ell(\ell+1)}{n^2}\right]\right\} \quad eq^n\ 10.30$$

for H

$$\langle r \rangle_{2,0} = \frac{2^2(a_0)}{1}\left\{1 + \frac{1}{2}\left[1 - \frac{0}{4}\right]\right\} = \left(4a_0 \cdot \frac{3}{2}\right)$$

$$= \underline{\underline{3.174\ \mathring{A}}}$$

$$\langle r \rangle_{2,1} = \cancel{\frac{4a_0}{1}\left[1 - \frac{1(1+1)}{4}\right] = 4a_0 \cdot \frac{1}{2}} =$$

$$= \frac{4a_0}{1}\left[1 + \frac{1}{2}\left[1 - \frac{2}{4}\right]\right] = \underline{\underline{2.645\ \mathring{A}}}$$

For Li^{2+}

$$\langle r \rangle_{2,0} = \frac{4a_0}{3}\left\{1 + \frac{1}{2}[1 - 0]\right\} = \frac{4a_0}{3} \cdot \frac{3}{2}$$

$$= \underline{\underline{1.058\ \mathring{A}}}$$

$$\langle r \rangle_{2,1} = \frac{4a_0}{3}\left[1 + \frac{1}{2}\left[1 - \frac{2}{4}\right]\right] = \underline{\underline{0.8817\ \mathring{A}}}$$

(24) <u>2p orbital</u> $\hat{L}^2 \psi_{2p} = \ell(\ell+1)\hbar^2 \psi_{2p}$

$$= 1(1+1)\hbar^2 \psi_{2p} = 2\hbar^2 \psi_{2p}$$

$$L^2 = 2\hbar^2 \qquad \underline{\underline{L = \sqrt{2}\hbar}}$$

$$\hat{L}_z \psi_{2p} = m_\ell \hbar \psi_{2p}$$

$$L_z = m_\ell \hbar = \underline{\underline{-\hbar, 0, +\hbar}}$$

<u>3d orbital</u> $\hat{L}^2 \psi_{3d} = \ell(\ell+1)\hbar^2 \psi_{3d}$

$$= 2(2+1)\hbar^2 \psi_{3d} = 6\hbar^2 \psi_{3d}$$

$$L^2 = 6\hbar^2 \qquad \underline{\underline{L = \sqrt{6}\hbar}}$$

$$\hat{L}_z \psi_{3d} = m\hbar \psi_{3d}$$

$$L_z = m\hbar = \underline{\underline{-2\hbar, -\hbar, 0, \hbar, 2\hbar}}$$

(25)

		radial nodes	angular nodes
3s	$L = \sqrt{\ell(\ell+1)}\,\hbar = \underline{\underline{0}}$	2	0
3p	$L = \sqrt{\ell(\ell+1)}\,\hbar = \underline{\underline{\sqrt{2}\hbar}}$	1	1
3d	$L = \sqrt{\ell(\ell+1)}\,\hbar = \underline{\underline{\sqrt{6}\hbar}}$	0	2

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orbital	angular nodes (= ℓ)	radial nodes (= $n-\ell-1$)	total nodes ($n-1$)
1s	0	0	0
2s	0	1	1
2p	1	0	1
3p	1	1	2
3d	2	0	2

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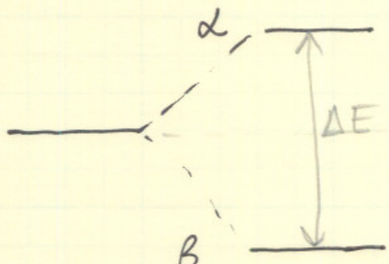
$$E = g_e \mu_B m_s B$$

$$g_e \mu_B B = (2.002322)(9.274 \times 10^{-24}\, J T^{-1})(1T)$$
$$= 1.85695 \times 10^{-23}\, J$$

$$E = m_s (1.85695 \times 10^{-23}\, J)$$

For the α spin state $\quad E_\alpha = \frac{1}{2}(1.85695 \times 10^{-23}\, J)$
$$= 9.28477 \times 10^{-24}\, J$$

For the β spin state $\quad E_\beta = -\frac{1}{2}(1.85695 \times 10^{-23}\, J)$
$$= -9.28477 \times 10^{-24}\, J$$



$$\Delta E = E_\alpha - E_\beta$$

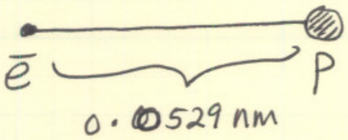
$$\Delta E = 1.85695 \times 10^{-23}\, J = \frac{hc}{\lambda}$$

$$\lambda = \frac{hc}{\Delta E} = \frac{(6.626 \times 10^{-34}\, Js)(2.99 \times 10^{8}\, ms^{-1})}{(1.85695 \times 10^{-23}\, J)}$$

$\lambda = 1.06689 \times 10^{-2}\ m$

$\underline{\underline{\lambda = 1.06689\ cm}}$ microwave region.

(46)



Classical energy $= \dfrac{q_1 q_2}{r} = \dfrac{(e)(-e)}{r} = \dfrac{-e^2}{r(4\pi\varepsilon_0)}$ SI units

$$= -\frac{(1.602\times10^{-19}\,C)^2}{(0.0529\,nm)} \times \frac{10^9\,nm}{m}\ \frac{1}{(4\pi\varepsilon_0)}$$

$$= -4.36034\times10^{-18}\ \frac{C^2}{m}\ \frac{1}{C^2 N^{-1} m^{-2}}$$

$$= -4.36034\times10^{-18}\ Nm$$

$$= \underline{\underline{-4.36034\times10^{-18}\ J}}$$

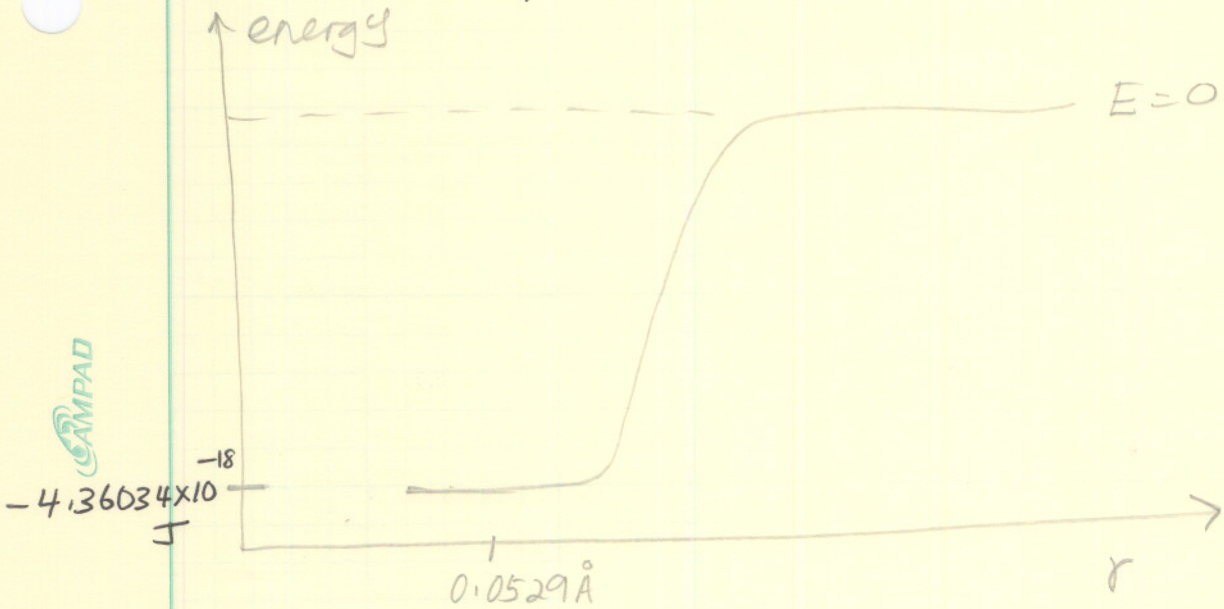
In the quantum mechanical treatment of the H atom (1e and 1p separated by a distance r)

energy $= -13.6\,eV\left(\dfrac{Z^2}{n^2}\right) = -13.6\,eV$ $(n=1)$

$$= -13.6\,eV \times \left(\frac{1.602\times10^{-19}\,J}{eV}\right) = \underline{\underline{-2.1787\times10^{-18}\ J}}$$

When the electron and the proton are infinite distance apart, classical energy = 0 (since $r=\infty$)

Classical picture



In a quantum mechanical system the potential energy term for a proton and an electron separated by a distance $r = \hat{V}$

$$\hat{V} = \int \psi_{1s}^{*}\left[\frac{-e^2}{(4\pi\varepsilon_0)r}\right]\psi_{1s}\,d\tau$$

$$= \frac{1}{\pi}\left(\frac{Z}{a_0}\right)^3 \int e^{-2Zr/a_0}\left(\frac{-e^2}{(4\pi\varepsilon_0)r}\right)d\tau$$

$$= \frac{1}{\pi}\left(\frac{Z}{a_0}\right)^3\left(\frac{-e^2}{4\pi\varepsilon_0}\right)\int_0^\infty r^{-1}e^{-2Zr/a_0}\,r^2dr\;\underbrace{\int_0^\pi \sin\theta\,d\theta\int_0^{2\pi}d\phi}_{=4\pi}$$

$$= \left(\frac{1}{\cancel{\pi}}\right)\left(\frac{Z}{a_0}\right)^3\left(\frac{-e^2}{4\pi\varepsilon_0}\right)(4\cancel{\pi})\int_0^\infty r\,e^{-2Zr/a_0}\,dr$$

$$= -\frac{Z^3}{}\left(e^2\right)\left(\frac{a_0^2}{}\right)$$

$$= -\left(\frac{Z}{a_0}\right)\left(\frac{e^2}{\pi \varepsilon_0}\right)\frac{1}{4}$$

$$= \left(-\frac{1}{0.529 \times 10^{-10}\, m}\right)\left[\frac{(1.602 \times 10^{-19} C)^2}{\pi (8.854 \times 10^{-12} C^2 N^{-1} m^{-2})}\right]\frac{1}{4}$$

$$= -4.3603 \times 10^{-18} J$$

A

(47) $E_{n_1} = -\frac{13.6\,ev}{n_1^2}$ $E_2 = -\frac{13.6\,ev}{n_2^2}$ $n_2 > n_1$

$$\Delta E = E_2 - E_1 = 13.6\,ev\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

For adjacent energy levels n_1 and n_2

$$(n_1+1) = n_2$$

$$\Delta E = 13.6\,ev\left(\frac{1}{n_1^2} - \frac{1}{(n_1+1)^2}\right)$$

$$\Delta E = kT = (1.381\times10^{-23}\,JK^{-1})(298.15\,K)$$

$$= 4.1175\times10^{-21}\,J = 2.570\times10^{-2}\,ev$$

$$\Rightarrow 2.570\times10^{-2}\,ev = 13.6\,ev\left[\frac{1}{n_1^2} - \frac{1}{(n_1+1)^2}\right]$$

$$1.889\times10^{-3} = \frac{(n_1+1)^2 - n_1^2}{n_1^2(n_1+1)^2} = \frac{2n_1+1}{n_1^2\underbrace{(n_1^2+2n_1+1)}_{\approx n_1^2}}$$

$$= \cancel{\frac{2n_1+1}{n_1^4+2n_1^3+1}}$$

$$= \frac{2n_1+1}{n_1^4} \approx \frac{2n_1}{n_1^4} \approx \frac{2}{n_1^3}$$

$\therefore$ $n_1 \approx 10.19 \approx 10$

$n_2 \approx$ ~~10~~ 11

~~48~~ B

Check the energy difference between $n=10$ and $n=11$ levels.

$$\Delta E = 13.6\,eV\left(\frac{1}{10^2} - \frac{1}{11^2}\right) = 2.360 \times 10^{-2}\,eV$$

Check the energy difference between $n=9$ and $n=10$

$$\Delta E = 13.6\,eV\left(\frac{1}{9^2} - \frac{1}{10^2}\right) = 3.190 \times 10^{-2}\,eV$$

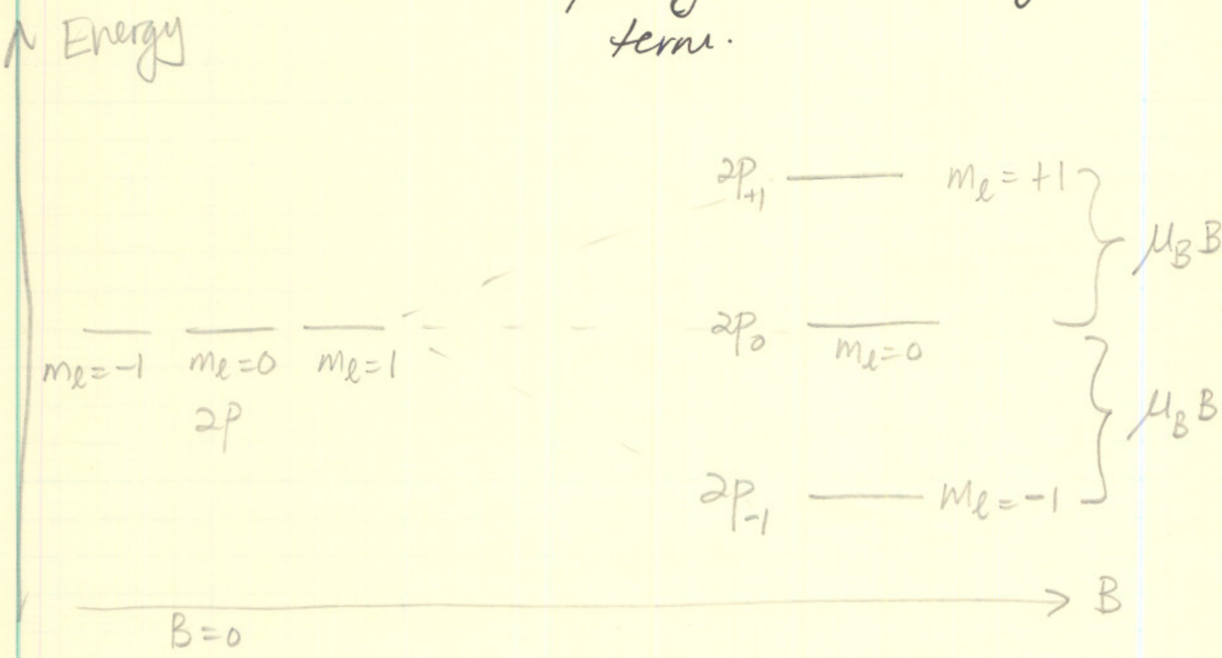
Check the energy difference between $n=11$ and $n=12$

$$\Delta E = 13.6\,eV\left(\frac{1}{11^2} - \frac{1}{12^2}\right) = 1.795 \times 10^{-2}\,eV.$$

$\therefore$ ΔE that is closest to kT is when energy change is between $n=10$ and $n=11$ levels.

(58) $$E_{nem} = \frac{-m_e e^4 Z^2}{2(4\pi\varepsilon_0)^2\hbar^2 n^2} + \mu_B m_e B$$

Splitting is caused by this energy term.



ψ_{2p_0} has the same energy as when $B=0$

$\psi_{2p_{-1}}$ has been decreased by $-\mu_B B$

ψ_{2p_1} has been increased by $\mu_B B$

$$\mu_B B = (9.274\times10^{-24}\,JT^{-1})(10T) = 9.274\times10^{-23}\,J$$

$$kT = (1.381\times10^{-23}\,JK^{-1})(298.15K) = 4.17745\times10^{-21}\,J$$

$\therefore\ \mu_B B << kT$

$\therefore$ all three levels can be occupied at room tempterature