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Quantum Mechanics 6 Ziyan Li

1.

(a) Stationary states : $|n, l, m\rangle$

Ignoring spin : 3 quantum numbers characterise stationary states (n, l, and m)

(b)

n → the principle quantum number

$n = 1, 2, 3 \cdots$

l → the orbital momentum quantum number

$l = 0, 1, 2, \cdots, n-1$

m → the ~~angular~~ magnetic quantum number

$m = -l, -l+1, \cdots, l-1, l$

(c)

$$E = -\frac{\hbar^2}{2\mu a_0^2}\frac{1}{n^2} \quad \text{if } \mu \approx \frac{m_p m_e}{m_p + m_e} \approx m_e$$

then $\boxed{E = -R\left(\frac{1}{n^2}\right)}$

where R= 13.6 eV is the Rydberg energy.

(d) First excited level :

$n = 2$, $l = 0, 1$

$m = 0$ $m = -1, 0, 1$

→ $\boxed{4 \text{ states}}$

second excited level :

$n=3$. $l = 0, 1, 2$

$m=0$

$m = -1, 0, 1$

$m = -2, 1, 0, 1, 2$

$\boxed{9 \text{ states}}$

(considering spin they should be multiplied by 2)

(e) The ground state wavefunction is

$$\langle r, \theta, \phi \mid 1, 0, 0 \rangle = \boxed{\frac{1}{\sqrt{\pi}\, a_0^{3/2}} e^{-r/a_0}}$$

where $a_0 = \frac{4\pi \varepsilon_0 \hbar^2}{m_e e^2} \simeq 5.29 \times 10^{-11}$ m is the Bohr radius

(f)

$$\cancel{\mu = \frac{m_p m_e}{m_p + m_e} = \frac{Z^2 m_e}{(Z+1) m_e} = \frac{Z}{Z+1}}$$

$$\mu = \frac{m_n m_e}{m_n + m_e}$$

(m_n = mass of nucleus

m_e = mass of electron)

(g) With μ replacing m_e and Ze^2 replacing e^2 in the expression for E we get

$$E_n = -\frac{Z^2\hbar^2}{2\mu a_0^2 n^2} = \frac{-Z^2e^2}{8\pi\varepsilon_0 a_0 n^2} = -\frac{Z^2\mu e^4}{2n^2(4\pi\varepsilon_0\hbar)^2}$$

$\therefore$ ~~$E_n \propto Z^2$~~ ~~$E_n \propto$~~

$$E_n \propto -Z^2\mu$$

(i) with the reduced mass the scale factor is

$$\frac{\mu}{m_e}$$

(ii) with the charge Ze the scale factor is

$$Z^2$$

(iii) The ground state radial wavefunction with Z and μ is

$$R'(r) \propto e^{-Zr/a_0}$$

$\therefore$ the radial scale is scaled with $\frac{1}{Z}$

2. The ground state wavefunction

$$\psi \propto e^{-Zr/a_0}$$

(a) $$\langle r \rangle = \frac{\int \psi^* r \psi r^2 dr}{\int \psi^* \psi r^2 dr}$$

$$= \frac{\int_0^\infty r^3 e^{-2Zr/a_0} dr}{\int_0^\infty r^2 e^{-2Zr/a_0} dr}$$

let $u = \frac{2Z}{a_0} r$

$du = \frac{2Z}{a_0} dr$

$dr = \frac{a_0}{2Z} du.$

$r = \frac{a_0}{2Z} u$

$$= \left(\frac{a_0}{2Z}\right) \frac{\int_0^\infty u^3 e^{-u} du}{\int u^2 e^{-u} du} = \frac{a_0}{2Z} \frac{3!}{2!}$$

$$= \boxed{\frac{3a_0}{2Z}}$$

(b) the most likely distance is the r at which ~~ψ~~ ψ is maximum

$$\because \psi \propto e^{-Zr/a_0}$$

$$\therefore \boxed{r_{max} = 0}$$ X

most likely is where most probability is.

$dP = |\psi(r)|^2 dr \, 4\pi r^2$

$\Rightarrow \frac{d}{dr}\left(|\psi|^2 4\pi r^2\right) = 0$

$\Rightarrow r_{max} = \frac{a_0}{Z}$

(c)

$$\langle \hat{V} \rangle = \langle \psi | \hat{V} | \psi \rangle$$

$$= \frac{\int \psi^* \left(\frac{-Ze^2}{4\pi\varepsilon_0 r}\right) \psi \, r^2 dr}{\int \psi^* \psi r^2 dr}$$

$$= -\frac{Ze^2}{4\pi\varepsilon_0}\frac{\int_0^\infty r e^{-2Zr/a_0}dr}{\int_0^\infty r^2 e^{-2Zr/a_0}dr} = \frac{Ze^2}{4\pi\varepsilon_0}\left(\frac{2Z}{a_0}\right)\frac{\int_0^\infty x e^{-x}dx}{\int_0^\infty x^2 e^{-x}dx}$$

$$= \frac{-Ze^2}{4\pi\varepsilon_0}\frac{\cancel{2Z}\,2Z\,(1!)}{\cancel{a_0}\,a_0\,(\cancel{2!})} = \frac{-Z^2e^2}{4\pi\varepsilon_0 a_0}$$

$$= -\frac{Ze^2}{4\pi\varepsilon_0 r_0}$$

$r_0 = \frac{a_0}{Z}$

(d) $\cancel{\langle K\rangle =}$

$$\langle T\rangle = \langle\psi|\hat{T}|\psi\rangle = \langle 1,0,0|\frac{\hat{p}_r^2}{2m_e} + \frac{\hat{L}^2}{2m_e r^2}|1,0,0\rangle$$

$= 0 \because l = 0$ for ground state.

$$= \frac{1}{2m_e}\langle\psi|\hat{p}_r^2|\psi\rangle$$

$$= \frac{1}{2m_e}\frac{\int_0^\infty \psi^* \hat{p}_r^2 \psi\,(r^2dr)}{\int_0^\infty \psi^*\psi\,(r^2dr)}$$

$$= \frac{1}{2m_e}\left(\left(\frac{a_0}{2Z}\right)^2(2!)\right)^{-1}\int_0^\infty \frac{1}{r^2}e^{-Zr/a_0}\left(-\hbar^2\right)\left[\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)e^{-Zr/a_0}\right]r^2dr$$

$\cancel{\hat{p}_r = -\frac{\hbar^2}{2m} - \frac{\hbar^2}{\hbar}\nabla}$

$$\hat{p}_r^2 = -\hbar^2\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)$$

$$= -\frac{\hbar^2}{2m_e}\left(\left(\frac{a_0}{2Z}\right)^2(2)\right)^{-1}\int_0^\infty dr\, e^{-Zr/a_0}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}e^{-Zr/a_0}\right)$$

$$\Rightarrow \frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}e^{-Zr/a_0}\right)$$

$$= \frac{\partial}{\partial r}\left(r^2\left(-\frac{Z}{a_0}\right)e^{-Zr/a_0}\right)$$

$$= \left(-\frac{Z}{a_0}\right)\left(2re^{-Zr/a_0} - \frac{Z}{a_0}r^2e^{-Zr/a_0}\right)$$

$$= \left(\frac{Z}{a_0}\right)^2 r^2 e^{-Zr/a_0} - \left(\frac{2Z}{a_0}\right) re^{-Zr/a_0}$$

$$\Rightarrow \int_0^\infty dr\, e^{-Zr/a_0}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}e^{-Zr/a_0}\right)$$

$$= \left(\frac{Z}{a_0}\right)^2\int_0^\infty dr\, r^2e^{-2Zr/a_0} - \left(\frac{2Z}{a_0}\right)\int_0^\infty dr\, re^{-2Zr/a_0}$$

$$= \left(\frac{Z}{a_0}\right)^2\left(\frac{a_0}{2Z}\right)^2(2!) - \left(\frac{2Z}{a_0}\right)\left(\frac{a_0}{2Z}\right)(1!)$$

$$= \frac{2!}{4} - 1 = \frac{1}{2} - 1 = -\frac{1}{2}$$

$$\therefore \langle T\rangle = +\frac{\hbar^2}{8m_e}\left(\frac{2Z}{a_0}\right)^2 = \frac{\hbar^2}{8m_e}\,\frac{4Z^2}{a_0^2}$$

$$\because a_0 = \frac{4\pi\varepsilon_0\hbar^2}{m_e e^2} \quad \therefore \frac{1}{m_e} = \frac{a_0e^2}{4\pi\varepsilon_0\hbar^2}$$

$$\therefore \langle T\rangle = \frac{\hbar^2}{8a_0^2}\,\frac{4Z^2a_0e^2}{4\pi\varepsilon_0\hbar^2} = \frac{Z^2e^2}{8\pi\varepsilon_0 a_0} = \boxed{\frac{Ze^2}{8\pi\varepsilon_0 r_0}}$$

$$r_0 = \frac{a_0}{Z}$$

(e)

$$\langle E \rangle = \langle T \rangle + \langle V \rangle$$

$$= \frac{Ze^2}{8\pi\varepsilon_0 r_0} + \left(-\frac{Ze^2}{4\pi\varepsilon_0 r_0}\right)$$

$$= \boxed{-\frac{Ze^2}{8\pi\varepsilon_0 r_0}}$$

agrees with the Bohr model.

3. Classically:, For $\cancel{Z}$ $Z=1$, $n=1$

Kinetic energy $T = \frac{e^2}{8\pi\varepsilon_0 a_0}$ (from 2.(d))

$\therefore \frac{1}{2} m_e v^2 = \frac{e^2}{8\pi\varepsilon_0 a_0}$, $a_0 = \frac{4\pi\varepsilon_0 \hbar^2}{m_e e^2}$

$\therefore v^2 = \frac{e^2}{4\pi\varepsilon_0 \cancel{m_e}} \frac{\cancel{m_e} e^2}{4\pi\varepsilon_0 \hbar^2} = \left(\frac{e^2}{4\pi\varepsilon_0 \hbar}\right)^2$

$= \left(\frac{e^2}{4\pi\varepsilon_0 \hbar c}\right) c^2 = \alpha^2 c^2$

$\rightarrow \boxed{v = \alpha c}$

Or From QM:

$\hat{\underline{p}} = -i\hbar \vec{\nabla}$ $\therefore \hat{\underline{v}} = \frac{\hat{\underline{p}}}{m} = -\frac{i\hbar}{m} \vec{\nabla}$

$\therefore \hat{v} \psi = -\frac{i\hbar}{m_e} \vec{\nabla} (e^{-r/a_0}) = -\frac{i\hbar}{m_e} \hat{r} \left(-\frac{1}{a_0}\right) e^{-r/a_0} = \vec{v} \psi$

ground state wave function

$\therefore \hat{v} = -\frac{i\hbar}{m_e a_0} \hat{r}$

$\therefore$ speed $v = |\vec{v}| = \frac{\hbar}{m_e a_0} = \frac{\hbar}{m_e} \left(\frac{4\pi\varepsilon_0 \hbar^2}{m_e e^2}\right)^{-1}$

$= \frac{\hbar}{m_e} \left(\frac{m_e e^2}{4\pi\varepsilon_0 \hbar^2}\right) = \frac{e^2}{4\pi\varepsilon_0 \hbar}$

$= \left(\frac{e^2}{4\pi\varepsilon_0 \hbar c}\right) c = \boxed{\alpha c}$

For the Fe ion $Z=26$

Ground state wave function $\propto e^{-Zr/a_0}$

$\rightarrow \quad \hat{v}\psi = \cancel{\frac{-i\hbar}{}} - \frac{i\hbar Z}{ma_0}\hat{r}\psi$

$\rightarrow \quad v = |\vec{v}| = \frac{\hbar Z}{ma_0} = Z\alpha c = \boxed{26\alpha c}$

relativistically

$$T = (\gamma - 1)mc^2 = \left(\frac{1}{\sqrt{1-\frac{v^2}{c^2}}} - 1\right)mc^2$$

$$= \left(\left(1-\frac{v^2}{c^2}\right)^{-\frac{1}{2}} - 1\right)mc^2 = \left(1 + \frac{1}{2}\frac{v^2}{c^2} + \frac{3}{8}\left(\frac{v^2}{c^2}\right)^2 + \dots - 1\right)mc^2$$

$$= \frac{1}{2}mv^2 + \frac{3}{8}m\frac{v^4}{c^2} + \dots$$

$\therefore$ For $Z=26$, the fractional error is

$$\frac{\frac{3}{8}m\frac{v^4}{c^2}}{\frac{1}{2}mv^2} = \frac{3}{4}\left(\frac{v}{c}\right)^2 \sim \frac{3}{4}\left(\frac{26}{137}\right)^2$$

$$\sim 0.03 = \boxed{3\%}$$

4.

Electric field strength is

$$E = \frac{e}{4\pi\varepsilon_0 a_0^2} = \frac{(1.6\times10^{-19})}{4\pi(8.85\times10^{-12})(5.29\times10^{-11})^2}$$

$$= 5.14\times10^{11}\ \text{V/m} \sim \underline{5\times10^{11}\ \text{V m}^{-1}}$$

charged electrodes cannot generate electric field as high as this because if the potential between the electrodes is too high then the medium between the electrodes will no longer be insulating any more. The medium will turn to be ~~conductive~~ conducting and current will flow. In this case the voltage cannot increase any more. So the electric field cannot increase indefinitely.

$$\vec{S} = \vec{E}\times\vec{H} = \frac{1}{\mu_0}\vec{E}\times\vec{B}$$

$$\therefore\ S = \frac{1}{\mu_0}EB = \frac{1}{\mu_0}E^2\frac{1}{c} = \frac{1}{\mu_0}\sqrt{\mu_0\varepsilon_0}\,E^2$$

$$= \sqrt{\frac{\varepsilon_0}{\mu_0}}E^2 = 10^{22}\ \text{W m}^{-2}$$

$$\cancel{E = \left(\sqrt{\frac{\mu_0}{\varepsilon_0}}E\right.}$$

$$E = \left(\sqrt{\frac{\mu_0}{\varepsilon_0}}S\right)^{\frac{1}{2}} = 1.9\times10^{12}\ \text{V/m}$$

comparable to 5×10^{11} V/m

5. For positronium the reduced mass

$$\mu = \frac{m_e^2}{2m_e} = \frac{m_e}{2}, \quad Z = 1$$

Bohr radius $\cancel{a_0}$ $a = \frac{4\pi\varepsilon_0\hbar^2}{\mu e^2} = 2\times\frac{4\pi\varepsilon_0\hbar^2}{m_e e^2} = 2a_0$

Energy levels.

$$E_n = -\frac{Z^2\mu e^2}{2n^2(4\pi\varepsilon_0\hbar)^2} = \boxed{-\frac{m_e e^2}{4n^2(4\pi\varepsilon_0\hbar)^2}}$$

$$= \frac{1}{2}E_{n,\text{hydrogen}}$$

For positronium in ground state:

$$\langle r\rangle = \cancel{\frac{3}{2}a_0}\ \frac{3}{2}a = \frac{3}{2}(2a_0) = 3a_0$$

$= 2\times$ radius of hydrogen

$\therefore$ The positronium atom is twice as big as a hydrogen atom

6. For muonium $\mu = \frac{206.7 m_e^2}{207.7 m_e} \sim 0.995 m_e$

$Z = 1$

$$\therefore \boxed{E_n = -\frac{0.995 m_e e^2}{2n^2 (4\pi \varepsilon_0 \hbar)^2}}$$

The muonium atom is $\frac{1}{0.995} \sim \boxed{1.005}$ times larger than a hydrogen atom

7. the energy levels of ~~hydrog~~ hydrogen is

$$E_n^H = -R_H \frac{1}{n^2} \qquad (R_H = 13.6eV)$$

Balmer series consists of transitions to $n=2$ from higher energy levels.

Frequency $= \nu$.

$$\rightarrow \quad h\nu_n = R_H \left(\frac{1}{2^2} - \frac{1}{n^2}\right)$$

$$\therefore \nu_n = \frac{R_H}{h}\left(\frac{1}{2^2} - \frac{1}{n^2}\right) \cancel{= (3.282\times10^{15})\left(\frac{1}{2^2}-\frac{1}{n^2}\right)}$$

$i=1$ ~~, n=3~~ $\qquad \therefore \nu_i = \frac{R_H}{h}\left(\frac{1}{2^2} - \frac{1}{(i+2)^2}\right)$

$$\cancel{\nu_n = 3.282\times10^{15}\left(\frac{1}{4}-\frac{1}{9}\right)}$$

For $i=1$

$$\nu_1^H = 0.456806 \times 10^{14}\ Hz$$

$$\nu_2^H = 0.616682 \times 10^{14}\ Hz$$

$$\nu_3^H = 0.690685 \times 10^{14}\ Hz$$

$$\nu_4^H = 0.730884 \times 10^{14}\ Hz$$

For the He^+ ion, energy levels

$$E_n^{He} = -R_{He}\frac{Z^2}{n^2} \quad \text{for } Z=2$$

Assume $R_{He} \sim R_H$ for now, then

$$E_n^{He} = \cancel{R_{He}} - R_H \frac{Z^2}{n^2} = -R_H \frac{4}{n^2}$$

consider the transitions to $n=4$ from higher energy levels

$$\cancel{h\nu_n^{He}} \Rightarrow h\nu_i^{He} = 4R_H\left(\frac{1}{4^2} - \frac{1}{(i+4)^2}\right)$$

If i is even, i.e. if $i=2m$, then

$$\nu_i^{He} = \nu_{2m}^{He} = \frac{4R_H}{h}\left(\frac{1}{4^2} - \frac{1}{(2m+4)^2}\right)$$

$$= \frac{R_H}{h}\left(\frac{1}{(4/2)^2} - \frac{1}{\left(\frac{2m+4}{2}\right)^2}\right)$$

$$= \frac{R_H}{h}\left(\frac{1}{2^2} - \frac{1}{(m+2)^2}\right) = \nu_m^H$$

= the m th Balmer line of H

Hence we call ν_i^{He} the pickering ~~*~~ series

and the even lines of pickering series are almost coincident with the Balmer series.

But they differ by a very tiny amount.

This difference arises from R_{He} is not exactly equal to R_H. This is caused by the fact that the mass of the nucleus is not infinite. we have to consider the ~~red~~ reduced mass.

The ~~frequen~~ ratio for frequencies between corresponding Balmer and Pickering lines should be

$$\frac{\nu_i^{He}}{\nu_{2i}^{H}} = \frac{R_{He}}{R_H}$$

$$R_{He} = \frac{1}{2}\mu_{He}\left(\frac{e^2}{4\pi\varepsilon_0\hbar}\right)^2 \qquad \cancel{\mu_{He} = \frac{2m_p + m_e}{2m_p}}$$

$$R_H = \frac{1}{2}\mu_H\left(\frac{e^2}{4\pi\varepsilon_0\hbar}\right)^2$$

$$\mu_{He} = \frac{4m_p m_e}{4m_p + m_e} \quad \left(m_{nucleus} = 2\times m_{proton} + 2\times m_{neutron} \approx 4m_p\right)$$

$$\mu_H = \frac{m_p m_e}{m_p + m_e}$$

$$\therefore \frac{\nu_i^{He}}{\nu_{2i}^{H}} \sim \frac{R_{He}}{R_H} \sim \frac{\mu_{He}}{\mu_H} \sim \frac{4m_p m_e}{4m_p + m_e}\,\frac{m_p + m_e}{m_p m_e}$$

$$\sim \frac{4(m_p + m_e)}{4(m_p) + m_e} \sim 1 + \frac{3m_e}{4m_p + m_e}$$

$$\sim \cancel{1.000273} \quad 1.000409$$

Compare the frequencies :

$$\frac{0.456987}{0.456806} \sim 1.000396$$

$$\frac{0.616933}{0.616682} \sim 1.000407$$

$$\frac{0.690967}{0.690685} \sim 1.000408$$

$$\frac{0.731183}{0.730884} \sim 1.000409$$

They are consistent under the corrections of reduced mass.

8. $z = r\cos\theta$

$$\langle r,\theta,\phi|2,0,0\rangle = u_{n=2}^{l=0}\, Y_{l=0}^{m=0}$$

$$= \frac{2}{(2a_0)^{3/2}}\left(1-\frac{r}{2a_0}\right)e^{-r/2a_0}\,\frac{1}{2}\sqrt{\frac{1}{\pi}}$$

$$\langle r,\theta,\phi|2,1,0\rangle = u_{n=2}^{l=1}\, Y_{l=1}^{m=0}$$

$$= \frac{r/a_0}{\sqrt{3}(2a_0)^{3/2}}e^{-r/2a_0}\,\frac{1}{2}\sqrt{\frac{3}{\pi}}\cos\theta$$

$\therefore \langle 2,0,0|z|2,1,0\rangle$

$$= \int r^2\sin\theta\,dr\,d\theta\,d\phi\,\frac{2}{(2a_0)^{3/2}}\left(1-\frac{r}{2a_0}\right)e^{-r/2a_0}\,\frac{1}{2}\sqrt{\frac{1}{\pi}}\ \times$$

$$r\cos\theta \times \frac{1}{\sqrt{3}(2a_0)^{3/2}a_0}\,r e^{-r/2a_0}\,\frac{1}{2}\sqrt{\frac{3}{\pi}}\cos\theta$$

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

$$\times\underbrace{\int_0^\pi d\theta\,\sin\theta\cos^2\theta}_{2/3}\times\underbrace{\int_0^{2\pi} d\phi}_{\cancel{2\pi}}$$

$$= \frac{2}{3a_0}\,\frac{1}{(2a_0)^3}\int_0^\infty dr\, r^4 e^{-r/a_0}$$

$$- \frac{2}{3a_0}\,\frac{1}{(2a_0)^4}\int_0^\infty dr\, r^5 e^{-r/a_0}$$

$$\int_0^\infty dr\, r^k e^{-r/a_0} \qquad u = \frac{r}{a_0} \quad du = \frac{dr}{a_0}$$

$$= \int_0^\infty (a_0 du)(a_0^k u^k) e^{-u} \qquad dr = a_0 du$$

$$r^k = a_0^k u^k.$$

$$= a_0^{k+1} \int_0^\infty \underbrace{du\, u^k e^{-u}}_{k!} = \cancel{a_0} a^{k+1} k!$$

$$\therefore \langle 2,0,0 | Z | 2,1,0 \rangle$$

$$= \frac{\cancel{2}}{3} \frac{1}{(2a_0)^3} \frac{1}{a_0} a_0^5 (4!) - \frac{2}{3} \frac{1}{(2a_0)^4} a_0^6 (5!)$$

$$= \left(\frac{\cancel{2}}{\cancel{3}} \times \frac{1}{\cancel{2} \times 2 \times \cancel{2}} \times \cancel{4} \times \cancel{3} \times 2 \times 1 - \frac{2}{\cancel{3}} \times \frac{1}{\cancel{3} \times \cancel{2} \times \cancel{2} \times \cancel{2}} \times 5 \times \cancel{4} \times \cancel{3} \times \cancel{2} \times 1 \right) a_0$$

$$= (2 - 5) a_0 = -3a_0$$

2. $E_n = -\frac{Z^2\hbar^2}{3\mu a_0^2 n^2} = -\frac{Z^2\hbar^2\mu e^4}{2n^2(4\pi\varepsilon_0\hbar)^2}$

$E_n \propto \mu$

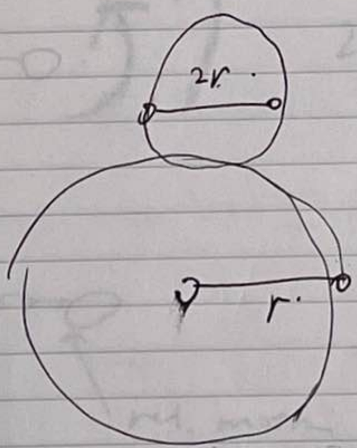
7 $E_{He^+} = E_H \frac{Z^2\mu}{\mu_H} \approx \cancel{4E_H}\ 4E_H$

$E_H^{(n)} = -\frac{m_e e^4}{2n^2(4\pi\varepsilon_0\hbar)^2} = -\frac{m_e e^4}{2(2n)^2(4\pi\varepsilon_0\hbar)^2}$

$= 4E_H^{(2n)}$

$\rightarrow \quad E_{He^+}^{(n)} = E_H^{(2n)}$

5.



Same size.

$\langle I \rangle = \frac{1}{2}$ factor

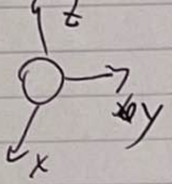
$dU = TdS - mdB$ $\qquad m = -\left(\frac{\partial U}{\partial B}\right)_S$

~~dF~~ $F = U - TS$ $\qquad$ but it's hard to keep S constant.

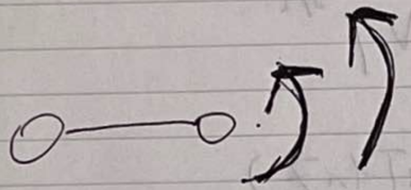
$dF = dU - TdS - SdT$

$dF = -SdT - mdB$

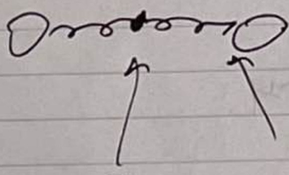
$m = -\left(\frac{\partial F}{\partial B}\right)_T$ it is easy to keep T constant.



3 translational D.O.F.



2 rotational D.o.f.



KE and PE.

rel. motion, 2-d.o.f.

CM

accounted by the 3-trans d.o.f already

$$C_V = -\frac{\partial}{\partial T}\left(\frac{\partial \ln Z}{\partial \beta}\right)_V = \frac{5}{2}k_B.$$

N particles,

$$C_V = \frac{5}{2}Nk_BT.$$

(independent)

partition function for N particles multiply.

indistinguishability ? ~~de~~ That means they are dependent.

6.

Partition Function

$$Z = Z_t Z_r Z_v$$

$$Z_t = \frac{V}{\lambda_{th}^3}, \quad Z_r = \frac{T}{\theta_R}, \quad Z_v \approx 1$$

$$\theta_R \ll T \ll \theta_v$$

$$\cancel{\lambda_{th}}$$

$$= V\left(\frac{2\pi m k_B T}{h^2}\right)^{3/2}$$

$$Z \propto V T^{5/2}$$

$$\cancel{S}$$

$$S = \frac{\partial}{\partial T}\left(k_B T \ln Z\right)$$

$$= k_B \ln Z + \frac{5}{2} k_B = \text{const.}$$

$$\Longrightarrow \quad V T^{5/2} = \text{const.}$$

$$PV = N k_B T$$

$$\rightarrow \quad P V^{7/5} = \text{const.}$$