Phys Chem Term 1 Rev sheet

$E = h\nu$

$= \frac{hc}{\lambda}$

$= hc\tilde{\nu}$

$\tilde{\nu} = -R_H\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$ [cm^{-1}]

$R_H = 109677.8\,cm^{-1}$ ×100

$= 10.96778 \times 10^6\,m$

Bohr 的假設:

- e/s move in circular orbit around tve charged nucleus
- certain orbits are allowed w/ integer values of n
- single photon is emitted / absorbed when an e⁻ moves from one orbit to another

- steps, 不連續
- 上落樓梯

emit / absorb photon

$L = I\omega$

$= \sum m_i r_i^2$

if one particle: $L = I\omega$

$= mr^2\omega$

$= mr\frac{v}{r}$

$= mrv$

Postulate L to have multiples of $\frac{h}{2\pi} = \hbar$

$m_e v r = n\hbar$

$v = \frac{n\hbar}{m_e r}$

$\frac{mv^2}{r} = \frac{e^2}{4\pi\varepsilon r^2}$

$\frac{n^2\hbar^2}{mr^2} = \frac{e^2}{4\pi\varepsilon_0 r}$

$\frac{n^2\hbar^2}{mr} = \frac{e^2}{4\pi\varepsilon_0}$

$\frac{n^2\hbar^2\varepsilon_0}{\pi m e^2} = r$

$E = KE + PE$

$= \frac{1}{2}mv^2 - \frac{e^2}{4\pi\varepsilon_0 r^2}$

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

$= -\frac{e^2}{8\pi\varepsilon_0 r}$

$= -\frac{e^2}{8\pi\varepsilon_0} \times \frac{\pi m e^2}{n^2\hbar^2\varepsilon_0}$

$= -\frac{e^4 m}{8\varepsilon_0^2 h^2}\left(\frac{1}{n^2}\right)$

$-hcR$

$R = \frac{e^4 m_e}{8\varepsilon_0^2 h^3 c}$

Bohr 修正: e⁻ & proton both rotate about a common centre of mass: μ

$\mu = \frac{m_e m_n}{m_e + m_n}$ ⇒ if $m_n >> m_e$: $\mu = \frac{m_e m_n}{m_n} = m_e$

$R = R_{calc} = \frac{e^4\mu}{8\varepsilon_0 h^3 c}$

$1800\,m_e = m_n$

Bohr model doesn't work:

- lines in atomic spectra of alkali metals ≈ as H atom
  - ↳ doublets cannot be explained
  - ↳ 四個 quantum numbers

For poly electronic atoms:

$E = hcz^2 R_x\left[\frac{1}{n^2}\right]$

z: atomic number

Absorption: $1s \rightarrow np \Rightarrow \Delta l = \pm 1$

Emission: 複雜的 transitions

$\Delta l = \pm 1$

- calc energy $\nu = -R_H\left(\frac{1}{n_2^2} - \frac{1}{n_1^2}\right)$

Ionization energy:

$IE = -R\left(\frac{1}{\infty^2} - \frac{1}{n^2}\right) = \frac{R}{n_1^2}$

spin: $\pm\frac{1}{2}$

$l + s = j$ → total L

orbital L

spin L

4 angular momentum &

symmetry conservation

Fine structure:

- termsymbol: $^{2s+1}l_j$ (multiplicity) → $j = l+s, l+s-1, \dots |l-s|$

l:	0	1	2	3
	S	P	D	F

- 要畫
- 根 selection rules:
- 數氫

$\Delta l = \pm 1$

$\Delta s = 0$

$\Delta j = 0, \pm 1$

如果有 field: $m_j = 0, \pm 1$

j has a quantized orientation: m_j

$m_j = j, j-1, \dots, -j$

splitting of lines: separation of m_j levels by B-field ⇒ Stark effect

B-field ⇒ Zeeman effect

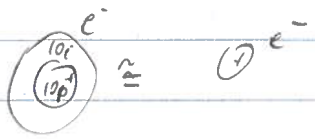
$E_{zeeman} = k g_j m_j$ (k: constant depending size of B-field; g_j: Lande g-factor)

Calculate g_j to know relative splitting of the levels:

$$g_j = \frac{j(j+1) + s(s+1) - l(l+1)}{2j(j+1)}$$

for sodium

↳ identical to Hatom



e⁻ don't spend all its time far from the nucleus

↳ for given value of n, e⁻s w/ low values of l spend more time near the nucleus "inside" the core e⁻s

↳ l ↓ → ↑↑ effective nuclear charge e⁻ experiences

∴ for given n: energies: s < p < d < f .....

↳ penetration of orbitals ↑↑ as l ↓↓

Energy level expressions: predicting energies of transitions

$$E_{nl} = -\frac{hc R_{Na}}{(n - \delta_{nl})^2}$$

δ_{nl}: quantum defect

- depends strongly on l, weakly on n
- quantifies degree of penetration of an e⁻ in given orbital

Na:

$\delta_{ns} \simeq 1.3$

$\delta_{np} \simeq 0.8$

$\delta_{nd} \simeq 0 (0.05)$

Can assume for d-orbitals:

↳ hardly penetrate the core

∴ $\delta_{sd} \approx 0$

for He: exciting one of the 2e⁻s

↳ really consider 1s¹n' as excited states

combine l s j

$L = l_1 + l_2, l_1 + l_2 - 1 \dots |L_1 - L_2|$

$s_1 s_2$ ∴ $S = \frac{1}{2} + \frac{1}{2} = 1$

$S = \frac{1}{2} - \frac{1}{2} = 0$

$J = L + S, L+S-1 \dots |L-S|$

singlet & triplet 分不開

↳ 因為 multiplicity