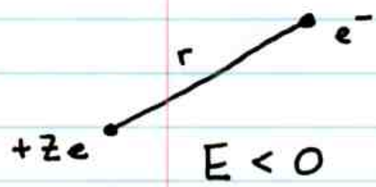
Atoms + Atomic Spectra

4. The Hydrogen-like (one-electron) Atom ($H, He^+, Li^{2+} \ldots$)



relative motion $\hat{H} = -\frac{\hbar^2}{2\mu}\nabla^2 - \frac{Ze^2}{r}$ (cgs)

$E < 0$ bound states

energy eigenvalues from Schrödinger equation:

$$E_n = -\frac{\mu e^4}{2\hbar^2} Z^2 \frac{1}{n^2} \quad ; \; n = 1, 2, 3, \ldots \quad \text{cgs units}$$

principal quantum number

$$\frac{1}{\mu} = \frac{1}{M_N} + \frac{1}{m_e} \approx \frac{1}{m_e} \qquad \mu \simeq m_e \text{ unless high accuracy required}$$

$\mu_H = 0.9993\ m_e$

Bohr radius: $a_0 = \frac{\hbar^2}{m_e e^2} \Rightarrow E_n \cong -\frac{e^2 Z^2}{2a_0 n^2} = -\frac{RZ^2}{n^2}$

(radius of lowest orbit for H in Bohr theory)

0.529 Å

Also $R\,(\text{Rydberg}) = \frac{m_e e^4}{2\hbar^2} = 13.605\,eV$

For atomic H:

$$R_H = \left(\frac{\mu_H}{m_e}\right) R \qquad E_n \overset{Z=1}{=} -R_H/n^2 \quad (\text{precise})$$

$\cong -13.600\,eV/n^2$

Spectroscopists often prefer wave numbers (cm^{-1}) to energy units:

$$E = h\nu = h\frac{c}{\lambda} = hc\,(1/\lambda) = hc\,\tilde{\nu}$$

$E/hc : cm^{-1} \qquad R_H/hc = \tilde{R}_H = 109{,}681\ cm^{-1}$

Although only the principal quantum number appears in the energy expression, two more quantum numbers come from the solution of the Schrödinger equation:

ℓ angular momentum quantum number m_ℓ : magnetic quantum number

(both are integers)

$0 \le \ell \le n-1$ $\ell=0$ "s" $\ell=1$ "p" $\ell=2$ "d" $\ell=3$ "f" $\ell>3$ g, h, i etc.

$-\ell \le m_\ell \le \ell$ $2\ell+1$ values $g_n = \sum_{\ell=0}^{n-1} \sum_{m_\ell=-\ell}^{\ell} 1 = n^2$

The energy eigenfunctions (position representation) contain all 3 quantum numbers; ℓ & m_ℓ are associated with the total angular momentum (orbital) of the electron and its projection on a space-fixed axis.

$$\Psi_{n\ell m_\ell}(r,\theta,\varphi) = N_{n,\ell,m} R_{n,\ell}(r)\, Y_{\ell,m_\ell}(\theta,\varphi) \qquad E<0$$

in text $d\tau = r^2 \sin\theta\, dr\, d\theta\, d\varphi$ associated Laguerre functions spherical harmonics

$$\hat{L}^2 \Psi_{n\ell m_\ell} = (\ )\hat{L}^2 Y_{\ell,m_\ell} = \ell(\ell+1)\hbar^2 \Psi_{n\ell m_\ell}$$

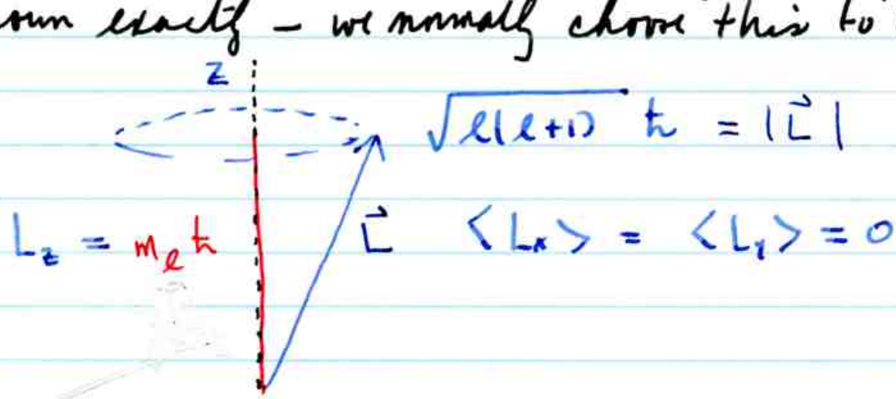
$$\hat{L}_z \Psi_{n\ell m_\ell} = m_\ell \hbar \Psi_{n\ell m_\ell}$$

all 3 operators commute so variables can be known exactly

$$\langle L_x \rangle = \langle L_y \rangle = 0$$

According to quantum mechanics, the components of L do not in general commute, so that only one component can be known exactly – we normally choose this to be L_z.

Vector "Picture"



Energy Levels and Spectra (H)

(continuum levels characterized by p^2, ℓ, m_ℓ)

"continuum"

$H^+ + e^-$

$n=\infty$ I.P. = 13.60 eV 0

$\vdots$

$n=3$ $\ell=0$ ($3s$) $\ell=1$ ($3p_{1,0,-1}$) $\ell=2$ ($3d_{2,1,0,-1,-2}$) $-R_H/9$

$n=2$ $\ell=0$ ($2s$) $\ell=1$ ($2p_{1,0,-1}$)   ($m_\ell = 1,0,-1$) $-R_H/4$

degeneracy $g_n = n^2$

$n=1$ $\ell=0$ ($1s$) $-R_H = -13.60\ \text{eV}$

Selection Rules: $(\mu)_{u\ell} \neq 0$ Δn = anything

$\vec{\mu} = -e\vec{r}$ $\Delta \ell = \pm 1$ (from Y_{ℓ, m_ℓ})

$\Delta m_\ell = 0, \pm 1$

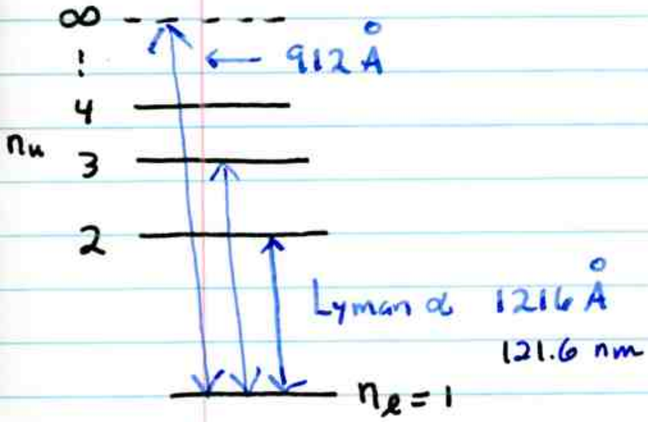
Via the Bohr Spectral Condition:

$$\nu_H = \frac{E_u - E_\ell}{h} \qquad \tilde{\nu}_H = \frac{E_u - E_\ell}{hc} = -\tilde{R}_H\left(\frac{1}{n_u^2} - \frac{1}{n_\ell^2}\right) = \frac{1}{\lambda_H}$$

Transitions divided into series based on wave length region and lower n.

($\Delta \ell$, Δm_ℓ selection rules non-restrictive)

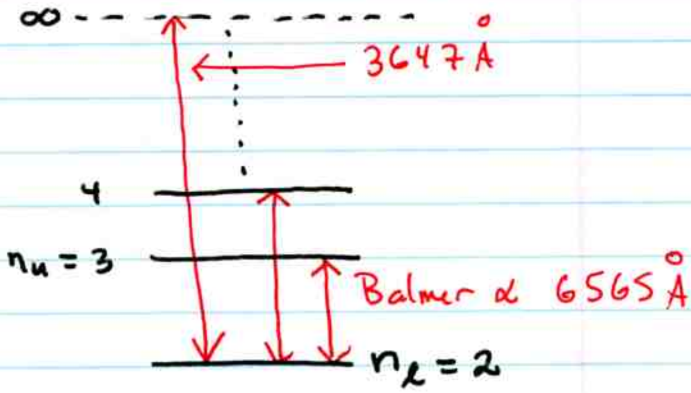
Lyman Series (UV)



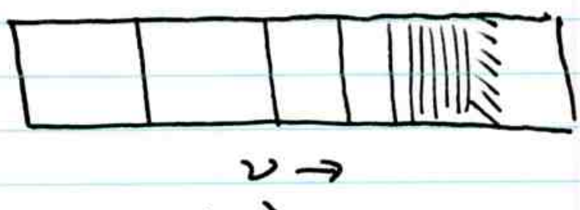
can be seen in absorption at low T

($1\,\text{Å} = 10^{-8}\,\text{cm} = 10^{-10}\,\text{m}$)

Balmer Series (visible)

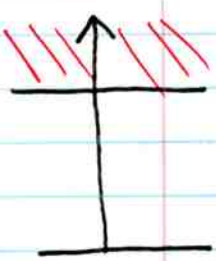


Photographic Plate For Series



The above transitions are known as "bound-bound."

Free- Bound Transitions



In absorption, occurs when photons of sufficient energy to ionize the electron are absorbed. Detailed examination reveals that transition intensity goes down sharply with amount of relative $H^+ - e^-$ energy or momentum.

In emission, occurs upon collisions:

$$H^+ + e^- \longrightarrow H(n, \ell, m_\ell) + h\nu$$

Free- free Transitions

- really inelastic collisions

"bremsstrahlung"

Rydberg States

In the simple Bohr theory of the H atom:

$r_n = a_0 n^2$ is the radius of the orbit of an electron with principal quantum number n. Although quantum mechanics is more complex, states with very high n have very large $\langle r \rangle$. Indeed, they approach the limit of ionization.

bound but distant

e.g. $n = 100$ $\quad r_n = 10^4 \underbrace{a_0}_{0.529\,\text{Å}} = 5.29 \times 10^3$ Å

$n = 10^4$ $\quad r_n = 10^8 a_0 = 0.529$ cm

Such states are known as Rydberg states.

Electron Spin

also: very detailed spectra

Some experiments (e.g. Zeeman effect, magnetic resonance) cannot be interpreted via the simple picture so far presented. These experiments require that individual electrons (and selected nuclei) have spin angular momentum. There is no classical counterpart to this notion.

For spin-½ particles: $\quad S^2 | \pm \rangle = s(s+1)\hbar^2 | \pm \rangle \quad s = ½$

$S_z | \pm \rangle = \underbrace{\pm ½}_{m_s} \hbar | \pm \rangle$

$| \pm \rangle$ sometimes represented as $\underset{\uparrow}{\alpha}, \underset{\downarrow}{\beta}$ $\quad \psi_{n l m_l m_s} = \psi_{n l m_l} | \pm \rangle$

adds degeneracy of 2 to all levels $\quad g_n = 2n^2$