Hydrogen(ic) Atom Primer: Chem. 1410 Oct. 22, 2007 ①

Historically, Ritz Combination Principle fits H emission spectra: $h\nu_{emission} = \boxed{R_H}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$; $n_2 > n_1$, R_H = 13.6 eV

Eg $n_1 = 1$, $n_2 = 2, 3, \ldots$ = Lyman series (UV) ; $n_1 = 2$, $n_2 = 3, 4, \ldots$ = Balmer Series (visible), etc.

Aspects of Hydrogenic Q.M:

$+Ze \xrightarrow{r} e^-$

Since $m_p / m_e = 1{,}823$ regard nucleus as fixed in space

So solve
$$\boxed{\left[-\frac{\hbar^2}{2m_e}\nabla^2 - \underbrace{\frac{Ze^2}{4\pi\epsilon_0 r}}_{V(r)\ \text{Coulomb}}\right]\psi(r,\theta,\varphi) = E\,\psi(r,\theta,\varphi)}$$

(1) $Z = 1$ for H atom

← NB: (2) if allow nucleus (mass m_N) to move, only correction is $m_e \to \mu \equiv \frac{m_e m_N}{(m_e + m_N)}$

Now note:
$$\nabla^2 = \frac{1}{r}\frac{\partial^2}{\partial r^2}(r\ ) + \frac{\hat{\Lambda}^2}{r^2} \quad ; \quad \hat{\Lambda}^2 = \text{"Legendrian" (see above)} = \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}$$

NB: $\hat{\Lambda}^2 Y_{\ell m}(\theta,\varphi) = -\ell(\ell+1)Y_{\ell m_\ell}(\theta,\varphi)$

Let $\psi(r,\theta,\varphi) = R(r)Y_{\ell m_\ell}$ $\overset{SE}{\Rightarrow}$
$$\left[-\frac{\hbar^2}{2m_e}\left\{\frac{1}{r}\frac{\partial^2}{\partial r^2}(r\ ) + \frac{\overset{-\ell(\ell+1)}{\hat{\Lambda}^2}}{r^2}\right\} - \frac{Ze^2}{4\pi\epsilon_0 r}\right]R(r)Y_{\ell m}(\theta\varphi) = E\,R(r)Y_{\ell m}(\theta\varphi)$$

$\rightarrow$ Radial Eq
$$-\frac{\hbar^2}{2m_e}\frac{1}{r}\frac{d^2}{dr^2}(rR(r)) + \overbrace{\left(\frac{\hbar^2\ell(\ell+1)}{2m_e r^2} - \frac{Ze^2}{4\pi\epsilon_0 r}\right)}^{V_{eff}(r)}R(r) = E\,R(r)$$

Finally, let $\chi(r) \equiv r R(r) \Rightarrow$ $\boxed{-\frac{\hbar^2}{2m_e}\frac{d^2}{dr^2}\chi(r) + V_{eff}(r)\chi(r) = E\,\chi(r)}$ reduced radial Eq. (standard 1-d SE!)

an line: $\boxed{\psi_{n,\ell,m_\ell}(r,\theta,\varphi) = N_{n\ell m_\ell}\,\rho^\ell L_{n\ell}(\rho)\,e^{-\rho/2}\,Y_{\ell m_\ell}(\theta,\varphi)}$, with $L_{n\ell}$ = Laguerre polyn.; $\rho \equiv \frac{2Zr}{na_0}$; $\begin{cases} n = 1,2,3 \\ \ell = n-1, n-2, \ldots, 0 \\ m_\ell = -\ell, \ldots, \ell \end{cases}$

"2"

$$\boxed{a_0 = \text{Bohr radius} = \frac{4\pi\epsilon_0\hbar^2}{m_e e^2} = 0.52\,\text{Å}}$$

, and...

corresponding $E_n = -R/n^2$; $n=1,2,3,\ldots$; $R = \dfrac{Z^2 m_e e^4}{32\hbar^2\pi^2\epsilon_0^2} = 13.6\,eV$ for H ($Z=1$)

(Review) Properties of Hydrogen(ic) Atom: Angular Momentum — Note $\hat{L}_x = \hat{y}\hat{p}_z - \hat{z}\hat{p}_y = \frac{\hbar}{i}\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right)$, etc

It can be shown that $-\hbar^2\hat{\Lambda}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2 = \hat{L}^2$

Then: $\hat{L}^2\, Y_{\ell m_\ell}(\theta,\varphi) = \hbar^2 \ell(\ell+1) Y_{\ell m_\ell}(\theta,\varphi)$ ← Spherical Harmonics are eigenfunctions of $\hat{L}^2$!

It can also be shown that $\hat{L}_z = \frac{\hbar}{i}\frac{\partial}{\partial\varphi}$

Thus: $\hat{L}_z Y_{\ell m_\ell}(\theta,\varphi) = \hbar m_\ell Y_{\ell m_\ell}(\theta,\varphi)$ $[m_\ell = -\ell,\ldots,\ell]$ ← Spherical Harmonics are eigenfunctions of $\hat{L}_z$!

Implication for Hydrogenic Atoms: $\psi_{n\ell m_\ell}(r,\theta,\varphi) = R_{n\ell}(r)\, Y_{\ell m_\ell}(\theta,\varphi)$

Hence $\hat{L}^2 \psi_{n,\ell,m_\ell}(r,\theta,\varphi) = \hbar^2\ell(\ell+1)\psi_{n,\ell,m_\ell}(r,\theta,\varphi)$; $\hat{L}_z \psi_{n,\ell,m_\ell}(r,\theta,\varphi) = \hbar m_\ell \psi_{n,\ell,m_\ell}(r,\theta,\varphi)$

↑ hydrogenic energy eigenfunctions are also ℓ-moment. eigenfunctions !

↑ hydrogenic energy eigenfunctions are also eigenfunctions of $\hat{L}_z$!

Note on orbital degeneracies $\hat{H}\left[\psi_{2,1,+1} \pm \psi_{2,1,-1}\right] = E_2\left[\psi_{2,1,+1} \pm \psi_{2,1,-1}\right]$

hydrogen(ic) Hamiltonian

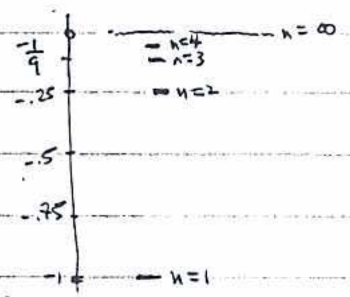
Look at $\psi_{2,1,+1} + \psi_{2,1,-1} = R_{n\ell}(r)\left[Y_{1,+1} + Y_{1,-1}(\theta,\varphi)\right] \propto R_{n\ell}(r)\sin\theta\cos\varphi \propto \psi_{2p_x}$

Likewise $\psi_{2,1,+1} - \psi_{2,1,-1} = R_{n\ell}(r)\left[Y_{1,+1} - Y_{1,-1}(\theta,\varphi)\right] \propto R_{n\ell}(r)\sin\theta\sin\varphi \propto \psi_{2p_y}$

} Chemists sometimes prefer these

More on Hydrogen atom properties ...

Energy level diagram [neglecting degeneracies!; cf. below]



Rydberg const $= Z^2(13.6\,\text{eV})$

Look again at standard; cf. Table 9.3 [Atkins 8th Ed.]

energy eigenfunctions: $\psi_{n,l,m_l}(\mathbf{r}) = R_{nl}(r)\, Y_{lm_l}(\theta,\varphi)$; $n=1,2,3\ldots$; $l=0,1,\ldots,n-1$; $m_l=-l,-l+1,\ldots,l-1,l$

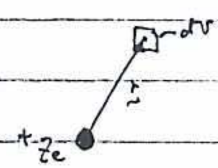
with $R_{nl}(r)$ given in Table 10.1 Atkins 8th Ed. ; E.g.: 1s $R_{10}(r) = 2\left(\frac{Z}{a_0}\right)^{3/2} e^{-\rho/2}$; $\rho = 2Zr/na_0$

"orbital" designation 2s $R_{20}(r) = \frac{1}{2\sqrt{2}}\left(\frac{Z}{a_0}\right)^{3/2}(2-\rho)\,e^{-\rho/2}$

Properties of the hydrogenic energy eigenfunctions or "orbitals"

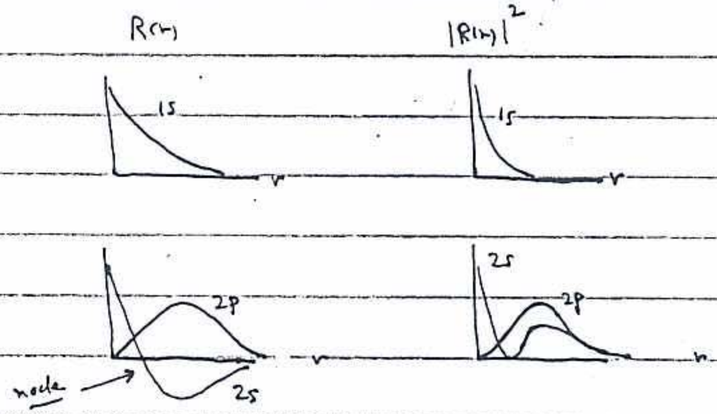
(a) Probability Amplitudes/Densities

(i) Note: $|\psi_{n,l,m_l}(\mathbf{r})|^2$ = Prob density to find electron at $\mathbf{r}$



$|\psi_{n,l,m_l}(\mathbf{r})|^2 dV$ = Probability to find electron in dV

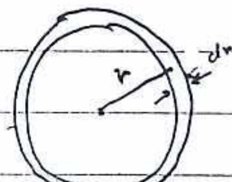
Thus examine:



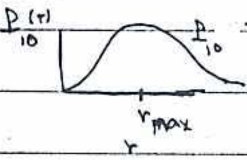
cf. Fig. 10.4, Atkins 8th Ed.

(ii) note $\underbrace{4\pi r^2 R_{n\ell}^2(r)}_{P_{n\ell}(r)}\, dr$ = prob. to find electron in spherical shell of radius r, thickness dr

"radial prob. density"



E.g., for 1s



$P_{10} = \bar{N} r^2 e^{-2r/a_0}$

$$0 = \frac{dP_{10}}{dr} \Rightarrow 0 = \frac{d}{dr}\left[r^2 e^{-2r/a_0}\right]$$

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

$\therefore\ \underbrace{r_{max} = a_0}$ = "most probable radius"

(b) Computing Expectation values; NB: Leibnitz' rule, $\int_0^\infty dx\, x^n e^{-\beta x} = \frac{n!}{\beta^{n+1}}$

(i) Understanding normalization: Look at 1s orbital $\psi_{1s}(\mathbf{r}) = N e^{-Zr/a_0}$

$$1 = \int d\mathbf{r}\, |\psi_{1s}(\mathbf{r})|^2 = \underbrace{\int_{-1}^{1} d(\cos\theta) \int_0^{2\pi} d\varphi}_{4\pi} \int_0^\infty dr\, r^2 N^2 e^{-2Zr/a_0} = 4\pi N^2 \cdot \frac{2!}{(2Z/a_0)^3} \Rightarrow \boxed{N^2 = \frac{Z^3}{\pi a_0^3}}$$

cf. $\psi_{1s}(\mathbf{r}) = \underbrace{R_{10}(r)}_{2\left(\frac{Z}{a_0}\right)^{3/2} e^{-\rho/2}} \underbrace{Y_{00}(\theta,\varphi)}_{\frac{1}{\sqrt{4\pi}}} \Rightarrow N = \left[\frac{Z^3}{\pi a_0^3}\right]^{\frac{1}{2}}$

(ii) Expectation values: Try $\langle r \rangle_{1s}$ for H atom ($Z=1$)

$$\langle r \rangle_{1s} = \int d\mathbf{r}\, \psi^*_{1s}(\mathbf{r})\, r\, \psi_{1s}(\mathbf{r}) = (4\pi)\left(\frac{1}{\pi a_0^3}\right) \underbrace{\int_0^\infty dr\, r^3 e^{-2r/a_0}}_{\frac{3!}{(2/a_0)^4}} = \boxed{\frac{3}{2} a_0}$$

Consequence of Degeneracy of l states

Note, e.g., $\hat{H}\left[\psi_{2,1,+1} \pm \psi_{2,1,-1}\right] = E_2\left[\psi_{2,1,+1} \pm \psi_{2,1,-1}\right]$

$\uparrow$ any hydrogenic Hamiltonian

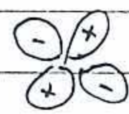
Thus, look at $\psi_{2,1,+1} + \psi_{2,1,-1} = R_{21}(r)\left[Y_{11}(\theta,\varphi) + Y_{1-1}(\theta,\varphi)\right] \propto R_{21}(r)\sin\theta\cos\varphi \propto \psi_{2p_x}$

" $-$ " " [" $-$ "] $\propto R_{21}(r)\sin\theta\sin\varphi \propto \psi_{2p_y}$

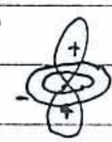
} chemists sometimes prefer these

Orbital Shapes: s - spherically symmetric [Fig. 10.10] ← Atkins 8th Ed.

p - dumbells [Fig. 10.15]

d - 4 4-leaf clovers  $d_{xy,yz,xz}$; $d_{x^2-y^2}$

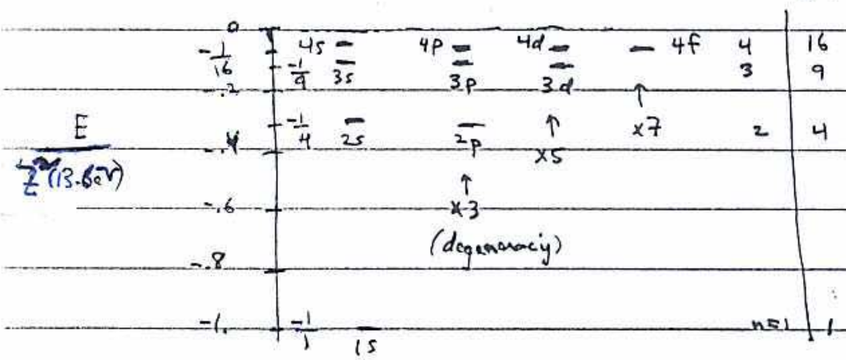
plus

1 "p-orbital w/ hula-hoop"  d_{z^2} [Fig. 10.16]

but note sign of lobes!

Energy Diagram, again (with degeneracies)

total degeneracy of n^{th} level $= n^2$



Note on ∠ momentum: Hydrogenic Energy Eigenfunctions are Simultaneously eigenfunctions of $\hat{L}^2, \hat{L}_z$.

Specifically, $\hat{L}^2 \underbrace{\psi_{n\ell m_\ell}(r,\theta,\varphi)}_{R_{n\ell}(r)\,Y_{n\ell}(\theta,\varphi)} = R_{n\ell}(r) \underbrace{\hat{L}^2 Y_{\ell m_\ell}(\theta,\varphi)}_{\hbar^2 \ell(\ell+1)\,Y_{\ell m_\ell}(\theta,\varphi)} = \hbar^2 \ell(\ell+1)\, \psi_{n\ell m_\ell}(r,\theta,\varphi)$

Same operator considered in "Particle on Sphere"

Similarly, $\hat{L}_z \psi_{n\ell m_\ell}(r,\theta,\varphi) = \hbar m_\ell \psi_{n\ell m_\ell}(r,\theta,\varphi)$

Finally, selection rules (telling which transitions are allowed/forbidden): $\Delta \ell = \pm 1$ ⇒ Grotrian Diagram

$\Delta m = -1, 0, 1$

$\Delta n =$ arbitrary

[Based on conservation of ∠ momentum; photon has spin ∠-momentum $= 1$]