PH585
AMO

Lecture #1

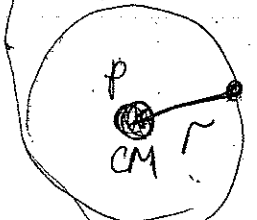
Review of hydrogenic atoms

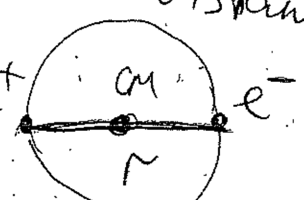
Hydrogenic atoms – isotopes of hydrogen (deuterium, tritium), ions (He^+, Li^{++}, ...), positronium (e^+e^-), muonium (μ^+e^-), muonic atoms, etc. $\Rightarrow$ core Ze + 1 electron (or muon) e^- (or μ^-)

$$H = \frac{p^2}{2\mu} - \frac{Ze^2}{4\pi\varepsilon_0 r}, \quad \mu = \frac{mM}{m+M}$$

m – mass of electron (or particle 1); M – core (nucleus) (or particle 2); μ – reduced mass; r – distance between particles

Ⓗ-atom





Recall: $H = \frac{M\dot{\vec{r}}_1^2}{2} + \frac{m\dot{\vec{r}}_2^2}{2} + V(\vec{r}_1, \vec{r}_2)$; then introduce $\vec{r}_{CM}$, $\vec{r}$ instead of $\vec{r}_1$, $\vec{r}_2$

$$H = \underbrace{H_{CM}}_{\frac{\vec{P}_{CM}^2}{2(M+m)}} + \underbrace{H}$$

$\frac{\vec{P}_{CM}^2}{2(M+m)}$ – motion of center of mass

H – motion of a "relative" particle

$\Leftarrow$ convenient $\Leftarrow$ since, $V(\vec{r}_1, \vec{r}_2) = V(|\vec{r}_1 - \vec{r}_2|) = V(r)$ – central potentials

Time-independent Schrödinger equation $\Rightarrow$ (2.)

$$\left[-\frac{\hbar^2}{2\mu}\vec{\nabla}^2 - \frac{Ze^2}{4\pi\varepsilon_0 r}\right]\Psi(\vec{r}) = E\,\Psi(\vec{r})$$

Solve in spherical coordinates ; $\Psi_{n\ell m}(r,\theta,\varphi) =$

$$= R_{n\ell}(r)\,Y_{\ell m}(\theta,\varphi)$$

principal quantum number (n); orbital angular momentum quantum number (ℓ); magnetic quantum number (m)

normalization

$$\underbrace{\int_0^\infty |R_{n\ell}|^2 r^2 dr}_{=1}\;\underbrace{\int_0^\pi\int_0^{2\pi} |Y_{\ell m}(\theta,\varphi)|^2 \sin\theta\, d\theta\, d\varphi}_{=1} = 1$$

$$\vec{L}^2\, Y_{\ell m}(\theta,\varphi) = \hbar^2 \ell(\ell+1)\, Y_{\ell m}(\theta,\varphi)$$

$$L_z\, Y_{\ell m}(\theta,\varphi) = \hbar m\, Y_{\ell m}(\theta,\varphi)$$

$$\left(-\frac{\hbar^2}{2\mu}\left[\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{d}{dr}\right) - \frac{\ell(\ell+1)}{r}\right] - \frac{Ze^2}{4\pi\varepsilon_0 r}\right) R_{n\ell}(r) = E R_{n\ell}(r)$$

$$\Downarrow$$

$$R_{n\ell}(r) = -\left[\left(\frac{2Z}{n a_\mu}\right)^3 \frac{(n-\ell-1)!}{2n[(n+\ell)!]^3}\right]^{1/2} e^{-\rho/2}\rho^\ell L^{2\ell+1}_{n+\ell}(\rho)$$

$$a_\mu = \frac{4\pi\varepsilon_0\hbar^2}{\mu e^2} = a_0\frac{m}{\mu}\;;\quad \rho = \frac{2Z}{n a_\mu} r$$

a_0: Bohr radius

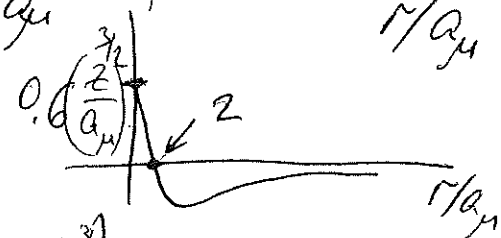
$n+\ell$ or $n-\ell-1$

associated Laguerre polynom

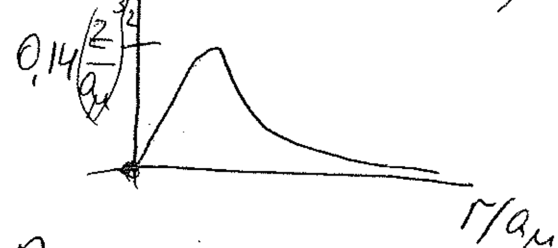
Examples of $R_{nl}(r)$:

$$R_{10}(r) = 2a_\mu^{-3/2} Z^{3/2} e^{-rZ/a_\mu}$$

$$R_{20}(r) = \frac{Z^{3/2}}{\left(2a_\mu^3\right)^{1/2}} \left(1 - \frac{Zr}{2a_\mu}\right) e^{-rZ/2a_\mu}$$



$$R_{21}(r) = \frac{Z^{3/2}}{\sqrt{6a_\mu^3}} \frac{r}{2a_\mu} e^{-rZ/2a_\mu}$$



etc.

<u>Overall:</u> at small r's $\Rightarrow$ $R_{nl}(r) \underset{r\to 0}{\sim} r^l$

Only at $l=0$ (s-states) $R_{nl}(0) \neq 0$

at large r's $\Rightarrow$ $R_{nl}(r) \underset{r\to\infty}{\sim} r^l \cdot \underbrace{r^{n-l-1}}_{} e^{-\frac{rZ}{na_\mu}} \sim$

$\sim e^{-\frac{rZ}{na_\mu}}$

dominated by exponent

highest power of L_{n+l}^{2l+1}

<u>Spherical harmonics</u> $\Rightarrow -l \leq m \leq l \Rightarrow$

associated Legendre polynom

$$Y_{lm}(\theta,\varphi) = (-1)^m \left[\frac{(2l+1)(l-m)!}{4\pi(l+m)!}\right]^{1/2} P_l^m(\cos\theta) e^{im\varphi}$$

$$Y_{l,-m}(\theta,\varphi) = (-1)^m Y_{lm}^*(\theta,\varphi)$$

$m \geq 0$

Examples of $Y_{lm}(\theta,\varphi)$:

$$Y_{00} = \frac{1}{\sqrt{4\pi}} \; ; \quad Y_{10} = \sqrt{\frac{3}{4\pi}}\cos\theta$$

$$Y_{1\pm1} = \mp\sqrt{\frac{3}{8\pi}}\sin\theta\, e^{\pm i\varphi}$$

Energy levels:

$$E_n = -\boxed{\frac{e^2 Z^2}{2a_\mu(4\pi\varepsilon_0)}}\frac{1}{n^2}\,, \quad n = 1, \ldots, \infty$$

" E_I ← ionization

For each $n \Rightarrow$ $l = 0, \ldots, n-1$

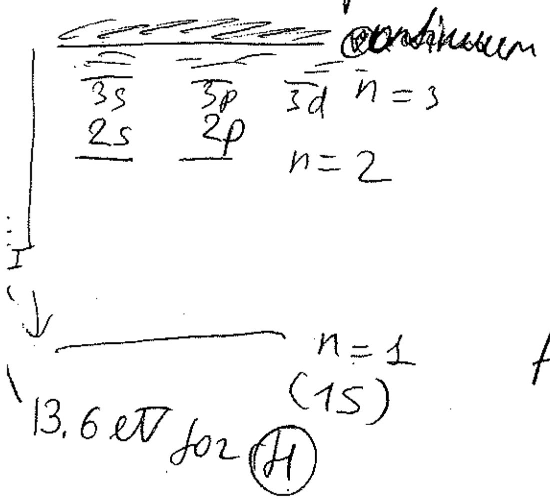
For each $l \Rightarrow 2l+1$ m's

$$g_n = \sum_{l=0}^{n-1}(2l+1) = n^2$$

↑ degeneracy of nth level

↑ $2n^2$ if spin is included

Note: degeneracy with respect to l is "accidental" (due to the particular form of Coulomb potential); in any other central potential $\Rightarrow E_{n,l}$



$l = 0 \; 1 \; 2 \; 3 \; 4$
$\;\;\;\;\; s \; p \; d \; f \; g$ } sub shells

$n = 1 \; 2 \; 3 \; 4$
$\;\;\;\;\; K \; L \; M \; N \; \ldots$ } shells

Also note: $a = a_0 \frac{m}{\mu}\frac{1}{Z}$

a → extent of wave function; $a_0 \frac{m}{\mu} = a_\mu$