Hydrogen atom 25/11/2020

1) Solution of stationary Schrodinger equation
   - properties of wave function
   - spectrum of hydrogen atom, specroscopic notation

2) Dimensions and orders of magnitude

3) Last comment about spin - orbic coupling

Ad 1. $V(r)$ - spherical symmetry

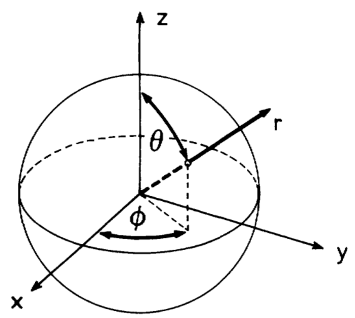
$$V(r) = -\frac{e^2}{4\pi\varepsilon_0 r}$$

$$H = -\frac{\hbar^2 \nabla^2}{2m} + V(r)$$

$\to E\psi = H\psi$

$$-\frac{\hbar^2\nabla^2}{2m} = -\frac{\hbar^2}{2m}\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)$$

$$+\frac{\hbar^2}{2m}\frac{1}{r^2}L^2$$




$$L^2 = -\hbar^2\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right]$$

$$\psi(r,\theta,\varphi) = Y(\theta,\varphi)\,R(r)$$

$$E\,Y(\theta,\varphi)R(r) = Y(\theta,\varphi)\left[-\frac{\hbar^2}{2m}\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + V(r)\right]R(r)$$

$$+\,R(r)\frac{1}{2mr^2}L^2\,Y(\theta,\varphi)$$

$$L^2 Y(\theta,\varphi) = \hbar^2 \ell(\ell+1) Y(\theta,\varphi)$$

$$L_z Y(\theta,\varphi) = \hbar m Y(\theta,\varphi)$$

$$H Y(\theta,\varphi) = E Y(\theta,\varphi)$$

$\ell = 0, 1, \ldots$

$-\ell \le m \le \ell$

$$Y_{\ell m}(\theta,\varphi) = N_{\ell m} e^{-im\varphi} P_\ell^m(\cos\theta)$$

spherical harmonic

$P_\ell^m(\cos\theta) \to$ Legendre polynomials

https://mathworld.wolfram.com/SphericalHarmonic.html

$$\int d^3r \, Y_{\ell m}(\theta,\varphi) Y^*_{\ell' m'}(\theta,\varphi) = \delta_{\ell\ell'} \delta_{mm'}$$

Radial equation:

$$E R(r) = \left[ -\frac{\hbar^2}{2m} \frac{1}{r^2} \frac{\partial}{\partial r}\left( r^2 \frac{\partial}{\partial r} \right) + V(r) + \frac{\hbar^2 \ell(\ell+1)}{2 m r^2} \right] R(r)$$

$$R(r) = \underline{N_{n\ell}} \, e^{-\rho} (2\rho)^\ell L^{2\ell+1}_{n-\ell-1}(2\rho)$$

$\rho = \frac{r}{a n}$ $\qquad$ $a$ - Bohr radius

$\qquad$ $n$ - integer

$L^{2\ell+1}_{n-\ell-1}(2\rho)$ — Laguerre polynomials

$n$ - principal quantum number

$a$; $\quad n = 0, 1, 2, \ldots$

m

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

$$E_H = \frac{\hbar^2}{2ma^2}$$

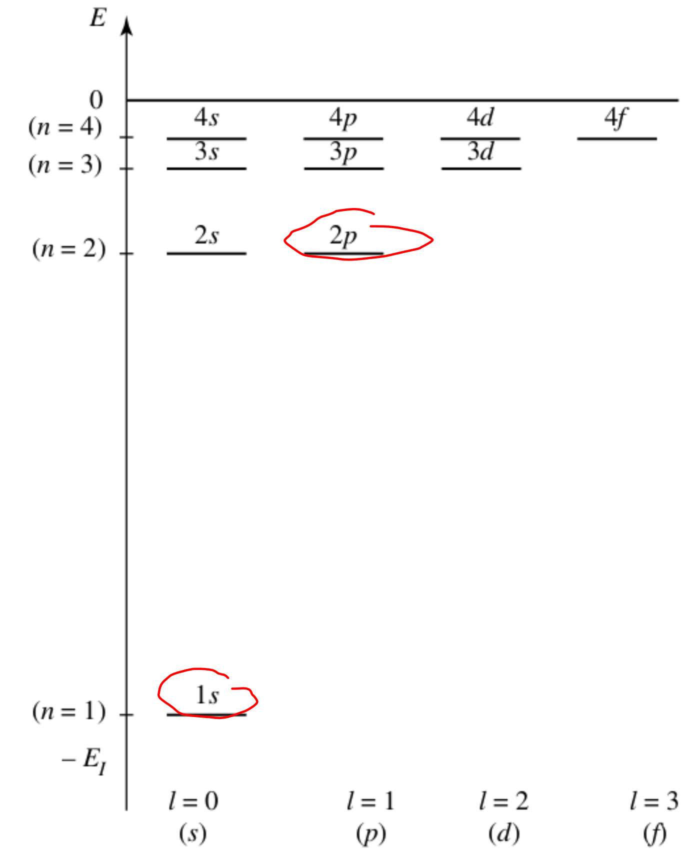



*Figure 4: Energy levels of the hydrogen atom. The energy $E_n$ of each level depends only on $n$. If $n$ is fixed, several values of $l$ are possible: $l = 0, 1, 2, \dots n-1$. To each of these values of $l$ correspond $(2l+1)$ possible values for $m$:*

$$m = -l,\ -l+1,\ \dots,\ l.$$

*Consequently, the level $E_n$ is $n^2$-fold degenerate.*

$n = 1, 2, 3, \dots +\infty$ ; $l = 0, 1, \dots, n-1$

Ad: 2) An expectation values of different powers of $r$

$$\langle r^k \rangle = \int d^3r\, r^k |\psi|^2$$

Kramer's relation:

$$\frac{s+1}{n^2}\langle r^s\rangle - (2s+1)a\langle r^{s-1}\rangle + \frac{s}{4}\left[(2l+1)^2 - s^2\right]a^2\langle r^{s-2}\rangle = 0$$

$s=0$

$$\frac{1}{n^2}\langle r^0\rangle - a\langle r^{-1}\rangle = 0 \Rightarrow \langle r^{-1}\rangle = \frac{1}{an^2}$$

9:36 $s=1$ $\langle r\rangle$ $s=2$ $\langle r^2\rangle$

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$$\langle r\rangle = \frac{a}{2}n^2\left(3 - \frac{l(l+1)}{n^2}\right)$$

$$\langle r^2\rangle = \frac{a^2}{2}n^4\left(5 - \frac{3l(l+1)-1}{n^2}\right)$$

$n \gg 1$ $\sigma_r = \sqrt{\langle r^2\rangle - \langle r\rangle^2}$

$$\sigma_r^2 = a^2n^4\frac{5}{2} - a^2n^4\left(\frac{3}{2}\right)^2 =$$

$$= a^2n^4\left(\frac{5}{2} - \frac{9}{4}\right) = a^2n^4\frac{1}{4}$$

$$\sigma_r = \sqrt{\sigma_r^2} \approx a n^2$$

relative error $\frac{\sigma_r}{\langle r\rangle} = \frac{an^2}{\frac{3}{2}an^2} = \frac{2}{3}\cdot\frac{1}{2}$

$$\frac{2\sigma_r}{\langle r\rangle} = 66,7\ldots\%$$

Bohr $\sigma_r \to 0$

$n=1,\ l=0 \qquad \psi_{100} = \frac{1}{\sqrt{\pi}} \cdot \frac{1}{a^{3/2}} e^{-r/a}$

$E_{rror} = \frac{\sigma_r}{\langle r \rangle} \qquad \int_0^\infty dx\, x^n\, e^{-ax} = \frac{n!}{a^{n+1}}$

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9:57 $\longrightarrow \quad \frac{\sigma_r}{\langle r \rangle} = \frac{1}{\sqrt{3}}$

$\underline{s = -1}$

$\langle r^{-2} \rangle = \frac{a}{4}\left( (2l+1)^2 - 1 \right) \langle r^{-3} \rangle$

$\rightarrow$ Feynman – Hellmann theorem

$H|\psi\rangle = \underline{E}|\psi\rangle$

$H(\lambda)|\psi(\lambda)\rangle = \underline{E}(\lambda)|\psi(\lambda)\rangle$

$E(\lambda) = \langle \psi(\lambda)| H(\lambda) |\psi(\lambda)\rangle$

$$\frac{dE}{d\lambda} = \left(\frac{d}{d\lambda}\langle\psi|\right) \underbrace{H(\lambda)|\psi\rangle}_{E|\psi\rangle} +$$

$$+ \langle\psi| \frac{dH}{d\lambda}|\psi\rangle + \underbrace{\langle\psi|H}_{\langle\psi|E}\left(\frac{d}{d\lambda}|\psi\rangle\right)$$

$$\frac{dE}{d\lambda} = \underbrace{\left[\left(\frac{d}{d\lambda}\langle\psi|\right)|\psi\rangle + \langle\psi|\left(\frac{d}{d\lambda}|\psi\rangle\right)\right]}\cdot E$$

$$+ \langle\psi|\frac{dH}{d\lambda}|\psi\rangle$$

$$\frac{d}{d\lambda}\left(\underbrace{\langle\psi|\psi\rangle}_{1}\right)$$

$$\frac{dE}{d\lambda} = \langle \psi | \underbrace{\frac{dH}{d\lambda}} | \psi \rangle$$

Radial part

$$H = -\frac{\hbar^2}{2m} \frac{d^2}{dr^2} + \frac{\hbar^2}{2m} \frac{\ell(\ell+1)}{r^2} - \frac{e^2}{4\pi\varepsilon_0 r}$$

$\lambda = \ell$ $\qquad\qquad$ $\lambda = e$

$$\frac{dH}{d\ell} = \frac{\hbar^2}{2m} \frac{2\ell+1}{r^2}$$

$$E = -\frac{E_H}{n^2} \qquad n = k + \ell + 1$$

$$\frac{dE}{d\ell} = \frac{dE}{dn} \frac{dn}{d\ell} = 2 E_H n^{-3}$$

$$\left\langle \frac{1}{r^2} \right\rangle = \frac{2}{a^2 n^3 (2\ell+1)}$$

$$\left\langle \frac{1}{r^3} \right\rangle = \frac{1}{a^3 n^3} \frac{2}{(2\ell+1)(\ell)(\ell+1)}$$

Comments:

$$\left\langle \frac{1}{r^2} \right\rangle = \frac{2}{a^2} \qquad \left\langle \frac{1}{r} \right\rangle = \frac{1}{a}$$

$$\psi_{100} = \frac{1}{\sqrt{\pi}} \frac{1}{a^{3/2}} e^{-r/a}$$

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