

Hydrogen-like atoms

Last time we obtained the energy levels for the hydrogen atom $E_{k,l} = -\frac{E_I}{(k+l)^2}$ \leftarrow ionization energy $k=1, 2, 3, \dots$

and radial part of the wave function

$$R_{k,l}(r) = \frac{u_{k,l}(r)}{r} = \frac{e^{-\frac{r}{a_0} \frac{1}{k+l}}}{r} \left(\frac{r}{a_0}\right)^{l+k} \sum_{q=0}^k C_q \left(\frac{r}{a_0}\right)^q$$

where $C_q = (-1)^q \left(\frac{2}{k+l}\right)^q \frac{(k-1)!}{(k-q-1)!} \frac{(2l+1)!}{q! (q+2l+1)!} C_0$

$$\int_0^\infty |R_{k,l}(r)|^2 r^2 dr = 1$$

determine from normalization

It is conventional to introduce a "principal quantum number" $n = k+l$, so that the energy levels $E_n = -\frac{E_I}{n^2}$, $n=1, 2, \dots$

Then, $l = n - k = n-1, n-2, \dots, 0$

With this new notation, the wave function

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

where $R_{nl}(r) = - \left(\frac{2}{na_0} \right)^{3/2} \frac{(n-l-1)!}{\sqrt{2n[(n+l)!]^3}} \left(\frac{2r}{na_0} \right)^l \cdot e^{-r/(na_0)}$ ②

$L_{n+l}^{2l+1} \left(\frac{2r}{na_0} \right)$
 ↑ sometimes labeled as $n-l-1$
 associated Laguerre polynomials

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

$$R_{10}(r) = 2a_0^{-3/2} e^{-r/a_0}$$

$$R_{20}(r) = \frac{1}{\sqrt{2}a_0^3} \left(1 - \frac{r}{2a_0} \right) e^{-r/2a_0}$$

$$R_{21}(r) = \frac{1}{\sqrt{6}a_0^3} \frac{r}{2a_0} e^{-r/2a_0}$$

etc.

Let's analyse the behavior of $R_{nl}(r)$:

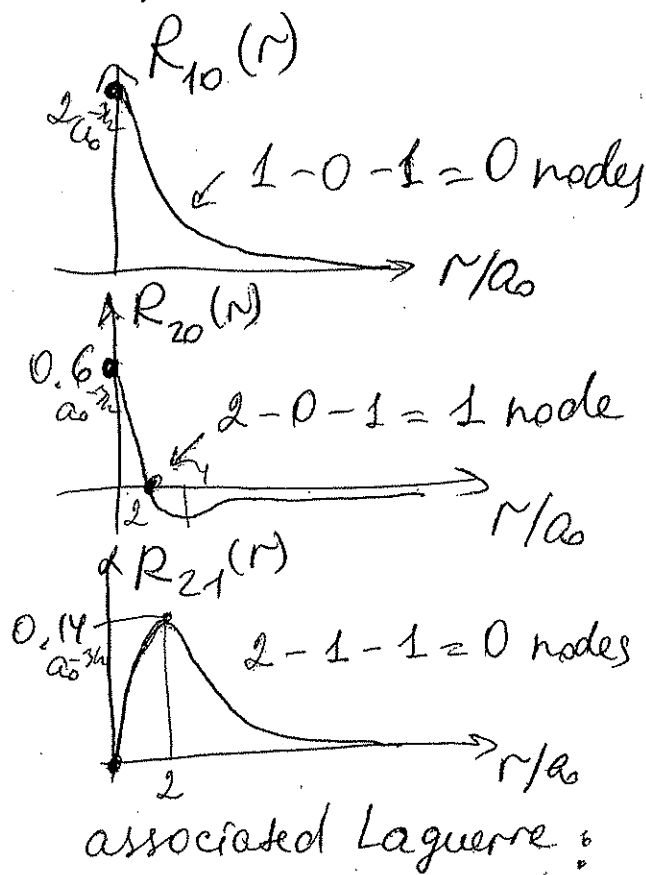
• for small r 's \Rightarrow

$$R_{nl}(r) \sim r^l$$

$\Downarrow r \rightarrow 0$

only at $l=0$ (so-called s-states)

$$R_{nl}(0) \neq 0$$



associated Laguerre:

$$L_1^1 = -1 = L_1^1(0)$$

$$L_2^1 = -4 + 2r \Rightarrow L_2^1(0) = -4$$

i.e. $L_{n+l}^{2l+1}(0) = \text{const}$

- at large r 's $\Rightarrow L_{n+l}^{2l+1}$ is dominated by (3)
the highest power of r ,
which is r^{n-l-1}
 $R_{nl}(r) \sim r^l \cdot r^{n-l-1} e^{-r/(na_0)} \sim e^{-r/na_0}$
 $r \rightarrow \infty$

- each function $R_{nl}(r)$ has $n-l-1$ radial nodes, since $L_{n+l}^{2l+1}(\frac{2r}{na_0})$ is a polynomial of $n-l-1$ degree

Degeneracy of the bound states

$$E_n = -\frac{E_I}{n^2} \leftarrow \begin{array}{l} \text{no dependence on } l \text{ and } m \\ \Downarrow \\ \text{degeneracy} \end{array}$$

Usually $\Rightarrow E_{n,l} \Rightarrow$ degeneracy with respect to l is a feature of the Coulomb potential
 $l = 0, \dots, n-1$

Degeneracy with respect to $m \Rightarrow$ a property of all central potentials (recall that the quantum number m does not appear in the Schrödinger equation $H\psi = E\psi$ at all!)
 for $\psi = \psi(r)$

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

↑
degeneracy
of the
nth level

↑
arithmetic
progression

$$\sum_{k=1}^n a_k = \frac{a_1 + a_n}{2} n$$

$$\text{---} \quad 2 \cdot \frac{0+n-1}{2} \cdot n + n = n(n-1) + n = n^2$$

Note: if we take into account spin, $g_n = 2n^2$
 ↑
 ↑ 0 2 1

Spectroscopic notation

A value of n characterizes an electron shell and contains n sub-shells, each one corresponding to one of the values of $l \Rightarrow$

$n = 1 \quad 2 \quad 3 \quad \dots \}$ shells
 K L M ...

$l = 0 \quad 1 \quad 2 \quad 3 \quad 4 \quad \dots \}$ sub-shells
 s p d f g ...

Example K-shell contains 1s sub-shell
 L-shell contains 2s and 2p sub-shells

All the results obtained for the hydrogen (5) atom can be applied to other one electron atoms or ions such as deuterium (1 proton + 1 neutron + 1 electron), tritium (1 proton + 2 neutrons + 1 electron), He^+ (2p + 2n + 1e), Li^{2+} (3p + 2n + 1e), etc.

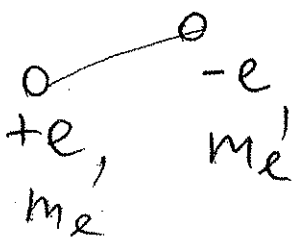
Recall that in such systems $V(r) = -\frac{Ze^2}{r}$, where Ze is a nuclear charge (e.g. $Z=2$ for He^+ , $Z=3$ for Li^{2+} , $Z=4$ for Be^{3+} , etc.)

Then, for such atoms $E_n = -\frac{Z^2 E_I^{(H)}}{n^2}$

Recall that $E_I^{(H)} = \frac{\mu e^4}{2\hbar^2}$, where $\mu \approx m_e$

Note that if m_{nucleus} is not $\gg m_e \Rightarrow$ then one also needs to take into account $\mu = \frac{m_1 m_2}{m_1 + m_2}$

Example positron - electron pair



$$\mu = \frac{m_e m_e}{m_e + m_e} = \frac{m_e}{2} \Rightarrow E_I = \frac{E_I^{(H)}}{2}$$

Also note that the Bohr radius changes $\textcircled{6}$

$$a_0(z) \approx \frac{a_0^{(H)}}{z} \quad (\text{if we don't take into account a change in } \mu) \quad \begin{matrix} \uparrow \\ \text{heavy nucleus} \end{matrix}$$

$$\text{If we do } \Rightarrow a_0^{(H)} = \frac{\hbar^2}{\mu e^2} \Rightarrow a_0 = a_0^{(H)} \frac{m_e}{\mu} \frac{1}{z}$$

\uparrow \uparrow \uparrow
 m_e μ z

for the hydrogen-like atom under consideration

Example

At what value of r the ~~electron~~ radial probability density of the electron in the 1s state of hydrogen atom reaches its maximum?

1s: $n=1, l=m=0 \Rightarrow$

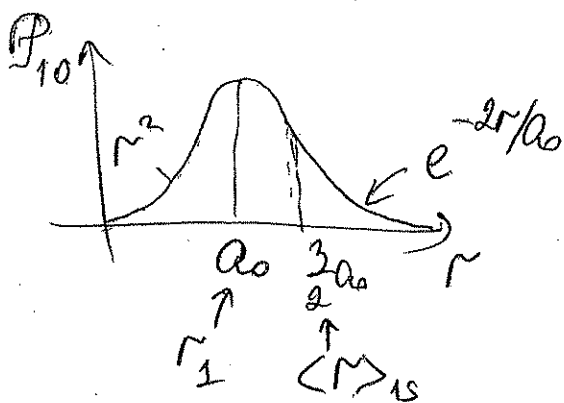
$$R_{10}(r) = 2a_0^{-3/2} e^{-r/a_0}$$

$$P_{10}(r) = r^2 |R_{10}(r)|^2 = 4a_0^{-3} r^2 e^{-2r/a_0}$$

\uparrow
need to find maximum of this!

The maximum occurs at r_1 such that ②

$$\left. \frac{dP_{10}(r)}{dr} \right|_{r_1} = 0 \Rightarrow 2r_1 - r_1^2 \cdot \frac{2}{a_0} = 0 \Rightarrow$$



$$\underline{r_1 = a_0}$$

So, in 1s state the maximal probability to find a particle is at a Bohr radius value, i.e. a_0

How does r_1 compare with the expectation value of r in this state? \Rightarrow

$$\langle r \rangle_{1s} = \int_0^{\infty} |R_{10}|^2 r \cdot r^2 dr = 4a_0^{-3} \int_0^{\infty} e^{-2r/a_0} r^3 dr =$$

$$= 4a_0^{-3} \cdot \left(\frac{a_0}{2}\right)^4 \cdot 3! = a_0 \cdot \frac{3}{2}$$

$$\int_0^{\infty} x^n e^{-x} dx = n! =$$

$$= \Gamma(n+1)$$

↑
Gamma-function

Why is $r_1 \neq \langle r \rangle_{1s}$? \Rightarrow

because the $P_{10}(r)$ is asymmetric with respect to its maximum \Rightarrow

although the most likely location of the electron is at $r_1 = a_0$, the average value of the measurement of its location is $\langle r \rangle_{1s} = \frac{3}{2}a_0$.

