

Quantum Mechanics 2

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Hydrogen Atom
Energy Eigenfunctions



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Energy Eigenvalues and Eigenfunctions

In [\[hydrogen 2\]](#), we have seen that the energy eigenvalues of hydrogen atoms are

$$E_n = -\frac{me^4}{(4\pi\epsilon_0)^2 2n^2 \hbar^2} = \frac{E_1}{n^2} = -\frac{13.6eV}{n^2}$$

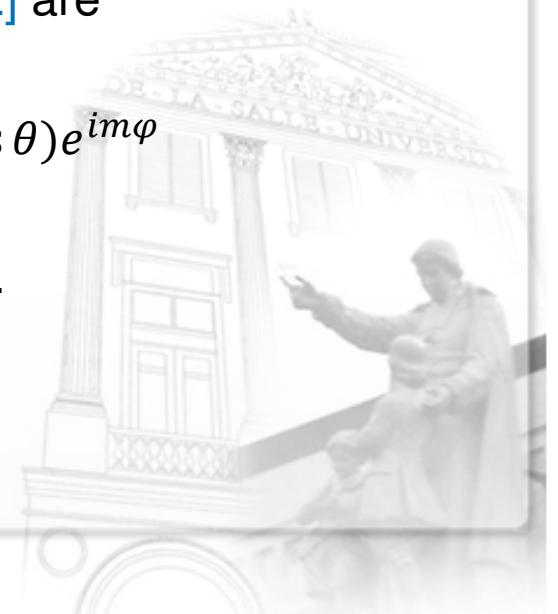
The energy eigenfunctions on the other hand are [\[see hydrogen 1\]](#)

$$u_{nlm}(r, \theta, \varphi) = R_{nl}(r)Y_{l,m}(\theta, \varphi)$$

where the spherical Harmonics [\[see Spherical Harmonics 2\]](#) are

$$Y_{l,m}(\theta, \varphi) = (-1)^m \sqrt{\frac{2l+1}{4\pi}} \sqrt{\frac{(l-m)!}{(l+m)!}} P_{l,m}(\cos \theta) e^{im\varphi}$$

with $P_{l,m}(\cos \theta)$ being the Associated Legendre polynomials.



Radial Function

To radial function are expressed as [hydrogen 1]

$$R(\rho) = G(\rho)e^{-\rho/2}$$

$$G(\rho) = \rho^l L(\rho)$$

where $L(\rho)$ are Associated Laguerre polynomials, and

$$\rho = \sqrt{\frac{8m|E|}{\hbar^2}} r = \sqrt{\frac{8m}{\hbar^2} \frac{me^4}{(4\pi\epsilon_0)^2 2n^2 \hbar^2}} r = \frac{2me^2}{(4\pi\epsilon_0)n\hbar^2} r = \frac{2r}{na_0}$$

with a_0 being the Bohr radius [Bohr]

$$a_0 = \frac{\hbar^2}{m} \left(\frac{e^2}{4\pi\epsilon_0} \right)^{-1} = 0.529\text{\AA}$$

Putting these together, we have

$$R_{nl}(\rho) = N\rho^l L_{n-l-1}^{2l+1}(\rho)e^{-\rho/2}$$



Normalization

Normalizing,

$$\int_0^{\infty} R_{nl}^* R_{nl} r^2 dr = |N|^2 \left(\frac{2}{na_0} \right)^{-3} \int_0^{\infty} \rho^{2l} L_{n-l-1}^{2l+1}(\rho) L_{n-l-1}^{2l+1}(\rho) e^{-\rho} \rho^2 d\rho = 1$$

Applying

$$\int_0^{\infty} e^{-\rho} \rho^{k+1} L_s^k(\rho) L_s^k(\rho) d\rho = \frac{(s+k)!}{s!} (2s+k+1)$$

where

$$s = n - l - 1$$

$$k = 2l + 1$$

$$s + k = n - l - 1 + 2l + 1 = n + l$$

$$2s + k + 1 = 2n - 2l - 2 + 2l + 1 + 1 = 2n$$



Normalized Eigenfunctions

Thus,

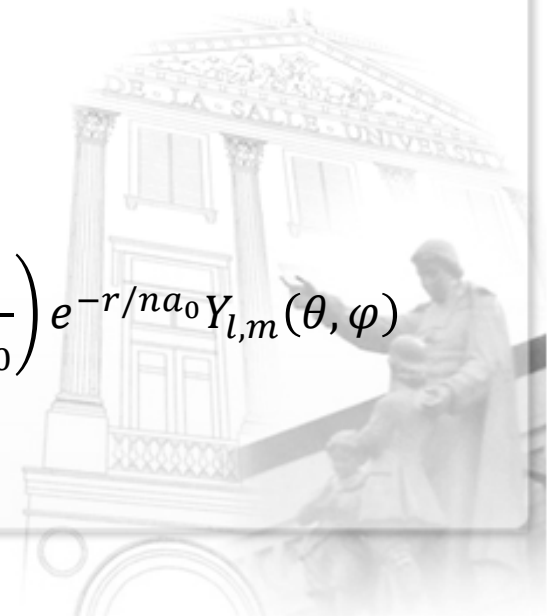
$$\begin{aligned} 1 &= |N|^2 \left(\frac{2}{na_0} \right)^{-3} \int_0^\infty \rho^{2l} L_{n-l-1}^{2l+1}(\rho) L_{n-l-1}^{2l+1}(\rho) e^{-\rho} \rho^2 d\rho \\ &= |N|^2 \left(\frac{2}{na_0} \right)^{-3} \frac{2n(n+l)!}{(n-l-1)!} \end{aligned}$$

and

$$N = \sqrt{\left(\frac{2}{na_0} \right)^3 \frac{(n-l-1)!}{2n(n+l)!}}$$

The full normalized energy eigenfunctions are thus

$$u_{nlm}(r, \theta, \varphi) = \left(\frac{2}{na_0} \right)^{3/2} \sqrt{\frac{(n-l-1)!}{2n(n+l)!}} \left(\frac{2r}{na_0} \right)^l L_{n-l-1}^{2l+1} \left(\frac{2r}{na_0} \right) e^{-r/na_0} Y_{l,m}(\theta, \varphi)$$



Quantum Numbers

The states are defined by the following quantum numbers

name	symbol	values
principal	n	1, 2, 3, ...
angular momentum	l	0, 1, 2, ..., $n - 1$
magnetic	m	$-l, -l + 1, \dots, l - 1, l$

Since energy is defined by the principal quantum number only, the hydrogen energy eigenstates are degenerate. The degree of degeneracy can be calculated as follows.

For each value of l , there are l negative values of m , l positive values, and a zero. Thus, the number of distinct values of m is $2l + 1$.

As l takes on values from 1, 2, ..., $n - 1$, the total number of degenerate states is

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

