# 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

$$E_n = -\frac{me^4}{(4\pi\varepsilon_0)^2 2n^2\hbar^2} = \frac{E_1}{n^2} = -\frac{13.6eV}{n^2}$$

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

$$\rho = \sqrt{\frac{8m|E|}{\hbar^2}}\, r = \sqrt{\frac{8m}{\hbar^2}\frac{me^4}{(4\pi\varepsilon_0)^2 2n^2\hbar^2}}\, r = \frac{2me^2}{(4\pi\varepsilon_0)n\hbar^2}\, r = \frac{2r}{na_0}$$

with $a_0$ being the Bohr radius [Bohr]

$$a_0 = \frac{\hbar^2}{m}\left(\frac{e^2}{4\pi\varepsilon_0}\right)^{-1} = 0.529\text{Å}$$

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,

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

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

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 | $n$ | $1, 2, 3, \ldots$ |
| angular momentum | $l$ | $0, 1, 2, \ldots, n-1$ |
| magnetic | $m$ | $-l, -l+1, \cdots, l-1, l$ |

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 $l$, the 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 $1, 2, \cdots, n-1$, the total number of degenerate states is

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