PHYS 3803: Quantum Mechanics I, Spring 2021

Lecture 26, May 04, 2021 (Tuesday)

- Reading: Hydrogen Atom—Griffiths 4.2
- Final Exam on May 11 (Tuesday) 1:30 pm–3:30 pm.

Topics for Today: Hydrogen Atom [Griffiths 4.2]

6.2 Radial wave Function

6.3 Fundamental Quantities Associated with Hydrogen Atom

6.4 Numerical Estimates

Next Lecture: Hydrogen Atom [Griffiths 4.2]

6.5 Comparison with Experiments

6.6 Degeneracy in Hydrogen Atom

6.7 Addition of Angular Momentum

6.2 Hydrogen Atom

Let us define the radial wave function as $R_{n,\ell}(r) \equiv u_{n,\ell}(r)/r$.

The solution of the differential equation for $u_{n,\ell}$ is

$$u_{n,\ell}(y) = e^{-\frac{1}{2}y} \sum_{k=0}^{n-\ell-1} a_k y^{k+\ell+1} = e^{-\frac{1}{2}y} y^{\ell+1} w(y)\,.$$

The differential equation that $w(y)$ satisfies is

$$y\frac{d^2w}{dy^2} + (2\ell + 2 - y)\frac{dw}{dy} + (n - \ell - 1)w(y) = 0\,.$$

An equation of the form

$$y\frac{d^2L_q}{dy^2} + (1 - y)\frac{dL_q}{dy} + qL_q = 0$$

is called the Laguerre equation and $L_q's$ are called Laguerre polynomials of order q.

The differential equation that $w(y)$ satisfies is

$$y\frac{d^2w}{dy^2} + (2\ell + 2 - y)\frac{dw}{dy} + (n - \ell - 1)w(y) = 0$$

The functions $L_q^p(y)$ are related to the L_q's by the relation

$$L_q^p(y) = \frac{d^p}{dy^p}L_q(y)\,, \quad q \geq p\,,$$

and they are known as the associated Laguerre polynomials. They are polynomials of order $q - p$ and satisfy the differential equation

$$y\frac{d^2L_q^p}{dy^2} + (p + 1 - y)\frac{dL_q^p}{dy} + (q - p)L_q^p = 0$$

Comparing this equation with the one satisfied by the w's, we see that

$$w(y) = L_{n+\ell}^{2\ell+1}(y)\;.$$

It is a good approximation to replace the reduced mass μ with m_e

$$\mu = \frac{m_p m_e}{m_p + m_e} \simeq m_e \, .$$

The radial wave function for the Hydrogen atom is

$$\begin{aligned} R_{n,\ell} &= N_{n,\ell} e^{-\frac{1}{2}y} y^{\ell} L^{2\ell+1}_{n+\ell}(y) \quad \text{where} \\ y &= 2\left(\frac{2m_e|E_n|}{\hbar^2}\right)^{1/2} r = \left(\frac{2m_e e^2}{\hbar^2 n}\right) r = \frac{2r}{n a_0} \quad \text{with} \\ E_n &= -\frac{m_e e^4}{2n^2\hbar^2} \quad \text{and} \quad a_0 \equiv \frac{\hbar^2}{m_e e^2} = \text{Bohr radius} \, . \end{aligned}$$

And the total wave function is

$$\psi_{n,\ell,m}(r,\theta,\phi) = R_{n,\ell}(r) Y_{\ell,m}(\theta,\phi) \, .$$

N.B Griffiths chooses the radial wave function as

$$R_{n,\ell} = N_{n,\ell} e^{-\frac{1}{2}y} y^{\ell} L^{2\ell+1}_{n-\ell-1}(y) \, .$$

Let us compare two slightly different conventions for the radial wave functions of the Hydrogen atom

- the Sakurai conventions (**our choice**), and
- the Griffiths conventions.

The Laguerre polynomials and the radial wave functions must be the same in both conventions:

$$L_q(y) = e^y \frac{d^q}{dy^q} \left(y^q e^{-y} \right) \ .$$

In the Sakurai conventions, the associated Laguerre polynomials are defined as

$$L_q^p(y) = \frac{d^p}{dy^p} L_q(y) \, .$$

Griffiths defines the associated Laguerre polynomials as

$$L_{q-p}^p(y) = (-1)^p \frac{d^p}{dy^p} L_q(y) \, .$$

Sakurai Conventions

It is convenient to evaluate the Laguerre polynomials with

$$L_q(y) = e^y \frac{d^q}{dy^q}\left(y^q e^{-y}\right) \,.$$

Exercise: Find L_0, L_1, L_2 and L_3.

Associated Laguerre polynomials

In the Sakurai conventions, the associated Laguerre polynomials are defined as

$$L_q^p(y) = \frac{d^p}{dy^p} L_q(y) \,.$$

Exercise: Find L_1^1, L_2^1, and L_3^3.

Laguerre polynomials

It is convenient to evaluate the Laguerre polynomials with

$$L_q(y) = e^y \frac{d^q}{dy^q}\left(y^q e^{-y}\right) \ .$$

For example,

$$\begin{aligned}
L_0(y) &= e^y \frac{d^0}{dy^0}\left(y^0 e^{-y}\right) = 1\,, \\
L_1(y) &= e^y \frac{d}{dy}\left(y e^{-y}\right) = -y + 1\,, \\
L_2(y) &= e^y \frac{d^2}{dy^2}\left(y^2 e^{-y}\right) = y^2 - 4y + 2\,, \\
L_3(y) &= e^y \frac{d^3}{dy^3}\left(y^3 e^{-y}\right) = -y^3 + 9y^2 - 18y + 6\,.
\end{aligned}$$

Associated Laguerre polynomials

In the Sakurai conventions, the radial wave function for the Hydrogen atom is

$$R_{n,\ell} \quad = \quad N_{n,\ell} e^{-\frac{1}{2}y} y^{\ell} L_{n+\ell}^{2\ell+1}(y) \, .$$

The associated Laguerre polynomials are defined as

$$L_q^p(y) = \frac{d^p}{dy^p} L_q(y) \quad \text{with} \quad L_q(y) = e^y \frac{d^q}{dy^q} \left(y^p e^{-y} \right) \, .$$

For example,

$$\begin{aligned}
L_1^1(y) \quad &= \quad \frac{d}{dy} L_1(y) = -1 \, , \quad n = 1 \, , \ell = 0 \\
L_2^1(y) \quad &= \quad \frac{d}{dy} L_2(y) = 2y - 4 \, , \quad n = 2 \, , \ell = 0 \\
L_3^3(y) \quad &= \quad \frac{d^3}{dy^3} L_3(y) = -6 \, , \quad n = 2 \, , \ell = 1 \, .
\end{aligned}$$

The normalization becomes

$$\begin{aligned}
\int R^*_{n,\ell} R_{n,\ell}\, r^2\, dr &= \left(\frac{n\hbar^2}{2m_e e^2}\right)^3 |N_{n,\ell}|^2 \int y^2 e^{-y} y^{2\ell} L^{2\ell+1}_{n+\ell}(y) L^{2\ell+1}_{n+\ell}(y) dy \\
&= \left(\frac{n\hbar^2}{2m_e e^2}\right)^3 |N_{n,\ell}|^2 \int y^{2\ell+2} e^{-y} L^{2\ell+1}_{n+\ell}(y) L^{2\ell+1}_{n+\ell}(y) dy \\
&= 1\,,
\end{aligned}$$

or

$$\left(\frac{n\hbar^2}{2m_e e^2}\right)^3 |N_{n,\ell}|^2 (2n) \frac{[(n+\ell)!]^3}{(n-\ell-1)!} = 1\,.$$

Choosing $N_{\ell,m}$ to be real and negative, we obtain

$$N_{\ell,m} = N^*_{\ell,m} = -\left[\left(\frac{2m_e e^2}{n\hbar^2}\right)^3 \frac{(n-\ell-1)!}{(2n)[(n+\ell)!]^3}\right]^{1/2} .$$

In the Sakurai conventions, the normalized radial wave functions are

$$R_{n,\ell} = -\left[\left(\frac{2}{na_0}\right)^3 \frac{(n-\ell-1)!}{(2n)[(n+\ell)!]^3}\right]^{1/2} \times e^{-\frac{1}{2}y} y^\ell L_{n+\ell}^{2\ell+1}(y) \quad \text{with}$$

$$y = 2\left(\frac{2m_e|E|}{\hbar^2}\right)^{1/2} r = \frac{2r}{na_0} \quad \text{and} \quad E_n = -\frac{m_e e^4}{2n^2\hbar^2}\,.$$

The first three radial functions are

$$R_{10} = 2\left(\frac{m_e e^2}{\hbar^2}\right)^{3/2} e^{-(m_e e^2/\hbar^2)r} = 2\left(\frac{1}{a_0}\right)^{3/2} e^{-r/a_0}\,,$$

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

$$R_{21} = \left(\frac{1}{2a_0}\right)^{3/2}\left(\frac{r}{\sqrt{3}a_0}\right) e^{-r/(2a_0)}\,, \quad \text{with}$$

$$a_0 = \frac{\hbar^2}{m_e e^2} \quad \text{(Bohr radius).}$$

Griffiths Conventions

It is convenient to evaluate the Laguerre polynomials with

$$L_q(x) = e^x \frac{d^q}{dx^q} \left(x^q e^{-x}\right) \,.$$

Exercise: Find L_0, L_1, L_2 and L_3.

Associated Laguerre polynomials

In the Griffiths conventions, the associated Laguerre polynomials are defined as

$$L^p_{q-p}(x) = (-1)^p \frac{d^p}{dx^p} L_q(x) \,.$$

Exercise: Find L^1_0, L^1_1, and L^3_0.

Laguerre polynomials

It is convenient to evaluate the Laguerre polynomials with

$$L_q(x) = e^x \frac{d^q}{dx^q} \left(x^q e^{-x} \right) \; .$$

For example,

$$\begin{aligned}
L_0(x) &= e^x \frac{d^0}{dx^0} \left(x^0 e^{-x} \right) = 1 \, , \\
L_1(x) &= e^x \frac{d}{dx} \left(x e^{-x} \right) = -x + 1 \, , \\
L_2(x) &= e^x \frac{d^2}{dx^2} \left(x^2 e^{-x} \right) = x^2 - 4x + 2 \, , \\
L_3(x) &= e^x \frac{d^3}{dx^3} \left(x^3 e^{-x} \right) = -x^3 + 9x^2 - 18x + 6 \, .
\end{aligned}$$

Associated Laguerre polynomials

In the Griffiths conventions, the radial wave function for the Hydrogen atom is

$$R_{n,\ell} \quad = \quad N'_{n,\ell} e^{-\frac{1}{2}x} x^{\ell} L^{2\ell+1}_{n-\ell-1}(x)\,.$$

The associated Laguerre polynomials are defined as

$$L^{p}_{q-p}(x) = (-1)^p \frac{d^p}{dx^p} L_q(x) \quad \text{with} \quad L_q(x) = e^x \frac{d^q}{dx^q}\left(x^q e^{-x}\right)\,.$$

For example,

$$\begin{aligned} L^1_0(x) \quad &= \quad L^p_{q-p}(x)(p=1,q=1) \;=\; (-1)^1 \frac{d}{dx} L_1(x) = 1\,,\; n=1\,,\ell=0 \\ L^1_1(x) \quad &= \quad L^p_{q-p}(x)(p=1,q=2) \;=\; (-1)^1 \frac{d}{dx} L_2(x) = -2x+4\,,\; n=2\,,\ell=0 \\ L^3_0(x) \quad &= \quad L^p_{q-p}(x)(p=3,q=3) \;=\; (-1)^3 \frac{d^3}{dx^3} L_3(x) = 6\,,\; n=2\,,\ell=1\,. \end{aligned}$$

In the Griffiths conventions, the normalized radial wave functions are

$$R_{n,\ell} \;=\; \left[\left(\frac{2}{na_0}\right)^3 \frac{(n-\ell-1)!}{(2n)[(n+\ell)!]^3}\right]^{1/2} \times e^{-\frac{1}{2}x} x^\ell L^{2\ell+1}_{n-\ell-1}(x) \quad \text{with}$$

$$x \;=\; 2\left(\frac{2m_e|E|}{\hbar^2}\right)^{1/2} r \;=\; \frac{2r}{na_0} \quad \text{and} \quad E_n = -\frac{m_e e^4}{2n^2\hbar^2}\,.$$

The first three radial functions are

$$R_{10} \;=\; 2\left(\frac{m_e e^2}{\hbar^2}\right)^{3/2} e^{-(m_e e^2/\hbar^2)r} \;=\; 2\left(\frac{1}{a_0}\right)^{3/2} e^{-r/a_0}\,,\;\; L^{2\ell+1}_{n-\ell-1} = L^1_0\,,$$

$$R_{20} \;=\; \left(\frac{1}{2a_0}\right)^{3/2}\left(2-\frac{r}{a_0}\right) e^{-r/(2a_0)} \quad \text{with} \quad L^{2\ell+1}_{n-\ell-1=1} = L^1_1\,,$$

$$R_{21} \;=\; \left(\frac{1}{2a_0}\right)^{3/2}\left(\frac{r}{\sqrt{3}a_0}\right) e^{-r/(2a_0)} \quad \text{with} \quad L^{2\ell+1=3}_{n-\ell-1=0} = L^3_0\,.$$

6.3 Fundamental Quantities Associated with Hydrogen Atom

Looking at the wave functions for the Hydrogen atom, we notice that there is a fundamental length scale that enters the solutions:

$$a_0 = \frac{\hbar^2}{m_e e^2}$$

that is the Bohr radius.

In terms of this quantity, we can write down the radial solutions as

$$R_{n,\ell}(r) \sim e^{-r/na_0} \left(\frac{2r}{na_0}\right)^{\ell} L_{n+\ell}^{2\ell+1}\left(\frac{2r}{na_0}\right)$$

Remembering that $L_{n+\ell}^{2\ell+1}$ is a polynomial of order $n-\ell-1$, the most dominant behavior for large r ($r \gg a_0$) would be

$$R_{n,\ell}(r) \sim (r)^{n-1} e^{-r/na_0} \ .$$

Then the probability for finding the electron in a special shell of radius r and thickness dr

$$\begin{aligned}\int_\Omega \psi^* \psi r^2 dr d\Omega &\sim R_{n,\ell}^2(r) r^2 dr \\ &= (r)^{2n} e^{-2r/na_0} dr \ .\end{aligned}$$

We can thus determine the radius of maximum probability as

$$\begin{aligned}\frac{d}{dr}\left((r)^{2n} e^{-2r/na_0}\right) &= 2nr^{2n-1} e^{-2r/na_0} - \frac{2}{na_0}(r)^{2n} e^{-2r/na_0} \\ &= \left(\frac{1}{na_0}\right)(r - n^2 a_0)(r)^{2n-1} e^{-2r/na_0} \\ &= 0\end{aligned}$$

or

$$r_* = n^2 a_0 \ .$$

Thus we see that the Bohr radius a_0 is the most probable value of r in the ground state and thus defines the natural size of the Hydrogen atom. We also see that $\langle r \rangle$ grows as n^2.

This theory also possesses a natural energy scale. Thus we define

$$R_y = \frac{m_e e^4}{2\hbar^2} = \text{ Rydberg.}$$

The the energy levels for the Hydrogen atom become

$$E_n = -\frac{R_y}{n^2} \ .$$

6.4 Numerical Estimates

Let's make an estimate for the value of a_0,

$$a_0 = \frac{\hbar^2}{m_e e^2} = \frac{(\hbar c)^2}{m_e c^2 e^2} = \frac{\hbar c}{m_e c^2}\frac{\hbar c}{e^2} \ .$$

Now we have

$$\begin{aligned} \hbar c &\simeq 2000 \ \ \mathrm{eV} \cdot \text{Å} \\ m_e c^2 &\simeq 0.5 \ \ \mathrm{MeV} \quad \text{and} \\ \alpha &= \frac{e^2}{\hbar c} = \frac{1}{137} \end{aligned}$$

that is the dimensionless fine structure constant.

Then

$$a_0 = \frac{2000 \ \ \mathrm{eV} \cdot \text{Å}}{5 \times 10^5 \ \ \mathrm{eV}} \times (137) \simeq 0.5 \ \ \text{Å}$$

where 1 Å$= 10^{-8}$ cm.

Furthermore

$$\begin{aligned} R_y &= \frac{m_e e^4}{2\hbar^2} = \frac{m_e c^2 e^4}{2(\hbar c)^2} = \frac{m_e c^2}{2}\left(\frac{e^2}{\hbar c}\right)^2 \\ &= \frac{5\times 10^5\ \text{eV}}{2} \times \left(\frac{1}{140}\right)^2 \simeq 13\ \text{eV}\,. \end{aligned}$$

A more accurate value for the Rydberg is

$$R_y = \frac{5.11\times 10^5\ \text{eV}}{2} \times \left(\frac{1}{137}\right)^2 \simeq 13.6\ \text{eV}\,.$$

Apply this value, we obtain

$$E_n = -\frac{R_y}{n^2} = -\frac{13.6}{n^2}\ \ \text{eV}\,.$$

Thus the ground state which is most tightly bound has an energy $E_1 = -13.6$ eV and therefore it would take 13.6 eV to release the electron from its ground state.

This is also known as the binding energy of the Hydrogen atom.