Finding Pi

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1 Introduction

A new derivation for for the Wallis Formula for pi was found by using the variational principle to find the energy levels of the hydrogen atom [Friedmann and Hagen, 2015]. However, in this derivation, a gaussian trial wave function was used for the hydrogen atom, however it is known that the true wave function is not a Gaussian but in fact goes as $\mathrm{e}^{-r\alpha_0}$. The purpose of this research is to follow the argument presented in the paper [Friedmann and Hagen, 2015] with the true wave function for the hydrogen atom and see if the Wallis Formula for π still emerges.

2 Original Paper

In this section, we will re-produce the method and results in the paper by Friedmann and Hagen with the trial wave function

$$\psi_{\alpha lm} = r^l \mathrm{e}^{-\alpha r^2} Y_l^m(\theta, \phi).$$

2.1 Finding the Expectation Value for the Hamiltonian

The expectation value will be given by:

$$\langle H(\alpha)\rangle = \frac{\langle\psi_{\alpha lm}|\hat{H}|\psi_{\alpha lm}\rangle}{\langle\psi_{\alpha lm}|\psi_{\alpha lm}\rangle}.$$

We shall first deal with the denominator:

$$\langle \psi_{\alpha lm} | \psi_{\alpha lm} \rangle = \int_{\mathbb{R}^3} \psi^* \psi \ d^3\mathbf{r}$$

The trial wave function is $r^l \mathrm{e}^{-\alpha r^2} Y_l{}^m(\theta, \phi)$ which is of the form $R(r) Y_l{}^m(\theta, \phi)$, we substitute this later form into our expression:

$$\begin{aligned} &= \int_{\mathbb{R}^3} r^2 (R(r))^2 Y_{l'}{}^{*m'}(\theta, \phi) Y_l{}^m(\theta, \phi) d^3\mathbf{r} \\ &= \int_0^\infty r^2 (R(r))^2 dr \int_0^\pi \int_0^{2\pi} Y_{l'}{}^{*m'}(\theta, \phi) Y_l{}^m(\theta, \phi) \sin\theta d\theta d\phi \end{aligned}$$

It is known that:

$$\int_0^\pi \int_0^{2\pi} Y_{l'}{}^{*m'}(\theta, \phi) Y_l{}^m(\theta, \phi) \sin\theta d\theta d\phi = \delta_{ll'} \delta_{mm'}$$

and since $l' = l$ and $m' = m$:

$$\int_0^\pi \int_0^{2\pi} Y_{l'}{}^{*m'}(\theta, \phi) Y_l{}^m(\theta, \phi) \sin\theta d\theta d\phi = 1$$

carrying on calculating the denominator:

$$\begin{aligned} \langle \psi_{\alpha lm} | \psi_{\alpha lm} \rangle &= \int_0^\infty r^2 (R(r))^2 dr \\ &= 2^{-\frac{5}{2} - l} \alpha^{-\frac{3}{2} - l} \Gamma(l + \frac{3}{2}) \end{aligned}$$

The hamiltonian operator is:

$$\hat{H} = \hat{K} + \hat{V} = \frac{-\hbar^2}{2m} \nabla^2 - \frac{e^2}{r}.$$

The expectation value for the potential energy is given by:

$$
\begin{aligned}
\langle \psi_{\alpha lm} | \hat{V} | \psi_{\alpha lm} \rangle &= \langle \psi_{\alpha lm} \left| \frac{-e^2}{r} \right| \psi_{\alpha lm} \rangle \\
&= \int_{\mathbb{R}^3} \psi^* \left(\frac{-e^2}{r} \right) \psi \ d^3\mathbf{r} \\
&= \int_{\mathbb{R}^3} \left(\frac{-e^2}{r} \right) (R(r))^2 {Y_{l'}}^{*m'}(\theta, \phi) {Y_l}^m(\theta, \phi) d^3\mathbf{r} \\
&= \int_0^\infty \left(\frac{-e^2}{r} \right) r^2 (R(r))^2 dr \int_0^\pi \int_0^{2\pi} {Y_{l'}}^{*m'}(\theta, \phi) {Y_l}^m(\theta, \phi) \sin\theta d\theta d\phi \\
&= \int_0^\infty -e^2 r (R(r))^2 dr \\
&= \frac{e^2 \Gamma(l+1)}{-2^{l+2} \alpha^{l+1}}
\end{aligned}
$$

Now dividing through by the normalisation condition found previously gives:

$$
\begin{aligned}
\frac{\langle \psi_{\alpha lm} | \hat{V} | \psi_{\alpha lm} \rangle}{\langle \psi_{\alpha lm} | \psi_{\alpha lm} \rangle} &= \frac{2^{\frac{5}{2}+l} \alpha^{\frac{3}{2}+l}}{\Gamma(l+\frac{3}{2})} \times \frac{e^2 \Gamma(l+1)}{-2^{l+2} \alpha^{l+1}} \\
&= -e^2 \frac{\Gamma(l+1)}{\Gamma(l+\frac{3}{2})} \sqrt{2\alpha}
\end{aligned}
$$

To make things easier to calculate the kinetic energy term, we will first use separation of variables to find the radial equation of the hamiltonian.

The time independent Schrodinger equation in spherical co-ordinates is:

$$
-\frac{\hbar^2}{2m} \left[\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial \psi}{\partial r} \right) + \frac{1}{r^2 \sin\theta} \frac{\partial}{\partial \theta} \left(\sin\theta \frac{\partial \psi}{\partial \theta} \right) + \frac{1}{r^2 \sin^2\theta} \left(\frac{\partial^2 \psi}{\partial \phi^2} \right) \right] + V\psi = E\psi
$$

We now substitute in $\psi = R(r)Y(\theta, \phi)$ into the equation:

$$
-\frac{\hbar^2}{2m} \left[\frac{Y}{r^2} \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) + \frac{R}{r^2 \sin\theta} \frac{\partial}{\partial \theta} \left(\sin\theta \frac{\partial Y}{\partial \theta} \right) + \frac{R}{r^2 \sin^2\theta} \left(\frac{\partial^2 Y}{\partial \phi^2} \right) \right] + VRY = ERY
$$

Dividing through by RY and multiplying by $-\frac{2mr^2}{\hbar^2}$ gives:

$$\left[\frac{1}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)-\frac{2mr^2}{\hbar^2}(V-E)\right]+\frac{1}{Y}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\left(\frac{\partial^2 Y}{\partial\phi^2}\right)\right]=0$$

The only way for this to be possible is if the radial equations and the angular equations were both equal to a constant. Since we are dealing with a spherically symmetric system, we will leave the angular equation alone and deal with the radial equation. Setting the radial equation equal to the constant $l(l+1)$:

$$\begin{aligned}\frac{1}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)-\frac{2mr^2}{\hbar^2}(V-E)&=l(l+1)\\ \frac{2}{Rr}\frac{dR}{dr}+\frac{1}{R}\frac{d^2R}{dr^2}-\frac{2m}{\hbar^2}V+\frac{2m}{\hbar^2}E&=\frac{l(l+1)}{r^2}R\\ -\frac{\hbar^2}{2m}\left(\frac{d^2R}{dr^2}+\frac{2}{r}\frac{dR}{dr}-\frac{l(l+1)}{r^2}R\right)+VR&=ER\end{aligned}$$

So the radial equation of the kinetic energy term for the Hamiltonian is:

$$-\frac{\hbar^2}{2m}\left(\frac{d^2R}{dr^2}+\frac{2}{r}\frac{dR}{dr}-\frac{l(l+1)}{r^2}R\right)$$

We can now calculate the expectation value for the kinetic energy term.

$$\begin{aligned}\langle\psi_{\alpha lm}|\hat{K}|\psi_{\alpha lm}\rangle&=\langle\psi_{\alpha lm}\left|-\frac{\hbar^2}{2m}\left(\frac{d^2}{dr^2}+\frac{2}{r}\frac{d}{dr}-\frac{l(l+1)}{r^2}\right)\right|\psi_{\alpha lm}\rangle\\ &=\frac{-\hbar^2}{2m}\int_{\mathbb{R}^3}\psi^*\left(\frac{d^2}{dr^2}+\frac{2}{r}\frac{d}{dr}-\frac{l(l+1)}{r^2}\right)\psi\; d^3\mathbf{r}\\ &=\frac{-\hbar^2}{2m}\int_0^\infty\left(\frac{d^2R}{dr^2}+\frac{2}{r}\frac{dR}{dr}-\frac{R(r)l(l+1)}{r^2}\right)r^2R(r)dr\int_0^\pi\int_0^{2\pi}Y_{l'}{}^{*m'}(\theta,\phi)Y_l{}^m(\theta,\phi)\sin\theta d\theta d\phi\end{aligned}$$

Computing the derivatives and simplifying gives:

$$=\frac{-\hbar^2}{2m}\left[\int_0^\infty -4\alpha l r^{2l+2}\mathrm{e}^{-2\alpha r^2}dr+\int_0^\infty -6\alpha r^{2l+2}\mathrm{e}^{-2\alpha r^2}dr+\int_0^\infty -4\alpha r^{2l+2}\mathrm{e}^{-2\alpha r^2}\right]$$

Using the subsitution, $t = 2\alpha r^2$ gives:

$$= \frac{-\hbar^2}{2m}\left[\int_0^\infty -l\frac{t^{l+\frac{1}{2}}\mathrm{e}^{-t}}{2^{l+\frac{1}{2}}\alpha^{l+\frac{1}{2}}}dt + \int_0^\infty -3\frac{t^{l+\frac{1}{2}}\mathrm{e}^{-t}}{2^{l+\frac{3}{2}}\alpha^{l+\frac{1}{2}}}dt + \int_0^\infty \frac{t^{l+\frac{3}{2}}\mathrm{e}^{-t}}{2^{l+\frac{3}{2}}\alpha^{l+\frac{1}{2}}}dt\right]$$
$$= \frac{-\hbar^2}{2m}\left(-\frac{l\Gamma(l+\frac{3}{2})}{2^{l+\frac{1}{2}}\alpha^{l+\frac{1}{2}}} - \frac{3\Gamma(l+\frac{3}{2})}{2^{l+\frac{3}{2}}\alpha^{l+\frac{1}{2}}} + \frac{\Gamma(l+\frac{5}{2})}{2^{l+\frac{3}{2}}\alpha^{l+\frac{1}{2}}}\right)$$

Dividing through by the normalisation condition gives:

$$\frac{\langle\psi_{\alpha lm}|\hat{K}|\psi_{\alpha lm}\rangle}{\langle\psi_{\alpha lm}|\psi_{\alpha lm}\rangle} = \frac{-\hbar^2}{2m}\left(\frac{\Gamma(l+\frac{5}{2})}{2^{l+\frac{3}{2}}\alpha^{l+\frac{1}{2}}} - \frac{l\Gamma(l+\frac{3}{2})}{2^{l+\frac{1}{2}}\alpha^{l+\frac{1}{2}}} - \frac{3\Gamma(l+\frac{3}{2})}{2^{l+\frac{3}{2}}\alpha^{l+\frac{1}{2}}}\right) \times \frac{2^{\frac{5}{2}+l}\alpha^{\frac{3}{2}+l}}{\Gamma(l+\frac{3}{2})}$$

Here we use the recursion relation $\Gamma(z+1) = z\Gamma(z)$:

$$= \frac{-\hbar^2}{2m}\left(\frac{(l+\frac{3}{2})\Gamma(l+\frac{3}{2})}{2^{l+\frac{3}{2}}\alpha^{l+\frac{1}{2}}} - \frac{l\Gamma(l+\frac{3}{2})}{2^{l+\frac{1}{2}}\alpha^{l+\frac{1}{2}}} - \frac{3\Gamma(l+\frac{3}{2})}{2^{l+\frac{3}{2}}\alpha^{l+\frac{1}{2}}}\right) \times \frac{2^{\frac{5}{2}+l}\alpha^{\frac{3}{2}+l}}{\Gamma(l+\frac{3}{2})}$$

Canceling the $\Gamma(l+\frac{3}{2})$ terms and tidying the exponents gives:

$$= \frac{-\hbar^2}{2m}[2\alpha(l+\frac{3}{2}-2l-3)]$$
$$= \frac{\hbar^2}{2m}(l+\frac{3}{2})2\alpha$$

So the expectation value of the Hamiltonian is found to be:

$$\langle H(\alpha)\rangle = \frac{\hbar^2}{2m}(l+\frac{3}{2})2\alpha - e^2\frac{\Gamma(l+1)}{\Gamma(l+\frac{3}{2})}\sqrt{2\alpha}. \tag{1}$$

2.2 Minimisation of Expectation Value

In order to minimise equation 1 we differentiate it with respect to α,

$$\frac{d\langle H(\alpha)\rangle}{d\alpha} = \frac{\hbar^2}{m}(l+\frac{3}{2}) - \frac{\sqrt{2}e^2\alpha^{-\frac{1}{2}}}{2}\frac{\Gamma(l+1)}{\Gamma(l+\frac{3}{2})}. \tag{2}$$

Setting equation 2 to zero and solving for α gives the value which corresponds to the ground state energy level.

$$\frac{\hbar^2}{m}(l+\frac{3}{2}) - \frac{\sqrt{2}e^2\alpha^{-\frac{1}{2}}}{2}\frac{\Gamma(l+1)}{\Gamma(l+\frac{3}{2})} = 0$$

$$\frac{\sqrt{2}e^2\alpha^{-\frac{1}{2}}}{2}\frac{\Gamma(l+1)}{\Gamma(l+\frac{3}{2})} = \frac{\hbar^2}{m}(l+\frac{3}{2})$$

$$\therefore \alpha = \left[\frac{m\sqrt{2}e^2\Gamma(l+1)}{2\hbar^2(l+\frac{3}{2})\Gamma(l+\frac{3}{2})}\right]^2$$

We now substitute this value for α into equation 1 to find the ground state energy level.

$$\langle H(\alpha)\rangle = \frac{\hbar^2}{m}(l+\frac{3}{2})\left[\frac{m\sqrt{2}e^2\Gamma(l+1)}{2\hbar^2(l+\frac{3}{2})\Gamma(l+\frac{3}{2})}\right] - e^2\frac{\Gamma(l+1)}{\Gamma(l+\frac{3}{2})}\left[\frac{m\sqrt{2}e^2\Gamma(l+1)}{\hbar^2(l+\frac{3}{2})\Gamma(l+\frac{3}{2})}\right]$$

$$\langle H(\alpha)\rangle = \frac{1}{(l+\frac{3}{2})}\left[\frac{\Gamma(l+1)}{\Gamma(l+\frac{3}{2})}\right]^2\left[\frac{me^4}{2\hbar^2} - \frac{me^4}{\hbar^2}\right]$$

$$\therefore \langle H(\alpha)\rangle = -\frac{me^4}{\hbar^2}\frac{1}{(l+\frac{3}{2})}\left[\frac{\Gamma(l+1)}{\Gamma(l+\frac{3}{2})}\right]^2$$

2.3 Forming the ratio

The accuracy of the approximation found can be measured by comparing it to the true value of the ground state for the hydrogen atom which is given by:

$$E_{0,l} = \frac{-me^4}{2\hbar^2}\frac{1}{(l+1)^2}.$$

So the ratio $\frac{\langle H(\alpha)\rangle}{E_{0,l}}$ is:

$$-\frac{me^4}{\hbar^2}\frac{1}{(l+\frac{3}{2})}\left[\frac{\Gamma(l+1)}{\Gamma(l+\frac{3}{2})}\right]^2 \times \frac{2\hbar^2}{-me^4}\frac{(l+1)^2}{1}$$

which simplifies to:

$$\frac{(l+1)^2}{l+\frac{3}{2}}\left[\frac{\Gamma(l+1)}{\Gamma(l+\frac{3}{2})}\right]^2. \qquad (3)$$

This ratio is plotted against l in figure 1 to identify it's behaviour at large values of l.

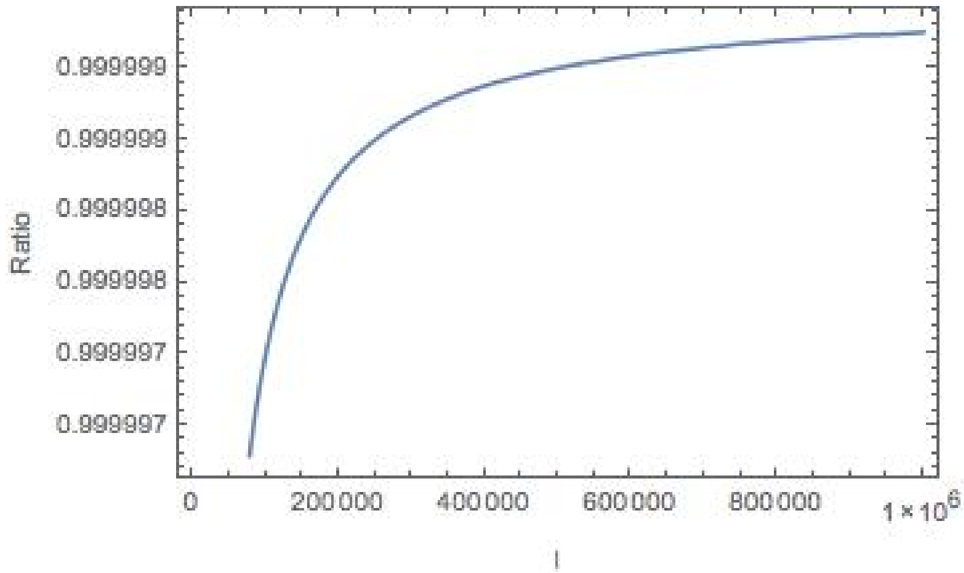

Figure 1: For large values of l, the limiting value of the ratio is 1

As shown in figure 1, in the limit as $l \to \infty$, the ratio in equation 3 approaches 1, i.e.

$$\lim_{l\to\infty} \frac{(l+1)^2}{l+\frac{3}{2}} \left[\frac{\Gamma(l+1)}{\Gamma(l+\frac{3}{2})}\right]^2 = 1.$$

2.4 Manipulating Expression (4) to (5)

$$\lim_{l\to\infty} \frac{(l+1)^2}{l+\frac{3}{2}} \left[\frac{\Gamma(l+1)}{\Gamma(l+\frac{3}{2})}\right]^2 = 1$$

$$\lim_{l\to\infty} \frac{1}{l+\frac{3}{2}} \left[\frac{(l+1)\Gamma(l+1)}{\Gamma(l+\frac{3}{2})}\right]^2 = 1$$

Since $z\Gamma(z) = \Gamma(z+1)$:

$$\lim_{l\to\infty} \frac{1}{l+\frac{3}{2}} \left[\frac{\Gamma(l+2)}{\Gamma(l+\frac{3}{2})}\right]^2 = 1$$

Since $\Gamma(m) = (m-1)!$:

$$\lim_{l\to\infty} \frac{1}{l+\frac{3}{2}} \left[\frac{(l+1)!}{\Gamma(l+\frac{3}{2})}\right]^2 = 1$$

Dealing with the denominator:

$$\begin{aligned}
\Gamma(l+\frac{3}{2}) &= \Gamma(l+\frac{1}{2}+1) \\
&= (l+\frac{1}{2})\Gamma(l+\frac{1}{2}) \\
&= (l+\frac{1}{2})(l-\frac{1}{2})\Gamma(l-\frac{1}{2}) \\
&= (l+\frac{1}{2})(l-\frac{1}{2})(l-\frac{3}{2})...(\frac{1}{2})\Gamma(\frac{1}{2})
\end{aligned}$$

Since $\Gamma(\frac{1}{2}) = \sqrt{\pi}$:

$$\Gamma(l+\frac{3}{2}) = (l+\frac{1}{2})(l-\frac{1}{2})(l-\frac{3}{2})...(\frac{1}{2})\sqrt{\pi}$$

which leads to:

$$\lim_{l\to\infty} \left[\frac{(l+1)!}{(l+\frac{1}{2})(l-\frac{1}{2})(l-\frac{3}{2})...(\frac{1}{2})\sqrt{\pi}}\right]^2 \frac{1}{l+\frac{3}{2}} = 1 \tag{4}$$

Now to get the Wallis Formula, we first rearrange equation 4 to get:

$$\lim_{l\to\infty} \left[\frac{(l+1)!}{\frac{1}{2}\cdot\frac{3}{2}\cdot\frac{5}{2}\cdot...\frac{(2l+1)}{2}}\right]^2 \frac{1}{2l+3} = \frac{\pi}{2}$$

We first deal with the numerator and notice that it can be expressed as:

$$(l+1)! = \prod_{j=1}^{l+1} j$$

However, since we have a $\frac{1}{2}$ for every single term in the denominator, for each iteration of j, there will be an additional factor of 2 in the numerator, giving:

$$(2(l+1))! = \prod_{j=1}^{l+1} 2j$$

But since it is squared, we will get:

$$(2(l+1)!)^2 = \prod_{j=1}^{l+1} (2j)(2j)$$

Since we have taken all the factors of $\frac{1}{2}$ from the denominator to the numerator, the denominator is now:

$$1 \cdot 1 \cdot 3 \cdot 3 \cdot 5 \cdot 5 \cdot 7 \cdot 7 ... (2l+1)(2l+1)(2l+3)$$

In terms of our iterator j, this line can be represented as $(2j-1)(2j+1)$ which ensures that it will terminate at $2l+3$. This completes the Wallis Product as we get:

$$\prod_{j=1}^{l+1} \frac{(2j)(2j)}{(2j-1)(2j+1)} = \frac{\pi}{2} \tag{5}$$

3 Using the exact wave function

In this section, we will carry out the same procedure as before, except we shall use the wave function:

$$\psi = r^l \mathrm{e}^{-\alpha r} Y_l^m$$

3.1 Calculating the Expectation Value of the Hamiltonian

The expectation value will be given by:

$$\langle H(\alpha) \rangle = \frac{\langle \psi_{\alpha l m} | \hat{H} | \psi_{\alpha l m} \rangle}{\langle \psi_{\alpha l m} | \psi_{\alpha l m} \rangle}.$$

Dealing with the denominator:

$$\langle\psi_{\alpha lm}|\psi_{\alpha lm}\rangle = \int_{\mathbb{R}^3} \psi^*\psi \ d^3\mathbf{r}$$

Substituting in our wave function $r^l \mathrm{e}^{-\alpha r} {Y_l}^m(\theta,\phi)$ in the form of $R(r){Y_l}^m(\theta,\phi)$:

$$\begin{aligned}
&= \int_{\mathbb{R}^3} r^2(R(r))^2 {Y_{l'}}^{*m'}(\theta,\phi){Y_l}^m(\theta,\phi) d^3\mathbf{r} \\
&= \int_0^\infty r^2(R(r))^2 dr \int_0^\pi \int_0^{2\pi} {Y_{l'}}^{*m'}(\theta,\phi){Y_l}^m(\theta,\phi)\sin\theta d\theta d\phi \\
&= \int_0^\infty r^{2l+2}\mathrm{e}^{-2\alpha r} dr
\end{aligned}$$

Using the substitution $t = 2\alpha r$

$$\begin{aligned}
&= \int_0^\infty \frac{t^{2l+2}}{2^{2l+3}}\alpha^{2l+3}\mathrm{e}^{-t} dt \\
&= \frac{\Gamma(2l+3)}{2^{2l+3}\alpha^{2l+3}}
\end{aligned}$$

Now finding the expectation value for the potential energy term:

$$\begin{aligned}
\langle\psi_{\alpha lm}|\hat{V}|\psi_{\alpha lm}\rangle &= \langle\psi_{\alpha lm}\left|\frac{-e^2}{r}\right|\psi_{\alpha lm}\rangle \\
&= \int_{\mathbb{R}^3} \psi^*\left(\frac{-e^2}{r}\right)\psi \ d^3\mathbf{r} \\
&= \int_{\mathbb{R}^3} \left(\frac{-e^2}{r}\right)(R(r))^2 {Y_{l'}}^{*m'}(\theta,\phi){Y_l}^m(\theta,\phi) d^3\mathbf{r} \\
&= \int_0^\infty \left(\frac{-e^2}{r}\right) r^2(R(r))^2 dr \int_0^\pi \int_0^{2\pi} {Y_{l'}}^{*m'}(\theta,\phi){Y_l}^m(\theta,\phi)\sin\theta d\theta d\phi \\
&= \int_0^\infty -e^2 r^{2l+1}\mathrm{e}^{-2\alpha r} dr
\end{aligned}$$

Using the substitution $t = 2\alpha r$:

$$\begin{aligned}
&= -e^2\int_0^\infty \frac{t^{2l+1}}{2^{2l+2}\alpha^{2l+2}} \\
&= -e^2\frac{\Gamma(2l+2)}{2^{2l+2}\alpha^{2l+2}}
\end{aligned}$$

Now dividing the result by the denominator:

$$\frac{\langle\psi_{\alpha lm}|\hat{V}|\psi_{\alpha lm}\rangle}{\langle\psi_{\alpha lm}|\psi_{\alpha lm}\rangle} = -e^2\frac{\Gamma(2l+2)}{2^{2l+2}\alpha^{2l+2}} \times \frac{2^{2l+3}\alpha^{2l+3}}{\Gamma(2l+3)}$$

Using the recursion relation $z\Gamma(z) = \Gamma(z+1)$:

$$\begin{aligned}
&= -e^2\frac{\Gamma(2l+2)}{2^{2l+2}\alpha^{2l+2}} \times \frac{2^{2l+3}\alpha^{2l+3}}{(2l+2)\Gamma(2l+2)} \\
&= -\frac{\alpha e^2}{l+1}
\end{aligned}$$

We now find the kinetic energy term using the radial equation found in the previous section.

$$\begin{aligned}
\langle\psi_{\alpha lm}|\hat{K}|\psi_{\alpha lm}\rangle &= \langle\psi_{\alpha lm}\bigg| - \frac{\hbar^2}{2m}\left(\frac{d^2}{dr^2} + \frac{2}{r}\frac{d}{dr} - \frac{l(l+1)}{r^2}\right)\bigg|\psi_{\alpha lm}\rangle \\
&= \frac{-\hbar^2}{2m}\int_{\mathbb{R}^3}\psi^*\left(\frac{d^2}{dr^2} + \frac{2}{r}\frac{d}{dr} - \frac{l(l+1)}{r^2}\right)\psi\ d^3\mathbf{r} \\
&= \frac{-\hbar^2}{2m}\int_0^\infty\left(\frac{d^2R}{dr^2} + \frac{2}{r}\frac{dR}{dr} - \frac{R(r)l(l+1)}{r^2}\right)r^2R(r)dr\int_0^\pi\int_0^{2\pi}{Y_{l'}}^{*m'}(\theta,\phi){Y_l}^m(\theta,\phi)\sin\theta d\theta d\phi
\end{aligned}$$

Computing the derivatives and simplifying gives:

$$= \frac{-\hbar^2}{2m}\int_0^\infty -2\alpha r^{2l+1}\mathrm{e}^{-2\alpha r}dr + \frac{-\hbar^2}{2m}\int_0^\infty -2\alpha l r^{2l+1}\mathrm{e}^{-2\alpha r}dr + \frac{-\hbar^2}{2m}\int_0^\infty \alpha^2 r^{2l+2}\mathrm{e}^{-2\alpha r}dr$$

Using the substitution $t = 2\alpha r$:

$$\begin{aligned}
&= \frac{-\hbar^2}{2m}\int_0^\infty -\frac{t^{2l+1}}{2^{2l+1}\alpha^{2l+1}}\mathrm{e}^{-t}dt + \frac{-\hbar^2}{2m}\int_0^\infty -l\frac{t^{2l+1}}{2^{2l+1}\alpha^{2l+1}}\mathrm{e}^{-t}dt + \frac{-\hbar^2}{2m}\int_0^\infty \frac{t^{2l+2}}{2^{2l+3}\alpha^{2l+1}}\mathrm{e}^{-t}dt \\
&= \frac{-\hbar^2}{2m}\left(-\frac{\Gamma(2l+2)}{2^{2l+1}\alpha^{2l+1}} - l\frac{\Gamma(2l+2)}{2^{2l+1}\alpha^{2l+1}} + \frac{\Gamma(2l+3)}{2^{2l+3}\alpha^{2l+1}}\right)
\end{aligned}$$

Dividing by the denominator gives:

$$\frac{\langle\psi_{\alpha lm}|\hat{V}|\psi_{\alpha lm}\rangle}{\langle\psi_{\alpha lm}|\psi_{\alpha lm}\rangle} = \frac{-\hbar^2}{2m}\bigg(-\frac{\Gamma(2l+2)}{2^{2l+1}\alpha^{2l+1}} - l\frac{\Gamma(2l+2)}{2^{2l+1}\alpha^{2l+1}} + \frac{\Gamma(2l+3)}{2^{2l+3}\alpha^{2l+1}}\bigg) \times \frac{2^{2l+3}\alpha^{2l+3}}{\Gamma(2l+3)}$$

Using the recursion relation $z\Gamma(z) = \Gamma(z+1)$:

$$\begin{aligned}
&= \frac{-\hbar^2}{2m}\bigg(-\frac{\Gamma(2l+2)}{2^{2l+1}\alpha^{2l+1}} - l\frac{\Gamma(2l+2)}{2^{2l+1}\alpha^{2l+1}} + \frac{(2l+2)\Gamma(2l+2)}{2^{2l+3}\alpha^{2l+1}}\bigg) \times \frac{2^{2l+3}\alpha^{2l+3}}{(2l+2)\Gamma(2l+2)} \\
&= \frac{-\hbar^2}{2m}\frac{-\Gamma(2l+2)}{2^{2l+3}\alpha^{2l+1}}\bigg(-4-4l+2l+2\bigg) \times \frac{2^{2l+3}\alpha^{2l+3}}{(2l+2)\Gamma(2l+2)} \\
&= \frac{\hbar^2}{2m}\alpha^2
\end{aligned}$$

So the Expectation Value for the Hamiltonian is:

$$\langle H(\alpha)\rangle = \frac{\hbar^2}{2m}\alpha^2 - \frac{\alpha e^2}{l+1}. \tag{6}$$

Seeing as there is no gamma function in the Hamiltonian, it is unlikely that any further analysis will yield any expression related to π or the Wallis Formula.

3.2 Minimising the expectation value

Differentiating equation 6 with respect to α gives:

$$\frac{d\langle H(\alpha)\rangle}{d\alpha} = \frac{\hbar^2}{m}\alpha - \frac{e^2}{l+1}. \tag{7}$$

Setting equation 7 equal to zero and solving for α gives the value corresponding to the ground state energy level as:

$$\alpha = \frac{me^2}{\hbar^2(l+1)}.$$

Now substituting this value into equation 6 gives our minimum energy level as:

$$\langle H(\alpha)\rangle = \frac{-me^4}{2\hbar^2(l+1)^2}. \tag{8}$$

Note that equation 8 is the exact result for the ground state energy level of the hydrogen, which is expected since we used the true wave function for the ground state of the hydrogen atom. Therefore the ratio of the exact known result to equation 8 is going to be equal to 1, i.e.

$$\frac{\langle H(\alpha)\rangle}{E_{0,l}} = 1.$$

4 Why does the gaussian give a formula for π?

In a bid to answer this question, we use the variational principle to compute the ground state energy level for the hydrogen atom using the general wave function

$$\psi_{\alpha lm} = r^l \mathrm{e}^{-\alpha r^q} Y_l{}^m(\theta, \phi). \tag{9}$$

Doing so gives the ratio between the true ground state energy level and the computed result in equation 9 as

$$\frac{4(l+1)^2)\left[\Gamma(\frac{2l+2}{q})\right]^2}{(2l+1)(2l+1+q)\Gamma(\frac{2l+1}{q})\Gamma(\frac{2l+3}{q})}. \tag{10}$$

To see how this ratio behaves in the limit as $l \to \infty$ for different q values, we produced the plot in figure 2.

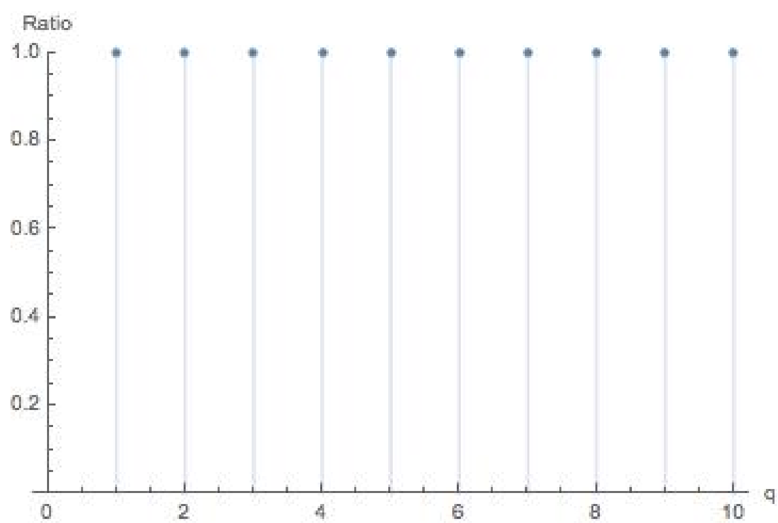

Figure 2: For large values of l, the limiting value of the ratio is always 1 for integer values of q

From figure 2, we can see that

$$\lim_{l\to\infty} \frac{4(l+1)^2)\left[\Gamma(\frac{2l+2}{q})\right]^2}{(2l+1)(2l+1+q)\Gamma(\frac{2l+1}{q})\Gamma(\frac{2l+3}{q})} = 1 \quad q \in \mathrm{Z}.$$

However, the only case where a formula for π is even possible is when $q = 2$, as this leads to half integer arguments in the gamma functions present in expression 10, which produces π. However, this does not answer why the gaussian wave function yields the Wallis Formula, it only confirms that it is the only one that can. In the following sections, we shall investigate the relationship between Wallis Integrals and the Gamma Function and also the uniqueness of Gaussians and the special properties that they have.

4.1 Wallis Integrals

In Wallis' original proof for the product, he compared the values of Wallis Integrals,

$$W_n = \int_o^{\frac{\pi}{2}} \sin^n(x)dx, \tag{11}$$

which can be represented using gamma functions depending on the parity of n. So if n is odd, i.e. $n = 2p + 1$, we get

$$W_{2p+1} = \frac{p!\Gamma(\frac{1}{2})}{(2p+1)\Gamma(p+\frac{1}{2})}, \tag{12}$$

and if n is even, $n = 2p$, the Wallis integral is

$$W_{2p} = \frac{\Gamma(\frac{1}{2})\Gamma(p+\frac{1}{2})}{2\Gamma(2p+1)}. \tag{13}$$

The proof of the Wallis Formula is presented in the following section.

4.1.1 Proof using Gamma Functions

Proof. Firstly, we shall use integration by parts on $W_n = \int_0^{\pi} \sin^n x dx$ as follows:

$$\int_0^{\frac{\pi}{2}} \sin^n x dx = \int_0^{\frac{\pi}{2}} \sin^{n-1} x \sin x dx$$

let $u = \sin^{n-1} x$ and $dv = \sin x dx$ and doing the integration by parts we get:

$$= \Big[-\sin^{n-1}(x)\cos(x) \Big]_0^{\frac{\pi}{2}} + \int_0^{\frac{\pi}{2}} \cos^2(x)(n-1)\sin^{n-2}(x)dx$$
$$= (n-1)\int_0^{\frac{\pi}{2}} \sin^{n-2}(x)\cos^2(x)$$

Since $\cos^2(x) = 1 - \sin^2(x)$,

$$W_n = (n-1)\int_0^{\frac{\pi}{2}} \sin^{n-2}(x)dx - (n-1)\int_0^{\frac{\pi}{2}} \sin^n(x)dx$$

This can be written in the W_n notation as:

$$W_n = (n-1)W_{n-2} - (n-1)W_n$$

$$\therefore \frac{W_n}{W_{n-2}} = \frac{n-1}{n}. \tag{14}$$

Now note that for $x \in [0, \frac{\pi}{2}]$, we have $0 \leq \sin x \leq 1$, which means the following inequalities are true for $x \in [0, \frac{\pi}{2}]$:

$$0 \leq \sin^{2n+2} x \leq \sin^{2n+1} x \leq \sin^{2n} x. \tag{15}$$

In terms of W_n notation, the inequalities in equation 15 are:

$$0 \leq W_{2n+2} \leq W_{2n+1} \leq W_2 n. \tag{16}$$

Dividing the inequalities in equation 16 by W_{2n} we get:

$$0 \leq \frac{W_{2n+2}}{W_{2n}} \leq \frac{W_{2n+1}}{W_{2n}} \leq 1. \tag{17}$$

From equation 14, we find that

$$\frac{W_{2n+2}}{W_{2n}} = \frac{2n+1}{2n+2},$$

which means that the inequalities in 17 become

$$0 \leq \frac{2n+1}{2n+2} \leq \frac{W_{2n+1}}{W_{2n}} \leq 1. \tag{18}$$

Now,

$$\lim_{n\to\infty} \frac{2n+1}{2n+2} = 1$$

and

$$\lim_{n\to\infty} 1 = 1,$$

so by the inequality in equation 18 and the squeeze theorem, we get that

$$\lim_{n\to\infty} \frac{W_{2n+1}}{W_{2n}} = 1. \tag{19}$$

Substituting equations 12 and 13 into 19, we get:

$$\begin{aligned}\frac{W_{2n+1}}{W_{2n}} &= \frac{n!\Gamma(\frac{1}{2})}{(2n+1)\Gamma(n+\frac{1}{2})} \times \frac{2\Gamma(2n+1)}{\Gamma(\frac{1}{2})\Gamma(n+\frac{1}{2})} \\ &= \frac{2n!(2n)!}{(2n+1)\left[\Gamma(n+\frac{1}{2})\right]^2}\end{aligned} \tag{20}$$

Since the limit of expression 20 at large n is 1 (equation 19) this leads to the Wallis Formula for π as follows:

$$\lim_{n\to\infty} \frac{2n!(2n)!}{(2n+1)\left[\Gamma(n+\frac{1}{2})\right]^2} = 1$$

Expanding the gamma function in the denominator using the recursion relation $\Gamma(m+1) = m\Gamma(m)$ gives

$$\lim_{n\to\infty} \frac{2n!(2n)!}{(2n+1)\left[(n-\frac{1}{2})(n-\frac{3}{2})(n-\frac{5}{2})...(\frac{1}{2})\sqrt{\pi}\right]^2} = 1$$

Rearrange to take π over to right hand side and re-write the denominator as:

$$\lim_{n\to\infty} \frac{n!(2n)!}{(2n+1)\left[(\frac{1}{2}\cdot\frac{3}{2}\cdot\frac{5}{2}\cdot ...(\frac{2n-5}{2})(\frac{2n-3}{2})(\frac{2n-1}{2}))\right]^2} = \frac{\pi}{2}$$

First note that the numerator can be expressed as:

$$n!(2n)! = \prod_{j=1}^{\infty} j \cdot 2j$$

However, since we have a $\frac{1}{2}$ for every single term in the denominator, for each iteration of j, there will be an additional factor of 2 in the numerator, giving:

$$(2n)!(2n)! = \prod_{j=1}^{\infty}(2j)(2j)$$

Since we have taken all the factors of $\frac{1}{2}$ from the denominator to the numerator, the denominator is now:

$$1\cdot 1\cdot 3\cdot 3\cdot 5\cdot 5\cdot 7\cdot 7...(2n-1)(2n-1)(2n+1)$$

In terms of our iterator j, this line can be represented as $(2j-1)(2j+1)$. This completes the Wallis Product as we get:

$$\prod_{j=1}^{\infty} \frac{(2j)(2j)}{(2j-1)(2j+1)} = \frac{\pi}{2} \tag{21}$$

■

4.1.2 Where does it all fall apart?

Taking a close look at expression 20 in the proof, we see that ultimately what leads to the formula for π is the presence of $\Gamma(n+\frac{1}{2})$ in the expression, where n is an integer. Comparing this to our general ratio in equation 10, we see that the only way we get that is for the case where $q = 2$. We can see it break down for other integer values for q quite quickly for a number of reasons. Firstly, and most importantly, we do not get a gamma function of the form $\Gamma(n + \frac{1}{2})$ where n is an integer, which is the only way to get π from these gamma functions. It seems that this could be achieved by using $q = 4$ and $q = 6$, however we do not get n as an integer, and even if we did, the remaining terms after using the recursion recursion relation will be $\Gamma(\frac{1}{4})$ and $\Gamma(\frac{1}{3})$ which are transcendental, so no analytic solution would be found, which is the second problem once we pass $q = 2$.

5 Conclusion

Following the procedure presented in [Friedmann and Hagen, 2015] using the exact wave function for the ground state of the hydrogen atom did not yield the Wallis formula. In fact no formula for π was found since as is expected from the variational method when the true wave function is used, the exact energy eigenvalue for the ground state energy level of the hydrogen atom was returned. This meant that the ratio formed that led to the Wallis formula in [Friedmann and Hagen, 2015], was in this case, exactly 1. Consequently, the result found in the original paper is artificial, and only arises due to the use of the Gaussian wave function.

References

[Friedmann and Hagen, 2015] Friedmann, T. and Hagen, C. R. (2015). Quantum mechanical derivation of the wallis formula for pi. *Journal of Mathematical Physics.*