

# Numerical Simulation of the Probability Distribution in a Wave Function\*

Numerical Methods

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# **Theoretical Framework**

## **Section One**

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# Quantum Mechanics

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## Wave Function

$$\psi(r) = \langle r | \psi \rangle \iff \langle \psi | \psi \rangle = \int_{-\infty}^{\infty} |\Psi(r, t)|^2 d\mathbf{r} = 1 \quad (1)$$

## Probability of the Wave Function

Under a closed interval, the generalization of it lies in the following formula:

$$P_{a_i \leq r_i \leq b_i}(t) = \int_I |\Psi(r, t)|^2 d^n r; \quad r, I \subset \mathcal{H} \quad (2)$$

where  $a_i, b_i$  are lower and upper limits in some vector space  $\mathcal{H}$ .

## Schrödinger Equation

$$i\hbar \frac{d}{dt} |\Psi(t)\rangle = \hat{H} |\Psi(t)\rangle \quad (3)$$

$$i\hbar \frac{\partial}{\partial t} \Psi(r, t) = \left[ \frac{-\hbar^2}{2m} \nabla^2 + V(r, t) \right] \Psi(r, t) \quad (4)$$

—Time Dependent Schrödinger Equation

$$\hat{H} |\Psi(r)\rangle = E |\Psi(r)\rangle \quad (5)$$

$$\left[ -\frac{\hbar^2}{2m} \nabla^2 + V(r) \right] |\Psi(r)\rangle = E |\Psi(r)\rangle \quad (6)$$

—Time Independent Schrödinger Equation

## Explanation

The Schrödinger equation is an equality which relates the state of a particle to its energy.

The values for the energy which makes the equality relation hold are called eigenvalues of the wave function. The Schrödinger equation helps us to determine them when boundary conditions are given.

## Hydrogen atom electron's wave function

$$\begin{aligned}\psi_{n\ell m}(r, \theta, \phi) &= R(r)Y_{\ell}^m(\theta, \phi) = R(r)\Theta(\theta)\Phi(\phi) \\ &= \sqrt{\left(\frac{2}{na_0^*}\right)^3 \frac{(n-\ell-1)!}{2n[(n+\ell)!]}} e^{-r/ma_0^*} \left(\frac{2r}{na_0^*}\right)^{\ell} \cdot L_{n-\ell-1}^{2\ell+1}\left(\frac{2r}{na_0^*}\right) \cdot Y_{\ell}^m(\theta, \phi)\end{aligned}$$

The meaning of the wave function for the electron in an hydrogen atom is that: for the coordinates  $r, \theta, \phi$ , the quantum energy level  $n = 1, 2, 3, 4, \dots$ , the quantum azimuthal number  $\ell = 0, 1, 2, 3, \dots, (n-1)$  and the quantum magnetic number  $m = -\ell, -\ell+1, -\ell+2, \dots, \ell$ .  $|\psi|^2$  is the probability of appearance for that electron at such given conditions and spatial point.

## Component Functions of the Hydrogen's Wave Function

$$Y_{\ell}^m(\theta, \phi) = (-1)^m \sqrt{\frac{2\ell+1}{4\pi} \frac{(\ell-m)!}{(\ell+m)!}} P_{\ell m}(\cos(\theta)) e^{im\phi} \quad (7)$$

—Spherical harmonic function

$$L_n^{(\alpha)} = \frac{x^{-\alpha} e^x}{n!} \frac{d^n}{dx^n} (e^{-x} x^{n+\alpha}) \quad (8)$$

—Laguerre polynomial function

$$P_{\ell}^m(x) = \frac{(-1)^m}{2^{\ell} \ell!} (1-x^2)^{m/2} \frac{d^{\ell+m}}{dx^{\ell+m}} (x^2-1)^{\ell}; \quad P_{\ell m}(x) = (-1)^m \frac{(\ell-m)!}{(\ell+m)!} P_{\ell}^m(x) \quad (9)$$

—Legendre polynomial in the spherical harmonic function



# Normalized Hydrogen Wave Functions

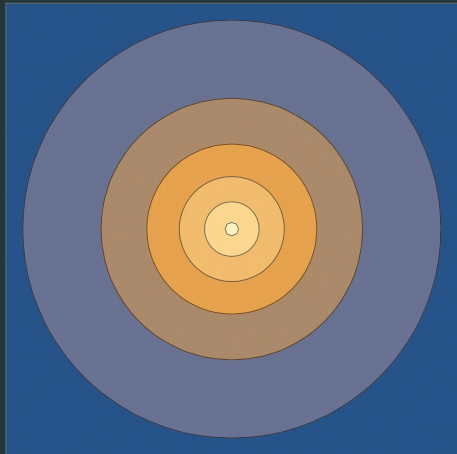
The following table shows the wave functions for the first three energy levels of an hydrogen atom

$n$	$\ell$	$m$	$E_l$	$\psi_{n\ell m}(r, \theta, \phi)$
1	0	0	1s	$\left(\sqrt{\pi}a_0^{3/2}\right)^{-1} e^{-r/a_0}$
2	0	0	2s	$\left(4\sqrt{2\pi}a_0^{3/2}\right)^{-1} \left[2 - \frac{r}{a_0}\right] e^{-r/2a_0}$
2	1	0	2p	$\left(4\sqrt{2\pi}a_0^{3/2}\right)^{-1} \frac{r}{a_0} e^{-r/2a_0} \cos(\theta)$

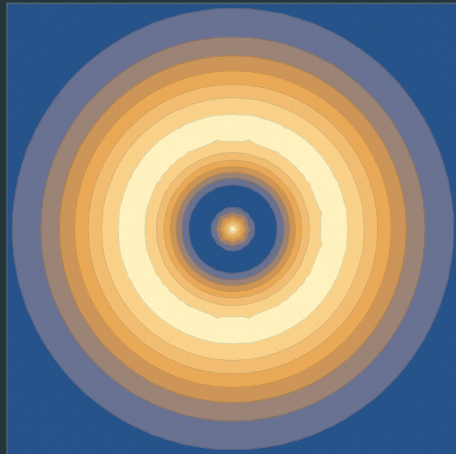
Where  $a_0 = \hbar^2 / me^2 \approx 0.0529mn$  is the first Bohr Radius.

# Hydrogen 1s and 2s Graphs

$$\langle \psi_{1,0,0} | \psi_{1,0,0} \rangle$$



$$\langle \psi_{2,0,0} | \psi_{2,0,0} \rangle$$



(Note that the wave functions has been plotted using cartesian coordinates and are not to scale so that we can visualize them better)

# Monte Carlo Integration Method

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Initial integral:

$$I(f) = \sum_{i=1}^N c_i f(x^{(i)}); x^{(i)} \equiv \left(x_d^{(i)}\right) \in \mathbb{E}^d, i = 1, \dots, N \quad (10)$$

from where we can obtain:

$$V = \int_{\Omega} d\bar{x} \quad (11)$$

$$I \approx Q_N \equiv V \frac{1}{N} \sum_{i=1}^N f(\bar{x}_i) = V \langle f \rangle; \quad \bar{x}_i \in \Omega \quad (12)$$

$$\lim_{N \rightarrow \infty} Q_N = I \quad (13)$$

Monte Carlo integration is numerical integration method using random numbers.

This method has better accuracy than successively applied Simpson's Rule or the Trapezoidal method. [11]

From equation (10) one can reshape the notation and rearrange the weights  $c_i$  expressing those as  $V/N$  (equal weights  $\forall f(x^{(i)})$ ).

So, equation (12) be obtained. This last equation is far more computable than the original Monte Carlo formula.

# Composite Quadrature Rule

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## Trapezoidal Rule

$$\begin{aligned}\int_a^b f(x)dx &= \frac{h}{2} \left( \sum_{i=0}^{N-1} f(x_i) \right) \\ &\quad + \frac{h}{2} (f(x_N) - f(x_0)) \\ &\quad - (x_N - x_0) \frac{h^2}{12} f''(\xi)\end{aligned}\quad (14)$$

## Midpoint Rule

$$\begin{aligned}\int_a^b f(x)dx &= h \sum_{i=0}^{N-1} f\left(x_i + \frac{1}{2}h\right) \\ &\quad + (x_N - x_0) \frac{h^2}{24} f''(\xi)\end{aligned}\quad (15)$$

### For both methods

**Where**  $\xi \in (a, b)$  is an arbitrary value

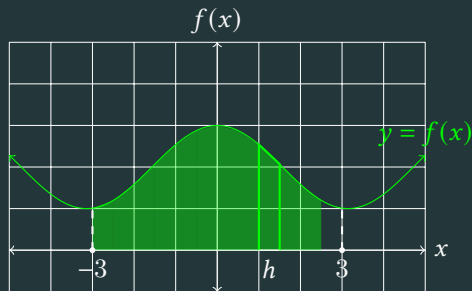
**is**  $h = (x_N - x_0)/N$  the width of a sub-interval

**being**  $[x_{i-1}, x_i]$ ,  $i = 1, 2, \dots, N$  sub-intervals of  $[a, b]$

**and**  $x_0 = a$ ,  $x_N = b$  [10]

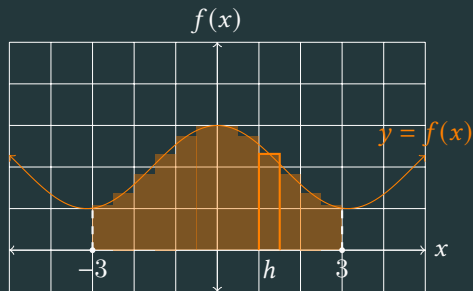
# Rules Representation

## Trapezoidal Rule



Note: the function plotted is  $f(x) = 2 + \cos(x)$

## Midpoint Rule



## Composite Quadrature Rule

Letting  $T(h)$  and  $M(h)$  denote the approximations to  $\int_a^b f(x)dx$  obtained by using respectively the trapezoidal and midpoint rules, the quadrature rule is:

$$\int_a^b f(x)dx \simeq \frac{2M(h) + T(h)}{3} \quad (16)$$

This rule has more accuracy for values of  $f$  at  $2N + 1$  equally spaced points  $x = x_0 + ih/2$ ,  $r = 0, 1, \dots, 2N$  [10] or which is equivalent, an odd number of sub-intervals for  $[a, b]$ .

The quadrature rule has then the extended form of

$$\int_a^b f(x)dx \simeq \frac{2M(h) + T(h)}{3} \quad (17)$$

$$\begin{aligned} &\simeq \frac{2}{3} \left( h \sum_{i=0}^{N-1} f \left( x_i + \frac{1}{2}h \right) + (x_N - x_0) \frac{h^2}{24} f''(\xi) \right) \\ &\quad + \frac{1}{3} \left( \frac{h}{2} \left( \sum_{i=0}^{N-1} f(x_i) \right) + (f(x_N) - f(x_0)) \right) - (x_N - x_0) \frac{h^2}{12} f''(\xi) \end{aligned} \quad (18)$$



**Probability of the Hydrogen Wave Function in a Closed  
Spatial Section  
Section Two**

# General Monte Carlo Integration for a Wave Function

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# Application of the Monte Carlo Method

The Monte Carlo integration method applied over the general wave function of the hydrogen atom is

$$I \approx \int_{\Omega} \lambda(\eta) d\eta \frac{1}{N} \sum_{i=1}^N |\psi_{n\ell m}(r_i, \theta_i, \phi_i)|^2 \quad (19)$$

where the integral of  $\lambda$  is an spatial volume section of a sphere as follows

$$\int_{\Omega} \lambda(\eta) d\eta = \int_{\phi_a}^{\phi_b} \int_{\theta_a}^{\theta_b} \int_{r_a}^{r_b} r^2 \sin(\phi) dr d\theta d\phi \quad (20)$$

$$= \int_{r_a}^{r_b} r^2 dr \int_{\phi_a}^{\phi_b} \sin(\phi) d\phi \int_{\theta_a}^{\theta_b} d\theta \quad (21)$$

$$= \left( \frac{r^3}{3} \Big|_{r_a}^{r_b} \right) \left( -\cos(\phi) \Big|_{\phi_a}^{\phi_b} \right) \left( \theta \Big|_{\theta_a}^{\theta_b} \right) \quad (22)$$

## Substitution

$$I \approx \left( \frac{r^3}{3} \Big|_{r_a}^{r_b} \right) \left( -\cos(\phi) \Big|_{\phi_a}^{\phi_b} \right) \left( \theta \Big|_{\theta_a}^{\theta_b} \right) \cdot \frac{1}{N} \sum_{i=1}^N |\psi_{n\ell m}(r_i, \theta_i, \phi_i)|^2 \quad (23)$$

—Numerical Monte Carlo  
Generalized Hydrogen Wave  
Function Integral

$$I \approx \Delta r \Delta \theta \Delta \phi \frac{1}{N} \sum_{i=1}^N |\psi_{n\ell m}(r_i, \theta_i, \phi_i)|^2 \quad (24)$$

—Equivalent Expression

The last numerical integral, is understood as

$$\Delta r = \left( \frac{r^3}{3} \Big|_{r_a}^{r_b} \right); \quad \Delta \theta = \left( \theta \Big|_{\theta_a}^{\theta_b} \right); \quad \Delta \phi = \left( -\cos(\phi) \Big|_{\phi_a}^{\phi_b} \right) \\ r_i \in [r_a, r_b]; \quad \theta_i \in [\theta_a, \theta_b]; \quad \phi_i \in [\phi_a, \phi_b] \quad (25)$$

Now, note that as we would expect of a normalized wave function:

$$0 \leq I \left( |\psi_{n\ell m}(r_i, \theta_i, \phi_i)|^2 \right) \quad (26)$$

And due the numerical error and that the integral of any squared normalized wave function is expected to be equal to one.

# Numerical simulation for the first hydrogen's atom wave function

## Procedure

$$\psi_{1,0,0}(r, \theta, \phi) = \left(\sqrt{\pi} a_0^{3/2}\right)^{-1} e^{-r/a_0} \quad (27)$$

—Hydrogen 1s Wave Function

$$|\psi_{1,0,0}(r, \theta, \phi)|^2 = \frac{1}{\pi a_0^3} e^{-2r/a_0} \quad (28)$$

—Squared Value

$$I \approx \Delta r \Delta \theta \Delta \phi \frac{1}{N} \sum_{i=1}^N \frac{1}{\pi a_0^3} e^{-2r/a_0} \quad (29)$$

—Substitution

## Implementation

With equation (29) we have an explicit media to simulate the absolute squared value in  $\psi_{1,0,0}$ .

Using python was possible to archive this. Now, the default parameters where:

$$r_a = 0; \quad r_b = 6.73E - 11$$

$$\theta_a = 0; \quad \theta_b = \pi$$

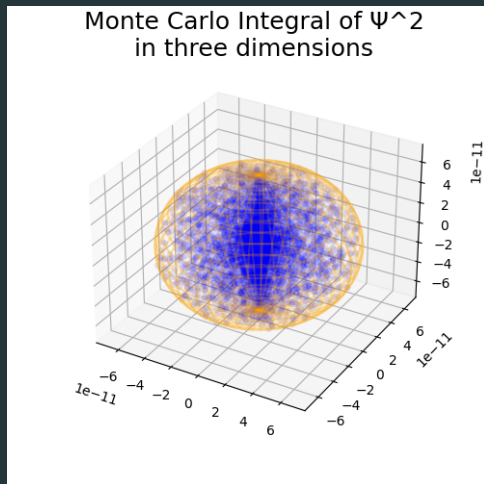
$$\phi_a = 0; \quad \phi_b = 2\pi$$

$$N = 7E + 03$$

(Note that  $r_b$  is close to  $a_0$ )

# Obtained 3D Cartesian Plot

## Graph



## Comments

Though the integral converges at a value near 1, if we play with the range of the radius we will obtain different predictions.

It can be attributed to the information reconstruction technique applied for this numerical method.

**Numerical Approximation for the Hydrogen 1s and 2s  
Squared Wave Functions Integral Values  
Section Four**

# Evaluating Hydrogen's 1s Squared Wave Function

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## Solution

For improper integrals which converges we can take suitable values for  $a$  and  $b$  so that the difference between  $a_i, b_i$  and  $a_j, b_j$  as finite integrals be small enough according to an error criteria  $\epsilon$ . The integral of  $|\psi_{1,0,0}(r)|^2 \equiv P_{1s}(r)$  would be

$$\int_0^{\infty} \frac{1}{\pi a_0^3} e^{-2r/a_0} dr \simeq \int_{r_a}^{r_b} \frac{1}{\pi a_0^3} e^{-2r/a_0} dr \quad (30)$$

taking the quadrature rule to approximate the value, it is:

$$\begin{aligned} \int_{r_a}^{r_b} \frac{1}{\pi a_0^3} e^{-2r/a_0} dr &\simeq \frac{1}{3} \left( h \sum_{i=0}^{N-1} P_{1s} \left( r_i + \frac{1}{2}h \right) + (r_N - r_0) \frac{h^2}{24} P_{1s}''(\xi) \right) \\ &+ \frac{1}{3} \left( \frac{h}{2} \left( \left( \sum_{i=0}^{N-1} P_{1s}(r_i) \right) + (P_{1s}(r_N) - P_{1s}(r_0)) \right) - (r_N - r_0) \frac{h^2}{12} P_{1s}''(\xi) \right) \end{aligned} \quad (31)$$

where the second derivative of  $P_{1s}$  is

$$\frac{d^2}{dr^2} P_{1s}(r) = \frac{d^2}{dr^2} \left( \frac{1}{\pi a_0^3} e^{-2r/a_0} \right) = \frac{4e^{-2r/a_0}}{\pi a_0^5} \quad (32)$$

# Iterative search for a suitable value for $r_b$ in the quadrature integral of $\psi_{1,0,0}$

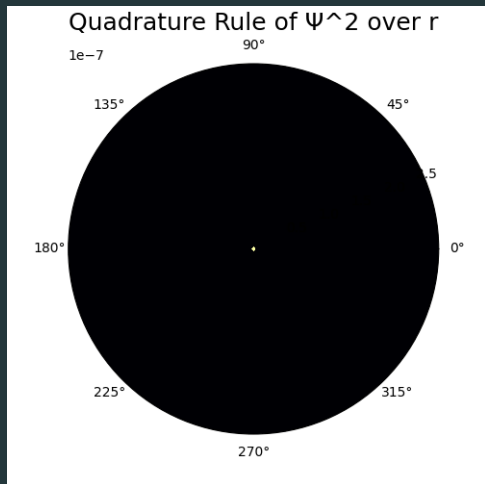
From  $r_b = a_0$  we are going to increment the value of the radius by  $1E - 11$  successively until we reach

$$\int_0^\infty |\psi_{1,0,0}(r)|^2 dr \simeq \int_0^{r_b} |\psi_{1,0,0}(r)|^2 dr = \int_0^{r_b} \left| \left( \sqrt{\pi} a_0^{3/2} \right)^{-1} e^{-r/a_0} \right|^2 dr = 1 \quad (33)$$

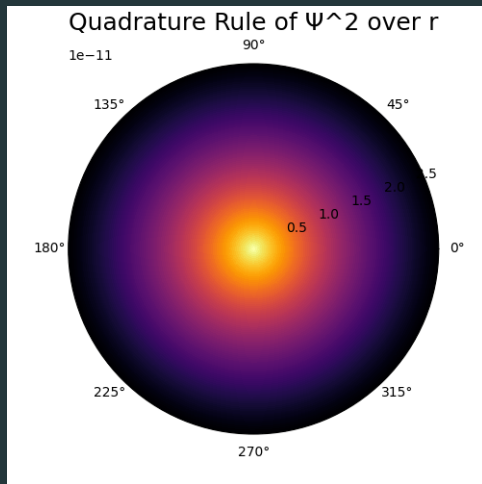
Iteration	$r_b$	$\int_0^{r_b}  \psi_{1,0,0}(r) ^2 dr$	Value Difference	Relative Error
26277	2,628129177212380E-07	1,015332651964350E+00	1,881808328490390E-03	1,533265196434710E-02
26278	2,628229177212380E-07	1,013454323442920E+00	1,878328521422560E-03	1,345432344292450E-02
26279	2,628329177212380E-07	1,011579468296590E+00	1,874855146339890E-03	1,157946829658460E-02
26280	2,628429177212380E-07	1,009708080105230E+00	1,871388191351910E-03	9,708080105232720E-03
26281	2,628529177212380E-07	1,007840152460660E+00	1,867927644577880E-03	7,840152460654840E-03
26282	2,628629177212380E-07	1,005975678966440E+00	1,864473494211480E-03	5,975678966443350E-03
26283	2,628729177212380E-07	1,004114653238060E+00	1,861025728387090E-03	4,114653238056270E-03
26284	2,628829177212380E-07	1,002257068902710E+00	1,857584335351440E-03	2,257068902704830E-03
26285	2,628929177212380E-07	1,000402919599380E+00	1,854149303323280E-03	4,029195993815460E-04
26286	2,629029177212380E-07	9,985521989788530E-01	1,850720620528820E-03	1,447801021147280E-03

## Obtained Graphs

$$r_a = 0, r_b = 2.6289491772072074E - 7, N = 100$$



$$r_a = 0, r_b = 2.6289491772072074E - 11, N = 100$$



## Evaluating Hydrogen's 2s Squared Wave Function

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## Solution - This is the Excel Application Problem we will Do

Being

$$\psi_{2,0,0}(r) = \left(4\sqrt{2\pi}a_0^{3/2}\right)^{-1} \left[2 - \frac{r}{a_0}\right] e^{-r/2a_0} \quad (34)$$

the wave function for the hydrogen atom at  $n = 2, \ell = 0, m = 0$  then, the square of its absolute value is

$$|\psi_{2,0,0}(r)|^2 = \left(\left(4\sqrt{2\pi}a_0^{3/2}\right)^{-1} \left[2 - \frac{r}{a_0}\right] e^{-r/2a_0}\right)^2 = (32\pi a_0^3)^{-1} \left[2 - \frac{r}{a_0}\right]^2 e^{-r/a_0} \quad (35)$$

the quadrature rule for this wave function is:

$$\int_0^\infty |\psi_{2,0,0}(r)|^2 dr \simeq \int_{r_a}^{r_b} (32\pi a_0^3)^{-1} \left[2 - \frac{r}{a_0}\right]^2 e^{-r/a_0} dr \quad (36)$$

Where  $r_a = 0$  by default; and the second derivative of  $|\psi_{2,0,0}(r)|^2 \equiv P_{2s}(r)$  is:

$$\frac{d^2}{dr^2} P_{2s}(r) = \frac{d^2}{dr^2} \left( (32\pi a_0^3)^{-1} \left[2 - \frac{r}{a_0}\right]^2 e^{-r/a_0} \right) = e^{-r/a_0} \left[ \frac{-8a_0 r + 14a_0^2 + r^2}{32\pi a_0^7} \right] \quad (37)$$

# Numerical Methods Code Implementations

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# Code Implementation - Monte Carlo Integration Method

```
1 def spherical_monte_carlo_integral(f: Callable[[float, float, float], float], r_a: float = 0,
2   r_b: float = a_0, theta_a: float = 0, theta_b: float = np.pi * 2,
3   phi_a: float = 0, phi_b: float = np.pi, samples=MONTE_CARLO_SAMPLING):
4   """
5   :param f: the function to be evaluated in spherical coordinates
6   :param r_a: initial radius
7   :param r_b: final radius
8   :param theta_a: initial polar angle
9   :param theta_b: final polar angle
10  :param phi_a: initial azimuthal angle
11  :param phi_b: final azimuthal angle
12  :param samples: the number of samples in the integral
13  :return: the approximate integral value for f
14  """
15  evaluated_volume: float = (((r_b-r_a) ** 3)/3)*(theta_b-theta_a)*(-np.cos(phi_b)+np.cos(phi_a))
16  r, theta, phi = uniform_spherical_interval(r_a, r_b, theta_a, theta_b, phi_a, phi_b, samples)
17  summation: float = 0
18  for r_i, theta_i, phi_i in zip(r, theta, phi): # combination
19      summation += f(r_i, theta_i, phi_i)
20  return (evaluated_volume * summation) / samples, r, theta, phi
```

# Code Implementation - Trapezoidal and Midpoint Rules

```
1 def trapezoidal_rule(f: Callable[[float], float], f_second: Callable[[float], float],
2                       a: float, b: float, n: int) -> float:
3     h = (b - a) / n
4     xi = (b - a) / 2 # rd.uniform(a + 0.1, b - 0.1)
5     summation = 0
6     for x_i in np.linspace(start=a, stop=b - h, num=n):
7         summation += f(x_i)
8     return (h / 2) * (summation + (f(b) - f(a))) - (b - a) * ((h ** 2) / 12) * f_second(xi)
9
10 def midpoint_rule(f: Callable[[float], float], f_second: Callable[[float], float],
11                   a: float, b: float, n: int) -> float:
12     h = (b - a) / n
13     xi = (b - a) / 2 # rd.uniform(a + 0.1, b - 0.1)
14     summation = 0
15     for x_i in np.linspace(start=a, stop=b - h, num=n):
16         summation += f(x_i + (h * 0.5))
17     return h * summation + (b - a) * ((h ** 2) / 24) * f_second(xi)
```



## Code Implementation - Composite Quadrature Rule

```
1 def quadrature_rule(f: Callable[[float], float], f_second: Callable[[float], float],
2     a: float, b: float, n: int) -> float:
3     """
4     :param f: the function to evaluate
5     :param f_second: the second derivative
6     :param a: the lower integration limit
7     :param b: the upper integration limit
8     :param n: the number of sub-intervals
9     :return: the approximate value for the integral of f
10    """
11    return ((2 * midpoint_rule(f, f_second, a, b, n)) + trapezoidal_rule(f, f_second, a, b, n)) / 3
```

# Conclusions







1. While here the search for an approximate radius for which a “redimensionalized” integral gives us the inner product of the Hydrogen 1s wave function, this method can be extended to more dimensions or even to lower dimensions.
2. The Quadrature rule applied to  $\psi_{1,0,0}$  (H 1s) and  $\psi_{2,0,0}$  (H 2s) had a great number of iterations even when  $a_0$  was chosen. It is a normal comportment, the quadrature rule used here is a composite rule made from the trapezoidal and midpoint rules, those attempts to predict the final behavior of a function given a finite interval. Since here the arbitrary choose of the initial interval  $[0, a_0]$  reconstruct poorly an accurate image of  $\psi_{1,0,0}$  we have to make the integral converge by means of successive iterations.
3. The scales worked over are difficult to correctly approach (in the sense of numerical precision) due our limitations in floating point arithmetic. We have x64-bit and x32-bit machines but the numbers and quantities here are often irrational numbers as  $\pi$ ,  $a_0$ ,  $e$ ,  $\hbar$ , it naturally leads to truncation errors.
4. The number of samples  $N$  in the Monte Carlo integration method does not affect the result range as such, this number gives us a better precision over the integral due the stochastic nature of this method.

**Thank you so much for paying attention!**

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