Numerical Simulation of the Probability Distribution in a Wave Function*

Numerical Methods

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Theoretical Framework
Section One

Contents

Quantum Mechanics

Wave Function

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

Probability of the Wave Function

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

$$P_{\mathrm{a}_i \le \mathrm{r}_i \le \mathrm{b}_i}(t) = \int_{\mathrm{I}} |\Psi(\mathrm{r},t)|^2 d^n\mathrm{r}; \quad \mathrm{r}, \mathrm{I} \subset \mathcal{H} \tag{2}$$

where $\mathrm{a}_i, \mathrm{b}_i$ are lower and upper limits in some vector space $\mathcal{H}$.

Schrödinger Equation

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

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

—Time Dependent Schrödinger Equation

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

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

—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

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

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

Component Functions of the Hydrogen's Wave Function

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

—Spherical harmonic function

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

—Legendre polynomial function

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

—Laguerre polynomial in the spherical harmonic function

Normalized Hydrogen Wave Functions

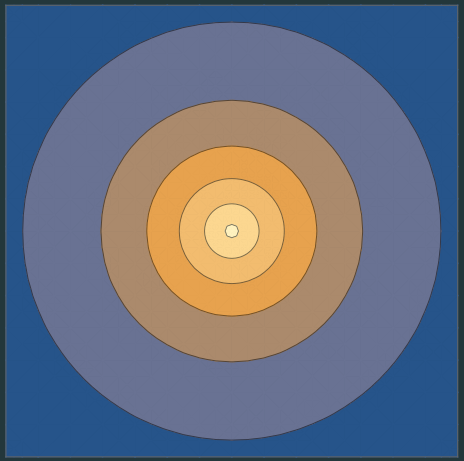
The following table shows the wave functions for the first three energy levels of an hydrogen atom

n	ℓ	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	$\left(4\sqrt{2\pi}a_0^{3/2}\right)^{-1}\frac{r}{a_0}e^{-r/2a_0}\cos(\theta)$

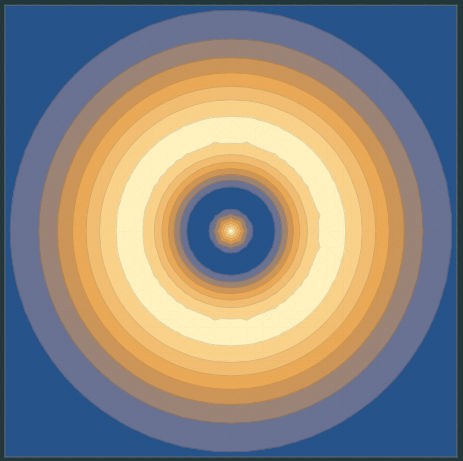
Where $a_0 = \hbar^2/me^2 \approx 0.0529mn$ is the first Bohr Radius.

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

Initial integral:

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

from where we can obtain:

$$V = \int_{\Omega} d\bar{\mathrm{x}} \tag{11}$$

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

$$\lim_{N \to \infty} Q_N = I \tag{13}$$

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

Trapezoidal Rule

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

Midpoint Rule

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

For both methods

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

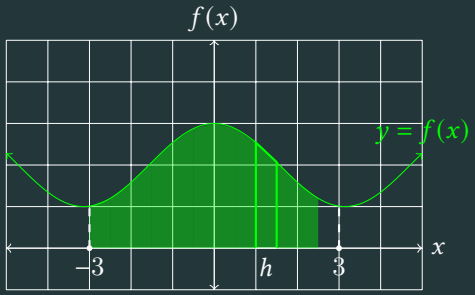
is $h = (x_N - x_0)/N$ the width of a sub-interval

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

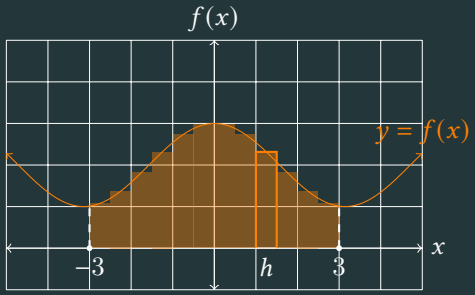
and $x_0 = a,\ x_N = b$ [10]

Rules Representation

Trapezoidal Rule



Midpoint Rule



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

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:

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

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

The quadrature rule has then the extended form of

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

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

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

General Monte Carlo Integration for a Wave Function

Application of the Monte Carlo Method

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

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

where the integral of λ is an spatial volume section of a sphere as follows

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

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

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

Substitution

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

—Numerical Monte Carlo Generalized Hydrogen Wave Function Integral

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

—Equivalent Expression

The last numerical integral, is understood as

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

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

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

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

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

—Hydrogen 1s Wave Function

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

—Squared Value

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

—Substitution

Implementation

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

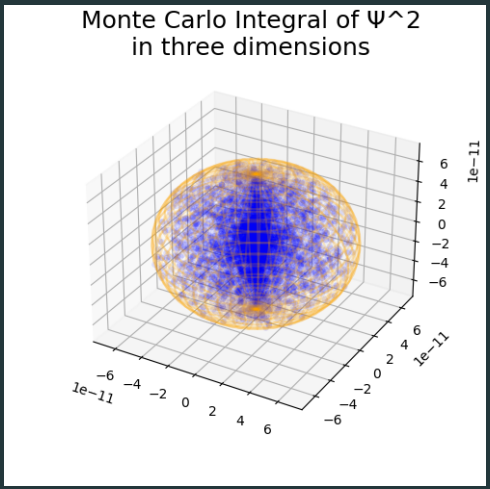
Using python was possible to archive this. Now, the default parameters where:

$$r_a = 0;\ \ r_b = 6.73E-11$$
$$\theta_a = 0;\ \ \theta_b = \pi$$
$$\phi_a = 0;\ \ \phi_b = 2\pi$$
$$N = 7E+03$$

(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 radious 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

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 ϵ. The integral of $|\psi_{1,0,0}(r)|^2 \equiv P_{1s}(r)$ would be

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

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

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

where the second derivative of P_{1s} is

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

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

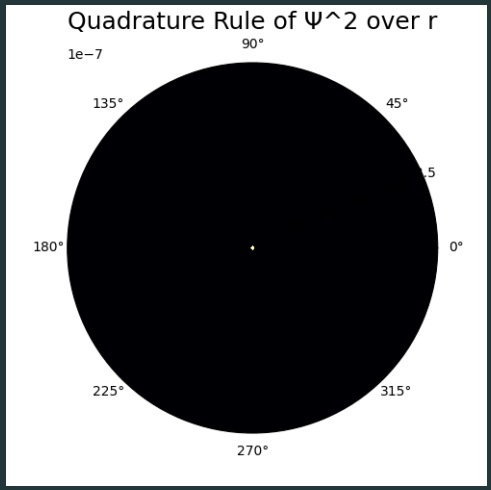
From $r_b = a_0$ we are going to increment the value of the radius by $1E-11$ successively until we reach

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

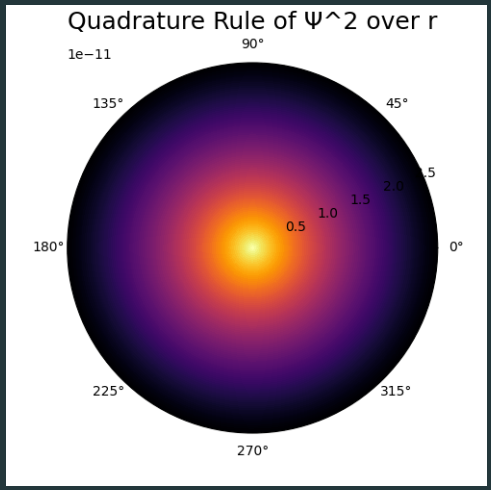
Iteration	r_b	$\int_0^{r_b} \lvert\psi_{1,0,0}(r)\rvert^2 dr$	Value Difference	Relative Error
26277	2,6281291772123 80E-07	1,015332651964350E+00	1,881808328490390E-03	1,533265196434710E-02
26278	2,6282291772123 80E-07	1,013454323442920E+00	1,878328521422560E-03	1,345432344292450E-02
26279	2,6283291772123 80E-07	1,011579468296590E+00	1,874855146339890E-03	1,157946829658460E-02
26280	2,6284291772123 80E-07	1,009708080105230E+00	1,871388191351910E-03	9,708080105232720E-03
26281	2,6285291772123 80E-07	1,007840152460660E+00	1,867927644577880E-03	7,840152460654840E-03
26282	2,6286291772123 80E-07	1,005975678966440E+00	1,864473494211480E-03	5,975678966443350E-03
26283	2,6287291772123 80E-07	1,004114653238060E+00	1,861025728387090E-03	4,114653238056270E-03
26284	2,6288291772123 80E-07	1,002257068902710E+00	1,857584335351440E-03	2,257068902704830E-03
26285	2,6289291772123 80E-07	1,000402919599380E+00	1,854149303323280E-03	4,029195993815460E-04
26286	2,6290291772123 80E-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

Solution - This is the Excel Application Problem we will Do

Being

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

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

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

the quadrature rule for this wave function is:

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

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

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

Numerical Methods Code Implementations

Code Implementation - Monte Carlo Integration Method

```python
def spherical_monte_carlo_integral(f: Callable[[float, float, float], float], r_a: float = 0,
    r_b: float = a_0, theta_a: float = 0, theta_b: float = np.pi * 2,
    phi_a: float = 0, phi_b: float = np.pi, samples=MONTE_CARLO_SAMPLING):
    """
    :param f: the function to be evaluated in spherical coordinates
    :param r_a: initial radius
    :param r_b: final radius
    :param theta_a: initial polar angle
    :param theta_b: final polar angle
    :param phi_a: initial azimuthal angle
    :param phi_b: final azimuthal angle
    :param samples: the number of samples in the integral
    :return: the approximate integral value for f
    """
    evaluated_volume: float = (((r_b-r_a) ** 3)/3)*(theta_b-theta_a)*(-np.cos(phi_b)+np.cos(phi_a))
    r, theta, phi = uniform_spherical_interval(r_a, r_b, theta_a, theta_b, phi_a, phi_b, samples)
    summation: float = 0
    for r_i, theta_i, phi_i in zip(r, theta, phi):  # combination
        summation += f(r_i, theta_i, phi_i)
    return (evaluated_volume * summation) / samples, r, theta, phi
```

Code Implementation - Trapezoidal and Midpoint Rules

```python
def trapezoidal_rule(f: Callable[[float], float], f_second: Callable[[float], float],
                     a: float, b: float, n: int) -> float:
    h = (b - a) / n
    xi = (b - a) / 2  # rd.uniform(a + 0.1, b - 0.1)
    summation = 0
    for x_i in np.linspace(start=a, stop=b - h, num=n):
        summation += f(x_i)
    return (h / 2) * (summation + (f(b) - f(a))) - (b - a) * ((h ** 2) / 12) * f_second(xi)

def midpoint_rule(f: Callable[[float], float], f_second: Callable[[float], float],
                  a: float, b: float, n: int) -> float:
    h = (b - a) / n
    xi = (b - a) / 2  # rd.uniform(a + 0.1, b - 0.1)
    summation = 0
    for x_i in np.linspace(start=a, stop=b - h, num=n):
        summation += f(x_i + (h * 0.5))
    return h * summation + (b - a) * ((h ** 2) / 24) * f_second(xi)
```

Code Implementation - Composite Quadrature Rule

```python
def quadrature_rule(f: Callable[[float], float], f_second: Callable[[float], float],
                    a: float, b: float, n: int) -> float:
    """
    :param f: the function to evaluate
    :param f_second: the second derivative
    :param a: the lower integration limit
    :param b: the upper integration limit
    :param n: the number of sub-intervals
    :return: the approximate value for the integral of f
    """
    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!

References

Sources i

- A. Lindner and D. Strauch, A Complete Course on Theoretical Physics. Springer, 2019, pp. 320.
- D. Griffiths J. and D. Schroeter F., Introduction to Quantum Mechanics. Cambridge University Press, 2019, pp. 21.
- R. Shankar, “Principles of Quantum Mechanics”. Springer, 2012, pp. 143, 145.
- “Schrodinger equation” http://hyperphysics.phy-astr.gsu.edu/hbase/quantum/Scheq.html (accessed: Sep. 20, 2020).
- “In Quantum Mechanics is there any difference between ψ and Ψ?” physics.stackexchange.com/questions/373993 (accessed: Sep. 20, 2020).
- P. Tipler A. and G. Mosca, Physics for Scientists and Engineers. Macmillan, 2007.

Sources ii

- “Hydrogen Wavefunctions” http://hyperphysics.phy-astr.gsu.edu/hbase/quantum/hydwf.html (accessed: Sep. 22, 2020).
- R. Cools and D. Nuyens, Monte Carlo and Quasi-Monte Carlo Methods. Springer, 2016. (1-46)
- “Classic Volume Examples using triple integrals” https://sites.math.washington.edu/~aloveles/Math324Fall2013/f13m324TripleIntegralExa (accessed: Sep. 24, 2020).
- G. Phillips M. and P. Taylor J., Theory and Applications of Numerical Analysis. Elsevier, 1996, pp. 162-180.
- I. T. Dimov, Monte Carlo Methods for Applied Scientists. World Scientific, 2008, pp. 48-52.