Numerical Simulation of the Probability Distribution of a Wave Function*

In Spherical, Semi-Spherical Spatial Sections and Infinite Intervals

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ABSTRACT

Context. Quantum mechanics has become a fundamental pillar on which the modern development of human race has take place. The hydrogen atom wave function is both, a symbol of this advance and is a very complex and beautiful discovery which was brought by solving the Schrodinger equation and is written in terms of representative analytical functions.

Aims. In this paper the author will take the hydrogen atom wave function and will try to approximate numerically its absolute squared value integral by means of a two simulations written in the Python programming language.

Methods. The Monte Carlo integration method as a composite Quadrature Rule built in terms of the Trapezoidal and Midpoint rules will be used.

Results. The simulations where properly constructed, this paper provided the formulas and theoretical means to do the coded implementations, as consequence an app parallel to this paper called "QLab" has two visual representations, one for the Monte Carlo integration method (applied with a small variation shown latter) and a second for a composite quadrature rule.

Key words. Wave function, Probability, Error, Integration, Interval, Monte Carlo Integration, Quadrature Rule.

1. Theoretical Framework

1.1. Wave Function

The wave function of a state is commonly understood as its representation in a real vector space:

$$\psi(\mathbf{r}) = \langle \mathbf{r}|\psi \rangle \tag{1}$$

where if $|\psi\rangle$ is a vector of a Hilbert space then $\psi(\mathbf{r})$ must be both normalizable and infinitely differentiable, with the requirement of $\langle \psi|\psi \rangle = 1$ being true. [1]

1.2. Probability of the wave function

The wave function is interpreted as a probability distribution which must be equal to 1. It is:

$$\int_{-\infty}^{\infty} |\Psi(\mathbf{r}, t)|^2 d\mathbf{r} = 1 \tag{2}$$

where the integral is applied over $\mathbf{r}$ and it is done such that it express the position as such in spherical coordinates.

This equation make us think about the probability for continuous statistical functions, which must be 1 for some range $[a, b]$ (here $a = -\infty, b = \infty$). Now, there also exists the measurement of the probability of finding a particle in some sector of the selected space, it is:

$$P_{\mathbf{a}_i \leq \mathbf{r}_i \leq \mathbf{b}_i}(t) = \int_{\mathbf{I}} |\Psi(\mathbf{r}, t)|^2 d^n\mathbf{r}; \quad \mathbf{r}, \mathbf{I} \subset \mathcal{H} \tag{3}$$

1.3. Time-dependent general Schrödinger equation

The Schrödinger equation is an equality which relates the state of a system 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.

The time dependent general Schrödinger equation [3] is

$$i\hbar \frac{d}{dt} |\Psi(t)\rangle = \hat{H} |\Psi(t)\rangle \tag{4}$$

Where the Hamiltonian operator $\hat{H}^1$ is:

$$\hat{H} = \hat{T} + \hat{V} \tag{5}$$

$$\hat{T} = \frac{\hat{\mathbf{p}} \cdot \hat{\mathbf{p}}}{2m} = \frac{\hat{p}^2}{2m} = -\frac{\hbar^2}{2m}\nabla^2; \qquad \hat{\mathbf{p}} = -i\hbar\nabla \tag{6}$$

$$\hat{V} = V = V(\mathbf{r}, t) \tag{7}$$

being $\hat{V}$ the potential energy, $\hat{T}$ the kinetic energy and $\hat{\mathbf{p}}$ the momentum operator. The equation can be written more completely as

$$i\hbar \frac{d}{dt} |\Psi(t)\rangle = \left[-\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{r}, t) \right] |\Psi(t)\rangle \tag{8}$$

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[1] Note that the sum of potential and kinetic energy is the total energy in the system.

Now, if the basis is relative to some point in the space we use [4]

$$i\hbar\frac{\partial}{\partial t}\Psi(\mathbf{r},t) = \left[\frac{-\hbar^2}{2m}\nabla^2 + V(\mathbf{r},t)\right]\Psi(\mathbf{r},t) \tag{9}$$

where instead of a normal derivative we indicate that Ψ depends on $\mathbf{r}$ (a position in the space) so that we present a more coherent notation.

1.4. Time-independent general Schrödinger equation

When time is not being considered, the Schrödinger equation has the form

$$\hat{H}\left|\Psi(\mathbf{r})\right\rangle = E\left|\Psi(\mathbf{r})\right\rangle \tag{10}$$

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{r})\right]\left|\Psi(\mathbf{r})\right\rangle = E\left|\Psi(\mathbf{r})\right\rangle \tag{11}$$

and is called time-independent Schrödinger equation. Here E is the value of the total energy. Alternatively, the notation

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{r})\right]\psi(\mathbf{r}) = E\psi(\mathbf{r}) \tag{12}$$

is also valid and does represent any different meaning, the main difference is that ψ sometimes is used for single particle systems and Ψ for multiple particle systems. [5]

Finally, it is important to mention that given suitable conditions (typically $\Psi(\mathbf{r},0)$) the time independent Schrödinger equation determines $\Psi(\mathbf{r},t)$ for all value of t. [2]

1.5. Hydrogen atom electron's wave function

The wave function for the hydrogen atom is obtained by solving the Schrodinger equation

$$\left(-\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{4\pi\epsilon_0 r}\right)\psi_{n\ell m}(r,\theta,\phi) = E\psi_{n\ell m}(r,\theta,\phi) \tag{13}$$

being the following its solution (the wave function can be separated into functions of each coordinate [6])

$$\psi_{n\ell m}(r,\theta,\phi) = R(r)Y_\ell^m(\theta,\phi) = R(r)\Theta(\theta)\Phi(\phi) \tag{14}$$

$$= \sqrt{\left(\frac{2}{na_0^*}\right)^3 \frac{(n-\ell-1)!}{2n[(n+\ell)!]}} e^{-r/ma_0^*}\left(\frac{2r}{na_0^*}\right)^\ell$$

$$\cdot L_{(n-\ell-1)}^{2\ell+1}\left(\frac{2r}{na_0^*}\right)\cdot Y_\ell^m(\theta,\phi) \tag{15}$$

this function is expressed in terms of other analytic functions which are simultaneously composed of some others as the spherical harmonic function:

$$Y_\ell^m(\theta,\phi) = (-1)^m\sqrt{\frac{2\ell+1}{4\pi}\frac{(\ell-m)!}{(\ell+m)!}}P_{\ell m}(\cos(\theta))e^{im\phi} \tag{16}$$

the associated Laguerre polynomial

$$L_n^{(\alpha)} = \frac{x^{-\alpha}e^x}{n!}\frac{d^n}{dx^n}\left(e^{-x}x^{n+\alpha}\right) \tag{17}$$

and the Legendre polynomial in the spherical harmonic

$$P_\ell(x) = \frac{1}{2^\ell\ell!}\frac{d^\ell}{dx^\ell}(x^2-1)^\ell \tag{18}$$

$$P_\ell^m(x) = \frac{(-1)^m}{2^\ell\ell!}(1-x^2)^{m/2}\frac{d^{\ell+m}}{dx^{\ell+m}}(x^2-1)^\ell \tag{19}$$

$$P_{\ell m}(x) = (-1)^m P_\ell^m(x) \tag{20}$$

now, 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 $\ell = 0,1,2,3,\ldots,(n-1)$ and the quantum magnetic number $m = -\ell,-\ell+1,-\ell+2,\ldots,l$.
Then $|\psi|^2$ is the probability of appearance for that electron at such given conditions and spatial point.

$$\langle\psi_{n\ell m}|\psi_{n\ell m}\rangle = \int_{\mathbf{S}}ds\ \psi_{n\ell m}^*\ \psi_{n\ell m} = \int_{\mathbf{S}}|\psi_{n\ell m}|^2\ ds$$
$$= \delta_{nn}\delta_{\ell\ell}\delta_{mm} = 1 \tag{21}$$

1.6. 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 $a_0 = \hbar^2/me^2 \approx 0.0529mn$. [7]

1.7. Monte Carlo integration method

Monte Carlo integration is a numerical integration method using random elements in the domain of a function, the Monte Carlo integral has better accuracy than successively applied Simpson's Rule or Trapezoidal method. The Monte Carlo numerical integral is defined taking as basis the integration of the following quadrature rule: [11]

$$I(f) = \sum_{i=1}^N c_i f(x^{(i)}); \ x^{(i)} \equiv \left(x_d^{(i)}\right) \in \mathbf{E}^d \tag{22}$$

where we can reshape the notation and fix the weights c_i expressing those as V/N (equal weights $\forall f(x^{(i)})$):

$$I(f) = \int_\Omega f(\bar{\mathbf{x}})d\bar{\mathbf{x}}; \quad \Omega \subset \mathbb{R}^n \tag{23}$$

where Ω is a region of $\mathbb{R}^n$. The value of the integral I can be approximated by

$$V = \int_\Omega d\bar{\mathbf{x}} \tag{24}$$

$$I \approx Q_N \equiv V\frac{1}{N}\sum_{i=1}^N f(\bar{\mathbf{x}}_i) = V\langle f\rangle; \quad \bar{\mathbf{x}}_i \in \Omega \tag{25}$$

$$\lim_{N\to\infty}Q_N = I \tag{26}$$

which for N tending to infinity is equal to the analytical integral due the law of large numbers.

1.7.1. Monte Carlo integral Error

The weighted Monte Carlo method has an estimated error

$$|\bar{\xi}_N - I| \leq x_\beta \sqrt{\frac{D\xi}{N}} \tag{27}$$

Where $\bar{\xi}_N$ is an estimation, I the analytical integral value, x_β a value which establishes a measure, $D\xi$ denotes the variance of ξ (a set of random samples) and N the number of samples. [11] For our current notation it is:

$$\text{Var}(f) \equiv \sigma_N^2 = \frac{1}{N-1} \sum_{i=1}^{N} \left(f(\bar{\mathbf{x}}_i) - \left(\frac{1}{N} \sum_{i=1}^{N} f(\bar{\mathbf{x}}_i) \right) \right)^2 \tag{28}$$

$$= \frac{1}{N-1} \sum_{i=1}^{N} (f(\bar{\mathbf{x}}) - \langle f \rangle)^2 \tag{29}$$

$$\therefore \text{Var}(Q_N) = \frac{V^2}{N^2} \sum_{i=1}^{N} \text{Var}(f) = V^2 \frac{\sigma_N^2}{N} \tag{30}$$

Being the following the error estimator of Q_n

$$\delta Q_N \approx \sqrt{\text{Var}(Q_n)} = V \frac{\sigma_N}{\sqrt{N}} \tag{31}$$

1.8. Trapezoidal rule

$$\int_{x_0}^{x_N} f(x)dx = \frac{h}{2} \left(\sum_{i=0}^{N-1} f(x_i) \right) + \frac{h}{2} (f(x_N) - f(x_0))$$
$$- (x_N - x_0) \frac{h^2}{12} f''(\xi) \tag{32}$$

where $\xi \in (a,b)$, $h = (x_N - x_0)/N$, this is the composed trapezoidal rule plus error term [10]. Where this rule is a metric generalization for $[x_{i-1}, x_i]$, $i = 0, 2, \ldots, N-1$ according to N sub intervals of $[a,b]$ where $x_0 = a$, $x_N = b$.

Now, note how $hf(x_i)/2$ builds a quasi rectangular area under the image of f, the following terms gives accuracy and corrects the error.

1.8.1. Error Bound

Suppose $|f''(x)| \leq K$ for M being it an upper bound of f'' in $a \leq x \leq b$ then the error for the trapezoidal rule is: [12] [13]

$$|E_T| \leq \frac{M(b-a)^3}{12N^2} \tag{33}$$

1.9. Midpoint rule

$$\int_{x_0}^{x_N} f(x)dx = h \sum_{i=0}^{N-1} f\left(x_i + \frac{1}{2}h \right) + (x_N - x_0) \frac{h^2}{24} f''(\xi) \tag{34}$$

where $\xi \in (a,b)$, $h = (x_N - x_0)/N$, $[x_{i-1}, x_i]$,
$i = 0, 2, \ldots, N-1$ according to N sub intervals of $[a,b]$
where $x_0 = a$, $x_N = b$. [10]

1.9.1. Error Bound

Suppose $|f''(x)| \leq K$ for M being it an upper bound of f'' in $a \leq x \leq b$ then the error for the midpoint rule is: [12] [13]

$$|E_M| \leq \frac{M(b-a)^3}{24N^2} \tag{35}$$

1.10. Quadrature rule

Let $T(h)$ and $M(h)$ denote the approximations to $\int_a^b f(x)dx$ obtained by using respectively the trapezoidal and midpoint rules

$$\int_a^b f(x)dx \simeq \frac{2M(h) + T(h)}{3} \tag{36}$$

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

The quadrature rule has then the extended form of

$$\int_a^b f(x)dx \simeq \frac{1}{3} \left(2M(h) + T(h) \right) \tag{37}$$

$$\simeq \frac{2}{3} \left(h \sum_{i=0}^{N-1} f\left(x_i + \frac{1}{2}h \right) + (x_N - x_0) \frac{h^2}{24} f''(\xi) \right)$$
$$+ \frac{1}{3} \left(\frac{h}{2} \left(\left(\sum_{i=0}^{N-1} f(x_i) \right) + (f(x_N) - f(x_0)) \right) \right)$$
$$- (x_N - x_0) \frac{h^2}{12} f''(\xi) \tag{38}$$

1.10.1. Error Bound

Given the error for the trapezoidal and midpoint rules, we can estimate the error bars for this composite quadrature rule as follows:

$$|E_Q| \leq \frac{M(b-a)^3}{12N^2} + \frac{M(b-a)^3}{24N^2} = \frac{M(b-a)^3}{8N^2} \tag{39}$$

where as before, M is an upper bound of f'' in $a \leq x \leq b$.

2. Probability of the Hydrogen Wave Function in a Closed Spatial Section

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

$$I \approx \int_\Omega \lambda(\eta) d\eta \, \frac{1}{N} \sum_{i=1}^{N} \left| \psi_{n\ell m}(r_i, \theta_i, \phi_i) \right|^2 \tag{40}$$

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

$$\int_\Omega \lambda(\eta) d\eta = \int_{\phi_a}^{\phi_b} \int_{\theta_a}^{\theta_b} \int_{r_a}^{r_b} r^2 \sin(\phi) dr d\theta d\phi \tag{41}$$

$$= \int_{r_a}^{r_b} r^2 dr \int_{\phi_a}^{\phi_b} \sin(\phi) d\phi \int_{\theta_a}^{\theta_b} d\theta \tag{42}$$

$$= \left(\frac{r^3}{3} \Big|_{r_a}^{r_b} \right) \left(-\cos(\phi) \Big|_{\phi_a}^{\phi_b} \right) \left(\theta \Big|_{\theta_a}^{\theta_b} \right) \tag{43}$$

The Monte Carlo integral of the wave function can be expressed as

$$I \approx \left(\frac{r^3}{3} \bigg|_{r_a}^{r_b} \right) \left(-\cos(\phi) \bigg|_{\phi_a}^{\phi_b} \right) \left(\theta \bigg|_{\theta_a}^{\theta_b} \right)$$
$$\cdot \frac{1}{N} \sum_{i=1}^{N} \left| \psi_{n\ell m}(r_i, \theta_i, \phi_i) \right|^2 \qquad (44)$$

being then

$$I \approx \Delta r \, \Delta \theta \, \Delta \phi \, \frac{1}{N} \sum_{i=1}^{N} \left| \psi_{n\ell m}(r_i, \theta_i, \phi_i) \right|^2 \qquad (45)$$

the numerical integral, where

$$\Delta r = \left(\frac{r^3}{3} \bigg|_{r_a}^{r_b} \right); \quad \Delta \theta = \left(\theta \bigg|_{\theta_a}^{\theta_b} \right); \quad \Delta \phi = \left(-\cos(\phi) \bigg|_{\phi_a}^{\phi_b} \right)$$
$$r_i \in [r_a, r_b]; \qquad \theta_i \in [\theta_a, \theta_b]; \qquad \phi_i \in [\phi_a, \phi_b] \qquad (46)$$

Finally, as we would expect of a normalized wave function

$$0 \leq I \left(\left| \psi_{n\ell m}(r_i, \theta_i, \phi_i) \right|^2 \right) \qquad (47)$$

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

2.1. Numerical simulation for the first hydrogen's atom wave function

Considering the first wave function

$$\psi_{1,0,0}(r, \theta, \phi) = \left(\sqrt{\pi} a_0^{3/2} \right)^{-1} e^{-r/a_0} \qquad (48)$$

which cleverly shows how the probability of finding the electron in $1s$ decreases as the radial distance increases.

The square of its absolute value is

$$\left| \psi_{1,0,0}(r, \theta, \phi) \right|^2 = \frac{1}{\pi a_0^3} e^{-2r/a_0} \qquad (49)$$

and represents the probability of finding the electron at a distance r for any angular directions θ, ϕ (azimuthal and polar angles respectively).
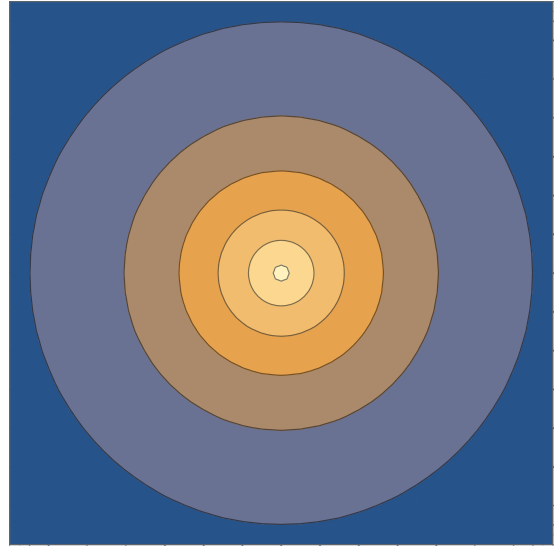
Replacing it on the previous derived formula we obtained, the finite numerical distribution probability of appearance for an electron in the hydrogen atom of electronic configuration $1s$ is

$$I \approx \Delta r \, \Delta \theta \, \Delta \phi \, \frac{1}{N} \sum_{i=1}^{N} \left| \psi_{1,0,0}(r_i, \theta_i, \phi_i) \right|^2 \qquad (50)$$

$$\approx \Delta r \, \Delta \theta \, \Delta \phi \, \frac{1}{N} \sum_{i=1}^{N} \left| \left(\sqrt{\pi} a_0^{3/2} \right)^{-1} e^{-r_i/a_0} \right|^2 \qquad (51)$$

$$\approx \Delta r \, \Delta \theta \, \Delta \phi \, \frac{1}{N} \sum_{i=1}^{N} \frac{1}{\pi a_0^3} e^{-2r_i/a_0} \qquad (52)$$

The following graph shows the inner product $\langle \psi_{1,0,0} | \psi_{1,0,0} \rangle$

Here at the point $r = 0$ (which should be physically impossible outside string theory) the value for the absolute square of the wave function reaches its peak at $\psi_{1,0,0} = (\pi a_0^3)^{-2}$. (Additionally, note that $r < 0$ is impossible to consider and it makes infinite any improper integral)[2]

3. Approximating Numerically Hydrogen's 1s Squared Wave Function Integral Value

3.1. Evaluating Hydrogen's 1s squared wave function

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

$$\int_0^\infty \frac{1}{\pi a_0^3} e^{-2r/a_0} dr \simeq \int_{r_a}^{r_b} \frac{1}{\pi a_0^3} e^{-2r/a_0} dr \qquad (53)$$

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

$$\int_{r_a}^{r_b} \frac{1}{\pi a_0^3} e^{-2r/a_0} dr \simeq$$
$$\frac{1}{3} \left(h \sum_{i=0}^{N-1} P_{1s} \left(r_i + \frac{1}{2} h \right) + (r_N - r_0) \frac{h^2}{24} P_{1s}''(\xi) \right)$$
$$+ \frac{1}{3} \left(\frac{h}{2} \left(\left(\sum_{i=0}^{N-1} P_{1s}(r_i) \right) + (P_{1s}(r_N) - P_{1s}(r_0)) \right) \right.$$
$$\left. - (r_N - r_0) \frac{h^2}{12} P_{1s}''(\xi) \right) \qquad (54)$$

where the second derivative of P_{1s} is

$$\frac{d^2}{dr^2} P_{1s}(r) = \frac{d^2}{dr^2} \left(\frac{1}{\pi a_0^3} e^{-2r/a_0} \right) = \frac{4 e^{-2r/a_0}}{\pi a_0^5} \qquad (55)$$

Now, note that r_a can be fixed to be equal zero due it is the minimum valid value for the radius of $\psi_{1,0,0}$ and therefore of P_{1s}.

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[2] This graph isn't plotted at scale.

3.2. Error Estimation

Given the error bound for the composite quadrature rule in equation (39), the value which makes $P_{1s}''(r)$ maximum in any interval $r_a = 0, r_b \in \mathbb{R}$ is 0. Therefore the error bound for the quadrature rule of $P_{1s}(r)$ is

$$\epsilon \approx \frac{P_{1s}''(0)(b-a)^3}{8N^2} = \frac{4}{\pi a_0^5}\frac{(b-a)^3}{8N^2} = \frac{(b-a)^3}{2N^2(\pi a_0^5)} \quad (56)$$

4. Approximating Numerically Hydrogen's 2s Squared Wave Function Integral Value

4.1. Evaluating Hydrogen's 2s squared wave function

Being

$$\psi_{2,0,0}(r) = \left(4\sqrt{2\pi}a_0^{3/2}\right)^{-1}\left[2 - \frac{r}{a_0}\right]e^{-r/2a_0} \quad (57)$$
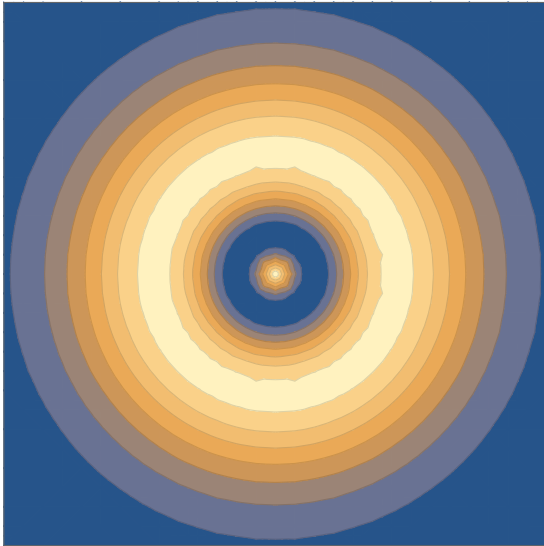
the wave function for the hydrogen atom at $n = 2, \ell = 0, m = 0$ then, the square of its absolute value is

$$|\psi_{2,0,0}(r)|^2 = \left(\left(4\sqrt{2\pi}a_0^{3/2}\right)^{-1}\left[2 - \frac{r}{a_0}\right]e^{-r/2a_0}\right)^2 \quad (58)$$

$$= \frac{1}{\left(4\sqrt{2\pi}a_0^{3/2}\right)^2}\left[2 - \frac{r}{a_0}\right]^2 e^{-r/a_0} \quad (59)$$

$$= \left(32\pi a_0^3\right)^{-1}\left[2 - \frac{r}{a_0}\right]^2 e^{-r/a_0} \quad (60)$$

and the correspondent graphic is:[3]

Now, the quadrature rule for this wave function is:

$$\int_0^\infty |\psi_{2,0,0}(r)|^2 dr \simeq \int_{r_a}^{r_b} \left(32\pi a_0^3\right)^{-1}\left[2 - \frac{r}{a_0}\right]^2 e^{-r/a_0} dr \quad (61)$$

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[3] This graph isn't plotted at scale.

the second derivative of $|\psi_{2,0,0}(r)|^2 \equiv P_{2s}(r)$ is:

$$\frac{d^2}{dr^2}P_{2s}(r) = \frac{d^2}{dr^2}\left(\left(32\pi a_0^3\right)^{-1}\left[2 - \frac{r}{a_0}\right]^2 e^{-r/a_0}\right) \quad (62)$$

$$= \frac{1}{32\pi a_0^3}\frac{d^2}{dr^2}\left(\left[2 - \frac{r}{a_0}\right]^2 e^{-r/a_0}\right) \quad (63)$$

$$= \frac{e^{-r/a}}{32\pi a_0^3}\frac{\left(-8a_0 r + 14a_0^2 + r^2\right)}{a_0^4} \quad (64)$$

$$= e^{-r/a}\left[\frac{-8a_0 r + 14a_0^2 + r^2}{32\pi a_0^7}\right] \quad (65)$$

and finally, the quadrature rule we obtain is:

$$\int_{r_a}^{r_b} \left(32\pi a_0^3\right)^{-1}\left[2 - \frac{r}{a_0}\right]^2 e^{-r/a_0} dr \simeq$$

$$\frac{1}{3}\left(h\sum_{i=0}^{N-1} P_{2s}\left(r_i + \frac{1}{2}h\right) + (r_N - r_0)\frac{h^2}{24}P_{2s}''(\xi)\right)$$

$$+ \frac{1}{3}\left(\frac{h}{2}\left(\left(\sum_{i=0}^{N-1} P_{2s}(r_i)\right) + (P_{2s}(r_N) - P_{2s}(r_0))\right)\right)$$

$$- (r_N - r_0)\frac{h^2}{12}P_{2s}''(\xi)\right) \quad (66)$$

5. Computer Implementing

The implementation was done in python, it consists of a program with two main modules, namely Monte Carlo Integral and Quadrature Rule, the development required `mathplotlib`, `pandas`, `numpy`, `tkinter`. `pandas` was needed to create Excel documents and do some experiments.

5.1. Numerical Approximations

5.2. Monte Carlo Integral

As clarification, it is good to mention that in the source code, the random generation for the coordinates was done in such way that no value for r, θ, ϕ were repeated, that would absolutely affect the result for the integral, specially the values of r because $\psi_{1,0,0}$ and $\psi_{2,0,0}$ depends only in such value and repeated values for the integral are taken as additional information.

The problem resides in that repeated values from a function's domain in an analytical integral are nonexistent, so, there will be negative consequences of using those repeated values concerning the precision of the integral.

Hence the implementation was done using:

```
numpy.random.uniform([l_a], [l_b], [n_samples])
```

Apart from that, because the coordinate system for all the wave functions associated to the hydrogen atom are given in spherical coordinates and due `mathplotlib` plots in cartesian coordinates there was needed a conversion from coordinate systems.

Table 1. Iterative search for a suitable value for r_b in the quadrature integral

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

The predetermined values taken for this method were:

$r_a = 0; \quad r_b = 6{,}73\text{E-}11$
$\theta_a = 0; \quad \theta_b = 2\pi$
$\phi_a = 0; \quad \phi_b = \pi$
$N = 7\text{E}+03$

Note: r_b was selected based on a_0 then increasing randomly r_b.

5.2.1. Error Estimation

Because the error in equation (31) is measured taking in consideration the randomly selected points, it isn't possible to provide a deterministic error estimation for this algorithm before its execution. Moreover with the fact that there are 7.000 randomly selected spherical coordinates we have quite the problem to expose such quantity of data in the paper.

However, the related python application QLab realizes this estimation every simulation.

5.3. Quadrature Rule

The quadrature rule applied to $\psi_{1,0,0}$ was estimated with successive iterations, table (1) shows the last iterations realized in Python taking as initial value $r_b = a_0$ and increasing it by 1E-11.

In addition, as we know the value for r_b we can estimate the error bound in the composite quadrature rule. It is:

$$E_Q = \frac{(r_b - r_a)^3}{2N^2(\pi a_0^5)} \tag{67}$$

where

$r_a = 0$
$r_b = 2{,}629029177212380\text{E-}07$
$N = 100$

and if we wanted an error bound of 10E-1 it would be necessary

$$\sqrt{\frac{(r_b - r_a)^3}{20(\pi a_0^5)}} = N = 8{,}34834411874894\text{E}+14 \tag{68}$$

sub-intervals. It turns out to be an `np.array` with `dtype float64` of 7.11 PiB.

6. Conclusions

1. The Monte Carlo integration method is cleverly useful, it can be adjusted or used to be suitable enough in complex problems. 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 one dimension.
2. The prediction done using the Monte Carlo integration here does not constitutes a proof about being able to find the electron of an hydrogen atom inside a strictly closed spatial. Certainly it does shows us a good approximation but it is due the value selected for the maximum radius r_b, one can truly notice exploring the QLab application (produced for corroborating this paper).
3. The Quadrature rule applied to $\psi_{1,0,0}$ and $\psi_{2,0,0}$ 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.
4. The scales which were worked here are difficult to correctly approach (in the sense of numerical precision) due our limitations in floating point arithmetic. Certainly 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.
5. 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.

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