

Numerical Simulations of the Probability Distributions in the Hydrogen's Atom Wave Functions*

Electric Physics, Simulation, Numerical Methods

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Aims and Methodology

Section One

Summary

Summary, aims and methodology

Aims

The main objective The main objective is to describe the MonteCarlo integral form of the real wave functions.

The specific objectives are: determine the MonteCarlo integral for the Wave Functions, find the error bounds of the integrals and to give an interpretation of the results.

Methods (methodology)

The theoretical framework brings elements susceptible of implementation, it provided the tools to develop the MonteCarlo integral of the hydrogen's atom wave functions. In experimentation phase the results were found.

Results

It was found from the integrals of the wave functions that the MonteCarlo integral constitutes a good approximation, the error estimate was the standard deviation.

Theoretical Framework

Section Two

Quantum Mechanics

Wave Function

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

$$\begin{aligned} \langle \psi_{n\ell m} | \psi_{n\ell m} \rangle &= \int_S ds \psi_{n\ell m}^* \psi_{n\ell m} = \int_S |\psi_{n\ell m}|^2 ds \\ &= \delta_{nn} \delta_{\ell\ell} \delta_{mm} = 1 \end{aligned} \quad (2)$$

Probability of the Wave Function

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

$$P_{a_i \leq r_i \leq b_i}(t) = \int_I |\Psi(\mathbf{r}, t)|^2 d^n \mathbf{r}; \quad \mathbf{r}, I \subset \mathcal{H} \quad (3)$$

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

Schrödinger Equation

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

$$i\hbar \frac{\partial}{\partial t} \Psi(\mathbf{r}, t) = \left[-\frac{\hbar^2}{2m} \nabla^2 + V(\mathbf{r}, t) \right] \Psi(\mathbf{r}, t) \quad (5)$$

—Time Dependent Schrödinger Equation

$$\hat{H} |\Psi(\mathbf{r})\rangle = E |\Psi(\mathbf{r})\rangle \quad (6)$$

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + V(\mathbf{r}) \right] |\Psi(\mathbf{r})\rangle = E |\Psi(\mathbf{r})\rangle \quad (7)$$

—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

$$\left(-\frac{\hbar^2}{2m} \nabla^2 - \frac{e^2}{4\pi\epsilon_0 r} \right) \psi_{n\ell m}(r, \theta, \phi) = E \psi_{n\ell m}(r, \theta, \phi) \quad (8)$$

—Schrödinger equation for the hydrogen atom

$$\begin{aligned} \psi_{n\ell m}(r, \theta, \phi) &= R(r) Y_\ell^m(\theta, \phi) = R(r) \Theta(\theta) \Phi(\phi) \\ &= \sqrt{\left(\frac{2}{na_0^*}\right)^3 \frac{(n-\ell-1)!}{2n[(n+\ell)!]}} e^{-r/ma_0^*} \left(\frac{2r}{na_0^*}\right)^\ell \cdot L_{n-\ell-1}^{2\ell+1} \left(\frac{2r}{na_0^*}\right) \cdot Y_\ell^m(\theta, \phi) \end{aligned} \quad (9)$$

—Solution for $\psi_{n\ell m}$

For the coordinates r, θ, ϕ , 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 $m = -\ell, -\ell + 1, -\ell + 2, \dots, l$. $|\psi|^2$ is the probability of appearance for an electron in the atom.

Component Functions of the Hydrogen's Wave Function

$$Y_\ell^m(\theta, \phi) = (-1)^m \sqrt{\frac{2\ell+1}{4\pi} \frac{(\ell-m)!}{(\ell+m)!}} P_{\ell m}(\cos(\theta)) e^{im\phi} \quad (10)$$

—Spherical harmonic function

$$L_n^{(\alpha)} = \frac{x^{-\alpha} e^x}{n!} \frac{d^n}{dx^n} (e^{-x} x^{n+\alpha}) \quad (11)$$

—Laguerre polynomial function

$$P_\ell^m(x) = \frac{(-1)^m}{2^\ell \ell!} (1-x^2)^{m/2} \frac{d^{\ell+m}}{dx^{\ell+m}} (x^2 - 1)^\ell; \quad P_{\ell m}(x) = (-1)^m P_\ell^m(x) \quad (12)$$

—Legendre polynomial in the spherical harmonic function

Normalized Hydrogen Wave Functions

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

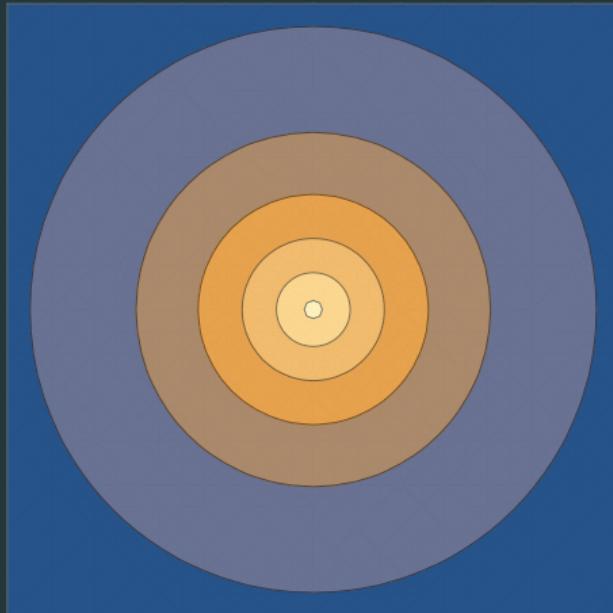
n	ℓ	m	E_l	$\psi_{nlm}(r, \theta, \phi)$
1	0	0	1s	$\left(\sqrt{\pi}a_0^{3/2}\right)^{-1} e^{-r/a_0}$
2	0	0	2s	$\left(4\sqrt{2\pi}a_0^{3/2}\right)^{-1} \left[2 - \frac{r}{a_0}\right] e^{-r/2a_0}$
2	1	0	2p	$\left(4\sqrt{2\pi}a_0^{3/2}\right)^{-1} \frac{r}{a_0} e^{-r/2a_0} \cos(\theta)$
2	1	± 1	2p	$\left(8\sqrt{\pi}a_0^{3/2}\right)^{-1} \frac{r}{a_0} e^{-r/2a_0} \sin(\theta) e^{\pm i\phi}$
3	0	0	3s	$\left(81\sqrt{3\pi}a_0^{3/2}\right)^{-1} \left[27 - 18\frac{r}{a_0} + 2\frac{r^2}{a_0^2}\right] e^{-r/3a_0}$
3	1	0	3p	$\left(81\sqrt{\pi}a_0^{3/2}\right)^{-1} \sqrt{2} \left[6 - \frac{r}{a_0}\right] \frac{r}{a_0} e^{-r/3a_0} \cos(\theta)$

n	ℓ	m	E_l	$\psi_{nlm}(r, \theta, \phi)$
3	1	0	3p	$\left(81\sqrt{\pi}a_0^{3/2}\right)^{-1} \sqrt{2} \left[6 - \frac{r}{a_0}\right] \frac{r}{a_0} e^{-r/3a_0} \cos(\theta)$
3	1	± 1	3p	$\left(81\sqrt{\pi}a_0^{3/2}\right)^{-1} \left[6 - \frac{r}{a_0}\right] \frac{r}{a_0} e^{-r/3a_0} \sin(\theta) e^{\pm i\phi}$
3	2	0	3d	$\left(81\sqrt{6\pi}a_0^{3/2}\right)^{-1} \frac{r^2}{a_0^2} e^{-r/3a_0} (3\cos^2(\theta) - 1)$
3	2	± 1	3d	$\left(81\sqrt{\pi}a_0^{3/2}\right)^{-1} \frac{r^2}{a_0^2} e^{-r/3a_0} \sin(\theta) \cos(\theta) e^{\pm i\phi}$
3	2	± 2	3d	$\left(162\sqrt{\pi}a_0^{3/2}\right)^{-1} \frac{r^2}{a_0^2} e^{-r/3a_0} \sin^2(\theta) e^{\pm i2\phi}$

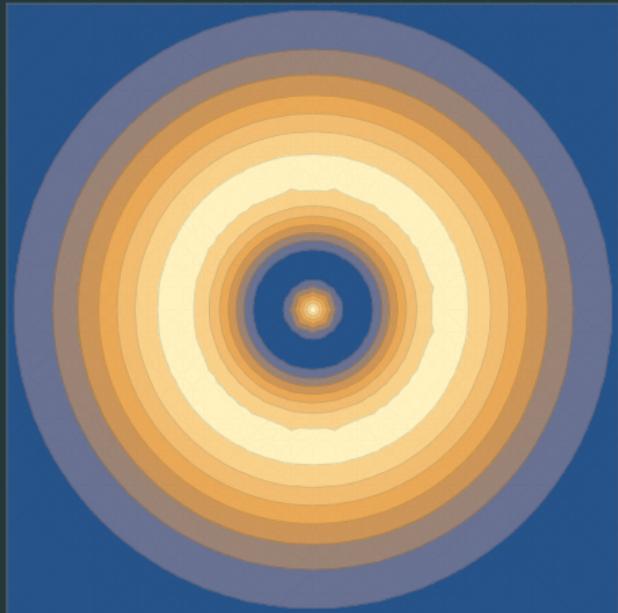
Where $a_0 = \hbar^2/m e^2 \approx 0.0529 mn$ is the first Bohr Radius.

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 have been plotted using cartesian coordinates and are not to scale so that we can visualize them better)

Monte Carlo Integration Method

Initial integral:

$$I(f) = \sum_{i=1}^N c_i f(x^{(i)}); \quad x^{(i)} \equiv \left(x_d^{(i)} \right) \in E^d \quad (13)$$
$$i = 1, \dots, N$$

from where we can obtain:

$$V = \int_{\Omega} d\bar{x} \quad (14)$$

$$I \approx Q_N \equiv V \frac{1}{N} \sum_{i=1}^N f(\bar{x}_i) = V \langle f \rangle; \quad \bar{x}_i \in \Omega \quad (15)$$

$$\lim_{N \rightarrow \infty} Q_N = I \quad (16)$$

Monte Carlo integration is numerical integration method using random sampling.

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

From equation (13) one can reshape the notation and rearrange the weights c_i expressing those as V/N (equal weights $\forall f(x^{(i)})$).

So, equation (15) be obtained. This last equation is far more computable than the original Monte Carlo formula.

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

$$I \approx \int_{\Omega} \Upsilon(v) dv \frac{1}{N} \sum_{i=1}^N |\psi_{n\ell m}(r_i, \theta_i, \phi_i)|^2 \quad (17)$$

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

$$\int_{\Omega} \Upsilon(v) dv = \int_{\phi_a}^{\phi_b} \int_{\theta_a}^{\theta_b} \int_{r_a}^{r_b} r^2 \sin(\phi) dr d\theta d\phi \quad (18)$$

$$= \int_{r_a}^{r_b} r^2 dr \int_{\phi_a}^{\phi_b} \sin(\phi) d\phi \int_{\theta_a}^{\theta_b} d\theta \quad (19)$$

$$= \left(\frac{r^3}{3} \Big|_{r_a}^{r_b} \right) \left(-\cos(\phi) \Big|_{\phi_a}^{\phi_b} \right) \left(\theta \Big|_{\theta_a}^{\theta_b} \right) \quad (20)$$

for $v = (r, \theta, \phi)$, $dv = dr d\theta d\phi$, $\Upsilon \mapsto r^2 \sin(\phi)$.

Substitution

$$I \approx \left(\frac{r^3}{3} \Big|_{r_a}^{r_b} \right) \left(-\cos(\phi) \Big|_{\phi_a}^{\phi_b} \right) \left(\theta \Big|_{\theta_a}^{\theta_b} \right) \cdot \frac{1}{N} \sum_{i=1}^N |\psi_{n\ell m}(r_i, \theta_i, \phi_i)|^2 \quad (21)$$

—Numerical Monte Carlo
Generalized Hydrogen Wave
Function Integral

$$I \approx \Delta r \Delta \theta \Delta \phi \frac{1}{N} \sum_{i=1}^N |\psi_{n\ell m}(r_i, \theta_i, \phi_i)|^2 \quad (22)$$

—Equivalent Expression

The last numerical integral, is understood as

$$\Delta r = \left(\frac{r^3}{3} \Big|_{r_a}^{r_b} \right); \quad \Delta \theta = \left(\theta \Big|_{\theta_a}^{\theta_b} \right); \quad \Delta \phi = \left(-\cos(\phi) \Big|_{\phi_a}^{\phi_b} \right) \\ r_i \in [r_a, r_b]; \quad \theta_i \in [\theta_a, \theta_b]; \quad \phi_i \in [\phi_a, \phi_b] \quad (23)$$

So, we denote the integral as

$$I_{\rho_a}^{\rho_b}(\psi_{n\ell m}) \approx V \Big|_{\rho_a}^{\rho_b} \frac{1}{N} \sum_{i=1}^N |\psi_{n\ell m}(r_i, \theta_i, \phi_i)|^2 \quad (24)$$

Considering $\rho_a = (r_a, \theta_a, \phi_a)$, $\rho_b = (r_b, \theta_b, \phi_b)$ as embedded spatial boundaries in the integral. Note that as we would expect of a normalized wave function:

$$0 \leq I \left(|\psi_{n\ell m}(r_i, \theta_i, \phi_i)|^2 \right) \leq 1 \quad (25)$$

Numerical solution for the first hydrogen's atom wave function

Procedure

$$\psi_{1,0,0}(r, \theta, \phi) = \left(\sqrt{\pi}a_0^{3/2}\right)^{-1} e^{-r/a_0} \quad (26)$$

—Hydrogen 1s Wave Function

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

—Squared Value

$$I \approx V \left| \int_{r_a}^{r_b} \frac{1}{N} \sum_{i=1}^N \frac{1}{\pi a_0^3} e^{-2r_i/a_0} \right|^2 \quad (28)$$

—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 compute the following default parameters^a:

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

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

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

$$N = 7E + 03$$

(Note that r_b is close to a_0)

^aSee the paper for further details

Results and Analysis

Section Three

Integral Representations for Real Valued Wave Functions

Integral Representations

Due the complexity of graphing complex valued vector functions those to be implemented won't involve complex values as result.

$\psi_{n\ell m}$		MonteCarlo Integral
1s		$V \left \frac{1}{N} \sum_{i=1}^N \left \left(\sqrt{\pi} a_0^{3/2} \right)^{-1} e^{-r_i/a_0} \right ^2 \right _{\rho_a}^{\rho_b}$
2s		$V \left \frac{1}{N} \sum_{i=1}^N \left \left(4\sqrt{2\pi} a_0^{3/2} \right)^{-1} \left[2 - \frac{r}{a_0} \right] e^{-r/2a_0} \right ^2 \right _{\rho_a}^{\rho_b}$
2p		$V \left \frac{1}{N} \sum_{i=1}^N \left \left(4\sqrt{2\pi} a_0^{3/2} \right)^{-1} \frac{r}{a_0} e^{-r/2a_0} \cos(\theta) \right ^2 \right _{\rho_a}^{\rho_b}$

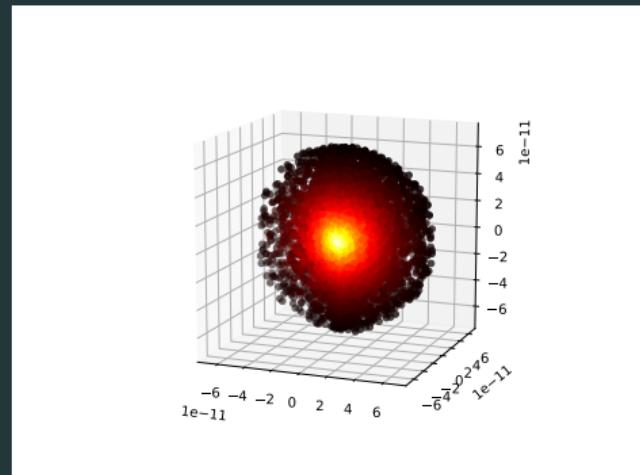
$\psi_{n\ell m}$	MonteCarlo Integral
$3s$	$V \left \frac{1}{N} \sum_{i=1}^N \left \left(81 \sqrt{3\pi} a_0^{3/2} \right)^{-1} \left[27 - 18 \frac{r}{a_0} + 2 \frac{r^2}{a_0^2} \right] e^{-r/3a_0} \right ^2 \right _{\rho_a}^{\rho_b}$
$3p$	$V \left \frac{1}{N} \sum_{i=1}^N \left \left(81 \sqrt{\pi} a_0^{3/2} \right)^{-1} \sqrt{2} \left[6 - \frac{r}{a_0} \right] \frac{r}{a_0} e^{-r/3a_0} \cos(\theta) \right ^2 \right _{\rho_a}^{\rho_b}$
$3d$	$V \left \frac{1}{N} \sum_{i=1}^N \left \left(81 \sqrt{6\pi} a_0^{3/2} \right)^{-1} \frac{r^2}{a_0^2} e^{-r/3a_0} (3 \cos^2(\theta) - 1) \right ^2 \right _{\rho_a}^{\rho_b}$

Stochastic Sampling and 3D Visualizations

Iterative Search

$H_{1s} (\psi_{1,0,0})$			
Iteration	$\int_0^{r_b} \psi ^2 dV$	r_b	δQ_N
130	0,9457019	6,5817721E-11	2,1031176%
131	0,9595269	6,5917721E-11	2,0185508%
132	0,9176160	6,6017721E-11	2,0389192%
133	0,9829230	6,6117721E-11	2,1481853%
134	1,0025933	6,6217721E-11	2,1479737%

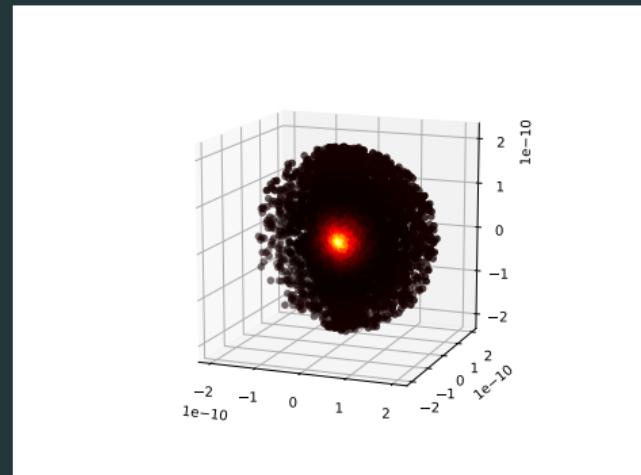
3D Plot



Iterative Search

$H_{2s} (\psi_{2,0,0})$			
Iteration	$\int_0^{r_b} \psi ^2 dV$	r_b	δQ_N
1311	0,9091722	1,8391772E-10	5,0342333%
1312	0,8510967	1,8401772E-10	4,7661942%
1313	0,9406232	1,8411772E-10	5,2906420%
1314	0,9496419	1,8421772E-10	5,0903240%
1315	1,0151406	1,8431772E-10	5,4509201%

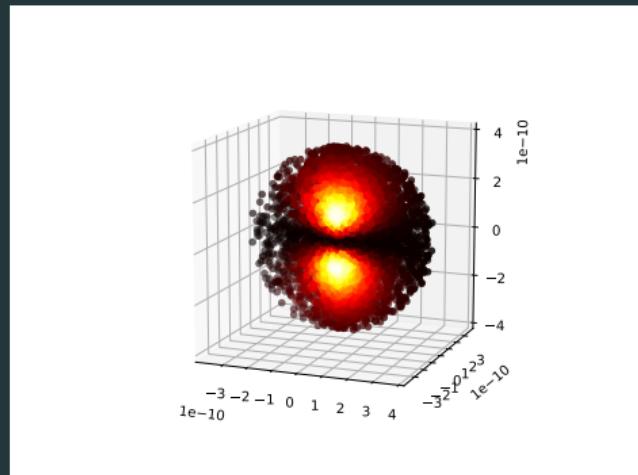
3D Plot



Iterative Search

$H_{2p}(\psi_{2,1,0})$			
Iteration	$\int_0^{r_b} \psi ^2 dV$	r_b	δQ_N
2171	0,9631911	2,6991772E-10	2,6748278%
2172	0,9848947	2,7001772E-10	2,6065623%
2173	0,9567920	2,7011772E-10	2,6329902%
2174	0,9284070	2,7021772E-10	2,6330210%
2175	1,0221785	2,7031772E-10	2,8217323%

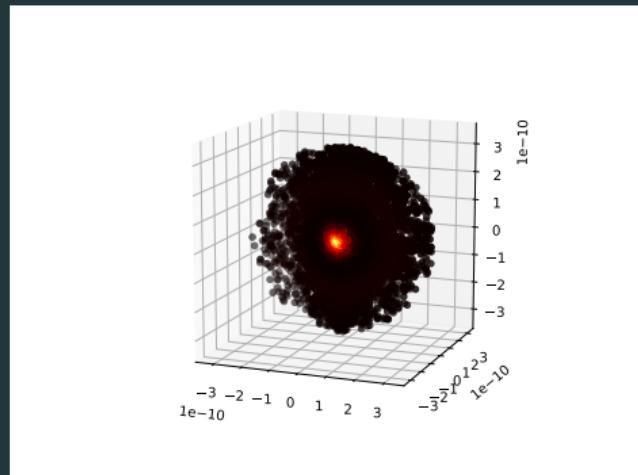
3D Plot



Iterative Search

$H_{3s} (\psi_{3,0,0})$			
Iteration	$\int_0^{r_b} \psi ^2 dV$	r_b	δQ_N
2719	0,8474818	3,2471772E-10	6,1158473%
2720	0,8570234	3,2481772E-10	6,4824615%
2721	0,9295840	3,2491772E-10	6,3611570%
2722	0,8450058	3,2501772E-10	6,0798280%
2723	1,0280992	3,2511772E-10	7,2012712%

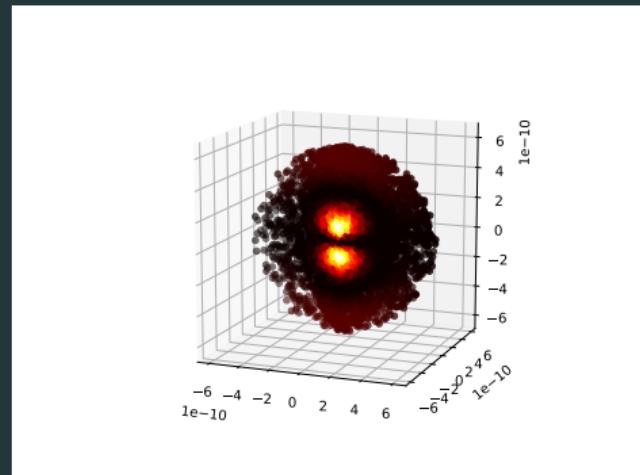
3D Plot



Iterative Search

$H_{3p}(\psi_{3,1,0})$			
Iteration	$\int_0^{r_b} \psi ^2 dV$	r_b	δQ_N
4519	0,9095951	5,0471772E-10	4,5325230%
4520	0,9494293	5,0481772E-10	4,5971247%
4521	0,8962857	5,0491772E-10	4,3819209%
4522	0,8631052	5,0501772E-10	4,3409817%
4523	1,0376629	5,0511772E-10	4,8082404%

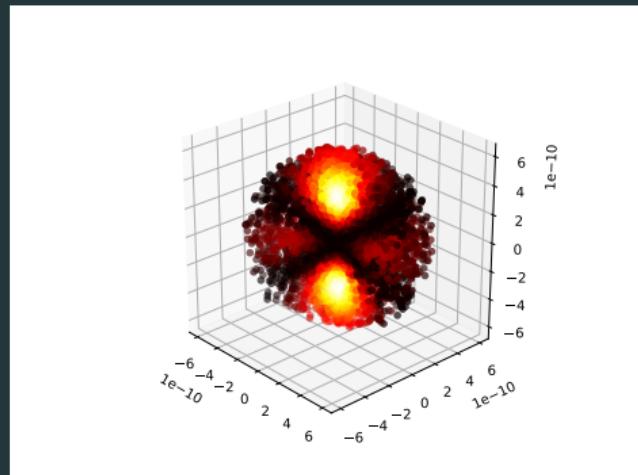
3D Plot



Iterative Search

H _{3d} ($\psi_{3,2,0}$)			
Iteration	$\int_0^{r_b} \psi ^2 dV$	r_b	δQ_N
5476	0,9643382	6,0041772E-10	3,7983305%
5477	0,9714497	6,0051772E-10	3,6970124%
5478	0,9762733	6,0061772E-10	3,8403023%
5479	0,9468050	6,0071772E-10	3,5944818%
5480	1,0085111	6,0081772E-10	3,8450384%

3D Plot



Code Implementation

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     evaluated_volume: float = (((r_b - r_a) ** 3) / 3) * (theta_b - theta_a)
6     * (-np.cos(phi_b) + np.cos(phi_a))
7     r, theta, phi = uniform_spherical_interval(r_a, r_b, theta_a, theta_b, phi_a, phi_b, samples)
8     psi_i = np.zeros(samples, dtype='float32')
9
10    i: int = 0
11    summation: float = 0
12    for r_i, theta_i, phi_i in zip(r, theta, phi):
13        psi_i[i] = f(r_i, theta_i, phi_i)
14        summation += psi_i[i]
15        i += 1
16
17    return (evaluated_volume * summation) / samples, r, theta, phi, evaluated_volume, psi_i
```

Code Implementation - Error Computation

```
1 def spherical_monte_carlo_estimation_error(f: Callable[[float, float, float], float],
2                                             r: np.ndarray, theta: np.ndarray, phi: np.ndarray, volume: float,
3                                             samples: int = MONTE_CARLO_SAMPLING):
4
5     summation: float = 0
6     for r_i, theta_i, phi_i in zip(r, theta, phi):
7         summation += f(r_i, theta_i, phi_i)
8     summation /= samples
9
10    sqrt_var_f: float = 0
11    for r_i, theta_i, phi_i in zip(r, theta, phi):
12        sqrt_var_f += (f(r_i, theta_i, phi_i) - summation) ** 2
13    sqrt_var_f = np.sqrt(sqrt_var_f / samples - 1)
14
15    return sqrt_var_f * volume / np.sqrt(samples)
```

Analysis and Conclusions

Analysis

1. Due that the general wave function implies quite a large amount of numerical computations and the fact that x64 bit machines truncates data which exceeds its registry capacity, it's better to look for a clearer alternative such as using the specific values of the wave functions to reduce systematic and numerical errors.
2. The obtained results are coherent so far as we can see, with a maximal error δQ_N in the samplings of 7,2012712%, it's certain that the overall estimation method for the frontier values in the MonteCarlo integral is suitable enough. We could reproduce more tries using a larger quantity of samples to decrement the error estimate and obtain greater accuracy results.
3. δQ_N representing the error estimation due the standard deviation is related to the geometrical form given by the specter of the wave function once it's plotted in the three dimensional space, because the points of data where the probability augments will be closer depending on the specter of it.

Conclusions

1. The Monte Carlo integration method is cleverly useful, it can be adjusted or used to be suitable enough in complex problems such as multivariate probability integrals.
2. The values of r_b obtained in each wave function matches an increasing pattern in radial distance for the energy levels. As we know, for higher energy levels the electrons in the hydrogen atom will be able to locate in greater radial distances from the nucleus. Hence, the evaluation via MonteCarlo Integration is correct and matches experimental results.
3. The values of $\int_0^{r_b} |\psi|^2 dV$ (probabilities) may suggest experimental areas where the likely to find the electron of a wave function is considerably higher than in other locations. Because the material to realize empirical sampling isn't at disposition this hypothesis cannot be verified.
4. Finally, δQ_N reinforces the accuracy of the results. Due to the geometrical shape of the wave function, a high error estimate indicates that the probability is relatively sparse in the space as well a low error estimator indicates that it's located on dense spatial sections.

Thank you for paying attention!

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