Role of the cut-off function for the ground state variational wavefunction of the hydrogen atom confined by a hard sphere

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A variational treatment of the hydrogen atom in its ground state, enclosed by a hard spherical cavity of radius $R_c$, is developed by considering the ansatz wavefunction as the product of the free-atom 1s orbital times a cut-off function to satisfy the Dirichlet boundary condition imposed by the impenetrable confining sphere. Seven different expressions for the cut-off function are employed to evaluate the energy, the cusp of the ansatz wavefunction as the product of the free-atom 1s orbital times a cut-off function to satisfy the Dirichlet boundary condition imposed

\[ \psi(\vec{r})|_{\vec{r} \notin \delta \Omega} = 0 \]

This simple model has been widely used to test new techniques to solve the Schrödinger equation (exact solutions) or to explore new trial variational wavefunctions to compare with the most accurate calculations [10]. One of the approximate methods is the direct variational method (DVM), in which the trial wavefunction is constructed as the product of a wave function, similar to the wave function of the free (unbounded) system, times a non-singular function $f_{\text{cut}}$, which vanishes on the boundary of the box $\delta \Omega$.

The selection of the cut-off term $f_{\text{cut}}$ in the literature has been arbitrary. Some authors have used different forms of cut-off function: linear [5-7], exponential [19], or $(1 - r/R_c)^n$, where $n$ is a positive integer number [20], etc. On the other hand, to our knowledge there is no systematic study about the effect of the cut-off function on the energy of the confined hydrogen atom, obtained in a variational way.

The objective of this work is to explore several criteria to decide which of the cut-off functions is the best. We tested seven trial wavefunction constructed as a product of the free 1s hydrogen-like orbital times seven different cut-off function $f_{\text{cut}}$. We compared the calculated physical quantities with the exact ones [9,10,33] to decide which of the trial wavefunctions give the best approximations.

The organization of this work is as follows: in Sec. 2 we present the methodology used to solve the confined hydrogen atom (CHA) problem within spherical impenetrable cavity using the direct variational method. We used seven different cut-off functions to compute the ground state energy and several expectation values of $r$ as functions of the confinement radius. In Sec. 3 we compute the Shannon entropy in coordinate space for the different trial wave functions of Sec. 2. In
Sec. 4 we compare the results obtained by using the different trial wave functions with the accurate numerical results [9-10,33]. Finally in Sec. 5 we give our conclusions.

2. The ground state energy of the CHA by using different cut-off functions

The Hamiltonian of the confined hydrogen atom, in atomic units, is given by

\[ H = -\frac{1}{2} \nabla^2 - \frac{1}{r} + U_c(r) \]

\[ U_c(r) = \begin{cases} 0, & r \leq R_c \\ \infty, & r > R_c \end{cases} \quad (1) \]

In the DVM, the ground state wavefunction \( \psi_t \) of the CHA is the product of a function \( \psi_f \), similar to the 1 s orbital of the free hydrogen atom, times a nonsingular cut-off function \( f_{\text{cut}} \), such that \( f_{\text{cut}}(r = R_c) = 0 \).

\[ \psi_t = \psi_f f_{\text{cut}}. \quad (2) \]

In this way \( \psi_t \) satisfies the Dirichlet boundary condition of the problem

\[ \psi_t(r = R_c, \theta, \varphi) = 0. \quad (3) \]

We propose the wave function \( \psi_f \) as the 1 s hydrogen-like wavefunction:

\[ \psi_f(r) = Ae^{-\alpha r}, \quad (4) \]

where \( A \) is the normalization constant and \( \alpha \) is the variational parameter.

The trial wavefunction for the ground state of the CHA, with its nucleus clamped at the origin of a sphere of radius \( R_c \) is given by:

\[ \psi_t(r, \theta, \varphi) = Ae^{-\alpha r} f_{\text{cut}}(r), \quad (5) \]

This function must be a decreasing function of \( r \) in the interval \([0, R_c]\) and it is valid for negative and positive energy values.

We use this trial wave function (5) and the variational method to minimize the energy functional \( E(\alpha) \), which is given by:

\[ E(\alpha) = \frac{\langle \psi_t | H | \psi_t \rangle}{\langle \psi_t | \psi_t \rangle}, \quad (6) \]

As we mentioned above the cut-off function \( f_{\text{cut}} \) is, in principle, arbitrary. We selected seven different cut-off functions to evaluate the quality with which they reproduce the energy of the CHA ground state and several expectation values of \( r \). The following seven trial wavefunctions are constructed by using the rule given by the Eq. (5):

I

\[ e^{-\alpha r} \left( 1 - \frac{r}{R_c} \right)^2. \]

II

\[ e^{-\alpha r} \left( 1 - \frac{r}{R_c} \right)^3. \]

III

\[ e^{-\alpha r} \left( 1 - \frac{r}{R_c} \right)^4. \]

IV

\[ e^{-\alpha r} \left( 1 - \frac{r}{R_c} \right)^2. \]

V

\[ e^{-\alpha r} \left( 1 - \frac{r}{R_c} \right)^2. \]

VI

\[ e^{-\alpha r} j_0 \left( \frac{X_{10} r}{R_c} \right). \]

VII

\[ e^{-\alpha r} \left( c_1 j_0 \left( \frac{X_{10}}{R_c} r \right) + c_2 j_0 \left( \frac{X_{20}}{R_c} r \right) \right), \]

where \( j_0 \) is the zeroth-order spherical Bessel function. \( X_{10} = \pi \) and \( X_{20} = 2\pi \) are the first and second zeros of the spherical Bessel function, \( c_1 \) and \( c_2 \) are linear variational parameters, respectively. \( j_0 \) is the wave function, with angular momentum \( l = 0 \), of the free particle in a spherical impenetrable box. The wave functions \( j_0(X_{10}/R_c r) \) and \( j_0(X_{20}/R_c r) \), are the ground state and the first excited state wave function of the free particle in a box, respectively. The wavefunction VII is the linear superposition of the two linearly independent wavefunctions.

We must note that all the differences in the calculated values of physical properties are due to the kind of cut-off function used.

According to the variational theorem, we must calculate the expectation value of the energy using the trial wavefunction. Thus, because of the symmetry of the problem, the integrals we need to calculate are:

\[ \langle \psi_t | H | \psi_t \rangle = \frac{\langle \psi_t | T | \psi_t \rangle + \langle \psi_t | V | \psi_t \rangle}{\langle \psi_t | \psi_t \rangle} \quad (7) \]

Where

\[ \langle \psi_t | V | \psi_t \rangle = - \int_0^{R_c} \left[ e^{-\alpha r} f_{\text{cut}}(r) \right]^2 r \, dr, \quad (8) \]

\[ \langle \psi_t | T | \psi_t \rangle = - \frac{1}{2} \int_0^{R_c} e^{-\alpha r} f_{\text{cut}}(r) \times \left[ \frac{1}{r^2} \frac{d}{dr} \left( r^2 \frac{d}{dr} (e^{-\alpha r} f_{\text{cut}}(r)) \right) \right] r^2 \, dr, \quad (9) \]
TABLE I. Ground state energy for the CHA, with seven different trial wavefunctions (see the text) by means of the variational method. These results are compared with the exact value [10]. Distances are in Bohrs, while energies are in Hartrees.

| \( R_c \) | I   | II  | III | IV  | V   | VI  | VII | Exact value |
|-----------|-----|-----|-----|-----|-----|-----|-----|-------------|
| 0.5       | 14.8971 | 14.8152 | 14.8774 | 15.0390 | 14.7621 | 14.7619 | 14.7480 |
| 0.6       | 9.6180   | 9.5657   | 9.6065   | 9.7117   | 10.4975  | 9.5419  | 9.5416 | 9.5277 |
| 0.7       | 6.5272   | 6.4921   | 6.5190   | 6.5924   | 7.1791   | 6.4842  | 6.4839 | 6.4699 |
| 0.8       | 4.5808   | 4.5565   | 4.5752   | 4.6279   | 5.0838   | 4.5577  | 4.5574 | 4.5434 |
| 0.9       | 3.2870   | 3.2699   | 3.2831   | 3.3220   | 3.6891   | 3.2765  | 3.2762 | 3.2622 |
| 1         | 2.3906   | 2.3784   | 2.3878   | 2.4170   | 2.7168   | 2.3884  | 2.3880 | 2.3740 |
| 1.2       | 1.2767   | 1.2705   | 1.2753   | 1.2924   | 1.5053   | 1.2838  | 1.2833 | 1.2693 |
| 1.5       | 0.4388   | 0.4371   | 0.4384   | 0.4464   | 0.5861   | 0.4515  | 0.4508 | 0.4370 |
| 1.7       | 0.1396   | 0.1394   | 0.1395   | 0.1441   | 0.2541   | 0.1535  | 0.1527 | 0.1391 |
| 2         | -0.1250  | -0.1240  | -0.1249  | -0.1232  | -0.0431  | -0.1108 | -0.1118 | -0.1250 |
| 3         | -0.4225  | -0.4206  | -0.4224  | -0.4237  | -0.3902  | -0.4116 | -0.4132 | -0.4240 |
| 4         | -0.4811  | -0.4796  | -0.4811  | -0.4824  | -0.4670  | -0.4741 | -0.4760 | -0.4833 |
| 5         | -0.4947  | -0.4937  | -0.4948  | -0.4956  | -0.4884  | -0.4906 | -0.4924 | -0.4964 |
| 6         | -0.4982  | -0.4976  | -0.4983  | -0.4988  | -0.4953  | -0.4959 | -0.4974 | -0.4993 |
| 7         | -0.4993  | -0.4989  | -0.4994  | -0.4996  | -0.4978  | -0.4979 | -0.4990 | -0.4999 |
| 8         | -0.4997  | -0.4995  | -0.4997  | -0.4999  | -0.4989  | -0.4988 | -0.4996 | -0.5000 |
| 9         | -0.4998  | -0.4997  | -0.4999  | -0.5000  | -0.4994  | -0.4993 | -0.4998 | -0.5000 |
| 10        | -0.4999  | -0.4998  | -0.4999  | -0.5000  | -0.4996  | -0.4996 | -0.4999 | -0.5000 |

and the overlap integral is given by

\[
\langle \psi_t | \psi_t \rangle = - \int_0^{R_c} (e^{-\alpha r} f_{cut}(r))^2 d\tau \tag{10}
\]

The energy functional as a function of the variational parameter \( \alpha \) for a given confinement radius \( R_c \) is the following:

\[
E_{var}(\alpha; R_c) = \langle \psi_t | H | \psi_t \rangle \tag{11}
\]

Minimizing \( E_{var} \) respect \( \alpha \) for a fixed value of \( R_c \), we find an upper limit for the ground state energy \( E \) of the CHA.

Most of the integrals involved in the calculation of the energy functional (11) are obtained in analytical form, except for the cut-off functions VI and VII. In order to minimize the energy functional, it is necessary to fix the value of \( R_c \) and vary \( \alpha \). We used the program Mathematica 9 and the command \texttt{FindMinimum} to obtain the minimum of Eq. (11) for each value of \( R_c \). The optimum values of the energy for every trial wavefunction as a function of \( R_c \) are shown in Table I. We also show the most accurate energy values [10], which we will call “the exact values”.

3. The Shannon entropy

The Shannon entropy in coordinate space is defined as [27,28]

\[
S_r = \int_{R_c}^0 d^3r |\psi_t|^2 \ln |\psi_t|^2 , \tag{12}
\]

where \( \psi_t \) is normalized to one. We must remember that the trial wavefunction has the following form \( \psi_t = Ae^{-\alpha r} f_{cut}(r)Y_{00}(\theta, \varphi) \), where \( A \) is the normalization constant and \( Y_{00}(\theta, \varphi) = 1/\sqrt{4\pi} \).

Gadre et al. used the Shannon entropy as a measure of the quality of the basis set for free atomic and molecular systems [27,28]. In their calculations they constructed a wave function as a linear combination of functions from a basis set. They observed that, on having increased the number of functions of the basis set, the constructed wavefunction approaches better the exact wavefunction of the system, and the Shannon entropy increases approaching the Shannon entropy of the exact wavefunction [9-10,33]. According to the Maximum Entropy Principle due to Jaynes [29] one must choose the trial wavefunction whose Shannon entropy is the highest among a set of functions that satisfy the appropriate constraints of the system. In this way, Shannon entropy could offer an alternative form to determine the quality of the trial wavefunction for confined systems.
4. Results

The optimized energies as a function of \(R_c\) for every trial wave function, appears in the Table I. We also calculate the relative percentage error defined in the following way:

\[
E_{rel} = \frac{E - E_{exact}}{E_{exact}} \times 100.
\] (13)

This quantity, \(E_{rel}\), is always positive because the energy calculated in a variational way \(E\) is always greater than the exact energy [9-10,33]. In Fig. 1 we plotted \(E_{rel}\) vs \(R_c\) for every trial wavefunction considered in this work.

From Table I, we see that for confinement radii less than 1.0 au, the trial wavefunction VI gives the lowest energy with \(f_{cut}(r) = j_0((X_{10}r)/R_c)\). This can be understood because in the strong confinement regime the system behaves like a free particle inside an impenetrable spherical box [25] whose radial wavefunctions are precisely the spherical Bessel functions [26]. For confinement radii between 0.8 and 1.7 au, the trial wavefunction II gives the lowest energy. From Fig. 1 we can observe that the wavefunctions VI and VII produce an overestimation of the energy in a neighborhood of \(R_c = 2\) au. We also can observe that the trial wavefunction IV overestimates the ground state energy for \(R_c < 2\) au.

As we can see from the Fig. 1, every trial wavefunction has a region in \(R_c\) at which it approaches better to the exact energy [9-10,33]. Nevertheless, the trial wavefunctions I - III are those that predict energies nearer to the exact value [9-10,33]. The wavefunction V gives the largest error in the region \(0.5 \leq R_c \leq 4\).

Finally, for \(R_c\) larger than 2.0 au all trial wavefunctions give good estimations for the ground state energy. This behavior is shown graphically in Fig. 1.

We calculated the Shannon entropy for each of the trial wavefunctions. The Shannon entropy for all trial wavefunctions have smaller values than the Shannon entropy for the exact wavefunction [9-10,33]. We define the Shannon entropy relative error \(S_{rel}\) as follows:

\[
S_{rel} = \frac{S_r - S_{trial}}{S_r} \times 100,
\] (14)

where \(S_r\) and \(S_{trial}\) are the Shannon entropy for the exact wavefunction [9-10,33] and for any trial wavefunction, respectively. In the Fig. 2 we show the relative error \(S_{rel}\) for each of the trial wavefunctions. For the region, \(0.5 < R_c < 0.8\) au, the trial wavefunctions that have values closer to the exact Shannon entropy [32] are I - III and VI - VII. While in the region \(0.8 < R_c < 2\) au, the trial wavefunctions with less error are I - III. For values, \(R_c > 2\) au, the trial wavefunction IV has the lowest errors. Whereas the wavefunction V produces the largest errors. The maximum error produced by the all wavefunction are reached near the \(R_c = 0.8\).

In the interval, [0.5,1.5], trial wavefunction II that produces small errors on the prediction of the Shannon entropy and in the energy whereas the function IV has similar behavior in for \(R_c > 5\) au. We conclude that the Gadre’s conjecture is not a good criterion to decide the quality of the trial wavefunctions.

In Fig. 3 we show the cusp condition at the origin of the trial wavefunctions I-VII as a function of \(R_c\). The cusp con-
The cusp condition of CHA produced by the seven different trial wavefunctions as a function of the confinement radius $R_c$.

Figure 3. The cusp condition of CHA produced by the seven different trial wavefunctions as a function of the confinement radius $R_c$.

The cusp condition at the origin of the exact wavefunction for CHA is equal to 1. Accordingly, the best trial wavefunction will be the one with the cusp closer to 1. As we can see, for large confinement radius all functions satisfy this requirement. However, as the confinement radius $R_c$ decreases the cusp condition for all trial functions start to move away from 1. In the region, $R_c \leq 2$ au, this difference begins to be noticeable. The wavefunctions V, VI and VII are those closer to one, reaching a value of 0.5 at $R_c \sim 0.5$ au. The cusp values for the rest of the trial functions are not good, few of them having a cusp value greater than 1.5, as for example, the wavefunction I, II and IV at, $R_c \sim 0.5$ au.

These two criteria, the Shannon entropy and the cusp condition, are not sufficient to decide which of trial wavefunctions approximates better to the exact one. To try to give a clearer answer to this question, we need to compute few expectation position values by using the trial wave functions I-VII and comparing those results with the exact ones.

The position expectation values are given by:

$$
\langle r^n \rangle = \frac{\langle \psi_t | r^n | \psi_t \rangle}{\langle \psi_t | \psi_t \rangle} \int_{0}^{R_c} (e^{-\alpha r} f_{cut}(r))^2 r^{n+2} dr
$$

whereas the relative error is the following:

$$
Error \langle r^n \rangle = \frac{\langle r^n \rangle - \langle r^n \rangle_{exacto}}{\langle r^n \rangle_{exacto}} \times 100.
$$

The relative error for $n = -1, 1$ and 2 are shown in Figs. 4-6. In Fig. 4 we show the relative error in the calculation of the expectation value $\langle r^{-1} \rangle$ as a function of the confinement radius, $R_c$, for all wavefunctions I-VII. For a confinement radius of $R_c = 0.5$ au all the trial wavefunc-
The confinement radius at which the CHA total energy becomes zero is called the critical cage radius $r_c$ [30,34,36]. Sommerfeld and Welker [30], and recently Ley-Koo [37] showed that $r_c$ can be obtained as a function of the zeros of the Bessel function of first class $J$ of order $2l + 1$.

$$r_c = \frac{1}{8}(\chi_{i,2l+1})^2,$$  \hspace{1cm} (17)

Where $\chi_{i,2l+1}$ denotes the $i$th zero of $J_{2l+1}$.

The exact value of the critical radius for the CHA ground state is equal to 1.8353. The critical radius predicted by the trial wave functions I-VII are: 1.83, 1.83, 1.79, 1.75, 1.69, 1.851 and 1.852, respectively. The wave functions I-III are the best to predict a critical cage radius.

Seven decades ago de Groot and ten Seldam [38] noted that each zero of the wave function, of some state of the free hydrogen atom, is a cage size $R_c$ for the confined atom, and the latter has the same energy as the state of the former. For example, the $2s$ wave function of the free hydrogen atom has a node at $r = 2$ au.[39-41] The ground state energy of the hydrogen atom confined in a box $R_c = 2$ au, is $-1/8$ au, that corresponds to the energy of the $2s$ state of the free hydrogen atom.

The wave function of the state $2s$ of the free hydrogen atom is

$$\psi_{2s} = N(2 - r)e^{-r/2} = (2N)(e^{-r/2})\left(1 - \frac{r}{2}\right),$$  \hspace{1cm} (18)

apart from the normalization, it is identical to the function I for $R_c = 2$ and $\alpha = 1/2$.

The first node of the wave function of any given state of the free hydrogen atom gives a cage of size $R_c$, in which case the ground state of the CHA has the same energy as the free hydrogen atom. This argument can be extended for the identification of the excited states of the CHA. However, this procedure gives the ground state energy of the CHA only for particular values of $R_c$.

5. Conclusions

In this work we used the direct variational method to compute the ground state energy of the confined hydrogen atom in an impenetrable spherical box. In this approach, the trial wavefunction is constructed as the product of the $1s$ hydrogen-like (free) orbital times a cut-off function. Seven different cut-off functions were used for calculations of the energy, cusp condition, Shannon entropy, $\langle r^{-1}\rangle$, $\langle r \rangle$, $\langle r^2 \rangle$ and the critical cage radius as a function of $R_c$.

We found that there are regions of $R_c$ for which certain trial wavefunctions predict a physical property with a small error, but in other regions the same wavefunctions predict it with a high error. For example, the trial wavefunctions VI and VII predict energy values with small errors in the region of strong confinement, $R_c < 1$, but large error in $1 \leq R_c \leq 3$. On the other hand, the wavefunction I-III give small errors in the energy for the region $R_c > 2$. It should be noted that
the functions I and III behave in much the same way, but the
calculations with the wavefunction of type I are more simple
than those with the wavefunction of type III. The trial
wavefunction V gives the larger errors in the estimation of
the energy, and for this reason it is not recommended for this
kind of computations.

According to the criterion on the degeneracy which results
from choosing the confinement radius, $R_c$, on the radial node
of the free wave function, the best function should be the
wavefunction I. However, this is apparent because this wave-
function I does not behave as the wave function of the free
particle, for small radii. A good trial wave function must be-
have as the wavefunction of a free particle in a box for small
values of $R_c$ and like a free $1s$ hydrogen wavefunction for
large values of $R_c$.

The best wavefunction is one that reproduces all the physi-
cal properties of the system with the lowest error comparing
with the exact ones. None of the wavefunctions studied in this
work satisfy this definition. We can conclude that, the wave-
functions VI and VII are very useful for strong confinement
(small $R_c$). For intermediate and large values of $R_c$ wave
functions of types I and II are the most recommendable.

One way to construct better trial wavefunctions for this
problem consists in the inclusion of more radial terms and
variational parameters in the radial wavefunction. For exam-
ple, Varshni [22] improved wavefunction I, as follows:

$$\psi = \left(1 - \frac{r}{R_c}\right)^\alpha e^{-\alpha r} (1 + \beta r),$$

Where $\alpha$ and $\beta$ are variational parameters.

Whereas, Montgomery [36] proposed a generalization of
Varshni’s wavefunction:

$$\psi = \left(1 - \frac{r}{R_c}\right)^\alpha (1 + \beta r) \left( e^{-\alpha r} \sum_p a_p r^p \right)$$

Where $a_p$, are linear variational parameters and $\alpha$ is a
non-linear variational parameter.

The last trial wavefunction gives energy and other physi-
cal properties near to the exact ones [10]. We must note that
Varshni [10] and Montgomery [36] used $(1 - (r/R_c))$ as a
cut-off function.

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