Comparative study of the scaling behavior of the Rényi entropy for He-like atoms

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Abstract. We solve the Schrödinger equation in the spherical or Hylleraas-coordinate systems, and within the framework of the Ritz’s variational principle. The eigenvalues, and the eigenfunctions \( \psi(r) \) in \( r \)- or Hylleraas-space for the \( 1s^2 \)-state of the He-like atoms as a function of two variational parameters are calculated. Using a simple scaling procedure, we calculate the scaled wavefunction as a function of the nuclear charge \( Z \). Given the density of states, \( \rho(r) \), the scaling behavior of the information entropies, e.g., Fisher, Shannon and Rényi’s entropies, with their powers and products, as functions of \( Z \) are calculated. Scaled wavefunctions for the \( 1s^2 \)-state of the He-like atoms, with exchange, have been used to study the scaling behavior. Our results agree with the published results. Furthermore, we present a simple logarithmic equation that shows the dependence of information entropies on \( Z \) for He-like atoms. The formulation enhances the computational efficiency of the entropies and other related quantities.

1. Introduction

In atomic and molecular physics [1], the electronic density \( \rho(r) \) plays a crucial role in calculating many measurable physical quantities that are related to the expectation values. Lately, \( \rho(r) \) has been introduced to calculate many information entropies [2], such as the Shannon [3], the Fisher [4] and the Rényi [5] entropies.

Recently, Rényi entropy and its power have been investigated in different areas of science and engineering [6]. Fisher information, \( I_\rho \), Shannon entropy, \( S_\rho \), and Rényi entropy, \( R_\beta \), are defined, respectively, as follows

\[
I_\rho \equiv \int \rho(r_1, r_2) \nabla (\ln[\rho(r_1, r_2)])^2 \, dr_1 dr_2, 
\]

(1)

\[
S_\rho \equiv -\int \rho(r_1, r_2) \ln[\rho(r_1, r_2)] \, dr_1 dr_2, 
\]

(2)

\[
R_\beta \equiv \frac{1}{1-\beta} \ln \int \rho(r_1, r_2)^\beta \, dr_1 dr_2, 
\]

(3)

where \( dr = r^2 \, dr \, d\Omega \) and \( d\Omega = \sin\theta \, d\theta \, d\phi \). In three dimensions, the Shannon entropy power, \( J_\rho \), is defined as [7]
The Fisher-Shannon information product, $P_\rho$, is defined by

$$P_\rho \equiv I_\rho J_\rho / 3, \quad (5)$$

which satisfies the uncertainty relation $P_\rho > 0$.

The quantity $I_\rho$ is considered as a gauge of the sharpness or concentration of the density $\rho(r)$. Moreover, the Fisher information, $I_\rho$, constitutes a measure of the gradient content of $\rho(r)$, which makes it quite sensitive even to small localized perturbations of $\rho(r)$. The Shannon entropy $S_\rho$ provides a measure of information about the density of states in the respective spaces. A more localized distribution $\rho(r)$, corresponds to the smaller value of $S_\rho$. The smaller $S_\rho$ is, the more concentrated the wave function of the state becomes. $S_\rho$ is a limit value of the Rényi entropy as $\beta \to 1$. In atomic systems, the Shannon entropy power, $J_\rho$, measures the spatial delocalization of the electronic cloud.

In this paper, we consider the simple uncorrelated two electron (i.e., He-Like structure) wavefunction $[1]$

$$\phi_1(r_1, r_2; a) = \frac{a^3}{\pi} e^{-a(r_1 + r_2)}, \quad (6)$$

where $a = Z - z_0$ and $z_0$ is the screening charge which we set to 5/16 (and also to 0 when no screening is employed). We also consider the asymmetric and exchange, but uncorrelated wavefunction $\phi_2$, given here as

$$\phi_2(r_1, r_2; a, b) = A \left[e^{-ar_1 - br_2} + e^{-br_1 - ar_2}\right], \quad (7)$$

where $a$ and $b$ are both variational parameters and $A$ is a normalization constant. The density of states in this context is given by

$$\rho_n(r_1, r_2; a, b) = |\phi_n(r_1, r_2; a, b)|^2, \quad (8)$$

subject to the normalization condition

$$(4\pi)^2 \int r_1^2 r_2^2 \rho(r_1, r_2; a, b) \, dr_1 dr_2 = 1. \quad (9)$$

Alternatively, for a wavefunction, $\phi_2$, the Hylleraas coordinate system may be used, in which $s = r_1 + r_2$, $t = r_1 - r_2$, and $u = r_{12}$, subject to the conditions $-u \leq u$, $0 \leq s \leq \infty$ and the volume element $d\tau = \pi^2 (s^2 - t^2) u$.

On the other hand, for the wavefunctions $\phi_1$, it is straightforward to show that the Shannon entropy takes the form

$$S_\rho = 6 + 2 \ln(\pi) - 6 \ln(a), \quad (10)$$

while the Rényi entropy takes the form

$$R_\beta = \frac{(2\beta - 2) \ln(a^3/\pi) - 6 \ln(\beta)}{1 - \beta} \to S_\rho, \quad (11)$$

which tends to $S_\rho$ as $\beta \to 1$. 

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Table 1. The quantities for seven He-like atoms, using the wavefunction \( \phi_2 \). The literature for energy is cited as Ref. [8]. All results are given in atomic units.

\[
\begin{array}{cccccccc}
 & \text{He} & \text{Li}^+ & \text{Be}^{2+} & \text{B}^{3+} & \text{C}^{4+} & \text{B}^{5+} & \text{O}^{6+} \\
Z & 2 & 3 & 4 & 5 & 6 & 7 & 8 \\
\hline
a & 1.1885 & 2.0789 & 2.9847 & 3.9012 & 4.8256 & 5.7561 & 6.6914 \\
b & 2.1831 & 3.2949 & 4.3897 & 5.4734 & 6.5491 & 7.6187 & 8.6834 \\
\hline
-E & 2.8744 & 7.247 & 13.621 & 21.996 & 32.371 & 44.746 & 59.121 \\
-E_{[8]} & 2.9037 & 7.279 & 13.655 & 22.030 & 32.406 & 44.781 & 59.156 \\
I_\rho & 11.502 & 28.995 & 54.491 & 87.990 & 129.48 & 178.98 & 236.48 \\
S_\rho & 5.4482 & 2.5234 & 0.5745 & -0.8920 & -2.0690 & -3.0521 & -3.8965 \\
R_1 & 5.4452 & 2.5229 & 0.5742 & -0.8920 & -2.0680 & -3.0527 & -3.8968 \\
J_\rho & 2.2085 & 0.3147 & 0.0858 & 0.0322 & 0.0147 & 0.0076 & 0.0043 \\
P_\rho & 8.4678 & 3.0422 & 1.5595 & 0.9472 & 0.6366 & 0.4564 & 0.3435 \\
R_2 & 3.5356 & 0.6415 & -1.2950 & -2.7550 & -3.9278 & -4.9082 & -5.7505 \\
R_3 & 2.6474 & -0.2354 & -2.1677 & -3.6254 & -4.7968 & -5.7762 & -6.6179 \\
\end{array}
\]

Table 2. The scaling properties found in Table 1.

\[
\begin{align*}
\alpha &= 0.9121 \ Z^{-0.6754} \\
\beta &= 1.0818 \ Z^{-0.0297} \\
E &= -0.996 \ Z^2 + 0.573 \ Z \\
J_\rho &= 45.32 \ Z^{-4.477} \\
P_\rho &= 39.464 \ Z^{-2.3} \\
R_1 &= -6.673 \ln(Z)+7.1536 \\
R_2 &= -6.676 \ln(Z)+8.0485 \\
R_3 &= -6.663 \ln(Z)+7.1536 \\
\end{align*}
\]

Table 3. Selected quantities for the three wavefunctions of the He-atom.

\[
\begin{array}{cccc}
 & \phi_1(z_0 = 0) & \phi_1(z_0 = 5/16) & \phi_2 \\
\hline
-E & 4.0 & 2.8476 & 2.8744 \\
R_1 & 4.1305 & 5.1496 & 5.4452 \\
R_2 & 2.2894 & 3.3088 & 3.5356 \\
R_3 & 1.4264 & 2.4458 & 2.6474 \\
I_\rho & 16.0 & 11.390 & 11.502 \\
\langle r_1^2 \rangle & 0.75 & 1.0535 & 1.2378 \\
\langle p_1^2 \rangle & 4.00 & 2.8476 & 2.8756 \\
\langle r_1^2 \rangle \langle p_1^2 \rangle & 3.00 & 3.00 & 3.5596 \\
\end{array}
\]

2. Results and Discussion

A symmetric and exchange wavefunction, \( \phi_2 \), is used to calculate the values for the Shannon and Rényi entropies and other related quantities such as the Shannon entropy power, Fisher-Shannon information product. The main results are displayed in table 1. From table 1, the following observations can be made:

- Given the variational parameters \( a \) and \( b \), good agreement with the exact values for the energy, at least to 3 decimal places, is observed. To facilitate the comparison with Ref. [8], their data has been truncated to only five digits.
- \( R_1 \) changes its sign for \( Z > 4 \). Furthermore, \( R_2 \) and \( R_3 \) also change their sign for \( Z > 2 \).
- The inequality of the product \( P_\rho > 0 \), is satisfied.
• The product and the power decrease gradually.

Table 2 lists the scaling laws for each quantity sought which was computed using curve-fitting. Furthermore, in this comparative study, table 3 provides a few quantities that present the following observations:

• Neglecting the electron-electron interaction in the unscreened wavefunction \( \phi_1(z_0 = 0) \) gives lower bounds on all quantities.

• Including the electron-electron interaction, as in the \( \phi_1(z_0 = 5/16) \), improves the results.

• Including the electron-electron interaction and exchange further improves the results.

• For both the unscreened wavefunction \( \phi_1(z_0 = 0) \) and the screened wavefunction \( \phi_1(z_0 = 5/16) \), the product \( \langle r_1^2 \rangle \langle p_1^2 \rangle = \langle r_2^2 \rangle \langle p_2^2 \rangle = 3 \), where the expectation values \( \langle r_i^2 \rangle \) and \( \langle p_i^2 \rangle \) for a single electron, are defined as follows

\[
\langle r_i^2 \rangle = (4\pi)^2 \int dr_1 dr_2 \ r_1^2 r_2^2 \left( |\phi_i| \right)^2,
\]

and

\[
\langle p_i^2 \rangle = (4\pi)^2 \int dr_1 dr_2 \ r_1^2 r_2^2 \phi_i \frac{1}{r_1} \partial_{r_1,r_1}(r_1 \phi_i).
\]

• The effect of the exchange of the two electrons for \( \langle r_1^2 \rangle \langle p_1^2 \rangle \) or \( \langle r_2^2 \rangle \langle p_2^2 \rangle \) for \( Z < 5 \) is vividly clear. However, it diminishes and may be neglected for values of \( Z \) greater than 5.

3. Conclusion

The scaled ground state wavefunction, in r-space, of two variational parameters is used to calculate the ground state energies for seven He-like atoms. In addition, the information entropies for Fisher, Shannon and Rényi have been calculated and their scaled expressions have been derived. The dependence of such quantities on the atomic number \( Z \) is clear. Furthermore, to a good degree of accuracy, we are able to deduce expressions for Rényi entropy and consequently Shannon entropy, and other related quantities employing simple equations. This helps in computing these quantities efficiently. To our knowledge, the results are new and encouraging to pursue further developments using the \( J \)-matrix method [9] and correlated wavefunctions with different potentials.

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