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Discontinuity of Shannon information entropy for two-electron atoms

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Abstract

Atomic Shannon information entropies are computed using Hyllerass-type basis functions for the helium isoelectronic series. As one varies the nuclear charge Z for the two-electron atoms, finite size scaling analysis shows that the system exhibits a critical point of the ground state energy at $\lambda_c = 1/Z_c = 1.0971 \pm 0.0005$ with a critical exponent $\alpha = 1$, $E(\lambda) \sim (\lambda - \lambda_c)^{\alpha}$. At the critical point, the ground state energy becomes degenerate with the hydrogenic threshold. The Shannon information entropy develops a step-like discontinuity at λ_c. Further analysis indicates that the entropy as a function of λ is proportional to the first derivative of the energy with respect to λ. The critical exponent for the entropy $\alpha_s = 0$, $S(\lambda) \sim (\lambda - \lambda_c)^{\alpha_s}$.

1. Introduction

Shannon information entropy measures the extent, spread, shape, uncertainty, and the information content of the underlying distribution from which it was derived [1]. Shannon proposed that the information entropy for a system with a continuous probability distribution $P(x)$ in one dimension could be characterized as [1]

$$S = -\int P(x)\ln P(x)\mathrm{d}x, \quad \int P(x)\mathrm{d}x = 1. \tag{1}$$

For atomic systems one can define the Shannon entropy in position space S_ρ, where the probability distribution is the electronic charge density $\rho(r)$. The momentum space Shannon entropy S_π of the electronic momentum density $\pi(p)$ is defined in a fully analogous way. The importance of the entropy sum $S_t = S_\rho + S_\pi$ is firmly established by noting that a stronger version of Heisenberg's uncertainty principle may be formulated for any quantum N-electron system [2,3],

$$S_t \geqslant 3N(1 + \ln\pi) - 2N\ln N. \tag{2}$$

Recently, numerical calculations demonstrate that the total entropy is invariant to scaling and could be used to measure basis set quality [3,4]. The total entropy also measures correlations in many-electron systems [5] and nuclei [6]. It has linear dependence on the logarithm of the number of particles in atoms, nuclei, atomic clusters [7,8] and even in correlated boson systems [6].

Shannon entropy in atomic calculations has further been related to various properties such as atomic ionization potential [9], molecular geometric parameters [10], chemical similarity of functional groups [11], characteristics of correlation methods for global delocalizations [12], molecular reaction paths [13], orbital-based kinetic theory [14], and highly excited states of single-particle systems [15].

In previous studies [16,17], using finite size scaling, we have shown that two-electron atoms exhibit a critical point as one varies the nuclear charge Z. At the critical point $\lambda_c = 1/Z_c = 1.0976 \pm 0.0004$ the ground state energy becomes degenerate with the hydrogenic threshold with a critical exponent $\alpha = 1$, $E(\lambda) \sim (\lambda - \lambda_c)^{\alpha}$. In the present work we calculate the atomic Shannon

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information entropies using Hyllerase-type basis functions for the helium isoelectronic series. At the critical point, the Shannon information entropy develops a step-like discontinuity at λ_c with a critical exponent α_s=0, $S(\lambda) \sim (\lambda - \lambda_c)^{\alpha_s}$.

2. Finite size scaling for two-electron atoms

The Hamiltonian for two-electron atoms in the scaled variable, $r \to r/Z$, is given by

$$H = -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{1}{r_1} - \frac{1}{r_1} + \frac{\lambda}{r_{12}}, \tag{3}$$

where $\lambda = 1/Z$ is the inverse of the nuclear charge Z and measures the strength of the interelectronic repulsion. By varying the parameter λ one can study the behavior of the energy for the helium isoelectronic sequence [16] starting from $\lambda = 1$, which corresponds to the stable H^- anion [18]. For this Hamiltonian, a critical point means the value of λ_c for which a bound state energy becomes degenerate with the hydrogenic threshold.

To apply the finite size scaling one has to choose a convenient basis set to obtain the lowest two eigenvalues, $E_0(\lambda)$ and $E_1(\lambda)$. Since our focus on the ground state $^1S_0$, we can choose the following Hylleraas-type basis sets [19,20]:

$$\Psi = \sum_{i,j,k} C_{i,j,k} \frac{1}{\sqrt{2}} (r_1^i r_2^j e^{-\alpha r_1 - \beta r_2} + r_1^j r_2^i e^{-\beta r_1 - \alpha r_2}) r_{12}^k, \tag{4}$$

in which i,j,k are indices defining the Pekeris shell [21] with $0 \leqslant i,j,k \leqslant N$ and $i+j+k \leqslant N$. N is the radius of the shell which determines the expansion length $M(N)$ of Eq. (4). Our numerical results show that $M(N) \sim N^{2.27}$. Such a systematic expansion of the wave function in the Hylleraas-type basis sets has been used extensively in calculations of the ground and excited states of the two-electron atoms [22–24,17].

In Eq. (4) α and β are the two hydrogenic exponents. For the ground state of helium in Eq. (3) we choose $\alpha = 2$ and $\beta \approx 2$ and $\alpha = 1$ and $\beta \approx 1$ for the H^- anion at $\lambda = 1$. As we increase the parameter λ to simulate the electron ionization we have found that $\beta = 0.21$ is the optimal choice for the wave function. Putting the trial wave function into the Schrödinger equation and diagonalizing the energy matrix, we obtain the eigenvalues and the eigenvectors **C**, the expansion coefficients in Eq. (4). All the numerical calculations were performed using 64-bit Fortran 95 codes.

Fig. 1 shows the behavior of the ground state energy as a function of λ for different values of $N = 5,6,7,\ldots,13$. The results are in complete agreement with our previous results [16,25]. In the present work, $\alpha = 1$ and $\beta = 0.21$ are fixed and the energy eigenvalues are obtained by systematically increasing the order N for the expansion in Eq. (4). In Fig. 1 the energy lines for

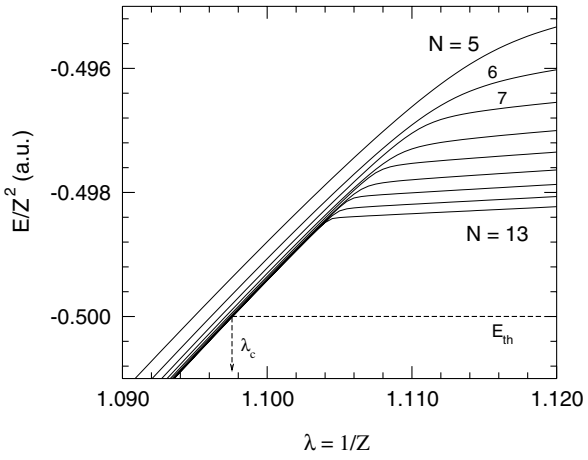

Fig. 1. The ground state scaled energy, E/Z^2, as a function of $\lambda = 1/Z$, where Z is the nuclear charge, for different basis set orders $N = 5,6,\ldots,13$. The dashed line corresponds to the threshold energy, $E_{th} = -0.5$ a.u.

each order N gradually go up at $\lambda < 1.104$ and bend over sharply at $\lambda = 1.104$. As $N \to \infty$ the true ground state energy becomes degenerate with the lowest continuum $E_0 = -1/2$ at λ_c [25].

Now, the finite size scaling analysis can be used to obtain the critical point. The phenomenological renormalization equation for finite systems of sizes N and $N+1$ is given by [16]

$$\left(\frac{E_1(N)}{E_0(N)}\right)^N = \left(\frac{E_1(N+1)}{E_0(N+1)}\right)^{N+1} \tag{5}$$

and has a fixed point at $\lambda_c^{(N)}$. It is expected that the succession of the crossing points $\lambda_c^{(N)}$ in the limit of infinite size to converge to the true λ_c. Fig. 2 shows the crossing points, which are the fixed points of Eq. (5), for $N = 5,6,7,\ldots,13$. The values of the fixed points as a function of N can be extrapolated to the limit $N \to \infty$ by using the Bulirsch and Stoer algorithm [17]. We obtain $\lambda_c = 1.0971$ as shown in the window of Fig. 2.

Next, we examine the conditional probability in order to visualize the attractive and repulsive forces which influence the system close to the critical point. This function represents the probability distribution seen by one electron given that the other electron is fixed at a certain distance. We define the conditional probability to find one electron at distance r_1 when the other is fixed at $r_2 = 1$ by

$$P(r_1)_{r_2=1} = \frac{2\pi}{r_1} \int_{|r_1-1|}^{r_1+1} |\Psi|^2 \, r_{12} \, dr_{12}. \tag{6}$$

Fig. 3 shows the three conditional probability curves corresponding to $\lambda < \lambda_c$, $\lambda = \lambda_c$, $\lambda > \lambda_c$ at $\lambda = 1.1050$, 1.1055, 1.1060, respectively. In order to compare the three curves, they were normalized such that the first maximum is one. For $\lambda < \lambda_c$ the leading maximum is at small distance, $r_1 \approx 2$ a.u., for $\lambda \to \lambda_c$ the two maxima

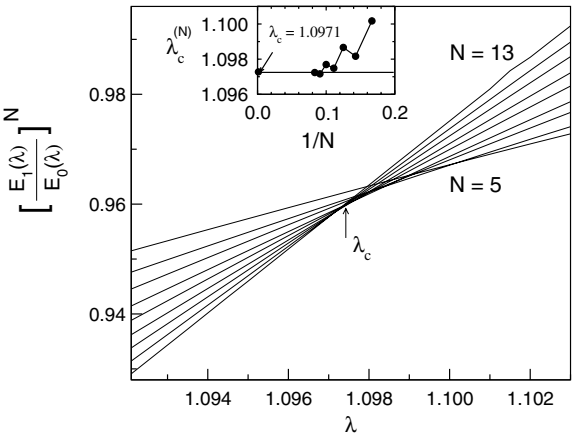

Fig. 2. The ratio between the ground state energy, E_0, and the second lowest eigenvalue, E_1, raised to a power N as a function of $\lambda = 1/Z$ for $N = 5, 6, \ldots, 13$. The small window shows the pseudocritical points, $\lambda_c^{(N)}$ as a function of $1/N$. The value of the extrapolated $\lambda_c = 1.0971$ is also shown as a dot.

reaches the same height and for $\lambda > \lambda_c$, the second maxima is getting larger and the nuclear charge cannot bind two electrons. Thus one electron move to infinity and become a free electron for $\lambda > \lambda_c$.

3. Criticality of Shannon information entropy

Information theory is the framework in which one attempts to measure the amount of information inherent in a system. Shannon information entropy for the two-electron systems with electronic charge distribution $\rho(r)$ is given by

$$S = -\int_0^\infty \rho(r) \ln \rho(r) 4\pi r^2 \, dr, \tag{7}$$

where the electron density $\rho(r_1)$ can be obtained from the wave function $\Psi(r_1, r_2, r_{12})$ by averaging over the other coordinates,

$$\rho(r_1) = \frac{2\pi}{r_1} \int_0^\infty \int_{|r_1 - r_2|}^{r_1 + r_2} |\Psi|^2 r_2 \, dr_2 \, r_{12} \, dr_{12}, \tag{8}$$

in which $\rho(r)$ is normalized to 1,

$$\int_0^\infty \rho(r) 4\pi r^2 \, dr = 1. \tag{9}$$

$\rho(r)$ is continuous over $0 \leqslant r \leqslant \infty$, representing a radial correlation of electron 1 with electron 2 bounded to the nucleus.

Fig. 4 shows the calculated entropy S from Eq. (7) as a function of λ for different values of N. For $\lambda < \lambda_c$, the entropy is about $S \approx 6.5$ and slowly increased for larger values of λ up to the critical point. At the critical point, the entropy develops a step-like discontinuity and the entropy jumps to higher value, $S \approx 10.7$. This behavior resemble the behavior of the first derivative of the energy with respect to λ, which develops a step-like discontinuity at λ_c. Fig. 5 shows the ratio of the two consecutive entropies raised to power N, $(S_{N+1}/S_N)^N$, as a function of λ. Each of the corresponding curves exhibits a sharp peak. The height of the peak is proportional to the entropy gradient. The peak increases rapidly as N becomes large while the position of the peak approaches $\lambda_c = 1.09$ which compares well with the most accurate estimate of $\lambda_c = 1.097$.

Now, let us determine the critical exponent α_s for the entropy

$$S(\lambda) \sim (\lambda - \lambda_c)^{\alpha_s}. \tag{10}$$

In our previous studies we have shown that the critical exponent for the energy is 1,

$$E(\lambda) = E(\lambda_c) + 0.235(\lambda - \lambda_c)^1, \tag{11}$$

where $E(\lambda_c) = -1/2$.

Our numerical results indicate that the entropy is proportional to the first derivative of the ground state energy with respect to λ. Fig. 6 show the first derivative of energy with respect to λ (solid lines) and the fitted entropy (dots) assuming the form

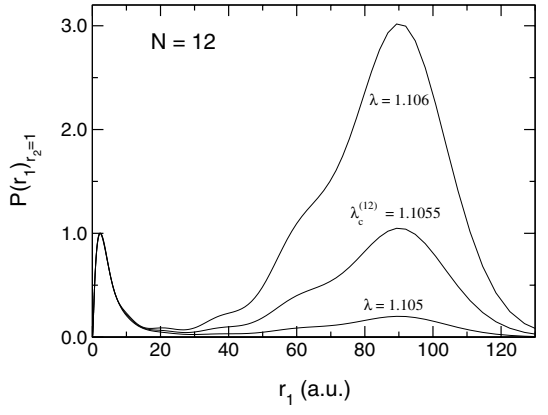

Fig. 3. Conditional probability distribution, $P(r_1)_{r_2=1}$, as a function of r_1 for $\lambda = 1.1050, 1.1055, 1.1060$ with basis set order $N = 12$. The three curves are scaled to 1 at $r_1 = 2.3$.

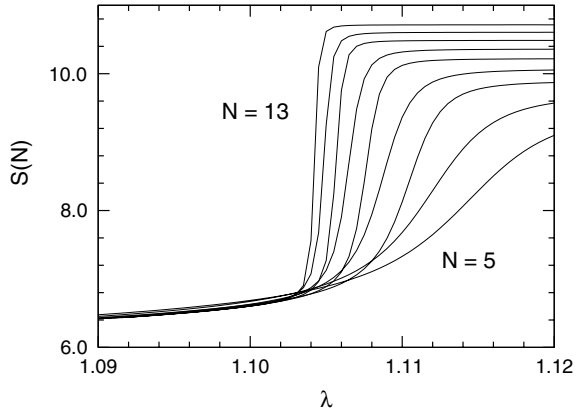

Fig. 4. Shannon information entropy $S(N)$ as a function of λ for $N = 5, 6, \ldots, 12$.

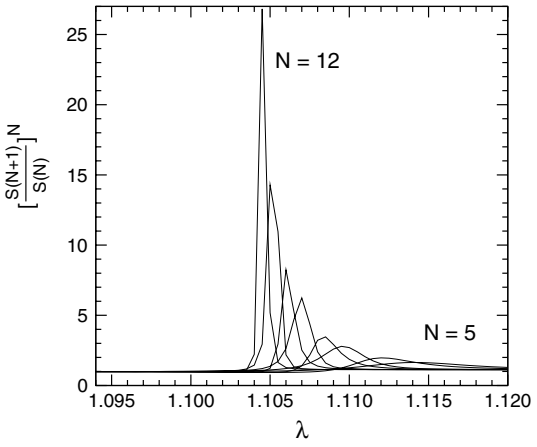

Fig. 5. The ratio between two consecutive entropies raised to power N, $(\{S(N+1)\}/S(N))^N$ as a function of λ for $N = 5,6,\ldots,13$.

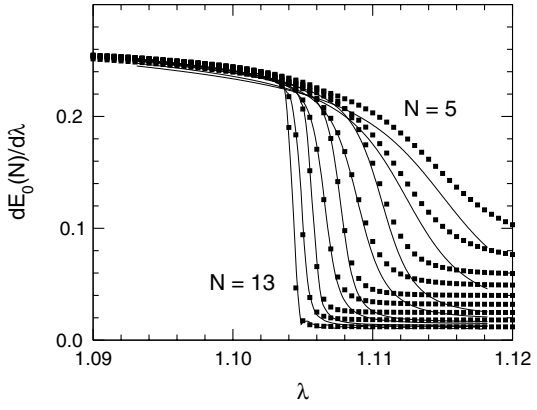

Fig. 6. The first derivative of energy, $dE_0(N)/d\lambda$ (solid lines) and the fitted derivative from the entropy $S(N) = 10.93 - 17.69\,dE_0(N)/d\lambda$ (dots) as a function of λ for $N = 5,6,\ldots,13$. Note that the entropy, $S(\lambda)$, is proportional to the first derivative of the energy with respect to λ.

$$S(\lambda) = a - b\frac{dE}{d\lambda} \tag{12}$$

with $a = 10.93$ and $b = 17.69$. For large values of N, the fitted results are good agreement with calculated first derivative of the ground state energy. From this numerical fit, the critical exponent for the entropy $\alpha_s = 0$ as $\lambda \to \lambda_c$.

4. Conclusions

The Shannon information entropies for the two electron atoms were calculated using a highly accurate wave function based on expansion in Hyllerase-type basis set. At the critical point $\lambda_c = 1/Z_c = 1.0976$, the entropy develops a step-like discontinuity which resemble the behavior of the first derivative of the energy with respect to λ. Numerical analysis shows that the entropy is indeed proportional to the first derivative of the ground state energy with respect to λ and thus its critical exponent $\alpha_s = 0$. This physical picture is consistent with the definition of Shannon information entropy which measures the delocalization or the lack of structure in the respective distribution. Thus S is maximal for uniform distribution that for an unbound system and is minimal when the uncertainty about the structure of the distribution is minimal. For two electron atoms the entropy S is minimal when the two electrons are bound in the ground state $\lambda < \lambda_c$ then develops a step-like discontinuity at λ_c and jumps to maximal value $S \approx 10.7$ for $\lambda > \lambda_c$.

Recently, we have established the analogy between symmetry breaking of electronic structure configurations and quantum phase transitions [26]. In particular for two electron atoms, the mapping between symmetry breaking and mean-field theory of phase transitions was shown by allowing the nuclear charge Z, the parameter which tunes the phase transition, to play a role analogous to temperature in classical statistical mechanics. In this study we have shown that one can add the entropy to this mapping. Here the Shannon information entropy develops a step-like discontinuity as a function of λ which "resemble" the step-like discontinuity of the thermodynamic entropy as a function of the temperature in a first order phase transition.

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