Finite size scaling for the atomic Shannon-information entropy

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We have developed the finite size scaling method to treat the criticality of Shannon-information entropy for any given quantum Hamiltonian. This approach gives very accurate results for the critical parameters by using a systematic expansion in a finite basis set. To illustrate this approach we present a study to estimate the critical exponents of the Shannon-information entropy $S \sim (\lambda - \lambda_c)^{\alpha_S}$, the electronic energy $E \sim (\lambda - \lambda_c)^{\alpha_E}$, and the correlation length $\xi \sim |\lambda - \lambda_c|^{-\nu}$ for atoms with the variable $\lambda = 1/Z$, which is the inverse of the nuclear charge Z. This was realized by approximating the multielectron atomic Hamiltonian with a one-electron model Hamiltonian. This model is very accurate for describing the electronic structure of the atoms near their critical points. For several atoms in their ground electronic states, we have found that the critical exponents $(\alpha_E, \nu, \alpha_S)$ for He ($Z=2$), C ($Z=6$), N ($Z=7$), F ($Z=9$), and Ne ($Z=10$), respectively, are (1, 0, 0). At the critical points $\lambda_c = 1/Z_c$, the bound state energies become absorbed or degenerate with continuum states and the entropies reach their maximum values, indicating a maximal delocalization of the electronic wave function. © *2004 American Institute of Physics.* [DOI: 10.1063/1.1785773]

I. INTRODUCTION

In statistical physics, the finite size scaling method provides a systematical way to extrapolate information available from a finite system to the thermodynamic limit.[1,2] Finite size scaling crossing points, the pseudocritical points, are the information needed in order to extrapolate to the thermodynamic limit, where singularities or phase transitions occur. Recently we have developed the finite size scaling methods to study phase transitions that are taking place at the absolute zero of temperature in atoms and molecules.[3] These transitions are not driven by temperature as in classical phase transitions but rather by quantum fluctuations as a consequence of the Heisenberg's uncertainty principle.[4,5] In this regard, the finite size corresponds not to the spatial dimension, as in statistical physics, but to the number of elements in a complete basis set used to expand the wave functions of a given Hamiltonian. Here the "thermodynamic limit" is achieved by extrapolation to the infinite basis set limit. The phase transitions occur by tuning parameters in the Hamiltonian.

Different finite size scaling methods were recently reviewed in quantum mechanics[6] and were successfully applied to atoms,[7] molecules,[8] three-body systems,[9] crossover phenomena and resonances[10] and critical conditions for stable dipole and quadrupole bound anions.[11,12] Critical phenomena described by energy operators are examined through varying the nuclear charges' or molecular fragments' separation distances. For atoms, the phase transitions at a critical point exploit a fundamental process of an electron leaving the atom, the ionization process.[7,11] For molecules and clusters the phase transitions are closely related to the symmetry breaking in the geometrical configurations of the molecular fragments.[8,9,13]

Shannon-information entropy[14] measures the delocalization or the lack of structure in the respective distribution.[15] Thus the entropy S is maximal for uniform distribution, that is, for an unbound system, and is minimal when the uncertainty about the structure of the distribution is minimal. Shannon proposed that the information entropy for a system with a probability distribution $P(x)$ in one dimension could be characterized by

$$S = - \int P(x) \ln P(x) dx; \quad \int P(x) dx = 1. \tag{1}$$

For atomic systems one may define the spatial Shannon entropy S_ρ using the electronic density ρ and its momentum space analog S_π. Such definitions result in that the sum $S_t = S_\rho + S_\pi$ provides a stronger version of the Heisenberg's uncertainty principle for any N-electron system,[16,17]

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

The total entropy has been used in recent years to measure correlations in many-electron systems[18] and nuclei.[19] Also, it is invariant to scaling and has been used to measure basis set quality.[17,20] Furthermore, it has a linear dependence on the logarithm of the number of particles in atoms, nuclei, atomic clusters,[21,22] and in correlated boson systems.[19] Shannon entropy has further been related to various properties such as molecular geometric parameters,[23] chemical similarity of different functional groups,[24] ionization potential,[25] global delocalizations,[26] molecular reaction paths,[27] orbital-based kinetic theory,[28] and highly excited states of single-particle systems.[29]

Recently, we studied the criticality of energy operator for a given quantum-mechanical system of either known atoms and molecules or models.[7-13] The theoretical calculations provided energetic information and made it possible to extract the critical exponent using the scaling function of energy. Most recently we revisited the simplest two-electron Helium atom in the Hylleraas coordinate.[30] The Hylleraas expansion approach to the wave function was even confirmed as the most accurate method in the Hilbert space

spanned by a single-exponent Slater-type basis set. After calculating both energy and electron density (and therefore entropy) and then fitting those accurate data we found an approximately linear relation between the entropy and the first derivative of the energy. In particular, we noted that close to the critical point such linear relation becomes true. These results show that the exponent of the entropy for helium is the exponent of the energy minus 1.

In this paper, we develop the finite size scaling method to obtain the critical parameters related to the atomic Shannon entropies. In Sec. II we review the scaling functions and establish relations among the critical exponents for the atomic Shannon entropy, the correlation length, and the electronic energy. In Sec. III we describe a one-electron model Hamiltonian used to approximate the multielectron Hamiltonian. In Sec. IV we present results and also the integrals needed for calculating the different energy matrix elements. Discussion and conclusions follow in Sec. V. Atomic units are used throughout the paper unless otherwise specified.

II. FINITE SIZE SCALING FOR THE CRITICALITY OF SHANNON-INFORMATION ENTROPY

The Hamiltonian for many interesting problems in quantum mechanics, in particular for atomic and molecular systems,[8] can be transformed to the following general form:

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{V}_\lambda, \tag{3}$$

where $\mathcal{H}_0$ is λ independent while $\mathcal{V}_\lambda$ is a λ dependent term and λ represents a free parameter. For electronic structure of atoms, λ is the inverse of the nuclear charge Z. At the critical point λ_c, a bound state described by the Schrödinger equation $\mathcal{H}\Psi = E\Psi$ becomes absorbed or degenerate with a continuum.

For a λ-independent complete and orthonormal basis set $\{\Phi_n\}$, spanning an infinite-dimensional Hilbert space L^2, the bound state can be expanded as

$$\Psi_\lambda = \sum_n^\infty C_n(\lambda)\Phi_n, \tag{4}$$

where n is an adequate set of quantum indices and $\{C_n(\lambda)\}$ the expansion coefficients which are generally λ dependent. In calculating the energy matrix, the expansion has to be truncated at order N, i.e., expanding up to a finite length, $M(N)$ which equals a finite dimension in the Hilbert space. For a finite basis set, the expectation value of any quantum operator $\mathcal{O}$ is given by

$$\langle\mathcal{O}\rangle^{(N)}(\lambda) = \sum_{i,j}^{M(N)} C_i^{(N)}(\lambda)C_j^{(N)}(\lambda)\mathcal{O}_{i,j}, \tag{5}$$

where $\mathcal{O}_{i,j}$ are the matrix elements of $\mathcal{O}$ in the basis set $\{\Phi_n\}$. In general, the mean value of the operator $\mathcal{O}$ is not analytical at $\lambda = \lambda_c$, and has the form

$$\langle\mathcal{O}\rangle \underset{\lambda\to\lambda_c^+}{\sim} (\lambda - \lambda_c)^{\mu_\mathcal{O}}, \tag{6}$$

where $\mu_\mathcal{O}$ is the critical exponent.

The finite size scaling hypothesis[31] assumes the existence of a scaling function for the truncated expansion such that

$$\langle\mathcal{O}\rangle^{(N)}(\lambda) \sim \langle\mathcal{O}\rangle F_\mathcal{O}(N/\xi^{(\infty)}(\lambda)), \quad \xi^{(\infty)}(\lambda) = |\lambda - \lambda_c|^{-\nu}, \tag{7}$$

with a different scaling function $F_\mathcal{O}$ for each different operator but with a unique scaling exponent ν. $\xi^{(\infty)}(\lambda)$ is the correlation length at $N\to\infty$.

Since $\langle\mathcal{O}\rangle^{(N)}(\lambda)$ is analytical in λ, the scaling function at $\lambda\to\lambda_c$ must behave like

$$F_\mathcal{O}(x) \sim x^{-\mu_\mathcal{O}/\nu}, \tag{8}$$

where $x = N(\lambda - \lambda_c)^\nu \to 0$. It follows that $\langle\mathcal{O}\rangle^{(N)}(\lambda)$ at λ_c depends on N as a power law

$$\langle\mathcal{O}\rangle^{(N)}(\lambda_c) \sim N^{-\mu_\mathcal{O}/\nu}; \quad N\to\infty. \tag{9}$$

Using Eq. (9) one may extrapolate the exponent $\mu_\mathcal{O}$ and ν (Ref. 31) from the crossings of the pseudocritical exponents $\mu_\mathcal{O}^{(N,N')}$ and $\nu^{(N,N')}$ for two consecutive expansions N, $N' = N+1$ (or $N+2$ if parity effects involve[32]),

$$\frac{\mu_\mathcal{O}^{(N,N')}}{\nu^{(N,N')}} = \frac{\ln(\langle\mathcal{O}\rangle_{\lambda_c}^{(N)}/\langle\mathcal{O}\rangle_{\lambda_c}^{(N')})}{\ln(N'/N)}. \tag{10}$$

At this point we may define the energy E exponent α_E as

$$E_\lambda \underset{\lambda\to\lambda_c^+}{\sim} (\lambda - \lambda_c)^{\alpha_E} \tag{11}$$

and obtained from Eq. (10) by replacing $\mathcal{O} \equiv \mathcal{H}$

$$\frac{\alpha_E^{(N,N')}}{\nu^{(N,N')}} = \Delta_\mathcal{H}(\lambda_c; N, N'), \tag{12}$$

where the notation $\Delta_\mathcal{H}$ is used for the right side of Eq. (10).

For unique exponents we start from Eq. (11) and take the derivative[32]

$$\frac{\partial E_\lambda}{\partial\lambda} \underset{\lambda\to\lambda_c^+}{\sim} (\lambda - \lambda_c)^{\alpha_E - 1}. \tag{13}$$

Using Hellmann-Feynman theorem

$$\frac{\partial E_\lambda}{\partial\lambda} = \left\langle\frac{\partial\mathcal{H}}{\partial\lambda}\right\rangle_\lambda = \left\langle\frac{\partial\mathcal{V}_\lambda}{\partial\lambda}\right\rangle_\lambda \tag{14}$$

and taking $\mathcal{O} = \partial\mathcal{V}_\lambda/\partial\lambda \equiv \mathcal{V}_\lambda'$ in Eq. (10) we have

$$\frac{\alpha_E^{(N,N')} - 1}{\nu^{(N,N')}} = \Delta_{\mathcal{V}_\lambda'}(\lambda_c; N, N'). \tag{15}$$

Given the electron probability ρ, atomic Shannon-information entropy S may be defined as the expectation value of the operator $\mathcal{I}_\rho$ in

$$S_\lambda = \langle -\ln\rho(\mathbf{r})\rangle_\lambda \equiv \langle\mathcal{I}_\rho\rangle_\lambda. \tag{16}$$

Its exponent α_S is then defined by

$$S_\lambda \underset{\lambda\to\lambda_c^+}{\sim} (\lambda - \lambda_c)^{\alpha_S}. \tag{17}$$

By replacing $\mathcal{O} = \mathcal{I}_\rho$ in Eq. (10), one obtains

$$\frac{\alpha_S^{(N,N')}}{\nu^{(N,N')}} = \Delta_{\mathcal{I}_\rho}(\lambda_c; N, N'). \tag{18}$$

From Eqs. (12), (15), and (18) we can obtain the pseudocritical exponents $\alpha_E^{(N,N')}$, $\nu^{(N,N')}$, and $\alpha_S^{(N,N')}$ by defining the following functions:

$$\Gamma_{\alpha_E}(\lambda,N,N')=\frac{\Delta_{\mathcal{H}}}{\Delta_{\mathcal{H}}-\Delta_{\mathcal{V}'_\lambda}},$$

$$\Gamma_\nu(\lambda,N,N')=\frac{1}{\Delta_{\mathcal{H}}-\Delta_{\mathcal{V}'_\lambda}}, \tag{19}$$

$$\Gamma_{\alpha_S}(\lambda,N,N')=\frac{\Delta_{\mathcal{I}_\rho}}{\Delta_{\mathcal{H}}-\Delta_{\mathcal{V}'_\lambda}}.$$

These functions are independent of the values of N and N' at the critical point $\lambda=\lambda_c$ and give the critical exponents

$$\alpha_E=\Gamma_{\alpha_E}(\lambda_c,N,N'); \quad \nu=\Gamma_\nu(\lambda_c,N,N');$$

$$\alpha_S=\Gamma_{\alpha_S}(\lambda_c,N,N'). \tag{20}$$

The finite size scaling equations are valid as an asymptotic expression, $N\to\infty$. However, with a finite basis set, pseudocritical exponents $\alpha_E^{(N,N')}$, $\nu^{(N,N')}$, and $\alpha_S^{(N,N')}$ can be obtained as a succession of values as a function of (N,N'). In order to obtain the extrapolated values α_E, ν, and α_S at $N\to\infty$ we used the algorithm of Bulirsch and Stoer.[33]

III. ONE-ELECTRON APPROXIMATION FOR ATOMIC HAMILTONIAN

A direct way to treat multielectron systems is to use *ab initio* electronic structure methods with Gaussian basis-set functions. This approach is widely applied in modern quantum chemistry computations. We have recently examined such Gaussian basis functions using finite size scaling method for simple molecular systems.[8] The problem of using Gaussian functions in finite size scaling analysis is that they do not form a complete basis set and are more localized than the Slater functions.

In the present work, we apply the one-electron approximation to the Hamiltonian [Eq. (3)] to avoid the complexity of the multielectron problem while producing the relevant main physics near the critical points. Let us start by considering an N-electron Hamiltonian for neutral atoms with infinite nuclear mass,[8]

$$H=\sum_{i=1}^{N}\frac{\mathbf{p}_i^2}{2m_i}-\sum_{i=1}^{N}\frac{1}{r_{0i}}+\lambda\sum_{i=1}^{N-1}\sum_{j=2,i<j}^{N}\frac{1}{r_{ij}}, \tag{21}$$

where p_i is the momentum of electron i with mass m_i, r_{0i} is the distance between electron i and the nucleus (index 0), and r_{ij} are the interelectron distances.

We decompose the Hamiltonian H into two parts: one represents the highest occupied orbital for electron N and the other for the atomic core with the remaining $N-1$ electrons,

$$H=H_{core}+h. \tag{22}$$

If we assume that the core is frozen, $\Psi=\Phi_{core}\psi$, and is in its ground state, $H_{core}\Phi_{core}=E_{core}\Phi_{core}$, with

$$H_{core}=\sum_{i=1}^{N-1}\frac{\mathbf{p}_i^2}{2m_i}-\sum_{i=1}^{N-1}\frac{1}{r_{0i}}+\frac{1}{Z}\sum_{i=1}^{N-2}\sum_{j=2,i<j}^{N-1}\frac{1}{r_{ij}}, \tag{23}$$

then h must satisfy $h\psi=(E-E_{core})\psi$ in which

$$h=\frac{\mathbf{p}_N^2}{2m_N}+V(r_{0N},r_{01},r_{02},...,r_{0(N-1)}), \tag{24}$$

and

$$V(r_{0N},r_{01},r_{02},...,r_{0(N-1)})$$

$$=-\frac{1}{r_{0N}}+\lambda\sum_{i=1}^{N-1}\frac{1}{r_{iN}}$$

$$=-\frac{1}{r_{0N}}+\frac{\lambda}{r_{0N}}\sum_{i=1}^{N-1}\frac{1}{|\hat{\mathbf{r}}_{0N}-|\mathbf{r}_{0i}|/r_{0N}|}, \tag{25}$$

where $\hat{\mathbf{r}}_{0N}$ stands for the unit vector of $\mathbf{r}_{0N}$. $V(r_{0N},r_{01},r_{02},...,r_{0(N-1)})$ is not a central potential and further approximation is needed. If we examine the limit $r_{0N}\ll r_{0i}$, as the electron N moves closer to the nucleus,

$$V(r_{0N},r_{01},r_{02},...,r_{0(N-1)})\to-\frac{1}{r_{0N}}. \tag{26}$$

However, in the limit $r_{0i}\ll r_{0N}$, the electron N is closer to the ionization region,

$$V(r_{0N},r_{01},r_{02},...,r_{0(N-1)})\to-\frac{1}{r_{0N}}+\frac{\gamma}{r_{0N}},$$

$$\gamma=(N-1)\lambda. \tag{27}$$

Generally, $r_{0i}\lesssim r_{0N}$ for all i electrons and the potentials should include a Coulomb repulsive term less than γ/r_{0N}. This may be approximated by a short-range interaction of the Yukawa type potential

$$V(r_{0N},r_{01},r_{02},...,r_{0(N-1)})$$

$$\approx V(r_{0N})=-\frac{1}{r_{0N}}+\frac{\gamma}{r_{0N}}(1-e^{-\delta r_{0N}}), \tag{28}$$

where δ expresses the interaction range and may be extrapolated using data available either from experiments or other theories according to the following equation:[34]

$$\delta=\frac{\delta_0(\gamma-\gamma_1)-\delta_1(\gamma-\gamma_0)}{(\gamma_0-\gamma_1)}. \tag{29}$$

Here (δ_0,γ_0) and (δ_1,γ_1) are parameters corresponding to the neutral atom and its isoelectronic negative ion (if the negative ion does not exist, the parameters corresponding to the positive ion are used), respectively.

Solving the one-electron model in $H\Psi=E\Psi$ and utilizing the solution Ψ we may construct the electron spatial density $\rho(\mathbf{r}_N)=|\Psi(\mathbf{r}_N)|^2$. Under spherically averaging approximation with electron radial density $\rho(r_N)$, the atomic Shannon entropy takes[30] the following form:

$$S=-\int_0^\infty \rho(r)\ln\rho(r)4\pi r^2 dr \tag{30}$$

with normalization

$$\int_0^\infty \rho(r)4\pi r^2 dr=1, \tag{31}$$

where $r\equiv r_N$ and $\rho(r)$ is continuous over $0\leq r\leq\infty$.

IV. RESULTS

For the one-electron problem, we expand the wave function in $H\Psi = E\Psi$,

$$\Psi(\mathbf{r}) = \sum_{n,l,m} R_{n,l}(r) Y_{l,m}(\Omega) \tag{32}$$

with

$$R_{n,l}(r) = \frac{1}{[(n+1)(n+2)]^{1/2}} e^{-r/2} L_{n-l}^{(2)}(r), \tag{33}$$

where n is the principal quantum number, l is the angular quantum number, and $m = -l, -l+1, \ldots, l-1, l$. $L_{n-l}^{(2)}(r)$ is the generalized Laguerre polynomial of order 2 and degree $(n-l)$. Here the order 2 is chosen only for convenience in the calculations. $\{R_{n,l}(r) Y_{l,m}(\Omega)\}$ constitutes a complete and orthogonal basis set for $l \le n-1$. In the spherical average, Eqs. (30) and (31), the spherical harmonic functions $Y_{l,m}(\Omega)$ are normalized to 4π.

A. Yukawa potential

Let us consider a system involving one electron moving in the Yukawa potential $V(r) = -e^{-\delta r}/r$, which is obtained from Eq. (27) by setting $\gamma = 1$. The corresponding Hamiltonian is $H = -\frac{1}{2}\nabla^2 - e^{-\delta r}/r$. By scaling $\delta r \to r$ and $H/\sigma^2 \to H$, the scaled Hamiltonian becomes

$$H = -\frac{1}{2}\nabla^2 - \lambda e^{-r}/r; \quad \lambda = \frac{1}{\delta}. \tag{34}$$

Next, we calculate the pseudocrossing points $\alpha_E^{(N,N')}$, $\nu^{(N,N')}$, and $\alpha_S^{(N,N')}$ using Eq. (19) between two consecutive sizes N and $N' = N+2$, with basis-set expansion $N = 2,4,\ldots,$ 58. By extrapolating N to infinity,[33] we obtain the critical exponents for the Shannon entropy α_S, the energy α_E, and the correlation length ν.

Figure 1 presents the pseudocritical exponent crossings for an s-state electron $l = 0$ in the Yukawa potential as a function of $\lambda = 1/\delta$. The extrapolated values of the three critical exponents $(\alpha_E, \nu, \alpha_S)$ are $(2, 1, -0.23)$, respectively. The energy and correlation length exponents are in full agreement with previous results.[32] The system exhibits a "continuous phase transition" as the s-state electron moves to the continuum at a threshold $E = 0$. The entropy is singular at $\lambda_c = 0.84$ with an exponent -0.23.

Figure 2 displays the pseudocritical exponent crossings for a p-state electron $l = 1$ with $N = 26$–68. The three exponents are $(\alpha_E = 1, \nu = \frac{1}{2}, \alpha_S = 0)$. The energy phase transition is of "first order" with $\lambda_c = 4.54$. All the exponent values are listed in Table I.

B. One-electron atoms

For one-electron atoms we expand the wave functions using Eqs. (32) and (33). First, we describe the calculations for the heliumlike atoms and show how the one-electron model approximates the two-electron systems. According to Eqs. (24) and (28) the approximate Hamiltonian includes an ionic core He^+ and a $1s$ electron,
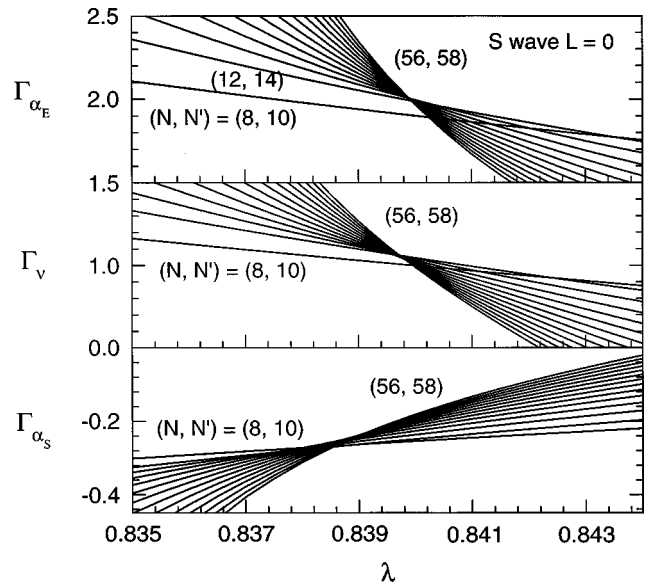

FIG. 1. The crossing points defining the pseudocritical exponents $\alpha_E^{(N,N')}$, $\nu^{(N,N')}$, and $\alpha_S^{(N,N')}$ for the Yukawa potential $(s, l = 0)$ as a function of parameter $\lambda = 1/\delta$ for $(N, N') = (8,10), (12,14), \ldots, (56,58)$.

$$h = -\frac{1}{2}\nabla^2 - \frac{1}{r} + \frac{\lambda}{r}(1 - e^{-\delta r}), \tag{35}$$

where $\delta = 0.22$ is calculated from Eq. (29) with $\delta_0 = 1.066$ and $\delta_1 = 0.881$.[34] h may approximate the full Hamiltonian

$$H = -\frac{1}{2}\nabla_1^2 + \left[-\frac{1}{2}\nabla_2^2 - \frac{1}{r_2} \right] - \frac{1}{r_1} + \frac{\lambda}{r_{12}}, \tag{36}$$

if H_{core}, the bracketed term in Eq. (36), is simply replaced by -0.5 a.u, the hydrogen ground-state energy, and r_1 by r.

Figure 3 shows the pseudocritical exponent curves for $N = 8$–58. From the figures we obtained the critical point
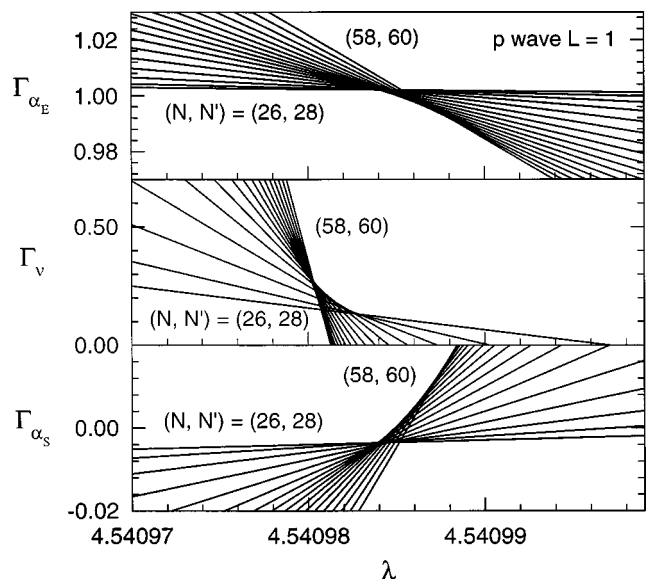

FIG. 2. The crossing points defining the pseudocritical exponents $\alpha_E^{(N,N')}$, $\nu^{(N,N')}$, and $\alpha_S^{(N,N')}$ for the Yukawa potential $(p, l = 1)$ as a function of parameter $\lambda = 1/\delta$ for $(N, N') = (26,28), (28,30), \ldots, (58,60)$.

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TABLE I. Critical charges Z_c and the extrapolated critical exponents α_E, ν, α_S for atomic systems with nuclear charges $Z=2,6,7,9,10$, and s state and p state for Yukawa potential.

Yukawa potential						
N	nl	λ_c		α_E	ν	α_S
1	$1s$	0.84		2	1	-0.23
1	$2p$	4.54		1	0.5	0
Atoms						
$N(=Z)$	nl	Z_c	$(Z-1)^{-1}$	α_E	ν	α_S
2(He)	$1s$	0.91	H^{-1}	1	0	0
6(C)	$2p$	4.97	B^{-1}	1	0	0
7(N)	$2p$	5.87	C^{-1}	1	0	0
9(F)	$2p$	7.87	O^{-1}	1	0	0
10(Ne)	$2p$	8.74	F^{-1}	1	0	0

$\lambda_c=1.096$. This value is in agreement with an exact calculation $\lambda_c=1.097$ using the full Hamiltonian and Hylleraas-type functions as basis sets.[30] The corresponding critical charge $Z_c=1/\lambda_c$ is 0.911. With this critical charge in mind we may draw a picture for the two-electron systems: at the critical point one of the $1s$ electrons is bounded by the nucleus while the other $1s$ electron moves away to infinity. For $Z>Z_c$, the system is stable and the two electrons are bounded. However, for $Z<Z_c$, the system is unstable. This analysis is useful to describe stability for a given isoelectronic atomic series.[34]

At the critical point $\lambda_c=1.096$, the extrapolated values of the three critical exponents are $\alpha_E=1$, $\nu=0$, $\alpha_S=0$ as shown in Fig. 3. The entropy exponent $\alpha_S=0$ confirms our previous analysis.[30] 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 is, for an unbound system, and is minimal when the uncertainty about the structure of the distribution is minimal.
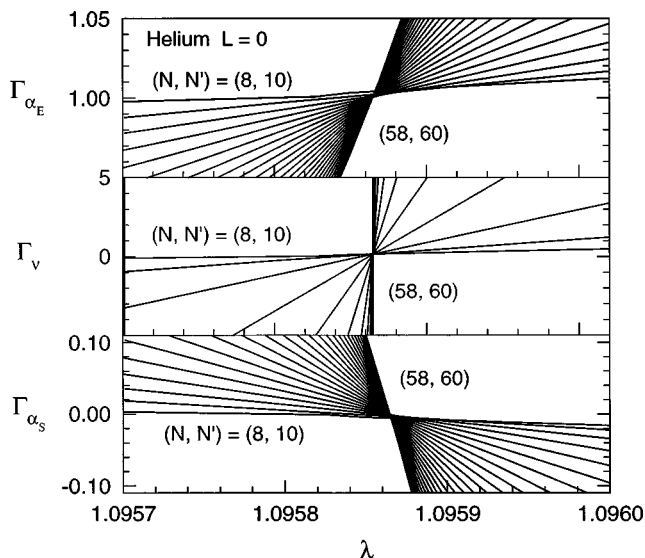

FIG. 3. The crossing points defining the pseudocritical exponents $\alpha_E^{(N,N')}$, $\nu^{(N,N')}$, and $\alpha_S^{(N,N')}$ for heliumlike atoms as a function of parameter $\lambda = 1/Z$ for $(N,N')=(8,10),(10,12),\ldots,(58,60)$.
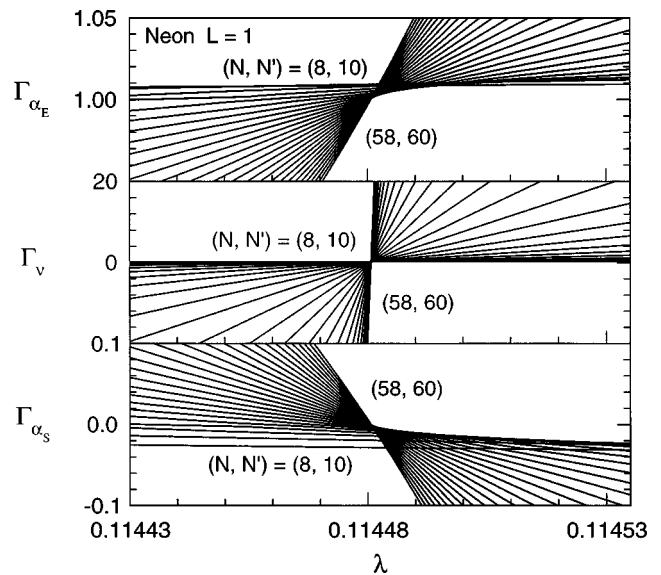

FIG. 4. The crossing points defining the pseudocritical exponents $\alpha_E^{(N,N')}$, $\nu^{(N,N')}$, and $\alpha_S^{(N,N')}$ for neonlike atoms as a function of parameter $\lambda = 1/Z$ for $(N,N')=(8,10),(10,12),\ldots,(58,60)$.

For two-electron atoms the entropy S is minimal when the two electrons are bound in the ground state $\lambda<\lambda_c$, and then develops a steplike discontinuity at λ_c and jumps to maximal value $S\approx 10.7$ for $\lambda>\lambda_c$.

Next we calculate the critical parameters for C (carbon), N (nitrogen), F (fluorine), and Ne (neon). C, N, and F have an open $2p$ orbital while Ne has a closed $2p$ orbital. Our calculations show that all these systems at their ground states undergo a first-order phase transitions. The critical points λ_c are 0.2013, 0.1704, 0.1270, and 0.1145, with the corresponding critical charges 4.97, 5.87, 7.87, and 8.73 for C, N, F, and Ne respectively. The excess charges $\Delta Z=Z-1/\lambda_c$ are 1.03, 1.13, 1.13, and 1.27 for 6-, 7-, 9-, and 10-electron atoms, respectively. This confirms the existence of stable anionic species B^{-1}, C^{-1}, O^{-1}, and F^{-1}.[32] However, there are no stable dianions because it requires an excess charge of 2.[32] For atoms with filled $2p$ orbitals, the three critical exponents are $\alpha_E=1$, $\nu=0$, $\alpha_S=0$ as shown in Fig. 4 with $N=8-58$. All the critical parameters are summarized in Table I.

V. DISCUSSION AND CONCLUSIONS

We presented a complete set of critical exponents α_E, ν, and α_S using finite size scaling analysis for the electronic energy, correlation length, and Shannon entropy,

$$E \underset{\lambda \to \lambda_c^+}{\sim} (\lambda-\lambda_c)^{\alpha_E}, \tag{37}$$

$$\xi \underset{\lambda \to \lambda_c^+}{\sim} |\lambda-\lambda_c|^{-\nu}, \tag{38}$$

$$S \underset{\lambda \to \lambda_c^+}{\sim} (\lambda-\lambda_c)^{\alpha_S}. \tag{39}$$

These exponents describe the singularity of the different quantities at the phase transition of the electron from a bound to a continuum state. These results were obtained by reduc-

ing a multiparticle Coulomb potential to a one-electron one-center atomic potential.[8] We examined the phase transition near the threshold for s-state ($l=0$) and p-state ($l=1$) Yukawa atoms, and atoms He ($Z=2$), C (6), N (7), F (9), and Ne (10). The method is general and can be used to treat the rest of the elements in the periodic table provided a good basis set and electron density.

Our data in Table I and Figs. 1–4 indicate the correspondence between the critical exponents and the interaction type. For all atoms with nuclear charge $Z=2,6,7,9,10$ their correlation length exponents are all 0, corresponding to a long-range Coulomb interaction as a dominant force. In contrast, the atoms with an electron in the Yukawa potential have positive exponents, corresponding to a short-range force which is more localized in the atomic scale than the Coulomb forces.

The atomic Shannon entropy exponents follow the trend for the correlation length exponents. For Coulomb atoms they have a common characteristic: at the critical point λ_c the entropy exponent is 0; as λ deviates from λ_c the entropy exponent varies dramatically. This shows a steplike, or discontinuous, change in the Shannon entropy of the atoms. Therefore, we conclude that the critical point is a point where atomic Shannon entropy reaches a maximum. At this point we have a delocalization of the electronic wave function. Such a property of the atomic Shannon entropy was recently described for the two-electron heliumlike atoms.[30]

Examining the critical exponents for the energy indicates that for the Yukawa atoms with an s-state electron it is of a continuous type while for p-state Yukawa atoms and atomic elements with nuclear charge $Z=2$, 6, 7, 9 and 10 it is of a first-order type. Combining the data of the ground state energy and Shannon entropy for atomic systems we can systematically map the quantum-mechanical quantities to their analogous classical quantities,

nuclear charge $Z=1/\lambda \leftrightarrow$ temperature T

electronic energy $E \leftrightarrow$ free energy G

number of basis functions $\leftrightarrow$ thermodynamic limit

atomic Shannon entropy $S \leftrightarrow$ thermodynamical entropy S.   (40)

Figure 5 presents an analogy between the behavior of the different thermodynamic quantities typical of liquid-gas first-order phase transition[35] and the critical behavior of the corresponding quantities for two-electron atoms. At first-order phase transition, the free energy G bends sharply as a function of the temperature T at the transition temperature T_d which leads to a discontinuity of the entropy S and infinite heat capacity C_p at constant pressure P. In analogy, the ground state energy for two-electron atoms E bends sharply at the transition point $\lambda_d^* = \lambda_c = 1/Z_c$; this leads to discontinuity of the Shannon information entropy and infinite "heat capacity," $C_\epsilon = \lambda (\partial S/\partial \lambda)$ with a zero external field. This analogy is very exciting and might give us a tool of classifying the electronic structure of atoms. Research is underway to classify all elements according to their types of "phase transition" and their consequences in chemical reactions.
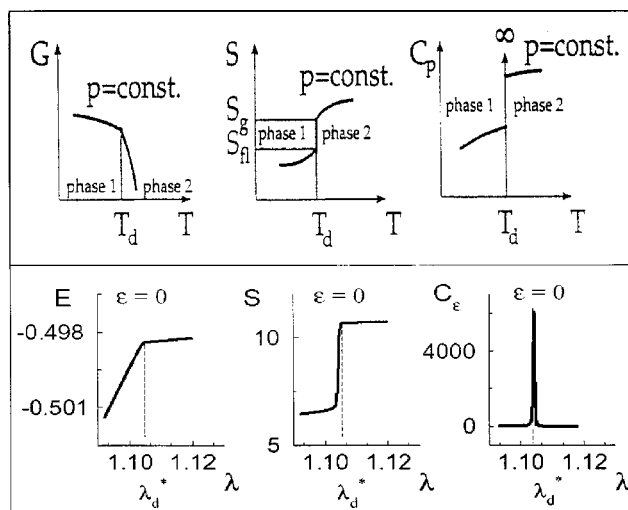

FIG. 5. Upper panel: Free energy G, entropy S, and specific heat C_p as a function of temperature for a typical first-order liquid-gas phase transition (Ref. 35). Lower panel: Ground state energy E, Shannon entropy S, and "electronic specific heat" C_ϵ as a function of the inverse of the nuclear charge Z, $\lambda = 1/Z$, for two-electron atoms in zero external field ϵ.

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APPENDIX: ENERGY MATRIX ELEMENTS

In order to calculate the energy matrix elements one needs to evaluate an integral as a product of four functions: two generalized Laguerre polynomials $L_n^{(\alpha)}(x)$ and $L_{n'}^{(\alpha)}(x)$, one exponential function e^{-x}, and one power law function x^α. The integrals with four power indices ($\alpha, \alpha+1, \alpha-1, \alpha-2$) were presented in Atomic, Molecular and Optical Handbook.[36] For convenience we list them with our corrections to the case ($\alpha-2$). All were evaluated with numerical methods.

$$\int_0^\infty x^\alpha e^{-x} L_n^{(\alpha)}(x) L_{n'}^{(\alpha)}(x) dx = \frac{\Gamma(n+\alpha+1)}{n!} \delta_{n,n'},$$

$$\int_0^\infty x^{\alpha+1} e^{-x} L_n^{(\alpha)}(x) L_{n'}^{(\alpha)}(x) dx$$
$$= \frac{\Gamma(n+\alpha+1)}{n!}[-n\delta_{n,n'+1} + (2n+\alpha+1)$$
$$\times \delta_{n,n'} - (n+\alpha+1)\delta_{n,n'-1}],$$

$$\int_0^\infty x^{\alpha-1} e^{-x} L_n^{(\alpha)}(x) L_{n'}^{(\alpha)}(x) dx$$
$$= \frac{\Gamma(n_< + \alpha+1)}{n_<! \alpha}, \quad \alpha>0,$$

$$\int_0^\infty x^{\alpha-2} e^{-x} L_n^{(\alpha)}(x) L_{n'}^{(\alpha)}(x) dx$$

$$= \frac{\Gamma(n_< + \alpha + 1)}{n_<! \alpha(\alpha^2 - 1)} [(n + n' - n_< + 1)\alpha + (n + n' + 1)],$$

$$\alpha > 1,$$

where $n_< = \min(n, n')$, α, n, and n' are integers, and $\Gamma(n+1) = 1 \times 2 \times 3...n$.

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