Critical parameters for the heliumlike atoms: A phenomenological renormalization study

Juan Pablo Neirotti, Pablo Serra, and Sabre Kais
Department of Chemistry, Purdue University, West Lafayette, Indiana 47907

(Received 9 October 1997; accepted 11 November 1997)

A mapping between the quantum few-body problem and its classical mechanics pseudo-system analog is used to study the critical parameters for the helium isoelectronic sequence. The critical point is the critical value of the nuclear charge Z_c for which the energy of a bound state becomes degenerate with a threshold. A finite-size scaling ansatz in the form of a phenomenological renormalization equation is used to obtain very accurate results for the critical point of the ground-state energy, $\lambda_c=1/Z_c=1.0976\pm0.0004$, as well as for the excited $2p^2\ ^3P$ state, $\lambda_c=1.0058\pm0.0017$. The results for the critical exponents α and ν are also included. © *1998 American Institute of Physics.* [S0021-9606(98)01407-X]

I. INTRODUCTION

Symmetry breaking and phase changes of a quantum system can take place as some parameters in its Hamiltonian are varied. For such transitions, crossing the phase boundary means that the quantum ground-state changes in some fundamental way.[1] In atomic and molecular physics, it has been suggested that there are possible analogies between critical phenomena and singularities of the energy.[2–4]

Recently it has been established for the N-electron atom[5] and simple molecular systems[6] at the large dimensional limit a new mapping between symmetry breaking of electronic structure configurations and mean-field theory of phase transitions. This analogy is shown by allowing the nuclear charge for atoms and the inverse of the internuclear distances for molecules to play a role analogous to temperature in statistical mechanics.

In this paper, we plan to study the analytical properties of the eigenvalues of the Hamiltonian for two-electron atoms as a function of the nuclear charge. This system, in the infinite-mass nucleus approximation, is the simplest few-body problem which does not admit an exact solution, but has well studied ground-state properties. The Hamiltonian in the scaled variables[7] has the form

$$\mathscr{H}(\lambda)=-\frac{1}{2}\nabla_1^2-\frac{1}{2}\nabla_2^2-\frac{1}{r_1}-\frac{1}{r_2}+\frac{\lambda}{r_{12}}=\mathscr{H}_0+\lambda\mathscr{V}, \tag{1}$$

where $\mathscr{H}_0$ is the unperturbed hydrogenic Hamiltonian, $\mathscr{V}$ is the Coulomb interelectronic repulsion and λ is the inverse of the nuclear charge Z. For this Hamiltonian, a critical point means the value of the parameter, λ_c, for which a bound state energy becomes absorbed or degenerate with the continuum.

An eigenvalue and an eigenvector of this Hamiltonian, Eq. (1), can be expressed as a power series in λ

$$E_n(\lambda)=\sum_{j=0}^{\infty}E_n^{(j)}\lambda^j, \tag{2}$$

$$\psi_n(\lambda)=\sum_{j=0}^{\infty}\psi_n^{(j)}\lambda^j. \tag{3}$$

Kato showed[8] that these series have a nonzero radius of convergence. This radius is determined by the distance from the origin to the nearest singularity in the complex plane λ^*. The study of the radius of convergence, λ^*, and whether or not this is the same as the critical value of λ_c has a long history with controversial results.[9–12] Recently, Morgan and co-workers[13] have performed a 401-order perturbation calculation to resolve this controversy over the radius of convergence of the $\lambda=1/Z$ expansion for the ground-state energy. They found numerically that $\lambda_c=\lambda^*\sim1.097\ 66$ which confirm Reinhardt's analysis of this problem using the theory of dilatation analyticity.[12] Ivanov[14] has applied a Neville–Richardson analysis of the data given by Morgan and coworkers and obtained $\lambda_c=1.097\ 660\ 79$.

Recently, in analogy with statistical mechanics, we presented phenomenological renormalization (PR) equations based on finite-size scaling (FSS) theory for the calculations of the critical points of the few-body quantum Hamiltonian.[15] Results show that the method gives very accurate results for the critical screening length for one-electron screened Coulomb potentials and the critical nuclear charge of the ground state for the two-electron atoms.[15]

In this paper, we will use the FSS approach to estimate the critical points as well as their critical exponents for the ground state and the triplet $2p^2\ ^3P$ state. In the next section we discuss the FSS method in general and its use for the quantum Hamiltonian. Section III goes into detail on the basis sets for the variational calculations. In Sec. IV we discuss the use of PR equation for estimating the critical parameters for the ground state, and in Sec. V present detailed calculations for excited states. Finally, we give the conclusions and project further research to extend the method to the N-electron atom and simple molecular systems.

II. FINITE-SIZE SCALING AND PHENOMENOLOGICAL RENORMALIZATION

The general idea of the FSS in classical statistical mechanics[16–19] is to extract information about a $(d+1)$-

dimensional lattice model in the neighborhood of the critical point by systematic numerical studies of the same d-dimensional model. This method gives a well defined procedure to extrapolate information obtained from a finite system to the thermodynamic limit. In our studies of the quantum Hamiltonian, the finite size corresponds not to the spatial dimension but to the number of elements in a truncated basis set used to expand the exact eigenfunction at a given order.[15]

The fact that a non-negative matrix could be interpreted as a transfer matrix of a classical *pseudo-system*, was recently used to study the ground-state properties of a d-dimensional quantum system, using the quantum Hamiltonian as the transfer matrix of a hypothetical $(d+1)$-dimensional statistical system.[1,17] In the present study, the Nth-order variational calculations, the two lowest energy levels $E_0^{(N)}$ and $E_1^{(N)}$ with orbital momentum $\ell=0$ are negative. If we take these levels, with opposite sign, as the eigenvalues of a transfer matrix for a classical pseudo-system, then we can define the correlation length of this finite pseudo-system as

$$\xi_N(\lambda)=-\frac{1}{\log(E_1^{(N)}(\lambda)/E_0^{(N)}(\lambda))}. \tag{4}$$

As λ_c is approached, in the limit $N\to\infty$, the characteristic length ξ grows without limit. Taking the order of the approximation N as the size of the pseudo-system, we have in virtue of the FSS ansatz that in the neighborhood of the critical point the behavior of the finite pseudo-system is determined by the scaled variable

$$y=\frac{N}{\xi(\lambda)}, \tag{5}$$

where ξ is the correlation length of the infinite system. If $y\sim 1$, the fluctuations are of the same order as of the size of the pseudo-system and critical effects are expected to occur. For $y\gg 1$ we expect bulklike behavior while for $y\ll 1$ the finite-size effects are manifested.

If a thermodynamical quantity K develops a singularity as a function of λ in the form

$$K(\lambda)=\lim_{N\to\infty} K_N(\lambda)\sim|\lambda-\lambda_c|^{-\rho}, \tag{6}$$

and in particular for the correlation length

$$\xi(\lambda)=\lim_{N\to\infty} \xi_N(\lambda)\sim|\lambda-\lambda_c|^{-\nu}, \tag{7}$$

the FSS ansatz assumes that

$$K_N(\lambda)\sim K(\lambda) f_K(y), \tag{8}$$

where $f_K(y)$ is an analytical function. For a finite N, K_N is also analytical, so the behavior of $f_K(y)$ must be

$$f_K(y)\underset{y\to 0}{\sim} y^{\rho/\nu}. \tag{9}$$

It follows that at λ_c

$$K_N(\lambda_c)\sim N^{\rho/\nu}, \quad N\to\infty. \tag{10}$$

If $K^{(q)}(\lambda)$ is the qth derivative of $K(\lambda)$, $K^{(q)}(\lambda)$ is also singular at λ_c

$$\frac{d^q}{d\lambda^q}K(\lambda)=K^{(q)}(\lambda)\sim|\lambda-\lambda_c|^{-\rho-q}, \tag{11}$$

and therefore

$$K_N^{(q)}(\lambda_c)\sim N^{(\rho+q)/\nu}; \quad N\to\infty. \tag{12}$$

Since $K^N(\lambda)$ is an analytical function in λ, it has a Taylor expansion around λ_c. Using Eq. (12) we find that $K_N(\lambda)$ can be expressed as

$$K_N(\lambda)\sim N^{\rho/\nu}\phi_K(N^{1/\nu}|\lambda-\lambda_c|), \quad N\to\infty, \tag{13}$$

where ϕ_K is a scaling function which is regular around λ_c.[16]

Since the FSS ansatz, Eq. (13), should be valid for any quantity which exhibits an algebraic singularity in the bulk, we can apply it to the correlation length ξ itself. Thus the correlation length in a finite system should have the form

$$\xi_N(\lambda)\sim N\phi_\xi(N^{1/\nu}|\lambda-\lambda_c|), \quad N\to\infty. \tag{14}$$

The special significance of this result was first realized by Nightingale[20] who showed how it could be reinterpreted as a renormalization group transformation of the infinite system. The phenomenological renormalization (PR) equation for finite systems of sizes N and N' is given by

$$\frac{\xi_N(\lambda)}{N}=\frac{\xi_{N'}(\lambda')}{N'}, \tag{15}$$

and has a fixed point at $\lambda^{(N,N')}$. It is expected that the succession of points $\{\lambda^{(N,N')}\}$ in the limit of infinite sizes to converge to the true λ_c. Using the definition of the correlation length, Eq. (4), then Eq. (15) at the fixed point can be written as

$$\left(\frac{E_1^{(N)}(\lambda^{(N,N')})}{E_0^{(N)}(\lambda^{(N,N')})}\right)^N=\left(\frac{E_1^{(N')}(\lambda^{(N,N')})}{E_0^{(N')}(\lambda^{(N,N')})}\right)^{N'}. \tag{16}$$

In general the best choice for N and N' is the value which minimizes $N-N'$,[21] that is $N'=N-1$ except when there are parity effects, then one has to take $N'=N-2$.[22,23] As far as N and N' are finite, the method is an approximation which can be improved by choosing N as large as possible. This method has the advantage that it is not necessary to know the threshold energy nor does it need the convergence of the series Eqs. (2) and (3).

There is no unique way to define the sequence $\{\lambda^{(N)}\}$, if for example, the threshold energy E_T is known, there is another alternative to obtain the sequence $\{\lambda^{(N)}\}$. This is can be done by using the following equation:

$$E_0^{(N)}(\lambda^{(N)})=E_T. \tag{17}$$

This approach is analogous to the first-order method (FOM) which has been used to study two-dimensional classical systems which display a first-order phase transition at $d=1$.[22]

III. BASIS SETS

The Hamiltonian (1) commutes with the total angular momentum operator $\mathscr{L}=\mathscr{L}_1+\mathscr{L}_2$. Using a complete λ-independent basis-set $\{\Phi_{K,\ell}\}$ with the property

$$\mathscr{L}^2\Phi_{K,\ell}=\ell(\ell+1)\Phi_{K,\ell}, \tag{18}$$

where K represents all the quantum numbers but ℓ, we can study the spectrum of $\mathscr{H}(\lambda)$ at each block of fixed ℓ. This will allow us to study excited states of the lowest symmetry of each block.

To carry out the FSS procedure one has to choose a convenient basis set to obtain the two lowest eigenvalues and eigenvectors of the finite Hamiltonian matrix. As basis functions for the FSS procedure we choose the following basis set functions:[24–26]

$$\Phi_{ijk,\ell}(\mathbf{x}_1,\mathbf{x}_2)=\frac{1}{\sqrt{2}}\,(r_1^i r_2^j e^{-(\gamma r_1+\delta r_2)}+r_1^j r_2^i e^{-(\delta r_1+\gamma r_2)}) \times r_{12}^k F_\ell(\theta_{12},\Omega), \tag{19}$$

where γ and δ are fixed parameters, r_{12} is the interelectronic distance and $F_\ell(\theta_{12},\Omega)$ is a suitable function of the angle between the positions of the two electrons θ_{12} and the Euler angles $\Omega=(\Theta,\Phi,\Psi)$. This function F_ℓ is different for each orbital-block of the Hamiltonian. For the ground state $F_0(\theta_{12},\Omega)=1$ and $F_1(\theta_{12},\Omega)=\sin(\theta_{12})\cos(\Theta)$ for the $2p^2\ ^3P$ state. These basis sets are complete for each ℓ-subspace.[25,26] The complete wave function is then a linear combination of these terms multiplied by variational coefficients determined by matrix diagonalization.

For the ground state the trial function must be symmetric under exchange of electrons. The trial function for the excited P-state is antisymmetric, because under the transformation $1\rightleftharpoons 2$ the angle Θ transforms to $\Theta\rightarrow\pi-\Theta$ so that $F_1\rightarrow -F_1$.

In the truncated basis set at order N, all terms are included such that $N\geqslant i+j+k$, so the number of trial functions $M(N)$ is

$$M(N)=\tfrac{1}{12}N^3+\tfrac{5}{8}N^2+\tfrac{17}{12}N+a_N, \tag{20}$$

where a_N is 1 ($\frac{7}{8}$) if N is even (odd).

The asymptotic behavior (large N) of the system is independent of the parameters of the trial functions. We adjust the values of the parameters in order to get a faster convergence of the PR equation Eq. (16). We found numerically that $\gamma=2$ and $\delta=0.15$ is a good choice for the ground state while $\gamma=0.5$ and $\delta=0.05$ is better for the triplet state.

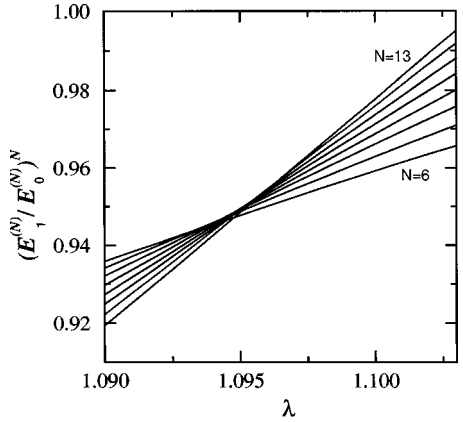

FIG. 1. The ratio between the ground-state energy and the second lowest eigenvalue raised to a power N as a function of λ for $N=6,7,...,13$.

TABLE I. Comparison of λ_c for the ground-state energy of the two-electron atoms.

Method	λ_c
FOM	$1.097\,66\pm 0.000\,02$
PR	1.0976 ± 0.0004
Fig. 6	1.0978 ± 0.0007
Ref.	$1.097\,660\,79$[a]

[a]From Ref. 14.

IV. NUMERICAL RESULTS FOR THE GROUND STATE

By diagonalizing the finite Hamiltonian matrix one can obtain the lowest two energy eigenvalues as a function of the order of the truncated basis set, $E_0^{(N)}$ and $E_1^{(N)}$. Using the PR equation, Eq. (16), one can look for its fixed point by taking the ratio of these two eigenvalues raised to a power N as a function of λ. Figure 1 shows the crossing points, which are the fixed points of Eq. (16), for $N=6,7,8,...,13$. The values of the fixed points as a function of N can be extrapolated to the limit $N\rightarrow\infty$ by using the Bulirsch and Stoer algorithm,[27] which is widely used for FSS extrapolation.[18] The extrapolated values of λ_c using the PR equation and FOM, Eq. (17), are given in Table I. The results are in excellent agreement with the best estimate of λ_c.

The behavior of the ground-state energy, $E_0^{(N)}$, as a function of λ for different values of N is shown in Fig. 2. When the value of N approaches the limit, $N\rightarrow\infty$, the true ground-state energy bends over sharply at λ_c to becomes degenerate with the lowest continuum at $E_0=-\frac{1}{2}$. This behavior can be seen in the finite order approximation, where the larger the value of N the more the energy curve bends toward a constant energy. In virtue of this behavior, we expect that the first derivative of the energy with respect to λ to develop a steplike discontinuity at λ_c. The first derivative is shown in Fig. 3 for $N=6,7,8,...,13$. As expected, the second derivative will develop a delta functionlike behavior as N is getting larger, as shown in Fig. 4.

The behavior of the ground-state energy and its first and second derivatives resemble the behavior of the free energy at a first-order phase transition. For the two-electron atoms, when $\lambda<\lambda_c$ the nuclear charge is large enough to bind two electrons, and this situation remains until the system reaches

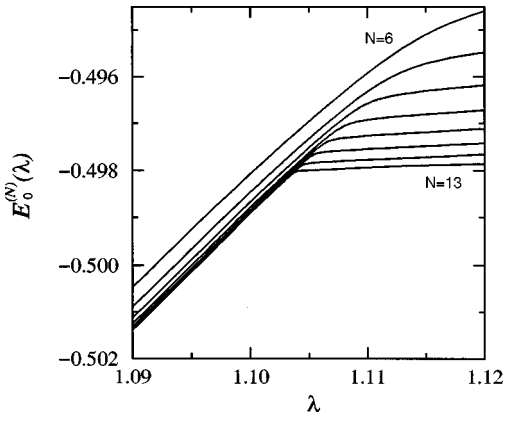

FIG. 2. Variational ground-state energy as a function of λ for $N=6,7,...,13$.

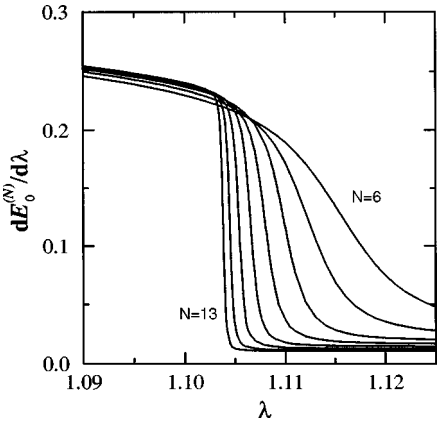

FIG. 3. First derivative of the ground-state energy as a function of λ for $N=6,7,...,13$.

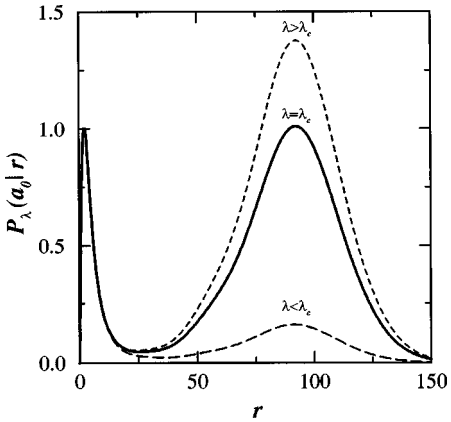

FIG. 5. Conditional probability $P_\lambda(a_0|r)$ in the twelfth-order approximation ($N=12$) for $\lambda=1.105>\lambda_c^{12}=1.104\,905$, $\lambda=\lambda_c^{12}$ and $\lambda=1.1045<\lambda_c^{12}$. The three curves are normalized such that the first maxima is one.

a critical point λ_c, which is the maximum value of λ for which the Hamiltonian has a bound state or the minimum charge necessary to bind two electrons. For $\lambda>\lambda_c$ one of the electrons jumps to infinity with zero kinetic energy.

V. CONDITIONAL PROBABILITY

Berry and co-workers[28] introduced the conditional probability as an aid in visualizing the attractive and repulsive forces which influence the dynamics of the electrons in the heliumlike atoms. This function represents the probability distribution seen by one electron given that the other electron is fixed at a certain distance. In this section we will use the same tool in order to examine the behavior of the system below and above the critical point.

We define the unnormalized conditional probability to find one electron at a distance r when the other is fixed at a distance a_0 by

$$P_\lambda(a_0|r)=\int d\Omega_1 d\Omega_2 r^2 |\psi_0(\lambda;\mathbf{x}_0,\mathbf{x})|^2, \tag{21}$$

where $d\Omega_1$ and $d\Omega_2$ the solid angular differentials, ψ_0 is the ground-state wave function, and $\mathbf{x}_0$ and $\mathbf{x}$ are the position vectors with modulus a_0 and r, respectively.

The plot of $P_\lambda(a_0=1|r)$ in the twelfth-order variational approximation, $N=12$, is shown in Fig. 5. This function has two local maxima. For $\lambda=1.1045<\lambda_c^{(12)}=1.104\,905$, the leading maxima is located at a distance about $2a_0$ from the origin and this position is independent of the order N. The other local maxima is located at a distance proportional to N but smaller than the first one. In this region, the nuclear charge is still large enough to bind the two electrons. In the limit $\lambda\to\lambda_c^-$ the second local maxima reaches the same height of the first one. For $\lambda=1.105>\lambda_c^{(12)}$ the second maxima at large distance is getting larger and the second electron is far away from the fixed one. In this region the nuclear charge cannot bind the two electrons, so one electron will move to infinity and become a free electron. The fact that the nuclear charge for H^- is below the critical point explains why this a stable ion. The position of the second local maxima scales linearly with N such that in the limit $N\to\infty$ it will be located at infinity. This is indeed a finite-size effect of the variational approximation because the asymptotic behavior of the one-electron radial density for $\lambda\leqslant\lambda_c$, has an exponential decay. This behavior resembles a first-order phase transition in which the system jumps from a state where the two electrons are bound to one with a hydrogenlike atom plus a free electron.

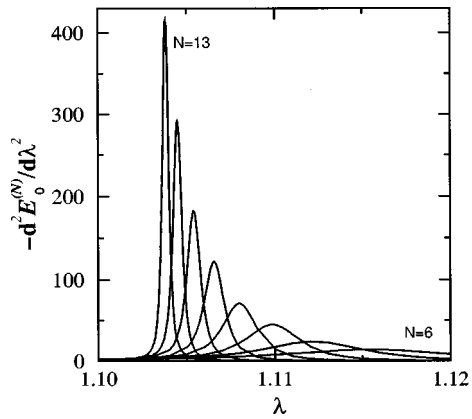

FIG. 4. Second derivative of the ground-state energy as a function of λ for $N=6,7,...,13$.

In Fig. 6 we plot the position of second maxima of the conditional probability, $x_{\max}^{(N)}$, as a function of λ for $N=4,5,6,...,11$. The steplike discontinuity tells us about the jump of the most probable position of one electron when the other is fixed at $a_0=1$. The position of this steplike discontinuity can be used as another possible definition of the pseudo-critical succession $\{\lambda^{(N)}\}$. The extrapolated value of this sequence, using the Bulirsh and Stoer algorithm,[27] is given in Table I. This value is in complete agreement with the previous results of PR and FOM methods.

VI. CRITICAL EXPONENTS

The convergence law of the results of the PR method is related to the corrections to the finite size scaling. From Eq. (10) we expect that at the critical value of nuclear charge the correlation length is linear in N. In Fig. 7 we plot the correlation length of the finite pseudo-system (evaluated at the exact critical point λ_c) as a function of the order N. The

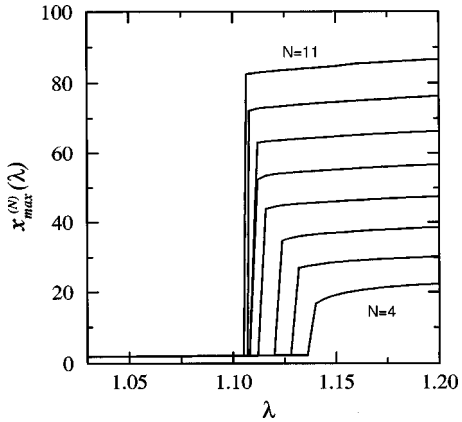

FIG. 6. Position of the highest maxima of the conditional probability $P_\lambda(a_0|r)$ as a function of λ for $N=4,5,...,11$.

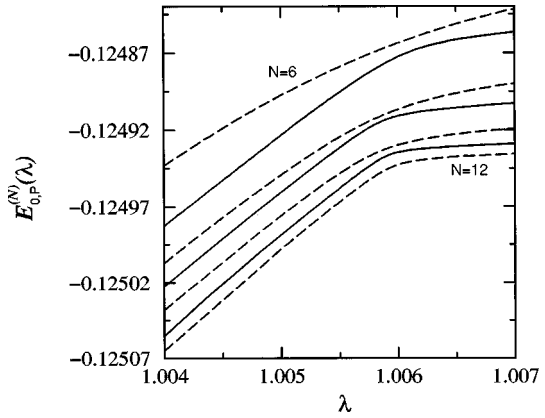

FIG. 8. Variational energy of the triplet $(2p^2\ ^3P)$ as a function of λ for $N=6,7,...,12$. The dashed curves correspond to even values of N while the solid lines to odd values of N.

linear behavior shows that the asymptotic Eq. (14) holds for very low values of N.

The classical critical exponent ν which describes the asymptotic behavior of ξ at λ_c can be obtained from Eqs. (12) and (15) for two different values of N and N'

$$\frac{1}{\nu}=\frac{\log\left[\left(\frac{d\xi_N}{d\lambda}\Big/\frac{d\xi_{N'}}{d\lambda}\right)_{\lambda=\lambda^{(N,N')}}\right]}{\log N-\log N'}-1. \tag{22}$$

Using this equation, Eq. (22), we can estimate the critical exponent ν. The extrapolated value is $\nu=1.00\pm0.02$ and the correlation length diverges as $\xi\sim|\lambda-\lambda_c|^{-\nu}$.

Hoffmann-Ostenhof's and Simon[31] have proved that $H(\lambda_c)$ has a square-integrable eigenfunction corresponding to a threshold energy $E(\lambda_c)=-\frac{1}{2}$ and noted that the existence of a bound state at the critical coupling constant λ_c implies that for $\lambda<\lambda_c$, $E(\lambda)$ approaches $E(\lambda_c)=-\frac{1}{2}$ linearly in $(\lambda-\lambda_c)$ as $\lambda\to\lambda_c^-$. Morgan and co-workers[13] confirmed this observation by their $1/Z$ perturbation calculations. They show that $E(\lambda)$ approaches $E(\lambda_c)=-\frac{1}{2}$ as

$$E(\lambda)=E(\lambda_c)+0.235(\lambda-\lambda_c). \tag{23}$$

Using the relation Eq. (10) from the FSS approach one can obtain the ratio of the critical exponents ρ/ν[29]

$$\frac{\rho}{\nu}=\frac{\log[K_N/K_{N'}]_{\lambda=\lambda^{(N,N')}}}{\log N-\log N'}. \tag{24}$$

Recently we presented a direct FSS approach to the quantum Hamiltonian where this equation can be obtained without the need to use any explicit analogy to classical statistical mechanics.[30] Now, we can estimate the critical exponent for the energy, α, by taking $K(\lambda)$ in Eq. (24) to be $(E_1^{(N)}-E_0^{(N)})$. We obtain the extrapolated value of $\alpha=1.04\pm0.07$, in agreement with the observation of Hoffmann-Ostenhof and Simon.[31]

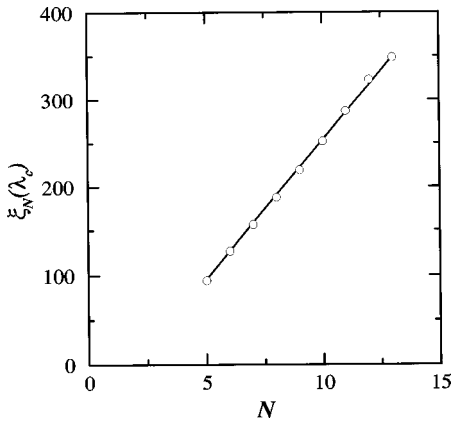

FIG. 7. Correlation length for the finite pseudo-system evaluated at the critical point λ_c as a function of N.

VII. EXCITED STATES

Having presented our results for the critical behavior of the ground-state energy of the helium isoelectronic sequence, we may now consider other excited states. The ground state is symmetric under electronic exchange and has a natural parity, which means its parity $\mathcal{P}=\mathcal{P}_1\mathcal{P}_2=(-1)^{\ell_1}(-1)^{\ell_2}$ is equal to $(-1)^{\ell}$,[32] where ℓ_i is the angular momentum number of the ith particle and $|\ell_1-\ell_2|\leq\ell\leq\ell_1+\ell_2$. All the S states have this parity because $\ell_1=\ell_2=\ell=0$. States with $\mathcal{P}=(-1)^{\ell+1}$ will be called states of unnatural parity. The triplet $2p^2\ ^3P$ has an unnatural parity.

For the H^- ion, Hill[33] proved that there is only one bound state with natural parity. This result along with Kato's proof[34] that the Helium atom has an infinite number of bound states seems to suggest that the critical point for the excited natural states is $\lambda=1$.

For the unnatural states of the H^- ion, we know from the work of Grosse and Pitner,[32] that there is just one unnatural bound state $2p^2\ ^3P$ for $\lambda=1$. An upper bound of $-0.125\ 35$ a.u. was estimated for this state by Midtdal[11] and Drake[35] which is below the threshold energy $E_T^P=-\frac{1}{8}$.

We performed a variational study of this level using the basis set defined in Eq. (19). As for the ground state, we obtained the lowest two eigenvalues which correspond to the block $\ell=1$. The energy for the triplet $2p^2\ ^3P$ state as a function of λ is shown in Fig. 8. The behavior is very similar to the one found for the ground state. The curves start to bend over sharply to a constant values as N gets larger. The true excited-state energy, in the limit $N\to\infty$, bends over

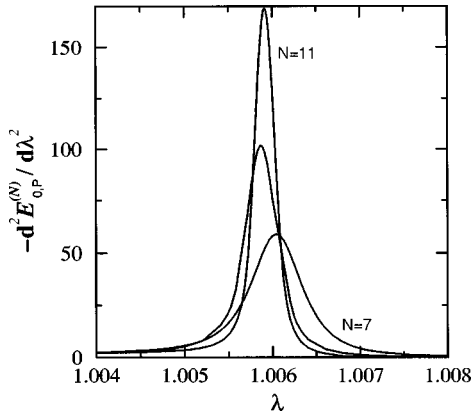

FIG. 9. Second derivative of the energy of the $(2p^2\ ^3P)$ as a function of λ for $N=7$, 9, and 11.

sharply at λ_c^P to become degenerate with the lowest continuum at $E_T^P=-\frac{1}{8}$. In Fig. 8 one can see a clear parity effects. The behavior of odd values of N is different from that of even values of N. This kind of parity effect has been observed in other statistical systems.[22] Figure 9 shows the behavior of the second derivative as a function of λ for odd values of N, and the corresponding even values of N have similar behavior and were omitted for clearity.

Taking the $\ell=1$ block as a transfer matrix of a pseudoclassical system, like the $\ell=0$ case, we can apply the PR equation, Eq. (16), to the present sector in order to obtain a sequence of pseudocritical λ as a function on $N,\{\lambda_P^{(N,N')}\}$. The extrapolated value of this sequence gives $\lambda_c^P=1.0058\pm0.0017$. Using the FOM procedure, which means getting a sequence of $\{\lambda_P^{(N)}\}$ by equating the energy at each order of approximation to the threshold energy $E_T^P=-\frac{1}{8}$, the extrapolated value is $\lambda_c^P=1.0057\pm0.0001$. This value is in complete agreement with the PR result. As far as we know the only estimate of λ_c for this triplet state is the one given by Brandas and Goscinski.[36] By applying a Darboux function anzatz[37,38] to the E_n's of Midtdal *et al.*[11] for n up to 27, they found $\lambda_c\sim1.0048$ which is in good agreement with our results.

VIII. CONCLUSIONS

By using a finite-size scaling ansatz in the form of a phenomenological renormalization equation for studying the critical parameters for the helium isoelectronic sequence, we have found the following: (i) The method is simple to implement and gives very accurate results for critical nuclear charge, which is the minimum charge necessary to bind two electrons. For the ground state we obtained $\lambda_c=1/Z_c=1.0976\pm0.0004$ and for the $2p^2\ ^3P$ state $\lambda_c=1.0058\pm0.0017$. These results are in complete agreement with perturbation calculations.[13] (ii) The FSS ansatz allows us to estimate the critical exponents. In this work we estimated the exponent ν which describes how the correlation length of the classical pseudo-system diverge at λ_c and the exponent α for the energy. We found that the energy approaches the threshold linearly in $(\lambda-\lambda_c)$ as $\lambda\rightarrow\lambda_c^-$ in agreement with rigorous results.[31] (iii) The electron leaves the atom as the nuclear charge decreases in a kind of ''first-order phase transition,'' which can be seen by examining the first and second derivative of the energy. The first derivative develops a steplike discontinuity where the second derivative develops a delta functionlike behavior at the critical point. (iv) The method can be generalized to treat the N-electron atoms if provided a convenient complete basis set. The lack of complete basis sets and the complexity of large atoms invites developing new approximations within the finite-size scaling approach. And finally, (v) FSS can be used to estimate the values of several critical parameters. This is a very useful procedure when one has to extend this method to much more complex systems such as molecular systems.

ACKNOWLEDGMENT

We would like to acknowledge the financial support of the Office of Naval Research (N00014-97-1-0192).

[1] S. L. Sondhi, S. M. Girvin, J. P. Carini, and D. Shahar, Rev. Mod. Phys. **69**, 315 (1997).
[2] F. H. Stillinger and D. K. Stillinger, Phys. Rev. A **10**, 1109 (1974).
[3] J. Katriel and E. Domany, Int. J. Quantum Chem. **8**, 559 (1974).
[4] D. R. Herschbach, J. Avery, and O. Goscinski, *Dimensional Scaling in Chemical Physics* (Kluwer, Dordercht, 1993).
[5] P. Serra and S. Kais, Phys. Rev. Lett. **77**, 466 (1996), Phys. Rev. A **55**, 238 (1997).
[6] P. Serra and S. Kais, Chem. Phys. Lett. **260**, 302 (1996), J. Phys. A **30**, 1483 (1997).
[7] E. A. Hylleraas, Z. Phys. **65**, 209 (1930).
[8] T. Kato, in *Perturbation Theory for Linear Operators*, 2nd ed. (Springer, New York, 1976).
[9] C. W. Scherr and R. E. Knight, Rev. Mod. Phys. **35**, 436 (1963).
[10] F. M. Stillinger Jr., J. Chem. Phys. **45**, 3623 (1966).
[11] J. Midtdal, Phys. Rev. A **138**, 1010 (1965).
[12] W. P. Reinhardt, Phys. Rev. A **15**, 802 (1977).
[13] J. D. Baker, D. E. Freund, R. N. Hill, and J. D. Morgan III, Phys. Rev. A **41**, 1247 (1990).
[14] I. A. Ivanov, Phys. Rev. A **51**, 1080 (1995).
[15] J. P. Neirotti, P. Serra, and S. Kais, Phys. Rev. Lett. **79**, 3142 (1997).
[16] M. E. Fisher, in *Critical Phenomena*, edited by M. S. Green Proceedings of the 51st Enrico Fermi Summer School, Varenna, Italy (Academic, New York 1971).
[17] M. N. Barber, *Finite-Size Scaling* in *Phase Transitions and Critical Phenomena*, edited by C. Domb and J. L. Lebowitz (Academic, New York 1983).
[18] V. Privman, *Finite Size Scaling and Numerical Simulations of Statistical Systems* (World Scientific, Singapore, 1990).
[19] P. J. Reynolds, H. E. Stanley, and W. Klein, Phys. Rev. B **21**, 1223 (1980).
[20] M. P. Nightingale, Physica A **83**, 561 (1976).
[21] R. R. dos Santos and L. Sneddon, Phys. Rev. B **23**, 3541 (1981).
[22] P. Serra and J. F. Stilck, Europhys. Lett. **17**, 423 (1992); Phys. Rev. E **49**, 1336 (1994).
[23] Z. Rácz, Phys. Rev. B **21**, 4012 (1980).
[24] G. W. F. Drake and Zong-Chao Yan, Chem. Phys. Lett. **229**, 489 (1994).
[25] E. A. Hylleraas, Z. Phys. **48**, 469 (1928); **54**, 347 (1929).
[26] A. K. Bhatia and A. Temkin, Rev. Mod. Phys. **36**, 1050 (1964).
[27] R. Bulirsch and J. Stoer, Numer. Math. **6**, 413 (1964).
[28] R. S. Berry and J. L. Krause, Phys. Rev. A **33**, 2865 (1986).
[29] J. L. Cardy, *Finite-Size Scaling* (Elsevier, New York, 1988).
[30] P. Serra, J. P. Neirotti, and S. Kais, Phys. Rev. A (submitted).
[31] M. Hoffmann-Ostenhof, T. Hoffmann-Ostenhof, and B. Simon, J. Phys. A **16**, 1125 (1983).
[32] H. Grosse and L. Pittner, J. Math. Phys. **24**, 1142 (1983).
[33] R. N. Hill, Phys. Rev. Lett. **38**, 643 (1977).
[34] T. Kato, Trans. Am. Math. Soc. **70**, 212 (1951).
[35] G. W. F. Drake, Phys. Rev. Lett. **24**, 126 (1970).
[36] E. Brändas and O. Goscinski, Int. J. Quantum Chem. **4**, 571 (1970).
[37] E. Brändas and O. Goscinski, Int. J. Quantum Chem. **6**, 59 (1972).
[38] G. A. Arteca, F. M. Fernández, and E. A. Castro, J. Chem. Phys. **84**, 1624 (1986).