Electronic Structure Critical Parameters From Finite-Size Scaling

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We present finite-size scaling and phenomenological renormalization equations for calculations of the critical points of the electronic structure of atoms and molecules. Results show that the method is efficient and very accurate for estimating the critical screening length for one-electron screened Coulomb potentials and the critical nuclear charge for two-electron atoms. The method has potential applicability for many-body quantum systems. [S0031-9007(97)04408-6]

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The analogies between quantum mechanical systems and statistical mechanics of classical systems has been the subject of study for many years. The correspondences between equilibrium statistical mechanics and quantum field theory are well established [1]. The Hamiltonian limit was widely used to obtain critical points and critical exponents [2] as well as mean-field phase diagrams for classical two-dimensional systems [3]. Recently, considerable interest has also been shown in the analogy between the quantum Hamiltonian and the transfer matrix in statistical mechanics. The fact that a non-negative matrix could be interpreted as a transfer matrix of a classical *pseudosystem* 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 [4,5]. In atomic and molecular physics, it has been suggested that there are possible analogies between critical phenomena and singularities of the energy [6–8]. In particular, it has been noted that, using a nonlinear variational approach, the energy curves of the two-electron atoms as a function of the inverse of the nuclear charge resemble the free energy curves as a function of the temperature for the Van der Waals gas [6]. Recently, Serra and Kais [9,10] have shown that symmetry breaking of the electronic structure configurations for the N-electron atoms and simple molecular systems at the large dimension limit can be studied as mean-field problems in statistical mechanics.

By virtue of the possibility of taking the lowest eigenvalues of a quantum Hamiltonian $\mathcal{H}(\lambda_1, \ldots, \lambda_k)$ of a set of parameters $\{\lambda_i\}$ as the leading eigenvalues of a transfer matrix of a classical *pseudosystem*, we present in this Letter a general method for studying the analytical behavior of energies of atoms and molecules near a *critical point* as a function of the parameters $\{\lambda_i\}$. In this context *critical* means the values of $\{\lambda_i\}$ for which a bound-state energy becomes absorbed or degenerates with the continuum. In our examples, we have considered only Hamiltonians with one parameter λ $(k = 1)$, but, as in statistical mechanics, the method is general and is not restricted to this condition [2,11].

In this Letter, we used the *finite-size scaling* (FSS) ansatz to obtain the critical points for electronic structure problems. The general idea of the FSS in classical statistical mechanics [12] 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. We apply the FSS ansatz to study the properties of a quantum Hamiltonian by a systematic finite basis-set expansion using a mapping between the quantum Hamiltonian and the statistical mechanics of a classical pseudosystem.

We can consider, without loss of generality, that the quantum Hamiltonian $\mathcal{H}(\lambda)$ has a well-defined ground-state energy below a critical point $\lambda < \lambda_c$. For a λ-independent complete basis set, the Nth-order approximation to the spectrum will be given by the eigenvalues of a finite $M(N) \times M(N)$ Hamiltonian matrix, with $M(N)$ being the number of elements of the truncated basis set at order N. Therefore, the leading eigenvalue of the finite matrix will be analytical, where the exact solution is nonanalytical at $\lambda = \lambda_c$. In order to obtain the value of λ_c from studying the eigenvalues of a finite-size Hamiltonian matrix, one has to define a sequence of pseudocritical parameters $\lambda^{(N)}$. Although there is no unique recipe to define such a sequence, one obvious possibility, if the threshold is known, is to define $\lambda^{(N)}$ as the value in which the ground-state energy in the Nth-order approximation, $E_0^{(N)}(\lambda)$, is equal to the threshold energy E_T,

$$E_0^{(N)}(\lambda^{(N)}) = E_T . \tag{1}$$

This approach is analogous to the first order method (FOM) in statistical mechanics which has been used to study two-dimensional classical systems which display a first order phase transition at $d = 1$ [11].

An alternative method to define the sequence of the pseudocritical values of λ is to calculate the first and second lowest eigenvalues of the $\mathcal{H}$ matrix for two different orders, N and N'. This method has the advantage that it is not necessary to know *a priori* the value of the threshold energy E_T. The pseudocritical parameter $\lambda^{(N,N')}$ is defined as the solution of the following equation:

$$\left(\frac{E_1^{(N)}(\lambda^{(N,N')})}{E_0^{(N)}(\lambda^{(N,N')})}\right)^N = \left(\frac{E_1^{(N')}(\lambda^{(N,N')})}{E_0^{(N')}(\lambda^{(N,N')})}\right)^{N'}, \tag{2}$$

where $E_0^{(N)}(\lambda)$ and $E_1^{(N)}(\lambda)$ are the ground state and the first excited eigenvalues of a sector of given symmetry of the $\mathcal{H}$ matrix.

This approach for the quantum system is inspired by the *phenomenological renormalization* (PR) [13] method, which is based on FSS arguments in statistical mechanics [12]. Using the PR method, one can obtain the critical points by searching for the fixed points of the phenomenological renormalization equation for a finite-size system. The key step is to calculate the correlation length ξ_N of the classical pseudosystem for a given basis set of order N. The correlation length of the classical pseudosystem is defined as

$$\xi_N(\lambda) = -\frac{1}{\ln[E_1^{(N)}(\lambda)/E_0^{(N)}(\lambda)]}\,. \qquad (3)$$

The PR consists of writing a renormalization equation for the correlation length of two finite systems of different orders N and N',

$$\frac{\xi_N(\lambda^{(N,N')})}{N} = \frac{\xi_{N'}(\lambda^{(N,N')})}{N'}\,. \qquad (4)$$

It is easy to see that Eq. (4) is equivalent to Eq. (2). In general, the best choice for N and N' is the value which minimizes $N - N'$ [2], that is, $N' = N - 1$, except when there are parity effects, then one has to take $N' = N - 2$ [11,14]. As far as N and N' are finite, the method is an approximation which can be improved by choosing N as large as possible.

To test the method, two cases with qualitatively different behavior near the critical point have been investigated. One with long-range interactions is the Hamiltonian of two-electron atoms, and the other with a short-range interaction is the Hamiltonian of a one-electron system with a screened Coulomb potential. For both systems the critical point is the value of the parameter entering its Hamiltonian, the nuclear charge for the first system and the screening length for the second, where the ground-state energy becomes degenerate with the lowest energy continuum. In both cases, the Hamiltonian $\mathcal{H}(\lambda)$ commutes with the total angular momentum $\vec{\mathcal{L}}$. Therefore, we can study independently each sector of the Hamiltonian, which corresponds to each eigenvalue of $\vec{\mathcal{L}}$. In this Letter, only the ground-state results with $\ell = 0$ were presented; studies of nonzero values of the angular momentum will be given elsewhere [15].

The Hamiltonian for the screened Coulomb potential in atomic units can be written as

$$\mathcal{H}(\lambda) = -\frac{1}{2}\nabla^2 - \frac{e^{-\lambda r}}{r} + C\,, \qquad (5)$$

where C is a constant added to the Hamiltonian in order to assure that the two lowest eigenvalues will have the same sign. It is known that, when the ground-state energy of this Hamiltonian is expressed as a power series in λ, the expansion is asymptotic and has a zero radius of convergence [16] and has the asymptotic formula $E_0 \simeq (\lambda_c - \lambda)^2 + O((\lambda_c - \lambda)^3)$ [17]. To carry out the calculations, we choose the following complete (nonorthogonal) basis set for S states:

$$\Psi_n(\vec{x}) = \frac{\alpha^{3/2}}{\sqrt{8\pi}\,(n+1)}\, e^{-\alpha r/2} L_n^{(1)}(\alpha r)\,, \qquad (6)$$

where α is a fixed parameter and $L_n^{(1)}$ are the generalized Laguerre polynomials of order 1 and degree n. In this case, the size of the $\mathcal{H}$ matrix of order N is $M(N) = N + 1$.

Because of parity effects, $N' = N - 2$ was taken in Eq. (2). The behavior of the ratio between the ground-state energy and the second lowest eigenvalue raised to power N as a function of λ for odd values of N is shown in Fig. 1(a). Also shown in Fig. 1(a) are the ten highest

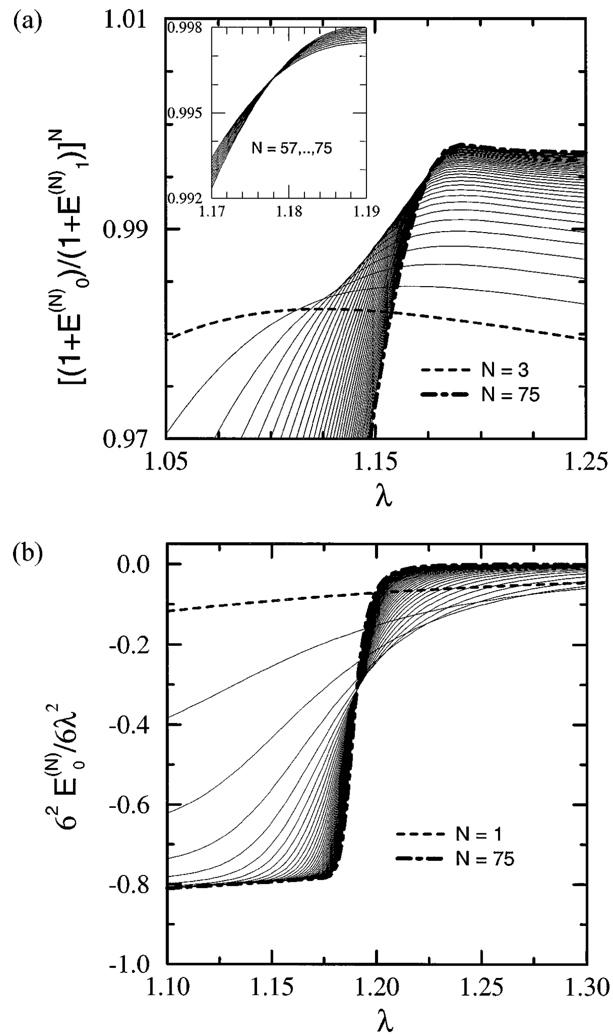

FIG. 1. For the screened Coulomb potential: (a) The ratio between the ground-state energy and the second lowest eigenvalue raised to a power N as a function of λ for odd values of $N = 3, 5, \ldots, 75$ as well as the ten highest odd values of $N = 57, 59, \ldots, 75$ (inset) in the neighborhood of the critical point $\lambda_c = 1.1906$. The constant $C = 1$ was added to the ratio as explained in the text. (b) The second derivative of the energy as a function of λ for odd values of $N = 1, 3, \ldots, 75$.

odd values of $N = 57, 59, \ldots, 75$ in the neighborhood of the critical point. The second derivative $\partial^2 E_0^{(N)}/\partial\lambda^2$ is shown in Fig. 1(b) for odd values of $N = 1, 3, \ldots, 75$. This function develops a discontinuity as a function of λ, reflecting the fact that the ground-state energy is a constant (which is equal to the threshold energy) for $\lambda > \lambda_c$. In both Figs. 1(a) and 1(b) only odd values of N are shown since the curves for even values of N are qualitatively identical.

In order to obtain the extrapolated value of the sequences $\lambda^{(N)}$ for FOM and the $\lambda^{(N,N')}$ for PR, we used the general algorithm of Bulirsch and Stoer [18] which is widely used for FSS extrapolations [2]. The extrapolated values of PR are shown in Fig. 2 and listed in Table I. Our result for λ_c is in complete agreement with the exact value obtained by numerical integration of the radial Schrödinger equation [19].

We may now consider another type of interaction, the long-range Coulomb potential in atoms. The scaled Hamiltonian of a multielectron atom can be written as

$$\mathcal{H}(\lambda) = \sum_i \left[-\frac{1}{2}\nabla_i^2 - \frac{1}{r_i} \right] + \lambda \sum_{i<j} \frac{1}{r_{ij}}, \quad (7)$$

where λ is the inverse of the nuclear charge. The ground-state $E_0(\lambda)$ has an expansion in powers of λ with a nonzero radius of convergence [20], and the behavior of the ground state near the threshold is $E_0(\lambda) \simeq (\lambda_c - \lambda) + O((\lambda_c - \lambda)^2)$ [17].

The FSS and PR equations are general and can be applied to the Hamiltonian of the multielectron atom [Eq. (7)]. In this Letter, we performed the test for the special case of two-electron atoms. Several techniques have been used to study the radius of convergence of $E_0(\lambda)$ for the two-electron atoms ([21] and references therein). Morgan and co-workers [21] performed a 401-order perturbation calculation in the λ expansion and confirm that the radius of convergence is equal to λ_c. Using the coefficients presented in Ref. [21], Ivanov [22] used the Neville-Richardson analysis to obtain a very accurate value for $\lambda_c = 1.097\,660\,79$.

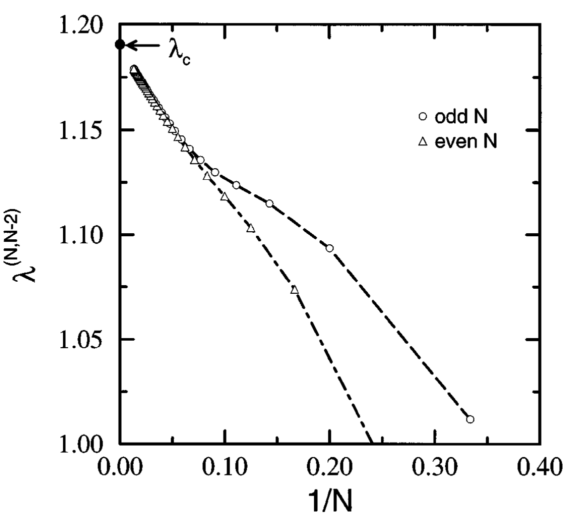

FIG. 2. $\lambda^{N,N-2}$ for the screened Coulomb potential as a function of the inverse of the system order for odd and even N. The value of the extrapolated λ_c is also shown by an arrow.

As a basis function for this procedure we choose the following trial functions [23,24]:

$$\Psi_{ijk}(\vec{x}_1, \vec{x}_2) = \frac{1}{\sqrt{2}} (r_1^i r_2^j e^{-(\alpha r_1 + \beta r_2)} + r_1^j r_2^i e^{-(\beta r_1 + \alpha r_2)}) r_{12}^k, \quad (8)$$

where α and β are fixed parameters and r_{12} is the interelectron distance. This set of trial functions, Eq. (8), is complete for the S states [24]. We took $\alpha = 2$ and $\beta = 0.15$. A more complete discussion of the behavior of the eigenvalues as functions of these parameters will be given elsewhere [15]. The finite order of the basis set is allowed to be $N \geq i + j + k$, so the number of trial functions is $M(N) = \frac{1}{12}N^3 + \frac{5}{8}N^2 + \frac{17}{12}N + a_N$, where a_N is 1 $(\frac{7}{8})$ if N is even (odd).

In the neighborhood of the critical point, the ratio between the ground-state energy and the second lowest eigenvalue raised to power N as a function of λ is shown in Fig. 3(a) for $N = 6, 7, \ldots, 13$. The behavior of the second derivative $\partial^2 E_0^{(N)}/\partial\lambda^2$ as a function of λ is shown in Fig. 3(b). This function develops a delta function like divergency as $N \to \infty$, as expected when the first derivative is discontinuous but finite.

Using the extrapolation method of Bulirsch and Stoer [2,18], we have found that the results of FOM and PR methods for λ_c are in complete agreement with the "exact" results as shown in Table I.

In summary, we have presented a PR method that is viable for obtaining information about the critical properties of isolated bound states of a large class of Hamiltonians. In particular, we calculated the critical screening length for a one-electron screened Coulomb potential and the critical charge for two-electron atoms. The results are in complete agreement with the exact numerical and large-order perturbation calculations. This

TABLE I. Comparison of λ_c for the screened Coulomb potential and the two-electron atoms.

Method	Parity	Screened Coulomb λ_c	He-like atoms λ_c
FOM, Eq. (1)	even	1.1906 ± 0.0001	1.097 66 ± 0.000 02
	odd	1.1907 ± 0.0002	
PR, Eq. (2)	even	1.1906 ± 0.0003	1.0976 ± 0.0004
	odd	1.1906 ± 0.0005	
Ref.		1.190 606 6[a]	1.097 660 79[b]

[a]From Ref. [19].
[b]From Ref. [22].

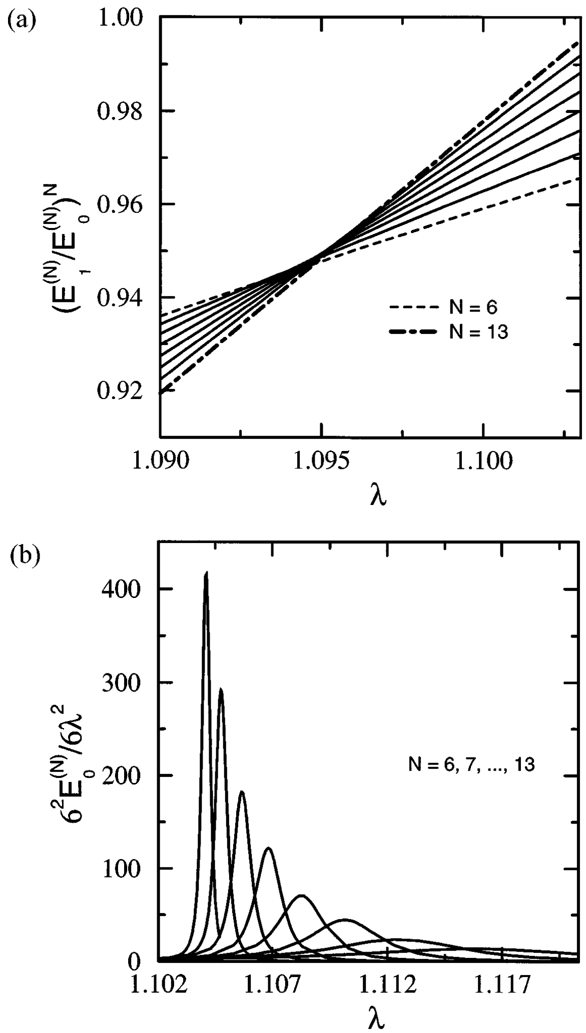

FIG. 3. For the two-electron atoms: (a) The ratio between the ground-state energy and the second lowest eigenvalue raised to a power N as a function of λ for $N = 6, 7, \ldots, 13$. (b) The second derivative of the energy as a function of λ for $N = 6, 7, \ldots, 13$.

method assures that the fixed point obtained by solving the PR equations is indeed a critical point, which means that the system has a different behavior above and below the critical point. Also, this method is efficient for the problems considered in this Letter and can be applied to the general Hamiltonian of multielectron atoms and molecules with no other requirements than knowing the matrix elements in a given basis set. Currently, there is no definitive estimate of λ_c other than for the He-like atoms [21]. Research is underway to estimate and examine the underlying structure of the critical parameters [15], such as the critical charges and the critical internuclear distances for multielectron atoms and simple molecular systems.

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